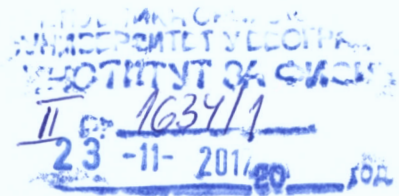Научном већу Института за физику у Београду
Београд, 23. 11. 2017.

Предмет: *Молба др Владимира Д. Стојановића за покретање поступка за реизбор у звање виши научни сарадник*

Молим Научно веће Института за физику у Београду да у складу са Правилником о поступку и начину вредновања и квантитативном исказивању научно-истраживачких резултата истраживача покрене поступак за мој реизбор у звање виши научни сарадник.

У прилогу достављам:

1. Мишљење руководиоца пројекта са предлогом чланова комисије за избор у звање виши научни сарадник
2. Стручну биографију
3. Преглед научне активности
4. Елементе за квалитативну оцену научног доприноса
5. Елементе за квантитативну оцену научног доприноса
6. Списак објављених радова и њихове копије
7. Податке о цитираности радова
8. Фотокопију решења о избору у претходно звање
9. Додатке

Са поштовањем,

Владимир Д. Стојановић
виши научни сарадник
Институт за физику у Београду

Научном већу Института за физику у Београду

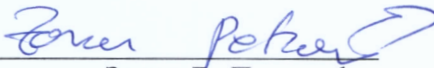Београд, 23.новембар 2017. године

Предмет: Мишљење руководиоца пројекта са предлогом чланова комисије за реизбор у звање виши научни сарадник

Др Владимир Д. Стојановић је запослен у Лабораторији за гасну електронику, у оквиру Института за Физику у Београду, Универзитета у Београду и ангажован је на пројектіма истраживања Министарства просвете, науке и технолошког развоја Републике Србије ОН171037, под називом "Фундаментални процеси и примене транспорта честица у неравнотежним плазмама, траповима и наноструктурама" и ИИИ41011 под називом "Примене нискотемпературних плазми у биомедицини, заштити човекове околине и нанотехнологијама"

За састав комисије за реизбор др Владимира Д. Стојановића звање виши научни сарадник предлажем:

(1) Др Жељка Д. Никитовић, научни саветник, Институт за физику, Универзитет у Београду, Београд
(2) Др Зоран М. Распоповић, виши научни сарадник, Институт за физику, Универзитет у Београду, Београд
(3) Др Јован М. Цветић, редовни професор, Електротехнички факултет, Универзитет у Београду, Београд

Руководилац пројекта ОН171037

Академик Зоран Љ. Петровић

Руководилац пројекта ИИИ41011

Научни саветник Невена Пуач

БИОГРАФСКИ ПОДАЦИ

Др Владимир Стојановић је рођен 1961. године у Београду где је завршио основну школу "Максим Горки" и XI београдску гимназију. Дипломирао је на Електротехничком факултету Универзитета у Београду 1987. године са просеком 9.13, где је и магистрирао 1992. године. Дипломски рад **Нумеричко израчунавање магнетске индукције методом електричних мрежа** награђен је од стране Привредне Коморе града Београда 1989. године.

Магистарски рад под називом **Електронски ексцитациони коефицијенти за побуђена стања азота на средњим и високим вредностима *E/N* (*E*-електрично поље, *N* –густина гаса),** комплетиран у Лабораторији за гасну електронику Института за физику, Универзитета у Београду, под руководством др Зорана Љ. Петровића и др Бранислава Јеленковића проглашен је најбољим магистарским радом за 1992. годину у Институту за физику.

Докторску дисертацију под називом **Моделовање Таунзендових пражњења на високим E/N и ниском притиску** је комплетирао у Институту за физику, у Лабораторији за гасну електронику под руководством академика Зорана Љ. Петровића и др Жељке Никитовић. Докторска дисертација је одбрањена на Електротехничком факултету Универзитета у Београду 13. марта 2008. године.

Кандидат је у радном односу од 20. децембра 1987. године и Институту за физику у Београду, који је прекинут 1995 године. Запослен је у Институту за физику од 30.08. 1997. године. У звање истраживач сарадник изабран је 29.6.1993. године, а у звање научни сарадник 19.11.2008. године.

У звање виши научни сарадник изабран је 24.04.2013. године.

Тренутно ради у групи академика Зорана Љ. Петровића са ангажовањем на два пројекта Министарства просвете, науке и технолошког развоја , у пројектном циклусу 2011-2017 (идентификациони број 132176)):

   Пројекат 41011 : Примене нискотемпературних плазми у биомедицини, заштити човекове околине и нанотехнологијама.

   Пројекат 171037 : Фундаментални процеси и примене транспорта честица у неравнотежним плазмама, траповима и наноструктурама.

Др Стојановић је до сада објавио укупно 50 радова у међународним часописима са ISI листе, од чега 1 категорије М21а, 23 категорије М21, 6 категорије М22, 17 категорије М23 и 3 категорије М24.

У периоду од избора у претходно звање у часопису Europhysics Letters објавио је 5 радова и 2 рада у тренутно најцењенијем часопису из ове области у Европи, Plasma Sources Sci. Technol.

У току је публиковање још 4 рада у врхунским међународним часописима.

До сада је био рецензент у часописима IEEE Transactions on Plasma Science и J. Phys. D: Appl. Phys.

Према подацима са Web of Science на дан 23. 11. 2017. године, радови су цитирани укупно 340 пута (не укључујући самоцитате), уз h-index једнак 8.

ПРЕГЛЕД НАУЧНЕ АКТИВНОСТИ

Научно-истраживачки рад др Владимира Стојановића одвијао се у области физике плазме и јонизованих гасова.

За време магистарских студија у Београду (1987-1991) кандидат је проучавао електронску ексцитацију азота у нискострујном пражњењу на ниском притиску.

Током израде докторске дисертације кандидат се бавио нумеричким моделирањем Таунзендовог пражњења на високим E/N (E-електрично поље, N-густина гаса) где је помоћу технике Монте Карло симулација анализиран транспорт ројева електрона, јона и брзих неутрала у гасу, у Лабораторији за гасну електронику Института за физику у Београду.

У периоду од докторирања наставио је да се бави нумеричким моделирањем транспорта честица Монте Карло техником. Успешно је отворио нову линију истраживања где у сарадњи са колегама из групе за гасну електронику ради у оквиру неколико тема. У наредном тексту је наведена листа тема док су у средњим заградама наведене досадашње публикације; симболом ";" одвојене су публикације искоришћене за добијање звања виши научни сарадник од оних које су предложене за реизбор истог. Теме које су отворене од последњег избора у научно звање осветљене су додатним објашњењима. Листа тема је:

1. Одређивање сетова ефективни пресека за електроне и јоне у гасовима методом роја [M21.9,M21.12, M22.4; M23.1, M21a.1,M21.20, M21.22,M33.2]

2. Моделовање експеримената на високим E/N и ниским притисцима [M21.12, M23.9-10; M23.11,M24.3,M33.1,M33.3,M34.24]

3. Кинетика електрона у смешама гасова [M21.11-13,21.16,M23.5-8; M23.11, M24.3]

4. Моделовање термализације електрона у гасу методом Монте Карло [M21.10; M34.24, M34.21]

5. Моделовање Доплеровог профила у пражњењу са водоником [M21.12,M23.9-10; M23.17, M33.3, M34.31]

6. Транспорт негативних јона у гасним пражњењима [M21.9,M22.4;M21.17-19,M22.5,M23.12-14,M24.1-2,M33.5,M34.9-10,M34.11,M34.13]

7. Транспорт метастабилних јона у гасном пражњењу [M21.15; M32.1]

8. Сетови пресека и транспортни параметри јона воде у воденој пари и атмосферским гасовима и њиховим смесама [M23.1, M23.17, M24.1, M33.4, M33.3, M33.8, M34.31, M34.29, M34.25, M34.23, M34.16, M34.14]

У склопу целина 1,2,5,6,7 настављено је изучавање Таунзендовог пражњења у гасу техником Монте Карло методе које је настављено комплетирањем резултата Монте Карло симулација за електроне, јоне и брзе неутралне честице. Сетови пресека (Phelps 2009) за тешке честице у водонику коришћени су у Монте Карло симулацијама да би се добио просторни профил H2 емисије који је поређен са експериментално добијеним просторним профилом H2 емисије на 10 kTd. Ови сетови пресека искоришћени су и за добијање иницијалних сетова пресека за расејање јона и брзих неутрала у воденој пари. Најважнији резултати се односе на моделовање Доплеровски проширене Halfa линије водоника, у пражњењима која у себи садрже компоненту услед ексцитације брзим

тешким честицама, јонима и неутралима. Добар фит облика линија је постигнут уз конволуцију инструменталног профила и додавања компоненте услед ексцицатице електронима. Припрема и слање неколико публикација за пражњење у чистом водонику је у току.

Део активности од претходног избора у звање је посвећен комплетирању резултата у Ar/H$_2$ смеси. У овом периоду је публикован један део резултата који се тиче електронског транспорта.

У циљу моделовања пражњења која садрже водену пару комплетиран је сет пресека за расејање електрона на воденој пари који представља екстензију сета пресека Phelpsa а који укључује сет пресека за ексцитацију које је мерила P. Thorn са сарадницима као и актуелне пресеке за парцијалну јонизацију. Сви ефективни пресеци су екстраполисани до енергија 10 keV. Помоћу тако добијеног сета пресека, Монте Карло симулацијама је показано слагање са експериментално мереним подацима за ефективни јонизациони коефицијент Hasegawa et al. (2007) одређених на ниским E/N.

У циљу добијана слагања са експерименталним резултатима Hasegawa et al. (2007) на високим E/N, формиран је сет пресека за анизотропно расејање електрона на молекулу воде који је укључио анизотропију ефективних пресека за јонизацију коришћењем диференцијалних пресека за b$^1\Sigma$ стање азота. Коришћење ових диференцијалних пресека поправило је већ постојеће слагање са ефективним јонизационим коефицијентом који су мерили Hasegawa и сарадници (2007). Овај сет пресека представља неопходан корак у добијању информација о термализацији електрона у воденој пари. Прелиминарни резултати просторне емисије Hα линије у воденој пари, добијени Monte Carlo симулацијом електронског транспорта, где смо користили поменуте сетове пресека, за услове Таунзендовог пражњења на 2 kTd, показали су слагање са експерименталним резултатима Škoro *et al.*(2011). Циљ одређивања сетова пресека за јоне у пражњењу водене паре постигнут је комплетирањем сетова пресека за расејање јона O$^-$ и H$_3^+$ на молекулу воде. У фази публиковања су сетови пресека за расејање O$^+$, O$_2$H$^+$ док се у израчунавањима користе прелиминарни сетови пресека за расејање H$^+$, H$_2^+$, H$_2$O$^+$ и H$_3$O$^+$ и брзих неутрала, H, на молекулу воде. Основна особина ових пресека је узимање у обзир диполног момента молекула воде у ефеквтни пресек за пренос импулса. Ендотермски процеси су представљени ефективним пресецима који су одређени на основу Денпо-Нанбу теорије.

9. *Транспорт позитивних јона у гасним пражњењима* [M21a.1,M21.18, M21.20, M21.22-23, M22.6, M23.15-17,M33.6-7,M34.30,M34.26-28,M34.22,M34.17-20,M34.4]

Транспорт позитивних јона у гасовима је тема коју је др Владимир Стојановић започео са колегама (др Жељка Никитовић, др Зоран Распоповић) из групе за гасну електронику и са Машинског Факултета, универзитета у Београду 2012.године (др Јасмина Јовановић). Потреба за базама података које би служиле за моделирање плазми за продукцију интегрисаних кола и наноструктура нужно укључује позитивне јоне за које се генерално сматра да постоји релативно добра покривеност са подацима. Међутим, за позитивне јоне са великим рекомбинационим потенцијалом ситуација је потпуно различита. Егзотермне реакције, које уједно врше и промену идентитета посматраних јона, на термалним и супратермалним енергијама драстично мењају транспортне особине ових јона (балк транспортни коефицијенти могу драстично одступати од флукс вредности) а тиме и утичу на особине неравнотежних плазми којима доминирају судари у гасу. По први пут је у литератури приказано одређивање транспортних параметара јона у индукованом поларизационом потенцијалу уз учешће егзотермних реакција асоцијације и реакција промене идентитета јона. Сетови пресека и транспортни параметери одређени су методом Монте Карло симулација. У Монте Карло симулацијама у којима је циљ био одређивање транспортних коефицијената, егзотермне реакције су третиране као губитак честица јона из роја. У периоду од претходног избора у звање др Стојановић је компилирао неколико сетова пресека и са својим колегама

одредио транспортне коефицијенте за јоне у гасу CF_4 (F^-, CF_3^+, Ar^+, Ne^+, He^+) и $F_2(F^-)$. Одредио је сет пресека за транспорт јона H^+ у н-бутанолу који се сматрају једним од основних конституената струје пражњења у бутанолу. У циљу моделовања транспорта H^+ у н-бутанолу одређени су и транспортни коефицијенти у овом гасу који се могу користити у глобалним моделима. Сличан сценарио одвијао се и са транспортом јона у гасу DXE (диметоксиетилен) који се користи као катализатор у физици чврстог стања. Одређивањем сетова пресека за алкалне јоне у гасу DXE Денпо-Нанбу теоријом др Стојановић је направио први корак у моделовању јонског транспорта у пражњењу DXE. Истовремено, транспорт алкалних јона (Li^+, K^+, Na^+) у DXE веома је занимљив због недавно измерених асоцијативних пресека који су омогућили студирање ефекта реакције асоцијације на транспортне параметре. Резултати Монте Карло симулација показали су велике разлике флукс и балк транспортних коефицијената у овом гасу. Коришћењем Денпо-Нанбу теорије која раздваја еластичне од реактивних процеса одређени су ефективни пресеци за расејање јона на молекулима који су послужили као полазна тачка у одређивању финалног сета пресека методом роја како помоћу апроксимативних семианалитичких израза добијених помоћу моментум трансфер теорије, тако и помоћу Монте Карло симулација које укључују детаље расејања и ефекте термалног кретања мете.

10. *Анализа масене спектроскопије јона радиофреквентног пражњења на ниском притиску у циљу функционализације карбонских наноструктура на површини* [M21.21, M33.9, M34.32, M34.29, M34.25]
У сарадњи са Институтом Техничких Наука САНУ (Проф. Др. Илијом Стефановићем) и Универзитетом у Орлеану (Проф. Др. Ј. Берндт и Проф.др. Е. Ковачевић) анализиране су реакиције у капацитивно спрегнутом РФ пражњењу кисеоника на ниском притиску.
У GREMI лабораторији, капацитивно спрегнуто РФ пражњење у кисеонику је анализирано помоћу масене спектроскопије. Добијени масени спектри неутрала и позитивних честица су мерени бочно у односу на правац између електрода на различитим растојањима између плазме и отвора на масеном спектрометру. Осим кисеоничних јона примећена је неочекивано висока концентрација јона и јонских кластера водене паре. У томе је примећен нуобичајено мали допринос H_2O^+ јона у односу на доприносе осталих нечистоћа водене паре. Др Стојановић је дискутујући могуће реакције које могу довести до продукције посматраних јона и масених спектара дошао до објашњења овог феномена који је објашњен у публикацији ранга M21.

ЕЛЕМЕНТИ ЗА КВАЛИТАТИВНУ ОЦЕНУ РАДА КАНДИДАТА

1. Квалитет научних резултата
1.1 Научни ниво и значај резултата, утицај научних радова

Др Владимир Стојановић је током научне каријере објавио преко 220 радова укључујући абстракте. Објавио је укупно 50 радова у међународним часописима са ISI листе, од чега 1 категорије М21а, 23 категорије М21 и 1 категорије М22 и 6 категорије М23. Укупан импакт фактор радова је 98.5. Од одлуке Научног већа о предлогу за стицање претходног научног звања др Стојановић је објавио 1 М21а рад, 7 М21 радова, 2 М22 рада, 7 М23 рада и 3 М24 рада. Укупан импакт фактор ових радова је 35.388. Квалитет научног рада др Владимира Стојановића се може проценити, између осталог, из угледа часописа у којима су радови објављени: др Стојановић је до сада објавио 6 радова у најугледнијем европском часопису у области физике Europhysics Letters (ИФ=1.957), 5 радова у најугледнијем часопису у области физике плазме и јонизованог гаса Plasma Sources Sci. Technol. (ИФ (2016) = 3.302), као и два чланка у часопису European Physical Journal D (ИФ(2016)=1.288).

Најзначајнији радови др Стојановића у последњих неколико година су:
[1] V. Stojanović, Z. Raspopović, Marić, and Z. Petrović, *Cross sections and transport of O⁻ in H₂O vapour at low pressures*, Eur Phys J D 69, 63 (2015), ИФ=1.24, цитиран до сада 4 пута без аутоцитата, **selected for the journal Highlights of 2016**, ИФ=2.546.

[2] Ž D Nikitović, Z M Raspopović and V D Stojanović,
Reduced mobility of He⁺ in CF₄,
Plasma Sources Sci. Technol. 26 (2017) 044004, ИФ=3.304.

[3] Ž. D. Nikitović, V. D. Stojanović, Z. M. Raspopović, *Modelling elastic momentum transfer cross-sections from mobility data*, Europhys. Lett. 114, 25001 (2016), doi: 10.1209/0295-5075/114/25001, ISSN 0295-5075, ИФ =2.095

[4] Ž. Nikitović, Z. Raspopović, V. Stojanović, and J. Jovanović, *Transport parameters of F⁻ ions in Ar/BF₃ mixtures*, EPL 108, 35004 (2014), ИФ=2.269, цитиран до сада 5 пута без аутоцитата.

[5] V. Stojanović, Z. Raspopović, J. V. Jovanović, J. De Urquijo, Z. Lj. Petrović, *Mobility of positive ions in CF₄*, J. Phys. Conf. Series 514, 012059 (2014), цитиран до сада 4 пута без аутоцитата.

У раду 1 помоћу технике Монте Карло симулација, добијени су транспортни коефицијенти O⁻ јона у воденој пари, који дрифтују у константном електричном пољу. По први пут је Денпо-Нанбу теорија примењена на случај расејања јона на поларном молекулу. Комплетни сет пресека за расејање ових јона на H₂O је одређен на основу познатих експериментални података и израчунавања помоћу Денпо-Нанбу теорије. У добијању финалног сета пресека коришћен је методројева. По први пут су у овом раду приказани транспортни параметри за услове од ниских до средњих вредности редукованог електричног поља уз узимање у обзир неконзервативних судара. Добијени подаци могу се користити у

условима ниских притисака где формирање кластера не утиче на транспорт ових јона, или и на високим притисцима заједно са моделом за формирање кластерске кинетике.

У раду 2 приказан је комплетан сет пресека за расејање He^+ јона на CF_4 који је базиран на експерименталним подацима за егзотермни пресек за пренос импулса који продукује јоне CF_2^+ и CF_3^+, као и ендотермским пресецима за пренос импулса који продукују CF^+, C^+ и F^+ јоне. Услед великог губитка посматраних јона транспортни коефицијенти ових јона нису могли бити измерени. Монте Карло методом су одређени транспортни коефицијенти He^+ јона на CF_4 који су неопходни да би се могло моделирати пражњење са овим јоном. Показано је да понашање редуковане мобилности јако зависи од енергијске зависности егзотермног пресека за реакције. Због егзотермних судара редукована мобилност добија вредности веће од вредности у поларизационом лимиту. Услед приближно константне колизионе учестаности за еластичне сударе флукс компонента редуковане мобилности је приближно константна до високих вредности E/N. Понашање балк компоненте, као и њен широки пик су, међутим, директна последица неконзервативних судара.

У раду 3 приказани су нови метод за једноставно одређивање ефективног пресека за пренос импулса којиме се предвиђа максимум криве за редуковану мобилност у функцији редукованог електричног поља као и температурну варијацију на ниским енергијама. У првом кораку је одређен транспортни пресек који одсликава податке за мобилност за системе са затвореном љуском, коришћењем Монте Карло методе. У другом, одредили смо највероватније реактивне процесе и компилирали ефективне пресеке из других експерименталних и теоријских података. На крају, еластични момeнтум трансфер пресек је одређен као разлика тоталног момeнтум трансфер пресека и компилираних реактивних пресека уз узимање ефеката угаоне расподеле при расејању. За случај $Ne^+ + CF_4$, Монте Карло симулацијама, са овако добијеним сетом пресека одредили смо транспортне коефицијенте у функцији редукованог електричног поља који до сада нису били познати. Дискутовани су ефекти неконзервативних судара на редуковану мобилност Ne^+ јона.

У раду 4 су по први пут у литератури приказани ефекти егзотермних реакција јона на транспортне коефицијенте у константном електричном пољу. Показано је да се без обзира на интензитет ефективног пресека за асоцијацију, ако је по облику исти као једини њему компетитивни ефективни пресек за еластични момeнтум трансфер добијају једнаки флукс и балк транспортни коефицијенти, Такође, у овом раду су приказане предикције нискоенергијских пресека и транспортне особине за F^- јоне у технолошки важном гасном пражњењу смеши Ar/BF_3 за коју не постоје подаци у литератури. Параметри роја су добијени у функцији E/N (E-електрично поље, N-густина гаса) и за температуру гаса T=300 K.

У раду 5 су дискутовани сетови пресека за расејање F^+ и CF_3^+ јона у гасу CF_4. Методом ројева уз коришћење методе Монте Карло симулација ефикасни пресеци су модификовани тако израчуната редукована мобилност фитује експерименталне податке за мобилност ових јона. Монте Карло симулацијом су израчунати транспортни параметри за позитивне јоне у гасу CF_4 у константном

електричном пољу на температури гаса Т=300 К у функцији редукованог електричног поља.

1.2 Позитивна цитираност научних радова кандидата
Према подацима са Web of Science на дан 23. 11. 2017. године, радови су цитирани укупно 340 пута (не укључујући самоцитате), уз h-index једнак 8 (видети прилог о цитираности).

1.3 Параметри квалитета часописа
Др Стојановић је током научне каријере објавио укупно 50 радова у међународним часописима са ISI листе, од чега 1 категорије М21а, 13 категорије М21 и 3 категорије М22. Укупан импакт фактор радова је 98.5. Од одлуке Научног већа о предлогу за стицање претходног научног звања др Стојановић је објавио 1 М21а рад, 8 М21 радова, 2 М22 рада и једно поглавље у зборнику водећег међународног значаја М13. Укупан импакт фактор ових радова је 35.388.

1.4 Степен самосталности и степен учешћа у реализацији радова у научним центрима у земљи и иностранству
Након докторских студија др Стојановић је наставио да се са својим колегама у Групи за гасну електронику бави темом коју је имао при изради доктората с тиме што је технике које је користио проширио на знатно комплексније случајеве, као што су пражњења на високим вредностима редукованог електричног поља у водонику и воденој пари. Самостално је компилирао сетове пресека за електроне, јоне и брзе неутрале до енергија од неколико keV. Помоћу Монте Карло симулација у којима су коришћени ови сетови пресека за расејање, показана су слагања како са транспортним коефицијентима на ниским Е/N (пре свега слагање са редукованом мобилношћу), јонизационим коефицијентима на средњим Е/N и слагањем са емисионим мерењима на високим Е/N.
Други покренути правац рада подразумева сарадњу са др З. Распоповићем у Институту за физику у Београду и са др Ј. Јовановић са Машинског факултета Универзитета у Београду, са којима је 2007 започет рад на одређивању транспортних особина негативних јона у гасовима, који учествују у моделовању електронегативних плазми, а од 2012 са др Ж. Никитовић, и позитивних јона, пре свега оних чије егзотермне реакције утичу на карактеристике плазме. Из ове проблематике објављено је неколико радова у врхунским међународним часописима.
Заједно са др Драганом Марић и др Николом Шкором покреће моделирање гасног пражњења у чистој воденој пари. По први пут су на Институту за физику, у оквиру ове теме, објављени експериментално-теоријски радови. Допринос др Стојановића у заједничким експериментално-теоријским радовима са др Илијом Стефановићем са Техничког Института САНУ и колегама из GREMI института, Универзитета у Орлеану, у Француској, др Ј. Берндтом и Е. Ковачевић се огледа у објашњавању масених спектара јона у радиофреквентном пражњењу, анализи и дискусији резултата, као и значајном учешћу у писању ових радова. Са проф. Ј. Јовановић са Машинског факултета, Универзитата у Београду је покренуто истраживање које се бави одређивањем транспортних особина јона у атмосферским гасовима. Заједно са дугогодишњом сарадницом проф др Жељком Никитовић покренута је сарадња са проф М. Мозетићем и др У. Цвелбаром, из Института Јожеф Штефан у Словенији на моделирању CF_4

плазми и смеса са радикалима. У већини поменутих активности остварена је сарадња са академиком Зораном Љ. Петровићем која је забележена како у захвалницама тако и у заједничким публикацијама.

2. Ангажованост у развоју услова за научни рад, образовању и формирању научних кадрова

У оквиру тема које су обрађиване у Групи за гасну електронику Института за физику у Београду развијена је сарадња са истраживачима који су радили дисертације са темама где је поред осталог била потребна експертиза везана за ове задатке (в. Прилог академика З.Љ. Петровића поводом избора у претходно звање):

Марија Радмиловић Рађеновић – коришћење Монте Карло симулације за прорачуне повратне дифузије и моделовања пробоја; заједнички радови**:

1. Z.Lj. Petrović, **V. Stojanović**, M. Radmilović
The influence of electrons reflected from the anode on ionization
(2000), XXth SPIG, Zlatibor, Yugoslavia, Contributed Papers,
Editors: Z.Lj. Petrović, M.M. Kuraica, N. Bibić and G. Malović, p.131.

2. M. Radmilović-Rađenović, Z.Lj. Petrović, **V. Stojanović**
Reflection of Electrons from the Anode
July (2001) Int. Sym. on Electron-Molecule Collisions and Swarms, Lincoln NE USA pp. 126-127.

А. Стринић – коришћење кода који је др Стојановић развио у својој дисертацији за моделовање мерења и добијање података о сударним процесима; заједнички радови**:

1. J. Spasojević, A. Strinić, **V.D. Stojanović**, Z.Lj. Petrović
Excitation of N$_2$ at very high *E/N* ratios
(1998), XIX SPIG, Zlatibor, Yugoslavia,
Contributed Papers, ed. N.Konjević, M.Ćuk and I. Videnović pp.179-182.
2. J.V. Spasojević, A. Strinić, **V. Stojanović** i Z.Lj. Petrović
Razdvajanje doprinosa elektrona i teških čestica u ekscitaciji na visokim *E/N*
(1997) Elektron Sto godina od otkrića; Vol. 7 Zbornik saopštenja (Ed. M.V. Kurepa)
Zavod za ud)benike i nastavna sredstva, Beograd pp. 89-92.
3. A. Strinić, J.V. Spasojević, **V.D. Stojanović** i Z. Lj. Petrović
Eksperimentalna provera ekscitacije teškim česticama
(2000) 10. Kongres fizi□ara Jugoslavije, Vrnja□ka Banja p. 603.

Ж. Никитовић – коришћење кода који је развио др Стојановић у својој дисертацији за моделовање мерења и добијање пподатака о сударним процесима; заједнички радови**:

1. Ž.D. Nikitović, A.I. Strinić, G.N. Malović, **V.D. Stojanović** i Z.Lj. Petrović
Modelovanje u neonu na visokim vrednostima *E/N*
Kongres fizičara Srbije i Crne Gore, Petrovac na Moru, 3-5. jun 2004. p. 3-111-114.

2. Željka D. Nikitović, Aleksandra I. Strinić, **Vladimir D. Stojanović**,
Gordana N. Malović and Zoran Lj. Petrović
A Monte Carlo simulation of collisional processes in a Townsend discharge in neon
Radiation Physics and Chemistry (2007) **76** pp.556-560.

А. Нина – коришћење Монте Карло кода за проверу неутрализације јона у пражњењу са цевчицама које су извор снопа неутрала; заједнички радови**:

1. M. Radmilović-Rađenović, A. Stojković, A. Strinić, **V. Stojanović**,

Ž. Nikitović, G.N. Malović and Z.Lj. Petrović

Modeling of a plasma etcher for charging free processing of nanoscale structures
Materials Science Forum (2006) **518** pp.57-62,
(ISBN: 0-87849-405-7) (ISSN: 0255-5476).

2. M. Radmilović-Rađenović, Z.Lj. Petrović, Ž. Nikitović, A. Strinić, **V. Stojanović**, A. Nina and B. Rađenović
Particle-in-cell Modelling of a Neutral Beam Source for Material Processing in Nanoscale Structures Fabrication
Materials Science Forum (2007) **555** pp.47-52,
(ISBN: 0-87849-405-7) (ISSN: 0255-5476).

М. Савић – помоћ на реализацији модела продукције секундарних електрона; заједнички радови**:
1. Z. Lj. Petrović, S. Dujko, Ž. Nikitović, **V. Stojanović**, M. Savić, M. Radmilović-Rađenović, D.   Marić, G. Malović and A. Banković
Theoretical foundations, numerical techniques and application of transport coefficients in modelling of plasmas and gas breakdown
(2009) *2nd International Conference On Advanced Plasma Technologies With 1st International   Plasma Nanoscience Symposium*, sep 29th-Oct 2nd , Piran, Slovenia, Conference Proceedings,
pp.28-31

** - овде су цитирани само радови током израде дисертација, док су публикације у часописима реализоване после одбрана и има знатно више заједничких радова.

Иако ни у једној од ових тема др Стојановић није био ментор, технике које ставио на располагање студентима и у чему им је помагао биле су суштински најважније за реализацију делова пројеката на којима су радили.

У току школске 2015/2016 др Стојановић је био ангажован на обављању студентских пракси за студенте физике Физичког факултета, Универзитета у Београду. Студент Марија Благојевић (индекс 2026/2015) је обавила своју праксу у Институту за физику упознавши се са методологијом рада нумеричких прорачуна транспорта јона у гасу, као и упознавање са базом података Кобсон за научне публикације. Отворена је могућност сарадње на теми одређивања ефикасних пресека за јоне у гасовима Денпо-Нанбу теоријом.
Овакво и слично ангажовање ће бити настављено и у наредном периоду.

Од претходног избора у звање Др Стојановић је објавио више од 40 конференцијских саопштења (М33.4-13, М34.4-32). За свако од њих направљен је репрезентативни постер који је прецизно представио како његов тако и рад групе у којој ради. Тако је не само повећана видљивост проблематике која се обавља у Институту за физику него и остварено образовање и формирање научних кадрова који су могли да виде посетиоци при поменутим саопштењима. У просеку су за сваку конференцију спремана по два саопштења у виду постера.

3. Нормирање броја коауторских радова, патената и техничких решења
Теоријски радови др Стојановића објављени у периоду након одлуке Научног већа о предлогу за стицање претходног научног звања су базирани на аналитичким прорачунима и комплексним нумеричким симулацијама и имају пет или мање аутора, тако да улазе са пуном тежином у односу на број коаутора.

Експериментално-теоријски радови подразумевају шире колаборације, у којима је учествовао др В. Стојановић са др И. Стефановић и др Д. Марић. Већина ових радова имају до седам аутора и такође улазе са пуном тежином у односу на број коаутора. Укупан број М бодова након одлуке Научног већа о предлогу за стицање претходног научног звања је 118.5.

4 . Руковођење пројектима, потпројектима и пројектним задацима

У досадашњем истраживачком и научном и стручном раду је био учесник на следећим пројектима Министарства за науку:
        2001-2004 „Физика нискотемпературних неравнотежних плазми" ОИ 1478
        2005-2010 „Физичке основе примене неравнотежних плазми у нанотехнологијама и третману материјала" ОИ 141025
        2011-   „Примене нискотемпературних плазми у биомедицини, заштити човекове околине и нанотехнологијама" III41011 Област: Биомедицина
        2011-   „Фундаментални процеси и примене транспорта честица у неравнотежним плазмама, траповима и наноструктурама" ON171037,
као и на међународном пројектима:
        FP6 IPB-CNP 026328: *"Reinforcing Experimental Centre for Non-Equilibrium Studies With Application in Nano-Technologies, Etching of Integrated Circuits and Environmental Research".
        2013-2017 учествовао је на међународном пројекту:
        COST Action TD1208 "Electrical Discharges with Liquids for Future Applications" (в. www.cost-plasma-liquids.eu/Database-of-Institutions/Institute -of-Physics-Belgrade-University-of-Belgrade/) (2013-2017)
        У току 2012 године био је руководилац програмског задатка:

Сударни процеси на високом E/N

што се може видети из извештаја Центра за неравнотежне процесе, Института за физику, Универзитета у Београду за 2012. годину или из документације за претходни избор у звање.

        На почетку каријере др Стојановић се бавио експерименталним мерењем транспортних коефицијената у слабострујним Таунзендовим пражњењима. Каријеру је наставио у домену нискотемпературске плазме и то у домену везаном за моделовање система ројева електрона и анализу добијених резултата. Нискотемпературне, неравнотежне плазме мастају у гасним пражњењима на ниским притисцима (мањим од 1 Torra) која се одржавају електричним и магнетним пољима којима се обезбеђује да електрони покрену дисоцијативне процесе и произведу саму плазму, али да при томе не дође до пораста температуре јона и неутрала. Такве плазме имају широку примену у најсавременијим технологијама. У микроелектроници ове плазме се користе за модификацију површина полупроводничких материјала Под модификацијом површина подразумевају се процеси депозиције танких слојева, процеси анизотропног нагризања плазмом и процеси чишћења и распршивања материјала. Неравнотежне плазме су нашле и бројне примене у развоју извора светлости, плазма екрана, извора јона, псеудо спарк прекидача, гасних ласера, за уклањање загађујучих гасова.

Од 2006. године др Стојановић почиње да се бави и транспортом негативних јона у гасовима и прављењем базе података за транспорт негативних јона у гасовима.

2012 објављује први рад који се бави транспортом позитивних јона у гасовима чиме се уједно отвара нови правац истраживања.

5. Активност у научним и научно-стручним друштвима

Активност у свим друштвима у којима је др Стојановић члан, у време претходног избора у звање, је настављена.

6. Утицајност научних резултата

Утицај научних резултата кандидата се огледа у броју цитата који су наведени у тачки 1. овог прилога као и у прилогу о цитираности. Значај резултата кандидата је такође описан у тачки 1.

7. Конкретан допринос кандидата у реализацији радова у научним центрима у земљи и иностранству

Кандидат је учесник у међународној сарадњи са:

Групом др Мирана Мозетича и Институту Јожеф Штефан у Словенији,
Групом проф Ј. Уркихо у *Centro de Ciencias Fısicas na Universidad Nacional Autonoma de Mexico* у Мексику,
са групом проф Т. Макабе на *Department of Electrical Engineering*, Keio University, у Јапану,
са центром LPTP на *Ecole Polytechnique* у Француској,
са GREMI Универзитетом у Орлеану у Француској (проф др Ј. Берндт и проф др Е. Ковачевић).

Настављен је правац рада који кандидат самостално развио на Институту за физику у Београду а односио се иницијално на расејање негативних јона на молекулима. То је примена Денпо-Нанбу теорије за одређивање ефективних пресека за реактивне процесе која је у протеклом периоду коришћена и за расејање позитивних јона на молекулу у индукованом поларизационом потенцијалу. У протеклом периоду, ова теорија је примењена и на случај реакција јона и молекула са великим диполним моментом као што је H_2O.

Поред нумеричких прорачуна др Стојановић је дао значајан допринос и у анализи резултата и писању ових радова.
Др Стојановић је значајно допринео сваком раду у коме је учествовао.

8 . Уводна предавања на конференцијама и друга предавања

Након претходног избора у звање др Стојановић је одржао једно предавања по позиву.
Прилог: позивно писмо за предавање налази се одмах уз абстракт за то предавање.
Био је коаутор на великом броју предавања по позиву на водећим међународним конференцијама (в. Списак објављених радова).

Пре претходног избора у звање др Стојановић је одржао 2 предавања по позиву од којих је у периоду од докторирања био аутор 1 предавања по позиву на међународним конференцијама и 1 предавања по позиву на домаћој конференцији. Био је такође коаутор на 16 предавања по позиву на водећим међународним конференцијама.

ЕЛЕМЕНТИ ЗА КВАНТИТАТИВНУ ОЦЕНУ РАДА КАНДИДАТА
-

Др Владимир Стојановић је током научне каријере објавио укупно 50 радова у међународним часописима са ISI листе, од чега 1 категорије М21а, 23 категорије М21, 6 категорије М22, 17 категорије М23 и 3 категорије М24. Према подацима са Web of Science на дан 23. 11. 2017. године, радови су цитирани укупно 340 пута (не укључујући самоцитате), уз h-index једнак 8. Од одлуке Научног већа о предлогу за стицање претходног научног звања др Стојановић је објавио 1 М21а рад, 7 М21 радова, 2 М22 рада, 7 М23 рада и 3 М24 радова. Укупан импакт фактор ових двадесет радова је 32.395.

Остварени резултати у периоду након одлуке Научног већа о предлогу за стицање претходног научног звања:

Категорија	М бодова по раду	Број радова	Укупно М бодова	Нормирани број М бодова
М13	3	1	3	2.5
М21а	10	1	10	10
М21	8	7	56	56
М22	5	2	10	10
М23	3	7	21	21
М24	3	3	9	9
М32	1.5	1	1.5	1.5
М33	1	13	13	12
М34	0.5	32	15.5	15.5

Поређење са минималним квантитативним условима за избор у звање виши научни сарадник:

Минималан број М бодова		Остварени резултати	Остварени нормирани резултати
Укупно	70	122.5	122
М10+М20+М31+М32+М33+М41+М42+М90	50	122.5	122
М11+М12+М21+М22+М23	35	100	99.5

СПИСАК РАДОВА ДР ВЛАДИМИРА СТОЈАНОВИЋА

Напомена: са звездицом (*) су означени радови публиковани после покретања избора у претходно звање. Радови су нумерисани уназад при чему су први радови из најранијег временског периода а последњи из најкаснијег.

Радови

Поглавља у монографијама и тематским зборницима **(М13)**

Радови објављени након претходног избора у звање

1*.Željka Nikitović, Martina Gilić, Milica Petrović, Nebojša Romčević, Zoran Raspopović, Vladimir Stojanović
The kinetic energy dependence of association reactions for alkali metal ions with dimethoxyethane
Proceedings of the IV Advanced Ceramics and Applications Conference,
Izdavač: Atlantic Press Springer
Editors: Bill Lee, Rainer Gadow, Vojislav Mitić
ISBN: 978-94-6239-213-7
DOI: 10.2991/978-94-6239-213-7
Copyright 2017,
Chapter No.26, стр. 375-387

Радови објављени пре претходног избора у звање

Радови у међународним часописима изузетних вредности (М21а)

Радови објављени након претходног избора у звање
1*.Ž. D. Nikitović, Z. M. Raspopović and V. D. Stojanović,
Reduced mobility of He^+ in CF_4, Plasma Sources Sci. Technol. 26, 044004 (2017), doi:10.1088/1361-6595/aa61db, ISSN 0963-0252, IF=3.302

Радови објављени пре претходног избора у звање

Радови у врхунским међународним часописима (М21)

Радови објављени након претходног избора у звање

23*. Ž. Nikitović, M. Gilić, Z. Raspopović, and V. Stojanović, *Comparison between transport parameters for K^+ and Li^+ in 1,2-dimethoxy ethane (DXE)*, Europhys. Lett. 116, 15002 (2016), doi: 10.1209/0295-5075/116/15002, ISSN 0295-5075, IF=2.095

22*.Ž. D. Nikitović, V. D. Stojanović, Z. M. Raspopović, *Modelling elastic momentum transfer cross-sections from mobility data*, Europhys. Lett. 114, 25001 (2016), doi: 10.1209/0295-5075/114/25001, ISSN 0295-5075, IF=2.095

21*. I. Stefanović, V. Stojanović, C. Boulmer-Leborgne, T. Lecas, E. Kovačević and J. Berndt, *Mass spectrometry of positive ions in capacitively coupled low pressure RF*

discharges in oxygen with water impurities, J. Phys. D: Appl. Phys. 49 (2016) 26520, doi:10.1088/0022-3727/49/26/265202, ISSN 0022-3727, IF=2.772

20*. Z. Raspopović, V. Stojanović, Ž. Nikitović, *Effect of exothermic reactions on the mobility of Ar^+ in CF_4*, Europhys. Lett., 111 (2015) 45001, doi: 10.1209/0295-5075/111/45001, ISSN 0295-5075, IF=2.269

19*. Ž. Nikitović, Z. Raspopović, V. Stojanović, and J. Jovanović, *Transport parameters of F^- ions in Ar/BF_3 mixtures*, Europhys. Lett. 108 (2014) 35004. doi: 10.1209/0295-5075/108/35004, ISSN 0295-5075, IF=2.269

Радови објављени после покретања претходног избора у звање

18*. J de Urquijo, J V Jovanović, A Bekstein, V Stojanović and Z Lj Petrović, *Ion mobilities and transport cross sections of daughter negative ions in N_2O and $N_2O–N_2$ mixtures*, Plasma Sources Sci. Technol. 22 (2013) 025004, doi:10.1088/0963-0252/22/2/025004, ISSN 0963-0252, IF=3.056

17*. V. Stojanović, Z. Raspopović, J. Jovanović, Z. Nikitović and Z. Lj. Petrović, *Transport of F^- ions in F_2*,
Europhys. Lett. 101 (2013) 45003. doi: 10.1209/0295-5075/101/45003, ISSN 0295-5075, IF=2.269

Радови објављени пре претходног избора у звање

16. Ž. Nikitović, **V. Stojanović** and Z. Lj. Petrović
Transport of electrons in Ar/H_2 mixtures
EPL Vol 99 (2012) 35003
ISSN: 0295-5075 doi: 10.1209/0295-5075/99/35003

15. **Vladimir D. Stojanović,** Zoran M. Raspopović, Jasmina Jovanović, Željka D., Nikitović, Svetlana B. Radovanov, Zoran Lj. Petrović,
Cross sections and transport properties of positive ions in BF_3 plasmas
Nuclear Instruments and Methods in Physics Research Section B 279 (2012) pp. 151-154, doi:10.1016/j.nimb.2011.10.052 (2011)

14.Ž. Nikitović, S. Radovanov, L. Godet, Z. Raspopović, O. Šašić, **V. Stojanović** and Z. Lj. Petrović,
Measurements and modeling of electron energy distributions in the afterglow of a pulsed discharge in BF_3
EPL Vol 95 (2011) 45003
ISSN: 0295-5075

13. Nikitović Ž., **Stojanović V**., Petrović Z. Lj, Cvelbar U., Mozetič M.
Transport coefficients for electron scattering in $CF_4/Ar/O_2$ mixtures with a significant presence of F_x or CF_x radicals
EPL Vol 91 Issue: 5 (2010) 55001
ISSN: 0295-5075 DOI: 10.1209/0295-5075/91/55001

12. Z. Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, **V. Stojanović** and M. Radmilović-Rađenović
Measurement and interpretation of swarm parameters and their application in plasma modelling
J. Phys.D:Appl. Phys. 42 (2009) 194002 (33pp) , IF=2.104
doi: 10.1088/0022- 3727/42/19/194002

11. Željka D Nikitović, **Vladimir D Stojanović,** Jean Paul Booth and Zoran Lj Petrović
Electron transport coefficients in mixtures of CF$_4$ and CF$_2$ radicals
Plasma Sources Sci. Technol. 18 (2009) 035008 (6pp)

10. Z Lj Petrović, **V Stojanović** and Ž. Nikitović
Modelling of thermalization of fast electrons in nitrogen at low pressures
Plasma Sources Sci. Technol. 18 (2009) 034017 (6pp)

9. J.V. Jovanović , Z.Lj. Petrović, and **V. Stojanović**
Cross Sections and Transport Properties of F$^-$ Ions in Ar, Kr and Xe
Nucl. Instr. And Meth. In Phys. Res. B (NIM B) 267(2) (2009) pp. 295-298.
doi: 10.1016/j. nimb.2008.10.037

8. Z. Lj. Petrović, M. Šuvakov, Ž. Nikitović, S. Dujko, O. Šašić, J. Jovanović, G. Malović and **V. Stojanović**
Kinetic phenomena in charged particle transport in gases, swarm parameters and cross section data.
Plasma Sources Sci. Technol. (2007) **16**, S1-S12.
doi:10.1088/0963-0252/16/1/S01 TOPICAL REVIEW

7. S. Vrhovac, **V. Stojanović**, B. Jelenković and Z. Petrović
Energy distribution of electrons in low-current self-sustained nitrogen discharge
J. Appl. Phys. (2001) **90** 5871.

6. A.A. Mihajlov, **V.D. Stojanović** and Z. Lj. Petrović
Resonant vibrational excitation/de-excitation of N$_2$(v) by electrons
J. Phys. D: Appl. Phys. (1999) **32** 2620.

5. V.D. Stojanović and Z. Lj. Petrović
Comparison of the results of Monte Carlo simulations with experimental data for electron swarms in N$_2$ from moderate to very high electric field to gas density ratios (*E/N*)
J. Phys. D: Appl. Phys. (1998) **31** 834.

4. Z. Lj. Petrović and **V.D. Stojanović**
The role of heavy particles in kinetics of low current discharges in argon at high electric field to gas density ratios
J. *Vac. Sci. Technol. A* (1998) **16** 329.

3. **V.D. Stojanović**, B.M. Jelenković and Z. Lj. Petrović
Excitation by electrons and fast neutrals in nitrogen discharges at very high electric field to gas density ratios

J. Appl. Phys. (1997) **81** 1601.

2. Z. Stokić, M.M.F.R. Fraga, J. Božin, **V. Stojanović**, Z. Lj. Petrović and B.M. Jelenković
Excitation of Balmer lines in low-current discharges of hydrogen and deuterium
Phys. Rev. A (1992) **45** 7463. IF=2.157

1. V.D. Stojanović, J. Božin, Z. Lj. Petrović and B.M. Jelenković,
Excitation of the C$^3\Pi_u$ state of N$_2$ and B$^2\Sigma_g^+$ state of N$_2^+$ by electrons at moderate and high values of *E/N*
Phys. Rev. A (1990) **42** 4983. IF=2.323

Радови у истакнутим међународним часописима (М22)

Радови објављени након претходног избора у звање

6*.Ž.D. Nikitović, M. D. Gilić, M. S. Petrović, N. Z. Romčević, Z. M. Raspopović, V. D. Stojanović, *Cross sections and Transport Properties for Na$^+$ in (DXE) Gas*, Sci. Sinter. 48, 379 (2016), doi:10.2298/SOS1603379N, ISSN 0350-820X, IF=0.781
Normiran broj poena: 4.17 iako je rad tipa numeričke simulacije.

5*.V. Stojanović, Z. Raspopović, D. Marić, and Z. Petrović, *Cross sections and transport of O$^-$ in H$_2$O vapour at low pressures*, Eur. Phys. J. D 69, 63 (2015), doi: 10.1140/epjd/e2015-50720-9, ISSN 1434-6060, IF=1.398

Радови објављени пре претходног избора у звање

4. Željka Nikitović, Aleksandra Strinić, Gordana Malović, **Vladimir Stojanović** and Zoran Lj. Petrović
Measurements and analysis of spatial profiles of 777.4 nm line in Townsend discharge in oxygen
Acta Chim. Slov. (2008) 55 pp.219-222 (ISSN: 1318-0207) IF=0.909
online at http://acta.chem-soc.si

3. Z. Lj. Petrović, J.V. Jovanović, **V. Stojanović**, Z. M. Raspopović and Z. Ristivojević
Cross Sections and Transport Properties of Cl⁻ Ions in Noble Gases
The European Physical Journal D 48 1 (2008) pp.87-94. IF=1.828

2. Z. Lj. Petrović, Z. M. Raspopović, **V. D. Stojanović**, J. V. Jovanović, G. Malović, T. Makabe and J. de Urquijo
Data and modeling of negative ion transport in gases of interest for production of integrated circuits and nanotechnologies.
Applied Surface Science,(2007) **253**, pp.6619-6640, IF=1.576

1. Željka D. Nikitović, Aleksandra I. Strinić, **Vladimir D. Stojanović**,

Gordana N. Malović and Zoran Lj. Petrović
A Monte Carlo simulation of collisional processes in a Townsend discharge in neon
Radiation Physics and Chemistry (2007) **76** pp.556-560, IF=0.882

Радови у међународним часописима (М23)

Радови објављени након претходног избора у звање

17*.V. Stojanović, Z. Raspopović, J. Jovanović, Ž.Nikitović, D. Marić, and Z. Petrović, *Cross sections and transport coefficients for H_3^+ ions in water vapour*, Eur. Phys. J. D 71, 283 (2017), doi: 10.1140/epjd/e2017-80295-2, ISSN 1434-6060, IF=1.288

16*.Ž.Nikitović, Z. Raspopović and V. Stojanović,
H^+ scattering in n-Butanol, Acta Phys. Polonica A, 132 (2017)1420, doi=10.12693/APhysPolA.132.1420, ISSN=0022-3727, IF=0.530
15*.Ž. Nikitović, V. Stojanović and Z. Raspopović,
Cross-Section and Transport Parameters of Ne^+ in CF_4, Acta Phys. Polonica A, 130 (2016) 1343, doi: 10.12693/APhysPolA.130.1343, ISSN=0022-3727, IF=0.530

14*.Ž. Nikitović, V. Stojanović and Z. Raspopović,
Rate Coefficients of F^- Ions in Ar/BF_3 Mixtures, Acta Phys. Polonica A, 127 (2015) 1634, doi: 10.12693/APhysPolA.127.1634, ISSN=0022-3727, IF=0.604

13*.V. Stojanović, Ž. Nikitović, J. Jovanović and Z. Raspopović,
Cross-Sections and Transport Properties of F^- Ions in F_2,
Acta Phys.Polonica A, 125 (2014) 46, doi: 10.12693/APhysPolA.125.46, ISSN=0022-3727, IF=0.604

12*.Ž. Nikitović, V. Stojanović, Z. Raspopović and J. Jovanović,
Transport Parameters of F^- Ions in BF_3, Acta Phys.Polonica A, 126 (2014) 724, doi: 10.12693/APhysPolA.126.724, ISSN=0022-3727, IF=0.604

11*.Ž. Nikitović and V. Stojanović,
Transport Coefficients in Mixtures Ar/H_2,
Acta Phys. Polonica A, 123 (2013) 73, doi: 10.12693/APhysPolA.123.73, ISSN 0022-3727, IF=0.604

Радови објављени пре претходног избора у звање

10. **V. Stojanović** and Ž. Nikitović
MODELING OF EXCITATION BY HEAVY PARTICLES IN PURE H_2 DISCHARGES AT HIGH E/N
Acta Physica Polonica A, vol.121 (2012) pp. 622-624

9. **Vladimir Stojanović**, Željka Nikitović and Zoran Lj. Petrović
On Anisotropy and Spatial Dependence of Doppler-Induced Broadening Due to Heavy-particle excitation
IEEE Transactions on Plasma Science, vol 39. No.11 (2011) pp.2592-2593

8. Željka Nikitović, **V. Stojanović** and M. Radmilović-Radjenović,
Transport Coefficients For Electrons in Mixtures $CF_4/Ar/O_2$ and CF, CF_2 or CF_3 Radicals,
Acta Physica Polonica A, vol.120 (2011) pp. 289-291

7. Ž. Nikitović and **V. Stojanović**
The influence of F, F_2 on electrons in BF_3
Hemijska industrija (2011) pp. 229-232
doi:10.2298/HEMIND110110014N

6.Ž. Nikitović, O. Šasić, Z. Raspopović, **V. Stojanović,** S. Radovanov, M. Mozetić and U. Cvelbar,
Modeling of Electron Kinetics in BF_3
Acta Physica Polonica A, vol.117(5) (2010) pp. 748-751

5.Ž. Nikitović, **V. Stojanović** and Z. Lj. Petrović
On the role of radicals in kinetics of plasma etchers in Ar/CF_4 mixtures
Acta Physica Polonica A, vol.115, (2009) pp. 765-767, IF=0.321

4**.** M. Radmilović-Rađenović, Z.Lj. Petrović, Ž. Nikitović, A. Strinić, **V. Stojanović**, A. Nina and B. Rađenović
Particle-in-cell Modelling of a Neutral Beam Source for Material Processing in Nanoscale Structures Fabrication
Materials Science Forum (2007) **555** pp.47-52,
(ISBN: 0-87849-405-7) (ISSN: 0255-5476).
online at http://www.scientific.net

3. M. Radmilović-Rađenović, A. Stojković, A. Strinić, **V. Stojanović**, Ž. Nikitović, G.N. Malović and Z.Lj. Petrović
Modeling of a plasma etcher for charging free processing of nanoscale structures
Materials Science Forum (2006) **518** pp.57-62,
(ISBN: 0-87849-405-7) (ISSN: 0255-5476).
online at http://www.scientific.net

2. Ž.D. Nikitović, A.I. Strinić, G.N. Malović, **V.D. Stojanović** and Z. Lj. Petrović
Modeling of absolute spatial emission profiles of Townsend discharges at high *E/N* in methane by a Monte Carlo technique.
Czech. J. Phys. (Suppl. B) (2006) **56**:B958-B962. IF=0.574

1. Zoran Petrović and **Vladimir Stojanović**
Anomalous Doppler broadening of Hydrogen lines due to excitation by fast neutrals in low pressure Townsend discharges
Mem. S.A.It. (2005) Vol. 7, 172

Радови у часописима међународног значаја верификованих посебном одлуком (М24)

Радови објављени након претходног избора у звање

3*.Ž.D. Nikitović, J.V. Jovanović, U. Cvelbar, M. Mozetić, V.D. Stojanović,
Modeling of the Effect of Radicals on Plasmas Used for Etching in Microelectronics
FME Transactions 44 (2016) 105-108, ISSN=1451-2092, doi:10.5937/fmet1601106N

2*.Z.M. Raspopović, V.D. Stojanović, U. Cvelbar, Ž.D. Nikitović, and J. V.Jovanović,
Role of Pressure in Transport of F- Ions in BF₃ Gas For Technological Applications
FME Transactions 43 (2015) 168-172, ISSN=1451-2092, doi:10.5937/fmet1502168R

1*.J.V. Jovanović, Z.M. Raspopović, V.D. Stojanović and Ž.D. Nikitović,
Transport of F- Ions in Gaseous Environment for Technological Applications
FME Transactions, 41 (2013) 163-166, ISSN=1451-2092

Предавања по позиву са међународних скупова штампана у целини (М31)

Радови објављени након претходног избора у звање

Радови објављени пре претходног избора у звање

1. Vladimir D. Stojanović
Modeling of Townsend discharges at high E/N and low pressure
Journal of Physics: Conference Series 133 (2008) 012008
24th Summer School and International Symposium on the Physics of Ionized Gases
edited by G. Malović, L. Č. Popović, M. S. Dimitrijević
August 25-29, 2008, Novi Sad, Serbia.

Предавања по позиву са међународних скупова штампана у изводу (М32)
Радови објављени након претходног избора у звање
1*.Vladimir Stojanović,
Denpoh-Nanbu Theory in Modelling Low Pressure Discharge
Contributed Papers & Abstracts of Invited Lectures, Topical Invited Lectures, Progress Reports and Workshop Lectures of the 28th Summer School and International Symposium on the Physics of Ionized Gases
The 4th International Workshop on Non-Equilibrium Processes (NonEqProc) (2016).
Издавач: Faculty of physics, University of Belgrade, Serbian Academy of Sciences and Arts, Belgrade, Serbia
(Ed.s. D. Marić, A. R. Milosavljević, B. Obradović, G. Poparić)
ISSN: нема, Serbia, Belgrade, од: 29.8.2016. до: 2. 9. 2016.
pp. 457-457

Радови објављени пре претходног избора у звање
1. V. Stojanović, Ž. Nikitović and Z. Lj. Petrović
Monte Carlo modeling of electrons and heavy particles in pure H₂ discharge
CEPAS 2011 & CEAMPP 2011 Ed. A. Milosavljević, S. Dujko, B. Marinković
5th Conference on Elementary Processes in Atomic Systems, Belgrade, Serbia, June 21-25, 2011, p.62

Саопштења са међународних скупова штампана у целини (М33)

Радови објављени након претходног избора у звање

Коауторска предавања по позиву

1*. Z.Lj. Petrović, **V. Stojanović**, N. Škoro, Ž. Nikitović, G. Malović, J. Sivoš, D. Marić
Development of fast neutral etching for integrated circuits and nanotechnologies fast neutrals in gas
Microelectronics Proceedings - MIEL 2014, 2014 29th International Conference
on, 12-14 May (2014) Belgrade, Serbia pp.17-24, ISBN: 978-1-4799-5295-3, DOI: 10.1109/MIEL.2014.6842079

2*.Zoran Lj. Petrović, Srđan Marjanović, Saša Dujko, Ana Banković, Olivera Šašić, Danko Bošnjaković, **Vladimir Stojanović**, Gordana Malović, Stephen Buckman, Gustavo Garcia, Ron White, James Sullivan and Michael Brunger
Kinetic Phenomena in Transport of Electrons and Positrons in Gases caused by the Properties of Scattering Cross Sections
XXVIII International Conference on Photonic, Electronic and Atomic Collisions (ICPEAC 2013) IOP Publishing,
The Institute of Modern Physics, Chinese Academy of Sciences (IMP)
(24-30 July, 2013 in Lanzhou, China)
J.Phys:Conf. Ser. 488 (2014) 012047 (9pp)
doi:10.1088/1742-6596/488/1/012047

3*.N. Škoro, D. Marić, **V. Stojanović**, J. Sivoš, G. Malović and Z. Lj. Petrović
Heavy-particle collisions in water vapour discharges at low pressures
Proceedings of the 23rd Europhysics Sectional Conference on the Atomic and Molecular Physics of Ionized Gases (ESCAMPIG)
(July 12-16, 2016, Bratislava, Slovakia)(2016)
Editors: V. Medvecká, P. Papp, J. Országh and Š. Matejčík). Izdavač:EPS.
pp.406-409

Радови саопштени на скуповима

4*.**V. Stojanović**, Z. Raspopović, D. Marić, and Z. Lj. Petrović
Cross sections and transport parameters of O^- ions in water vapour
XXVII SPIG, August 26-29, 2014, Belgrade, Serbia, ISBN 978-86-7762-600-6, Publisher: Institute of Physics,Belgrade & Klett izdavačka kuća d.o.o. (Ed.s. D. Marić, A. R. Milosavljević, Z. Mijatović) pp. 142-145

5*. Z. Raspopović, Ž. Nikitović, **V. Stojanović**, J. Jovanović and Z. Lj. Petrović
Modelling of F^- ions in Ar/BF_3 mixtures
XXVII SPIG, August 26-29, 2014, Belgrade, Serbia, ISBN 978-86-7762-600-6, Publisher: Institute of Physics,Belgrade & Klett izdavačka kuća d.o.o. (Ed.s. D. Marić, A. R. Milosavljević, Z. Mijatović) pp. 150-153

6*. Ž Nikitović, M. Gilić, Z. Raspopović, M. Petrović, M. Petrović and **V. Stojanović**
Cross section and transport parameters for K^+ in dimethoxyethane
XXVIII SPIG, August 29-September 2, 2016, Belgrade, Serbia, ISBN 978-86 -84539-14-6, Publisher: University of Belgrade, Faculty of Physics (Ed.s. D. Marić, A. R. Milosavljević, B. Obradović, G. Poparić) pp. 112-115

7*. Ž. Nikitović, Z. Raspopović and **V. Stojanović**
Transport properties of He$^+$ in CF$_4$
XXVIII SPIG, August 29-September 2, 2016,Belgrade, Serbia, ISBN 978-86-84539-14-6, Publisher: University of Belgrade, Faculty of Physics (Ed.s. D. Marić, A. R. Milosavljavić, B. Obradović, G. Poparić) pp. *116-119*

8*. **V. Stojanović**, J. Jovanović, D. Marić, and Z. Lj. Petrović
Cross sections for scattering and mobility of OH$^-$ and H$_3$O$^+$ ions in H$_2$O
XXVIII SPIG, August 29-September 2, 2016,Belgrade, Serbia, ISBN 978-86-84539-14-6, Publisher: University of Belgrade, Faculty of Physics (Ed.s. D. Marić, A. R. Milosavljavić, B. Obradović, G. Poparić) pp. *128-131*

9*. I. Stefanović, **V. Stojanović**, J. Jovanović, C. Pattya, S. Hussain, E. Kovačević and J. Berndt
Mass spectra analysis of RF nitrogen plasma for functionalization of carbon nanostructures
XXVIII SPIG, August 29-September 2, 2016, Belgrade, Serbia, ISBN 978-86-84539-14-6, Publisher: University of Belgrade, Faculty of Physics (Ed.s. D. Marić, A. R. Milosavljavić, B. Obradović, G. Poparić) pp. *272-275*

10*. **Vladimir Stojanović**, Nikola Škoro, Jelena Sivoš, Gordana Malović, Dragana Marić and Zoran Petrović
Modeling emission from water vapor dc discharge at low pressure
XXVIII SPIG, August 29-September 2, 2016, Belgrade, Serbia, ISBN 978-86-84539-14-6, Publisher: University of Belgrade, Faculty of Physics (Ed.s. D. Marić, A. R. Milosavljavić, B. Obradović, G. Poparić) pp. *328-331*

11*. Zoran M. Raspopović, Željka D. Nikitović, Sanja D. Tošić and **Vladimir D. Stojanović**
Cross section set and transport properties of Ne$^+$ in CF$_4$
Conference Program
ICPEAC 2015, XXIX International Conference on Photonic, Electronic, and Atomic Collisions
(22-28 JULY 2015 TOLEDO·SPAIN)
Edited by: Fernando Martín, Gustavo García, Luis Méndez, Luca Argenti, Alicia Palacios, WE-048 p.123
J. Phys. Conf. Series 635 (2015) 022099 doi:10.1088/1742-6596/635/2/022099

12*.Vladimir Stojanović, Zoran Raspopović, Željka Nikitović and Zoran Lj. Petrović,
Cross sections and transport parameters for F$^-$ ions in BF$_3$,
e-book abstracts:http:\icpig2013.net\buscador\index.html
31st International Conference on Phenomena in Ionized Gases (ICPIG),2013
Granada, Spain, од: 14.07.2013. до: 19.07.2013.
Editor: dr. F.J. Gordillo-Vasquez
PS4-007, 3pp.

13*. Nevena Puač,Vladimir Stojanović, Zoran Raspopović, Željka Nikitović, and Zoran Lj. Petrović,
Cross section set and transport properties for Ar$^+$ in CF$_4$,

Радови пре претходног избора у звање

Koautorska predavanja po pozivu

14. Z.Lj. Petrović, **V. Stojanović**, Ž. Nikitović
Electron, ion and atom collisions leading to anomalous Doppler Broadening in hydrogen
AIP Conf. Proc. -- September 28, 2007 -- Volume 938, pp. 237-244
SPECTRAL LINE SHAPES IN ASTROPHYSICS:
VIth Serbian Conference on Spectral Line Shapes in Astrophysics (VI SCSLSA)
June 11-15 2007, Sremski Karlovci, Serbia, eds. Milan S. Dimitrijević and Luka È. Popović
Online ISSN 1551-7616

15. Z. Lj. Petrović, Ž. Nikitović and **V. D. Stojanović**
MODELING OF ANOMALOUS DOPPLER BROADENED LINES, THERMALIZATION OF ELECTRONS AND THE ROLE OF RADICALS IN DISCHARGES AT HIGH E/N
Journal of Physics: Conference Series **133** (2008) 012003, elektronska publikacija 9. nov.2008, papirna kasnije
24th Summer School and International Symposium on the Physics of Ionized Gases
edited by G. Malović, L. Č. Popović, M. S. Dimitrijević
August 25-29, 2008, Novi Sad, Serbia.

16. Z. Lj. Petrović, S. Dujko, A. Banković, J. Jovanović, O. Šašić,
Ž. Nikitović, **V. Stojanović** and J. P. Marler
Electron and Position Swarms: Collision and Transport Data and Kinetic Phenomena
Proceedings of the Seventeenth International
Conference on GAS DISCHARGES AND THEIR APPLICATIONS
Cardiff University *7th – 12th September 2008*
Editor: J. E. Jones, D.Sc. pp. 71-80.

17. Z. Lj. Petrović, M. Radmilović-Rađenović, D. Marić, G. Malović, **V. Stojanović** and Ž. Nikitović
Basic Phenomena and Data for Modelling of Interactions Between Surfaces and Gas Discharges
6th solid states surfaces and interfaces **November 24-27**, 2008, Smolenice Castle, Slovak Republic, pp. 39-42.

18. Z. Lj. Petrović, S. Dujko, Ž. Nikitović, **V. Stojanović**, M. Savić, M. Radmilović-Rađenović, D. Marić, G. Malović and A. Banković

Theoretical foundations, numerical techniques and application of transport coefficients in modelling of plasmas and gas breakdown
(2009) *2nd International Conference On Advanced Plasma Technologies With 1st International Plasma Nanoscience Symposium*, sep 29th-Oct 2nd , Piran, Slovenia, Conference Proceedings, pp.28-31

19. Zoran Lj. Petrović, Saša Dujko, Olivera Šašić, **Vladimir Stojanović** and Gordana Malović,
Kinetic phenomena in charged paricle transport in gases and plasmas
AIP Conference Proceedings vol. 1438, pp. 17-22 (2012); doi: 10.1063/1.4707849
The 17th International Conference On Atomic Processes in Plasmas) ICAPiP

Radovi saopšteni na skupovima

20. **V. Stojanović** , Z.Lj. Petrović, J. Božin, B.M. Jelenković
Excitation of $C^3\Pi_u$ of N_2 and $B^2\Sigma_g^+$ of N_2^+ at high *E/N*,
(1988), SPIG 88, Sarajevo, Yugoslavia, Proc. Contrib. Papers p.124.

21. **V. Stojanović**, Z.Lj. Petrović, J. Božin, B.M. Jelenković
Excitation of $B^2\Omega_g^+$ of N_2^+ by electrons at high *E/N*
(1988), IX ESCAMPIG, Lisbon, Portugal, p.313.

22. J. Božin, **V. Stojanović**, Z.Lj. Petrović, B.M. Jelenković
Excitation coefficients for the $C^3\chi_u$ of N_2 and $B^2\Omega_g^+$ of N_2^+ at high electric fields to gas density ratios
(1989), ICPIG, Book of contributed papers, ed. J.M. Labat, Beograd, Yugoslavia, **3** 558.

23. **V. Stojanović**, J. Božin, Z. Stokić, Z. Petrović, B. Jelenković
Electron excitation coefficient for the a state of H_2 in discharges at high electric field to gas density ratio
(1990), Proc. SASP (Symposium on Atomic and surface Physics), Ed's T.D. Mark and F. Howorka, Obertaun, Austria p.160.

24. J. Božin, Z. Stokić, **V. Stojanović**, Z. Petrović, B. Jelenković
Electron Excitation Coefficients for the Continuous Spectrum of Deuterium
(1990), 17th EPS Fusion Conference Ed. G.Briffod, Adri Nijsen-Vis and Schuller Amsterdam, Holland, pp.1405-1408.

25. Z. Stokić, J.V. Božin, **V. Stojanović**, Z. Lj. Petrović, B.M. Jelenković
Electron Excitation of $a^3\Omega_g$ state of deuterium in D_2 discharges at moderate and high values of *E/N*
(1990) X ESCAMPIG 1990, Orleans, France, Ed. Prof. B. Dubreuil
Europhysics Conference Abstracts, **14E** 138.

26. Z. Stokić, **V. Stojanović**, J. Božin, Z. Petrović, B.M. Jelenković
Ionization and excitation by electrons in H_2 at moderate and high *E/N*
(1991), ICPIG, Ciocco, Italy, Contributed Papers 4, p.149.

27. B.M. Jelenković, Z. Stokić, **Vladimir Stojanović**, Zoran Petrović

Monte Carlo simulations of electron kinetics at high *E/N* in N$_2$
(1991), ISPC-10 (International Symposium on Plasma Chemistry), Bochum,
Germany, Ed.s Ute Ehlemann, H.G.Lergon and K.Wiesemann, p .3.2.24.

28. S.B. Radovanov , Z. Lj. Petrović, S.A. Bzenić, S.B. Vrhovac, **V. Stojanović**, B.M.
Jelenković
Spectroscopic studies of discharges in hydrogen
(1991), (International Symposium on Plasma Chemistry), Bochum, Germany, Ed.s
Ute Ehlemann, H.G.Lergon and K.Wiesemann, p. 2.1.14.

29. Z.Lj. Petrović, **V.D. Stojanović**
Monte Carlo simulation of electron kinetics at high *E/N*
(1992), Proc. Tenth International Conference on Gas Discharges and
their applications, vol. II, GD92, Swansea, UK, p.832.

30. **V.D. Stojanović**, Z.Lj. Petrović
**Monte Carlo simulation of emission in nitrogen taking into account simple
models of electron reflection and emission at anode boundary**
(1994), 6th APP and 11th AIPC, Brisbane, Australia, p.97.

31. **V.D. Stojanović**, Z. Lj. Petrović
Monte Carlo Simulation of Electron Transport at very High *E/N*
(1995) International Symposium on Electron and Photon- Molecule Collisions and
Swarms, ed. T. Rescigno, Berkeley, USA, H-5

32. **V.D. Stojanović**, Z.Lj. Petrović
Ar$^+$ swarms in argon at high *E/N*
(1996) Proc. 18th SPIG, Ed.s B. Vujičić and S. ourović, (Kotor, Yugoslavia) p.124.

33. **V.D. Stojanović**, B.M. Jelenković, Z.Lj. Petrović
Heavy particle excitation in nitrogen at very high *E/N*
(1996) Proc. 13th ESCAMPIG-96 (ed. P. Lukac, I. Kosinar, J. Skalny) (Poprad,
Slovakia) p.65. (1996) Europhysics conference abstracts **20E** 65.

34. V.D. Stojanović, Z.Lj. Petrović
**Arrival time spectrum of electron and ion avalanches at very high *E/n* in
nitrogen**
(1996) Proc. First Belarussian-Yugoslav symposium on Physics and Diagnostics of
Laboratory and Astrophysical Plasma PDP-I 96 (Ed. V.S. Burakov and M.S.
Dimitrijević) (Minsk, Belarus) p.35.

35. **V.D. Stojanović**, Z.Lj. Petrović
**The effect of reflection of fast electrons from the anode: Monte Carlo simulation
of low current discharges at very high *E/N***
(1997) XIII ICPIG, Toulouse, France, Proceedings Contributed Papers, Editors: M. C.
Bordage and A. Gleizes I-34.

36. **V. Stojanović**, Z.Lj. Petrović
**Monte Carlo simulation of non-equilibrium electron and heavy particle
transport at very high *E/N***

(1997) ICRP-3/SPP-14, Nara, Japan, VIb-5 p. 233.

37. Z.Lj. Petrović, **V.D. Stojanović**
Monte Carlo simulation of spatial line emission profiles in low current argon discharges at high *E/N*
(1997), International Symposium on Electron-Molecule Collisions and Ion and Electron Swarms, Ed. M. Allan, Engelberg, Switzerland P 64/1.

38. A.A. Mihajlov, **V.D. Stojanović**, Z.Lj. Petrović
Rate coefficients for resonant electron induced excitation between two vibrational levels of nitrogen
(1998), Proc. XIV ESCAMPIG 98, Malahide, Ireland, Europhys. Abstracts **22H** 96.

39. J. Spasojević, A. Strinić, **V.D. Stojanović**, Z.Lj. Petrović
Excitation of N_2 at very high *E/N* ratios
(1998), XIX SPIG, Zlatibor, Yugoslavia, Contributed Papers, ed. N.Konjević, M.Ćuk and I. Videnović pp.179-182.

40. A.A. Mihajlov, **V.D. Stojanović** and Z.Lj. Petrović
Resonant vibrational excitation of $N_2(v)$ by electrons
(1998), XIX SPIG, Zlatibor, Yugoslavia, Contributed Papers ed. N. Konjević, M. Ćuk and I. Videnović, pp.81-84.

41. Z.Lj. Petrović, **V. Stojanović**, M. Radmilović
The influence of electrons reflected from the anode on ionization
 (2000), XXth SPIG, Zlatibor, Yugoslavia, Contributed
 Papers, Editors: Z.Lj. Petrović, M.M. Kuraica, N. Bibić and G. Malović, p.131.

42. **V.D. Stojanović,** Z.Lj. Petrović
Validity of perturbation theory for ion transport at very high *E/N*
 (2002), 34th EGAS, Sofia, Bulgaria, P2-64.

43. J.V. Jovanović, S. Dujko, **V. Stojanović,** S.B. Vrhovac, Z.Lj. Petrović
Momentum transfer of ion transport under the influence of resonant charge transfer collisions: the   case of argon and neon ions in parent gases
(2002), Proc. 21st SPIG (Symposium on physics on ionized gases) Ed. M.K. Radović and M.S. Jovanović, Sokobanja, Yugoslavia, pp. 160-163.

44. **V. D. Stojanović**, Z.Lj. Petrović,
Non-hydrodinamic effects for N_2^+ ion transport close to the boundaries
(2003), Fifth General Conference of the Balkan Physical Union, BPU-5, *Proceedings*, Ed. S. Jokić, I. Milošević, A. Balaž and Z. Nikolić, 25-29. avgust, Vrnjačka Banja, Serbia and Montenegro,   content on CD-ROM , ISBN 86-902537-4-2

45. **V. D. Stojanović**, M. Radmilović-Rađenović, Z.Lj. Petrović,
Modelling of electron reflection from the anode
(2003), International Symposium on Electron-Molecule Collisions and Swarms, 30 July – 2 August, Pruhonice near Prague, Czech Republic.

46. A.I. Strinić, Ž.D. Nikitović, G.N. Malović, **V.D. Stojanović**, Z.Lj. Petrović
Modeling of spatial emission profiles of high E/N in neon by Monte Carlo technique
Seventeenth European Conference on Atomic & Molecular Physics of Ionized Gases (ESCAMPIG 17), edited by Victor Ciupina, Geavit Musa and Rodica Vladoiu, published by European Physical Society, Constanta-Romania, September 1-5 (2004) p. 90-91.

47. A. Strinić, Ž. Nikitović, **V.D. Stojanović**, G. Malović, Z.Lj. Petrović
Monte Carlo simulation Townsend discharges in neon
XXVIIth ICPIG, Eindhoven, the Netherlands (2005) 1-3.

48. J.V. Jovanović, Z.Lj. Petrović, Z.M. Raspopović, **V. Stojanović**
Cross sections and transport proprerties of Cl⁻ ions in Ar
2006, in 18th European Conference on The Atomic and Molecular Physics of Ionized Gases,
ESCAMPIG XVIII, Lecce, Italy, 225.

49. **V.D. Stojanović**, Z.Lj. Petrović
337.1 nm And 391.4 nm Emission as a Consequence of Electron Thermalization in Pure N_2
SPIG 2006, 23rd Summer School and International Symposium on the Physics of Ionized Gases, Kopaonik, Serbia, August 28 – September 1, 2006,
Contributed papers & Abstracts of Invited Lectures, Topical Invited lectures and progress reports, Editors, N.S. Simonović, B.P. Marinković and Lj. Hadžievski, p.101.

50. Zeljka Nikitović, Aleksandra Strinić, **Vladimir Stojanović**, Olivera Sasić, Gordana Malović, Zoran Lj. Petrović
Townsend Discharges in Methane at Very High E/N
SPIG 2006, 23rd Summer School and International Symposium on the Physics of Ionized Gases, Kopaonik, Serbia, August 28 – September 1, 2006,
Contributed papers & Abstracts of Invited Lectures, Topical Invited lectures and progress reports, Editors, N.S. Simonović, B.P. Marinković and Lj. Hadžievski, p139.

51. Ž.Nikitović, **V. Stojanović**, Z.Lj. Petrović
Electron transport in X/CF_4 mixtures (X=F,F_2,CF,CF_2,CF_3) and modelling of high E/N discharges in hydrogen
5th EU-Japan Joint Symposium on Plasma Processing, Editors: Z.Lj. Petrović, N. Mason, S. Hamaguchi, M. Radmilović-Rađenović, 7–9 March 2007, Zemun, Serbia, Po-3

52. J.V. Jovanović, Z.Lj. Petrović, Z.M. Raspopović, **V. Stojanović**
Cross Sections and Transport Properties of Negative Halogen Ions in Noble Gases
5th EU-Japan Joint Symposium on Plasma Processing, Editors: Z.Lj. Petrović, N. Mason, S. Hamaguchi, M. Radmilović-Rađenović, 7–9 March 2007, Zemun, Serbia, Po-6

53. Ž.Nikitović, G. Malović, A. Strinić, **V. Stojanović**, O. Šašić, Z.Lj. Petrović
Electron and fast neutral excitation in Townsend discharges in helium, neon, oxygen and methane
5th EU-Japan Joint Symposium on Plasma Processing, Editors: Z.Lj. Petrović, N. Mason, S. Hamaguchi, M. Radmilović-Rađenović, 7–9 March 2007, Zemun, Serbia, Po-9

54. Ž. Nikitović, **V. Stojanović**, Z. Lj. Petrović
Electron transport in X/CF$_4$ mixtures (X=F, F$_2$, CF, CF$_2$, CF$_3$) and modelling of high *E/N* discharges
XXVII International Conference on Phenomena in Ionized Gases, 15 - 20 July 2007, Prague, Czech Republic, pp.121-123, ISBN 978-80-87026-01-4

55. **V. D. Stojanović**, Ž. D. Nikitović and Z. Lj. Petrović
The effect of anisotropy of the scattering of heavy particles on modeling of the Doppler profile in pure H$_2$ discharge
24rd Summer School and International Symposium on the Physics of Ionized Gases, August 25- 29, 2008, Novi Sad, Serbia (2008) pp.87-91

56. **V. D. Stojanović**, Z. M. Raspopović, J. V. Jovanović, Ž. D. Nikitović and Z. Lj. Petrović
Electron detachment of H$^-$ ions in hydrogen discharge
24rd Summer School and International Symposium on the Physics of Ionized Gases, August 25- 29, 2008, Novi Sad, Serbia (2008) pp.91-95

57. Ž. D. Nikitović,**V. D. Stojanović** and Z. Lj. Petrović
Modelling of high *E/N* in mixtures of CF$_4$ and its radicals
24rd Summer School and International Symposium on the Physics of Ionized Gases, August 25- 29, 2008, Novi Sad, Serbia (2008) pp.103-107

58. Petrović Z. Lj., Jovanović J. V., **Stojanović V.**
Cross sections and transport properties of negative bromine ions in Kr and Xe
17th International Conference on Gas discharges and their applications, 2008, GD2008, Cardiff, *7th – 12th September 2008*
Editor: J. E. Jones, D. Sc. pp. 577-580.

59. Zoran Lj. Petrović, **Vladimir Stojanović**, Željka Nikitović
Modeling of Fast Neutral Transport in Low Pressure Discharges
The 7th EU-Japan Joint Symposium on Plasma Processing 23rd to 26th April 2009, Chateau Liblice, Liblice, Czech Republic, p. 25

60. Ž. Nikitović, M. Radmilović-Rađenović, **V. Stojanović** and Z. Lj. Petrović
Modeling of the effect of radicals on plasmas used for etching in microelectronics
(2009), 29th ICPIG, July 12-17, 2009, Cancún, México, Conference Proceedings on CD ROM PA5-4

61. Ž. Nikitović, **V. Stojanović**, N. Puač, and Z.Lj. Petrović
Transport coefficients for electron scattering in mixtures of CF$_4$, Ar and O$_2$

(2009) ISPC 19, International Symposium on Plasma Chemistry, Book of Abstracts, p.338
Ed. A. von Keudell, J. Winter, M. Boke, V. Schulz-von der Gathen, July 27-31, 2009, Ruhr-University, Bochum, Germany, Conference Proceedings on CD ROM P2.2.15

62. **Vladimir D. Stojanović**, Željka D. Nikitović and Zoran Lj. Petrović,
Effect of Anode Surface on Doppler Profile in Townsend discharge in Pure Hydrogen
AIP Conf. Proc. 1203, 318 (2010); doi:10.1063/1.3322458
7th General Conference of the Balkan Physical Union BPU-7 (2009), 9-13. september, Alexandroupolis, Greece

63. Ž. Nikitović, **V. Stojanović** and Z. Lj. Petrović
Modelling of discharges at high *E/N* in mixtures of CF$_4$, O$_2$ and Ar
(2009) 2nd International Conference On Advanced Plasma Technologies With 1st International Plasma Nanoscience Symposium, sep 29th-Oct 2nd , Piran, Slovenia, Conference Proceedings, pp.140-142.

64. Ž. D. Nikitović,**V. D. Stojanović**, Z. Lj. Petrović, Uroš Cvelbar and Miran Mozetič
The influence of F$_2$ molecules on kinetics of electrons in BF$_3$
3rdInternational Conference on Advanced Plasma Technologies, Slovenia, Bohinj, Jun 14th-16th, 2010, p.63-65

65. Željka Nikitović, **Vladimir Stojanović**, Zoran Lj. Petrović, Uroš Cvelbar, Miran Mozetič, Svetlana Radovanov
Electron kinetics in mixtures in BF$_3$ and F$_2$
20th Europen Conference on the Atomic and Molecular Physics of Ionized Gases, Novi Sad, Serbia, 13-17 July 2010., 2-52.

66. **Vladimir Stojanović,** Željka Nikitović, Zoran Lj. Petrović
Monte Carlo modeling of electrons and heavy particles in pure H$_2$ discharge
20th Europen Conference on the Atomic and Molecular Physics of Ionized Gases, Novi Sad, Serbia, 13-17 July 2010., 2-53.

67. Željka Nikitović, **Vladimir Stojanović**, and Zoran Lj. Petrović
Transport coefficients for electron scattering in mixtures of CF$_4$,Ar and O$_2$
25thSummer School and International Symposium on the Physics of Ionized Gases, August 30- September 3, 2010, Donji Milanovac, Serbia Publ. Astron. Obs. Belgrade No. 89 (2010) 75-78 ISSN 0373-3742

68. **V. Stojanović**, Ž. Nikitović, Z. Lj. Petrović
Modeling particle energy distribution functions in Ar/H$_2$ discharge
30th ICPIG
August 28th – September 2nd 2011, Belfast, Northern Ireland, UK, A2-243.

69. Ž. Nikitović, **V. Stojanović,** Z. Lj. Petrović
Modeling in Ar/H$_2$ discharge
*21th Europen Conference on the Atomic and Molecular Physics of Ionized Gases (ESCAMPIG),*Viana do Castelo, Portugal, July 10-14, 2012 P1.1.8.

70. **V. Stojanović**, Z. M. Raspopović, J. Jovanović, Ž. Nikitović, Z. Lj. Petrović
Detachment rate for negative ions in Ar/BF₃ discharges
*21ᵗʰ Europen Conference on the Atomic and Molecular Physics of Ionized Gases (ESCAMPIG),*Viana do Castelo, Portugal, July 10-14, 2012 P2.1.5.

71. Ž. Nikitović, **V. Stojanović** and Z. Lj. Petrović
MONTE CARLO SIMULATIONS INAr/H₂ MIXTURES
26th Summer School and International Symposium on the Physics of Ionized Gases
August 27th -31st, 2012, Zrenjanin Serbia, Editors: Milorad Kuraica
Zoran Mijatović, ISBN 978-86-7031-242-5, S3.22, 223-227

72. **V. Stojanović**, Z. Raspopović, J. Jovanović, Ž.Nikitović, Z. Lj. Petrović
TRANSPORT OF F⁻ IONS IN F₂
26th Summer School and International Symposium on the Physics of Ionized Gases
August 27th -31st, 2012, Zrenjanin Serbia, Editors: Milorad Kuraica
Zoran Mijatović, ISBN 978-86-7031-242-5, S3.51, 341-345

73. **V. Stojanović**, J. Sivoš, D. Marić, N.Škoro, Z. Lj. Petrović
MONTE CARLO SIMULATION OF ELECTRON TRANSPORT IN H₂O VAPOUR
26th Summer School and International Symposium on the Physics of Ionized Gases
August 27th -31st, 2012, Zrenjanin Serbia, Editors: Milorad Kuraica
Zoran Mijatović, ISBN 978-86-7031-242-5, S3.51, 35-38

Саопштења са међународних скупова штампана у изводу (М34)

Радови објављени након претходног избора у звање
Коауторство предавања по позиву у изводу

3*. Zoran Lj. Petrović**,** Nevena Puač,Dragana Marić, Saša Dujko, Saša Gocić, Željko Mladenović, **Vladimir Stojanović** and Gordana Malović
Data and modeling of discharges containing water vapour
ISPC 23, July 31th to August 4th, 2017, Montreal, Canada

2*. N. Škoro, D. Marić, **V. Stojanović**, J. Sivoš, G. Malović and Z. Lj. Petrović
Heavy-particle processes in low-pressure water vapour discharge
28th Summer School and International Symposium on the Physics of Ionized Gases (August 29-September 2, 2016, Belgrade, Serbia)(2016)

1*. Z.Lj. Petrović, S. Marjanović, S. Dujko, A. Banković, O. Šašić, D. Bošnjaković, **V. Stojanović,** G. Malović, S. J. Buckman, G. Garcia, R. D. White, J. P. Sullivan, M. J. Brunger
XXVIII International Conference on Photonic, Electronic and Atomic Collisions (ICPEAC), 24-30 July 2013, Lanzhou, China

Саопштено на скуповима

2017

32*. V. Stojanović, J. Jovanović, I. Stefanović, E. Kovačević, J. Berndt, D.Marić, Z.Lj. Petrović,
Rate coefficients for reactive processes of water impurity ions in N_2
BOOK OF ABSTRACTS
XX International Symposium on Electron-Molecule Collisions and Swarms
(22-24 July, Amaroo on Mandalay Resort, Magnetic Island, Queensland, Australia)(2017)
Editors: James Sullivan, Michael Bromley, David Cassidy, Ilya Fabrikant, Ron White
PST41, pp.98

31*. V. Stojanović, D.Marić, J. Jovanović, Z.Lj. Petrović,
Mobility of H_2O^+ in water vapour
BOOK OF ABSTRACTS
XX International Symposium on Electron-Molecule Collisions and Swarms
(22-24 July, Amaroo on Mandalay Resort, Magnetic Island, Queensland, Australia)
(2017)
Editors: James Sullivan, Michael Bromley, David Cassidy, Ilya Fabrikant, Ron White
PST40, pp.97

30*.Željka Nikitović, Zoran Raspopović, and Vladimir Stojanović
Transport properties of Ar^+ in Ar/CF_4 mixtures for technological applications
Programme and The Book of Abstracts
NINETEENTH ANNUAL CONFERENCE YUCOMAT, 2017,
Издавач: Materials Research Society of Serbia
Editors: prof. dr Dragan Uskoković and dr Velimir Radmilović
Herceg Novi, Montenegro, од: 04.09.2017. до: 08.09.2017.
P.S.B.5., pp. 59

29*. **V. Stojanović**, J. Jovanović, D. Marić and Z. Lj. Petrović
Cross sections and mobility of H_2O^+ ions in H_2O
COST Action TD1208, International Conference on Plasmas With Liquids (ICPL2017),
CONFERENCE PROGRAM BOOK OF ABSTRACTS
March 5-9 2017, Prague, Czech Republic, pp 39

28*. Željka Nikitović, **Vladimir Stojanović**, Zoran Raspopović, and Zoran Lj. Petrović,
Transport Parameters of Ar+ ions Mixtures Ar/CF_4
70th Annual Gaseous Electronics Conference
(06.11.2014 - 10.11.2014, 2017, Pittsburgh, Pennsylvania, USA)
http://meetings.aps.org/Meeting/GEC17/Session/GT1.59   Topic number r

2016
27*. Vladimir Stojanović, Željka Nikitović, Nikola Škoro and Zoran Raspopović
Reduced mobility of He^+ in CF_4
Proceedings of the 23rd Europhysics Conference on the Atomic and Molecular Physics of Ionized Gases. Bratislava: European Physical Society as a Europhysics conference, 2016.
Editors: V. Medvecká, P. Papp, J. Országh and Š. Matejčík). Izdavač:EPS-
ISBN 979-10-96389-02-5.

23rd Europhysics Sectional Conference on the Atomic and Molecular Physics
of Ionized Gases (ESCAMPIG) (July 12-16, 2016, Bratislava, Slovakia)(2016)
P02-06-05

26*. Željka D. Nikitović, Zoran M. Raspopović, **Vladimir D. Stojanović**,
Monte Carlo simulations of He$^+$ in CF$_4$
Programme and The Book of Abstracts
EIGHTEENTH ANNUAL CONFERENCE YUCOMAT, 2016,
Издавач: Materials Research Society of Serbia
Editors: prof. dr Dragan Uskoković and dr Velimir Radmilović
од: 05.09.2016. до: 10.09.2016. Herceg Novi, Montenegro
P.S.A.21., pp. 81

25*. J. Jovanović, Z. Raspopović, **V. Stojanović**, J. Jovanović, D. Marić and Z. Lj.
Petrović
Mobility of OH- and H$_3$O$^+$ ions in H$_2$O
COST Action TD1208, International Conference on Electrical Discharges With
Liquids (ICEDL2016),
Editors: Arif Demir, Elşen Veli, Elif Kaçar, Hayriye S. Pamuk, Jale Y. Süngü
13-17 March 2016, Kocaeli University, Turkey, pp 51

24*. Zoran Lj. Petrović, **Vladimir Stojanović**, Nikola Škoro, Jelena Sivoš, Dragana
Marić and Gordana Malović
*Effects of Electrons and Heavy Particles on Halpha Emission in Pure H$_2$O DC
Discharge at High E/N (E-Electric Field, N-Gas Density)*
69th Annual Gaseous Electronics Conference (GEC)
(October, 10-14, 2016, Bochum, Germany)
Bul. Am. Phys. Soc., Series II, Volume 61, No 9, pp.73-73, ISSN: 0003-0503
http://meetings.aps.org/link/BAPS.2016.GEC.MW6.47

23*. Z.Lj. Petrović, **V. Stojanović**, J. Jovanović, and D. Marić
Transport parameters for positive ions in pure H$_2$O DC discharge
69th Annual Gaseous Electronics Conference (GEC)
(October, 10-14, 2016, Bochum, Germany)
Bul. Am. Phys. Soc., Series II, Vol. 61, No 9, pp.70-71, ISSN: 0003-0503
http://meetings.aps.org/link/BAPS.2016.GEC.MW6.34

2015
22*.Nebojša Romčević, Milica Petrović, Martina Gilić, **Vladimir Stojanović**, Željka
Nikitović and Zoran Raspopović,
*Cross sections and transport properties for alkali metal ions with dimethoxyethane
(DXE)*
ADVANCED CERAMICS AND APPLICATIONS IV, 2015,
Издавач: Serbian Ceramic Society
Editors: Vojislav Mitić, Olivera Milošević, Lidija Mančić, Nina Obradović,
Belgrade, Serbia, од: 21.09.2015. до: 23.09.2015.
P25, од стр. 74 до стр. 74

21*.**Vladimir Stojanović**, Željka Nikitović and Zoran Lj. Petrović,

Modelling light emission from DC discharge tube filled with CH$_4$ gas
4th International Conference on the Physics of Optical Materials and Devices, ICOM2015, Book of Abstracts
Издавач: Institut za nuklearne nauke Vinča
Editors: dr Miroslav Dramićanin, dr Bruno Viana, dr Rachid Mahiou
ISBN: 978-86-7306-134-4
Budva, Montenegro, од: 31.08.2015. до: 04.09.2015.
P4-45-439, од стр. 298 до стр. 298

20*.Željka Nikitović, Zoran Raspopović and **Vladimir Stojanović**,
Transport parameters of Ne$^+$ in CF$_4$ for technological applications
SEVENTEENTH ANNUAL CONFERENCE YUCOMAT, 2015,
Издавач: Materials Research Society of Serbia
Editors: prof. dr Dragan Uskoković and dr Velimir Radmilović
Herceg Novi, Montenegro, од: 31.08.2015. до: 04.09.2015.
P.S.A.12., од стр. 60 до стр. 60

19*.Milica Petrović, Martina Gilić, **Vladimir Stojanović**, Željka Nikitović, Zoran Raspopović, Nebojša Romčević,
The kinetic energy dependence of association reactions for alkali metal ions with dimethoxyethane
SEVENTEENTH ANNUAL CONFERENCE YUCOMAT, 2015,
Издавач: Materials Research Society of Serbia
Editors: prof. dr Dragan Uskoković and dr Velimir Radmilović
Herceg Novi, Montenegro, од: 31.08.2015. до: 04.09.2015.
P.S.A.8., од стр. 58 до стр. 58

18*.Zoran M. Raspopović, Željka D. Nikitović, Sanja Tošić, **Vladimir D. Stojanović**,
Cross section set and transport properties of Ne$^+$ in CF$_4$
ICPEAC, 2015,
Editors: Fernando Martín, Gustavo García, Luis Méndez, Luca Argenti, Alicia Palacios
Toledo, Spain, од: 22.07.2015. до: 28.07.2015.
WE-048 од стр.123 до стр.123

17*.**Vladimir Stojanović**, Zoran Raspopović, Jasmina Jovanović, Željka Nikitović,
Transport parameters of Ar$^+$ in CF$_4$,
Book of Abstracts
XIX International Symposium on Electron-Molecule Collisions and Swarms, POSMOL 2015,
(од: 17.07.2015. до: 21.07.2015, Lisboa, Portugal)
Editors: Paulo Limão-Vieira, Filipe Ferreira da Silva, Guilherme Meneses, Emanuele Lange, Tiago Cunha
E52, од стр. 76 до стр.76
ISBN: 978-989-20-5845-0,

16*. **V. Stojanović**, Z. Raspopović, D. Marić and Z. Lj. Petrović
Cross Sections and Transport Properties of OH$^-$ ions in H$_2$O
COST Action TD1208, 2nd Annual Meeting
Electrical Discharges with Liquids for Future Applications

15*.Željka Nikitović, **Vladimir Stojanović**, Zoran Raspopović, Jasmina Jovanović and Zoran Lj. Petrović,
Mobility of Ar$^+$ in CF$_4$
68th Annual Gaseous Electronics Conference/9th International Conference on Reactive Plasmas/33rd Symposium on Plasma Processing
(12.10.2015 - 16.10.2015, 2015, Honolulu, Hawaii, USA)
Bul. Am. Phys. Soc., vol. 60, No 9 (2015) ISSN: 0003-0503
http://meetings.aps.org/link/BAPS.2015.GEC.GT1.85

2014
14*. Srđan Marjanović, Zoran Raspopović, Željka Nikitović, Vladimir Stojanović and Zoran Lj. Petrović
Mobility of H$^+$ ions in water monomer gas
Europhysics Conference Abstract Booklet
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13*. Srđan Marjanović, Zoran Raspopović, Željka Nikitović, Vladimir Stojanović and Zoran Lj. Petrović

Transport parameters of F$^-$ ions in mixtures Ar/BF$_3$
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12*.Dragana Marić, Jelena Sivoš, Nikola Škoro, **Vladimir Stojanović**, Srđan Marjanović, Ana Banković, Saša Dujko, Gordana Malović and Zoran Petrović
Atomic and molecular processes of interest for modeling of discharges in liquids
6th Conference on Elementary Processes in Atomic Systems – CEPAS 2014
Contributed Papers
(July 9th - 12th, 2014, Bratislava, Slovakia) (2014)
Editors: Š. Matejčik, P. Papp, O. Bogar
pp.121-DA122

11*. Željka Nikitović, **Vladimir Stojanović**, Zoran Raspopović, Jasmina Jovanović and and Zoran Lj. Petrović,
Transport Parameters of F$^-$ ions Mixtures Ar/BF$_3$
67th Annual Gaseous Electronics Conference
(02.11.2014 - 07.11.2014, 2014, Raleigh, North Carolina, USA)
Bul. Am. Phys. Soc., vol. 59, No 9, pp.41-41 (2014) ISSN: 0003-0503
http://meetings.aps.org/link/BAPS.2014.GEC.MW1.12

10*. Vladimir Stojanović, **Nenad Ivanović**, Marija Radmilović-Rađenović, Zoran Raspopović, Aleksandar Bojarov and Zoran Petrović,
Transport properties of negative ions in HBr plasmas
67th Annual Gaseous Electronics Conference
(02.11.2014 - 07.11.2014, 2014, Raleigh, North Carolina, USA)
Bul. Am. Phys. Soc., vol. 59, No 9, pp.42-42 (2014) ISSN: 0003-0503
http://meetings.aps.org/link/BAPS.2014.GEC.GT1.54

9*. Jasmina Jovanović, **Vladimir Stojanović**, Zoran Raspopović and Zoran Petrović,
Cross Sections and Transport Properties of Br^- ions in Ar
67th Annual Gaseous Electronics Conference
(02.11.2014 - 07.11.2014, 2014, Raleigh, North Carolina, USA)
Bul. Am. Phys. Soc., vol. 59, No 9, pp.64-64 (2014) ISSN: 0003-0503
http://meetings.aps.org/link/BAPS.2014.GEC.GT1.49

2013
8*. **V. Stojanović**, Z. Raspopović, J. Jovanović, J. Urquijo, Z. Lj. Petrović,
Cross secton set for CF_3^+ ions in CF_4
Programme and Book of Abstracts
XVIII International Symposium on Electron-Molecule Collisions and Swarm
POSMOL 2013
(19-21 July, 2013, Kanazawa, Japan)
Editors: Y. Nagashima et al.
POSMOL, E-27, p.67

7*. **V. Stojanović,** Z. Raspopović, J. Jovanović, Ž. Nikitović, Z. Lj. Petrović
Cross sections and non-equilibrium rate coefficients for F^- ions in BF_3
5th Central European Symposium on Plasma Chemistry, Balatonalmadi, Hungary, 25-29 August 2013, ISBN 978-615-5270-04-8, editors: R. Hohol and Z. Heiszler, P-FUN7, p. 114

6*. **V. Stojanović**, Z. Raspopović, J. Jovanović, Ž. Nikitović and Z. Lj. Petrović
Transport Properties of Fluorine Ions in BF_3
66th Annual Gaseous Electronics Conference
(September 30 - October 4, 2013, Princeton, New Yersey, USA)
Bul. Am. Phys. Soc., Series II, Vol. 58, No. 8 (2013) ISSN: 0003-0503
http://meetings.aps.org/link/BAPS.2013.GEC.CT1.22

5*.**V. Stojanović**, N. Škoro, D. Marić, Z. Raspopović and Z. Lj. Petrović
Kinetics of charged particles in CF_4 at high values of reduced electric field
66th Annual Gaseous Electronics Conference
(September 30 - October 4, 2013; Princeton, New Jersey, USA)
Bul. Am. Phys. Soc., series II, vol. 58, No. 8 (2013) ISSN: 0003-0503
http://meetings.aps.org/link/BAPS.2013.GEC.CT1.5

4*.**V. Stojanović**, Z. Raspopović, J. Jovanović, J. Urquijo, and Z. Lj. Petrović,
Mobility of positive ions in CF_4
18th International summer School on Vacuum, Electron and Ion Technologies
(7-11 October 2013, Sozopol, Bulgaria) (2013)

Радови објављени пре претходног избора у звање

Коауторска предавања по позиву

6. Z. Lj. Petrović, G. Malović, O. Šašić, J. Jovanović, Ž. Nikitović, **V. Stojanović**, S. Dujko, A. Banković and J de Urquijo
ELECTRON AND POSITRON SWARMS: COLLISION AND TRANSPORT DATA AND KINETIC PHENOMENA
Chemical physics of low temperature plasmas (31 Jan- 2 Feb 2011, Bari, University of Bari)

5. Z. Lj. Petrović, S. Dujko, J. Jovanović, O. Šašić, S. Dupljanin, G. Malović, Ž. Nikitović, **V. Stojanović**, A. Banković
Kinetic phenomena and data for cross sections for electrons, positrons and negative ions in ionized gases
21 Symposium on Plasma Science for Materials
October 8-11, 2008, Huangshan, China, p.49.

4. Z. Lj. Petrović, Ž. Nikitović and **V. D. Stojanović**
Modeling of anomalous doppler broadened lines, thermalization of electrons and the role of radicals in discharges at high E/N
CONTRIBUTED PAPERS & ABSTRACTS OF INVITED LECTURES, TOPICAL INVITED LECTURES AND PROGRESS REPORTS
24th Summer School and International Symposium on the Physics of Ionized Gases edited by G. Malović, L. Č. Popović, M. S. Dimitrijević
August 25-29, 2008, Novi Sad, Serbia, p. 14.

3. Z. Lj. Petrović, D. Marić, Ž. Nikitović, C. M. O. Mahony, P. D. Maguire, M. Radmilović-Rađenović, N. Škoro and **V. Stojanović**
Voltampere Characteristics of Low Current Micro Discharges and Transport Coefficients in CF_x/CF_4 Mixtures
The 6th EU-Japan Joint Symposium on Plasma Processing (EU-Japan JSPP)
April 21-23, 2008, Okinawa, Japan, pp. 16-17.

2. Z. Lj. Petrović, J. Jovanović, O. Šašić, Ž. Nikitović, **V. Stojanović**, S. Dujko, A. Banković, J. P. Marler, G. Malović
Transport of Charged Particles and Fast Neutrals in Low Pressure Gases and Discharges
Second Workshop&Training School on Low Cost Applications of Plasma Technology in Industry and Environment 10-15 November 2007, Al-Azhar University, Nasr City, Cairo, Egypt .

1. Nikitović Ž. D., Strinić A. I., Radmilović-Rađenović M. D., Malović G. N., **Stojanović V. D.,** Šamara V. M., Petrović Z. Lj.
Heavy particle excitation and delay distance in oxygen
22nd Summer School and International Symposium on the Physics of Ionized Gases, August 23-27, 2004, Tara, Serbia and Montenegro (2004) pp.145-149.

Радови саопштени на скуповима

48. Ž. Nikitović, **V. Stojanović**, Z. Lj. Petrović
TRANSPORT COEFFICIENTS IN MIXTURES Ar/H$_2$
FOURTEENTH ANNUAL CONFERENCE YUCOMAT 2012, editor: prof. Dr Dragan Uskoković
Herceg Novi, September 3-7, 2012, P.S.A.31., p.65

47. **Vladimir Stojanović**, Željka Nikitović, Zoran Raspopović, Jasmina Jovanović, Svetlana Radovanov, Zoran Petrović
Rate Coefficients for Ion Production by Electrons and Ions in BF$_3$ Gas
64th Annual Gaseous Electronics Conference
November 15-18, 2011, Salt Lake City, Utah, USA p.62 MR2 4
Bul. Am. Phys. Soc. Vol. 56 No.15 (2011) ISSN: 0003-0503

46. **Vladimir Stojanović**, Željka Nikitović, Zoran Petrović
Electron Transport in Ar/H$_2$ Mixtures
64th Annual Gaseous Electronics Conference
November 15-18, 2011, Salt Lake City, Utah, USA p.34 FTP1 34
Bul. Am. Phys. Soc. Vol. 56 No.15 (2011) ISSN: 0003-0503

45. **Vladimir Stojanović**, Željka Nikitović, Zoran Petrović
Anisotropy of H$_\alpha$ Lines in Low Current Discharges in H$_2$ Discharges at High *E/N*
64th Annual Gaseous Electronics Conference
November 15-18, 2011, Salt Lake City, Utah, USA p.71 PR2 5
Bul. Am. Phys. Soc. Vol. 56 No.15 (2011) ISSN: 0003-0503

44. **V. Stojanović**, Ž. Nikitović and Z.Lj. Petrović
Heavy Particle Contribution to Doppler Profile in Ar/H$_2$ Mixture
XVII International Symposium on Electron Molecule Collisions and Swarms
(ed. P. van der Burgt, National University of Ireland Maynooth) 22-25 July 2011
Maynooth, Ireland p. 81.

43. **V. Stojanović**, Z. Raspopović, J. Jovanović, Ž. Nikitović, S. Radovanov and Z.Lj. Petrović
Transport Properties of Positive Ions in BF$_3$ Plasmas
XVII International Symposium on Electron Molecule Collisions and Swarms
(ed. P. van der Burgt, National University of Ireland Maynooth) 22-25 July 2011
Maynooth, Ireland p. 82.

42. **V. Stojanović**, Ž. Nikitović, Z. Lj. Petrović
MODELLING OF ELECTRONS AND HEAVY PARTICLES IN PURE H$_2$ DISCHARGE
The Thertheent Annual Conference "YUCOMAT", Book of Abstracts Editor: Prof. dr Dragan P. Uskoković, September 5-September 9, 2011 Herceg-Novi, Montenegro (2011) [P.S.B.18.] 36.

41. **V. Stojanović**, Z. Raspopović, J. Jovanović, S. Radovanov, Ž. Nikitović, and Z. Lj. Petrović
Transport properties of positive ions in BF$_3$ plasmas

CEPAS 2011 & CEAMPP 2011 Ed. A. Milosavljević, S. Dujko, B. Marinković
5th Conference on Elementary Processes in Atomic Systems, Belgrade, Serbia, June 21-25, 2011, p.67.

40. Z. Lj. Petrović ,**V. Stojanović** and Ž. Nikitović
Doppler Broadening induced by fast heavy particles in molecular hydrogen
42nd Annual Meeting of the APS Division of Atomic, Molecular and OpticalPhysics
Volume 56, Number 5, June 13–17, 2011, Atlanta, Georgia (2011) Q1.00056

39. Zoran Petrović, Željka Nikitović, Svetlana Radovanov, **Vladimir Stojanović**
Modeling of heavy particle collisions in high E/N discharges in helium
63rd Annual Gaseous Electronics Conference and 7thInternational Conferenceon
Reactive Plasmas *Volume 55, No. 7*
October 4–8, 2010, Paris, France (2010) p.59 DTP13

38. Ž. Nikitović, **V. Stojanović** and Z. Lj. Petrović
Transport coefficients in mixtures $CF_4/Ar/O_2$
The Twenth Annual Conference "YUCOMAT", Book of Abstracts, Editor: Prof. dr
Dragan P. Uskoković, September 6-September 10, 2010 Herceg-Novi, Montenegro
(2010) [P.S.B.35.] 195.

37. Zoran Petrović, **Vladimir Stojanović**, Željka Nikitović
Role of anisotropic particle scattering in hydrogen Townsend discharge
Division of Atomic &Molecular Physics and Photonic Interactions
May 25-29, 2010, Hyatt Regency hotel, Houston, Texas, p.53 E1 150

36. Željka Nikitović, **Vladimir Stojanović** and Zoran Lj. Petrović
Time resolved H emission in pure hydrogen discharge
Frontiers in Low Temperature Plasma Diagnostics 8
19th - 23th April 2009, Blansko, Czech Republic, p. 73

35. Ž. Nikitović, **V. Stojanović** and Z. Lj. Petrović,
TRANSPORT COEFFICIENTS IN MIXTURES BF_3, F_2 AND F
The Eleventh Annual Conference "YUCOMAT", Book of Abstracts, Editor: Prof. dr
Dragan P. Uskoković 31 August - 4 September 2009, Herceg-Novi, Montenegro
(2009) [P.S.A.41] 105.

34. Željka Nikitović, **Vladimir Stojanović**, Zoran Petrović
Transport Coefficients and Cross Section Set for Electron Scattering in mixtures CF_4, Ar and O_2
62nd Annual Gaseous Electronics Conference
October 20-23, 2009, Saratoga Springs, New York, USA p.77 URP 9
Bul. Am. Phys. Soc. Vol. 54 No.12 (2009) ISSN: 0003-0503

33. Zoran Lj. Petrović, Željka Nikitović, Olivera Šašić, Zoran Raspopović,**Vladimir Stojanović**, Svetlana Radovanov
Transport Coefficients for Electrons in BF_3
62nd Annual Gaseous Electronics Conference
October 20-23, 2009, Saratoga Springs, New York, USA p.22 GT1 6
Bul. Am. Phys. Soc. Vol. 54 No.12 (2009) ISSN: 0003-0503

32. **V. Stojanović**, Ž. Nikitović, Z.Lj. Petrović, Z.Raspopović and J. Jovanović
Effects of H⁻ ions produced at the surface in Townsend discharge
 (2009) XI International Symposium on Electron-molecule Molecule Collisions and Swarms, BOOK OF ABSTRACTS, 29.july-1.avgust, York University, Toronto, Canada, p.59

31. **Vladimir D. Stojanović**, Željka D. Nikitović and Zoran Lj. Petrović,
Effect of anode surface on Doppler profile in Townsend discharge in pure hydrogen
(2009), *7th General Conference of the Balkan Physical Union,* BPU-7, Book of Abstracts, 9-13. september, Alexandroupolis, Greece, p.65

30. Željka Nikitović, **Vladimir Stojanović** and Zoran Lj. Petrović
Time resolved Hα emission in pure hydrogen discharge
Frontiers in Low Temperature Plasma Diagnostics 8
Book of Abstracts, 19th - 23th April 2009, Blansko, Czech Republic, p. 73

29. **Vladimir Stojanović**, Željka Nikitović, Zoran Petrović
Arrival Time Spectra of Heavy Particles in Hydrogen Discharge
61st Annual Gaseous Electronics Conference
October 13-17, 2008, Dallas, Texas USA p.40 FTP1 104
Bul. Am. Phys. Soc. Vol. 53 No.10 (2008) ISSN: 0003-0503

28. **Vladimir Stojanović**, Željka Nikitović, Zoran Petrović
Thermalization of High Energy Electrons in Nitrogen
61st Annual Gaseous Electronics Conference
October 13-17, 2008, Dallas, Texas USA p.40 FTP1 98
Bul. Am. Phys. Soc. Vol. 53 No.10 (2008) ISSN: 0003-0503

27. Ž. Nikitović, **Vladimir Stojanović**, Z. Lj. Petrović,
The role of radicals in kinetics of plasma etchers in Ar/CF$_4$ mixtures
The Tenth Yugoslav Materials Research Society Conference "YUCOMAT", Book of Abstracts, Editor: Prof. dr Dragan P. Uskoković 8-12 September 2008, Herceg-Novi, Montenegro (2008) [P.S.B.16] 105

26. **Vladimir D. Stojanović**
Modeling of Townsend discharges at high E/N and low pressure
CONTRIBUTED PAPERS & ABSTRACTS OF INVITED LECTURES, TOPICAL INVITED LECTURES AND PROGRESS REPORTS
24th Summer School and International Symposium on the Physics of Ionized Gases
edited by G. Malović, L. Č. Popović, M. S. Dimitrijević,
August 25-29, 2008, Novi Sad, Serbia, p. 20

25. Zoran Lj. Petrović, Olivera Šašić, Zoran Raspopović, Željka Nikitović, **Vladimir Stojanović**, Svetlana Radovanov, Ludovic Godet
Transport coefficients for electrons in BF$_3$
19th Europhysics Conference on the Atomic and Molecular Physics of Ionized Gases, Granada, Spain, 15-19 July 2008., 3-80.

24. O. Šašić, Z. Raspopović, Ž. Nikitović, **V. Stojanović** and Z. Lj. Petrović
Modelling electron kinetics in BF$_3$
4th Conference on Elementary Processes in Atomic Systems Cluj-Napoca, Romania, June 18-20, 2008., We-9.

23. Ž. Nikitović, **V. Stojanović** and Z. Lj. Petrović
Electron Transport in X/CF$_4$ Mixtures (X=F, F$_2$, CF, CF$_2$, CF$_3$)
23rd Symposium on Plasma Physics and Technology
June 16-19. 2008. Prague, Czech Republic, p. 109

22. **V.D. Stojanović**, Ž.D. Nikitović, Z.Lj. Petrović,
Modelling Hα emission in Hydrogen by Monte Carlo simulation
15th International Symposium on Electron Molecule Collisions and Swarms & XIV International Workshop on Low Energy Positron and Positronium Physics, August 1-4, 2007, University of Reading, United Kingdom, p.69

21. Željka Nikitović, **Vladimir Stojanović**, Zoran Petrović
Transport Coefficients and Cross Section Set for Electron Scattering in mixtures CF$_4$ and CF$_2$
60th Annual Gaseous Electronics Conference
October 2-7, 2007, Arlington, Virginia p.42 MWP1 29
Bul. Am. Phys. Soc. Vol. 52 No.8 (2007) ISSN: 0003-0503

20. **Vladimir Stojanović**, Željka Nikitović, Zoran Petrović
Hα emission in pure hydrogen Townsend discharge obtained by a Monte Carlo simulation
60th Annual Gaseous Electronics Conference
October 2-7, 2007, Arlington, Virginia p.27 FTP1 39.
Bul. Am. Phys. Soc. Vol. 52 No.8 (2007) ISSN: 0003-0503.

19**.** M. Radmilović-Radjenović, Z.Lj. Petrović, Ž. Nikitović, A. Strinić, **V. Stojanović**, A. Nina, B. Radjenović
Particle-in-Cell Modeling of a Neutral Beam Source for Material Processing in Nanoscale Structures Fabrication
The Eighth Yugoslav Materials Research Society Conference "YUCOMAT", Book of Abstracts, Editor: Prof. dr Dragan P. Uskoković 4-8 September 2006, Herceg-Novi, Serbia (2006) [P.S.A.4.] 66

18. Željka Nikitović, Aleksandra Strinić, **Vladimir Stojanović**, Olivera Šašić, Gordana Malović, Zoran Petrović
Townsend discharge in Methane at Very High E/N
59th Annual Gaseous Electronics Conference, October 10-13, 2006, Ohio State, USA, (2006) Bul. Am. Phys. Soc. Vol. 51 No.5, p.70.

17. Zoran Petrović, **Vladimir Stojanović**
Monte Carlo simulation of Hα emission in hydrogen Townsend discharge
59th Annual Gaseous Electronics Conference, October 10-13, 2006, Ohio State, USA, (2006) Bul. Am. Phys. Soc. Vol. 51 No.5, p.64.

16. Zoran Petrović, **Vladimir Stojanović**

Monte Carlo simulation of 337.1 nm and 391.4 nm emission due to the electron thermalization in Nitrogen.
59th Annual Gaseous Electronics Conference, October 10-13, 2006, Ohio State, USA (2006) Bul. Am. Phys. Soc. Vol. 51 No.5, p.24.

15. Ž. D. Nikitović, A. I. Strinić, G. N. Malović, **V. D. Stojanović**, O. M. Šašić, Z. Lj. Petrović
Modeling of Spatial Emission of High E/N in Methane by Monte Carlo Technique
22nd SYMPOSIUM ON PLASMA PHYSICS AND TEHNOLOGY
June 26-29, 2006, Praha, Czech Republic, p. 50.

14. A. Stojković, Ž. Nikitović, A. Strinić, **V. Stojanović**, M. Radmilović-Rađenović, Z.Lj. Petrović
Modelling of a plasma etcher for charging free processing of nanoscale structures
The Seventh Yugoslav Materials Research Society Conference "YUCOMAT", Book of Abstracts, Editor: Prof. dr Dragan P. Uskoković 12-16 September 2005, Herceg-Novi, Serbia and Montenegro [P.S.C.24.] (2005) 150.

13. Ž. Nikitović, A. Strinić, G. Malović, **V.D. Stojanović**, Z. Petrović
Monte Carlo simulations of low current Townsend discharges in Neon
14th International Symposium on Electron – Molecule Collisions and Swarms, Ed: Sergio d A. Sanchez, Romarly F. da Costa, Marco A. Lima, Campinas, Brazil (2005) p.78 .

12. Željka D. Nikitović, Aleksandra I. Strinić, **Vladimir D. Stojanović**, Zoran Lj. Petrović
Townsend discharges in neon at very high E/N
57th Annual Gaseous Electronics Conference
September 26-29 (2004) Bunratty, Ireland, p.26
(2004) Bul. Am. Phys. Soc. 49 (5) (2004) 26 ES1 37.

11. **V. D. Stojanović**, Z.Lj. Petrović,
Non-hydrodinamic effects for N_2^+ ion transport close to the boundaries
(2003), Fifth General Conference of the Balkan Physical Union, BPU-5, Book of Abstracts, Ed. S. Jokić, I. Milošević, A. Balaž and Z. Nikolić, 25-29. avgust, Vrnjačka Banja, Serbia and Montenegro, p. [SP08-003] p.208   ISBN 86-902537-4-2

10. M. Radmilović-Rađenović, Z.Lj. Petrović, **V. Stojanović**
Reflection of Electrons from the Anode
July (2001) International Symposium on Electron-Molecule Collisions and Swarms, Lincoln NE USA pp. 126-127.

9. S. Vrhovac, **V.D. Stojanović**, B.M. Jelenković, Z.Lj. Petrović
Electron energy distribution function in N_2 Townsend discharge - measurements and Monte Carlo simulations
 (1998), Proc. 51st GEC (Gaseous Electronics Conference) and 4th ICRP (International Conference on Reactive Plasmas), Maui,USA, (1998) Bull.Am.Phys. Soc. 1469 **43** (JTP7 1).

8. **V. Stojanović**, B.M. Jelenković, Z.Lj. Petrović
Excitation by Electrons and fast neutrals in N₂ discharges at high *E/N*
(1996) Proc. 49th GEC, Argonne, USA, MPB-12, (1996) Bull. Am.Phys. Soc. **41**
1296.

7. Z.Lj. Petrović, **V.D. Stojanović**, B.M. Jelenković, A.V. Phelps
Monte Carlo simulations of electron kinetics at very high *E/N*
(1992), IEEE International Conference on Plasma Science, Tampa, Florida, USA,
6B1- 176.

M52. Rad publikovan u nacionalnom časopisu (vrednost rezultata=1.5)

2. Ž. D. Nikitović, **V. D. Stojanović** and Z. Lj. Petrović
Određivanje elektronskih transportnih koeficijenata za smeše BF₃ sa F i F₂
NOVI MATERIJALI 19 (2010) **6**, pp.1-4

1. Ž. Nikitović, **V. Stojanović** and Z. Lj. Petrović
Elektronski transportni koeficijenti za smešu CF₄ sa F i F₂
NOVI MATERIJALI 17 (2008) **6**, pp.1-5 (YU ISSN 0354-2300)

M63. Радови саопштени на скуповима националног значаја штампани у целини (вредност резултата=0.5)

Радови објављени након претходног избора у звање

1*.Ж.Д. Никитовић и **В.Д. Стојановић**
ЕЛЕКТРОНСКИ ТРАНСПОРТНИ КОЕФИЦИЈЕНТИ ЗА СМЕШУ Ar/H₂
 XII Конгрес физичара Србије,
(28.април-2.мај, 2013, Врњачка Бања, Србија)
Уредници: Јарослав Лабат, Никола Цветановић, Иван Дојчиновић
p.345-350 (ISBN 978-86-86169-08-2)

Радови објављени пре претходног избора у звање

14. Željka Nikitović,**Vladimir Stojanović** i Zoran Lj. Petrović
Uticaj F₂ na transportne koeficijente u smešama sa CF₄ i BF₃
Zbornik radova 54. Konferencije ETRAN, Društvo za ETRAN, Institut IMTEL
Beograd, Donji Milanovac 7-10. juna (2010) NM1.4

13. Željka D. Nikitović, **Vladimir D. Stojanović** i Zoran Lj. Petrović
TRANSPORTNI KOEFICIJENTI ZA RASEJANJE ELEKTRONA U SMEŠAMA CF₄ , CF₂ I F₂
(2009) in Zbornik radova 51. Konferencije za ETRAN, Vrnjačka Banja, Serbia, June
15-18.

12. Željka Nikitović, **Vladimir Stojanović**, Olivera Šašić, Zoran Raspopović i Zoran
Lj. Petrović

ODREĐIVANJE TRANSPORTNIH KOEFICIJENATA U SMEŠI BF₃ I F₂
Palić, 8-12. juna (2008) NM 1.8

11. Željka Nikitović, **Vladimir Stojanović,** Olivera Šašić, Zoran Raspopović i Zoran Lj. Petrović
Modeling of Nonequilibrium Townsend Transport Coefficients for Electrons in BF₃ and F₂ mixtures
1ˢᵗNational Conference on Electronic, Atomic, Molecular and Photonic Physics Ed. Aleksandar R. Milosavljević, Dragutin Šević and Bratislav P. Marinković, Zaječar, 15-18. maja (2008) pp.49-53

10. Željka Nikitović, **Vladimir Stojanović**, Olivera Šašić i Zoran Lj. Petrović
Transportni koeficijenti i preseci za rasejanje elektrona u smesama CF₃ i CF₄
 (2007), in Zbornik radova 51. Konferencije za ETRAN.

9. Željka Nikitović, Aleksandra Strinić, **Vladimir Stojanović**, Olivera Šašić, Gordana Malović i Zoran Petrović
Modelovanje neravnotežnog Townsendovog pražnjenja u metanu
(2006), in Zbornik radova 50. Konferencije za ETRAN, ed. M. Milošević, Z. Jakšić, N. Mitrović, i V. Potkonjak No. IV, Beograd, pp. 241-244

8. Željka Nikitović, Aleksandra Strinić, **Vladimir Stojanović**, Gordana Malović i Zoran Petrović
Uticaj refleksije elektrona sa anode na prostornu zavisnost emisije u Taunzendovom pražnjenju,
Zbornik radova 49. Konferencije za ETRAN, Ed. Miodrag Milošević, Zoran Jakšić, Dušan Božić, Veljko Potkonjak, Budva, 5-10. juna 2005. tom IV, pp.109-111. (predavanje)

7. Ž.D. Nikitović, A.I. Strinić, G.N. Malović, **V.D. Stojanović** i Z.Lj. Petrović
Modelovanje u neonu na visokim vrednostima *E/N*
Kongres fizičara Srbije i Crne Gore, Petrovac na Moru, 3-5. jun 2004. p. 3-111-114.

6. A. Strinić, J.V. Spasojević, **V.D. Stojanović** i Z. Lj. Petrović
Eksperimentalna provera ekscitacije teškim česticama
 (2000) 10. Kongres fizičara Jugoslavije, Vrnjačka Banja p. 603.

5. J.V. Spasojević, A. Strinić, **V. Stojanović** i Z.Lj. Petrović
Razdvajanje doprinosa elektrona i teških čestica u ekscitaciji na visokim *E/N*
(1997) Elektron Sto godina od otkrića; Vol. 7 Zbornik saopštenja (Ed. M.V. Kurepa) Zavod za udžbenike i nastavna sredstva, Beograd pp. 89-92.

4. **V. Stojanović** i Z. Lj. Petrović
Neravnotežni transport elektrona na veoma visokim *E/N*
(1997) Elektron Sto godina od otkrića; Vol. 7 Zbornik saopštenja (Ed. M.V. Kurepa) Zavod za ud〉benike i nastavna sredstva, Beograd pp. 77-80.

3. **V.D. Stojanović** i Z. Lj. Petrović
Monte Carlo simulacija neravnotežnog transporta elektrona u azotu

(1995), IX kongres fizičara, Petrovac na Moru, p.125.

2. **V. Stojanović** , J. Božin, Z. Lj. Petrović i B.M. Jelenković
Odreπivanje ekscitacionog koeficijenta u gasovima u zavisnosti od odnosa električnog polja i gustine gasa
(1989) VI Jugoslavenski skup iz fizike atomskih sudara (Brioni,Yugoslavia) p.14.

M64. Saopštenja sa skupa nacionalnog značaja štampana u izvodu (vrednost rezultata=0.2)

5.**Vladimir Stojanović**, Željka Nikitović i Zoran Lj. Petrović
Transport elektrona u Ar/H$_2$ smeši
Zbornik apstrakta i program 55. Konferencije ETRAN, Društvo za ETRAN, Institut IMTEL Beograd, Banja Vrućica 6-9. juna (2011) NM1.4, p. 55

4.Željka Nikitović,**Vladimir Stojanović** i Zoran Lj. Petrović
Uticaj F$_2$ na transportne koeficijente u smešama sa CF$_4$ i BF$_3$
Zbornik apstrakta i program 54. Konferencije ETRAN, Društvo za ETRAN, Institut IMTEL Beograd, Donji Milanovac 7-10. juna (2010) NM1.4, p. 59

3.Željka Nikitović,**Vladimir Stojanović** i Zoran Lj. Petrović
TRANSPORTNI KOEFICIJENTI ZA RASEJANJE ELEKTRONA U SMEŠAMA CF$_4$, CF$_2$ I F$_2$
Zbornik apstrakta i program 53. Konferencije ETRAN, Ed. Zoran Jakšić, Zorica Nikolić, Veljko Potkonjak, Vrnjačka Banja, 15-18. juna (2009) NM1.2-1-4, p. 62

2. Željka Nikitović, **Vladimir Stojanović**, Olivera Šašić, Zoran Raspopović i Zoran Lj. Petrović
ODREĐIVANJE TRANSPORTNIH KOEFICIJENATA U SMEŠI BF$_3$ I F$_2$
Program i zbornik apstrakta 52. Konferencije ETRAN
Palić, 8-12. juna (2008) NM 1.8, p. 56

1. Željka Nikitović, **Vladimir Stojanović**, Olivera Šašić i Zoran Lj. Petrović
TRANSPORTNI KOEFICIJENTI I PRESECI ZA RASEJANJE ELEKTRONA U SMEŠAMA CF$_3$ I CF$_4$
PROGRAM I ZBORNIK APSTRAKTA 51. KONFERENCIJE ZA ETRAN, HERCEG NOVI-IGALO, 4-8. JUNA (2007) NM 1.3, P.56

M70. МАГИСТАРСКА ТЕЗА I DOKTORSKA ДИСЕРТАЦИЈА

Одбрањена докторска дисертација (М71(вредност резултата=6))

1. Моделовање Таунзендових пражњења на високом E/N и ниском притиску, Владимир Д. Стојановић, Електротехнички факултет, Универзитет у Београду, Београд, Србија (март 2008).

Одбрањена магистарски рад (М72(вредност резултата=3))

1. Електронски ексцитациони коефицијенти за побуђена стања азота на средњим и високим вредностима E/N (E - електрично поље, N - густина гаса), В. Стојановић, Електротехнички факултет Универзитета у Београду (април 1992).

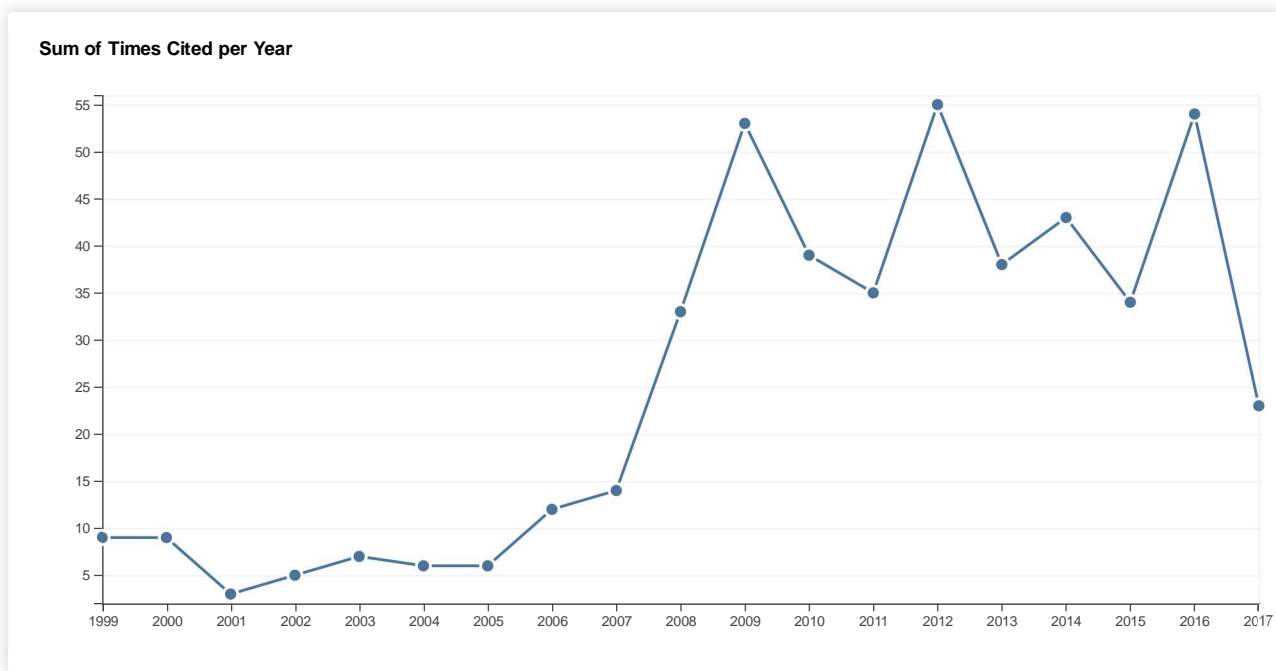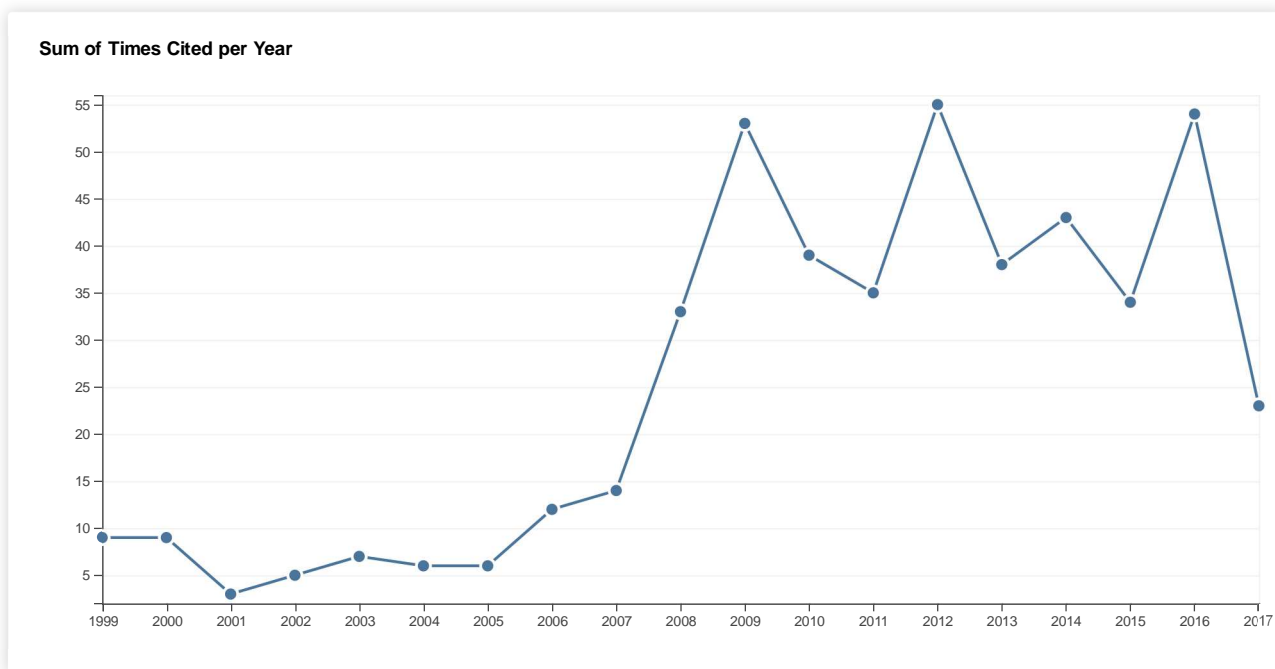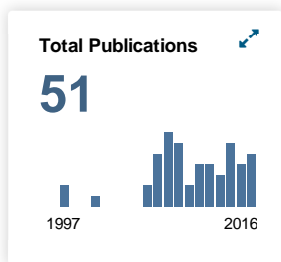| Web of Science | InCites | Journal Citation Reports | Essential Science Indicators | EndNote | Publons | | Vladimir ▼ | Help | English ▼ |

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1. **Measurement and interpretation of swarm parameters and their application in plasma modelling** By: Petrovic, Z. Lj; Dujko, S.; Maric, D.; et al. JOURNAL OF PHYSICS D-APPLIED PHYSICS Volume: 42 Issue: 19 Article Number: 194002 Published: OCT 7 2009	17	13	19	10	0	109	12.11
2. **Kinetic phenomena in charged particle transport in gases, swarm parameters and cross section data**	4	1	6	3	0	74	6.73

By: Petrovic, Z. Lj; Suvakov, M.; Nikitovic, Z.; et al.
Conference: 18th European Sectional Conference on Atomic and Molecular Physics of Ionized Gases Location: Lecce, ITALY Date: JUL 12-16, 2006
PLASMA SOURCES SCIENCE & TECHNOLOGY   Volume: 16   Issue: 1   Pages: S1-S12   Published: FEB 2007

3. **Comparison of the results of Monte Carlo simulations with experimental data for electron swarms in N-2 from moderate to very high electric field to gas density ratios (E/N)**

By: Stojanovic, VD; Petrovic, ZL
JOURNAL OF PHYSICS D-APPLIED PHYSICS   Volume: 31   Issue: 7   Pages: 834-846   Published: APR 7 1998

3	0	1	1	0	63	3.15

4. **The role of heavy particles in kinetics of low current discharges in argon at high electric field to gas number density ratio**

By: Petrovic, ZL; Stojanovic, VD
Conference: International Workshop on Basic Aspects of Nonequilibrium Plasmas Interacting with Surfaces (BANPIS 97) Location: SHIRAHAMA, JAPAN Date: JAN 26-27, 1997
Sponsor(s): USAF, Off Sci Res, Asian Off Aerosp Res & Dev; Japan Soc Appl Phys
JOURNAL OF VACUUM SCIENCE & TECHNOLOGY A-VACUUM SURFACES AND FILMS   Volume: 16   Issue: 1   Pages: 329-336   Published: JAN-FEB 1998

2	0	1	0	0	62	3.10

5. **Data and modeling of negative ion transport in gases of interest for production of integrated circuits and nanotechnologies**

By: Petrovic, Z. Lj.; Raspopovic, Z. M.; Stojanovic, V. D.; et al.
Conference: 4th International Workshop on Basic Aspects of Non-Equilibrium Plasmas Interacting with Surface Location: Mt Fuji, JAPAN Date: JAN 30-FEB 01, 2006
Sponsor(s): 21st Century Ctr Excellence; Keio Univ; Open Univ, Ctr Atomic & Mole Engn; Japan Soc Appl Phys
APPLIED SURFACE SCIENCE   Volume: 253   Issue: 16   Pages: 6619-6640   Published: JUN 15 2007

4	6	7	1	0	41	3.73

6. **Energy distributions of electrons in a low-current self-sustained nitrogen discharge**

By: Vrhovac, SB; Stojanovic, VD; Jelenkovic, BM; et al.
JOURNAL OF APPLIED PHYSICS   Volume: 90   Issue: 12   Pages: 5871-5877   Published: DEC 15 2001

0	1	1	1	0	21	1.24

7. **Cross sections and transport properties of Cl- ions in noble gases**

By: Petrovic, Z. Lj.; Jovanovic, J. V.; Stojanovic, V.; et al.
EUROPEAN PHYSICAL JOURNAL D   Volume: 48   Issue: 1   Pages: 87-94   Published: JUN 2008

2	1	0	1	0	17	1.70

8. **Electron transport coefficients in mixtures of CF4 and CF2 radicals**

By: Nikitovic, Zeljka D.; Stojanovic, Vladimir D.; Booth, Jean Paul; et al.
PLASMA SOURCES SCIENCE & TECHNOLOGY   Volume: 18   Issue: 3   Article Number: 035008   Published: AUG 2009

0	0	2	2	0	14	1.56

9. **Cross sections and transport properties of positive ions in BF3 plasmas**

By: Stojanovic, V. D.; Raspopovic, Z. M.; Jovanovic, J. V.; et al.
Conference: 5th International Conference on Elementary Processes in Atomic Systems (CEPAS) Location: Belgrade, SERBIA Date: JUN 21-25, 2011
Sponsor(s): Univ Belgrade, Inst Phys; Serbian Acad Sci & Arts (SASA); Republ Serbia, Minist Educ & Sci; Serbian Phys Soc; Serv Cooperat dact culturelle Ambassade France Serbie; Osterreichisches Kulturforum Belgrad
NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH SECTION B-BEAM INTERACTIONS WITH MATERIALS AND ATOMS   Volume: 279   Pages: 151-154   Published: MAY 15 2012

2	3	0	1	0	8	1.33

10. **On the Role of Radicals in Kinetics of Plasma Etchers in Ar/CF4 Mixtures**

By: Nikitovic, Z.; Stojanovic, V.; Petrovic, Z. Lj.
Conference: 10th Annual Conference of the Materials-Research-Society-of-Serbia Location: Herceg Novi, MONTENEGRO Date: SEP 08-12, 2008
Sponsor(s): Mat Res Soc Serbia
ACTA PHYSICA POLONICA A   Volume: 115   Issue: 4   Pages: 765-767   Published: APR 2009

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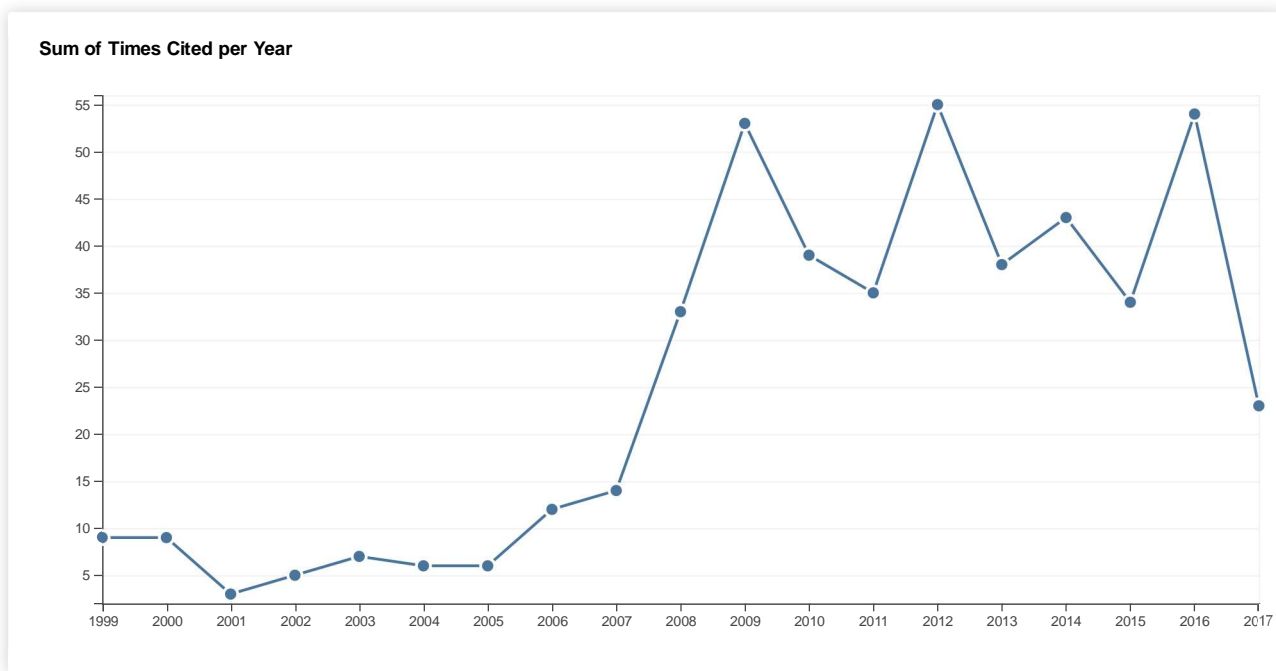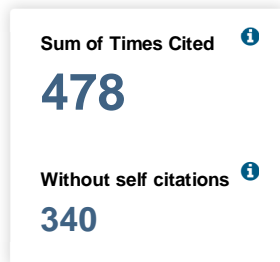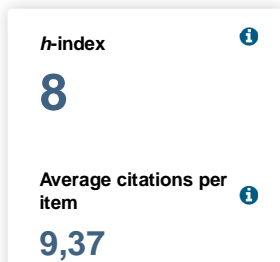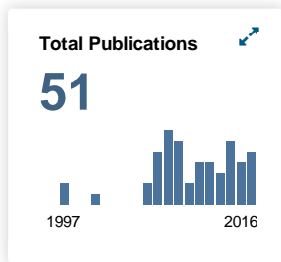
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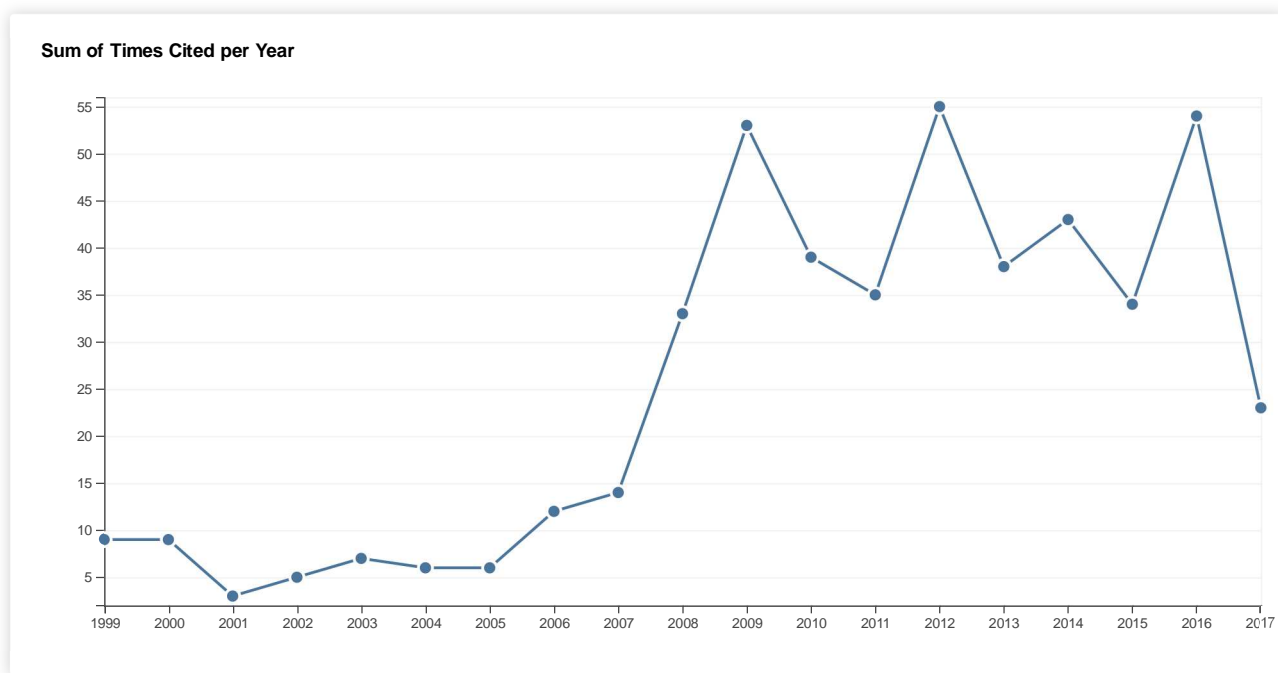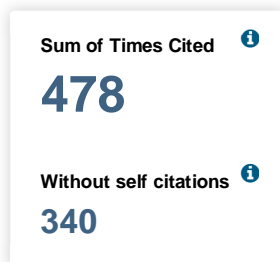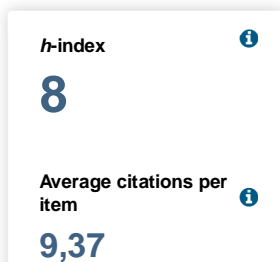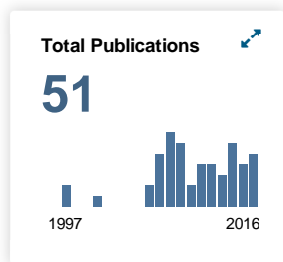**Search**   My Tools ▼   Search History   Marked List   **51**

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11. **Transport parameters of F- ions in Ar/BF3 mixtures**							
By: Nikitovic, Z.; Raspopovic, Z.; Stojanovic, V.; et al. EPL Volume: 108 Issue: 3 Article Number: 35004 Published: NOV 2014	0	1	4	0	0	5	1.25

☐	12.	**Mobility of positive ions in CF4**						
✅		By: Stojanovic, V.; Raspopovic, Z.; Jovanovic, J. V.; et al. Edited by: VandeSanden, MCM; Dimitrova, M; Ghelev, C Conference: 18th International Summer School on Vacuum, Electron and Ion Technologies (VEIT) Location: Sozopol, BULGARIA Date: OCT 07-11, 2013 Sponsor(s): Dutch Inst Fundamental Energy Res; Inst Elect; Bulgarian Acad Sci; AllData; Astel; Minist Educ & Sci Republ Bulgaria 18TH INTERNATIONAL SUMMER SCHOOL ON VACUUM, ELECTRON AND ION TECHNOLOGIES (VEIT2013) Book Series: Journal of Physics Conference Series Volume: 514 Article Number: 012059 Published: 2014	0	3	2	0	0	5	1.25
☐	13.	**Ion mobilities and transport cross sections of daughter negative ions in N2O and N2O-N-2 mixtures**						
✅		By: de Urquijo, J.; Jovanovic, J. V.; Bekstein, A.; et al. PLASMA SOURCES SCIENCE & TECHNOLOGY Volume: 22 Issue: 2 Article Number: 025004 Published: APR 2013	0	1	3	0	0	5	1.00
☐	14.	**Cross sections and transport of O- in H2O vapour at low pressures**						
✅		By: Stojanovic, Vladimir; Raspopovic, Zoran; Maric, Dragana; et al. EUROPEAN PHYSICAL JOURNAL D Volume: 69 Issue: 3 Article Number: 63 Published: MAR 6 2015	0	2	1	1	0	4	1.33
☐	15.	**On Anisotropy and Spatial Dependence of Doppler-Induced Broadening Due to Heavy-Particle Excitation**						
✅		By: Stojanovic, Vladimir; Nikitovic, Zeljka; Petrovic, Zoran Lj IEEE TRANSACTIONS ON PLASMA SCIENCE Volume: 39 Issue: 11 Special Issue: SI Pages: 2592-2593 Part: 1 Published: NOV 2011	1	0	0	0	0	4	0.57
☐	16.	**Measurements and modeling of electron energy distributions in the afterglow of a pulsed discharge in BF3**						
✅		By: Nikitovic, Z.; Radovanov, S.; Godet, L.; et al. EPL Volume: 95 Issue: 4 Article Number: 45003 Published: AUG 2011	2	0	0	0	0	4	0.57
☐	17.	**Modeling of Electron Kinetics in BF3**						
✅		By: Nikitovic, Z.; Sasic, O.; Raspopovic, Z.; et al. Conference: 11th Annual Conference of the Materials-Research-Society- of-Serbia (YUCOMAT 2009) Location: Heroeg Novi, MONTENEGRO Date: AUG 31-SEP 04, 2009 Sponsor(s): Mat Res Soc Serbia ACTA PHYSICA POLONICA A Volume: 117 Issue: 5 Pages: 748-751 Published: MAY 2010	2	0	0	0	0	4	0.50
☐	18.	**A Monte Carlo simulation of collisional processes in a Townsend discharge in neon**						
✅		By: Nikitovic, Zeljka D.; Strinic, Aleksandra I.; Stojanovic, Vladimir D.; et al. Conference: 3rd Conference on Elementary Processes in Atomic Systems Location: Univ Miskole, Miskole, HUNGARY Date: AUG 31-SEP 02, 2005 Sponsor(s): Univ Miskole, Dept Phys; European Phys Soc RADIATION PHYSICS AND CHEMISTRY Volume: 76 Issue: 3 Pages: 556-560 Published: MAR 2007	0	0	0	0	0	4	0.36
☐	19.	**Transport Parameters of F- Ions in BF3**						
✅		By: Nikitovic, Z.; Stojanovic, V.; Raspopovic, Z.; et al. ACTA PHYSICA POLONICA A Volume: 126 Issue: 3 Pages: 724-726 Published: SEP 2014	0	0	3	0	0	3	0.75
☐	20.	**Transport of F- ions in F-2**						
✅		By: Stojanovic, V.; Raspopovic, Z.; Jovanovic, J.; et al. EPL Volume: 101 Issue: 4 Article Number: 45003 Published: FEB 2013	1	0	2	0	0	3	0.60

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☐ 21. **Transport coefficients for electron scattering in CF4/Ar/O-2 mixtures with a significant presence of F-x or CFx radicals** By: Nikitovic, Z.; Stojanovic, V.; Petrovic, Z. Lj; et al. EPL Volume: 91 Issue: 5 Article Number: 55001 Published: SEP 2010	0	0	0	0	0	3	0.38

22. **Kinetic Phenomena in Transport of Electrons and Positrons in Gases caused by the Properties of Scattering Cross Sections**

By: Petrovic, Zoran Lj; Marjanovic, Srdan; Dujko, Sasa; et al.
Book Group Author(s): IOP
Conference: 28th International Conference on Photonic, Electronic and Atomic Collisions (ICPEAC) Location: Chinese Acad Sci, Inst Modern Phys, Lanzhou, PEOPLES R CHINA Date: JUL 24-30, 2013
Sponsor(s): Natl Nat Sci Fdn China; Chinese Acad Sci; Int Union Pure & Appl Phys; Inst Modern Phys; Youth Innovat Promot Assoc, Inst Modern Phys
XXVIII INTERNATIONAL CONFERENCE ON PHOTONIC, ELECTRONIC AND ATOMIC COLLISIONS (ICPEAC)   Book Series: Journal of Physics Conference Series   Volume: 488   Article Number: UNSP 012047   Published: 2014

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23. **Modeling of thermalization of fast electrons in nitrogen at low pressures**

By: Petrovic, Z. Lj; Stojanovic, V.; Nikitovic, Z.
Conference: 19th European Sectional Conference on Atomic and Molecular Physics of Ionized Gases Location: Granada, SPAIN Date: JUL 15-19, 2008
Sponsor(s): Spanish Natl Res Council (CSIC)
PLASMA SOURCES SCIENCE & TECHNOLOGY   Volume: 18   Issue: 3   Article Number: 034017   Published: AUG 2009

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24. **Cross-sections and transport properties of F- ions in Ar, Kr and Xe**

By: Jovanovic, J. V.; Petrovic, Z. Lj.; Stojanovic, V.
Conference: 4th Conference on Elementary Processes in Atomic Systems Location: Cluj Napoca, ROMANIA Date: JUN 18-20, 2008
Sponsor(s): Babes Bolyai Univ, Fac Phys; Hungarian Acad Sci, Inst Nucl Res
NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH SECTION B-BEAM INTERACTIONS WITH MATERIALS AND ATOMS   Volume: 267   Issue: 2   Pages: 295-298   Published: JAN 2009

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25. **Electron, ion and atom collisions leading to anomalous Doppler broadening in hydrogen**

By: Petrovic, Zoran Lj.; Stojanovic, Vladimir D.; Nikitovic, Zeljka D.
Edited by: Popovic, LC; Dimitrijevic, MS
Conference: 6th Serbian Conference on Spectral Line Shapes in Astrophysics Location: Sremski Karlovci, SERBIA Date: JUN 11-15, 2007
Sponsor(s): Minist Sci; Inst Mihailo Pupin; PORTAL; ITESON
SPECTRAL LINE SHAPES IN ASTROPHYSICS   Book Series: AIP Conference Proceedings   Volume: 938   Pages: 237-+   Published: 2007

0   0   0   0   0   2   0.18

26. **Modeling of absolute spatial emission profiles of Townsend discharges at high E/N in methane by a Monte Carlo technique**

By: Nikitovic, Z. D.; Strinic, A. I.; Malovic, G. N.; et al.
Conference: 22nd Symposium on Plasma Physics and Technology Location: Prague, CZECH REPUBLIC Date: JUN 26-29, 2006
CZECHOSLOVAK JOURNAL OF PHYSICS   Volume: 56   Supplement: B   Pages: B958-B963   Part: 5   Published: 2006

1   0   0   0   0   2   0.17

27. **Modeling of a plasma etcher for charging free processing of nanoscale structures**

By: Radmilovic-Radjenovic, M.; Stojkovic, A.; Strinic, A.; et al.
Edited by: Uskokovic, DP; Milonjic, SK; Rakovic, DI
Conference: 7th Conference of the Yugoslav-Materials-Research-Society (Yu-MRS) Location: Herceg Novi, SERBIA MONTENEG Date: SEP 12-16, 2005
Sponsor(s): Yugoslav Mat Res Soc
RECENT DEVELOPMENTS IN ADVANCED MATERIALS AND PROCESSES   Book Series: Materials Science Forum   Volume: 518   Pages: 57-62   Published: 2006

1   0   0   0   0   2   0.17

28. **Effect of exothermic reactions on the mobility of Ar+ in CF4**

By: Raspopovic, Z.; Stojanovic, V.; Nikitovic, Z.
EPL   Volume: 111   Issue: 4   Article Number: 45001   Published: AUG 2015

0   0   1   0   0   1   0.33

29. **Cross-Sections and Transport Properties of F- Ions in F-2**

By: Stojanovic, V.; Nikitovic, Z.; Jovanovic, J.; et al.
ACTA PHYSICA POLONICA A   Volume: 125   Issue: 1   Pages: 46-48   Published: JAN 2014

0   1   0   0   0   1   0.25

30. **Transport Coefficients in Mixtures Ar/H-2**

By: Nikitovic, Z.; Stojanovic, V.
ACTA PHYSICA POLONICA A   Volume: 123   Issue: 1   Pages: 73-75

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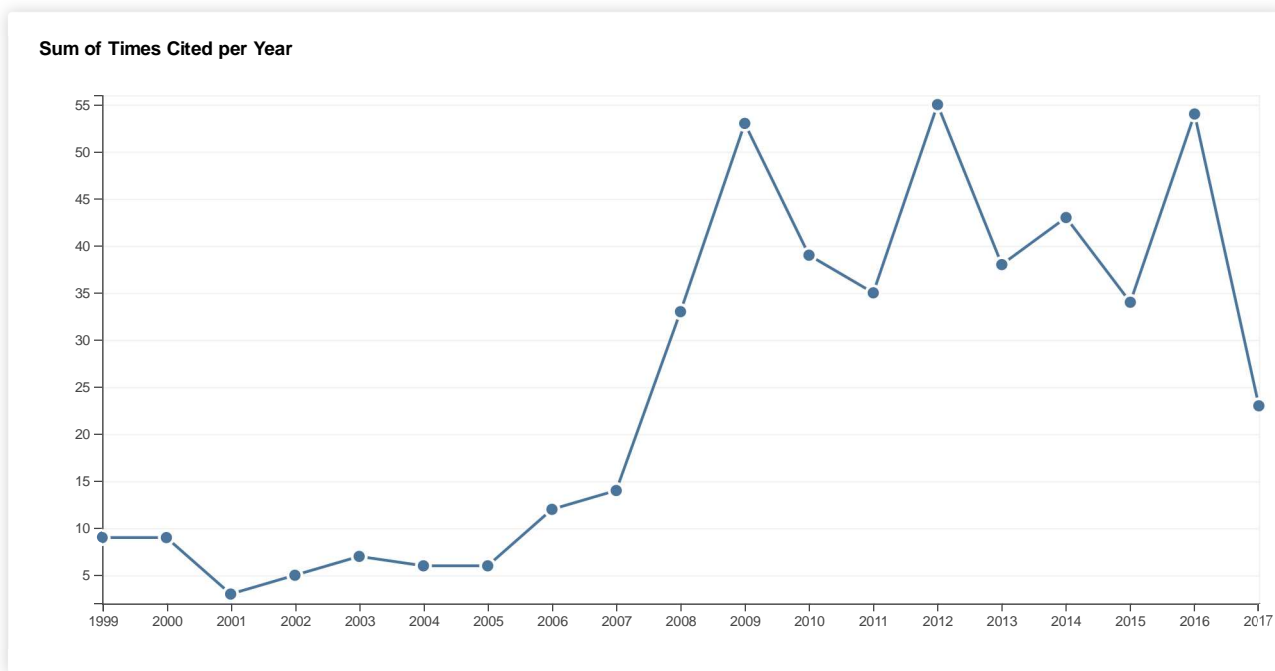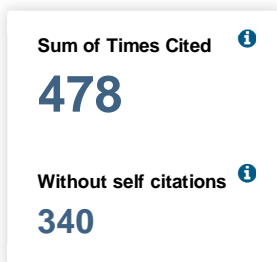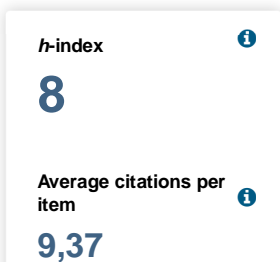Search   My Tools ▾ | Search History | Marked List 51

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31. **Transport of electrons in Ar/H-2 mixtures** By: Nikitovic, Z.; Stojanovic, V.; Petrovic, Z. Lj. EPL Volume: 99 Issue: 3 Article Number: 35003 Published: AUG 2012	0	0	0	0	0	1	0.17

☐	32.	**The influence of F and F-2 on kinetics of electrons in BF3**							
✓		By: Nikitovic, Zeljka D.; Stojanovic, Vladimir D. HEMIJSKA INDUSTRIJA Volume: 65 Issue: 3 Pages: 229-232 Published: MAY-JUN 2011	0	0	0	0	0	1	0.14
☐	33.	**Measurements and analysis of spatial profiles of 777.4 nm line in a townsend discharge in oxygen**							
✓		By: Nikitovic, Zeljka; Strinic, Aleksandra; Malovic, Gordana; et al. ACTA CHIMICA SLOVENICA Volume: 55 Issue: 1 Pages: 219-222 Published: 2008	0	0	0	0	0	1	0.10
☐	34.	**Particle-in-cell modelling of a neutral beam source for material processing in nanoscale structures fabrication**							
✓		By: Radmilovic-Radjenovic, M.; Petrovic, Z. Lj.; Nikitovic, Z.; et al. Edited by: Uskokovic, DP; Milonjic, SK; Rakovic, DI Conference: 8th Conference of the Yugoslav-Materials-Research-Society (Yu-MRS) Location: Herceg Novi, MONTENEGRO Date: SEP 04-08, 2006 Sponsor(s): Yugoslav Mat Res Soc RESEARCH TRENDS IN CONTEMPORARY MATERIALS SCIENCE Book Series: Materials Science Forum Volume: 555 Pages: 47-+ Published: 2007	1	0	0	0	0	1	0.09
☐	35.	**Cross-Section and Transport Parameters of Ne+ in CF4**							
✓		By: Nikitovic, Z.; Stojanovic, V.; Raspopovic, Z. ACTA PHYSICA POLONICA A Volume: 130 Issue: 6 Pages: 1343-1345 Published: DEC 2016	0	0	0	0	0	0	0.00
☐	36.	**Comparison between transport parameters for K+ and Li+ in 1, 2-dimethoxy ethane (DXE) gas**							
✓		By: Nikitovic, Z.; Gilic, M.; Raspopovic, Z.; et al. EPL Volume: 116 Issue: 1 Article Number: 15002 Published: OCT 2016	0	0	0	0	0	0	0.00
☐	37.	**Cross Sections and Transport Properties for Na+ in (DXE) Gas**							
✓		By: Nikitovic, Zeljka D.; Gilic, Martina D.; Petrovic, Milica S.; et al. SCIENCE OF SINTERING Volume: 48 Issue: 3 Pages: 379-386 Published: SEP-DEC 2016	0	0	0	0	0	0	0.00
☐	38.	**Mass spectrometry of positive ions in capacitively coupled low pressure RF discharges in oxygen with water impurities**							
✓		By: Stefanovic, Ilija; Stojanovic, Vladimir; Boulmer-Leborgne, Chantal; et al. JOURNAL OF PHYSICS D-APPLIED PHYSICS Volume: 49 Issue: 26 Article Number: 265202 Published: JUL 6 2016	0	0	0	0	0	0	0.00
☐	39.	**Modeling elastic momentum transfer cross-sections from mobility data**							
✓		By: Nikitovic, Z. D.; Stojanovic, V. D.; Raspopovic, Z. M. EPL Volume: 114 Issue: 2 Article Number: 25001 Published: APR 2016	0	0	0	0	0	0	0.00
☐	40.	**Rate Coefficients of F- Ions in Ar/BF3 Mixtures**							
✓		By: Nikitovic, Z.; Stojanovic, V.; Raspopovic, Z. ACTA PHYSICA POLONICA A Volume: 127 Issue: 6 Pages: 1634-1636 Published: JUN 2015	0	0	0	0	0	0	0.00

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41. **Cross section set and transport properties of Ne+ in CF4** By: Raspopovic, Z.; Nikitovic, Z.; Tosic, S.; et al. Edited by: Diaz, C; Rabadan, I; Garcia, G; et al. Conference: 29th International Conference on Photonic, Electronic, and Atomic Collisions (ICPEAC) Location: Toledo, SPAIN Date: JUL 22-28, 2015	0	0	0	0	0	0	0.00

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Physics Conference Series   Volume: 635   Article Number: UNSP 022099
   Published: 2015

42. **Development of Fast Neutral Etching for Integrated Circuits and Nanotechnologies Fast Neutrals in Gas**

By: Petrovic, Z. Lj.; Stojanovic, V.; Skoro, N.; et al.
Book Group Author(s): IEEE
Conference: 29th International Conference on Microelectronics (MIEL)
Location: Belgrade, SERBIA Date: MAY 12-14, 2014
Sponsor(s): IEEE Serbia & Montenegro Sect ED SSC Chapter; IEEE Elect
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43. **Modeling of Excitation by Heavy Particles in Pure H-2 Discharges at High E/N**

By: Stojanovic, V.; Nikitovic, Z.
ACTA PHYSICA POLONICA A   Volume: 121   Issue: 3   Pages: 622-624
   Published: MAR 2012

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44. **Kinetic Phenomena In Charged Particle Transport In Gases And Plasmas**

By: Petrovic, Zoran Lj.; Dujko, Sasa; Sasic, Olivera; et al.
Edited by: Aggarwal, K; Shearer, F
Conference: 17th International Conference on Atomic Processes in Plasmas
(ICAPiP) Location: Queens Univ, Belfast, NORTH IRELAND Date: JUL 19-22,
2011
Sponsor(s): Royal Astronom Soc; European Off Aerosp Res & Dev; AF Off;
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1438   Pages: 17-22   Published: 2012

0	0	0	0	0	0	0.00

45. **Transport Coefficients For Electrons in Mixtures CF4/Ar/O-2 and CF, CF2 or CF3 Radicals**

By: Nikitovic, Z.; Stojanovic, V.; Radmilovic-Radjenovic, M.
Conference: 12th Annual YUCOMAT Conference Location: Herceg Novi,
SERBIA Date: SEP 06-10, 2010
ACTA PHYSICA POLONICA A   Volume: 120   Issue: 2   Pages: 289-291
   Published: AUG 2011

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46. **Effect Of Anode Surface on Doppler Profile in Townsend Discharge in Pure Hydrogen**

By: Stojanovic, Vladimir D.; Nikitovic, Zeljka D.; Petrovic, Zoran Lj
Edited by: Angelopoulos, A; Fildisis, T
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Location: Alexandroupolis, GREECE Date: SEP 09-13, 2009
Sponsor(s): Balkan Phys Union; Hellen Phys Soc; Univ Crete; Univ Athens; Univ
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VOLS 1 AND 2   Book Series: AIP Conference Proceedings   Volume: 1203
   Pages: 318-323   Published: 2009

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47. **Modeling of Townsend discharges at high E/N and low pressure**

By: Stojanovic, V. D.
Edited by: Malovic, G; Popovic, L; Dimitrijevic, M
Conference: 24th Summer School and International Symposium on Physics of
Ionized Gases Location: Novi Sad, SERBIA Date: AUG 25-29, 2008
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PHYSICS OF IONIZED GASES   Book Series: Journal of Physics Conference
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48. **MODELING OF TOWNSEND DISCHARGES AT HIGH E/N AND LOW PRESSURE**

By: Stojanovic, V. D.
Edited by: Malovic, G; Popovic, LC; Dimitrijevic, MS
Conference: 24th Summer School and International Symposium on Physics of
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☐   49.   **THE EFFECT OF ANISOTROPY OF THE SCATTERING OF HEAVY PARTICLES ON MODELLING OF THE DOPPLER PROFILE IN PURE H(2) DISCHARGE**
✅

By: Stojanovic, V. D.; Nikitovic, Z. D.; Petrovic, Z. Lj.
Edited by: Malovic, G; Popovic, LC; Dimitrijevic, MS
Conference: 24th Summer School and International Symposium on Physics of Ionized Gases Location: Novi Sad, SERBIA Date: AUG 25-29, 2008
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☐   50.   **ELECTRON DETACHMENT OF H(-) IONS IN HYDROGEN DISCHARGE**
✅

By: Stojanovic, V. D.; Raspopovic, Z. M.; Jovanovic, J. V.; et al.
Edited by: Malovic, G; Popovic, LC; Dimitrijevic, MS
Conference: 24th Summer School and International Symposium on Physics of Ionized Gases Location: Novi Sad, SERBIA Date: AUG 25-29, 2008
24TH SUMMER SCHOOL AND INTERNATIONAL SYMPOSIUM ON THE PHYSICS OF IONIZED GASES, CONTRIBUTED PAPERS   Book Series: PUBLICATIONS OF THE ASTRONOMICAL OBSERVATORY OF BELGRADE--SERIES   Issue: 84   Pages: 91-94   Published: 2008

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By: Nikitovic, Z. D.; Stojanovic, V. D.; Petrovic, Z. Lj. Edited by: Malovic, G; Popovic, LC; Dimitrijevic, MS Conference: 24th Summer School and International Symposium on Physics of							

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НАУКЕ И ТЕХНОЛОШКОГ РАЗВОЈА
Комисија за стицање научних звања

Број:06-00-75/1316
24.04.2013. године
Б е о г р а д

На основу члана 22. става 2. члана 70. став 6. Закона о научноистраживачкој делатности ("Службени гласник Републике Србије", број 110/05 и 50/06 – исправка и 18/10), члана 2. става 1. и 2. тачке 1 – 4.(прилози) и члана 38. Правилника о поступку и начину вредновања и квантитативном исказивању научноистраживачких резултата истраживача ("Службени гласник Републике Србије", број 38/08) и захтева који је поднео

Инсшишуш за физику у Беоīраду

Комисија за стицање научних звања на седници одржаној 24.04.2013. године, донела је

ОДЛУКУ
О СТИЦАЊУ НАУЧНОГ ЗВАЊА

Др Владимир Сшојановић
стиче научно звање
Виши научни сарадник

у области природно-математичких наука - физика

О Б Р А З Л О Ж Е Њ Е

Инсшишуш за физику у Беоīраду

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Комисија за стицање научних звања је по предходно прибављеном позитивном мишљењу Матичног научног одбора за математику, рачунарске науке и механику на седници одржаној 24.04.2013. године разматрала захтев и утврдила да именовани испуњава услове из члана 70. став 6. Закона о научноистраживачкој делатности ("Службени гласник Републике Србије", број 110/05 и 50/06 – исправка и 18/10), члана 2. става 1. и 2. тачке 1 – 4.(прилози) и члана 38. Правилника о поступку и начину вредновања и квантитативном исказивању научноистраживачких резултата истраживача ("Службени гласник Републике Србије", број 38/08) за стицање научног звања **Виши научни сарадник,** па је одлучила као у изреци ове одлуке.

Доношењем ове одлуке именовани стиче сва права која му на основу ње по закону припадају.

Одлуку доставити подносиоцу захтева, именованом и архиви Министарства просвете, науке и технолошког развоја у Београду.

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научни саветник
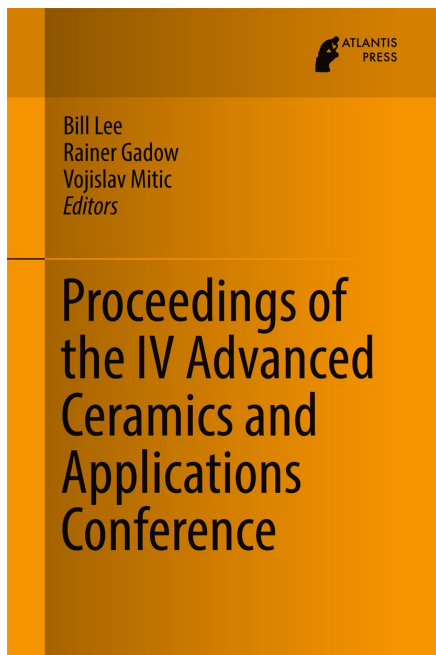
Bill Lee, Rainer Gadow, Vojislav Mitic (Eds.)

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Reduced mobility of He$^+$ in CF$_4$

Ž D Nikitović, Z M Raspopović and V D Stojanović

Institute of Physics, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

E-mail: zeljka@ipb.ac.rs

Abstract

This paper is devoted to a presentation of a cross section set for the scattering of He$^+$ ions in CF$_4$, which is assessed by using available experimental data for exothermic charge transfer cross sections that produce CF$_3^+$ and CF$_2^+$ ions and endothermic charge transfer cross sections that produce CF$^+$, C$^+$ and F$^+$ ions. Due to the significant particle losses, experimental transport coefficients have not been measured. Transport properties of He$^+$ ions in CF$_4$ needed for modeling discharges containing mentioned ions are calculated by the Monte Carlo method at a temperature of $T = 300$ K. Significant differences between flux and bulk transport coefficients are noticed, which is important for fluid models that exploit flux transport coefficients as input data.

Keywords: He$^+$, CF$_4$, Monte Carlo simulation, cross sections, transport coefficients

(Some figures may appear in colour only in the online journal)

1. Introduction

He-CF$_4$ mixtures are used in gas electron multipliers for various imaging purposes (x-rays, charged particles, thermal neutrons and dark matter detection) [1]. Bursts of electron multiplication affect the production of various ions that may affect time distribution of detected particles [2]. Experimental transport coefficients needed as input data for models for the transport of He$^+$ ions in CF$_4$ gas are missing. Although some experimental points for scattering cross sections of He$^+$ ions in CF$_4$ are obtained by Fisher *et al* [3], a cross section set that can be used in modelling is not established yet. Quantum-mechanical calculation of a particular cross section is a demanding task requiring knowledge of ion-molecule potential energy surface, which has to be constructed from the structure of the reactants. Less calculation-intensive methods such as Denpoh–Nanbu theory [4–6] require knowledge about thermodynamic formation data and are applicable for a range of molecules. Although in this case thermodynamic formation data are known, such an approach is hard to apply, since reaction does not proceed via the excited (HeCF$_4^{+*}$) complex but via excited states of CF$_4^+$ (CF$_4^{+*}$). It is also more appropriate to select threshold energies for reaction products from threshold energies of CF$_4^+$ states [7] than from enthalpies of formation.

Charge transfer reactions of ions with molecules are important elementary processes in modeling kinetics in all kinds of plasmas. In many cases, cross sections for these reactions are known to represent the most significant part of the cross section set. It can be concluded from observation of the line spectra of excited F atoms obtained in spectrometric measurements [7] in CF$_4$ that the charge transfer reaction is a dominant process in collisions with inert gas ions. That argument appears sufficient in neglecting other possible reactions.

The aim of the present paper is to report on a topic important both for fundamental studies and for applications. We assessed the cross section set for He$^+$ in CF$_4$ by using existing experimental data [3] for charge transfer collisions producing radical ions of CF$_4$. In the following section we will discuss compilation of existing data and establish one possible cross section set. Next we describe the calculation of transport parameters and at the end discuss our results. Flux and bulk reduced mobilities, calculated from flux and bulk drift velocities by Monte Carlo simulation are significantly different in the region of moderate E/N.

2. Cross section set

Our aim in this section will be to establish the cross section set since only the cross section set contains relevant information to calculate transport properties of selected ion in particular gas. In our selected case the general knowledge

Figure 1. Cross section set for $He^+ + CF_4$.

Figure 2. Mean energy and characteristic energy for He^+ in CF_4 as a function of E/N.
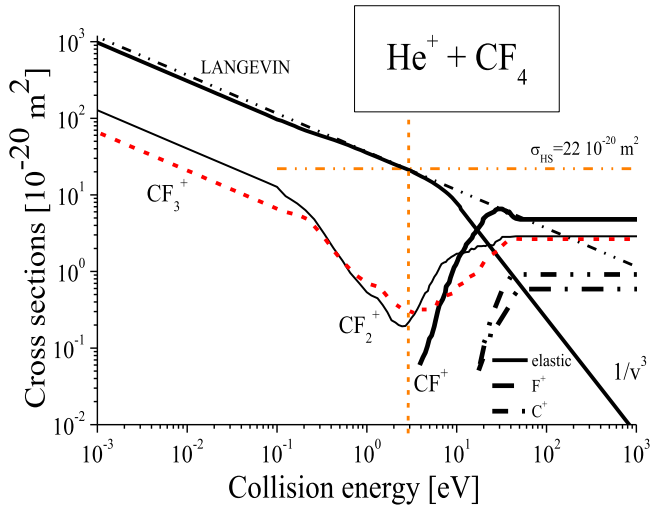
about the total cross section indicates that at low energies it would be affected by long-range attractive forces while at high energies by repulsive forces.

For small energies, when interaction potential is very close to induced dipole potential, one may assume that the total momentum transfer cross section is $\sigma_{mt} = 1.105\ \sigma_L$, where σ_L is the Langevin's cross section [8]. The Langevin's cross section was determined by using the average polarizability of the gas. The average polarizability of CF_4 is poorly determined [3] and may produce discrepancies in the calculated mobilities of ions in CF_4 [9, 10]. As a consequence, this would affect plasma parameters prediction in modeling. We adopted the value of $3.86\ 10^{-30}\ m^3$ used by Stojanović *et al* [9] who found excellent agreement between experimental and calculated reduced mobility of CF_3^+ ions in CF_4.

From the exothermic cross section measurements of Fisher *et al* [3] for CF_2^+ and CF_3^+ production from $He^+ + CF_4$, one may conclude that scattering is appropriate to describe induced polarization potential up to 0.2 eV, thus assuming that charge transfer reactions are the dominant interaction one may obtain for the elastic momentum transfer cross section by deducing experimental reactive cross sections [3] from assumed total momentum transfer cross section.

When the collision energies are larger than the crossing point between the $1.105\ \sigma_L$ curve and the hard sphere (HS) cross section (represents purely the repulsive part of the potential), repulsive interaction is beginning to dominate [3]. At the crossing point (~3 eV) the elastic momentum transfer cross section is smoothly connected to the $1/v^3$ trend [11, 12], where v is the center-of-mass velocity (see figure 1). This trend assumes that repulsive interaction is with anisotropic (forward) scattering probability.

Finally, in the cross section set all exothermic and endothermic cross sections of Fisher *et al* [3] are included. Reactive cross sections were approximated by constant values at all ion kinetic energies above 50 eV by using the data for production ratio between observed ions as suggested in [13].
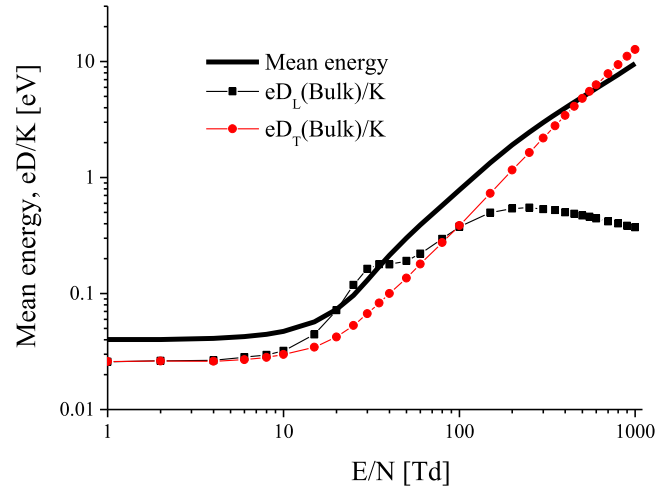
Although the cross sections for CF_2^+ and CF_3^+ production are almost an order of magnitude lower than the total momentum transfer cross section their magnitude below 0.3 eV is significant and has to be known if ion transport at lower temperatures has to be modelled. From the calculations of Krstić and Shultz [11] assuming validity of capture theories down to about 0.1 meV extrapolation of the experimental measurements [3] towards low energies is safely done by $1/v$ trend. Below 0.1 meV we used extrapolation with the constant cross section.

3. Transport coefficients

Transport properties needed for modeling CF_4 discharges containing He^+ ions are calculated by the Monte Carlo method. A code that properly takes into account thermal collisions was used [14]. It has passed all relevant benchmarks [6] and was tested in our work on several types of charged particles [6, 15]. Swarm parameters of He^+ in CF_4 for a temperature of $T = 300$ K are presented.

The calculated transport parameters are the mean energy, characteristic energy, drift velocity, diffusion coefficients and rate coefficients for ions [16]. Note that these transport parameters are the only information present in the literature up to now and there are no published experimental data for the transport coefficients of He^+ in CF_4.

In figure 2 we present the mean energy, obtained as an average of particle ensemble [14, 16] and compare it to characteristic energies (diffusion coefficient normalized to mobility eD/K in units of eV, where $K = v_d/E$ and v_d is the drift velocity of the ion) determined in the direction of the field and transversal to the electric field. In figure 2 values that are taking into account only bulk values of transport coefficients that can be experimentally determined [17] are shown. They can be compared with values obtained when experimental measurements become available.

Characteristic energy curves above 200 eV show that the energy in the longitudinal direction is significantly affected by
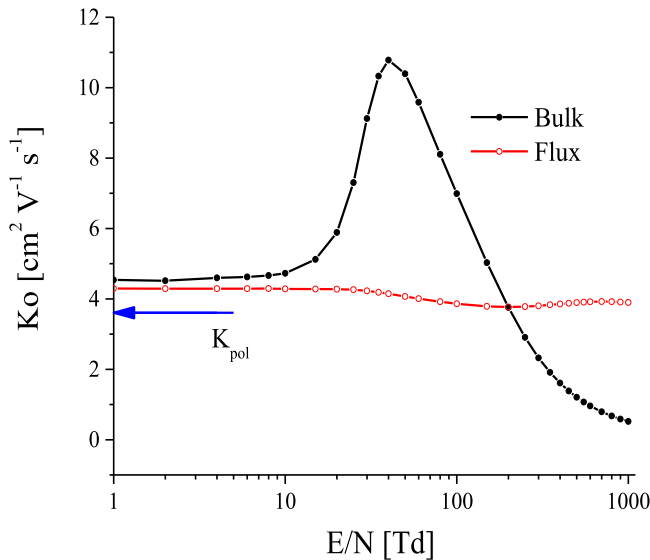
Figure 3. The bulk and flux reduced mobility for He$^+$ in CF$_4$ as a function of E/N.

Figure 4. The transversal and longitudinal diffusion coefficients for He$^+$ in CF$_4$ as a function of E/N.

non-conservative collisions. Note that the mean energy cannot be directly measured in experiments. Mapping of mean energy versus E/N may be used directly to provide the data in fluid models in situations when local field approximation fails. As visible on the figure the energy increases from 10 Td and before that a thermal value of 0.04 eV.

The mobility K of an ion is a quantity defined as the velocity attained by an ion moving through a gas under the unit electric field. One often exploits the reduced or standard mobility defined as:

$$K_0 = \frac{v_d}{N_0 E} N, \qquad (1)$$

where N is the gas density at elevated temperature T, $N_0 = 2.69 \cdot 10^{25}$ m^{-3} and E is the electric field. Let us remind the reader that the bulk drift velocity ($W = \mathrm{d}\langle x \rangle / \mathrm{d}t$) is a reaction corrected flux drift velocity ($w = \langle v \rangle$): $W = w + S$, where S is the term representing a measure of the effect of reactions on the drift velocity. For flux mobility are responsible elastic collisions. The difference between bulk and flux reduced mobilities is a consequence of energy-dependent reactions.

Generally both flux and bulk reduced mobilities converge, when $E \to 0$, $T \to 0$, to a polarization limit value, when interaction between ion and molecule can be described with induced polarization potential (if one neglects reactions). The polarization limit value for our studied case is $K_{pol} = 3.608$ cm^2 V^{-1} s^{-1} (see figure 3). If exothermic reactions take place, as in the our case, then reduced mobility acquires larger values since the elastic cross section is smaller at the expense of exothermic cross sections [5].

Flux and bulk values of reduced mobility for He$^+$ ions in CF$_4$ as a function of E/N (E-electric field strength, N-gas number density) are shown in figure 3.

Due to the exothermic processes producing CF$_2^+$ and CF$_3^+$ reduced mobility at lowest E/N is larger than polarization limit value. Flux reduced mobility is nearly flat at
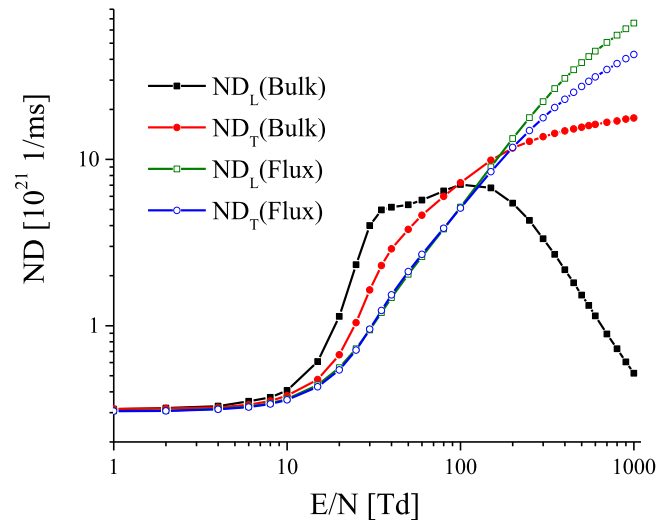
these E/Ns since collision frequency for elastic scattering is nearly constant [5]. When collision frequency for elastic collisions begins to decrease one would expect the increase of the flux reduced mobility. This is not happening since endothermic reactions remove high-energy ions from the swarm front. This shifts the center of mass of ions backward.

At the low E/N tail of thermal energy distribution function (EDF), decreasing part of the collision frequency for reactions allows the increase of ions energy at the front of the swarm. This affects the center of mass of the ions moving ahead (source term S is positive) and bulk reduced mobility is increasing.

For the ion energies larger than thermal, by increasing reduced electric field, EDF in a wider range senses the drop of high energy ions in the front of the swarm due to the exothermic reactions and so bulk reduced mobility is increasing steeply.

For the energies for which collision frequency for reactions begins to increase, fast ions are removed from the swarm front and bulk reduced mobility decreases with E/N.

Thus, the significant peak in the bulk reduced mobility at about 35 Td is obtained as a result of difference in energy dependence of elastic and exothermic cross sections [18].

Transversal and longitudinal diffusion coefficients are given in figure 4. At very low energies due to the similarity of the cross sections for elastic and exothermic scattering, flux and bulk diffusion coefficients are similar. Very large non-conservative effects, almost a reminder of the positron transport [19], are noticed at higher E/Ns. Similar to the results for drift velocity, flux diffusion coefficients are significantly larger than the bulk values at largest E/N's, due to the reactive collisions.

In figure 5 we show rate coefficients for elastic momentum transfer and for all reactive processes as a function of E/N. The rate coefficients as the final output of our calculations are needed as input in fluid equations for the description of ion transport in CF$_4$ gas.
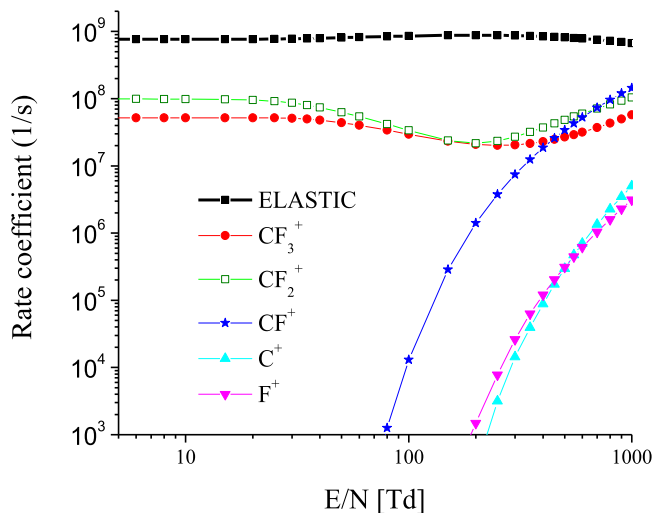
Figure 5. Rate coefficients for momentum transfer and for production reactions as a function of E/N.

Calculated rate coefficients are valid for swarm conditions. The precision of the calculated rate coefficients depends on the precision of the measured cross section, which is stated to be 50%–60% [3]. At higher energies, where cross sections for reactions are extrapolated, precision of the calculated rate coefficients is lower. This precision is fortunately increasing due to the measured cross sections ratio at 861 eV [13]. Note that exothermic rate coefficients obtained from capture theories are constant and are significantly different from the rate coefficients obtained in this work.

4. Conclusion

In this work we determined elastic momentum transport cross sections as a function of energy for He^+ scattering on CF_4 that can be used in modelling transport of He^+ in CF_4 gas. We exploited data for a simple theoretical total momentum transfer cross section and obtained an elastic momentum transfer cross section by deducing all experimentally obtained charge transfer cross sections. In that we assumed that measured charge transfer cross sections are the collisions with the highest probability. Thus, in this paper we have assessed the cross section set for He^+ ions in CF_4 that can be used as an independent input in the modelling transport of He^+ ions. This assessment was performed by using measured charge transfer cross sections.

Since to the best of our knowledge no direct information exists in the literature on how the mobility of high recombination energy ions such as He^+ ions behaves in CF_4, we calculated transport parameters by using the Monte Carlo simulation method [5, 18].

In this paper we have obtained and discussed both flux and bulk reduced mobility data. Data for swarm coefficients for positive and negative ions are needed for hybrid and fluid

codes and the current focus on liquids or liquids in the mixtures with rare gases dictates the need to produce data compatible with those models. In view of the present interest in models of liquids and/or liquids in mixtures with rare gases, data for swarm coefficients for positive and negative ions are needed for hybrid and fluid codes.

References

[1] Fraga M M F R, Fraga F A F, Fetal S T G, Margato L M S, Ferreira Marques R and Policarpo A J P L 2003 *Nucl. Instrum. Methods Phys. Res.* A **504** 88
Kaboth A *et al* 2008 *Nucl. Instrum. Methods Phys. Res.* A **592** 63
[2] Bošnjaković D 2016 *PhD Dissertation,* Faculty of Electrical Engineering, University of Belgrade, Belgrade
[3] Fisher E R, Weber M E and Armentrout P B 1990 *J. Chem. Phys.* **92** 2296
[4] Denpoh K and Nanbu K 1998 *J. Vac. Sci. Technol.* A **16** 1201
[5] Nikitović Ž, Raspopović Z, Stojanović V and Jovanović J 2014 *Europhys. Lett.* **108** 35004
[6] Petrović Z Lj, Raspopović Z M, Stojanović V D, Jovanović J V, Malović G, Makabe T and de Urquijo J 2007 *Appl. Surf. Sci.* **253** 6619
[7] Motohashi K, Takahashi T, Takahashi N and Tsurubuchi S 2005 *J. Phys. B: At. Mol. Opt. Phys.* **38** 3339
[8] McDaniel E W, Čermak V, Dalgarno A, Ferguson E E and Friedman L 1970 *Ion-Molecule Reactions* (New York: Wiley)
[9] Stojanović V, Raspopović Z, Jovanović J V, de Urquijo J and Petrović Z Lj 2014 *J. Phys.: Conf. Series* **514** 012059
[10] Georgieva V, Bogaerts A and Gijbels R 2003 *J. Appl. Phys.* **93** 2369
[11] Krstić P S and Schultz D R 2009 *J. Phys. B: At. Mol. Opt. Phys.* **42** 065207
[12] Raspopović Z, Stojanović V and Nikitović Ž 2015 *Europhys. Lett.* **111** 45001
[13] Parker J E and El-Ashhab F S M 1983 *Int. J. Mass Spectrom. Ion. Phys.* **47** 159
[14] Ristivojević Z and Petrović Z Lj 2012 *Plasma Sources Sci. Technol.* **21** 035001
[15] de Urquijo J, Jovanović J V, Bekstein A, Stojanović V and Petrović Z Lj 2013 *Plasma Sources Sci. Technol.* **22** 025004
[16] Petrović Z Lj, Dujko S, Marić D, Malović G, Nikitović Ž, Šašić O, Jovanović J, Stojanović V and Radmilović-Radjenović M 2009 *J. Phys. D: Appl. Phys.* **42** 194002
[17] Robson R E 1991 *Aust. J. Phys.* **44** 685
[18] Nikitović Ž D, Stojanović V D and Raspopović Z M 2016 *Europhys. Lett.* **114** 25001
[19] White R D *et al* 2014 *Appl. Radiat. Isot.* **83** 77

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Comparison between transport parameters for K$^+$ and Li$^+$ in 1, 2-dimethoxy ethane (DXE) gas

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Abstract – In this paper, a theoretical study of 1, 2-dimethoxy ethane (DXE) and K$^+$/Li$^+$ binary mixture in low-temperature plasmas is reported. The most probable reactions of alkali metal ions K$^+$ and Li$^+$ with dimethoxy ethane molecule and its fragment ions are selected in order to obtain appropriate gas phase enthalpies of formation for the products. The scattering cross-sections set as a function of kinetic energy and transport parameters as a function of E/N (E is the electric field, N the gas density) were obtained by using the Monte Carlo technique.

Introduction. – Transport properties of species in gas plasmas are of great importance in understanding the nature of molecular and ionic interactions in gas mixtures [1–3]. These properties include the mean energy, drift velocity, diffusion coefficients, ionization and chemical reaction coefficients, chemical reaction coefficients for ions and (rarely) excitation coefficients, and they are very useful in chemical industries for the design of many types of transport and process equipment.

The ether-based molecule 1,2-dimethoxy ethane (DXE) is a clear colorless volatile liquid at room temperature and atmospheric pressure [4]. As being the smallest oligomer, *i.e.*, the building block of the polyethylene oxide (PEO) polymer, it has a widespread application in the medical and pharmaceutical field [5–7]. Nevertheless, DXE is also used as a precursor in the production of ceramics [8] or as a sole compound to and other chemicals such as those used in lithium batteries production [9–12], superconductor production [13], nanoparticles synthesis [14–16], in etherification [17] etc.

Being a suitable medium for a number of chemical reactions, it forms chelate complexes with metal cations. Having all that in mind, it would be of great importance to observe a binary gas mixture of DXE and K$^+$ or Li$^+$. To the best of our knowledge, the transport properties of such mixtures in gas plasmas have received no attention.

At atmospheric-pressure three-body reactions of ions are of increasing importance for the reaction kinetics. In many modeling cases information about the

three-body processes is missing. The Denpoh-Nanbu theory (DNT) [18] can be exploited to calculate cross-section sets as a function of the kinetic energy for cases where no or limited information is available about scattering data [19]. Nikitović *et al.* [20] showed how radiative association for three-body reactions can be included in cross-section sets obtained by the DNT. The approach presented in [20] was compared with the existing experimental data for association cross-section as a function of pressure [21] and showed good agreement at energies below a few eV. Such information is of great importance in atmospheric-pressure plasmas containing complex molecules such as DXE and can be highly valuable in modeling clustering in various plasmas.

In all of the reactions studied experimentally to date [22,23], the only produced ions were the association complexes Li$^+$(DXE) and K$^+$(DXE). Therefore, in this work we will apply the approach in [20] to the case of alkali ions in DXE.

In this paper we selected the most probable reactions of alkali metal ions K$^+$ and Li$^+$ with dimethoxy ethane (DXE) molecule (and its most probable products) for thermodynamic threshold energies below about 15 eV. Appropriate gas phase enthalpies of formation [24] for the products were used to calculate thermodynamic thresholds.

Although DXE consists of many atoms its dipole moment is negligible, so the simplest capture theories can be applied. The scattering cross-sections as a function

Table 1: Heats of formation $\Delta_f H^0$ at 298 K(kJ/mol).

Species	$\Delta_f H^0$	Species	$\Delta_f H^0$
Li	159.4	Li$^+$	679.6
K	89	K$^+$	507.8
DXE	−340	DXE$^+$	557
C$_3$H$_8$O$_2$	−364	C$_3$H$_8$O$_2^+$	562
C$_2$H$_6$O	793.1	C$_2$H$_6$O$^+$	775.4
C$_2$H$_4$O	821.1	C$_2$H$_4$O$^+$	−165.8
CH$_4$O	−201.6	CH$_4$O$^+$	845.3
CH$_2$O	−108.7	CH$_2$O$^+$	940.5
CH$_4$	−74.5	CH$_4^+$	1132.0
CO	−110.53	CO$^+$	1241.59
H$_2$	0.0	H$_2^+$	1488.3

Table 2: X$^+$-DXE reaction paths (X = Li, K) showing reaction products and the corresponding thermodynamic threshold energies Δ.

No.	Products	Li$^+$	K$^+$
1	X$^+$ + DXE	0	0
2	X + C$_4$H$_{10}$O$_2^+$	3.905	4.9561
3	X$^+$ + C$_3$H$_8$O$_2$ + CH$_2$	3.793	3.793
4	X + C$_3$H$_8$O$_2^+$ + CH$_2$	7.999	9.050
5	X + C$_3$H$_8$O$_2$ + CH$_2^+$	8.724	9.775
6	X$^+$ + C$_2$H$_6$O + CH$_2$ + CO	4.513	4.513
7	X + C$_2$H$_6$O$^+$ + CH$_2$ + CO	9.147	10.198
8	X + C$_2$H$_6$O + CH$_2^+$ + CO	9.444	10.495
9	X + C$_2$H$_6$O + CH$_2$ + CO$^+$	13.135	14.186
10	X + C$_2$H$_4$O$^+$ + C$_2$H$_6$O	4.7353	5.7862
11	X + C$_2$H$_4$O + C$_2$H$_6$O$^+$	4.5322	5.5831
12	X$^+$ + CH$_2$O + C$_2$H$_6$ + CO	0.3811	0.3811
13	X + CH$_2$O$^+$ + C$_2$H$_6$ + CO	5.8636	6.9145
14	X + CH$_2$O + C$_2$H$_6^+$ + CO	6.5145	7.5654
15	X + CH$_2$O + C$_2$H$_6$ + CO$^+$	9.0031	10.054
16	X$^+$ + CH$_4$O + C$_3$H$_4$ + H$_2$O	0.8620	0.8620
17	X + CH$_4$O$^+$ + C$_3$H$_4$ + H$_2$O	6.3207	7.3716
18	X + CH$_4$O + C$_3$H$_4^+$ + H$_2$O	5.8305	6.8814
19	X + CH$_4$O + C$_3$H$_4$ + H$_2$O$^+$	8.0818	9.1328
20	X$^+$ + C$_4$H$_6$ + 2H$_2$ + O$_2$	5.0307	5.0307
21	X + C$_4$H$_6^+$ + 2H$_2$ + O$_2$	9.2012	10.2521
22	X + C$_4$H$_6$ + 2H$_2$ + O$_2^+$	15.064	16.115
23	X + C$_4$H$_6$ + H$_2^+$ + H$_2$ + O$_2$	11.716	12.7674

of kinetic center of mass energy is calculated with the DNT [18,25].

Calculation of the cross-section. − DXE selected in this study is of *trans, trans, trans* conformation [22] and is known not to have permanent dipole moment in its ground state. The average polarizability 9.94×10^{-30} m^3 [22] is used for the DXE target. Similar to our recent papers [26] the DNT method is used to separate elastic from reactive endothermic collisions by accounting for the thermodynamic threshold energy and branching ratio according to the Rice-Rampsperger-Kassel (RRK) theory [18]. Within the RRK theory the internal energy is being distributed among an empirical number of s equivalent effective modes of the complex selected from the total number of atoms involved in the complex.

Appropriate gas phase enthalpies of formation for the products [23] (table 1) were used to calculate thermodynamic thresholds (table 2). The cross-section for the exothermic reaction (EXO) forming a molecular ion X$^+$ in DXE is commonly represented by ion capture cross-section:

$$\sigma_{\mathrm{exo}} = \beta\sigma_{\mathrm{L}}, \qquad (1)$$

where σ_{L} is the orbiting cross-section [27] and β is the probability of a specific exothermic reaction.

By combining the relation (1) and the thermal rate coefficient we determined the probability of exothermic reaction and the contributions of association cross-section and elastic cross-section. In the low-energy limit [2,23], the cross-sections are similar due to dominant polarization of the target. At higher energies reactive collisions including the non-conservative collisions become efficient for various possible processes.

The elastic momentum transfer cross-section be modified in order to fit approximate mobility peak characteristic for presented systems. This is done using the swarm method [28,29] and the reduced mobilities (experimental [30] or theoretical values [31]) in the peak region for these ions in neutrals of equal or similar reduced mass. From Langevin's cross-section we deduced experimental

Fig. 1: (Color online) Cross-section set for scattering of K$^+$ with DXE. "ASSOC" denotes the experimentally obtained association cross-section [22] while theoretical curves are denoted in the legend.

association cross-sections and theoretical endothermic cross-sections in order to obtain elastic momentum transfer cross-section. The elastic momentum transfer cross-sections for elastic collisions of K$^+$ with DXE is presented in fig. 1. In fig. 2 we present cross-sections for Li$^+$ in DXE.
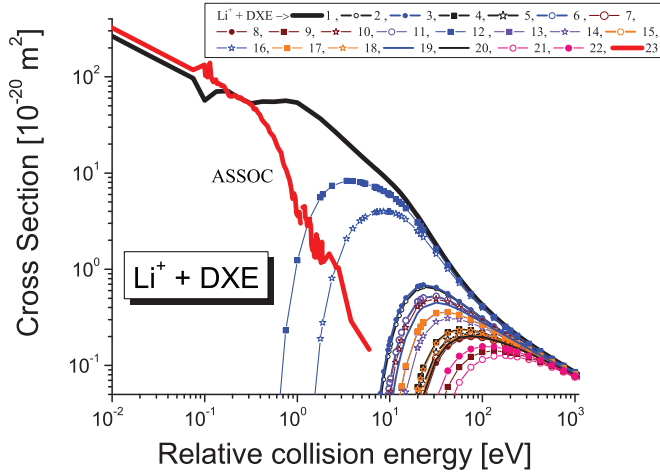
Fig. 2: (Color online) Cross-section set for scattering of Li$^+$ with DXE. "ASSOC" denotes the experimentally obtained association cross-section [22] while theoretical curves are denoted in the legend.

Fig. 3: (Color online) Mean energy as a function of E/N for K$^+$ and Li$^+$ in DXE.

Agreement with experiment is satisfactory for energies below 1 eV. A further step in both cases will be to add more reactions with multiple radicals that will increase the thermodynamic threshold and generally increase the number of reactions. This may potentially improve agreement with experimental data for cross-sections for association reaction.

In all mentioned experimental cases, the cross-sections show a clear pressure dependence, which indicates the occurrence of collisional stabilization of complex by secondary collisions. The effect of secondary collisions can be eliminated completely by linear extrapolation of the cross-section data to zero reactant pressure. The same trend is easily achieved with theoretical data which have to include effects of all possible reactions providing our theoretical cross sections can be exploited and also used in many other cases.

Transport parameters. – Generally speaking, plasma modelling and simulations requires the use of swarm parameters. The non-equilibrium regime in discharges can be well represented under a broad range of conditions by using the Boltzmann kinetic equation or by following individual evolutions of all ions with Monte Carlo technique. In our Monte Carlo code swarm of ions is traced until they reach hydrodynamic regime when transport properties are calculated [25,26,29]. Internal excitation of the DXE is neglected in the cross-section calculation although is included with association cross-section where we exploited experimental data. Agreement of measured association cross-section at very low energies with Langevin's trend indicate that the effect of internal excitation of the molecule is of less importance than reactive collisions in selected conditions.

We have used a Monte Carlo code that properly takes into account thermal collisions [32]. The code has passed
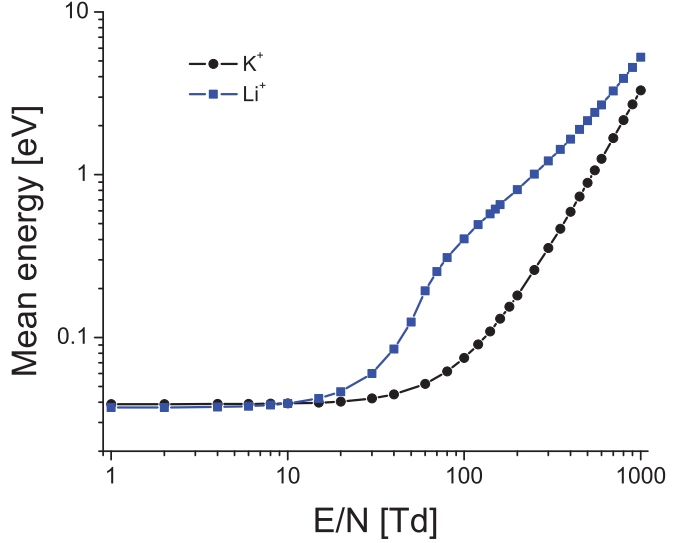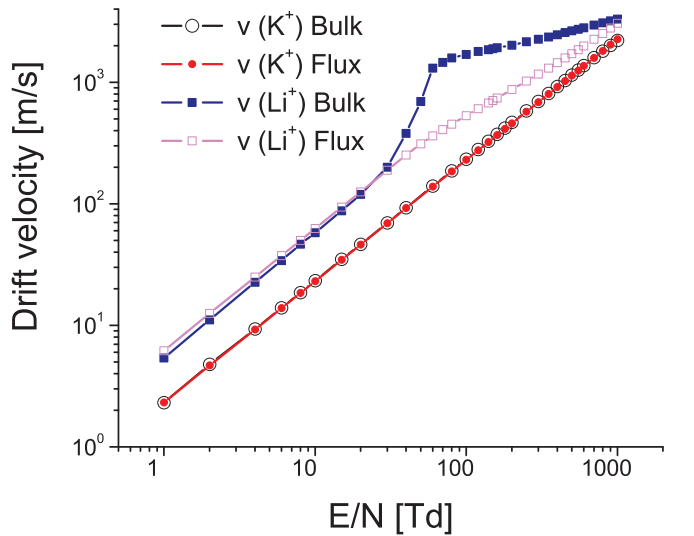
Fig. 4: (Color online) Flux and bulk drift velocity as a function E/N for K$^+$ and Li$^+$ in DXE.

all the relevant benchmarks [25] and has been tested in our work on several types of charged particles [25,33].

In fig. 3 we show the mean energy as a function of collision energy for K$^+$ and Li$^+$ in DXE. The mean energy cannot be directly measured in experiments. The difference in the mean energies of Li$^+$ and K$^+$ is visible because of the big attachment for Li$^+$ above 20 Td.

Flux and bulk drift velocities [34–36] for K$^+$ in DXE as a function of E/N are given in fig. 4. The drift velocities obtained by Monte Carlo simulation calculated in real space (bulk) and in velocity space (flux) values which are obtained as $\langle v \rangle$ and dx/dt, respectively. The mass of Li$^+$ is smaller than the mass of K$^+$, so as a consequence the drift velocity of Li$^+$ is bigger. In the case of K$^+$, due to
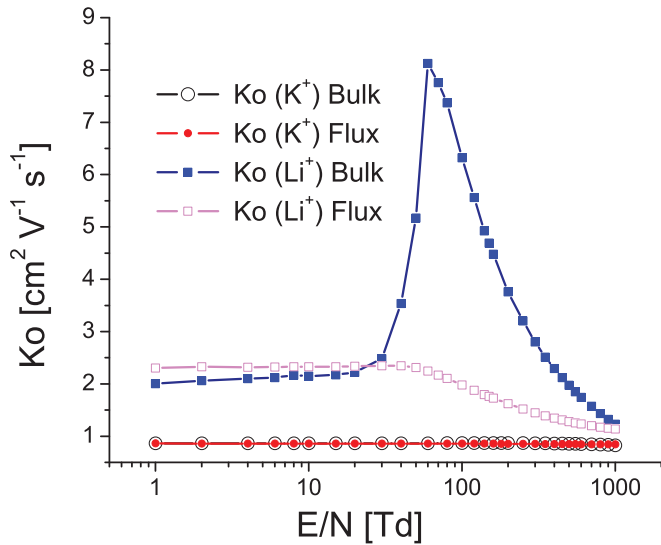
Fig. 5: (Color online) Reduced mobility as a function E/N for K^+ and Li^+ in DXE.
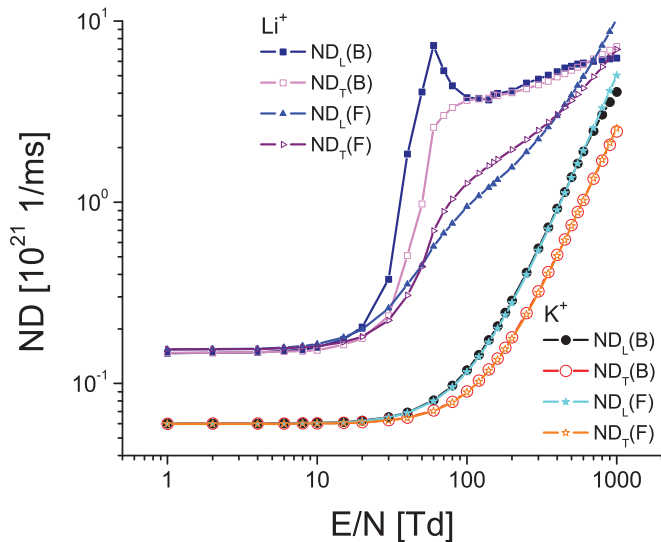
Fig. 6: (Color online) Longitudinal and transversal diffusion coefficients as a function E/N for K^+ and Li^+ in DXE.

weak non-conservation, there is no important difference between the flux and bulk velocity.

The mobility K of an ion is a quantity defined as the velocity attained by an ion moving through a gas under the unit electric field. One often exploits the reduced or standard mobility defined as

$$K_0 = \frac{v_d}{N_0 E} N, \qquad (2)$$

where v_d is the drift velocity of the ion, N is the gas density at elevated temperature T, $N_0 = 2.69 \cdot 10^{25} \, \mathrm{m}^{-3}$ and E is the electric field.

In fig. 5 we show the results of Monte Carlo simulation for reduced mobility for K^+ and Li^+ in DXE as a function of E/N. Due to reactive collisions bulk and flux values

of reduced mobility are separated. The reduced mobility for K^+ is constant but increasing the resolution shows its structure, while the mobility for Li^+ sharply rises at energies 0.3–2 eV because of resonant association.

Longitudinal and transversal diffusion coefficients for K^+ and Li^+ in DXE as a function of E/N are shown in fig. 6. The peak is visible only in the behavior of longitudinal diffusion coefficients. With the increase of E/N the longitudinal diffusion decreases as a consequence of the big attachment for Li^+.

However, there are no published experimental data for the longitudinal and transverse diffusion coefficients of K^+ and Li^+ in DXE so far.

Conclusion. – The Denpoh-Nanbu theory, supplemented with the swarm method was used to calculate the elastic collisions of K^+ and Li^+ on DXE. Calculated cross-sections are used to obtain transport parameters for K^+ and Li^+ in DXE gas.

DXE is a technologically important gas. Cross-sections and transport data for it have been calculated by a simple theory. Adding a database of measured transport coefficients would open the possibility of refining the calculations.

$$* * *$$

REFERENCES

[1] Todd B. and Young J. B., *J. Power Sources*, **110** (2002) 186.
[2] Mason E., *J. Chem. Phys.*, **27** (1957) 782.
[3] Golzar K., Amjad-Iranagh S., Amani M. and Modarress H., *J. Membr. Sci.*, **451** (2014) 117.
[4] Wang Y., Liu C. and Zhang Y., *Plasma Sci. Technol.*, **7** (2005) 2839.
[5] Park S., Choi H., Lee J., Lee Y., Ku J., Lee S. and Nam T., *Arch. Pharm. Res.*, **39** (2016) 302.
[6] Heckmann V. G., Becker G., Homer S., Richard H., Kraft H. and Dvortsak P., *Z. Naturforsch. B*, **56** (2001) 146.
[7] Tasaki K. and Abe A., *Polym. J.*, **17** (1985) 641.
[8] Kumar N., Yang Y., Noh W., Girolami G. S. and Abelson J. R., *Chem. Mater.*, **19** (2007) 3802.
[9] McCloskey B. D., Burke C. M., Nichols J. E. and Renfrew S. E., *Chem. Commun.*, **51** (2015) 12701.
[10] Cheng Y., Stolley R. M., Han K. S., Shao Y., Arey B. W., Washton N. M., Mueller K. T., Helm M. L., Sprenkle V. L., Liu J. and Li G., *Phys. Chem. Chem. Phys.*, **17** (2015) 13307.
[11] Chung S.-H. and Manthiram A., *J. Phys. Chem. Lett.*, **5** (2014) 1978.
[12] Shui J.-L., Karan N. K., Balasubramanian M., Li S.-Y. and Liu D.-J., *J. Am. Chem. Soc.*, **134** (2012) 16654.

[13] BUCHANAN W. D., GUINO-O M. A. and RUHLANDT-SENGE K., *Inorg. Chem.*, **49** (2010) 7144.

[14] BALDWIN R. K., PETTIGREW K. A., RATAI E., AUGUSTINE M. P. and KAUZLARICH S. M., *Chem. Commun.* (2002) 1822.

[15] PICKERING A. L., MITTERBAUER C., BROWNING N. D., KAUZLARICH S. M. and POWER P. P., *Chem. Commun.* (2007) 580.

[16] HAWA T. and ZACHARIAH M. R., *J. Phys. Chem. C*, **112** (2008) 14796.

[17] CHE P., LU F., SI X. and XU J., *RSC Adv.*, **5** (2015) 24139.

[18] DENPOH K. and NANBU K., *J. Vac. Sci. Technol. A*, **16** (1998) 1201.

[19] GEORGIEVA V., BOGAERTS A. and GIJBELS R., *J. Appl. Phys.*, **93** (2003) 2369.

[20] NIKITOVIĆ Ž., STOJANOVIĆ V., RASPOPOVIĆ Z. and JOVANOVIĆ J., *Acta Phys. Pol. A*, **126** (2014) 724.

[21] PETROVIĆ M., GILIĆ M., STOJANOVIĆ V., NIKITOVIĆ Ž., RASPOPOVIĆ Z. and ROMČEVIĆ N., *YUCOMAT, Herceg Novi, Montenegro, August 31–September 4 (2015)*, abstract P.S.A.8.

[22] KOIZUMI H. and ARMENTROUT P. B., *J. Chem. Phys.*, **119** (2003) 12819.

[23] SATOH Y., TAKEBE M. and IINUMA K., *J. Chem. Phys.*, **87** (1987) 6250.

[24] LIAS S. G., BARTMESS J. E., XEBMAN J. F., HOLMES J. L., LEVIN R. D. and MALLARD W. G., *J. Phys. Chem. Ref. Data, Suppl. 1*, **17** (1988) 1.

[25] PETROVIĆ Z. LJ., RASPOPOVIĆ Z. M., STOJANOVIĆ V. D., JOVANOVIĆ J. V., MALOVIĆ G., MAKABE T. and DE URQUIJO J., *J. Appl. Surf. Sci.*, **253** (2007) 6619.

[26] STOJANOVIĆ V., RASPOPOVIĆ Z., JOVANOVIĆ J., NIKITOVIĆ Ž. and PETROVIĆ Z. LJ., *EPL*, **101** (2013) 45003.

[27] McDANIEL E. W., ČERMAK V., DALGARNO A., FERGUSON E. E. and FRIEDMAN L., *Ion-Molecule Reactions* (Willey Interscience) 1970.

[28] NIKITOVIĆ Ž., STOJANOVIĆ V., ŠAŠIĆ O., RASPOPOVIĆ Z. and PETROVIĆ Z., *ETRAN, Palić, Srbija, 8–12. juna (2008)*, abstract NM 1.8.

[29] NIKITOVIĆ Ž., RASPOPOVIĆ Z., STOJANOVIĆ V. and JOVANOVIĆ J., *EPL*, **108** (2014) 35004.

[30] VIEHLAND L. A. and MASON E. A., *At. Data. Nucl. Data Tables*, **60** (1995) 37.

[31] Viehland database, www.lxcat.net, retrieved in 2016.

[32] RISTIVOJEVIĆ Z. and PETROVIĆ Z. LJ., *Plasma Sources Sci. Technol.*, **21** (2012) 035001.

[33] DE URQUIJO J., JOVANOVIĆ J. V., BEKSTEIN A., STOJANOVIĆ V. and PETROVIĆ Z. LJ., *Plasma Sources Sci. Technol.*, **22** (2013) 025004.

[34] ROBSON R. E., *Aust. J. Phys.*, **44** (1991) 685.

[35] RASPOPOVIĆ Z., SAKADŽIĆ S., PETROVIĆ Z. LJ. and MAKABE T., *J. Phys. D*, **33** (2000) 1298.

[36] PETROVIĆ Z. LJ., DUJKO S., MARIĆ D., MALOVIĆ G., NIKITOVIĆ Ž., ŠAŠIĆ O., JOVANOVIĆ J., STOJANOVIĆ V. and RADMILOVIĆ-RADJENOVIĆ M., *J. Phys. D: Appl. Phys.*, **42** (2009) 194002.

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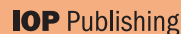
Modeling elastic momentum transfer cross-sections from mobility data

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Abstract – In this letter we present a new method to simply obtain the elastic momentum transfer cross-section which predicts a maximum of reduced mobility and its sensitivity to the temperature variation at low energies. We first determined the transport cross-section which resembles mobility data for similar closed-shell systems by using the Monte Carlo method. Second, we selected the most probable reactive processes and compiled cross-sections from experimental and theoretical data. At the end, an elastic momentum transfer cross-section is obtained by subtracting the compiled cross-sections from the momentum transfer cross-section, taking into account the effects of the angular scattering distributions. Finally, the cross-section set determined in such a way is used as an input in a final Monte Carlo code run, to calculate the flux and bulk reduced mobility for $Ne^+ + CF_4$ which were discussed as functions of the reduced electric field E/N (N is the gas density) for the temperature $T = 300 \, K$.

Introduction. – Cold plasmas are often exploited in new technologies where they favorably offer non-intrusive production or modification of various substances [1]. The main characteristics of these plasmas are their high electron temperature and low gas temperature where the non-equilibrium behavior of a large number of species takes place [2]. The present computer resources allow studies of complex global models [3,4] describing the behavior of such plasmas by taking into account a very large number of particles. In such cases the knowledge of the ion-neutral reaction and transport parameters for ions resurges as interesting mostly in cases in which reactive processes take place [5–7]. In spite of great efforts and numerous results [8–15], the knowledge about ion-molecule reactions holding a prominent place in the descriptions of these plasmas, is far from satisfactory. The main reason for that are the poorly known ion scattering properties in various gases that must be guessed in order to obtain transport properties during modelling [12,16–18].

Quantum-mechanical calculation of the ion-neutral scattering cross-sections requires the knowledge of accurate potential energy surfaces which are known only to within limits of appropriate (usually very complex) theories [19], while experiments at low energies are sensitive to small stray fields and many other technical problems.

Thus, simple and effective methods based on known principles are highly valuable.

Calculation of the cross-section. – Due to the lack of experimental and theoretical mobility data Gatland *et al.* [20] found that all the experimental mobility curves can be unified into a single mobility curve by using a model interaction potential. Their interaction potential predicts a peak in reduced mobility (Ko) and suggests generalized mobility curves for alkali ions in rare gases (closed-shell systems). The generalized mobility curves are defined as Ko normalized by a polarization limit (PL) value K_{PL} [6,20] as a function of the effective temperature normalized to the well depth of the potential minimum. Takebe [21] made a further step in the unification of mobility data. Apart from similar conclusions as in [20], *e.g.* that the ratio $Komax/K_{PL}$ dominantly depends on the observed ion, he showed that transport of ions proceeds in the presence of clustering collisions and found out that the activation energy for the reversible process accounts for half of the potential well depth. Takebe's reduced mobilities in the $T \to 0$ limit were slightly above the PL values. Takebe's approach is justified only for closed-shell systems but presents a good base for upgrading for more complex systems. By following a vast amount of data in [10] one
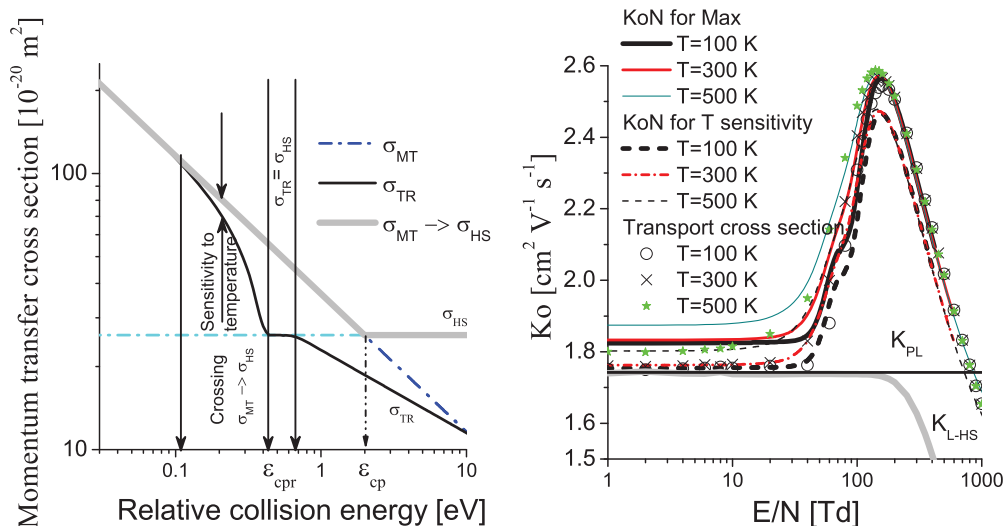
Fig. 1: (Colour online) (a) Transport cross-sections as a function of relative collision energy and (b) reduced mobility as a function of E/N where temperature T is used as a parameter.

may conclude that for a broad range of systems mobility behaves similarly to closed-shell systems, *i.e.*, where, apart from the association reaction, other reactions are negligible and the dominant effect on transport comes from the elastic momentum transfer cross-section. Since at low pressures the association cross-section is few percent of the elastic momentum transfer cross-section and is dominant at low collision energies, at $T \to 0$, $E \to 0$ affects the reduced mobility which goes to values slightly higher than the polarization limit. For the same reasons the association will not significantly affect the mobility peak. We than exploited a hard-sphere cross-section in order to define the maximum cross-section for reactive collisions.

Modelling the transport cross-section by mobility curve.

In order to model the transport cross-section one may exploit either numerical solutions of Boltzmann's kinetic equation or the stochastic Monte Carlo (MC) method [22, 23]. In this work we used the well-tested MC code [23].

Central information about the interaction is drawn from the differential cross-section with all the possible quantum-mechanical effects stored within, not exclusively from interaction potentials. Thus, in the MC modeling the momentum of the transfer cross-section σ_{MT} [22,24–26] with the assumption of isotropic scattering in the center-of-mass frame is very often used. The idea behind is the need to properly account for ion momentum losses which also appear in balance equations [12] and are desired in modeling many technologically interesting cases. Ion mobility is exactly described with σ_{MT}, at low energies where the average distance at which the ion and the molecule collide is within the range of the ion-induced dipole potential $\sim r^{-4}$. The same potential for the reaction coefficient gives a constant value calculated from the known gas polarizability and reduced mass of ion and gas.

Average polarizabilities for most gaseous atoms/molecules are generally known [27] so simple approximations

based on them are useful for a wide range of systems. For r^{-4} the potential momentum transfer cross-section $\sigma_{MT} = \sigma_{DL} = 1.105 \cdot \sigma_L$ has the same energy dependence ($\sim \varepsilon^{-0.5}$) as Langevin's cross-section σ_L [17] and a constant mobility (see solid line denoted by K_{PL} in fig. 1(b)) is obtained analytically by the so-called mean-free time theories such as, for example, the theory in [22]. In this case the obtained mobility is not a function of temperature and pressure [6,26] and is taken as a limiting case for the polarization attraction between ion and neutral [17]. If for the same potential, Langevin's cross-section is used either partially or fully to describe the loss of particles, for example, the association reaction [5] reduced mobility increases. Generally inelastic collisions cause the decrease of mobility [28] while reactive collisions increase the mobility [6] which in general can be limited by the possibility of inverse reactions. Both reduced mobility and reaction rate coefficients are easily calculated by the MC code [24], where σ_{MT} is used as previously explained. The calculated values are precise (reproducible) to a few significant digits depending on the computing resources [4,24].

A hard-sphere (HS) cross-section σ_{HS} [29,30] is often used to represent ion transport [24,30] at high collision energies (see fig. 1(a)) where actually the repulsive nature of collisions becomes dominant. Scattering in this case, described by a potential $\sim r^{-n}$ ($n \to \infty$), is isotropic in the center-of-mass frame [24] and is exactly represented by $\sigma_{MT} = \sigma_{HS}$ in Monte Carlo codes. At the same time σ_{HS} is used as a starting point in theories of ion reactions, for example as a good approximation in cases in which processes of charge transfer dominate [29,31] so it can be a potentially good approximation for more complex cases. If one crudely joins the above-mentioned approximations simply by using $\sigma_{MT} = 1.105 \cdot \sigma_L$ below ε_{cp} and $\sigma_{MT} = \sigma_{HS}$ above ε_{cp}, trying to describe ion mobility in a wider energy range (see thick solid line in fig. 1(a)) than the MC

Table 1: Characteristic values for mobility peaks with respect to polarization limit values in percent [10,33] and appropriate E/N values in Td ($1\,\mathrm{Td} = 10^{-17}\,\mathrm{Vcm^2}$).

		^{4}He	^{20}Ne	^{40}Ar	^{84}Kr	^{131}Xe	^{222}Rn
^{7}Li$^+$	$K\mathrm{omax}/K\mathrm{o_{PL}}(\%)$	71	59	62	66	65	–
	E/N (Td)	48	50	117	112	144	–
^{11}Be$^+$	$K\mathrm{omax}/K\mathrm{o_{PL}}(\%)$	47	47	68	61	52	52
	E/N (Td)	30	40	165	190	265	263
^{23}Na$^+$	$K\mathrm{omax}/K\mathrm{o_{PL}}(\%)$	57	42	46	47	50	56
	E/N (Td)	34	53	151	156	156	174
^{27}Al$^+$	$K\mathrm{omax}/K\mathrm{o_{PL}}(\%)$	37	35	37	43	40	41
	E/N (Td)	20	38	129	173	213	223
^{39}K$^+$	$K\mathrm{omax}/K\mathrm{o_{PL}}(\%)$	36	27	33	34	37	43
	E/N (Td)	27	44	131	155	185	171
^{40}Ca$^+$	$K\mathrm{omax}/K\mathrm{o_{PL}}(\%)$	36	27	33	34	37	43
	E/N (Td)	27	44	131	155	185	171

code [22,23] which properly takes into account thermal collisions [10], gives a reduced mobility in fig. 1(b) (solid line labelled by $K_{\mathrm{L\text{-}HS}}$). $K_{\mathrm{L\text{-}HS}}$ at $T = 300\,\mathrm{K}$ overlaps the PL curve and is a uniformly decreasing function at high average energies.

It is commonly accepted that the mobility peak represents the average energy where attractive intermolecular forces balance repulsive forces [24,32]. The height of the peak is best represented with respect to the polarization limit value, while the E/N's scale can be well normalized by the well depth of the interaction potential [20,21].

In table 1 are shown the mobility peak values obtained from the newest theoretical data for the reduced ion mobility for closed-shell systems [10] which are the best fit to all the existing experimental data, all normalized at the polarization limit value ($K\mathrm{omax}/K_{\mathrm{PL}}$). It is evident that $K\mathrm{omax}$ mainly depends on ion species in closed-shell systems, so one may pull a more general conclusion that $K\mathrm{omax}/K_{\mathrm{PL}}$ decreases with the increase of the ion atomic number in inert gases, and even in minor cases a small discrepancy exists from such average trend. With the increase of the atomic number $K\mathrm{omax}/K_{\mathrm{PL}}$ are at higher E/N's since less collision energy is transferred from the laboratory system with lighter ions to the gas for the similar effect.

For our test case (^{20}Ne$^+$ + ^{88}CF$_4$) we chose ^{23}Na$^+$ + ^{84}Kr as nearest closed-shell system due to its similarity with the atomic number and polarizability value.

From table 1, one may see that the mobility peak for the Na$^+$ ion is 46% relatively to the polarization limit data and is characteristic not only for Kr [21] but also for all closed-shell atoms. Thus, by analogy, the mobility peak for Ne$^+$ + CF$_4$ should be very similar to the peak for Na$^+$ + Kr if one neglects the different reactivity of these two systems. For Na$^+$ + Kr both interaction potential and bulk of the experimental measurements for the transport coefficients are available [33–36], so in the following we will refer to these data in order to model the mobility of Ne$^+$ in CF$_4$. The theoretical data for $K\mathrm{o}$ from [36] (see also [10]) give an excellent fit of the data in [33,34] at $T = 300\,\mathrm{K}$ so as to be used also for the description of the temperature variation of the reduced mobility. We selected data for temperatures $T = 100\,\mathrm{K}$, $300\,\mathrm{K}$ and $500\,\mathrm{K}$ and normalized them at the Ne$^+$ + CF$_4$ polarization limit (solid lines denoted as "$K\mathrm{oN}$ for Max" in fig. 1(b)). Ne$^+$ has slightly lower atomic number than Na$^+$ and so slightly higher $K\mathrm{omax}/K_{\mathrm{PL}}$ for which we used 49% at $E/N = 155\,\mathrm{Td}$.

Most probable processes in Ne$^+$ + CF$_4$ scattering. It is known [29,37] that the scattering probability for Ne$^+$ on CF$_4$ is largest for charge transfer that has been measured with a guided ion beam apparatus [29] (CF$_3^+$, CF$_2^+$ and CF$^+$) for energies below 50 eV and where also the absence of NeCF$_4^+$ and CF$_4^+$ was notified. The cross-section extrapolation up to 1000 eV was done according to the emission measurements of Motohashi *et al.* [37] and data in [31]. The line spectra of excited atoms obtained in spectrometric measurements in CF$_4$ indicate that the charge transfer reaction is by far the most dominant process in collisions with inert-gas ions, so other processes such as Ne excitation can be safely neglected. Having in mind measurements of the charge transfer cross-sections for F$^+$ and C$^+$ production at high energies [31] we also deduced these cross-sections by using similarities with data for other radical ions [29,31], from He$^+$ + CF$_4$ scattering data [29], and for the emission cross-sections in [37]. Thresholds for the production of all radical ions were selected from the data for ionization energies for CF$_4$ [29].

Since it is not known whether dissociative processes proceed from excited CF$_4$ or a NeCF$_4^+$ complex, we calculated the dissociation cross-sections by using basic gas phase enthalpies of formation for CF$_4$ and products [29]. With the same input data we calculated thermodynamic thresholds and used them as cross-section thresholds.
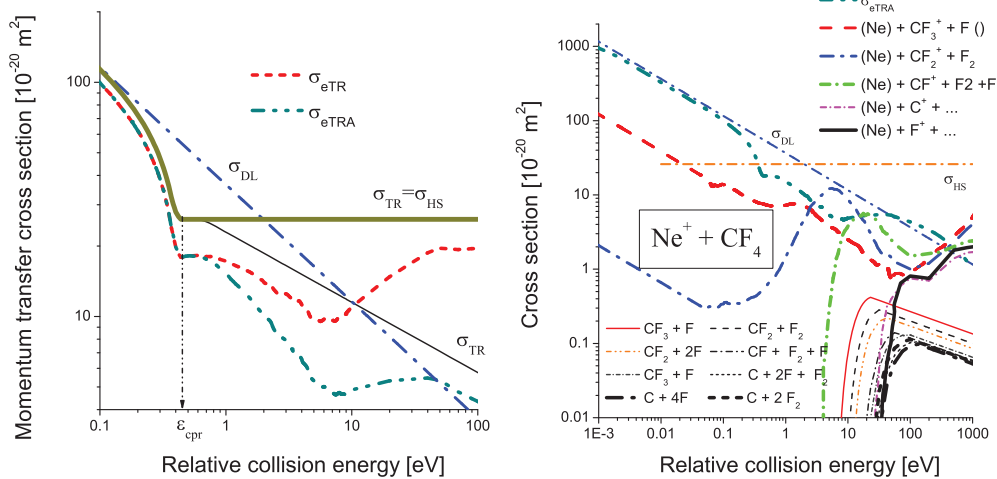
Fig. 2: (Colour online) (a) Momentum transfer cross-section and (b) cross-section set as a function of collision energy for $Ne^+ + CF_4$.

Modelling the elastic momentum transfer cross-section.
Since reactive collisions reduce the total number of trajectories, then σ_{TR} can be obtained by deducing all non-continuing trajectories represented by reactive cross-sections. The same is easily implemented in Monte Carlo codes by simply removing the particle followed from the simulation. This introduces non-conservativity in transport coefficients dividing them into flux and bulk coefficients [38]. Due to the uncertainties related to the reactive cross-sections it is possible that at high collision energies the sum of the reactive cross-sections be higher than σ_{TR}. With that in mind the momentum transfer cross-section is approximated by $\sigma_{TR} = \sigma_{HS}$ for collision energies $\varepsilon > \varepsilon_{cp}$ (see fig. 2(a)) in order to account for the possible reactions and if combined to a soft-sphere cross-section which is the one actually determined from the mobility of the closed-shell system to take into account scattering anisotropy. If now reactive cross-sections are subtracted, then the resulting cross-section σ_{eTR} represents all the elastic and inelastic losses. Now we may correct σ_{eTR} for more realistic angular dependences at high collision energies by applying the function $A(\varepsilon)$ to obtain the cross-section $\sigma_{eTRA} = A\sigma_{eTR}$ in fig. 2(a). If inelastic collisions can be neglected σ_{eTRA} represents the elastic momentum transfer cross-section $\sigma_{elm} \sim \sigma_{eTRA}$ which can be easily treated in Monte Carlo codes. If inelastic scattering is included in σ_{eTRA} the momentum balance will still be holding providing a precise calculation of the ion drift velocity and consequently of the flux. For the case of the previously derived σ_{eTRA} and reactive processes selected for $Ne^+ + CF_4$, one may claim that the cross-section set for $Ne^+ + CF_4$ is derived, which recovers the transport properties described by the given transport cross-section for a similar closed-shell system and set of reactive cross-sections (fig. 2(b)).

The mobility of high recombination energy ions such as Ne^+ ions in CF_4 is not measured up to now although the
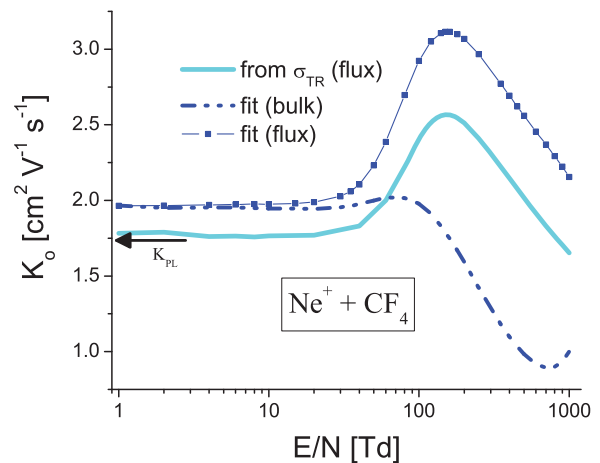
Fig. 3: (Colour online) Reduced mobility as a function E/N for Ne^+ ions in CF_4 gas for temperature $T = 300\,K$.

small reactivity at low E/N does not present a significant difficulty.

Transport parameters. – The reduced mobility for Ne^+ ions in CF_4 as a function of E/N (E is the electric-field strength, N the gas number density) compared with bulk and flux values is shown in fig. 3. The bulk drift velocity ($W = d\langle x \rangle /dt$) is the reaction corrected flux drift velocity ($w = \langle v \rangle$): $W = w + S$, where S is the term representing a measure of the effect of the reactions on the drift velocity. The difference between bulk and flux reduced mobility is a consequence of the energy-dependent reactions.

Very different values of flux and bulk reduced mobility are obtained (above about 20 Td), both with peaks of different height, as a consequence of reactive collisions. A large mobility peak appears for the flux component of the reduced mobility, while a much smaller peak appears in the bulk component of the reduced mobility. The flux

reduced mobility peaks at the same E/N values where the reduced mobility peak is obtained from the momentum transfer cross-section corresponding to the closed-shell system.

Conclusion. – We presented a simple and effective method to obtain an elastic momentum transfer cross-section for a modeled system from mobility data for a similar closed-shell system. The method can be described in a step-by-step manner as follows. A similar closed-shell system is used as a reference system with the absence of reactivity. For that system the elastic momentum transfer cross-section (σ_{TR}) as a function of energy is deduced by using Monte Carlo simulations where possible clustering reactions and temperature-dependent mobility data are taken into account. The momentum transfer cross-section of the modeled system is then constructed from σ_{TR} by using its polarization limit and atomic mass. At the same time at high energies a hard-sphere cross-section is used in order to recover the reactivity of the modeled system by subtracting from it the reactive cross-sections. By taking into account the angular dependence of the reference system one finally arrives at an elastic momentum transfer cross-section as a function of the collision energy and at the assessment of the cross-section set.

The method is applied for the case of Ne$^+$ scattering on CF$_4$ for which the cross-section set is determined. By using the Monte Carlo technique in the final run we calculated transport parameters and discussed flux and bulk mobility as a function of E/N, which were not available up to now.

$* * *$

REFERENCES

[1] MAKABE T. and PETROVIĆ Z., *Plasma Electronics: Applications in Microelectronic Device Fabrication* (Taylor and Francis, CRC Press, New York) 2006; PETROVIĆ Z. LJ., MAGUIRE P., RADMILOVIĆ-RADJENOVIĆ M., RADETIĆ M., PUAČ N., MARIĆ D., MAHONY C. and MALOVIĆ G., in *Nanotechnology for Electronics, Photonics and Renewable Energy*, edited by KORKIN A. *et al.* (Springer) 2010, p. 85.
[2] ROBSON R. E., WHITE R. D. and PETROVIĆ Z. LJ., *Rev. Mod. Phys.*, **77** (2005) 1303.
[3] MURAKAMI T., NIEMI K., GANS T., O'CONNELL D. and GRAHAM W. G., *Plasma Sources Sci. Technol.*, **22** (2013) 015003; VAN GAENS W. and BOGAERTS A., *J. Phys. D: Appl. Phys.*, **46** (2013) 275201.
[4] SAMUKAWA S., HORI M., RAUF S., TACHIBANA K., BRUGGEMAN P., KROESEN G., WHITEHEAD J. C., MURPHY A. B., GUTSOL A. F., STARIKOVSKAIA S., KORTSHAGEN U., BOEUF J.-P., SOMMERER T. J., KUSHNER M. J., CZARNETZKI U. and MASON N., *J. Phys. D: Appl. Phys.*, **45** (2012) 253001.
[5] NIKITOVIĆ Ž., RASPOPOVIĆ Z., STOJANOVIĆ V. and JOVANOVIĆ J., *EPL*, **108** (2014) 35004.
[6] RASPOPOVIĆ Z., STOJANOVIĆ V. and NIKITOVIĆ Ž., *EPL*, **111** (2015) 45001.
[7] STOJANOVIĆ V., RASPOPOVIĆ Z., JOVANOVIĆ J. V., DE URQUIJO J. and PETROVIĆ Z. LJ., *J. Phys.: Conf. Ser.*, **514** (2014) 012059.
[8] NEDNER-SCHATTEBURG G. and BONDYBEY V. E., *Chem. Rev.*, **100** (2000) 4059.
[9] JALILI A. H., BEHNEJAD H., AFSAHI G., GHARIBI M. and VIEHLAND L. A., *Chem. Phys. Lett.*, **584** (2013) 49.
[10] Viehland database, www.lxcat.net, retrieved on May 4, 2016.
[11] ARMENTROUT P. B., ERVIN K. M. and RODGERS M. T., *J. Phys. Chem.*, **112** (2008) 10071.
[12] PHELPS A. V., *Phys. Rev. E*, **79** (2009) 066401.
[13] TROE J., *J. Phys. Chem. A*, **110** (2006) 2831.
[14] PETRIE S. and BOHME D. K., *Top. Curr. Chem.*, **225** (2003) 37; BOHME D. K. and SCHWARZ H., *Angew. Chem., Int. Ed.*, **44** (2005) 2336; BOHME D. K., *Can. J. Chem.*, **86** (2008) 177.
[15] GEPPERT W. D. and LARSSON M., *Chem. Rev.*, **113** (2013) 8872.
[16] PHELPS A. V., *J. Appl. Phys.*, **76** (1994) 747.
[17] KRSTIĆ P. S. and SCHULTZ D. R., *J. Phys. B: At. Mol. Opt. Phys.*, **42** (2009) 065207.
[18] PETROVIĆ Z. LJ. and STOJANOVIĆ V. D., *J. Vac. Sci. Technol. A*, **16** (1998) 329.
[19] FALCETTA M. F., DORKO M. J. and SISKA P. E., *J. Chem. Phys.*, **113** (2000) 11044.
[20] GATLAND I. R., VIEHLAND L. A. and MASON E. A., *J. Chem. Phys.*, **66** (1977) 537.
[21] TAKEBE M., *J. Chem. Phys.*, **78** (1983) 7223.
[22] SKULLERUD H., *J. Phys. B: At. Mol. Phys.*, **6** (1973) 728.
[23] RISTIVOJEVIĆ Z. and PETROVIĆ Z. LJ., *Plasma Sources Sci. Technol.*, **21** (2012) 035001.
[24] MASON E. A. and MCDANIEL E. W., *Transport Properties of Ions in Gases* (John Wiley and Sons, New York) 1988, p. 560.
[25] DENPOH K. and NANBU K., *J. Vac. Sci. Technol. A*, **16** (1998) 1201.
[26] PETROVIĆ Z. LJ., RASPOPOVIĆ Z. M., STOJANOVIĆ V. D., JOVANOVIĆ J. V., MALOVIĆ G., MAKABE T. and DE URQUIJO J., *J. Appl. Surf. Sci.*, **253** (2007) 6619.
[27] HAYNES W. M. (Editor), *CRC Handbook of Chemistry and Physics*, 96th edition (CRC Press) 2015.
[28] OHTSUKI K., HANANOE M. and MATSUZAWA M., *Phys. Rev. Lett.*, **95** (2005) 213201.
[29] FISHER E. R., WEBER M. E. and ARMENTROUT P. B., *J. Chem. Phys.*, **92** (1990) 2296.
[30] MC DANIEL E. W., ČERMAK V., DALGARNO A., FERGUSON E. E. and FRIEDMAN L., *Ion-Molecule Reactions* (Wiley Interscience) 1970.
[31] PARKER E. and EL-ASHHAB F. S. M., *Int. J. Mass Spectrom. Ion Phys.*, **47** (1983) 159.
[32] JOVANOVIĆ J. and PETROVIĆ Z. LJ., *J. Phys.: Conf. Ser.*, **162** (2009) 012004.
[33] ELLIS H. W., THACKSTON M. G., MC DANIEL E. W. and MASON E. A., *At. Data Nucl. Data Tables*, **31** (1984) 113.

[34] THACKSTON M. G., SANCHEZ M. S., NEELY G. N., POPE W. M., EISELE F. L., GATLAND I. R. and MCDANIEL E. W., *J. Chem. Phys.*, **73** (1980) 2012.

[35] KOUTSELOS A. D., MASON E. A. and VIEHLAND L. A., *J. Chem. Phys.*, **93** (1990) 7125.

[36] VIEHLAND L. A., LOZEILLE J., SOLDAN P., LEE E. P. F. and WRIGHT T. G., *J. Chem. Phys.*, **119** (2003) 3729.

[37] MOTOHASHI K., TAKAHASHI T., TAKAHASHI N. and TSURUBUCHI S., *J. Phys. B: At. Mol. Opt. Phys.*, **38** (2005) 3339.

[38] ROBSON R. E., *Aust. J. Phys.*, **44** (1991) 685.

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Mass spectrometry of positive ions in capacitively coupled low pressure RF discharges in oxygen with water impurities

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Abstract

A capacitively coupled RF oxygen discharge is studied by means of mass spectroscopy. Mass spectra of neutral and positive species are measured in the mid plane between the electrodes at different distances between plasma and mass-spectrometer orifice. In the case of positive ions, as expected, the largest flux originates from O_2^+. However, a significant number of impurities are detected, especially for low input powers and larger distances. The most abundant positive ions (besides O_2^+) are NO^+, NO_2^+, $H^+(H_2O)$, and $H^+(H_2O)_2$. In particular, for the case of hydrated hydronium ions $H^+(H_2O)_n$ ($n = 1, 2$) a surprisingly large flux (for low pressure plasma conditions) is detected. Another interesting fact concerns the H_2O^+ ions. Despite the relatively high ammount of water impurities H_2O^+ ions are present only in traces. The reaction mechanisms leading to the production of the observed ions, especially the hydrated hydronium ions are discussed.

Keywords: water cluster ions, RF oxygen plasma, mass spectrometry

(Some figures may appear in colour only in the online journal)

1. Introduction

In common reactors used for reactive plasma processing some amounts of impurities are usually present; often to an unknown level. These impurities can have an immense influence on plasma properties [1] and thus increase the complexity of chemical reactions in plasma processes.

One of the most common impurities—present both in low pressure and high pressure plasmas- is certainly water. The sources of water are different; in atmospheric pressure plasma jets operating in contact with liquids, water is unavoidable specie. But water impurities can also originate from some chemical process in reactive plasma, from desorption by chemical sputtering or they can intrude from the environment just by opening the chamber and exposing it to the atmosphere. Once deposited on the chamber walls or electrodes, water cannot be efficiently pumped out and diminishes for example significantly the lifetimes of argon metastable in plasmas [2].

It is important to stress that although low pressure plasmas are very often used, for example for surface functionalisation (where even traces of water can play an important role for the formation of surface functional groups) the analysis of water ions and water ion clusters is rather rare. One interesting example for the formation of water clusters in low pressure plasmas concerns astrophysical applications [3]. More investigations have been performed in the field of high pressure discharges.

Very often impurities in plasmas are detected from observations based on optical emission spectroscopy [2] but also with other more indirect methods, such as measuring the decay times of metastable Ar^m or He^m [2, 4]. Impurities from the feed gas, especially water molecules, are reported to be responsible for the fast quenching of the He^m metastable atoms [4].

Another diagnostic commonly used for the characterisation of processing plasmas is mass spectrometry. Besides the

detection of neutral species, plasma ion mass spectrometry allows in addition the (energy resolved) detection of fluxes of positive ions [5]. Recently, it was shown for a plasma jet operated at high pressure that the dominant positive ions originate from ion clusters of water molecules $H^+(H_2O)_n$, $n = 1, 2,\ldots$, where the maximum neutral water content was 3790 ppm H_2O in He [6].

Here we present the mass spectra of positive ions in radiofrequency oxygen plasma used for the functionalization of carbon—based nanostructures. The ion mass spectra will be discussed by considering relevant ion–neutral reactions and their reaction rates. An unexpected large flux of hydrated hydronium ions $H^+(H_2O)_n$ ($n = 1, 2$) is detected under low pressure plasma conditions. These ions are generated in plasma chemical reactions of water and other impurities present in the vacuum chamber. Under laboratory conditions, $H^+(H_2O)$ (hydronium ion or protonated water) is used for example in Proton Transfer Reaction Mass Spectrometry [7, 8] and is usually produced in atmospheric pressure corona discharges. In this paper we show how the relative yield of O_2^+ ions and ions originating from impurities (such as $H^+(H_2O)_n$) depend on the discharge power, and on the distance between the plasma source and the entrance of the mass spectrometer. In addition, the relative abundance of different water cluster ions ($H^+(H_2O)$, mass $m = 19$ amu and $H^+(H_2O)_2$, mass 37 amu) are analyzed.

2. Experiment

The experiments are performed in a radio frequency (RF) discharge at 13.56 MHz (figure 1). The circular electrodes have a diameter of 120 mm and a distance of 50 mm. The distance between the stainless—steel electrodes can be varied without opening the discharge chamber. The lower electrode is grounded while the upper electrode is powered. In the present experiment, the input powers in the range from 3 W to 15 W are used giving a stable discharge. This set-up is normally used for the plasma based treatment of sensitive surfaces.

The vacuum system consists of a large cylindrical vessel (610 mm in diameter and 650 mm high). The vacuum is maintained by a turbo molecular vacuum pump and rotary—van pump as a back-up. After opening the chamber (e.g. by changing the samples) a background pressure of 5–7 × 10^{-8} mbar can be achieved after few hours of pumping. A continuous gas supply is introduced from a high pressure cylinder ALPHAGAZ™ 1 from Air Liquide and controlled by a system of flow controllers (MKS). The global oxygen purity of ALPHAGAZ™ 1 is 99.998%. 0.002% or 20 ppm (particles per million) of impurities consist of: hydrocarbons C_nH_m (<500 ppb (particle per billion) in total), H_2O (<2 ppm), CO (0.2 ppm), CO_2 (<0.2 ppm), Ar (<10 ppm), and N_2 (<5 ppm). During the experiment the gas pressure is kept constant at 0.1 mbar by reducing the pumping speed.

For mass spectroscopy a HIDEN EQP 1000 quadruple mass spectrometer (QMS)—equipped with an energy analyzer—is used. Besides for the rest gas analysis i.e. the detection of neutral species, the QMS is also used for the detection of ions
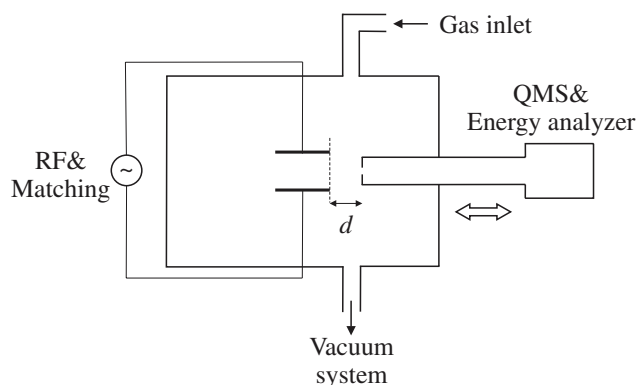
Figure 1. Experimental set-up. QMS is movable to and from the plasma source, giving the possibility to measure ion fluxes at different distances d.
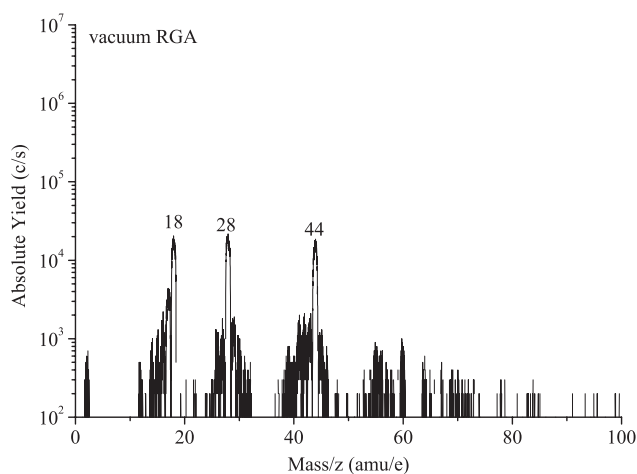
Figure 2. Residual gas analysis of the discharge chamber before introducing the working gas. Mass 18 amu reveals the presence of water, mass 28 amu nitrogen and mass 44 amu CO_2 impurities. Other impurities, such as H_2, have a much lower abundance. Total residual gas pressure is 1.3×10^{-5} mbar. There is no oxygen impurity.

and for measuring the energy distribution of the arriving ions. The latter is necessary for determining the sampling energy for optimal ion signal, which can be different for different ions due to the nature of collisions experienced by the specific ions during their travel from the plasma to the QMS.

The QMS is mounted perpendicular to the electrode axis on a mechanical rail, which is used to move QMS to and away from the electrodes. This system allows the measurements of ion fluxes and their energy distribution at different distances d from the plasma source (see figure 1); in this particular experiment it is 50 mm and 93 mm from the electrode perimeter. The QMS is electrically grounded and on the same potential as the lower electrode and the chamber walls.

3. Results

Prior to the start of the experiment, a rest gas analysis of the empty discharge chamber is made. The measured mass spectrum of the evacuated chamber is presented in figure 2. The most abundant masses are 18 amu, 28 amu and 44 amu. These
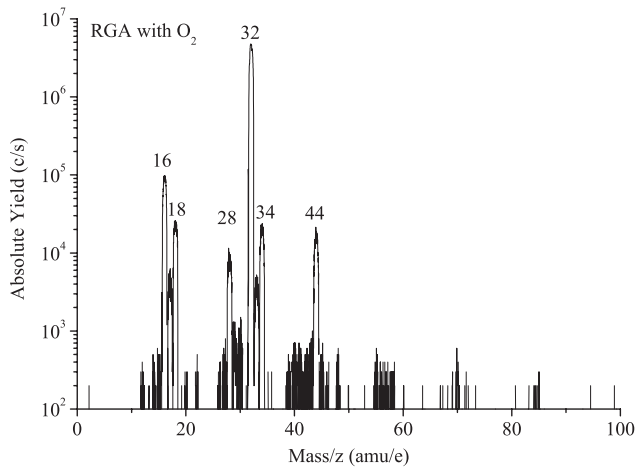
Figure 3. Residual gas analysis in the discharge chamber with the total gas pressure of 0.1 mbar and under 20 sccm gas flow-rate of oxygen. Beside the oxygen, there are different impurity species: water (mass 18 amu), nitrogen (mass 28 amu), and CO_2 (mass 44 amu). Mass 16 amu (atomic oxygen), 17 amu (OH), 33 amu (HO_2) and 34 amu (H_2O_2) are produced in chemical reactions in mass spectrometers ion source.

masses are assigned to water, nitrogen and carbon dioxide, respectively. In a recent report [9] the feed gas humidity is found to be the source of water impurity in an atmospheric pressure cold plasma jet. The authors find out that the type of pipes used for the gas feed and their flushing time strongly influences the water content. The mass spectrum in figure 2 reveals the absence of oxygen (mass 32) and furthermore, the N_2 : CO_2 ratio excludes a leakage of ambient air as a source of impurities. Some traces of molecular hydrogen (2 amu) should be noticed too. Nevertheless, in our experiment the RGA spectrum represents more a fingerprint of the operation history of the chamber than the water intrusion through a gas feed.

Figure 3 presents a RGA mass spectrum measured at 0.1 mbar total gas pressure and a constant oxygen flow of 20 sccm. After introducing the oxygen gas, the largest peak is at mass 32 amu. As usual, mass 16 amu (atomic oxygen O) is produced due to the ionization of O_2 by electron collisions in the ion source of the mass spectrometer. Some other detected species have a similar origin, such as OH (17 amu), HO_2 (33 amu) and H_2O_2 (34 amu). In comparison with figure 2, the relative content of water and CO_2 undergoes an insignificant change. Nevertheless, the N_2 yield is two times and the H_2 several times less than before introducing oxygen.

Figure 4 presents ion mass spectra detected at different distances from the discharge (a) 50 mm and (b) 93 mm away from the electrodes at 6 eV sampling energy. As it is expected, the most prominent ion is O_2^+. However, ($H^+(H_2O)$ is the second largest, followed by other ions that have their origin in impurities, such as NO^+ and NO_2^+. Some amount of protonated water clusters of higher number ($H^+(H_2O)_2$) at mass 37 amu is present. At 3.6 W input power, even very low yields of mass 55 amu ($H^+(H_2O)_3$) are detected. Traces of other ions such as $H_2O_2^+$, HO_2^+, and CO_2^+ are detected too. At the larger distance, the number of ions drops at least two times, except of NO^+ which drops only about 20% compared to the value at 50 mm.

With increasing power, the signal of the main positive ion O_2^+ increases, independently from the distance between the plasma and the orifice. The trend for the impurities is rather opposite. With respect to the plasma—orifice distance, the contribution of the 'impurity ions' becomes larger at larger distances, reaching almost 50% of the total flux for the 3.6 W cases.

The total ion yield versus RF input power is depicted on figure 5 (The total ion yield is defined as a sum of the absolute ion yields in the spectrum $\sum_i Y_i^a$, where Y_i^a denotes absolute yield of ion *a* expressed in counts per second.). By increasing the input RF power, the plasma density increases, which is reflected well by the increase of the total ion yield.

4. Discussion

As shown in figure 4, the most abundant positive ions are (besides O_2^+) NO^+, NO_2^+, $H^+(H_2O)$ and $H^+(H_2O)_2$. Regarding the relatively high amount of water impurities, one striking characteristic of the ion mass spectra presented on figure 4 is the very low signal at the $m/e = 18$, which indicats a very low flux of H_2O^+.

The origin of the mesured ion mass spectra will be analyzed in the following text by discussing possible reaction paths that are described in the literature.

Due to their high kinetic energy, electrons play the main role in low pressure discharges for the production of both negative and positive ions. Electrons in pure oxygen plasmas produce mainly O_2^+ ions [10], which density depends on electron temperature and density. When water wapor molecules are colliding with electrons, H_2O^+ and OH^+ are the mainly produced ions. Electron collisions with N_2 impurities cause the production of N_2^+ and N^+ ions and indirectly also the production of NO^+ ions through reactions with O_2.

Another possible source of H_2O^+ can be exothermic charge-transfer (CT) collisions of O^+ ions with H_2O molecules [11]. However, O^+ is efficiently removed in CT collisions with O_2 producing O_2^+, and it is therefore not observed in the present mass spectrum. The formation of H_2O^+ due to to endothermic CT reactions of water molecules with O_2^+ ions is also an inefficient process. In addition, H_2O^+ could be also formed in charge transfer collisions of OH^+, H^+, and H_2^+ with H_2O [12].

The main loss chanel of H_2O^+ are the collisions with neutral oxygen moleculs, which exclusively produces O_2^+ [12, 13]

$$H_2O^+ + O_2 \rightarrow O_2^+ + H_2O \quad k = 1.5 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}. \quad (1)$$
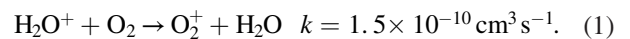
This gives for a O_2 pressure of 0.1 mbar a relatively short lifetime of about 2.6 μs, which is the main reason why H_2O^+ is minimized in the spectrum. Another important loss process for all positive ions is their diffusion to the walls.

According to Fehsenfeld *et al* [14], NO^+ is known as a positive ion 'sink' in ionized air since (nearly) every combination of positive oxygen or nitrogen ions, and oxygen (nitrogen) neutrals can react exothermically to give NO^+, and most of these reactions are rapid. Apart of NO^+ produced in the chamber there is also insignificant NO^+ present as a product of electron ionization of impurity NO.
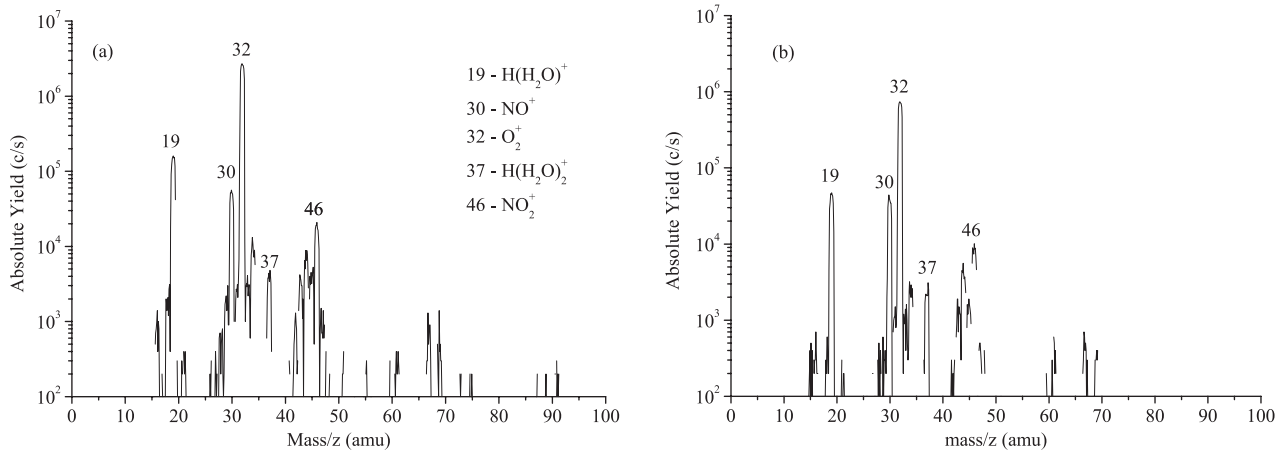
Figure 4. Ion mass spectra of oxygen plasma for two different distances of the QMS sampling orifice to the discharge: (a) 50 mm away from the electrodes, (b) 93 mm away. Most prominent ions are labelled. Discharge conditions are: pressure $p = 0.1$ mbar, flow rate 20 sccm and discharge power $P = 7.6$ W.
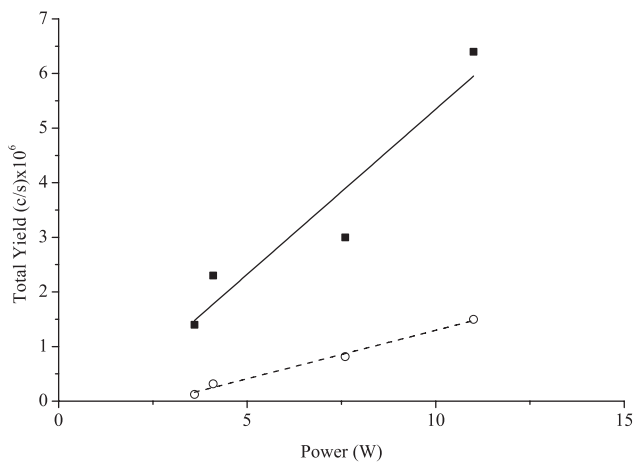
Figure 5. Total ion yield versus RF input power measured at two different distances of sampling orifice and plasma. Solid squares—50 mm and opened circles—93 mm distance. Solid and dashed lines are least square approximation of data, respectively.

Table 1. Relative yields of different ions (%) versus input RF power at two plasma—sampling orifice's distances.

Distance (mm)	50				93			
Power (W)	3.6	4.1	7.6	11	3.6	4.1	7.6	11
O_2^+	83	90	90	97	56	71	87	92
$H^+(H_2O)$	5.3	4.3	5.4	1.3	14	12	5.8	3.6
$H^+(H_2O)_2$	1.1	0.8	0.2	0.01	4.2	1.7	0.26	0.05
NO^+	4.5	3.5	1.9	0.8	19	12	4.5	3
NO_2^+	2.2	1.4	0.6	0.4	5.9	3	1.1	.45

$$O_2H + O_2H + M \rightarrow H_2O_2 + O_2 + M, \ k = (1.5 \pm 0.2) \cdot 10^{-12}$$
$$\times \exp[(19 \pm 31)/T] + 1.7 \cdot 10^{-33} \cdot [M] \cdot \exp[1000/T].$$
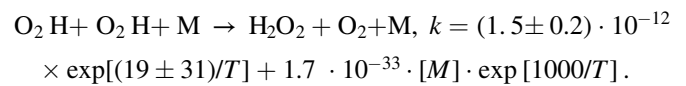
This reaction can be enhanced in the presence of H_2O and possibly other molecules.

The most interessting product of ion–neutral reactions in our plasma are hydrated hydronium ions $H^+(H_2O)_n$. According to table 1, the $H^+(H_2O)_n$ ion flux makes up to 20% of the total ion flux at 3.6 W discharge power and 93 mm plasma—sampling orifice's distance. $H^+(H_2O)_n$ cluster ions are also important constituents of the terrestrial atmosphere [14]. Particularly, hydrated hydronium ions are the most abundant species in the *D* region of the ionosphere (altitude 60–90 km) [14]. It is interesting to notice that the pressures in *D* region ranges between 1–10 Pa, which agrees well with the gas pressure in this experiment (although the energy distribution of those ions are different.)

In almost every report concerning this subject, the appearance of $H^+(H_2O)$ (often written as H_3O^+) in mass spectra is related to the formation of $H^+(H_2O)_n$ by proton transfer reaction

$$H_2O^+ + H_2O \rightarrow H_3O^+ + H. \tag{2}$$
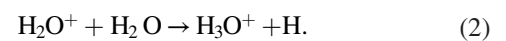
However, due to the low H_2O^+ density measured in our experiment (particularly due to the fast charge transfer reaction with

NO_2^+ ion (46 amu) appears from charge transfer reactions of NO_2 with other ions (O_2^+, OH^+,...), which is the main channel for the NO_2^+ production [13]. Nevertheless, electron impact ionization of NO_2 produces only about 10% of NO_2^+ and 90% of NO^+. NO_2 is introduced into the system either as impurity or produced in different reactions with neutrals [15, 16]. It is known that O atom absorption on surfaces [17, 18] causes the production of NO and NO_2 molecules, which can be easily converted to positive ions in collisions with O_2^+ ions.

According to available data [12] $H_2O_2^+$ (34 amu) is mainly produced in charge transfer collisions of O_2^+ with H_2O_2 [19]. H_2O_2 is most likely produced in neutral (three body) reactions such as [20]

$$OH + OH \rightarrow H_2O_2,$$

with the rate coefficient $k = 1.51 \times 10^{-17}$ m^3 s^{-1} [12, 21]. The principal source of H_2O_2 in the upper troposphere and the stratosphere is the reaction [22]:

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Figure 6. (a) Contribution of mass $m = 19$ amu in relative yield spectrum. Solid line—53 mm distance, dotted—dashed line 93 mm distance. (b) Ratio of relative ion yields of masses 19 amu and 37 amu (m(17)/m(37)) as a function of input power, at a distances 50 mm and 93 mm.

O_2 (1)) it is not clear whether reaction (2) is the only channel for the production of H_3O^+.

It is known for example from ionospheric experiments, that ions O_2^+ and NO^+ clustered with water contribute to the production of proton hydrates [23, 24]. i.e. to the production of H_3O^+ and $H^+(H_2O)_n$.

The association of O_2^+ ions with water molecules resulting in the formation of $O_2^+ \cdot H_2O$ [25] is inefficient for our conditions, as confirmed by the absence of $O_2^+ \cdot (H_2O)_n$ ions in the spectra (figure 4) and for all discharge powers.

Independent from the production mechanism, once H_2O^+ is formed, it can be the starting point for the production of higher water cluster ions via reversibile, fast *exothermic* reactions with water (oxygen stabilized association cluster reactions with H_2O):

$$H^+ \cdot (H_2O)_{n-1} + H_2O + (M) \rightarrow H^+ \cdot (H_2O)_n + (M), \qquad (3)$$
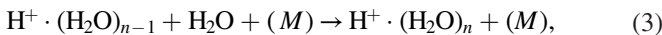
where $n = 1,2,3,\ldots$ and third body partners are $M = H_2O$ or O_2.

However, the reactions (3) are third order reactions, which are not so efficient at lower pressures [26] and very rare due to the low density of H_2O. Consequently, the mass spectra at figure 4 displays a significantly higher signal of $H^+(H_2O)$ ions than of $H^+(H_2O)_2$ ions or even larger water cluster ions. The third body partner in the reaction (3) strongly influences the relative abundance of ion water clusters of different masses, which can be different with the higher background pressure and different type of the background gas.

Another reason that the larger water cluster ions are not observed are reactions with H_2O and O_2:

(a) Endothermic chain reactions with H_2O:

$$H^+(H_2O)_n + H_2O \rightarrow H^+(H_2O)_{n-1} + 2H_2O - \Delta E_n, \qquad (4)$$
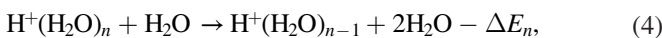
which are important only for higher n's [27];

(b) Reactions with the more abundant O_2:

$$H^+(H_2O)_n + O_2 \rightarrow H^+(H_2O)_{n-1} + H_2O + O_2 - \Delta E_n. \qquad (5)$$
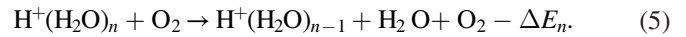
Figure 6(a) shows the relative ion yield of mass 19 amu in the ion mass spectrum as a function of power. (The relative ion yield is defined as absolute ion yield normalized to the total ion yield.)

The decrease of the relative yield of hydronium water clusters with increase of power (see figure 6(a)) is expected due to the nearly constant amount of water in the system and the increasing number of radicals and ions produced at higher powers. Moreover, it is known that the abundance of protonated water clusters in water wapor strongly depends on the collision energy [28, 29]. In general, the size of the cluster ions decreases for higher collision energies and one may expect higher $H^+(H_2O)$ peaks with increasing power input as it is observed in figure 6(b)).

As previously noticed, the total ion yied depends strongly on (i) discharge power and (ii) sampling distance. The results show that in this pressure range the influence of the ion collisions with the backgroun gas on their path to QMS is significant. The collisions with the background can change the energy distribution of the sampled ions as well as their lost by inellastic collisions. Although the increase of total ion yield with the discharge power is expected, the strong decay of the total yield with the sampling distance is more complicated to explain. Cosidering different solid angles, the expected yield at 93 mm ($Y(93)$) should be 30% of the yield at 50 mm ($Y(50)$) (figure 5). This value agrees well at higher powers (7.6 W and 11 W). Nevertheless, the total ion yield ratio at 3.6 W is $Y(93): Y(50) = 1:10$ and the difference can be explained by losses of O_2^+ in different inellastic collisions. Further invesigations, including a kinetic model for ion transport in collisional sheat, are necessary to revail observed behaviour.

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5. Conclusion

The measurements show that the composition of the ion flux depends strongly on the apllied discharge power and the distance of the plasma from the orifice of the mass spectrometer. For large powers and small distances the dominant ion species is—as expected—the O_2^+ ion. The situation changes dramtically for smaller RF—input powers and larger distances. In this case the impurity ions can make up to about 50% of the total ion flux. Particularly, at 3.6 W discharge power and 93 mm away from the discharge the relative ion yield of ion water clusters $(H^+(H_2O)_n$ ($n = 1, 2$) with $n = 1$ and $n = 2$) makes almost 20% of the total ion yield. The analysis of possible reaction paths explains well the sources of the impurity ions and their products in oxygen plasma at low pressure.

The analysis of the ion fluxes and their dependance from the discharge conditions is particularly important for plasma-surface treatments. It is necessary to understand the sources of impurities detected on different surfaces during and after plasma-surface treatments. Eventually, this will lead to a better understanding and controlling of the plasma functionalization, particularly of novel carbon and oxide materials (e.g. carbon nanotubes, ZnO nanorods).

Acknowledgments

References

[1] Martensa T, Bogaerts A, Brok W J M and Dijk J V 2008 *Appl. Phys. Lett.* **92** 041504

[2] Stefanović I, Kuschel T, Schröter S and Böke M 2014 *J. Appl. Phys.* **116** 113302

[3] Sinha H S S, Oyama K-I and Watanabe S 2013 *J. Geophys. Res.: Space Phys.* **118** 583

[4] Winter J, Santos Sousa J, Sadeghi N, Schmidt-Bleker A, Reuter S and Puech V 2014 *Plasma Sources Sci. Technol.* **24** 025015

[5] Ferreira J A and Tabarés F L 2009 *Plasma Sources Sci. Technol.* **18** 034019

[6] Bruggeman P, Iza F, Lauwers D and Gonzalvo Y A 2010 *J. Phys. D: Appl. Phys.* **43** 012003

[7] Pavlik M and Skalny J D 1997 *Rapid Commun. Mass Spectrom.* **11** 1757

[8] Hansel A, Jordan A, Holzinger R, Prazeller P, Vogel W and Lindinger W 1995 *Int. J. Mass Spectrom. Ion Process.* **149/50** 609

[9] Winter J, Wende K, Masur K, Iseni S, Dünnbier M, Hammer M U, Tresp H, Weltmann K-D and Reuter S 2013 *J. Phys. D: Appl. Phys.* **46** 295401

[10] Stoffels E, Stoffels W W, Vender D, Kando M, Kroesen G M W and Hoog F J 1995 *Phys. Rev.* E **51** 2425

[11] Dressler R A, Gardner J A, Cooke D L and Murad E 1991 *J. Geophys. Res.* **96** 13795

[12] Avtaeva S V, General A A and Kelman V A 2010 *J. Phys. D: Appl. Phys.* **43** 315

[13] Shul R J, Passarella R, DiFazio L T Jr, Keesee R G and Castleman A W Jr 1988 *J. Phys. Chem.* **92** 4941

[14] Fehsenfeld F C, Mosesman M and Ferguson E E 1971 *J. Chem. Phys.* **55** 2120

[15] Spanel P and Smith D 2000 *Rapid Commun. Mass Spectrum.* **14** 646

[16] Murakami T, Niemi K, Gans T, O'Connell D and Graham W G 2013 *Plasma Sources Sci. Technol.* **22** 015003

[17] Castillo M, Herrero V J and Tanarro I 2001 *Plasma Sources Sci. Technol.* **11** 368

[18] Guerra V, Marinov D, Guaitella O and Rousseau A 2014 *J. Phys. D: Appl. Phys.* **47** 224012

[19] Lindinger W, Albritton D L, Howard C J, Fehsenfeld F C and Ferguson E E 1975 *J. Chem. Phys.* **63** 5220

[20] Vasko C A, Liu D X, van Veldhuisen E M, Iza F and Bruggeman P J 2014 *Plasma Chem. Plasma Process.* **34** 1081

[21] Medodovic S and Locke B R 2007 *J. Phys. D: Appl. Phys.* **40** 7734

Medodovic S and Locke B R 2009 *J. Phys. D: Appl. Phys.* **42** 049801 (corrigendum)

[22] Christensen L E, Okumura M, Sander S P, Salawitch R J, Toon G C, Sen B, Blavier J F and Jucks K W 2002 *Geophys. Res. Lett.* **29** 1299

[23] Ferguson E E 1975 *Interactions Between Ions and Molecules* ed P Ausloos (New York: Plenum) p 377

[24] Ferguson E E and Fehsenfeld F C 1969 *J. Geophys. Res. Space Phys.* **74** 5743

[25] Keesee R G and Castleman A W Jr 1986 *J. Phys. Chem. Ref. Data* **15** 1011

[26] Hamon S, Speck T, Mitchell J B A, Rowe B and Troe J 2005 *J. Chem. Phys.* **123** 054303

[27] Good A, Durden D A and Kebarle P 1970 *J. Chem. Phys.* **52** 212

[28] Wroblewski T, Ziemczonek L, Gazda E and Karwasz G P 2003 *Radiat. Phys. Chem.* **68** 313

[29] Kebarle P, Searles S K, Zolla A, Scarborough J and Arshadi M 1967 *J. Am. Chem. Soc.* **89** 6393

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Effect of exothermic reactions on the mobility of Ar$^+$ in CF$_4$

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Abstract – In this letter we present a cross-section set and transport properties for Ar$^+$ scattering on CF$_4$ for relative energies up to 1000 eV. Monte Carlo simulation method is applied to accurately calculate transport parameters in hydrodynamic regime. We present new data for Ar$^+$ ions in CF$_4$ as a function of reduced electric fields E/N (N-gas density) where the gas temperature T_{g} is used as a parameter. Values of the reduced mobility are discussed. Discrepancy of reduced mobility for $T_{\mathrm{g}} \to 0$ and $E \to 0$ from the polarization limit was previously theoretically considered but rarely measured especially in the presence of exothermic reactions. We find that internally resonant exothermic dissociative charge transfer cross-section for CF$_3^+$ production significantly increases zero-field ion mobility with respect to the polarization limit.

Introduction. – Transport of Ar$^+$ plays a significant role in various etching and deposition processes [1], in dark-matter detection [2] and in many other scientific and technological applications. In this letter the objective will be to study the transport of Ar$^+$ in CF$_4$. Since quantitative information about ion-molecule reactions is essential for understanding the production and transport of ions in electrical discharges, it is necessary to have the cross-section set. Although for this particular case some experimental cross-sections exist, neither complete cross-section set [3] was established nor transport parameters were known. These data, although closely related, are both needed in plasma modeling.

Transport parameters in the presence of exothermic reactions (recombination energy of the ion is higher than the ionization potential of the gas particles) are generally less studied. In our selected case the reason is a large rate coefficient for exothermic reactions (resonant [4]) that limits the number of ions necessary for the determination of mobility. By using Monte Carlo simulations one may calculate transport parameters for the cases that are out of the reach of experimental efforts, provided the complete cross-section set is known. We expected that the reduced mobility data, as a function of E/N, will be significantly affected by the presence of exothermic reactions. Taking into account the existing rate coefficient for reactions, we also discussed the possibility of measuring the mobility for Ar$^+$ in CF$_4$ in time-of-flight (TOF) experiments.

In the following we have presented and explained the assessment of the cross-section set. Then we showed and discussed the results of our Monte Carlo simulations for which the cross-section set was used as input data. We presented the rate coefficients, the mean energies and the reduced mobility data, as a function of E/N where the gas temperature was used as a parameter. Finally we discussed the discrepancy of zero-field mobility data from polarization limit in the presence of exothermic collisions in the range from room to very low temperatures.

Mobility and polarization limit. – In standard textbooks [1] transport of ions at low electric fields is commonly explained by frequent elastic collisions with gas particles. Elastic collisions proceed according to the interaction potential between ion and gas molecule proved to be able to predict transport properties of ions such as ion mobility [5]. The measured ionic mobility data are often used as a first test in establishing the complete cross-section set [6].

When elastic collisions proceed in the long-range part of the induced polarization potential one obtains zero-field mobility in the so-called polarization limit. Due to their simplicity, expressions connecting the polarization term of the potential to the mobility are very useful and popular [1] and for many cases are satisfactorily accurate [7,8]. Studies of the mobility of inert-gas ions in atomic gases show that discrepancy from polarization limit is not larger than about 20% [7] allowing simple

extraction of total momentum transfer cross-section from zero-field mobility.

Zero-field mobility is close to the polarization limit only when the ion-atom collision energy is very low compared to the well depth of the interaction potential [9]. For example for a gas at $T_g = 77$ K the polarization limit may just be approached for some selected cases while at room temperature the thermal energy for the same cases can be comparable with the well depth of the interaction potential and so discrepancy from the polarization limit is large [10]. In recent experiments (TOF) for measuring mobility at very low temperature ($T_g = 4.35$ K, see, for example, [9] and/or [11]) it has been possible to prove that zero-field mobilities appear very close to the polarization limit, *i.e.* higher than the polarization limit when reflecting the association of ion with gas particles. Zero-field mobilities can also be lower by some degrees due to a rotational excitation [12]. Since the mobility of ions at temperatures close to the room temperature is not far from the polarization limit value [13] it is often used as an approximate value for mobility [14,15].

Low-field transport of ions in gases in many cases proceeds partially via exothermic reactions [16] that generally appear as a consequence of higher recombination potential (RE) of ions with respect to ionization potential (AE) of the gas target. That has been for a long time the most active research area in the field of electron capture collisions of ions with gas targets both experimentally and theoretically [16,17]. That list is however rarely used to complete cross-section sets that include exothermic reactions mainly due to the lack of knowledge of other cross-sections.

Ion mobility for the case of exothermic reactions [16] was experimentally studied only for few cases (He$^+$ + Ne [18], Ne$^+$ + Ar [10]), the main reason being the disappearance of the followed particles and the appearance of product ions (non-conservative collisions) [19] or simply "vanishing mobility" [20]. Note that in these cases exothermic cross-sections are small due to the large energy defect ($\Delta\varepsilon = RE - AE > 3$ eV and 5.8 eV, respectively). In contrast there are cases, in which exothermic reactions are dominant, such as Ar$^+$ + CF$_4$ ($\Delta\varepsilon \sim 0$) with no available information of how mobility behaves. One then may exploit a theoretical approach based on Monte Carlo simulations and complete cross-section set to reach such information.

Assessment of the cross-section set. – The cross-section sets for ion transport are rare due to a broad range of specific methods relevant for the quantification of the particular cross-section. The main problem in heavy-particle scattering, precisely selecting the state of the projectile and target before the collision, is still very complicated so databases for ion scattering [7,10] are not yet well filled with data. Phelps established the first world-wide accessible database with "complete" cross-section sets [21] tested for each particular case either for swarm conditions of spatially resolved measurement of emission

or ion mobility values. Another range of cross-section sets was established by measurements of ionic transport coefficients [10].

In the following section we will establish a cross-section set for Ar$^+$ scattering on CF$_4$ from 0.1 meV to 1000 eV which will be used to calculate transport properties. Generally one can distinguish three characteristic energy ranges: low-energy regime where polarization scattering is dominant, medium-energy regime where polarization scattering is gradually replaced by hard-sphere repulsion, and high-energy approximation regime.

Low-energy regime. At the lowest presented energies polarization scattering is appropriate as also observed in guided beam experiments [16]. Thus one may use simple scattering models [1,22] if a reliable value of the average polarizability of CF$_4$ is provided [23,24]. Stojanović *et al.* [23] found excellent agreement for the mobility of CF$_3^+$ ions in CF$_4$ by using the value $3.86 \cdot 10^{-30}$ m^3 [23] as an acceptable value for the average polarizability of CF$_4$. A similar value was previously found appropriate by Jarvis *et al.* [25]. It is also generally accepted that dipole and quadruple moments are negligible (see, for example, [16]) in the analyses with CF$_4$. Fisher *et al.* [16] by measuring the fast charge transfer reaction for CF$_3^+$ production proved that the internal states of the target which are populated, are those closest to the recombination energy of the projectile [4,25]. This has been for a long time the most active research area in the field of electron capture collisions of ions with gas targets both experimentally and theoretically [16,17] giving as a final output an extensive list of available exothermic cross-sections. That list is however rarely used to complete cross-section sets that include exothermic reactions mainly due to the lack of knowledge of other cross-sections.

Medium- and high-energy regimes. Smooth extrapolation above 0.1 eV towards higher energies will take into account hard-sphere cross-section. Fisher *et al.* [16] presented a measurement for CF$_3^+$ production cross-section that is larger than Langevin's value at the medium energies. It seemed reasonable to adopt the author's explanation who attributed such behavior to a potential change from polarization potential to hard-sphere potential. Thus, extrapolation of the elastic momentum transfer cross-section approximately beyond the crossing point of Langevin's and hard-sphere (HS) cross-section [16] was done by smoothly connecting to $1/v^3$ trend [19], where v is the center-of-mass velocity (see fig. 1). Adopted $1/v^3$ dependence of the elastic momentum transfer cross-section [22] followed also naturally from the trend of difference between Langevin's and CF$_3^+$ production cross-section.

Reactive cross-sections were extrapolated by constant values for relative kinetic energies above 50 eV, having in mind the work by Motohashi *et al.* [26] where slow oscillatory behaviour of the emission cross-sections was found at high projectile energies and almost constant reaction
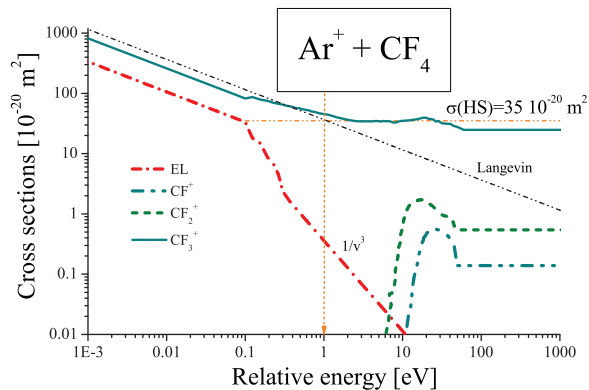
Fig. 1: (Colour on-line) Cross-section set as a function of relative energy for Ar^+ on CF_4.
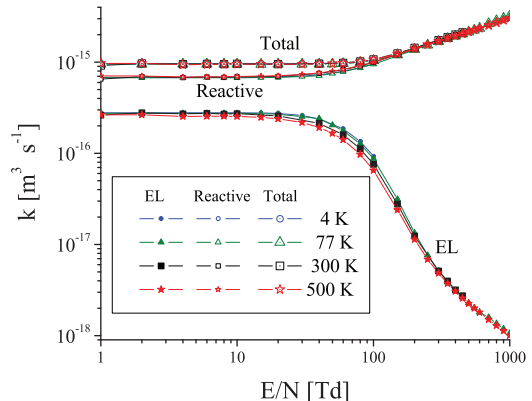

Fig. 2: (Colour on-line) Rate coefficients as a function of E/N for the sum of all processes (Total), sum of all reactive processes (Reactive) and elastic momentum transfer (EL). The gas temperature is used as parameter.

probability was found over a wide energy range. The resulting cross-section is shown in fig. 1.

Calculation of transport properties. – A Monte Carlo simulation method appropriate to calculate transport parameters [27,28] of Ar^+ ions in CF_4 at elevated temperature [29] is used. In Monte Carlo simulations exothermic reactive collisions are followed in a similar way as all non-conservative collisions, *i.e.* followed swarm particle dissappear from the swarm after the exothermic collision. This produced change of the swarm particle number in the whole energy range introducing non-conservativity in kinetic equations and thus division of transport parameters to flux and bulk ones [27].

Due to the competition of exothermic and elastic processes and specific sampling methods [30] necessary in conditions of low number of swarm particles, calculations of transport parameters are very time consuming. In order to keep the number of ions in the swarm constant, for any ion that disappears in the reaction we added another one by randomly sampling characteristic for the reaction of the remaining ions.

Behavior of ion swarm in the presence of exothermic processes. The external electric field induces a spatial distribution of the average ion energy in the direction of the swarm [31] causing the ions in the front to be fast while those in the tail to be slow. Note that the distributions in perpendicular directions are always uniform and equal to the average swarm energy.

If the exothermic collision frequency is an increasing function of ion energy, ions are removed from the regions of higher energy and one has a swarm "cooling" [32]. Swarm "heating" [32] occurs when the collision frequency is a decreasing function of ion energy.

Generally, the presence of non-conservative collisions causes the drift velocity to be more complex, *i.e.* one may define the bulk drift velocity as a measure of center-of-mass displacement in time ($W = \mathrm{d}\langle x \rangle/\mathrm{d}t$) [33] and flux drift velocity $w = \langle v \rangle$ that describes the ion flux. The bulk drift velocity is the reaction-corrected flux drift velocity:

$w = W + S$, where S is the term representing a measure of the effect of reactions on the drift velocity. It is necessary to discuss both since bulk values are those obtained from TOF experiments while flux values are those used as input data in modelling (fluid equations). Exothermic collisions cause differences between flux and bulk drift velocities at low E/N while endothermic collisions affect the swarm at high E/N.

Role of rate coefficients. For collisions with $1/v$ cross-section dependence (below 0.1 eV in our case) the collision frequencies are constant and also are the rate coefficients for $E/N < 10$ Td (1 Td $= 10^{-21}$ Vm^2) as shown in fig. 2. A slight decrease of momentum transfer rate coefficient with temperature occurs as a consequence of momentum transfer cross-section decrease for those temperatures where ions from the energy distribution function tail overcome 0.1 eV (when the elastic momentum transfer cross-section decreases). The rate coefficient for exothermic reaction rapidly increases from an almost constant value at $E/N > 100$ Td. For $E/N > 300$ Td the temperature dependence dissappears.

According to Langevin's theory ([22], see table 1) if each collision within orbiting distance results in a reaction, it is actually a measure of collision frequency and gives an upper limit to the value of the rate constant.

The collisional rate coefficients, k_c, calculated using Langevin's theory [5] and reaction efficiency, calculated as the ratio k_r/k_c, where k_r is the thermal rate coefficient for reactive processes, are presented in table 1. The average value of all experimental measurements is $7.6 \cdot 10^{-10}$ cm^3 molecule s^{-1} while the average reaction efficiency is 84%.

Average energy in the presence of exothermic collisions. The swarm energy is thermal due to the constant collision frequency of the exothermic process at low energies, for temperatures under 77 K, when $E/N \rightarrow 0$. For higher temperatures (300 K and 500 K in fig. 3) swarm energies are lower than thermal, *i.e* swarm "cooling" is present

Table 1: Thermal reaction rate constants and reaction efficiency for production of CF_3^+ ions.

Reference	This work (1–10 Td) 300 K	[16]	[34]	[16]	[35]	[25]	[22]
Total Rate (10^{-10} cm^3 s^{-1})	6.803	7.0 ± 2.6	8.15	8.0 ± 1.6	6.4 ± 1.3	8.1	8.8
Reaction efficiency (%)	77.3	79.5	92.6	90.1	72.7	92	84
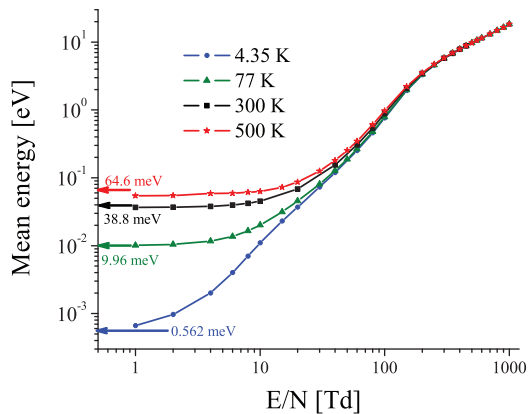
Fig. 3: (Colour on-line) Mean energy as a function of E/N at selected temperatures. With arrows we denoted the thermal energies at elevated temperatures T_g calculated as $3/2\ k_B T_g$ (k_B is the Boltzmann constant).

Fig. 4: (Colour on-line) Reduced mobility calculated with bulk and flux values of the drift velocities as a function of E/N with gas temperature as a parameter (in the legend's parentheses).

(fig. 3). For $E/N \geq 300$ Td, the increase of the energy diminishes as a consequence of the rapid increase of the reactive collisions ($E/N > 100$ Td).

Flux and bulk reduced mobility. In this letter the reduced mobility [5] for ions in a gas is calculated by using drift velocity sampling in Monte Carlo simulation. A zero-field mobility is defined as the reduced mobility extrapolated to the zero field ($E/N = 0$). Langevin's reduced mobility of Ar$^+$ ions in CF$_4$ in the polarisation limit is $K_{pol} = 1.3452$ cm^2/Vs.

In fig. 4 we show the reduced mobility for Ar$^+$ ions in CF$_4$ obtained from bulk drift velocity (lines denoted by "bulk") a result that can be compared with reduced mobility from TOF experimental measurements which according to our knowledge are not available at present. If one takes into account the rate coefficient for reactive collisions (fig. 2), then the distance at which the initial number of swarm particles reduces to one particle is about 1.5 cm for pressure $p = 0.0071$ torr ($E/N = 10$ Td).

Due to the competition between elastic and exothermic collisions within orbiting distance the zero-field reduced mobility is more than three times higher ($T_g = 4.35$ K) than the polarization limit value. This discrepancy is significantly higher than the observed one for any of existing measurements.

For $E/N < 10$ Td and low temperatures, the exothermic collision frequency is constant and corresponds to the energies below 0.1 eV. This causes the equality of the bulk and flux reduced mobilities [15] since the ions from the

front and the tail are removed with equal rate [27]. For higher temperatures the bulk reduced mobility is decreasing with temperature because of an increasing number of ions removed from the regions of higher energy (from the swarm front). That results in a shift in the centre-of-mass position. At the same time, flux reduced mobilities increase with temperature since the number of elastic collisions decreases.

Zero-field flux mobilities are less dependent on temperature than bulk values since they are more dependent on elastic collisions.

By increasing E/N the bulk reduced mobility is decreased since the exothermic collision frequency is increased. The increase of the flux reduced mobility with E/N is a consequence of the elastic cross-section decrease which in turn increases the ion velocity. With further increase of E/N elastic cross-sections decrease causing also the fast ions to shift the swarm center-of-mass forward.

At 150 Td the maximum of flux reduced mobility is a result of the significant reduction of high-energy ions in exothermic collisions. A further gradual flux reduced mobility drop appears due to the loss of elastic collisions which are replaced with exothermic collisions. In such a way fast particles are removed from the swarm.

The peak in bulk reduced mobility at about 300 Td appears at an average energy of 5.5 eV, where approximately additional exothermic reactions begin and where elastic collisions vanish. In these circumstances a drop of bulk reduced mobility beyond 300 Td is related to those Ar$^+$ ions

obtaining forward velocities as slow ones. Since the further bulk velocity increase does not depend on elastic collisions, the swarm of particles behaves as a beam attenuated by the insignificant number of endothermic collisions.

For $E/N > 300$ Td temperature effects are negligible for temperatures up to 500 K.

Conclusion. – By using measured charge transfer cross-sections we assessed the complete cross-section set for Ar$^+$ ions in CF$_4$ that is used as an input in Monte Carlo simulations in order to calculate transport parameters.

Focusing on calculated reduced mobility data as a function of E/N, in this letter we found that it is necessary to discuss both flux and bulk reduced mobility data. We have shown that zero-field ion mobility in the presence of exothermic collisions does not vanish but is significantly higher than in the case without exothermic collisions. We predicted that, although large losses of swarm particles in reactive collisions make measurement of mobility difficult, the possibility of such measurements exists.

$$* * *$$

REFERENCES

[1] Lieberman M. A. and Lichtenberg A. J., *Principles of Plasma Discharges and Materials Processing* (Wiley, New York) 1994.
[2] Kaboth A., Monroe J., Ahlen S., Dujmić D., Henderson S., Kohse G., Lanza R., Lewandowska M., Roccaro A., Sciolla G., Skvorodnev N., Tomita H., Vanderspek R., Wellenstein H., Yamamoto R. and Fisher P., *Nucl. Instrum. Methods Phys. Res. A*, **592** (2008) 63.
[3] Pancheshnyi S., Biagi S., Bordage M. C., Hagelaar G. J. M., Morgan W. L., Phelps A. V. and Pitchford L. C., *Chem. Phys.*, **398** (2012) 148.
[4] Parker E. and El-Ashhab F. S. M., *Int. J. Mass Spectrom. Ion Phys.*, **47** (1983) 159.
[5] Mason E. A. and McDaniel E. W., *Transport Properties of Ions in Gases* (John Wiley and Sons, New York) 1988.
[6] Petrović Z. Lj., Raspopović Z. M., Stojanović V. D., Jovanović J. V., Malović G., Makabe T. and de Urquijo J., *Appl. Surf. Sci.*, **253** (2007) 6619.
[7] http://nl.lxcat.net/data/set_type.php.

[8] Viehland L. A. and Mason E. A., *At. Data Nucl. Data Tables*, **60** (1995) 37.
[9] Saito N., Kojima T. M., Kobayashi N. and Kaneko Y., *J. Chem. Phys.*, **100** (1994) 5726.
[10] www.ruf.rice.edu/~atmol.
[11] Sanderson J., Tanuma H., Kobayashi N. and Kaneko Y., *J. Chem. Phys.*, **103** (1995) 7098.
[12] Ohtsuki K., Hananoe M. and Matsuzawa M., *Phys. Rev. Lett.*, **95** (2005) 213201.
[13] Fuji T. and Meisels G. G., *J. Chem. Phys.*, **75** (1981) 5067.
[14] de Urquijo J., Bekstein A., Ruiz-Vargas G. and Gordillo-Vazquez F. J., *J. Phys. D: Appl. Phys.*, **46** (2013) 035201.
[15] Nikitović Ž., Raspopović Z., Stojanović V. and Jovanović J., *EPL*, **108** (2014) 35004.
[16] Fisher E. R., Weber M. E. and Armentrout P. B., *J. Chem. Phys.*, **92** (1990) 2296.
[17] Martinez H. and Yousif F. B., *Phys. Rev. A*, **69** (2004) 062701.
[18] Wright T. G., Gray B. R., Viehland L. A. and Johnsen R., *J. Chem. Phys.*, **129** (2008) 184307.
[19] Saporoschenko M., *J. Chem. Phys.*, **49** (1968) 768.
[20] Phelps A. V., *J. Phys. Chem. Ref. Data*, **21** (1992) 883.
[21] Phelps A., http://jila.colorado.edu/~avp.
[22] Gioumousis G. and Stevenson D. P., *J. Chem. Phys.*, **29** (1958) 294.
[23] Stojanović V., Raspopović Z., Jovanović J. V., de Urquijo J. and Petrović Z. Lj., *J. Phys.: Conf. Ser.*, **514** (2014) 012059.
[24] Georgieva V., Bogaerts A. and Gijbels R., *J. Appl. Phys.*, **93** (2003) 2369.
[25] Jarvis G. K., Kennedy R. A., Mayhew C. A. and Tuckett R. P., *Int. J. Mass Spectrom.*, **202** (2000) 323.
[26] Motohashi K., Takahashi T., Takahashi N. and Tsurubuchi S., *J. Phys. B: At. Mol. Opt. Phys.*, **38** (2005) 3339.
[27] Robson R. E., *Aust. J. Phys.*, **44** (1991) 685.
[28] Robson R. E., White R. D. and Petrović Z. Lj., *Rev. Mod. Phys.*, **77** (2005) 1303.
[29] Ristivojević Z. and Petrović Z. Lj., *Plasma Sources Sci. Technol.*, **21** (2012) 035001.
[30] Raspopović Z. M., Sakadžić S., Bzenić S. A. and Petrović Z. Lj., *IEEE Trans. Plasma Sci.*, **27** (1999) 1241.
[31] White R. D., Robson R. E. and Ness K. F., *Aust. J. Phys.*, **48** (1995) 925.
[32] Nolan A. M., Brennan M. J., Ness K. F. and Wedding A. B., *J. Phys. D: Appl. Phys.*, **30** (1997) 2865.
[33] Ness K. F. and Robson R. E., *Phys. Rev. A*, **34** (1986) 2185.
[34] Pabst M. J. K., Tan H. S. and Franklin J. L., *Int. J. Mass Spectrom. Ion Phys.*, **20** (1976) 191.
[35] Chau M. and Bowers M. T., *Int. J. Mass Spectrom. Ion Phys.*, **24** (1977) 191.

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Transport parameters of F⁻ ions in Ar/BF₃ mixtures

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Transport parameters of F$^-$ ions in Ar/BF$_3$ mixtures

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Abstract – In this paper we show predictions for the low-energy cross-sections and transport properties for the F$^-$ in Ar/BF$_3$ mixtures which does not exist in the literature. These data are needed for modelling in numerous applications of technologically important Ar/BF$_3$ discharges. Results for transport coefficients as a function of E/N (E is the electric field, N the gas density) were obtained by using the Monte Carlo technique. The Monte Carlo method is applied to obtain swarm parameters at the temperature $T = 300$ K.

Introduction. – Negative ions are abundant in plasmas in fluor-containing molecules that are also relevant for a wide range of applications. One should bear in mind that the electron affinity of the F atom is the largest of all atoms and also that electronegative plasmas containing F$^-$ ions are highly reactive [1]. Understanding reaction kinetics is limited to scarce and often inconsistent data. Knowing the plasma chemistry and behavior of the negative ions in the plasmas is thus a key to the control of plasma processing devices. Negative ions determine the kinetics of the electronegative plasmas and their presence may change the nature of plasmas critically. Additionally, the recent progress of discharge modeling and simulation [2] has made contributions to a deeper understanding of the discharge phenomena and to the optimization of the reactor design or finding operating conditions. One such example is plasma implantation where Boron dopant penetration in silicon is achieved by a pulsed DC plasma system (PLAD) most widely employing BF$_3$ gas [3,4]. Ionized atoms are accelerated directly into a crystal substrate to add atoms selectively. Uniform plasma and implantation with normal ion incidence are the main goals in this technological process. Control over the number density of negative ions, such as F$^-$ and BF$_4^-$, increases the efficiency of implantation. Modelling of such plasmas requires knowledge of transport parameters of all abundant particles [2].

Plasma enhanced chemical vapor deposition (PECVD) using BF$_3$ gas is successfully used for the synthesis of cubic boron nitride (cBN) films with extreme properties similar to a diamond. In a fluorine-dominated environment the low-pressure PECVD [5,6] produces low-energy negative ions [7] affecting the chemistry near the surface. There is a large gap in understanding the chemical kinetics data relevant to ion-BF$_3$ collisions that make the progress in the synthesis of cBN films almost empirical. The BF$_3$ gas is also a working medium in neutron detectors [8] where electron-ion pairs were produced in neutron encounters. The signal detected due to the ion transport produces false counts and should be avoided. In order to trace such signals cross-sections and rate coefficients are needed for ion transport. In the first part of this work, we have extended Denpoh and Nanbu's technique (DN) for endothermic reactions [9] with exothermic association reaction to calculate the transport cross-section set for F$^-$ scattering on Ar/BF$_3$ appropriate for the low energies of F$^-$ ions. Next, by using the Monte Carlo technique developed by Ristivojević and Petrović [10] we have presented the calculated transport parameters as a function of the reduced DC electric field E/N.

Calculation of the cross-section set. – An accurate calculation of the cross-sections would involve determination of the ion-neutral interaction potential energy surface, followed by quantum-mechanical calculations of the ion-neutral scattering processes [11]. All these tasks are tractable only if a certain level of approximation is introduced. Significant simplification in the calculation appears when some statistical theory is applied.

The cross-sections for scattering of BF$_4^-$ ions on Ar and BF$_3$ and for F$^-$ ions on BF$_3$ are calculated by using the DN theory [9] separating elastic from detachment
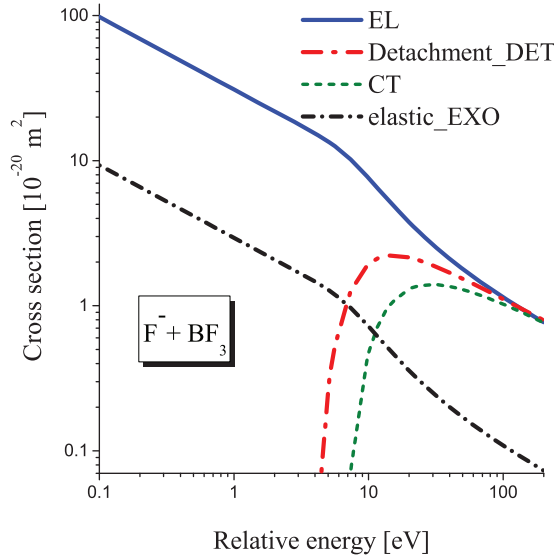
Fig. 1: (Colour on-line) The cross-section set for F^- ions in BF_3. EL is the elastic cross-section, CT the charge transfer, DET the electron detachment, EXO the association reaction.

Fig. 2: (Colour on-line) Cross-sections for F^- in Ar.

collisions. The cross-sections for F^- on Ar [12] were used to calculate rate coefficients for detachment. Dipole polarizability $3.31 \cdot 10^{-30} \, \mathrm{m}^3$ [13] and $1.64 \cdot 10^{-30} \, \mathrm{m}^3$ [14] is used for the BF_3 and Ar target, respectively.

Similar to our recent paper [15] DN's method is used to separate elastic from reactive endothermic collisions by accounting for the thermodynamic threshold energy and branching ratio according to the Rice-Rampsperger-Kassel (RRK) theory [9]. Within the RRK theory the internal energy is being distributed among an empirical number of s equivalent effective modes of the complex selected from the total number of atoms involved in the complex.

The cross-section for the exothermic reaction (EXO) forming a super halogen molecular ion BF_4^- is commonly represented by ion capture cross-section:

$$\sigma_{exo} = \beta \sigma_L, \qquad (1)$$

where σ_L is the orbiting cross-section [11] and β is the probability of a specific exothermic reaction.

By combining the relation (1) and the thermal rate coefficient, we determined the probability of exothermic reaction and the contributions of association cross-section (EXO) and elastic cross-section (EL) (fig. 1). In the low-energy limit the cross-sections are similar due to the dominant polarization of the target. At higher energies reactive collisions including the non-conservative collisions become efficient for various possible processes.

A cross-section set for F^- ions in Ar tested at low energies is presented by [16] (see fig. 2).

Discussion and results. – A correct treatment to obtain transport parameters of higher accuracy would be to follow solutions of the quantum-mechanical generalization of the Boltzmann equation that includes the effects of inelastic collisions and internal energy states [17]. The Monte Carlo simulation methods are generally built around the same initial principles as related kinetic equations. In this work we apply the Monte Carlo simulation designed for swarm particles [18].

The transport coefficients include drift velocity, diffusion coefficients, ionization and attachment coefficients and chemical reaction coefficients for ions [2]. Excitation coefficients are also measured but seldom used in modeling.

Swarm parameters are generally applied to plasma modeling and simulations. At the same time, the non-equilibrium regime in discharges is well represented under a broad range of conditions by using the Boltzmann equation with the collision operator representing only binary collisions.

In this work the Monte Carlo simulation technique for ion transport accounts for a finite gas, and the temperature of the background gas particles [10] is used to calculate the swarm parameters of F^- in Ar/BF_3 mixtures for temperature $T = 300 \, \mathrm{K}$. The Monte Carlo simulation is suited to the limitations of the swarm theory. Thus for the present case the code perfectly satisfies the demands required for the calculation of transport coefficients for ion transport in a dilute gas in equilibrium at the temperature T. A possible limitation imposed by the calculation of the collision frequency with the total cross-section instead of the differential cross-section [10] is relaxed simply by analyzing the interaction potential and particles geometry which actually reflect the central force.

A critical review of the experimentally obtained transport properties of gaseous halogen ions is presented in [19]. In this paper [19] only (experimental) data for the reduced mobility for F^- in Ar can be found. In our letter we give all transport parameters for F^- ions in both Ar and BF_3.
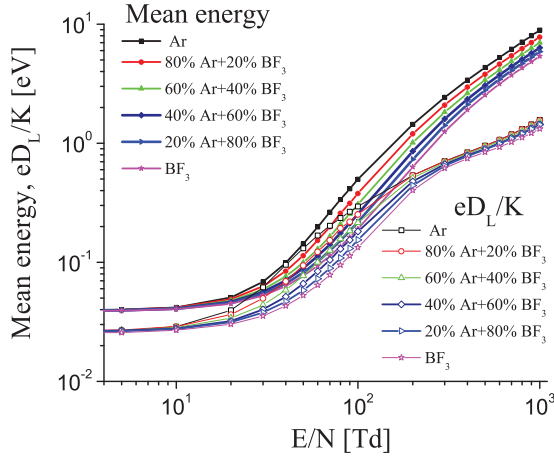
Fig. 3: (Colour on-line) Mean and characteristic energy of F$^-$ ions in BF$_3$ gas as a function of E/N at $T = 300\,\mathrm{K}$.
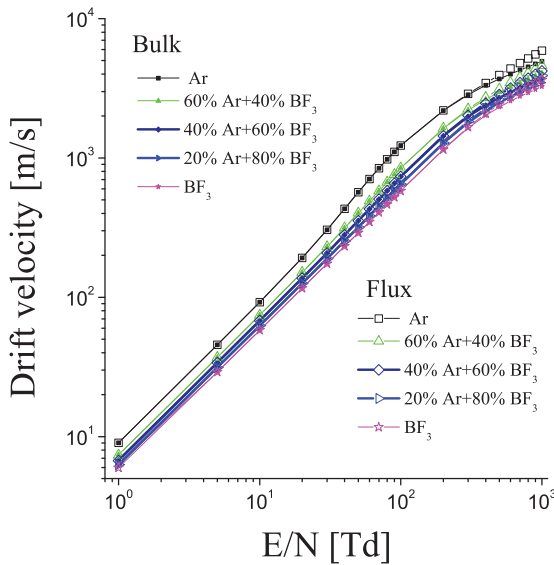

Fig. 4: (Colour on-line) The bulk and flux drift velocity of F$^-$ ions in Ar/BF$_3$ as a function of E/N at $T = 300\,\mathrm{K}$.
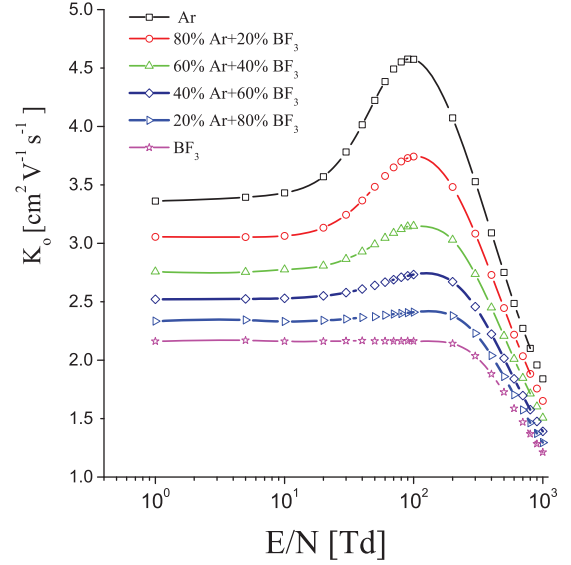

Fig. 5: (Colour on-line) The reduced mobility of F$^-$ ions in Ar/BF$_3$ as a function of E/N at $T = 300\,\mathrm{K}$.
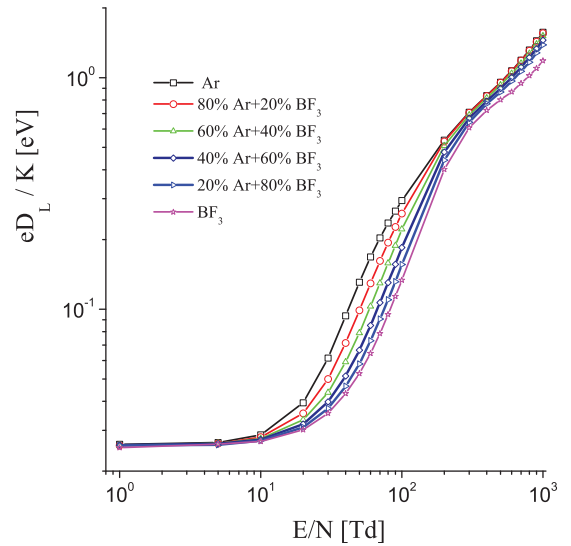
Fig. 6: (Colour on-line) The longitudinal diffusion coefficients for F$^-$ ions in Ar/BF$_3$ as a function of E/N at $T = 300\,\mathrm{K}$.

In fig. 3 we show the characteristic energies (diffusion coefficient normalized to mobility eD/K in units of eV) based on longitudinal (D_L) diffusion coefficients. We also show the mean energy, a parameter which cannot be directly measured in experiments, but a map of mean energy *vs.* E/N may be used directly to provide the data in fluid models especially when the local field approximation fails. As seen in fig. 3, the mean energy increases from about 10 Td. The Monte Carlo code [10] gives good results in which for all mixtures Ar/ BF$_3$ the mean energy converges to the thermal mean energy $3/2\ kT = 0.038778$ eV, while the thermal $eD/K = kT$ converges to 0.025852 eV (longitudinal (D_L) and transverse (D_T) diffusion coefficients).

The flux and bulk drift velocities [2,20,21] for F$^-$ in Ar/BF$_3$ as a function of E/N are given in fig. 4. The drift velocities obtained by the Monte Carlo simulation are calculated in real space (bulk) and in velocity space (flux)

values which are obtained as $\langle v \rangle$ and $\mathrm{d}x/\mathrm{d}t$, respectively. The bulk and flux values of the drift velocity begin to differ above 100 Td but very little.

The mobility K of an ion is the quantity defined as the velocity attained by an ion moving through a gas under the unit electric field. One often exploits the reduced or standard mobility defined as

$$K_0 = \frac{v_d}{N_0 E} N, \qquad (2)$$

where v_d is the drift velocity of the ion, N is the gas density, at elevated temperature T, E is the electric field.

In fig. 5 we show the results of the Monte Carlo simulation for the reduced mobility as a function of E/N. Non-conservative collisions of F$^-$ ions producing BF$_4^-$ ions

are only slightly modifying the mobility curve obtained for the case of inclusion of only endothermic processes ($\beta = 0$).

Longitudinal diffusion coefficients for F$^-$ ions in Ar/BF$_3$ as a function of E/N are shown in fig. 6. Note that the difference between the flux and bulk values of diffusion coefficients, which have the same origin, have the same initial value as drift velocities. There are no published experimental data for the longitudinal and transverse diffusion coefficients of F$^-$ in Ar/BF$_3$.

Conclusion. – In this paper we present new transport coefficients for low and moderate reduced electric fields E/N (N is the gas density) and accounting for the non-conservative collisions.

The cross-section set has been determined by using a simple theory and transport data for the gas BF$_3$, which is technologically very important.

The Monte Carlo technique was applied to carry out calculations of the mean energy, drift velocity and diffusion coefficients as a function of reduced DC electric field.

The results are a good base for modelling, which could be further improved by adding a data base of the measured values of transport coefficients and then performing the analysis again.

$$* * *$$

REFERENCES

[1] Hiraoka K., Nasu M., Katsuragawa J., Sugiyama T., Ignacio E. W. and Yamabe S., *J. Phys. Chem. A*, **102** (1998) 6916.
[2] Petrović Z. Lj., Dujko S., Marić D., Malović G., Nikitović Ž., Šašić O., Jovanović J., Stojanović V. and Radmilović-Radjenović M., *J. Phys. D: Appl. Phys.*, **42** (2009) 194002.
[3] Koo B.-W., Fang Z., Godet L., Radovanov S. B., Cardinaud C., Cartry G., Grouillet A. and Lenoble D., *IEEE Trans. Plasma Sci.*, **32** (2004) 456.
[4] Nikitović Ž., Radovanov S., Godet L., Raspopović Z., Šašić O., Stojanović V. and Petrović Z. Lj., *EPL*, **95** (2011) 45003.
[5] Yamamoto H., Matsumoto S., Okada K., Yu J. and Hirakuri K., *Diam. Relat. Mater.*, **15** (2006) 1357.
[6] Zhang W., Bello I., Lifshitz Y., Chan K., Meng X., Wu Y., Chan C. and Lee S.-T., *Adv. Mater.*, **16** (2004) 1405.
[7] Choi S. J. and Kushner M., *J. Appl. Phys.*, **74** (1993) 853.
[8] Padalakshmi M. and Shaikh A. M., *Pramana J. Phys.*, **71** (2008) 1177.
[9] Denpoh K. and Nanbu K., *J. Vac. Sci. Technol. A*, **16** (1998) 1201.
[10] Ristivojević Z. and Petrović Z. Lj., *Plasma Sources Sci. Technol.*, **21** (2012) 035001.
[11] McDaniel E. W., Čermak V., Dalgarno A., Ferguson E. E. and Friedman L., *Ion-Molecule Reactions* (Willey-Interscience) 1970.
[12] Petrović Z. Lj., Raspopović Z. M., Stojanović V. D., Jovanović J. V., Malović G., Makabe T. and De Urquijo J., *Appl. Surf. Sci.*, **253** (2007) 6619.
[13] Szmytkowski C., Piotrowicz M., Domaracka A., Klosowski L., Ptasinska-Denga E. and Kasperski G., *J. Chem. Phys.*, **121** (2004) 1790.
[14] McDaniel E. W., *Atomic Collisions: Electron and Photon Projectiles* (John Wiley & Sons) 1989.
[15] Stojanović V., Raspopović Z., Jovanović J., Nikitović Ž. and Petrović Z. Lj., *EPL*, **101** (2013) 45003.
[16] Jovanović J. and Petrović Z. Lj., *J. Phys.: Conf. Ser.*, **162** (2009) 012004.
[17] Kumar K., *Aust. J. Phys.*, **33** (1980) 449; Viehland L. A., Lin S. L. and Mason E. A., *Chem. Phys.*, **54** (1981) 341; Ness K. F. and Viehland L. A., *Chem. Phys.*, **148** (1990) 255; Viehland L. A. and Chang Y., *Mol. Phys.*, **110** (2012) 259.
[18] Kumar K., Skullerud H. R. and Robson R. E., *Aust. J. Phys.*, **33** (1980) 343.
[19] Viehland L. A. and Mason E. A., *At. Data. Nucl. Data Tables*, **60** (1995) 37.
[20] Robson R. E., *Aust. J. Phys.*, **44** (1991) 685.
[21] Robson R. E., White R. D. and Petrović Z. Lj., *Rev. Mod. Phys.*, **77** (2005) 1303.

Ion mobilities and transport cross sections of daughter negative ions in N_2O and $N_2O–N_2$ mixtures

Ion mobilities and transport cross sections of daughter negative ions in N₂O and N₂O–N₂ mixtures

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Abstract
A pulsed Townsend apparatus is used to measure the mobility of a single negative ion species
in N₂O and N₂O–N₂ gas mixtures. The range of the density-normalized electric field, E/N, is
6.5–100 Td (1 Townsend = 10^{-17} V cm²) over the pressure range 10–250 Torr and temperature
range 295–300 K. Based on previous work it is shown that the most likely drifting ion is $N_2O_2^-$.
A reaction scheme involving ion conversion and electron detachment is presented, ending with
the formation of a stable $N_2O_2^-$ ion. The momentum transfer integral cross section for $N_2O_2^-$ in
pure N₂O and N₂ gases is derived from the above measurements. The unfolded cross sections
are used as an initial guess and then further improved by ensuring good agreement between
Monte Carlo calculated mobilities and the experimental results for the N₂O–N₂ mixture.

(Some figures may appear in colour only in the online journal)

1. Introduction

Nitrous oxide is a gas of widespread use in different types
of glow discharges that find application in many scientific
and technological fields, including spectroscopy, kinetics
and plasma-enhanced chemical vapour deposition. In RF
discharges, N₂O constitutes the major component of N₂O–
SiH₄ mixtures, commonly used to deposit SiO₂ thin films [1],
which find an application as interlayer dielectrics for integrated
circuits, and in the fabrication of optical waveguides. In
addition, nitrous oxide is used in the deposition of other
materials such as SiO_xN_y [2], phosphosilicate glass layers
[3] and aluminium oxides [4]. Microwave discharges in
mixtures of N₂O with inert gases are efficient sources of
oxygen atoms and their properties have received attention as
well [5]. Another popular type of glow discharges are those
produced in hollow cathodes [6]. A review of cross sections
and transport data for negative ions required to model plasma
processing technologies in nanoelectronics was published by
Petrovič *et al* [7].

Nitrous oxide is one of the greenhouse gases, hence an

important contributor to global warming. N₂O is an important
factor and a stable chemical compound noted among the gases
that destroy the ozone layer, thereby influencing the electrical
parameters and the active processes in ozone formation [8].
The permanent increase of nitrous oxide concentration in the
atmosphere (about 0.2–0.3% per year) imposes the necessity
for a search to limit its emission. Because of its importance in
significant dissociative attachment and detachment reactions
[9] in the atmosphere and the formation of metastable
fragments upon dissociation [10], N₂O can be a very active
species in any discharge situation, hence there is a need for
cross sections, spectroscopic and swarm data.

The $N_2O_2^-$ anion was for the first time detected by
Moruzzi and Dakin [11] in their low-energy swarm experiment.
Klots and Compton [12] produced $N_2O_2^-$ ions from the low-
energy electron attachment to N₂O clusters. Coe *et al* [13]
observed $N_2O_2^-$ by injecting electrons into the high-pressure
region of a free expansion jet of N₂O. By infrared matrix
isolation spectroscopy, Milligan and Jacox [14] recorded the
first spectrum of $N_2O_2^-$. Using photoelectron spectroscopy of
negative ions, Posey and Johnson [15] found evidence for three

distinct isomers of $N_2O_2^-$ by varying ion source reagents and conditions.

There have been a number of experimental attempts to measure the electron affinity of N_2O using techniques such as charge exchange [9, 16], electron attachment [17], collisional ionization [18] and dissociative electron attachment to N_2O [19]. In addition, there have been some studies on N_2O dimers, trimers or even larger clusters [20]. Recently, interesting work on the formation of $N_2O_2^-$ in corona discharges in oxygen and N_2/O_2^- mixtures has been carried out [21]. These workers have been able to measure the mobility of this species in the above drift gases. To our knowledge, no experimental or theoretical results of transport data or cross sections of $N_2O_2^-$ ions in pure N_2O or in N_2O–N_2 mixtures are available.

The purpose of this paper is to provide measured mobilities and sets of collision cross sections that may be used in the simulation of plasmas containing $N_2O_2^-$. The procedure used here to determine the elastic momentum transfer cross section consists in applying the momentum transfer theory (MTT) as an initial step and also to make further adjustments, thereby saving a great deal of computation time. For higher energies, an extrapolation of the elastic cross section was made, together with the application of the detachment cross section. The resulting sets of elastic and detachment collision cross sections were validated eventually with some minor adjustments by using an optimized Monte Carlo (MC) code. Systematic comparisons were made of the anion mobility from the time-resolved measurements of $N_2O_2^-$ transients in N_2O and in binary mixtures with N_2. Only slight adjustments were made to the cross sections in the last stage to obtain the best agreement possible between the experimental data and the MC calculations. The MC calculations are claimed to provide exact results, limited only by the statistical uncertainty and the accuracy of the cross section.

Following this introduction, section 2 is devoted to an account of the time-resolved technique used to measure electron detachment and negative ion mobility ($N_2O_2^-$) in N_2O and its mixtures with N_2. In earlier papers [22], we have explained in detail the MTT and the MC simulation procedure to obtain the collision cross section sets, hence these two techniques will not be explained thoroughly here. In section 3, we will give a brief overview of the calculation of the elastic collision cross section based on the MTT approximation and related formulae. Finally, we present the best cross section set obtained from comparison of the MTT and MC results with the experimental data.

2. Experimental

2.1. The apparatus

The time-resolved pulsed Townsend method relies on the measurement of the total displacement current due to electrons and ions drifting through a parallel-plate capacitor [23–25]. The discharge is initiated by the instantaneous release of photoelectrons from the cathode by the action of UV light from a nitrogen laser (337 nm, 1 ns duration, 1 mJ). These photoelectrons, under the action of the electric field between

the electrodes, will move towards the anode. During their passage, according to the gas or gas mixture and the E/N range, the electrons may ionize and/or attach to the gas neutrals. Since the electrons are more mobile (by a factor of 100 or more) than the ions, these will remain virtually in their positions of formation during the electron transit. On a much slower time scale, the ions move towards the cathode or the anode, depending on their charge. This enables the distinction of two types of current contributions, namely the fast, or electronic component, and the second, slow, or ionic component [25, 26].

The measurements were carried out for a fixed gap distance of 3.1 cm, at room temperature in the range 293–300 K. The uncertainty in the drift velocity measurements was estimated as 3–5%, and was obtained from the known possible systematic errors and, additionally, by averaging the drift velocity over a series of measurements at the same E/N value and different pressures. The stated purities of N_2 and N_2O were 99.999% and 99.5%, respectively, and were injected into the discharge vessel without further purification. The overall pressure range was 10–250 Torr. Ionic components of the pulses were measured with a 10^7 V/A transimpedance amplifier and linear bandwidth of 400 kHz.

2.2. The reaction scheme

The mid-energy range of electrons corresponding to the E/N range 10–100 Td covered in this study is 0.5–3.5 eV (see figure 3 below), hence we shall only deal with reactions that are likely to occur over this range. Dissociative electron attachment in N_2O leading to the formation of O^- takes place via the reaction [9]

$$e^- + N_2O \rightarrow O^- + N_2 \tag{1}$$
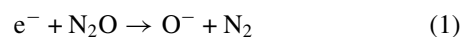
with an energy threshold of 0.2 eV. The exothermic reaction of O^- with N_2O

$$O^- + N_2O \rightarrow NO^- + NO + 0.14\,eV \tag{2}$$

may be followed by collisional electron detachment of NO^- as

$$NO^- + N_2O \rightarrow e^- + NO + N_2O + 0.12\,eV. \tag{3}$$
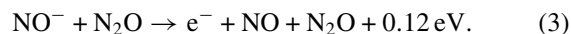
Reactions (2) and (3) have been studied together by several groups using drift tube, afterglow and ion-cyclotron resonance techniques [9]. For the mean energies of O^- in this study, ranging between 0.039 and 0.12 eV, the effective rate constant, k, for the combined reactions (2) and (3) measured by these groups is $(1–2) \times 10^{-10}$ $cm^3\,s^{-1}$. NO^- is regarded as an intermediate species that detaches readily since its electron affinity is only 0.026 eV [27], which is almost half the thermal energy at 300 K. Over the pressure range 10–250 Torr of measurement of the ionic pulses, the mean lifetime for collisions, $\tau = 1/kN$, ranges between 30 ns and 1.2 ns, respectively, a time which is much shorter than the electron transit times, $T_e = d/v_e$, of 440 ns and 240 ns for E/N values of 10 and 100 Td, respectively, a gap distance $d = 3.1$ cm and electron drift velocities, v_e, taken from [28]. This means that formation and destruction of O^- with NO^- as an intermediate take place only at the very early stages of ion drift, thereby
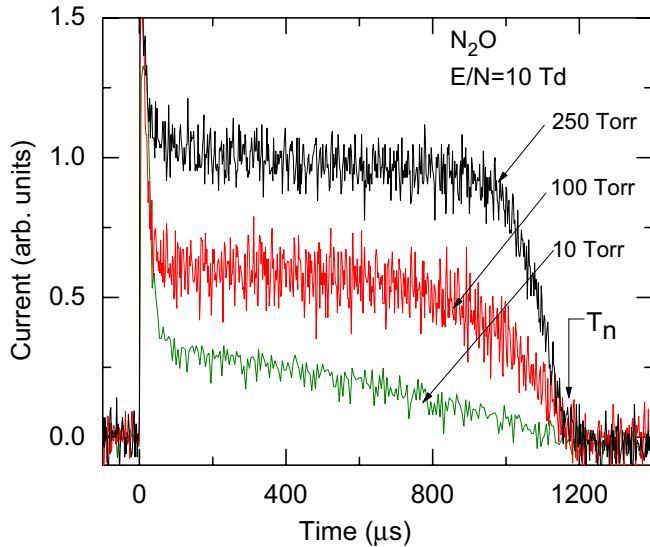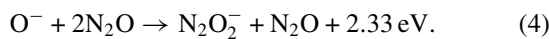
Figure 1. Negative ion transients N_2O at $E/N = 10$ Td, measured over the pressure range 10–250 Torr. The negative ion transit time, T_n, is indicated.
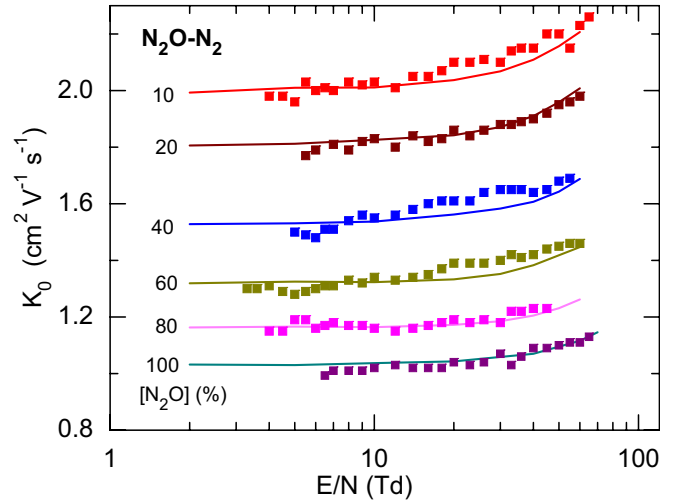

Figure 2. Reduced mobility of $N_2O_2^-$ in N_2O and N_2O–N_2. Symbols: measured values from inspection of the ion transit time (see figure 1); solid lines: Monte Carlo calculations (see section 3).

eliminating the concern of an influence of reactions (2) and (3) on the evaluation of the ionic transit time, T_n, from which the ion mobility is derived. The direct collisional detachment of O^- is disregarded in this study since its electron affinity is 1.46 eV [29], a value which is over 10 times the maximum mean energy of this ion under the present conditions.

A second, three-body, exothermic ion–molecule reaction of O^- with N_2O, which is very likely to occur under the present conditions, is [11, 15]

$$O^- + 2N_2O \rightarrow N_2O_2^- + N_2O + 2.33\,\text{eV}. \quad (4)$$

Thus, for the conditions of our experiment the dominant negative ion is $N_2O_2^-$.

2.3. Determination of the mobility of $N_2O_2^-$

The negative ion transit time, T_n, in this case of $N_2O_2^-$, is determined as indicated in figure 1 by the arrow. A further discussion of this procedure can be found in [30]. It can be seen from the three transients of figure 1 that the mobility, and hence the ion species, does not change over the wide pressure range 10–250 Torr. The negative ion drift velocity is then $v_n = d/T_n$ and, the reduced mobility is calculated by

$$K_0 = \frac{v_n}{N_0(E/N)}, \quad (5)$$

where $N_0 = 2.69 \times 10^{19}\,\text{cm}^{-3}$ is the gas density under standard conditions of pressure and temperature. The reduced mobilities of $N_2O_2^-$ in N_2O and in N_2O–N_2 mixtures are plotted in figure 2 as a function of E/N. The overall uncertainties in the mobility data, derived from averaging several measured values at the same E/N and different pressures, are in the range ±3–5%.

The mobility calculations to be described below are also shown in figure 2, where one sees an overall good agreement with the measured data.

3. Calculation of the collision cross sections and mobility of $N_2O_2^-$

While it is possible to calculate the cross sections from the potentials, the calculation is certainly not trivial and, in particular, it is not easy to estimate which range of energies may be covered by those calculations. On the other hand, the preparation of cross section sets for plasma models may involve a certain degree of extrapolation or interpolation that should be applied bearing in mind the energy range of the ions in the plasmas that are usually studied.

The procedure used here is to first determine the cross sections using the MTT, which consists of a specific simplification of the Boltzmann equation collision operator and a specific procedure to determine approximate distribution functions. When swarms develop in uniform and constant fields, the theory yields simple analytical solutions that may be surprisingly accurate (to within 15%) and may thus provide a basis for an efficient modelling of plasmas. MTT is exact only for the constant collision frequency model in the absence of reactions. A more detailed explanation of the theory and the equations that are used for the calculations of cross sections may be found in our previous paper [22] and here we will give only a brief overview of the equations used.

Considering ions with number density N in a neutral gas in equilibrium at temperature T_0, and assuming that the density gradients are weak, we have the following simple approximate balance equations for the mobility and mean energy of ions, respectively [31, 32]:

$$K = \frac{q}{m v_m} = \frac{v_n}{E} \quad (6)$$

and

$$\varepsilon = \tfrac{1}{2}m_0 v_n^2 + \tfrac{3}{2}k_B T_0, \quad (7)$$

where q and m are the charge and mass of the ion, respectively, m_0 is the mass of the neutral molecule, v_n is the ion drift velocity, E is the electric field, k_B is the Boltzmann constant,
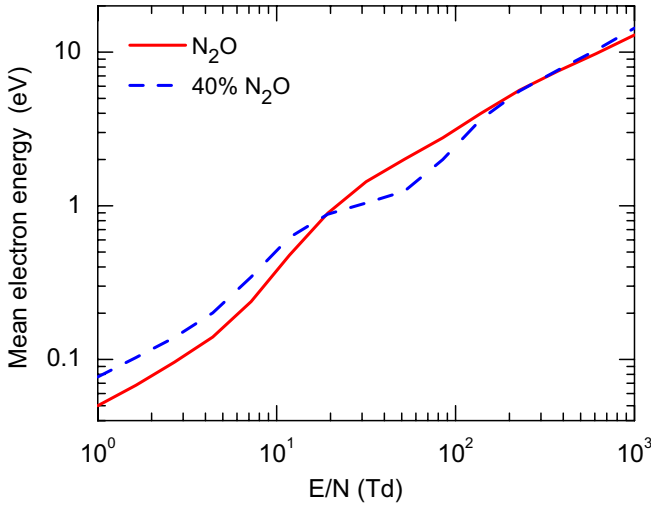
Figure 3. Mean electron energy as a function of E/N in N_2O and 40% N_2O–N_2.

and ε is the mean energy of ions in the centre of mass reference frame consisting of two parts: a field part represented by $\frac{1}{2}m_0 v_n^2$ and a thermal part represented by $\frac{3}{2}k_B T_0$. The total momentum transfer collision frequency in the centre of mass reference frame, v_m, is given by

$$v_m = N\sqrt{\frac{2\varepsilon}{\mu}}\sigma_m, \qquad (8)$$

where σ_m denotes the total momentum transfer cross section and μ is the reduced mass, $\mu = mm_0/(m + m_0)$.

Over the region of interest, the mean electron energies lie between 0.5 and 3.5 eV (figure 3), hence we have limited the range of measurement to the low E/N range in which no ionization takes place; in other words, over this low-energy range the most important scattering process will be elastic scattering and the reactive process would be electron detachment. Equations (6)–(8) are solved readily, and experimental results for the reduced mobility could provide cross sections up to 0.1 eV mean ion energy. The MTT is used only as the initial step to fit the experimental results and obtain the cross sections.

In the next step further and final adjustments are made in order to achieve good agreement between experimental data and MCS. Simulations are proved to give results in agreement to better than 0.1% with other benchmark calculations [33].

Proceeding in a similar fashion as in our previous work [7] we have calculated the elastic and detachment cross sections according to the procedure of Denpoh and Nanbu [34], given explicitly in [35]. The procedure resolves elastic and reactive collisions [22]. The detachment cross section of $N_2O_2^-$ was calculated from the threshold around 0.28 eV up to 100 eV for both gases. These cross sections were used as the initial guess for our fits and were kept outside the range of our swarm data.

We performed all the calculations under the assumption of isotropic scattering for elastic scattering and detachment. The final sets of cross sections are given in figures 4(*a*) and (*b*). It should be noted that the cross sections had to be modified from the original Langevin energy dependence at low energy

values. The departure from Langevin cross sections has often been noticed [7]. Above the limit of sensitivity of our data we maintain the Langevin cross sections and use the same energy dependence for extrapolating to the low energy limit.

The mean energy of $N_2O_2^-$ in N_2, calculated from the measured mobilities, is shown in figure 5. Apart from measuring the mobility of $N_2O_2^-$ in pure N_2O, we also measured it in mixtures containing 10–80% N_2O in N_2, as shown in figure 2. In general, fairly good agreement is achieved between experimental and our final MC results.

It is worth noting from figures 4 and 5 that our previous assumption of no electron detachment effects in $N_2O_2^-$ (figure 4) is now confirmed by the calculations since the calculated mean energies of $N_2O_2^-$ in N_2O are significantly smaller than the thresholds for electron detachment (0.3–0.4 eV).

4. Discussion

We have presented original measurements of the reduced mobility and the corresponding derived cross section sets concerning the interaction of $N_2O_2^-$ with N_2O and N_2O–N_2 mixtures. To our knowledge, no previous data have been published in the literature. The measurement of the mobility is reported over the density-reduced electric field strength, E/N, 6.5–100 Td by a time-resolved pulsed Townsend technique. To substantiate the identity of the drifting negative ion, a comprehensive reaction scheme, based on previous research, is presented. Even though we could vary the N_2O gas pressure from 10 to 250 Torr, we found no particular dependence of the reduced mobility of $N_2O_2^-$. A recent study on negative ion formation in pure H_2O revealed the formation of cluster species of the type $OH^-(H_2O)_n$ ($n = 1–3$) over the pressure range 2–16 Torr. This clustering phenomenon is explained in terms of the very large dipole moment of H_2O (1.85 D), in contrast to the relatively small dipole moment of N_2O (0.166 D).

Two further issues are worth addressing. The first deals with electron detachment from $N_2O_2^-$. In their drift tube-mass spectrometer experiment (0.1–8 Torr N_2O pressure range in the drift region) Moruzzi and Dakin [11] found that the most abundant ionic species were $N_3O_2^-$ and $N_2O_2^-$. However, $N_3O_2^-$ is a tertiary species formed from the secondary species NO^- (reaction (2)) by

$$NO^- + N_2O \rightarrow N_3O_2^-. \qquad (9)$$
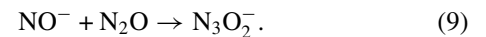
Thus, with NO^- being so easily destroyed by electron detachment due to its small electron affinity of 0.02 eV, it is very unlikely that $N_3O_2^-$ is the negative ion in question since, on the other hand, $N_2O_2^-$ is formed directly from O^-. Moreover, corona discharge studies assisted by drift tube-mass spectrometry [21] report copious amounts of $N_2O_2^-$ formed in such an environment. No traces of $N_3O_2^-$ were found.

The second issue deals with the formation of N_2O^- by the reaction

$$e + 2N_2O \rightarrow N_2O^- + N_2O, \qquad (10)$$
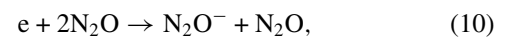
with a small three-body rate constant of $(6\pm1) \times 10^{-33}$ cm^6 s^{-1} [36] at thermal energies. The study of Chantry [37] on
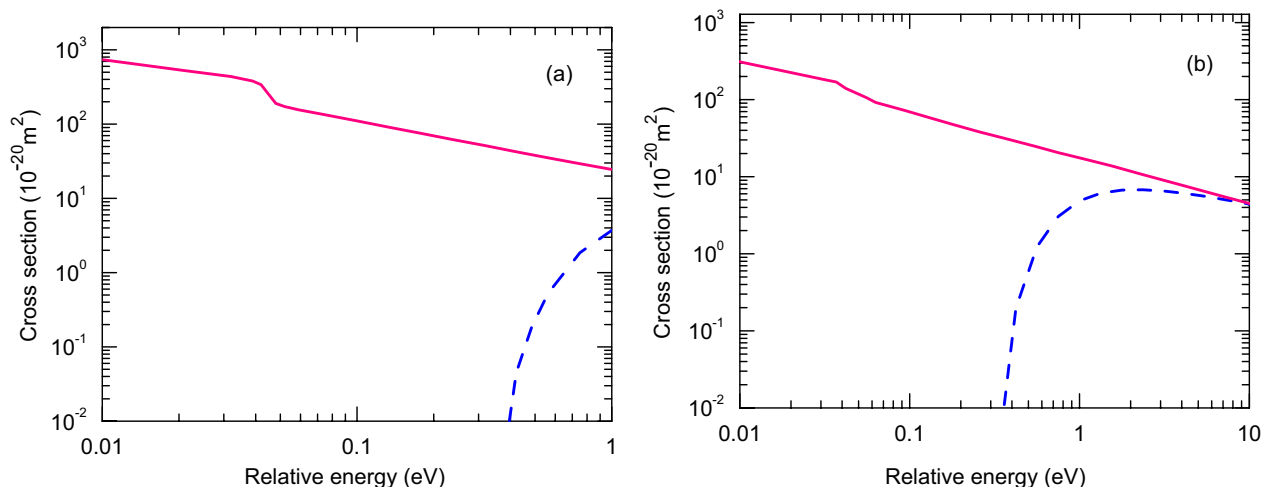
Figure 4. Cross section sets for (*a*) the $N_2O_2^-$–N_2O system and (*b*) the $N_2O_2^-$–N_2 system. Solid line: momentum transfer cross section; dashed line: detachment cross section.
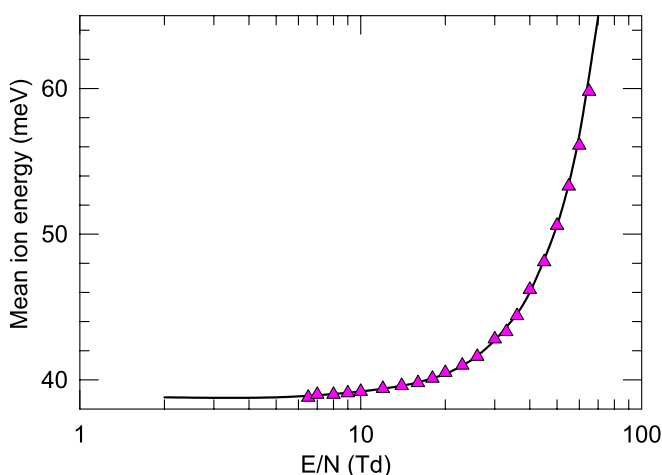

Figure 5. Calculated mean energy of $N_2O_2^-$ in N_2O as a function of E/N. The solid line is the Monte Carlo calculation and the triangles are the calculated values from the measured negative ion drift velocities, using equation (7) (transformed to the laboratory frame of reference).

the effects of temperature (295–1040 K) on the dissociative attachment cross section in N_2O showed that the production of O^- from N_2O was very sensitive to temperature at collision energies close to thermal, while it was insensitive above 2.3 eV. This finding has been related to two states of N_2O^- involved in the production of O^- from N_2O below about 4 eV [37]. The strong dependence of the cross section at thermal energies and up to about 1.5 eV is ascribed to the lowest state (ground state) of N_2O^-, due to excitation of the bending and vibration modes. The temperature-independent peak at 2.25 eV is ascribed to the second N_2O^- state. Furthermore, the shape of the density-normalized attachment coefficient in N_2O is typical of dissociative attachment [28]. Thus, the small amount of N_2O^- formed at low collision energies (low E/N) would dissociate into O^- and N_2, and therefore contribute with O^- to reaction (2).

The measured mobility data were used to determine the cross sections at very low energies. The cross sections were extrapolated to higher energies based on energy dependences for other negative ions. Due to the lack of additional experimental data such as diffusion coefficients or differential cross sections, we were not able to separate the isotropic and anisotropic components of the cross section [38]. The cross sections provided here should be employed with the assumption of isotropic scattering.

These data may be used [39] in the simulations of plasmas containing $N_2O_2^-$, which cover most atmospheric discharges and atmospheric-pressure plasmas [40]. In spite of the lack of a mass analyser in the system, we have given strong evidence for the predominance of $N_2O_2^-$ in the discharge. For this, we have provided some examples in previous publications dealing with the drift of negative ions in O_2 and SF_6 [41, 42].

The procedure used here to determine the cross sections is to first apply the MTT, which is fast, albeit of limited accuracy. The MTT is used to modify the cross sections until the transport data fit the experimental results. Finally, all the calculations are performed from a MC simulation that has been shown to be very accurate and satisfies all the benchmark tests [33]. Thus, the present final results should be associated only with the exact MC procedure.

Acknowledgments

References

[1] Smith D L and Alimonda A S 1993 *J. Electrochem. Soc.* **140** 149
Kushner M J 1993 *J. Appl. Phys.* **74** 6538
Fernandez-Lima F, Rodriguez J A, Pedrero E, Fonseca Filho H D, Llovera A, Riera M, Dominguez C, Behar M

and Zawislak F C 2006 *Nucl. Instrum. Methods Phys. Res.* B **243** 200

[2] Lam D K W 1984 *Appl. Opt.* 23 2744

[3] Takamatsu A, Shibata M, Sakai H and Yoshimi T 1982 *J. Electrochem. Soc.* **131** 1865

[4] Kim Y C, Chun J S and Lee W J 1995 *Thin Solid Films* **258** 67

[5] Piper L G and Rawlins W T 1986 *J. Phys. Chem.* **90** 321

[6] Arcos T, Domingo C, Herrero V J, Sanz M M, Schulz A and Tanarro I 1998 *J. Phys. Chem.* A **102** 6282

[7] Petrovič Z Lj, Raspopovič Z M, Stojanovič V D, Jovanovič J V, Malovič G, Makabe T and de Urquijo J 2007 *Appl. Surf. Sci.* **253** 6619

[8] Skalny J D, Matejčik S, Mikoviny T, Eden S and Mason N J 2004 *J. Phys. D: Appl. Phys.* **37** 1052

[9] Lindinger W, Albritton D L, Fehsenfeld F C and Ferguson E E 1975 *J. Chem. Phys.* **63** 3238
Chantry P J 1969 *J. Chem. Phys.* **51** 3369
Wentworth W E, Chen E and Freeman R 1971 *J. Chem. Phys.* **55** 2075
Marx R, Mauclaire G, Fehsenfeld F C, Dunkin D B and Ferguson E E 1973 *J. Chem. Phys.* **58** 3267
Parkes D A 1972 *J. Chem. Soc. Faraday Trans.* **168** 613
Warman J M, Fessenden R W and Bakale G 1972 *J. Chem. Phys.* **57** 2702
Skalny J D, Orszagh J, Mason N J, Rees J A, Aranda-Gonzalvo Y and Whitmore T D 2008 *J. Phys. D: Appl. Phys.* **41** 085202

[10] Barnett S M, Mason N J and Newell W R 1991 *Chem. Phys.* **153** 283

[11] Moruzzi J L and Dakin J J 1968 *J. Chem. Phys.* **49** 5000

[12] Klots C E and Compton R N 1978 *J. Chem. Phys.* **69** 1636

[13] Coe J V, Snodgrass J T, Freidhofl C B, McHugh K M and Bowen K H 1987 *J. Chem. Phys.* **87** 4302

[14] Milligan D E and Jacox M E 1971 *J. Chem. Phys.* **55** 3404

[15] Posey L A and Johnson M A 1988 *J. Chem. Phys.* **88** 5383

[16] Paulson J F 1966 *Adv. Chem.* **58** 28
Ferguson E E, Fehsenfeld F C and Schmeltekopf A L 1967 *J. Chem. Phys.* **47** 3085

[17] Bardsley J N 1969 *J. Chem. Phys.* **51** 3384
Wentworth W E, Chen E and Freeman R 1971 *J. Chem. Phys.* **55** 2075

[18] Nalley S J, Compton R N, Schweinler H C and Anderson V E 1973 *J. Chem. Phys.* **59** 4125

[19] Suter H U and Greber T 2004 *J. Phys. Chem.* B **108** 14511
McCarthy M C, Allington J W R and Sullivan K O 1999 *Mol. Phys.* **96** 1735

[20] Valdes H and Sordo J A 2004 *J. Phys. Chem.* A **108** 2062
Gorelsky S I, Ghosh S and Solomon E I 2006 *J. Am. Chem. Soc.* **128** 278
Hanel G, Fiegele T, Stamatovic A and Märk T D 2001 *Int. J. Mass Spectrom.* **205** 65

[21] Sabo M and Matejčik Š 2011 *Anal. Chem.* **83** 1985
Sabo M, Matúška J and Matejčik Š 2011 *Talanta* **85** 400
Sabo M, Pálenik J, Kučera M, Han H, Wang H, Chu Y and Matejčik Š 2010 *Int. J. Mass Spectrom.* **293** 23

[22] Vrhovač S B and Petrovič Z Lj 1996 *Phys. Rev.* E **53** 4012

Vrhovač S B, Petrovič Z Lj, Viehland L A and Santhanam T S 1999 *J. Chem. Phys.* **110** 2423
Jovanovič J V, Vrhovač S B and Petrovič Z Lj 2002 *Eur. Phys. J.* D **21** 335
Petrovič Z Lj, Jovanovič J V, Stojanovič V, Raspopovič Z M and Ristivojevič Z 2008 *Eur. Phys. J.* D **48** 87

[23] Raether H 1964 *Electron Avalanches and Breakdown in Gases* (London: Butterworths)

[24] Hunter S R and Christophorou L G 1984 *Electron–Molecule Interactions and Their Applications* vol 2 (New York: Academic)

[25] de Urquijo J, Basurto E and Hernández-Ávila J L 2001 *J. Phys. D: Appl. Phys.* **34** 2151

[26] Hinojosa G and de Urquijo J 2003 *J. Phys. D: Appl. Phys.* **36** 2510

[27] Travers M J, Cowles D C and Ellison G B 1989 *Chem. Phys. Lett.* **164** 449

[28] Dupljanin S, de Urquijo J, Šašič O, Basurto E, Juarez A M, Hernández-Ávila J L, Dujko S and Petrovič Z Lj 2010 *Plasma Sources Sci. Technol.* **19** 025005

[29] Branscomb L M 1958 *J. Chem. Phys.* **29** 452

[30] de Urquijo J, Bekstein A, Ruiz-Vargas G and Gordillo-Vázquez F J 2013 *J. Phys. D: Appl. Phys.* **46** 035201

[31] Viehland L A and Mason E A 1995 *At. Data Nucl. Data Tables* **60** 37

[32] Viehland L A and Kirkpatrick C C 1996 *Chem. Phys.* **202** 285

[33] Ristivojevič Z and Petrovič Z Lj 2012 *Plasma Sources Sci. Technol.* **21** 035001

[34] Denpoh K and Nanbu K 1998 *J. Vac. Sci. Technol.* A **16** 1201

[35] Georgieva V, Bogaerts A and Gijbels R J 2003 *Appl. Phys.* **93** 2369
Georgieva V 2005 *PhD Thesis* Universiteit Antwerpen

[36] Warman J M and Fessenden R W 1968 *J. Chem. Phys.* **49** 4719
Phelps A V and Voshall R E 1968 *J. Chem. Phys.* **51** 3246

[37] Chantry P J 1969 *J. Chem. Phys.* **51** 3369
Christophorou L G 1984 *Electron–Molecule Interactions and Their Applications* vol 1 (Orlando, FL: Academic) pp 533–4, 565–6

[38] Phelps A V 1994 *J. Appl. Phys.* **76** 747

[39] Petrović Z Lj, Šuvakov M, Nikitović Ž, Dujko S, Šašić O, Jovanović J, Malović G A and Stojanović V 2007 *Plasma Sources Sci. Technol.* **16** S1
Petrović Z Lj, Dujko S, Marić D, Malović G, Nikitović Ž, Šašić O, Jovanović J, Stojanović V and Radmilović-Radjenović M 2009 *J. Phys. D: Appl. Phys.* **42** 194001

[40] Kutasi K 2010 *J. Phys. D: Appl. Phys.* **43** 05520
Kutasi K, Guerra V and Paulo A S 2011 *Plasma Sources Sci. Technol.* **20** 035006
Malovič G, Puac N, Lazovic S and Petrovič Z Lj 2010 *Plasma Sources Sci. Technol.* **19** 034014

[41] Juárez A M, de Urquijo J, Hinojosa G, Hernández-Ávila J L and Basurto E 2010 *Plasma Sources Sci. Technol.* **19** 034005

[42] de Urquijo J, Bekstein A, Ducasse O, Ruiz-Vargas G, Yousfi M and Benhenni M 2009 *Eur. Phys. J.* D **55** 637

Transport of F$^-$ ions in F$_2$

Transport of F⁻ ions in F₂

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Abstract – Transport properties of F⁻ ions in F₂ in DC fields were calculated using the Monte Carlo simulation technique. In the absence of a more reliable theory or experiments we have employed a simple technique to predict the cross-sections and to separate elastic from reactive collisions. We present reaction rate coefficients, characteristic energies, mean energy and drift velocities for the conditions of low and moderate reduced electric fields E/N (E is the electric field, N the gas density) accounting also for the non-conservative collisions.

Introduction. – F₂ molecules, either as a part of the gas mixture or formed in plasma chemical processes [1] are frequently present in numerous processing plasmas. For example, F₂ may be produced in a pulsed plasma implantation system that is the basis for the doping of integrated circuit components [2]. In such a system it is necessary to create a uniform plasma over the entire wafer that can be more than 500 mm wide. To achieve such a goal one needs to understand a number of processes of particles interacting with gas molecules or the surfaces. Time-resolved measurements of the ion energy distributions in the cathode boundary [3] indicated a possible role of charge-transfer collisions between singly charged ions of various masses.

In this paper we study the energy-dependent scattering and transport processes for F⁻ ions in the F₂ gas. The paper is divided into two parts. In the first part we determine the scattering cross-sections for inelastic and elastic (including charge transfer) collisions of F⁻ ions. In the second part we study transport of these ions in the background F₂ gas. The basic assumption is that the density of ions is so low that they do not perturb the background gas and external field. Experiments that mimic these conditions are known as swarm experiments and typically these conditions may be achieved when the ratio of ion to molecule densities is below 10^{-7}. In such experiments and simulations results are independent of pressure the only scaling being through E/N and pd (where p is the pressure and d is the gap or the distance). Using the basic cross-sections and simulations we hope

to explore the effects of non-conservative processes on the transport properties of F⁻ ions. We hope that these data may contribute to the complete kinetics of plasmas in electronegative gases and in particular in the presence of F₂, which is either applied as a participant in the gas mixtures for plasma chemical processing or is sometimes created in plasma chemistry [1].

Non-equilibrium discharges are usually modeled either by fluid models, fluid models with correction for the non-locality or hybrid models. The basic input to such models are transport coefficients obtained for the swarm conditions [4–8]. Kinetic codes, (PIC and full kinetic codes) require cross-sections while hybrid codes use both. In this paper we provide both the cross-sections and transport coefficients that may be used in all such codes. Importantly the transport coefficients are consistent with the cross-sections and therefore may be used to validate different approaches.

The swarms are ensembles of charged particles traveling through gas under the influence of the external field and dissipating the energy and momentum in collisions with the background gas [5,9]. It is assumed that probabilities of colliding with products of other collisions are null and that perturbation of electric field is null hence the external voltage defines the field. In other words, the Debye radius of such systems is much greater than the size of the discharge vessel. In addition, in swarm experiments all primary products are proportional to the electron density, which is small. All the results of the subsequent reactions between those products are present in even

smaller numbers so the second-level processes do not affect the system. The transport coefficients include the drift velocity, diffusion coefficients, ionization and attachment coefficients and chemical reaction coefficients for ions. Excitation coefficients are also measured, but seldom used in modeling.

Using swarm data allows models of higher-density low-temperature plasmas to treat collisions through transport and rate coefficients. It makes it possible for these models to deal with space charge effects and field distribution separately but in a self-consistent way [6,7].

In this paper we provide transport coefficients for F^- ions in F_2 because these data have been lacking up to this point. In a standard swarm experiment it would be difficult to produce F^- ions in the gas directly, but in gas discharge low-temperature plasma those are readily produced. In order to produce the transport data we use our set of cross-sections in the relevant energy range and then perform a numerical experiment mimicking a real drift tube experiment. These studies have been known to provide excellent agreement and in that sense the results are as accurate as the input cross-sections.

It has been well established in experiments that the predominant ion in low-temperature plasmas for the processing of integrated circuits [1,2,10,11] and in excimer lasers is F^- [12]. F_2^- is formed in F_2 for low energies well below $0.2\,eV$. Dissociative attachment leading to F^- has a threshold of few eV. Mean energies of electrons in most discharges are between $2\,eV$ and $6\,eV$, well in the range of dissociative attachment. Hence there are very few electrons at thermal energies and as a result F^- is more abundant.

Finally it should be noted that swarm coefficients for ions [13] are of greater use than those for the electrons. The reason is that negative ions are mostly trapped in the potential distribution and are close to thermal energy. Higher energy cross-sections are needed for those formed in sheaths by attachment. In general, data for negative ions in gases of interest for processing have been in limited supply and this paper is a contribution with the goal of extending the existing database [5].

Monte Carlo technique and the cross-section data. – The cross-sections for scattering of F^- on F_2 molecule are calculated by using a simple procedure that has been known as Nanbu's theory [4,14]. It allows separation of elastic from reactive endothermic collisions. In this theory reactive collisions are treated by accounting for the thermodynamic threshold energy and branching ratio according to the Rice-Rampsperger-Kassel (RRK) theory [14]. Our procedure is an implementation of this theory and its inherent approximations. We have used the value of $1.2611\ 10^{-30}\,m^3$, recommended by Spelsberg and Meyer [15] for the polarizability of F_2, ionization potentials for F_2 and F from [16] and the bond values between atoms from ref. [17]. The usual procedure would be to unfold the cross-sections from the the measured transport

Table 1: F^--F_2 endothermic reaction paths considered in the model and the corresponding thermodynamic threshold energies [6–8].

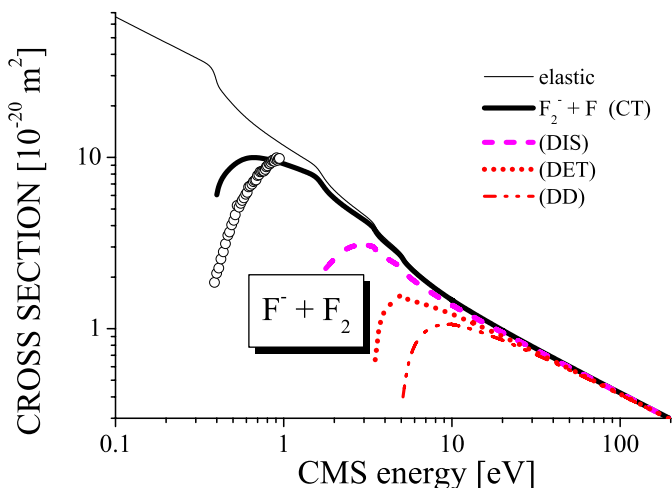| No.	Reaction	$\Delta\,(eV)$
1	$F_2^- + F$ (CT)	-0.38
2	$F^- + 2F$ (DIS)	-1.602
3	$F + F_2 + e^-$ (DET)	-3.4012
4	$F + 2F + e^-$ (DD)	-5.0032

Fig. 1: (Colour on-line) Cross-section set for F^- ions in F_2. Open circles denote the data of Chupka *et al.* [20] placed on absolute scale by assuming maximum value as obtained by Nanbu's theory.

coefficients and thermo-chemical data in a separate drift tube experiment, but to our knowledge no such data are available.

The Monte Carlo technique was applied to perform calculations of transport parameters as well as rate coefficients in DC electric fields. In this paper we have used a Monte Carlo code that properly takes into account the thermal collisions [18]. The code has passed all the tests and the benchmarks that were covered in our earlier studies [18]. Bulk and flux values of the drift velocity [19] are presented for a range of reduced electric fields E/N including the range where effects of the charge transfer collisions take place.

Discussion and results. – Most probable reaction paths, based on thermochemical data [15–17] are shown in table 1. We found them relevant for the selected domain of low F^- energies in F_2.

In fig. 1. we show calculated cross-sections for F^- scattering on F_2. The cross-section for the charge transfer (CT) producing F_2^- ion measured by Chupka *et al.* [20], is also shown in the same figure.

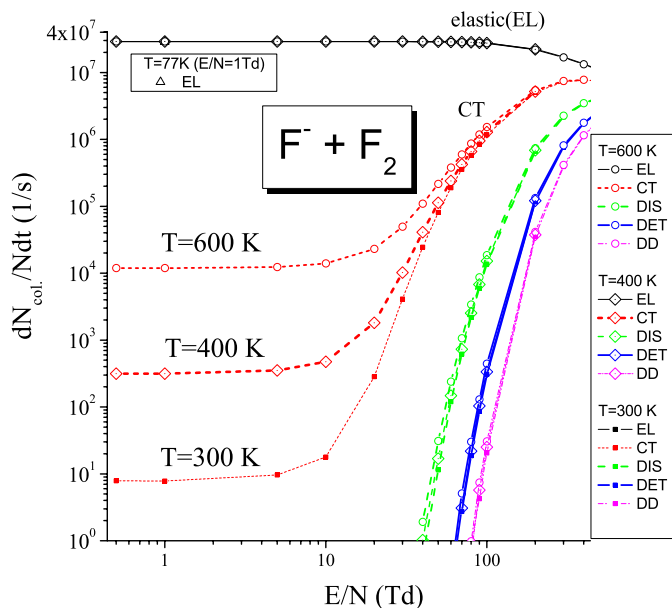Transport parameters were calculated for the room gas temperature of $T = 300\,K$. Calculated rate coefficients for

Fig. 2: (Colour on-line) Rate coefficients for F$^-$ ions in F$_2$ as a function of E/N.

Fig. 3: (Colour on-line) Bulk and flux values of drift velocity, for F$^-$ ions in F$_2$ as a function of E/N.

processes presented in table 1 and in fig. 1 are shown in fig. 2. The rate for CT with its low threshold of 0.39 eV overlaps with the thermal distribution function of participants in a collision and thus a plateau exists at low E/N. The value of the plateau is very low but it increases rapidly as the temperature of the gas is increased. The temperature for the most part does not affect elastic scattering as the total cross-section does not depart much from the cross-section consistent with the constant collision frequency. As for the rates of inelastic processes, the temperature makes a small, hardly observable, effect as the thresholds are considerably higher than the thermal energy.

Flux and bulk drift velocities [5,8,19] as a function of E/N are given in fig. 3. The drift velocities are not affected by the temperature and mobility is almost constant. Yet we observe effect of reactive collisions affecting the splitting of flux and bulk drift velocity components above 40 Td. The first mention of non-conservative effects in ion transport was given in [4].

In addition, in fig. 4. we show characteristic energies (diffusion coefficient normalized by mobility eD/μ in units eV) associated with longitudinal (L) and transverse (T) diffusion. We also show the mean energy, which cannot be directly measured in experiments. A map of the mean energy $vs.$ E/N may be used directly to provide data in fluid models especially when the local field approximation fails. The data shown in figs. 2–4 constitute all the data required to perform modeling of F$^-$ ion transport in low-temperature plasmas such as plasmas for treatment of integrated circuits or excimer lasers.

The experimental cross-section is consistent with our predictions, but it has a lower value in the threshold
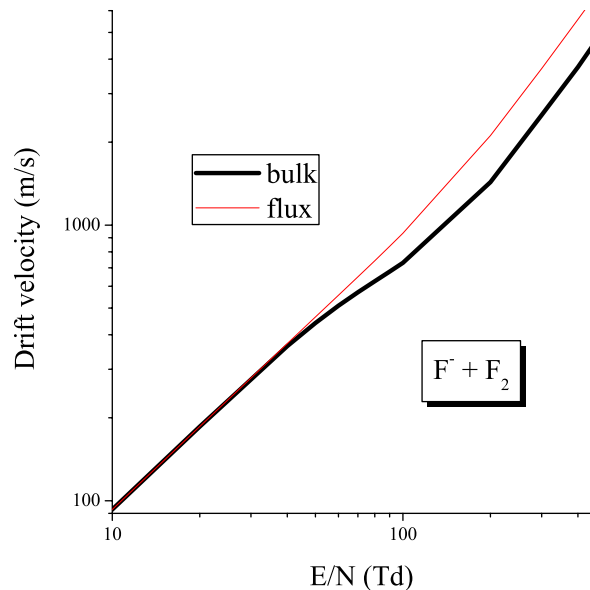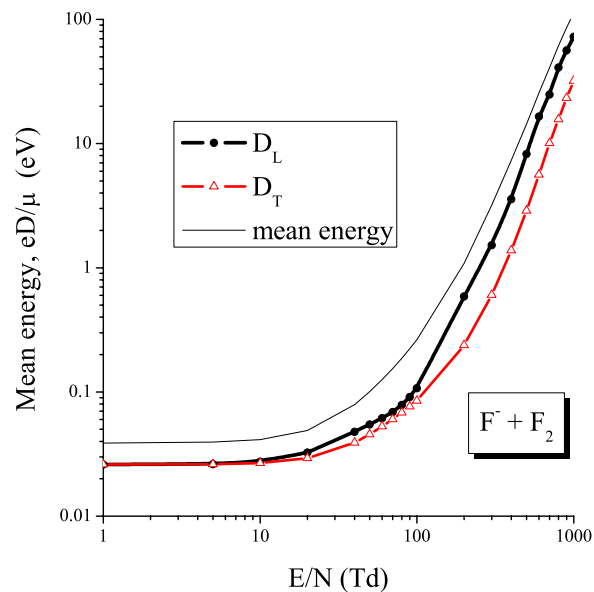
Fig. 4: (Colour on-line) Characteristic energies (longitudinal and transverse) and mean energy for F$^-$ ions in F$_2$.

region. This would reduce the temperature effect and push the increasing part to somewhat higher E/N's.

Conclusion. – In this paper we have given predictions for the cross-sections and transport coefficients of negative F$^-$ ions in F$_2$ which did not exist in literature. In principle, experiments and applications in pure F$_2$ are unlikely but one can use mixture laws [5,21] to predict the properties in mixtures containing F$_2$. The use of transport data or the use of cross-sections [22] in plasma modeling requires a wide range of data. The data for negative ions are not covered as well as for other particles. Measurements

of transport data with high accuracy would strongly challenge these results and produce a basis to improve them. Yet, in most applications, these ions and F_2 are not present in large abundances [11] and thus this set would allow very accurate results for mixtures.

$$* * *$$

REFERENCES

[1] CURLEY G. A., MARIC D., BOOTH J.-P., CORR C. S., CHABERT P. and GUILLON J., *Plasma Sources Sci. Technol.*, **16** (2007) S87.

[2] RADOVANOV S., GODET L., DORAI R., FANG Z., KOO B. W., CARINAUD C., CARTRY G., LENOBLE D. and GROULLET A., *J. Appl. Phys.*, **98** (2005) 113307.

[3] NIKITOVIĆ Ž., RADOVANOV S., GODET L., RASPOPOVIĆ Z., ŠAŠIĆ O., STOJANOVIĆ V. and PETROVIĆ Z. LJ., *EPL*, **95** (2011) 45003.

[4] PETROVIĆ Z. LJ., RASPOPOVIĆ Z. M., STOJANOVIĆ V. D., JOVANOVIĆ J. V., MALOVIĆ G., MAKABE T. and DE URQUIJO J., *Appl. Surf. Sci.*, **253** (2007) 6619.

[5] PETROVIĆ Z. LJ., DUJKO S., MARIĆ D., MALOVIĆ G., NIKITOVIĆ Ž., ŠAŠIĆ O., JOVANOVIĆ J., STOJANOVIĆ V. and RADMILOVIĆ-RAĐENOVIĆ M., *J. Phys. D: Appl. Phys.*, **42** (2009) 194002.

[6] MAKABE T. and PETROVIĆ Z., *Plasma Electronics: Applications in Microelectronic Device Fabrication* (Taylor and Francis, CRC Press, New York) 2006.

[7] LIEBERMAN M. A. and LICHTENBERG A. J., *Principles of Plasma Discharge and Materials Processing* (Wiley, Hoboken) 2005.

[8] ROBSON R. E., WHITE R. D. and PETROVIĆ Z. LJ., *Rev. Mod. Phys.*, **77** (2005) 1303.

[9] HUXLEY L. G. H. and CROMPTON R. W., (Wiley Interscience) 1974.

[10] JAUBERTEAU J. L., MEEUSEN G. J., HAVERLAG M., KROESEN G. M. W. and DE HOOG F. J., *Appl. Phys. Lett.*, **55** (1989) 2597.

[11] BOOTH J. P., CURLEY G., MARIC D. and CHABERT P., *Plasma Sources Sci. Technol.*, **19** (2010) 015005.

[12] OHWA M. and OBARA M., *Appl. Phys. Lett.*, **51** (1987) 959.

[13] MASON E. A. and MCDANIEL E. W., *Transport Properties of Ions in Gases* (Wiley-Interscience Publication, New York) 1988.

[14] DENPOH K. and NANBU K., *J. Vac. Sci. Technol. A*, **16** (1998) 1201.

[15] SPELSBERG D. and MEYER W., *J. Chem. Phys.*, **101** (1994) 1282.

[16] MC DANIEL E. W., *Atomic Collisions-Electron and Photon Projectiles* (John Willey & Sons, New York) 1989.

[17] STOCKDALE J. A., NELSON D. R., DAVIS F. J. and COMPTON R. N., *J. Chem. Phys.*, **56** (1972) 3336.

[18] PETROVIĆ Z. LJ., JOVANOVIĆ J. V., STOJANOVIĆ V., RASPOPOVIĆ Z. M. and RISTIVOJEVIĆ Z., *Eur. Phys. J. D*, **48** (2008) 87.

[19] ROBSON R. E., *Aust. J. Phys.*, **44** (1991) 685.

[20] CHUPKA W. A., BERKOWITZ J. and GUTMAN D., *J. Chem. Phys.*, **55** (1971) 2724.

[21] JOVANOVIĆ J. V., VRHOVAC S. B. and PETROVIĆ Z. LJ., *Eur. Phys. J. D*, **28** (2004) 91.

[22] NAKANO N., SHIMURA N., PETROVIĆ Z. LJ. and MAKABE T., *Phys Rev. E*, **49** (1994) 4455.

Regular Article

Cross sections and transport of O⁻ in H₂O vapour at low pressures[⋆]

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Abstract. The transport properties of O⁻ ions in water vapour drifting in DC fields were obtained by using the Monte Carlo simulation technique with the scattering cross section sets assessed on the basis of Denpoh and Nanbu's technique and available experimental data. A swarm method is applied to determine recommended cross section set. For the first time in this work we present the transport parameters for the conditions of low to moderate reduced electric fields E/N (N is gas density) accounting for the effect of non-conservative collisions. The data are applicable in the limit of low pressures where cluster formation does not affect the transport or may be applied at higher pressures together with a model of cluster formation kinetics.

1 Introduction

The interest in application of plasmas in medicine, some nanotechnologies and environmental remediation [1–5] has drawn the attention to studies of discharges in water and in proximity to water [6] although other liquids are of interest as well. Current studies show that in such systems, discharge is usually produced in water vapour either from evaporating liquid electrode or in bubbles created by an induced phase transition within the liquid. Mechanisms of breakdown in liquid without bubble formation are still under discussion [7,8]. More generally, all atmospheric discharges contain some degree of water vapour [9–12]. It is therefore of interest to determine how discharges are created in water vapour and to provide elementary transport data for the charged particles [13–17]. One of the key points must be to have an accurate knowledge of the electrical properties of water vapour and in particular of its breakdown potential [18,19]. Complicated chemistry and poor data for a range of processes of particles interacting with gas and surface require further insights and more data. In particular the data for transport and cross sections of ions are missing, especially having in mind that ions as well as electrons may have a wide range of energies, thereby affecting the profiles of electric field. In this work we analyse and provide scattering cross sections and transport coefficients of O⁻ ions in H₂O gas and we ex-plore the resulting effects of non-conservative processes on the transport properties of O⁻ ions.

The Monte Carlo technique was applied to perform calculations of the transport parameters as well as rate coefficients in DC electric fields. We have used a Monte Carlo code that properly takes thermal collisions into account [20]. This term implies the collisions where thermal energy of targets cannot be neglected and has to be included in momentum and energy balances. Under those conditions one cannot determine the collision probabilities for projectile and for the target separately, a compound probability has to be calculated. Simplified, albeit still more complex procedures have been proposed and tested providing a proper decay of energy in the low E/N limit. The code used here is the same as in [20] and has thus passed all the relevant benchmarks [20] and has been tested in our work on several types of charged particles [21,22].

2 Cross sections and calculated transport coefficients

In what follows, we will present two sets of cross sections. The first is based on experimental data and the second on the Denpoh and Nanbu's (DN) theory [23].

2.1 The available cross section data – cross section set S1

The scattering cross sections of O⁻ in H₂O, measured by Hasted and Smith [24] for electron detachment (DET) and

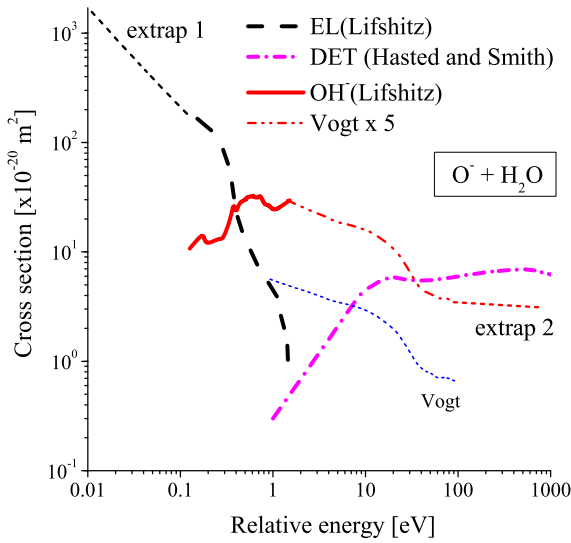a e-mail: draganam@ipb.ac.rs

Fig. 1. Cross section set for O^- + H_2O based on experimental results (S1). Cross section for the electron detachment (DET) is measured by Hasted and Smith [24], with the threshold taken from [26]. Lifshitz [25] measured cross sections for elastic scattering (EL) and for OH^- production (OH^-). The elastic cross section is extrapolated to low energies, based on the DN theory (extrap 1). Cross section for the OH^- production is extrapolated to higher energies by multiplying the results of Vogt [27] by a factor of 5 (dash-dot-dot line). (Original data of Vogt are represented by the thin dotted line.) Extension of Lifshitz cross section by using Vogt's scaled cross section up to 1 keV is indicated by "extrap 2".

Table 1. Products and the corresponding thermodynamic threshold energies Δ for the reactions O^- + H_2O.

No.	Products of reaction O^- + H_2O	Δ (eV)
1	O^- + H_2O (EL)	0.
2	OH^- + OH	-0.36
3	H_2O_2 + e^- (DET)	-0.43
	O + H_2O + e^-	-1.46

Lifshitz [25] for elastic scattering and OH^- formation at low energies, are shown in Figure 1 (thick lines) and processes are listed in Table 1 with their thresholds. We found them relevant for the selected domain of low O^- energies in water vapour. Preliminary results dealing with the present calculation have been presented in [28].

A cross section set S1 is completed (Fig. 1) based on these experimental data and applying extrapolations. For extrapolation at the lowest energies (dashed line labelled by "extrap 1" in Fig. 1) we have taken into account that polarisation and dipole forces are expected to be important over the energy range from 20 meV to few eV. This extrapolation is actually identical to our results for elastic scattering obtained by DN theory [23] as described in the next section.

OH^- production cross section of Lifshitz [25] was extrapolated towards high energies by using the data of Vogt [27]. The experimental data of Vogt [27] are consider-

ably lower than those of Lifshitz [25] but extend to higher energies. Note that Lifshitz explained OH^- production cross section solely through a complex formation, assuming that direct reaction is negligible, while Vogt explained his data by direct reaction only. Since both Lifshitz's cross sections [25] presented in Figure 1 are consistently measured (the same experiment), we assumed that it was reasonable to scale and connect the data of Vogt (dashed line, labelled in legend as "Vogt × 5") to the data of Lifshitz for OH^- production (energy range from 1.5 eV to 100 eV). The scaled cross section is then extended up to 1000 eV (dashed line labelled by "extrap 2" in Fig. 1). Extrapolations to high energy were necessary to enable calculations in the tail of the ion energy distribution function, i.e. to avoid possible numerical problems to the code due to a few ions that may achieve high energies.

2.2 Cross section set based on Denpoh and Nanbu's theory (S2)

The cross sections measured by Lifshitz [25] which were the basis of the cross section set S1 were interpreted by the author as a consequence of a long lived complex formation. Thus we have calculated a cross section set by using Denpoh and Nanbu's theory (this theory is explained well in [21,23] and our procedure has been shown in detail in [21]) that assumes complex formation and is modified to treat endothermic reactions with polar molecules by the locked dipole model [29]. In DN theory a reactive collision is treated by selecting the thermodynamic threshold energy and branching ratio according to the Rice-Rampsperger-Kassel (RRK) theory [23]. We have used the data for polarizability and dipole moment of H_2O as used by Clary [30] and selected heats of formation and electron affinities from reference [31]. The threshold for electron detachment (DET) has been taken from reference [26]. The obtained cross section set was corrected to fit the reduced mobility calculated by the SACM (Statistical Adiabatic Channel Model) approximation [32] (thick lines in Fig. 2) and is labelled S2 in what follows. The zero field mobility is $K_0 = 0.984$ cm^2 V^{-1} s^{-1} at $T = 300$ K.

Experimental elastic cross section (EL in Fig. 1) agrees well with the theoretical one up to 0.35 eV, but it falls more rapidly towards higher energies. Theoretical reactive cross section for OH^- production is about three times lower than experimental results of Lifshitz [25]. A possible variation of parameters in Denpoh and Nanbu's theory that increases this cross section worsens the other two cross sections.

It is now worth pointing again at the experimental measurements of Vogt [27] for reaction 2 in Table 1 (thin line in Fig. 2) that is in a good agreement with the present result of DN theory. On the other hand, Vogt explained his results by direct O^- excitation only, while DN theory and Lifshitz' explanation are based on complex formation. Note that the cross section for direct excitation is expected to be significantly lower than that proceeding with complex formation, so one may assume that process involving complex formation is relevant for OH^- reaction.
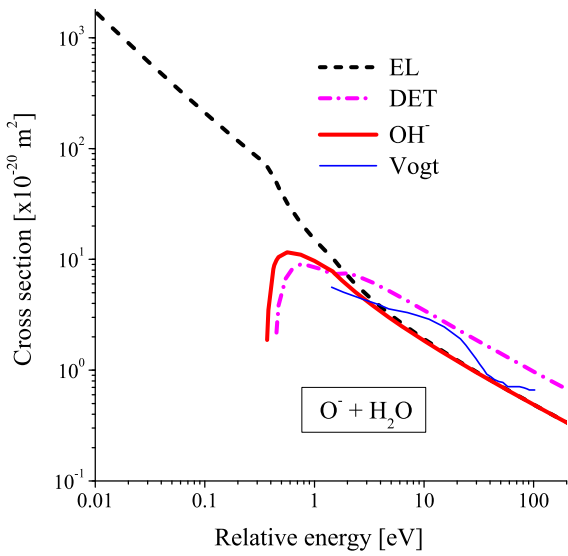
Fig. 2. Cross section set S2 for O^- + H_2O based on the ND theory [23] is shown by thick lines. We show the experimental data of Vogt [27] by a thin line. EL stands for the elastic cross section, DET for detachment and OH^- for the production of OH^-.

The experimental uncertainty of the measured cross sections is as given in the papers where data were published. More importantly the discrepancies between different sources for the reaction cross section are up to an order of magnitude. The theoretical cross section is based on an approximate theory and input data that may introduce uncertainties that are difficult to assess. In both cases the best way to proceed would be to provide swarm data and normalize the set of cross sections as a whole. Only in that case one would be able to assign the uncertainty and minimize it. At the present, however, we have to use those data as better data are not available. The uncertainty introduced in transport coefficients due to our simulation is very small and for a given set of cross sections it is of the order of 0.3%.

2.3 Transport parameters

Transport parameters obtained by Monte Carlo simulation for the cross section sets S1 and S2 described above are shown in Figures 3–7. Note that these transport parameters are the only information present in the literature up to now, there are no published experimental data for the transport coefficients of O^- in pure H_2O.

Cross sections S2 fall rapidly at higher energies which is a characteristic of DN theory, so that all transport parameters are generally higher than for the case S1 at high E/N. Since at relatively high energies the total cross section S2 becomes very low and simulation may not be in equilibrium with the local electric field E/N, we show only results below 600 Td.

The endothermic (reactive) collisions affect the drift velocity at high E/N values (Fig. 3). Since the total collision frequency for endothermic reactions increases with
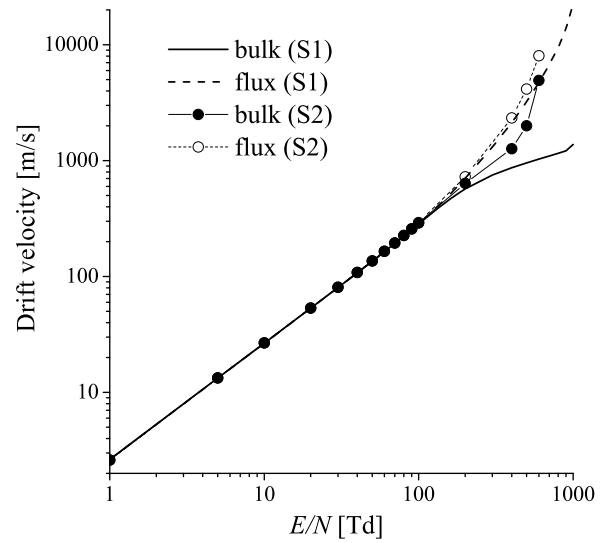
Fig. 3. Bulk and flux drift velocities for O^- ions in water vapour as a function of E/N obtained by Monte Carlo simulation at $T = 300$ K, by using cross section sets S1 and S2.
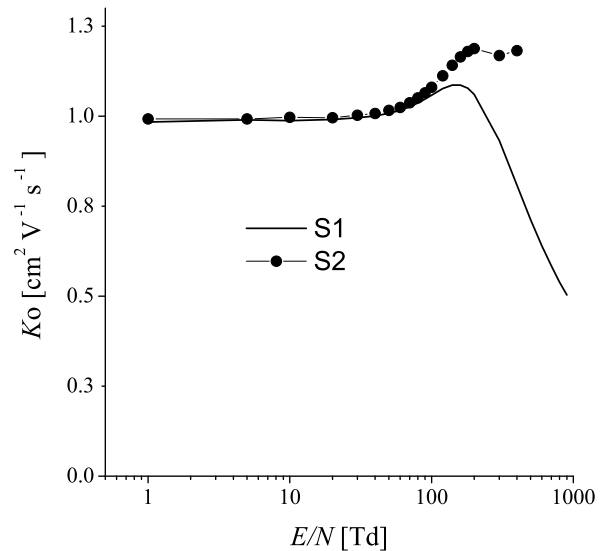
Fig. 4. Mobilities of O^- ions in water vapour as a function of E/N obtained by Monte Carlo simulation at $T = 300$ K by using cross section sets S1 and S2.

energy at high E/N thereby the dominant loss of the fast ions happens at the front of the swarm. This shifts the swarm's centre of mass towards the lower values. Thus, the bulk values (real space drift velocity $d\langle x \rangle/dt$) are lower than the flux values (velocity space drift velocity $\langle v \rangle$).

Due to the lower cross section for non-conservative processes in S2, at energies above their thresholds bulk drift velocities are closer to the flux values (as compared to the S1 results). Thus the difference between the bulk values for S1 and S2 increases with E/N (see Fig. 3). This observation indicates a possibility to distinguish between the two sets of cross sections by comparing flux and bulk
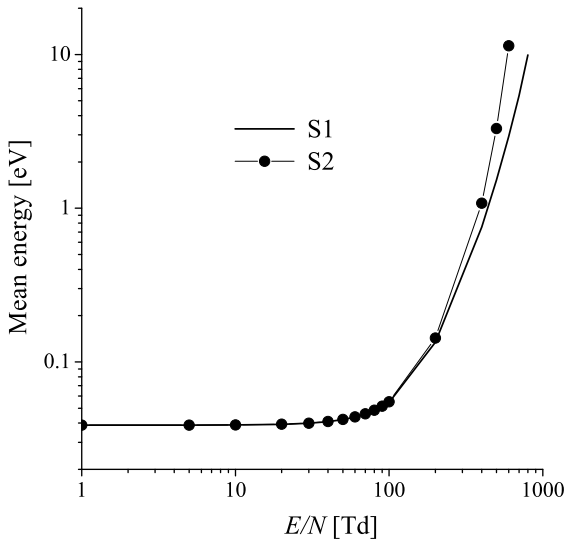
Fig. 5. Mean energies for O^- ions in water vapour as a function of E/N obtained by Monte Carlo simulation at $T = 300$ K by using cross section sets S1 and S2.
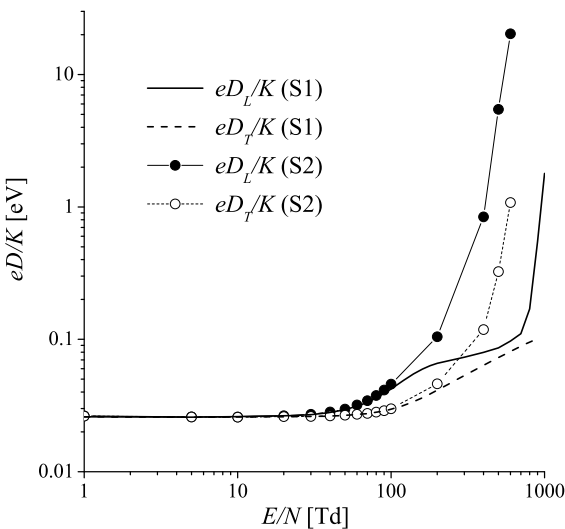

Fig. 6. Longitudinal and transverse characteristic energies for O^- ions in water vapour as a function of E/N obtained by Monte Carlo simulation at $T = 300$ K, by using cross section sets S1 and S2.

values in experiments. However, in this case there are no such measurements and it would be hard to find examples of experimental devices where such measurements could become available.

Values of the reduced mobility as a function of E/N shown in Figure 4 are sampled by using bulk drift velocities (i.e. mean velocities in real space), as those are measured in most experiments [33–35]. When the experimental or calculated data are to be used in modelling one needs to make a distinction between bulk and flux and apply the data according to the equations that are being used [34,35].

Effects of non-conservative processes become significant above 100 Td (Fig. 3). The mobility peak, representing a balance between repulsive and attractive forces appears at about 150 Td for S1 set and above 200 Td for S2 set, as seen in Figure 4.

The mean energy and the characteristic energies (longitudinal L and transverse T) are shown in Figures 5 and 6. A similar increase with E/N may be observed for diffusion coefficients, resulting in a significant increase of the characteristic energy, especially in the direction of the field (Fig. 6).

Longitudinal and transverse bulk and flux diffusion coefficients are given in Figures 7a and 7b and one should notice the very large non-conservative effects almost a reminder of the positron transport [16]. Note that the difference between the flux and bulk values of diffusion coefficients for S2 is relatively small as compared to the S1 results.

Finally, in Figure 8 we present rates for different processes for sets S1 and S2 together. Here the rate for detachment is separated from that for OH^- formation. While detachment is considerably smaller it becomes equal to OH^- formation at the highest E/Ns and also one should be aware of each process separately as products are different. Comparing rates for reactions between two models, the differences between S1 and S2 results are approximately one order of magnitude different. That is consistent with the choice of the cross sections that cover well the spread of data in the literature and within the observed experimental discrepancies as reported in [25].

Formation of $O^- \cdot H_2O$ produced in three body collisions [26] is not included in our work. We assumed that processes presented in Table 1 describe O^- transport well for low pressures where binary collision regime holds and where the contribution of the three body collisions is negligible.

3 Conclusion

O^- and OH^- are the principal negative ions in discharges in water vapour. Having in mind the current interest in discharges in and close to liquids it is important to provide a complete set of cross sections that would serve as the basis for modelling such plasmas/discharges.

The present data may be expected to be valid as a complete representation of O^- kinetics for the water vapour at low enough pressures so that clustering does not affect the results. A similar procedure as employed in the model S2 may be applied to provide collisions with most buffer gases and thus cover mixtures with a small abundance of water vapour. In addition, the data may be used as the basis to help analyse the transport when clustering is important [36].

We have proposed two cross section sets based either on experimental data or on theoretical calculations (by using the Danpoh and Nanbu's theory) and those sets were used in a simulation to produce the swarm data. We would recommend the theoretical cross section set S2 as it is fully self-consistent and it agrees with elastic scattering in [25] at low energies, OH^- formation from [27] and is also consistent with the detachment cross section in [24].
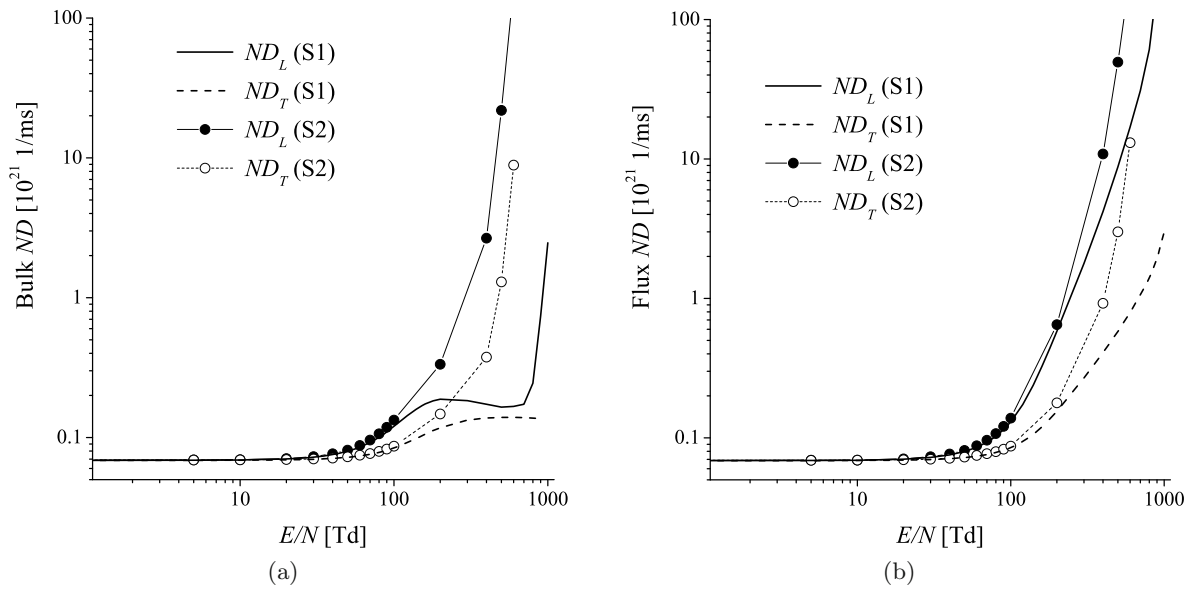
Fig. 7. Diffusion coefficients for O^- ions in water vapour as a function of E/N obtained by Monte Carlo simulation at $T = 300$ K by using cross section sets S1 and S2: (a) bulk diffusion coefficients, (b) flux diffusion coefficients.
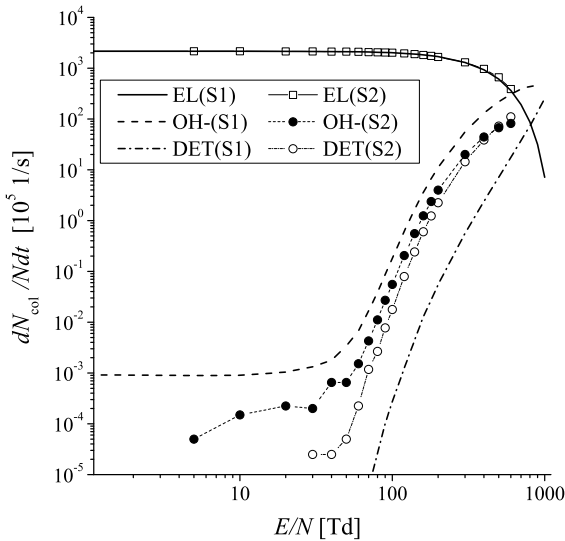

Fig. 8. Rate coefficients for collisions of O^- ions in water vapour as a function of E/N obtained by Monte Carlo simulation at $T = 300$ K, by using cross section sets S1 and S2.

energies may have considerable contribution greater than that extrapolated from our study.

In addition to presenting the cross section and transport data we show here effects of non-conservative collisions on ion transport (that have been discussed to our knowledge for the first time for ions in [21]). Due to non-conservative cross sections that quickly become larger than the elastic scattering cross section differences between flux and bulk transport coefficients are quite large – comparable to the strongest cases observed for electrons, even positrons. Set S2 does not show such large effects as the reactive cross sections are smaller and are falling off with energy but still its non-conservative discrepancy between bulk and flux properties is significant.

Data for swarm parameters and cross sections for ions are needed for kinetic, hybrid and fluid codes and it would be essential to carry out some measurements of ion transport to be able to make these results more accurate. Realistic experiments, however, will require somewhat higher pressures to achieve local hydrodynamic equilibrium and thus could be prone to cluster formation [36].

In this paper, we showed transport properties for the O^- in water vapour which are not available in the literature. These data are needed for modelling in numerous applications where water vapour is often present in various abundances [9–12,37] thus similar cross sections for the ions in standard buffer gases would be required Present results are also of interest for interpretation of the breakdown mechanisms [7,8,38] and early stages in the development of the discharges.

This set, however, leads to very low cross sections at higher energies and thus some of the transport coefficients such as the mean energy become exceedingly high. It would be interesting to see whether a runaway of O^- ions may occur in water vapour and thus confirm such cross section shapes. Tests of runaway, however, would require exact modelling of a particular experiment (pressure, geometry, etc.) and careful consideration both in simulations and even more so in experiments. In addition one would need to establish whether some new processes at higher energies open up and also whether elastic scattering at higher

References

1. K.R. Stalder, G. Nersisyan, W.G. Graham, J. Phys. D **39**, 3457 (2006)
2. T. Hagino, H. Kondo, K. Ishikawa, H. Kano, M. Sekine, M. Hori, Appl. Phys. Express **5**, 035101 (2012)
3. M. Laroussi, Plasma Processes Polym. **2**, 391 (2005)
4. S. Lazović, N. Puač, M. Miletić, D. Pavlica, M. Jovanović, D. Bugarski, S. Mojsilović, D. Maletić, G. Malović,P. Milenković, Z.Lj. Petrović, New J. Phys. **12**, 083037 (2010)
5. K. Kutasi, J. Loureiro, J. Phys. D **40**, 5612 (2007)
6. P. Bruggeman, D. Schram, M.Á. González, R. Rego, M.G. Kong, C. Leys, Plasma Sources Sci. Technol. **18**, 025017 (2009)
7. I. Marinov, O. Guaitella, A. Rousseau, S.M. Starikovskaia, Plasma Sources Sci. Technol. **22**, 042001 (2013)
8. A. Starikovskiy, Plasma Sources Sci. Technol. **22**, 012001 (2013)
9. T. Murakami, K. Niemi, T. Gans, D. O'Connell, W.G. Graham, Plasma Sources Sci. Technol. **22**, 015003 (2013)
10. W. Van Gaens, A. Bogaerts, J. Phys. D **46**, 275201 (2013)
11. P. Bruggeman, C. Leys, J. Phys. D **42**, 053001 (2009)
12. J.D. Skalny, J. Orszagh, N.J. Mason, J.A. Rees, Y. Aranda-Gonzalvo, T.D. Whitmore, Int. J. Mass Spectrom. **272**, 12 (2008)
13. G. Ruíz-Vargas, M. Yousfi, J. de Urquijo, J. Phys. D **43**, 455201 (2010)
14. Y. Itikawa, N. Mason, J. Phys. Chem. Ref. Data **34**, 1 (2005)
15. R.E. Robson, R.D. White, K.F. Ness, J. Chem. Phys. **134**, 064319 (2011)
16. R.D. White, W. Tattersall, G. Boyle, R.E. Robson, S. Dujko, Z.Lj. Petrović, A. Banković, M.J. Brunger, J.P. Sullivan, S.J. Buckman, G. Garcia, Appl. Radiat. Isotopes **83**, 77 (2014)
17. J. de Urquijo, E. Basurto, A.M. Juarez, K.F. Ness, R.E. Robson, M.J. Brunger, R.D. White, J. Chem. Phys. **141**, 014308 (2014)
18. N. Škoro, D. Marić, G. Malović, W.G. Graham, Z.Lj. Petrović, Phys. Rev. E **84**, 055401(R) (2011)
19. M. Radmilović-Radenović, B. Radenović, Ž. Nikitović, Š. Matejčik, M. Klas, Nucl. Instrum. Methods Phys. Res. B **279**, 103 (2012)
20. Z. Ristivojević, Z.Lj. Petrović, Plasma Sources Sci. Technol. **21**, 035001 (2012)
21. Z.Lj. Petrović, Z.M. Raspopović, V.D. Stojanović, J.V. Jovanović, G. Malović, T. Makabe, J. de Urquijo, Appl. Surf. Sci. **253**, 6619 (2007)
22. J. de Urquijo, J.V. Jovanović, A. Bekstein, V. Stojanović, Z.Lj. Petrović, Plasma Sources Sci. Technol. **22**, 025004 (2013)
23. K. Denpoh, K. Nanbu, J. Vac. Sci. Technol. A **16**, 1201 (1998)
24. J.B. Hasted, R.A. Smith, Proc. Roy. Soc. London A **235**, 349 (1956)
25. C. Lifshitz, J. Phys. Chem. **86**, 3634 (1982)
26. F.C. Fehsenfeld, E.E. Ferguson, J. Chem. Phys. **61**, 3181 (1974)
27. D. Vogt, Int. J. Mass. Spectrom. Ion Phys. **3**, 81 (1969)
28. V. Stojanović, Z. Raspopović, D. Marić, Z.Lj. Petrović, Contributed Papers, *27th SPIG, Belgrade, August 26–29, 2014*, p. 142
29. J.V. Dugan, J.L. Magee, J. Chem. Phys. **47**, 3103 (1967)
30. D.C. Clary, Chem. Phys. Lett. **232**, 267 (1995)
31. UMIST RATE12 astrochemistry.net, http://udfa.ajmarkwick.net/
32. J.A. de Gouw, M. Krishnamurthy, S.R. Leone, J. Chem. Phys. **106**, 5937 (1997)
33. Z.Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, V. Stojanović, M. Radmilović-Radenović, J. Phys. D **42**, 194002 (2009)
34. R.E. Robson, Aust. J. Phys. **44**, 685 (1991)
35. S. Dujko, A.H. Markosyan, R.D. White, U. Ebert, J. Phys. D **46**, 475202 (2013)
36. J. de Urquijo, A. Bekstein, G. Ruiz-Vargas, F.J. Gordillo-Vázquez, J. Phys. D **46**, 035201 (2013)
37. R.D. White, M.J. Brunger, N.A. Garland, R.E. Robson, K.F. Ness, G. Garcia, J. de Urquijo, S. Dujko, Z.Lj. Petrović, Eur. Phys. J. D **68**, 125 (2014)
38. D. Marić, M. Savić, J. Sivoš, N. Škoro, M. Radmilović-Radjenović, G. Malović, Z.Lj. Petrović, Eur. Phys. J. D **68**, 155 (2014)

Cross Sections and Transport Properties for Na$^+$ in (DXE) Gas

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Abstract:
    In this work we select most probable reactions of alkali metal ion Na$^+$ with dimethoxyethane (DXE) molecule. Appropriate gas phase enthalpies of formation for the products were used to calculate scattering cross section as a function of kinetic energy with Denpoh-Nanbu theory. Calculated cross sections were compared with existing experimental results obtained by guided ion beam tandem mass spectrometry. Three body association reactions of ions with DXE is studied and compared to experimental results. Calculated cross sections were used to obtain transport parameters for alkali metal ion in DXE gas.
Keywords: DXE molecule, Na$^+$, Monte Carlo simulation, Denpoh-Nanbu method.
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1. Introduction

        Field-assisted sintering technique/Spark plasma sintering (FAST/SPS) is a low voltage, direct current (DC) pulsed current activated, pressure-assisted sintering and synthesis technique [1]. It has been widely applied in materials processing in recent years.
        Cold plasmas are often used in new technologies where they offer methods for nonintrusive production or modification of specific substances [2]. Main characteristics of these plasmas are their high electron temperature and low gas temperature. Dimethoxy-containing compounds, such as dimethoxyethane (DXE), can be produced from dimethyl ether by using dielectric barrier discharge (DBD) plasmas containing water vapor at atmospheric pressure [3]. As clear and colorless liquid at room temperature and atmospheric pressure, DXE is used as a precursor in production of ceramics [4] or as a sole compound to make other chemicals such as those used in lithium batteries production [5-8], superconductor production [9], nanoparticles synthesis [10-12], in etherification [13] etc.
        Very limited information exists about processes taking place in these or similar complex plasmas. Therefore in this study we will analyze transport properties of ions in DXE gas since ions are not only inducing products of reactions but also large number of radicals.
        At atmospheric pressure three body reactions of ions are of increasing complexity for modeling reaction kinetics. In many modeling cases information about the three body processes is missing. Denpoh-Nanbu theory (DNT) [14] can be exploited to calculate cross section sets as a function of the kinetic energy for cases where no or limited information is available about scattering data [15]. Nikitović et al. [16] showed how radiative association for three body reactions can be included into cross section set obtained by DNT. Approach presented in [16] is compared with existing experimental data for association cross section as a function of pressure [17] and showed good agreement at energies below few eV. Such information is of great importance in atmosferic pressure plasmas containing complex

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molecules such as DXE and can be highly valuable in modeling clustering in various plasmas.

In this work we applied the approach of [16] for the case of alkali ions scattering on DXE molecule since in all reactions studied experimentally [18, 19] the only product that included alkali ions/atoms is the association complex Li[+](DXE) and similarly Na[+](DXE) and K[+](DXE). In the following text we will present cross section set for Na^{+} + DXE scattering which includes association cross section for Na^{+} (DXE) complex. Alkaline metals are of great interest for possible applications [20].

In this paper we firstly selected the most probable reactions of alkali metal ion Na^{+} with dimethoxyethane (DXE) molecule (and its most probable products) for thermodynamic threshold energies below about 15 eV. Appropriate gas phase enthalpies of formation [21] for the products were used to calculate thermodynamic thresholds.

Although DXE consists of many atoms its dipole moment is negligible, so the simplest capture theories can be applied. Scattering cross section as a function of kinetic center of mass energy is calculated with DNT [14, 22]. Calculated cross sections for three body association reaction of selected ions with DXE were compared with existing experimental results obtained by guided ion beam tandem mass spectrometry [18].

2. Calculation of the cross section set

The scattering cross sections of alkali ion Na^{+} on DXE are calculated by using the DNT [14] separating elastic from reactive collisions. DXE is known not to have dipole moment in its ground state. The dipole polarizability of 9.94×10^{-30} m^3 [18] is used for the DXE target. Similar to our recent papers [23], DN method is used to separate elastic from reactive endothermic collisions by accounting the thermodynamic threshold energy and branching ratio according to the Rice-Rampsperger-Kassel (RRK) theory [14]. Within the RRK theory the internal energy is being distributed among an empirical number of s equivalent effective modes of the complex selected from the total number of atoms involved in the complex.

Appropriate gas phase enthalpies of formation for the products [19] (Table I) were used to calculate thermodynamic thresholds (Table II). The cross-section for the exothermic reaction (EXO) forming a molecular ion X$^+$ in DXE is commonly represented by ion capture cross-section:

$$\sigma_{exo} = \beta \, \sigma_L, \qquad (1)$$

where σ_L is the orbiting cross-section [24] and β is the probability of a specific exothermic reaction.

Tab. I Heats of formation at 298 K (kJ/mol).

Species	$\Delta_f H^0$	Species	$\Delta_f H^0$
Li	159.4	Li$^+$	679.6
Na	107.3	Na$^+$	603.1
K	89	K$^+$	507.8
DXE	-340	DXE$^+$	557
$C_3H_8O_2$	-364	$C_3H_8O_2^+$	562
C_2H_6O	793.1	$C_2H_6O^+$	775.4
C_2H_4O	821.1	$C_2H_4O^+$	-165.8
CH_4O	-201.6	CH_4O^+	845.3
CH_2O	-108.7	CH_2O^+	940.5
CH_4	-74.5	CH_4^+	1132.0
CO	-110.53	CO$^+$	1241.59
H_2	0.0	H_2^+	1488.3

Tab. II X^+ - DXE reaction paths (X=Li, Na, K) showing reaction products and the corresponding thermodynamic threshold energies Δ.

No	products		Δ (eV)	
		Li^+	Na^+	K^+
1	$X^+ + DXE$	0	0	0
2	$X + C_4H_{10}O_2^+$	3.905	4.158	4.9561
3	$X^+ + C_3H_8O_2 + CH_2$	3.793	3.793	3.793
4	$X + C_3H_8O_2^+ + CH_2$	7.999	8.252	9.050
5	$X + C_3H_8O_2 + CH_2^+$	8.724	8.977	9.775
6	$X^+ + C_2H_6O + CH_2 + CO$	4.513	4.513	4.513
7	$X + C_2H_6O^+ + CH_2 + CO$	9.147	9.400	10.198
8	$X + C_2H_6O + CH_2^+ + CO$	9.444	9.697	10.495
9	$X + C_2H_6O + CH_2 + CO^+$	13.135	13.388	14.186
10(EXO1)	$X^+ + C_2H_4O + C_2H_6O$	-0.1016	-0.1016	-0.1016
11	$X + C_2H_4O^+ + C_2H_6O$	4.7353	4.9882	5.7862
12	$X + C_2H_4O + C_2H_6O^+$	4.5322	4.7851	5.5831
13(EXO2)	$X^+ + C_3H_8O + CO$	-0.2625	-0.2625	-0.2625
14	$X^+ + CH_2O + C_2H_6 + CO$	0.3811	0.3811	0.3811
15	$X + CH_2O^+ + C_2H_6 + CO$	5.8636	6.1165	6.9145
16	$X + CH_2O + C_2H_6^+ + CO$	6.5145	6.7674	7.5654
17	$X + CH_2O + C_2H_6 + CO^+$	9.0031	9.256	10.054
18	$X^+ + CH_4O + C_3H_4 + H_2O$	0.8620	0.8620	0.8620
19	$X + CH_4O^+ + C_3H_4 + H_2O$	6.3207	6.5736	7.3716
20	$X + CH_4O + C_3H_4^+ + H_2O$	5.8305	6.0834	6.8814
21	$X + CH_4O + C_3H_4 + H_2O^+$	8.0818	8.3347	9.1328
22	$X^+ + C_4H_6 + 2H_2 + O_2$	5.0307	5.0307	5.0307
23	$X + C_4H_6^+ + 2H_2 + O_2$	9.2012	9.454	10.2521
24	$X + C_4H_6 + 2H_2 + O_2^+$	15.064	15.317	16.115
25	$X + C_4H_6 + H_2^+ + H_2 + O_2$	11.716	11.969	12.7674
26(EXO3)	$X + CH_4 + C_3H_6^+ + O_2$	-2.4304	-2.1775	-1.3794
27(EXO4)	$X + C_4H_8^+ + H_2 + O_2$	-1.8717	-1.6189	-0.8208
28(EXO5)	$X^+ + C_3H_8 + H_2 + CO_2$	-1.6376	-1.6376	-1.6376
29(EXO6)	$X + C_3H_6^+ + 2H_2 + CO_2$	-5.7366	-5.4837	-4.6857

By combining the relation (1) and thermal rate coefficient we determined the probability of exothermic reaction and the contributions of association cross section and elastic cross section. In the low energy limit the cross sections are similar due to dominant polarization of the target. At higher energies reactive collisions including the non-

conservative collisions become efficient for various possible processes.

Elastic momentum transfer cross section is modified in order to fit approximate mobility peak characteristic for presented systems. Swarm method [25, 26] is exploited to modify the cross section for elastic momentum transfer where for reduced mobility in the peak region (experimental [27] or theoretical values [28]) similarity with ions of equal or similar reduced mass is targeted. Elastic momentum transfer cross section for elastic collisions of Na$^+$ and DXE is presented in Fig. 1.
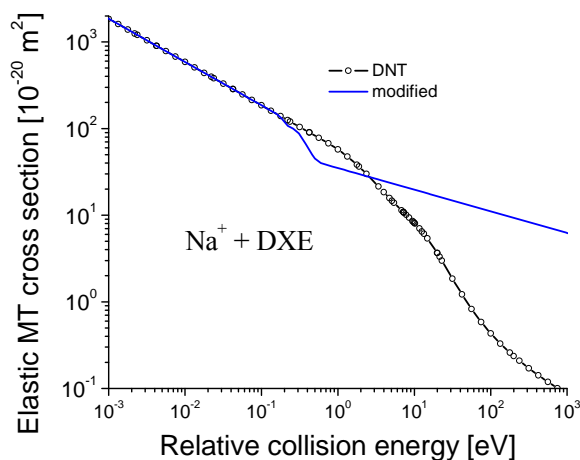
Fig. 1. Elastic momentum transfer cross section as a function of collision energy for Na$^+$ and DXE.

Agreement with experiment is satisfactory for energies below 1 eV. A further step in all cases will be to add more reactions with multiple radicals that will increase the thermodynamic threshold and generally increase the number of reactions. This may potentially improve agreement with experimental data for cross sections for association reaction.

In all mentioned experimental cases, the cross sections show a clear pressure dependence, which indicates the occurrence of collision stabilization of complex by secondary collisions. The effect of secondary collisions can be eliminated completely by linear extrapolation of the cross section data to zero reactant pressure. The same trend is easily achieved with theoretical data providing our theoretical cross sections can be exploited and also used in many other cases.

3. Transport parameters

The transport coefficients include the mean energy, the drift velocity, diffusion coefficients, ionization and attachment coefficients and chemical reaction coefficients for ions. Excitation coefficients are also measured but seldom used in modeling.

Swarm parameters as a function of reduced electric field E/N in DC electric fields is generally applied to plasma modeling and simulations.

We have used a Monte Carlo code that properly takes into account thermal collisions [29]. The code has passed all the relevant benchmarks and has been tested in our work on several types of charged particles.

In Fig. 2 we show the mean energy, which cannot be directly measured in experiments but a map of the mean energy versus E/N may be used directly to provide the data in fluid models especially when the local field approximation fails.
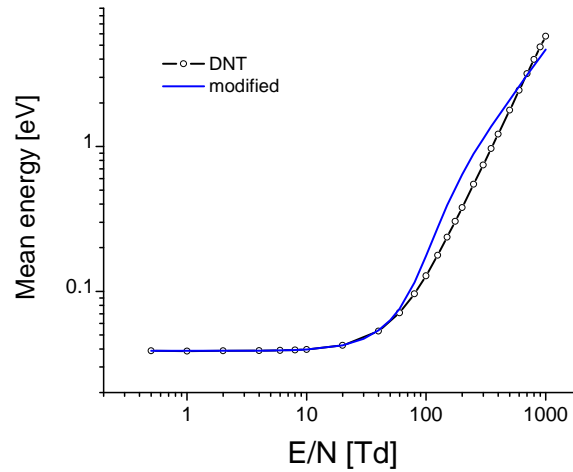
Fig. 2. Mean energy as a function E/N for Na$^+$ ions in DXE gas.

Flux and bulk drift velocities [30-32] as a function of E/N are given in Fig. 3. The drift velocities obtained by Monte Carlo simulation calculated in real space (bulk) and in velocity space (flux) values which are obtained as <v> and dx/dt, respectively.
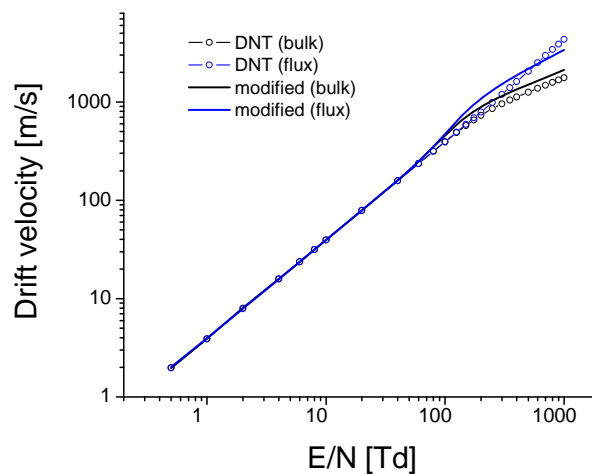
Fig. 3. Flux and bulk drift velocity as a function E/N for Na$^+$ ions in DXE gas.

The mobility K of an ion is the quantity defined as the velocity attained by an ion moving through a gas under the unit electric field. One often exploits the reduced or standard mobility defined as:

$$K_0 = \frac{v_d}{N_0 E} N \,, \tag{2}$$

where v_d is the drift velocity of the ion, N is the gas density at elevated temperature T and E is the electric field.

In Fig. 4 we show the results of Monte Carlo simulation for reduced mobility as a function of E/N. Due to reactive collisions bulk and flux values of reduced mobility are separated.
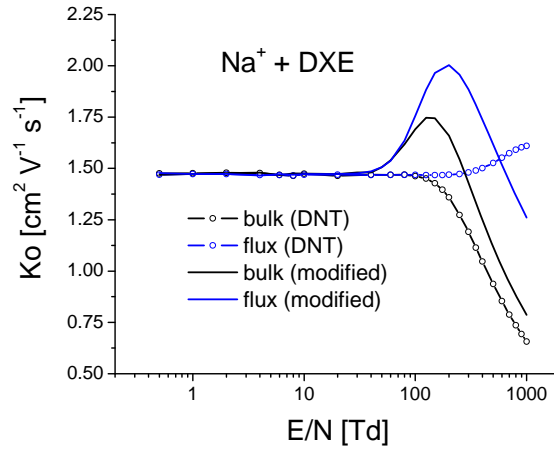
Fig. 4. Reduced mobility as a function E/N for Na$^+$ ions in DXE gas.

Longitudinal (a) and transversal (b) diffusion coefficients for Na$^+$ in DXE as a function of E/N are shown in Fig. 5. The peak is visible only in the behavior of longitudinal diffusion coefficients. However, there are no published experimental data for the longitudinal and transverse diffusion coefficients of Na$^+$ in DXE so far.

a)

b)
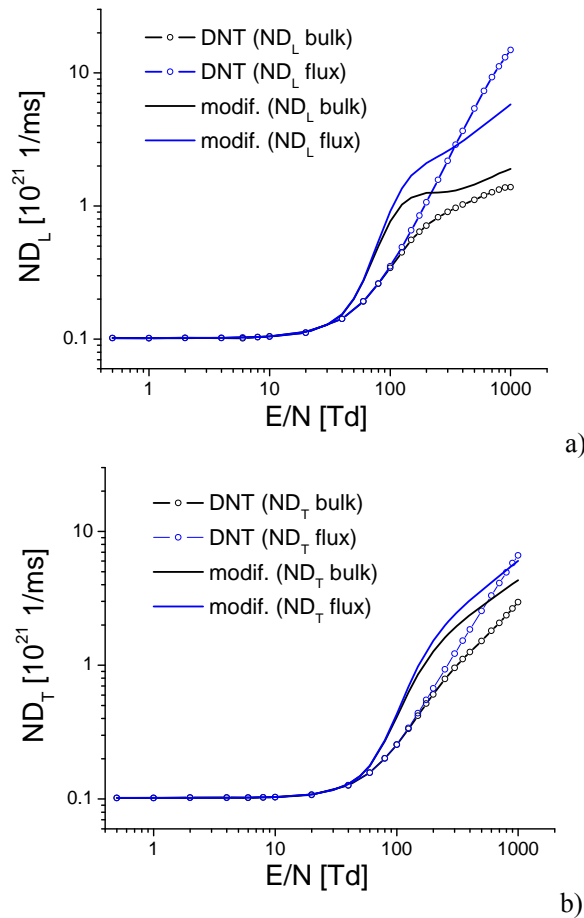
Fig. 5. a) Longitudinal and b) transversal diffusion coefficients as a function E/N for Na$^+$ ions in DXE gas.

4. Conclusion

Cross sections for elastic collisions of Na+ and DXE are calculated using Denpoh-Nanby theory and modified with help of swarm method. Calculated cross sections are used to obtain transport parameters for Na$^+$ in DXE gas.

Peak for flux reduced mobility values is shifted in energy and intensity with respect to peak for bulk values.

The cross sections and transport data for technologically very important gas DXE have been determined by using simple theory. While it is a good basis for modeling it would be much better to add a data base of measured transport coefficients and then to perform the analysis again.

Acknowledgements

5. References

1. O. Guillon, J. Gonzales-Julian, B. Dargatz, T. Kessel, G. Schierning, J. Rathel, M. Herrmann, Advanced Engineering Materials 16 (2014) 830-849.
2. K. Rajeswari, U. S. Hareesh, R. Subasri, Dibyendu Chakravarty, R. Johnson, Science of Sintering 42 (2010) 259-267.
3. Y. Wang, C. Liu, Y. Zhang, Plasma Sci. & Technology 7, No. 3 (2005) 2839-2841.
4. N. Kumar, Y. Yang, W. Noh, G. S. Girolami, and J. R. Abelson, Chem. Mater. 19 (2007) 3802-3807.
5. B. D. McCloskey, C. M. Burke, J. E. Nichols and S. E. Renfrew, Chem. Commun. 51 (2015) 12701-12715.
6. Y. Cheng, R. M. Stolley, K. S. Han, Y. Shao, B. W. Arey, N. M. Washton, K. T. Mueller, M. L. Helm, V. L. Sprenkle, J. Liu and G. Li, Phys. Chem. Chem. Phys. 17 (2015) 13307-14.
7. S.-H. Chung and A. Manthiram, J. Phys. Chem. Lett. 5 (2014) 1978−1983.
8. J.-L. Shui, N. K. Karan, M. Balasubramanian, S.-Y. Li and D.-J. Liu, J. Am. Chem. Soc. 134 (2012) 16654−16661.
9. W. D. Buchanan, M. A. Guino-o, and K. Ruhlandt-Senge, Inorg. Chem. 49 (2010) 7144-7155.
10. R. K. Baldwin, K. A. Pettigrew, E. Ratai, M. P. Augustine, S. M. Kauzlarich, Chem. Commun. (2002) 1822-1823.
11. A. L. Pickering, C. Mitterbauer, N. D. Browning, S. M. Kauzlarich, and P. P. Power, Chem. Commun. (2007) 580-582.
12. T. Hawa and M. R. Zachariah, J. Phys. Chem. C 112 (2008) 14796-14800.
13. P. Che, F. Lu, X. Si and J. Xu, RSC Adv. 5 (2015) 24139- 24143.
14. K. Denpoh and K. Nanbu, J. Vac. Sci. Technol. A 16 (3) (1998) 1201-1207.
15. V. Georgieva, A. Bogaerts and R. Gijbels, J. Appl. Phys. 93 (2003) 2369-2379.
16. Ž. Nikitović, V. Stojanović, Z. Raspopović and J. Jovanović, Acta Phys. Pol. A No. 3, Vol. 126 (2014) 724-726.
17. Milica Petrović, Martina Gilić, Vladimir Stojanović, Željka Nikitović, Zoran Raspopović, Nebojša Romčević, SEVENTEENTH ANNUAL CONFERENCE YUCOMAT, Herceg Novi, Montenegro, August 31-September 4 (2015) P.S.A.8.
18. H. Koizumi, P. B. Armentrout, J. Chem. Phys. 119 (2003) 12819-12829.
19. Y. Satoh, M. Takebe, K. Iinuma, J. Chem. Phys. 87 (1987) 6250.

20. I. A. Nafeaa, A. F. Zekry, M. G. Khalifa, A. B. Farag, N. A. El-Hussiny, M. E. H. Shalabi, Science of Sintering 47 (2015) 319-329.
21. S. G. Lias, J. E. Bartmess, J. F. Xebman and J. L. Holmes, R. D. Levin and W. G. Mallard, J. Phys. Chem. Ref. Data, Supl. 1 Vol. 17 (1988) 1.
22. Z. Lj. Petrović, Z. M. Raspopović, V. D. Stojanović, J. V. Jovanović, G. Malović, T. Makabe and J. de Urquijo, Appl. Surf. Science 253 (2007) 6619-6640.
23. V. Stojanović, Z. Raspopović, J. Jovanović, Ž. Nikitović and Z. Lj. Petrović, EPL 101 (2013) 45003.
24. McDaniel E. W., Čermak V., Dalgarno A., Ferguson E. E. and Friedman L., Ion-Molecule Reactions (Willey-Interscience) 1970.
25. Ž. Nikitović, V. Stojanović, O. Šašić, Z. Raspopović and Z. Petrović, Zbornik radova 52. konferencije ETRAN, Palić, Srbija, 8-12. juna (2008) NM 1.8.
26. Ž. Nikitović, Z. Raspopović, V. Stojanović and J. Jovanović, EPL 108 (2014) 35004.
27. L. A. Viehland and E. A. Mason, At. Data. Nucl. Data Tables 60 (1995) 37-95.
28. http://nl.lxcat.net/data/set type.php.
29. Z. Ristivojević and Z. Lj. Petrović, Plasma Sources Sci. Technol. 21 (2012) 035001.
30. R. E. Robson, Aust. J. Phys. 44 (1991) 685-692.
31. Z. Raspopović, S. Sakadžić, Z. Lj. Petrović and T. Makabe, J. Phys. D 33 (2000) 1298-1302.
32. Z. Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, V. Stojanović and M. Radmilović-Radjenović, J. Phys. D: Appl. Phys. 42 (2009) 194002.

Садржај: *У овом раду смо изабрали највероватније реакције за јоне алкалног метала Na⁺ са DXE молекулом. Одговарајуће енталпије гаса су коришћене за израчунавање пресека за сударе у функцији кинетичке енергије помоћу Denpoh-Nanbu теорије. Израчунати пресеци упоређени су са постојећим експерименталним резултатима добијеним помоћу тандем масене спектрометрије јонских снопова. Испитана је асоцијативна реакција три тела за јоне са DXE и упоређена је са експерименталним резултатима. Израчунати пресеци су коришћени за добијање транспортних параметара за јоне алкалног метала у DXE гасу.*
Кључне речи: *DXE молекул, Na⁺, Монте Карло симулације, Denpoh-Nanbu метод*

Transport Coefficients in Mixtures Ar/H$_2$

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In this work we present electron transport coefficients for electrons in Ar/H$_2$ mixtures for the conditions used in plasma assisted technologies for semiconductor production i.e. in moderate to very high reduced electric field E/N (E — electric field, N — gas density). We used a two term numerical solution of the Boltzmann equation at the lowest E/N and mean energies and also Monte Carlo simulation technique at moderate and high E/N. We show that a good agreement with experimental data exists for low and moderate E/N and that based on the tests for pure H$_2$ and Ar we can model properly the high E/N development. Results were obtained for abundances of H$_2$ from 1% to 50%. Such data are required to test the sets of cross-section data which are necessary in kinetic models for this mixture and also to produce transport coefficients for fluid models. Hydrogen is used for etching of organic compounds, most importantly low k dielectrics, at the same time argon as a buffer gas is added to control the mean energy and distribution function. Besides, operation at high E/N allows the generation of fast neutrals for charging free etching on nanometer scales.

1. Introduction

In a number of technologies argon is a typical buffer gas which allows control of electron temperature (mean energy may be quite high and one may support the selected processes with high threshold). Mixtures with hydrogen in rf plasmas may be useful for ashing of photoresists in microelectronic processing, but may also be used in a broader range of procedures.

In this paper we study the kinetics of electrons at E/N by using Monte Carlo simulations that have been well tested for similar discharges in Ar, H$_2$, and N$_2$. We focus on a special role that electrons have in plasmas and at high E/N discharges, leaving out heavy particle collisions which will be dealt with separately. Another motivation is to provide the transport data for the electrons in the mixtures of Ar and H$_2$ for modeling of such plasmas and also to point out the need to employ a more detailed kinetic modeling in sheath regions. These results can be used as the basis for modeling of anomalously broadened Doppler profiles which are particularly pronounced in Ar–H$_2$ mixtures [1], fast neutral plasma etchers for organic dielectrics and the whole range of plasma ashing/cleaning devices.

2. The Monte Carlo technique

A swarm is an ensemble of particles which move as a collective, do not interact mutually, and their motion is determined only by collisions with the atoms or molecules of the gas through which they move and the possibly present electric field. The behaviour of a swarm of electrons moving through a neutral gas can be described by transport coefficients. The basic transport coefficients

are the drift velocity, the diffusion coefficient, the characteristic energy and the coefficients for ionisation and attachment.

Transport coefficients are measured for two reasons: because of possible direct use of these results in the analysis of experiments or modelling, and also because of the determination of the cross section for scattering.

Determination of cross-sections is a complex process consisting of several steps [2]. The first step is collecting sets of maximally precise experimental data (w — the drift velocity, eD_{t}/μ — the characteristic energy, the ionisation, excitation and coefficient of capture) for a wide range of E/N values. The range of cross-section energies to be covered depends on the width of the range E/N.

In the following step a test set of cross-sections is defined. One chooses a complete set of cross-sections for all processes which exist in the energy range from 0 eV to the energy 10 times higher than the maximum mean energy of the electrons. This set is based on the best possible results obtained in experiments with swarms or crossed beams, and in theoretical calculations. It is necessary to know the characteristics of the components, the energy limits of the cross-sections and which cross-sections are tied.

Transport coefficients are obtained by using a two term approximation (TTA) to the electron Boltzmann equation [3] and by Monte Carlo simulations [4, 5] (MCS). The TTA technique is very frequently used in plasma modeling in spite of its limited accuracy [6].

We use the argon cross-sections from our calculations for argon electron (and ion) swarms [7]. For hydrogen we use the data defined in the data base of Petrović and Phelps [8]. Both sets are based on accurate low energy cross-sections that were tested aginst the best swarm data at low E/N and have been tested against the emission profiles at high E/N and energy distribution functions. Thus there is no reason to question the application

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of such set for the mixture of two gases covering similar energies.

3. Discussion and results

In Fig. 1 we show the electron energy distribution function (EEDF) for the mixture of Ar and a small yet variable percentage of H_2 for the reduced electric field $E/N = 10$ Td. This example shows that the effect of hydrogen addition from 1% to 50% reduces number of electrons in 10 eV energy group by two orders of magnitude. The shape of the EEDF changes considerably and the highest energy electrons are depleted as hydrogen is added.
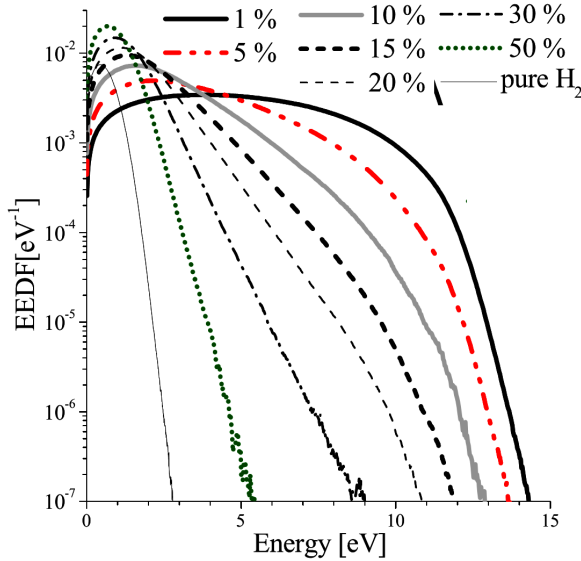
Fig. 1. EEDF obtained by MCS for a broad range of the Ar/H_2 mixtures where the parameter is taken as a percentage composition of hydrogen in the mixture.

Figure 2 shows electron drift velocity in the mixture Ar/H_2 as a function of E/N. Even a smallest addition of H_2 completely changes the shape of the drift velocity and induces effect of negative differential conductivity (NDC). The range of NDC is, however, reduced by a further increase of hydrogen concentration and is eventually lost beyond 15% of added hydrogen. In drift velocity plots we have also used the ELENDIF code [3] to calculate drift velocity at lower energies where the Monte Carlo simulation becomes inefficient (for higher H_2 abundances lower energies extend to higher E/N). Agreement with the experimental results of Engelhardt and Phelps [9] (EXP) confirms that a well-chosen set of sections is used to describe the behaviour of electrons in Ar/H_2 mixtures.

In Fig. 3 we show the mean energy of electrons in the mixture Ar/H_2 as a function of E/N. These results were obtained by the Monte Carlo code when H_2 is present from 1–20%.
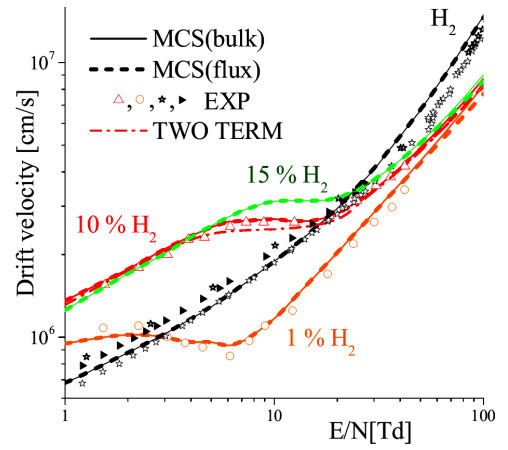
Fig. 2. Electron drift velocity for the mixture of Ar and H_2. Experimental values for pure H_2 are from Dutton [10].
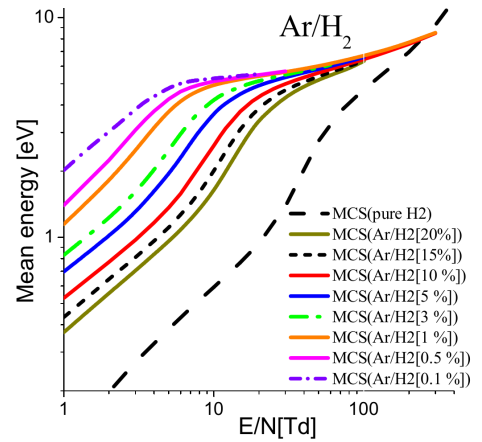
Fig. 3. Mean electron energy for the mixture of Ar and H_2.

There are notable changes in energy due to adding a secondary maximum hydrogen at lower E/N, where the influence of inelastic losses of electrons in collisions with hydrogen greatest.

The resulting transport coefficients are in agreement with existing experimental results, confirming that the effective scattering cross-section set which we have chosen can be used as a basis for modeling non-equilibrium conditions in the Ar/H_2 mixture gas discharges.

4. Conclusion

In this paper we show calculated electronic transport coefficients for the Ar/H_2 mixture under conditions where the dominant influence is exercised in the collisions of electrons with Ar and in conditions in which the influence of H_2 [11, 12] is significant. The resulting transport coefficients are in agreement with existing experimental results. We confirmed that the set of effective scattering

cross-section we have chosen can be used as a basis for modeling non-equilibrium regions in the gas discharges with Ar/H$_2$ mixture.

Acknowledgments

References

[1] M. Miyauchi, Y. Miyoshi, Z.Lj. Petrović, T. Makabe, *Solid-State Electron.* **51**, 1418 (2007).

[2] R.W. Crompton, *Adv. At. Mol. Opt. Phys.* **32**, 97 (1994).

[3] W.L. Morgan, B.M. Penetrante, *Comp. Phys. Commun.* **58**, 127 (1990).

[4] Z.Lj. Petrović, V.D. Stojanović, *J. Vac. Sci. Technol. A* **16**, 329 (1998).

[5] Ž. Nikitović, V. Stojanović, J.P. Booth, Z.Lj. Petrović, *Plasma Sources Sci. Technol.* **18**, 035008 (2009).

[6] S. Dujko, R.D. White, K.F. Ness, Z.Lj. Petrović, R.E. Robson, *J. Phys. D, Appl. Phys.* **39**, 4788 (2006).

[7] V. Stojanović, Ž. Nikitović, Z. Petrović, *Bul. Am. Phys. Soc.* **56**, FTP1 34 (2011).

[8] Z.Lj. Petrović, A.V. Phelps, *Phys. Rev. E* **80**, 066401 (2009).

[9] A.G. Engelhardt, A.V. Phelps, *Phys. Rev.* **133**, A375 (1962).

[10] J. Dutton, *J. Phys. Chem. Ref. Data* **4**, 577 (1975).

[11] V.D. Stojanović, Ž.D. Nikitović, Z.Lj. Petrović, in: *7th General Conf. of the Balkan Physical Union, Book of Abstracts, Alexandroupolis (Greece)*, 2009, p. 65.

[12] M. Hayashi, private communication, 1992.

Cross-Sections and Transport Properties of F⁻ Ions in F₂

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We present the new results for the simple scattering cross-section set and proposed transport coefficients for F⁻ ions in F₂ that can be used in such models. Nanbu's theory based on thermodynamic threshold energies and separating elastic and reactive collisions is used to calculate cross-sections for binary collisions of ions with atoms and molecules. Direct MC method is applied to obtain swarm parameters at temperature of $T = 300$ K.

1. Introduction

The goal of this work is to present data for modeling of complex low temperature collisional plasmas containing F⁻ ions by using a global [1–3] and other plasma models. The negative halogen ions are abundant in various forms of nonequilibrium plasmas relevant to applications such as excimer lasers [4, 5] and electrical discharges, biomedical devices, nanotechnologies and in radiation chemistry in the atmosphere. For example, it is experimentally found that negative ions are effective for increasing the etch rate and improving the etch profile [6]. F⁻ ions are also unavoidable part of production of cBN films [7].

For example, F₂ may be produced in pulsed plasma implantation system that is the basis for establishing doping of integrated components. In such a system it is necessary to create uniform plasma over the entire wafer that could be more than 500 mm wide. To achieve such a goal one needs to understand a number of processes of particles interacting with either gas molecules or surfaces. Time resolved measurements of ion energy distributions in the cathode boundary [8] indicated a possible role of charge-transfer collisions between singly charged ions of various masses.

In this paper we study the energy dependent scattering and transport processes for F⁻ ions in F₂ gas.

2. Monte Carlo technique and the cross-section data

The cross-sections for scattering of F⁻ on F₂ molecule are calculated by using Nanbu's theory [9, 10] that within same framework treats elastic and reactive endothermic collisions. In Nanbu's theory reactive collision is treated by accounting for thermodynamic threshold energy and branching ratio according to the Rice–Rampsperger–Kassel (RRK) theory [9]. In the RRK theory of uni-molecular reaction rates excited molecular

complex is treated as excited activated complex where internal energy is distributed among equivalent oscillators-vibrational modes of the complex.

Our procedure is a direct implementation of this theory and approximation. We have used value 1.2611×10^{-30} m³, for polarizability of F₂ recommended by Spelsberg and Meyer [11], ionization potentials for F₂ and F⁻ from [12] and the bond values between atoms in Ref. [13]. One is usually applying procedure where unfolding the cross-sections is coming from the measured transport coefficients and thermo-chemical data known from a separate drift tube and other experiments. According to our knowledge no such data are available.

In Monte Carlo (MC) technique used in this study collision frequency in case of thermal collisions of a test ion particle is not calculated by MC integration technique [14] but by using piecewise calculation [15]. That method is based on assumption that most cross-sections are defined numerically at limited number of points with linear interpolation for mid points.

The MC technique was applied to perform calculations of transport parameters as well as rate coefficients in DC electric fields. In this paper we have used a MC code that properly takes into account the thermal collisions [15]. The code has passed all the tests and the benchmarks that were covered in our earlier studies [15, 16]. For example the distinction should be made between [17, 18] the so called bulk (b) and flux (f) transport properties such as drift velocity

$$\boldsymbol{v}_b = \frac{\mathrm{d}}{\mathrm{d}t} \sum_{i=1}^{n} \boldsymbol{r}_i, \quad \boldsymbol{v}_f = \sum_{i=1}^{n} \boldsymbol{v}_i. \tag{1}$$

3. Discussion and results

In Fig. 1 we show calculated cross-sections for F⁻ scattering on F₂. Cross-section for charge transfer (CT) producing F₂⁻ ion measured by Chupka et al. [19] is shown in the same figure.

Transport parameters were calculated for the room gas temperature of $T = 300$ K. The rate for CT with its low threshold of 0.39 eV overlaps with the thermal distribution function of participants in a collision and thus a

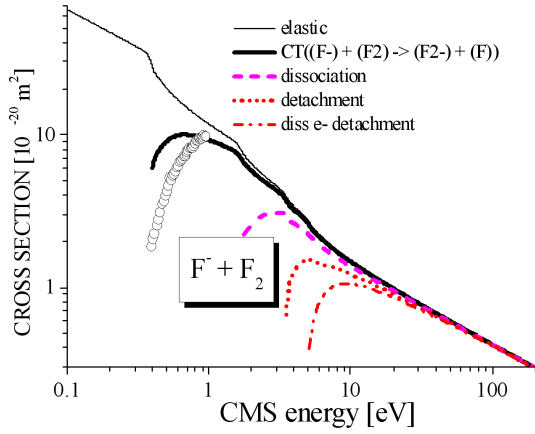---

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Fig. 1. Cross-section set for F^- ions in F_2. Open circles denote the data of Chupka et al. [19] placed on absolute scale by assuming maximum value as obtained by Nanbu's theory.

plateau exists at low E/N. The value of the plateau is very low but it increases rapidly as the temperature of the gas is increased.

The temperature for the most part does not affect elastic scattering as the total cross-section does not depart much from the cross-section consistent with the constant collision frequency.

As for the rates of inelastic processes the temperature makes a small, hardly observable, effect as the thresholds are considerably higher than the thermal energy.
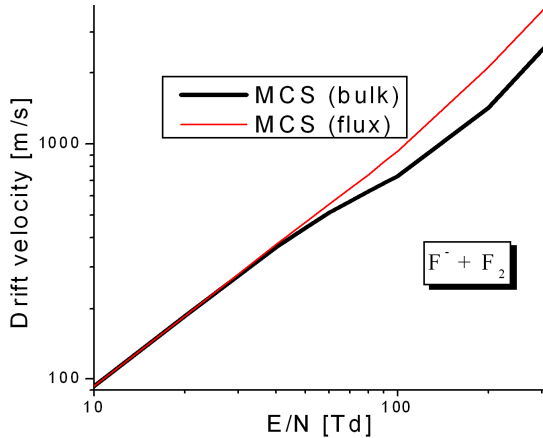
Fig. 2. Flux and bulk values of drift velocity for F^- ions in F_2 as a function of E/N.

Flux and bulk drift velocities [20, 18, 21] as a function of E/N are given in Fig. 2. The drift velocities obtained by MC simulation were calculated in real space (bulk) and in velocity space (flux) values which are obtained as $\langle v \rangle$ and dx/dt, respectively. In most plasma assisted applications exploiting low temperature conditions the drift velocities are not affected by the gas temperature and ion mobility is almost constant. Yet we observe effect of reac-

tive collisions affecting the splitting of flux and bulk drift velocity components above 40 Td (1 Td = 10^{-21} V m^2). Since accuracy of the ion implantation model is based on the precise determination of the flux and ion velocities at the surface of the electrode, then the difference between bulk and flux drift velocity represents the error in flux calculations. The first mention of non-conservative effects in ion transport was given in [12].

Longitudinal and transverse bulk diffusion coefficients for F^- ions in F_2 as a function E/N are shown in Fig. 3. They are necessary in modeling ionic diffusion losses in global models [3]. Let us note that difference between flux and bulk values of diffusion coefficients since having the same origin have the same initial value as drift velocities. There are no published experimental data for the longitudinal and transverse diffusion coefficients of F^- in F_2.
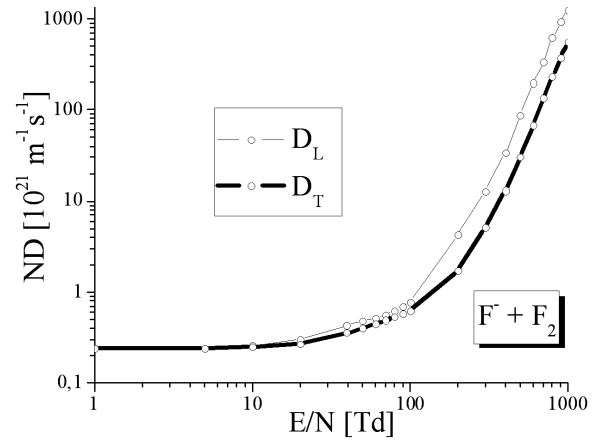
Fig. 3. The diffusion coefficients for F^- ions in F_2 obtained by MC simulation as a function of E/N at $T = 300$ K.

From the modeler's point of view, specifically for purpose of modeling a specific application, distinguishing between flux and bulk transport coefficients affects accuracy of numerical calculations [22].

4. Conclusion

The cross-sections for scattering of F^- ions on molecule are calculated by using Nanbu's theory [9] separating elastic from reactive collisions.

Monte Carlo technique was applied to carry out calculations of the drift velocity and diffusion coefficients as a function of reduced electric field in DC electric fields.

The cross-sections and transport data for technologically very important gas F_2 have been determined by using simple theory. While it is a good basis for modeling it would be much better to add a data base of measured transport coefficients and then to perform the analysis again.

Acknowledgments

References

[1] M.A. Lieberman, A.J. Lichtenberg, *Principles of Plasma Discharge and Materials Processing*, Wiley, Hoboken 2005.

[2] C. Lee, M.A. Lieberman, *J. Vac. Sci. Technol. A* **13**, 308 (1995).

[3] J.T. Gudmundsson, M.A. Lieberman, *Plasma Sources Sci. Technol.* **7**, 1 (1998).

[4] M. Takahashi, K. Maeda, T. Kitamura, M. Takasaki, S. Horiguchi, *Opt. Commun.* **116**, 269 (1995).

[5] P.X. Hien, B.-H. Jeon, Do A. Tuan, *J. Phys. Soc. Jpn.* **82**, 034301 (2013).

[6] J. Matsui, N. Nakano, Z.Lj. Petrović, T. Makabe, *Appl. Phys. Lett.* **78**, 883 (2001).

[7] H. Yamamoto, S. Matsumoto, K. Okada, J. Yu, K. Hirakuri, *Diamond Relat. Mater.* **15**, 1357 (2006).

[8] S. Radovanov, L. Godet, R. Dorai, Z. Fang, B.W. Koo, C. Carinaud, G. Cartry, D. Lenoble, A. Groullet, *J. Appl. Phys.* **98**, 113307 (2005).

[9] K. Denpoh, K. Nanbu, *J. Vac. Sci. Technol. A* **16**, 1201 (1998).

[10] Z.Lj. Petrović, Z.M. Raspopović, V.D. Stojanović, J.V. Jovanović, G. Malović, T. Makabe, J. De Urquijo, *Appl. Surf. Sci.* **253**, 6619 (2007).

[11] D. Spelsberg, W. Meyer, *J. Chem. Phys.* **101**, 1282 (1994).

[12] E.W. Mc Daniel, *Atomic Collisions-Electron and Photon Projectiles*, Wiley, New York 1989.

[13] J.A. Stockdale, D.R. Nelson, F.J. Davis, R.N. Compton, *J. Chem. Phys.* **56**, 3336 (1972).

[14] T. Simko, V. Martisovits, J. Bretagne, G. Gousset, *Phys. Rev. E* **56**, 5908 (1997); S. Longo, P. Diomede, *Europ. Phys. J. Appl. Phys.* **26**, 177 (2004).

[15] Z.Lj. Petrović, J.V. Jovanović, V. Stojanović, Z.M. Raspopović, Z. Ristivojević, *Eur. Phys. J. D* **48**, 87 (2008).

[16] R.E. Robson, R.D. White, Z.Lj. Petrović, *Rev. Mod. Phys.* **77**, 1303 (2005).

[17] Z.Lj. Petrović, V.D. Stojanović, *J. Vac. Sci. Technol. A* **16**, 329 (1998).

[18] Z. Raspopović, S. Sakadžić, Z.Lj. Petrović, T. Makabe, *J. Phys. D* **33**, 1298 (2000).

[19] W.A. Chupka, J. Berkowitz, D. Gutman, *J. Chem. Phys.* **55**, 2724 (1971).

[20] R.E. Robson, *Aust. J. Phys.* **44**, 685 (1991).

[21] Z.Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, V. Stojanović, M. Radmilović-Rađenović, *J. Phys. D, Appl. Phys.* **42**, 194002 (2009).

[22] V. Stojanović, Z. Raspopović, J. Jovanović, S. Radovanov, Ž. Nikitović, Z. Petrović, *Nucl. Instrum. Methods Phys. Res. B* **279**, 151 (2012).

Transport Parameters of F⁻ Ions in BF₃

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In this work we presented the new results for energy dependent cross-sections and transport coefficients as a function of E/N for F⁻ ions in BF₃ gas. Results were obtained by using the Monte Carlo technique for cross-section set determined on the basis of the Nanbu theory. Monte Carlo method is applied to obtain swarm parameters at temperature of $T = 300$ K.

1. Introduction

F⁻ ions are abundant in plasmas relevant for a wide range of applications. Knowledge of the plasma chemistry and behavior of the negative ions in the plasmas is thus a key to control plasma processing devices. Additionally, the recent progress of discharge modeling and simulation have made contributions to a deeper understanding of the discharge phenomena and to the optimization of reactor design or operating conditions. Boron dopant penetration in silicon is technologically achieved by DC pulsed plasma system (PLAD) most widely applying BF₃ gas [1, 2]. Uniform plasma and implantation with normal ion incidence are the main goals in this technological process. Control over the number density of negative ions, in such a case being F⁻ and BF₄⁻, increase efficiency of implantation. Modeling of such plasmas requires knowledge of transport parameters of all abundant particles [3].

In this work, we employ the Nanbu theory [4] to calculate transport cross-section set for F⁻ ions scattering on BF₃ molecule appropriate for low energies of F⁻ ions. By using Monte Carlo technique of Ristivojević and Petrović [5] we calculated transport parameters as a function of E/N (E — electric field, N — gas density).

2. Calculation of the cross-section set

According to the Nanbu theory elastic and reactive endothermic collisions are separated and treated by accounting for the thermodynamic threshold energy and branching ratio according to the Rice–Rampsperger–Kassel (RRK) theory [4]. Within the RRK theory an excited molecular complex is treated as excited activated complex where the internal energy is distributed among s equivalent vibrational modes of the complex.

Accounting for long range polarisation forces we exploited polarizability of 3.31×10^{30} m³ for BF₃ [6]. For

F⁻ + BF₃ system characteristic low energy reactive channels are shown in Table.

The cross-section for exothermic reaction (EXO) forming a super halogen molecular ion BF₄⁻ is commonly represented by ion capture cross-section:

$$\sigma_{\mathrm{exo}} = \beta \sigma_L, \tag{1}$$

where σ_L is the orbiting cross-section [7] and β is the probability of a specific exothermic reaction. It is also known that stabilization of the excited activated complex proceeds either radiatively or collisionally [8] for reaction EXO in Table. at room temperatures and pressures of about 0.5 Torr (67 Pa). Similar situation appears in the case where BF₄⁻ energies from the surface sputtering of cluster BF₃ ions [9]. In Ref. [8] Herd and Babcock concluded that magnitudes of collisional stabilization, radiative stabilization, and unimolecular decomposition back to initial reactants are comparable in these conditions. Since non-associative reactions share the same collisional complex the total probability of all selected reactions equals 1, so one can account cross-section for exothermic reaction as $\sigma_{\mathrm{exo}} = \beta \sigma_{e0}$, where β is selected to define elastic cross-section contribution as $\sigma_e = (1 - \beta)\sigma_{e0}$. σ_{e0} is the elastic cross-section (EL) obtained by Nanbu theory for endothermic reactions. Now one can determine β by calculating rate coefficient for association reaction and comparing with experimental data.

TABLE

F⁻–BF₃ reaction paths considered in the model and the corresponding thermodynamic threshold energies Δ.

No	Reaction path	Δ [eV]
1	F₂⁻+BF₂ (CT)	–5.6 [13]
2	F⁻+BF₃ + e⁻ (DET)	–3.4012 [14]
3	BF₄⁻ EXO)	+3.58 [12]

Thermal rate coefficient for association reaction 3 (Table) is determined experimentally by Babcock and Streit [10] by flowing afterglow technique and has a value 9.4×10^{-11} cm³/molecule/s for $T = 300$ K. By combining the relation (1) and thermal rate coefficient we determined the probability of exothermic reaction and

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thus contributions of association cross-section (EXO) and elastic cross-section (EL) (Fig. 1). In the low energy limit the cross-sections are similar due to dominant polarization of the target. At higher energies reactive collisions including the nonconservative collisions become efficient for different possible processes.
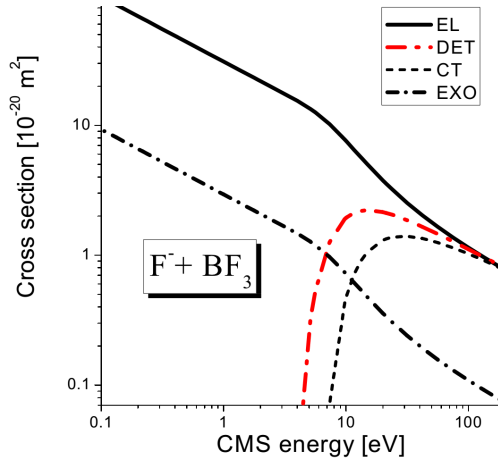

Fig. 1. Cross section set for F^- ions in BF_3.

3. Transport parameters

The transport coefficients include the drift velocity, diffusion coefficients, ionization and attachment coefficients and chemical reaction coefficients for ions [3]. Excitation coefficients are also measured but seldom used in modeling.

Swarm parameters are generally applied to plasma modeling and simulations. At the same time, the non-equilibrium regime in discharges is well represented under a broad range of conditions by using the Boltzmann equation with collisional operator representing only binary collisions.

In this work a Monte Carlo simulation technique for ion transport that accounts for finite gas temperature of the background gas particles [5] is used to calculate swarm parameters of F^- ions in gas for temperature $T = 300$ K.

The critical review of experimentally obtained transport properties of gaseous halogen ions is presented in [11].

In Fig. 2 we show characteristic energies (diffusion coefficient normalized by mobility D/K in units eV) longitudinal (L) and transverse (T) to the direction of electric field. We also show the mean energy, which cannot be directly measured in experiments but a map of mean energy versus E/N may be used directly to provide the data in fluid models especially when local field approximation fails. As visible in the figure the energy increases from 10 Td.

The mobility K of an ion is the quantity defined as the velocity attained by an ion moving through a gas under unit electric field. One often exploits the reduced
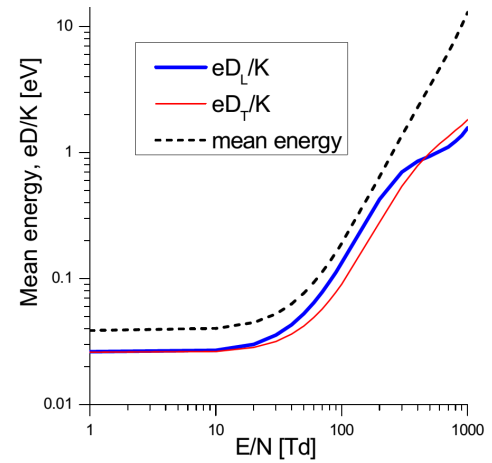
Fig. 2. Mean and characteristic energy of F^- ions in BF_3 as a function of E/N.
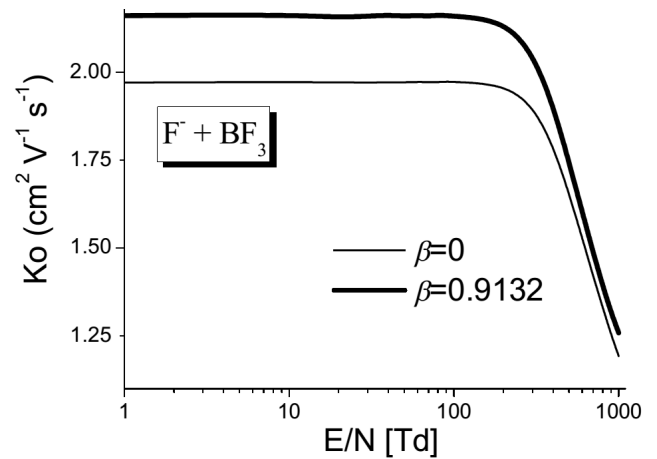
Fig. 3. Reduced mobility of F^- ions in BF_3 as a function of E/N.
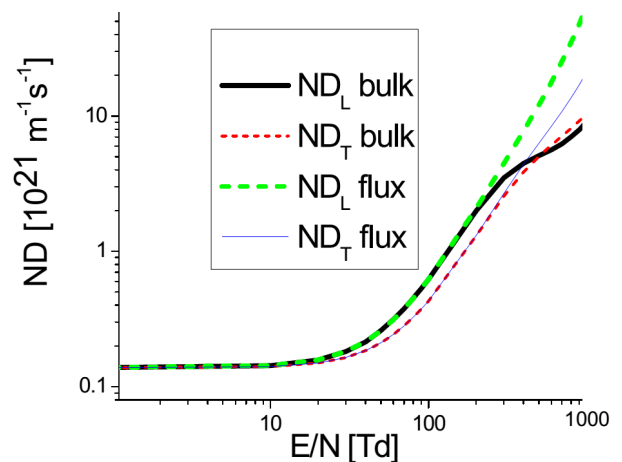
Fig. 4. The diffusion coefficients for F^- ions in BF_3 gas as a function of E/N at $T = 300$ K.

or standard mobility defined as:

$$K_0 = \frac{v_d}{N_0} NE, \qquad (2)$$

where v_d is the drift velocity of the ion, N is the gas density at elevated temperature T, E is the electric field.

In Fig. 3 we show the results of Monte Carlo simulation for reduced mobility as a function of E/N. Nonconservative collisions of F^- ions producing BF_4^- ions are only slightly modifying mobility curve obtained for two values of parameter β.

Longitudinal and transverse bulk and flux diffusion coefficients for F^- ions in BF_3 as a function of E/N are shown in Fig. 4. Note that the difference between flux and bulk values of diffusion coefficients which have the same origin have the same initial value as drift velocities. There are no published experimental data for the longitudinal and transverse diffusion coefficients of F^- in BF_3.

4. Conclusion

In this paper we show predictions for the low energy cross-sections and transport coefficients of negative F^- ions in BF_3 which did not exist in literature.

Monte Carlo technique was applied to carry out calculations of the mean energy, drift velocity and diffusion coefficients as a function of reduced electric field in DC electric fields.

In Monte Carlo technique used in presented study collision frequency in case of thermal collisions of a test ion particle is not calculated by Monte Carlo integration technique [15] but by using piecewise calculation [16]. The piecewise calculation is based on assumption that most cross-sections are defined numerically at limited number of points with linear interpolation for mid points.

The cross-section set have been determined by using a simple theory and transport data for gas BF_3, which is technologically very important. There results are a good base for modeling, but it could be further improved by adding a data base of the measured values of transport coefficients and then perform the analysis again.

Acknowledgments

References

[1] B.-W. Koo, Z. Fang, L. Godet, S.B. Radovanov, C. Cardinaud, G. Cartry, A. Grouillet, D. Lenoble, *IEEE Trans. Plasma Sci.* **32**, 456 (2004).

[2] Ž. Nikitović, S. Radovanov, L. Godet, Z. Raspopović, O. Šašić, V. Stojanović, Z. Lj. Petrović, *EPL* **95**, 45003 (2011).

[3] Z.Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, V. Stojanović, M. Radmilović-Rađenović, *J. Phys. D: Appl. Phys.* **42**, 194002 (2009).

[4] K. Denpoh, K. Nanbu, *J. Vac. Sci. Technol. A* **16**, 1201 (1998).

[5] Z. Ristivojević, Z. Petrović, *Plasma Sources Sci. Technol.* **21**, 035001 (2012).

[6] C. Szmytkowski, M. Piotrowicz, A. Domaracka, L. Klosowski, E. Ptasinska-Denga, G. Kasperski, *J. Chem. Phys.* **121**, 1790 (2004).

[7] E.W. McDaniel, V. Čermak, A. Dalgarno, E.E. Ferguson, L. Friedman, *Ion–Molecule reactions*, Wiley-Interscience, New York 1970.

[8] C.R. Herd, L.M. Babcock, *J. Phys. Chem.* **91**, 2372 (1987).

[9] X.L. Zhao, A.E. Litherland, *Nucl. Instrum. Methods Phys. Res. B* **259**, 223 (2007).

[10] L.M. Babcock, G.E. Streit, *J. Phys. Chem.* **88**, 5025 (1984).

[11] L.A. Viehland, E.A. Mason, *At. Data. Nucl. Data Tables* **60**, 37 (1995).

[12] G.L. Gutsev, P. Jena, R.J. Bartlett, *Chem. Phys. Lett.* **292**, 289 (1998).

[13] K.A.G. MacNeil, J.C.J. Thynne, *J. Phys. Chem.* **74**, 2257 (1970).

[14] E.W. Mc Daniel, *Atomic Collisions-Electron, Photon Projectiles*, Willey & Sons, New York 1989.

[15] T. Simko, V. Martisovits, J. Bretagne, G. Gousset, *Phys. Rev. E* **56**, 5908 (1997); S. Longo, P. Diomede, *European Phys. J. Applied Physics* **26**, 177 (2004).

[16] Z.Lj. Petrović, J.V. Jovanović, V. Stojanović, Z.M. Raspopović, Z. Ristivojević, *Eur. Phys. J. D* **48**, 87 (2008).

Rate Coefficients of F⁻ Ions in Ar/BF₃ Mixtures

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Transport parameters of F⁻ ions in mixtures Ar/BF₃ in DC fields were calculated using Monte Carlo simulation technique assuming the scattering cross-section set assembled on the basis of Nanbu's technique separating elastic from reactive collisions. In this work we present characteristic energy and rate coefficients for low and moderate reduced electric fields E/N (N — gas density) and account for the non-conservative collisions.

1. Introduction

Negative ions are abundant in plasmas containing fluorine molecules and which are also relevant for a wide range of applications. One should bear in mind that electron affinity of F atom is the largest of all atoms and also that electronegative plasmas containing F⁻ ions are highly reactive. Knowledge of the plasma chemistry and behavior of negative ions in plasmas is thus necessary in order to model plasma processing devices. Additionally, recent progress of discharge modeling and simulation has made contributions to a deeper understanding of the discharge phenomena and to the optimization of reactor design or finding operating conditions.

Plasma enhanced chemical vapour deposition (PECVD) using BF₃ gas is successfully used for the synthesis of cubic boron nitride (cBN) films with extreme properties similar to diamond. In a dominant fluorine environment low pressure PECVD [1, 2] produces the low energy negative ions [3] that affect the chemistry near the surface. The large gaps in understanding of chemical kinetics relevant to the ion–BF₃ collisions make the progress in the synthesis of cBN films almost empirical. BF₃ gas is also a working medium in neutron detectors [4] where electron–ion pairs are produced in neutron encounters. The signal detected due to ion transport produces false counts that should be avoided. In order to trace such signals, cross-sections and rate coefficients are needed for ion transport.

2. Monte Carlo technique

The cross-sections for scattering of BF₄⁻ ions on Ar and BF₃, and for F⁻ ions on BF₃ are calculated by using Nanbu's theory [5, 6] separating elastic from detachment collisions. The cross-sections for F⁻ on Ar [7] are used to calculate rate coefficients for detachment. The dipole polarizability of 3.31×10^{-30} m³ [8] and 1.64×10^{-30} m³ [9] is used for BF₃ and Ar target, respectively.

Similar to our recent papers [10, 11] Nanbu's theory is used to separate elastic from reactive endothermic

collisions by accounting for the thermodynamic threshold energy and branching ratio according to the Rice–Rampsperger–Kassel (RRK) theory [5]. Within the RRK theory internal energy is being distributed among empirical number of s equivalent effective modes of the complex selected from the total number of atoms involved in the complex.

The cross-section for exothermic reaction (EXO) forming a super halogen molecular ion BF₄⁻ is commonly represented by ion capture cross-section

$$\sigma_{\text{exo}} = \beta \sigma_{\text{L}}, \qquad (1)$$

where σ_{L} is the orbiting cross-section [12] and β is the probability of a specific exothermic reaction. When reactive processes come into play, according to Nanbu's theory elastic collisions are competing with reactive collisions and as a consequence none of cross-sections is following Langevin's cross-section energy dependence. Monte Carlo technique of Ristivojević and Petrović [13] is used to calculate the transport parameters as a function of E/N.

3. Transport coefficients

A correct approach to obtain transport parameters of higher accuracy would be to follow the solutions of quantum mechanical generalization of the Boltzmann equation than to include the effects of inelastic collisions and internal energy states [14, 15]. The Monte Carlo simulation methods are generally built around the same initial principles as the related kinetic equations. In this work we apply the Monte Carlo simulation designed for swarm particles [16].

The calculated transport coefficients are the drift velocity, diffusion coefficients, ionization and attachment coefficients, and chemical reaction coefficients for ions [17]. Excitation coefficients are also measured but seldom used in modeling.

Swarm parameters are generally applied to plasma modeling and simulations. At the same time, the non-equilibrium regime in discharges is well represented under a broad range of conditions by using the Boltzmann equation with the collision operator representing only binary collisions.

In this work a Monte Carlo simulation technique for ion transport that accounts for finite gas temperature of the

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background gas particles [13] is used to calculate swarm parameters of F^- ions in gas for temperature $T = 300$ K.

Apart from mobility data for F^- in Ar [18], other transport parameters for F^- were measured neither for Ar nor for BF$_3$.
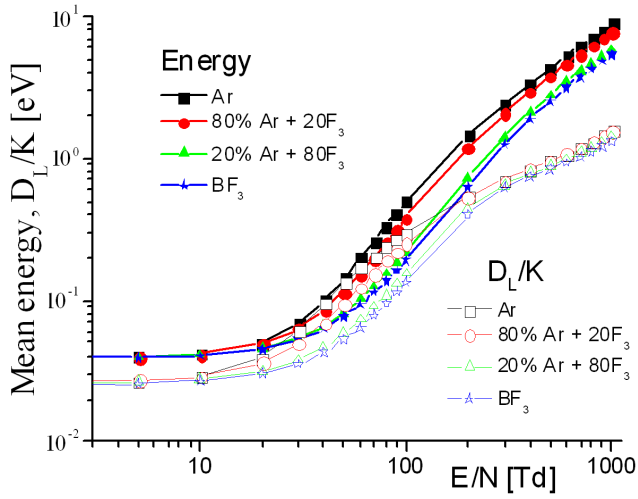

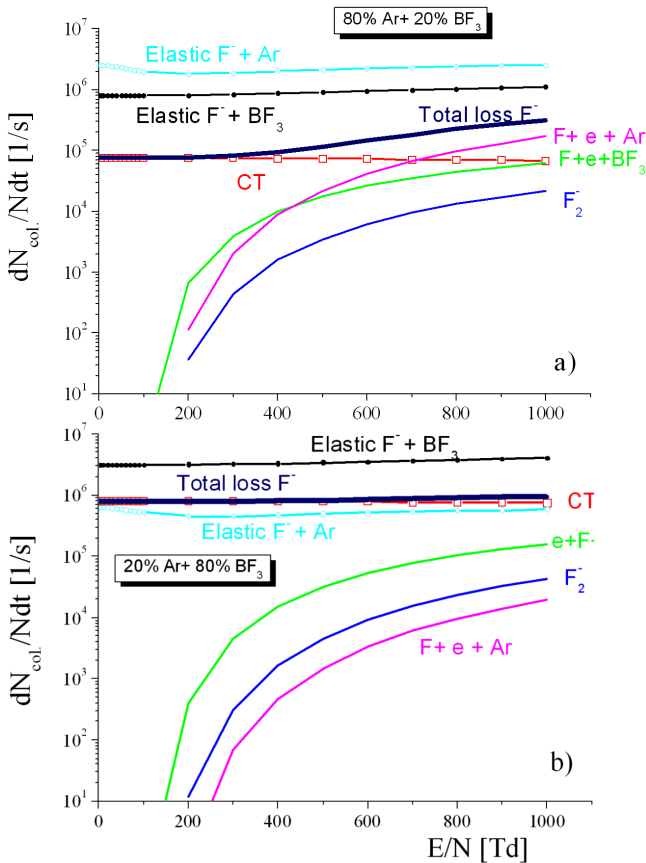Fig. 1.   Mean and characteristic energies of F^- ions in Ar/BF$_3$ mixtures as a function of E/N.

Fig. 2.   Rate coefficients for F^- ions in Ar/BF$_3$ mixtures as a function of E/N.

In Fig. 1 we show the characteristic energies (diffusion coefficient normalized by mobility D/K in units of eV) longitudinal (L) and transverse (T) to the direction of electric field. We also show the mean energy, which cannot be directly measured in experiments but a map of the mean energy versus E/N may be used directly to provide the data in fluid models especially when local field approximation fails. As visible in Fig. 1 the mean energy and the characteristic energies increase from about 20 Td.

In order to test the Monte Carlo code [13] for the case of mixtures we calculated mean energy and characteristic energy at lowest E/N. Obtained values for all mixtures converged exactly to the thermal mean energy $(3/2)kT = 0.038778$ eV and the thermal $eD/K = kT$ i.e. to 0.025852 eV (longitudinal $(D = D_{\mathrm{L}})$ and transverse $(D = D_{\mathrm{T}})$ diffusion coefficients) as expected.

Calculated rate coefficients for processes are presented in Fig. 2. Rate coefficients are important for applications of the global model to Ar/BF$_3$ mixtures. We are presenting rate coefficients for charge transfer (CT), elastic scattering of F^- in Ar, elastic scattering of F^- in BF$_3$, and total loss of F^- for (a) 80% Ar + 20%BF$_3$ and (b) 20% Ar + 80%BF$_3$.

Transversal diffusion coefficients for F^- ions in Ar/BF$_3$ mixtures as a function of E/N are shown in Fig. 3. Note that the difference between the flux and bulk values of diffusion coefficients, which have the same origin, have the same initial value as drift velocities. There are no published experimental data for the longitudinal and transverse diffusion coefficients of F^- in Ar/BF$_3$.
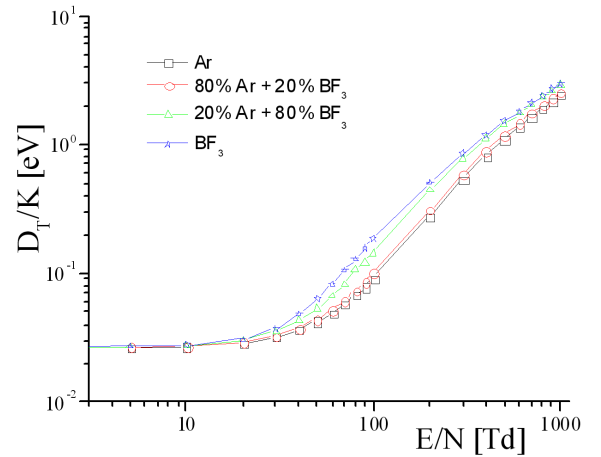
Fig. 3.   The transversal diffusion coefficients for F^- ions in Ar/BF$_3$ mixtures as a function of E/N.

4. Conclusion

In this paper we show transport properties for the F^- in mixtures Ar/BF$_3$ which do not exist in the literature. The complete cross-section set has been determined by extending Nanbu's theory.

The results are believed to be a good base for modeling, which could be further improved when measured values of transport coefficients become available and then perform the analysis again.

References

[1] H. Yamamoto, S. Matsumoto, K. Okada, J. Yu, K. Hirakuri, *Diam. Relat. Mater.* **15**, 1357 (2006).

[2] W. Zhang, I. Bello, Y. Lifshitz, K. Chan, X. Meng, Y. Wu, C. Chan, S-T. Lee, *Adv. Mater.* **16**, 1405 (2004).

[3] S.J. Choi, M. Kushner, *J. Appl. Phys.* **74**, 853 (1993).

[4] M. Padalakshmi, A.M. Shaikh, *J. Pramana Phys.* **71**, 1177 (2008).

[5] K. Denpoh, K. Nanbu, *J. Vac. Sci. Technol. A* **16**, 1201 (1998).

[6] Z.Lj. Petrović, Z.M. Raspopović, V.D. Stojanović, J.V. Jovanović, G. Malović, T. Makabe, J. De Urquijo, *Appl. Surf. Sci.* **253**, 6619 (2007).

[7] J. Jovanović, Z.Lj. Petrović, *J. Phys. Conf. Ser.* **162**, 012004 (2009).

[8] C. Szmytkowski, M. Piotrowicz, A. Domaracka, L. Klosowski, E. Ptasinska-Denga, G. Kasperski, *J. Chem. Phys.* **121**, 1790 (2004).

[9] E.W. Mc Daniel, *Atomic Collisions-Electron and Photon Projectiles*, Wiley, New York 1989.

[10] V.D. Stojanović, Z.M. Raspopović, J.V. Jovanović, S.B. Radovanov, Ž.D. Nikitović, Z.Lj. Petrović, *Nucl. Instrum. Methods Phys. Res. B* **279**, 151 (2012).

[11] V. Stojanović, Ž. Nikitović, Z. Raspopović, J. Jovanović, *Acta Phys. Pol. A* **125**, 46 (2014).

[12] E.W. McDaniel, V. Čermak, A. Dalgarno, E.E. Ferguson, L. Friedman, *Ion–Molecule Reactions*, Wiley-Interscience, New York 1970.

[13] Z. Ristivojević, Z. Petrović, *Plasma Sources Sci. Technol.* **21**, 035001 (2012).

[14] K. Kumar, *Aust. J. Phys.* **33**, 449 (1980).

[15] L.A. Viehland, Y. Chang, *Mol. Phys.* **110**, 259 (2012).

[16] K. Kumar, H.R. Skullerud, R.E. Robson, *Aust. J. Phys.* **33**, 343 (1980).

[17] Z.Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, V. Stojanović, M. Radmilović-Radjenović, *J. Phys. D Appl. Phys.* **42**, 194002 (2009).

[18] L.A. Viehland, E.A. Mason, *At. Data Nucl. Data Tables* **60**, 37 (1995).

Cross-Section and Transport Parameters of Ne⁺ in CF₄

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A cross-section set for scattering Ne⁺ ions in CF₄ is assessed by using available experimental data for charge transfer cross-sections. In this paper we present new results for the mean energy, reduced mobility and diffusion coefficients for low and moderate reduced electric fields E/N (N — gas density) and account for the non-conservative collisions. The Monte Carlo method is used to calculate transport properties of Ne⁺ ions in CF₄ at temperature of $T = 300$ K.

1. Introduction

Charge transfer reactions of ions with molecules are unavoidable elementary processes in modeling kinetics in terrestrial, industrial, and astrophysical plasmas in dark matter detection [1]. Motivational factors for this study are identified and this paper reports on a topic important both for fundamental studies and for applications.

Tetrafluoromethane or CF₄ molecule which has widely been used in aluminium manufacturing and semiconductor industries has an extremely long life time (≈ 50000 years) and the highest atmospheric abundance of all perfluorocarbons [2]. It is, therefore, very important to develop replacing materials or methods to decompose efficiently CF₄ molecules in order to reduce man-made greenhouse gases.

Line spectra of excited atoms obtained in spectrometric measurements in CF₄ indicate that the charge transfer reaction is dominant process in collisions with inert gas ions. In selected cases charge transfer cross-sections is representing the most significant part of a cross-section set.

The cross-section data for dissociative excitation of CF₄ [3] are essential in estimating the degree of importance of many related processes. In this work we assessed cross-section set for Ne⁺ in CF₄ by using existing experimental data [4] for charge transfer collisions producing radical ions of CF₄.

Since no direct information is found in the literature how mobility of high recombination energy ions such as Ne⁺ ions behaves in CF₄ we also calculated transport parameters by using the Monte Carlo simulation technique [5].

2. Cross-section set

The experimentally measured reaction cross-sections presented by Fisher et al. [4] were extrapolated toward lowest energies according to Langevin's cross-section trend (curves with labels CF⁺, CF₂⁺, CF₃⁺) and shown

in Fig. 1. These curves were used to determine the elastic momentum transfer cross-section ("EL" in Fig. 1) assuming the total momentum transfer cross-section σ_{mt} is known. At low energies less than 1 eV we assumed that σ_{mt} is Langevin's cross-section and elastic momentum transfer cross-section is determined by deducing all reactive cross-sections.
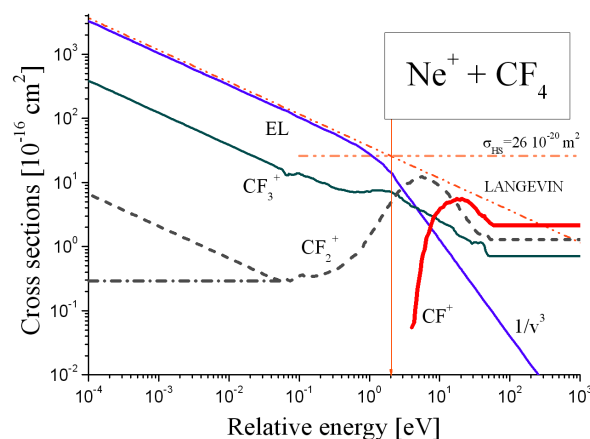

Fig. 1. Cross-section set for Ne⁺ + CF₄.

The Langevin cross-section was determined by using the polarizability of the gas. The average polarizability of CF₄ is not well established [4] and may produce discrepancy for calculated mobility of ions in CF₄ [6, 7] and thus affect plasma parameters prediction in modeling. We adopted value of 3.86×10^{-30} m³ used by Stojanović et al. [6] who found excellent agreement between experimental and calculated mobility of CF₃⁺ ions drifting in CF₄ gas. Extrapolation of the elastic momentum transfer cross-section trend beyond crossing point (see vertical arrow in Fig. 1) of the Langevin and hard sphere (σ_{HS}, see dash-dot-dot line in Fig. 1) cross-section [1] is done by smoothly connecting to $1/v^3$ trend [8] where v is the center-of-mass velocity (see Fig. 1).

At all ion kinetic energies above 50 eV reactive cross-sections are extrapolated by constant values taking into account measured ratio of reactive cross-sections at high energies [9].

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The effects of various extrapolations (short dot-dashed and dashed line in Fig. 1) of unusual behavior at low energy, observed for measurements of the cross-section leading to formation of CF_2^+ (where irrespective of the Ne^+ spin state exothermic behavior of reaction is expected) is found negligible on mobility.

3. Transport parameters

The Monte Carlo technique was applied to perform calculations of transport parameters. Information about the cross-sections is used during the integration of the collision frequency to get kinematics after the collisions. By using the statistical methods transport parameters (mean energy, drift velocity and diffusion coefficients) were determined after their temporal relaxation.

We have used a Monte Carlo code that properly takes into account thermal collisions [10]. The code has passed all the relevant benchmarks [11] and has been tested in our work on several types of charged particles [11, 12].

Results of Monte Carlo simulations are shown in Figs. 2–4. Note that these transport parameters are the only information present in the literature up to now, there are no published experimental data for the transport coefficients of Ne^+ in CF_4.

In Fig. 2 we show the mean energy, which cannot be directly measured in experiments but a map of mean energy versus E/N may be used directly to provide the data in fluid models especially when local field approximation fails. The mean energy having thermal value of 0.039 eV increases above 10 Td.
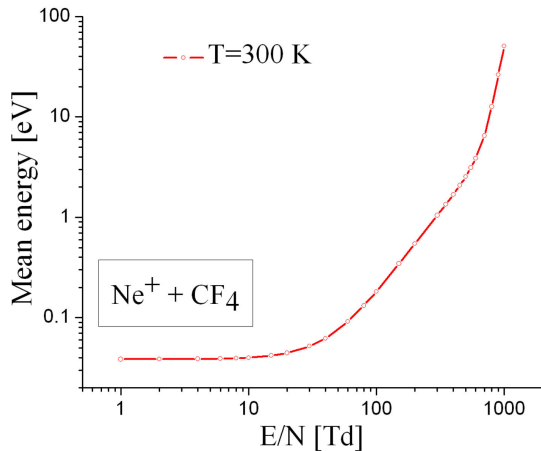
Fig. 2. The mean energy for Ne^+ in CF_4 as a function of E/N.

Generally, the presence of non-conservative collisions causes the drift velocity to be more complex i.e. one may define bulk drift velocity as a measure of center of mass displacement in time ($W = d\langle x \rangle / dt$) [13] and flux drift velocity $w = \langle v \rangle$ that describes ion flux. Bulk drift velocity is reaction corrected flux drift velocity: $w = W + S$, where S is the term representing a measure of the effect of reactions on the drift velocity.

Reduced mobility for Ne^+ ions as a function of E/N (E — electric field, N — gas density) compared with Langevin's value is shown in Fig. 3.
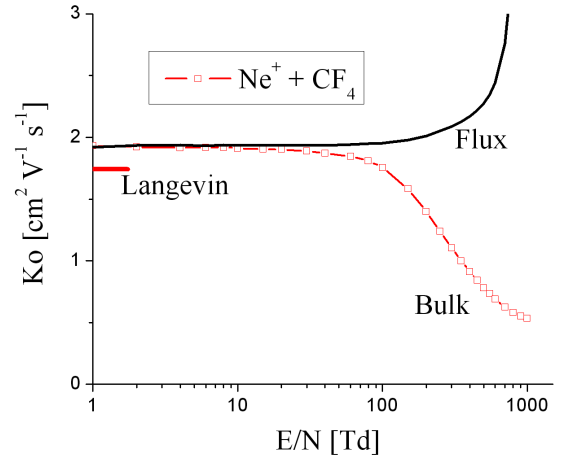
Fig. 3. The bulk and flux reduced mobility for Ne^+ in CF_4 as a function of E/N.

For $E/N < 50$ Td, exothermic collision frequency is approximately corresponding to the energies below 0.1 eV. This causes the equality of the bulk and flux reduced mobilities [14, 15] since the ions from the front and the tail are removed with equal rate [16].

For higher E/N the bulk reduced mobility is decreasing with E/N because of an increasing number of ions removed from the regions of higher energy (from swarm front). That results in a shift in the centre-of-mass position. At the same time, flux reduced mobilities increase with E/N since number of elastic collisions decrease.

Due to exothermal collisions mobility is 10% higher than the polarisation limit ($E \rightarrow 0$ and $T \rightarrow 0$) value (see the mark "Langevin" in Fig. 3) predicted by the Langevin theory. The mobility which is shown is the same at smaller temperatures because of the constant collision frequency on small energies.

Bulk and flux longitudinal diffusion coefficients [13] were calculated by time averaging the position (x) and velocity (v_x) (direction of the electric field) of each swarm particle

$$D_L(\text{bulk}) = 0.5 \frac{d}{dt} \left(\langle x^2 \rangle - \langle x \rangle^2 \right),$$

$$D_L(\text{flux}) = \langle x v_x \rangle - \langle x \rangle \langle v_x \rangle,$$

respectively. The same procedure is used for transversal diffusion coefficients ($\langle y \rangle = \langle z \rangle = 0$, $\langle v_y \rangle = \langle v_z \rangle = 0$). All calculated diffusion coefficients are shown in Fig. 4.

One should notice the very large non-conservative effects, almost a reminder of the positron transport [17]. Similarly to the results for drift velocity flux diffusion coefficients are significantly larger than bulk values. The decrease of the bulk longitudinal diffusion from 200 Td to 600 Td is especially interesting due to a significant increase of the collision frequency for reactive collisions.
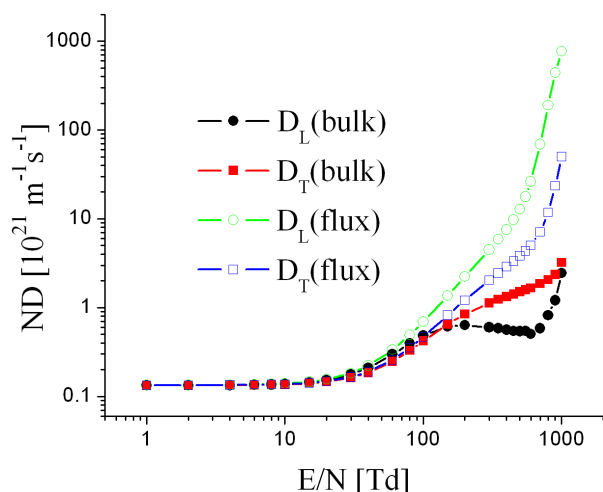
Fig. 4. The transversal and longitudinal diffusion coefficients for Ne$^+$ in CF$_4$ as a function of E/N.

4. Conclusion

By using measured charge transfer cross-sections we assessed the complete cross-section set for Ne$^+$ions in CF$_4$ that is used as an input in Monte Carlo simulations in order to calculate transport parameters.

Focusing on calculated reduced mobility data as a function of E/N, in this paper we found that is necessary to discuss both flux and bulk reduced mobility data.

Data for swarm parameters for ions are needed for hybrid and fluid codes and the current focus on liquids or liquids in the mixtures with rare gases dictates the need to produce data compatible with those models.

Acknowledgments

References

[1] A. Kaboth, J. Monroe, S. Ahlen, D. Dujmi, S. Henderson, G. Kohse, R. Lanza, M. Lewandowska, A. Roccaro, G. Sciolla, N. Skvorodnev, H. Tomita, R. Vanderspek, H. Wellenstein, R. Yamamoto, P. Fisher, *Nucl. Instrum. Methods Phys. Res. A* **592**, 63 (2008).

[2] M. Aslam, K. Khalil, R.A. Rasmussen, J.A. Culbertson, J.M. Prins, E.P. Grimsrud, M.J. Shearer, *Environ. Sci. Technol.* **37**, 4358 (2003).

[3] K. Motohashi, T. Takahashi, N. Takahashi, S. Tsurubuchi, *J. Phys. B At. Mol. Opt. Phys.* **38**, 3339 (2005).

[4] E.R. Fisher, M.E. Weber, P.B. Armentrout, *J. Chem. Phys.* **92**, 2296 (1990).

[5] Z.Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, V. Stojanović, M. Radmilović-Radjenović, *J. Phys. D Appl. Phys.* **42**, 194002 (2009).

[6] V. Stojanović, Z. Raspopović, J.V. Jovanović, J. de Urquijo, Z.Lj. Petrović, *J. Phys. Conf. Series* **514**, 012059 (2014).

[7] V. Georgieva, A. Bogaerts, R. Gijbels, *J. Appl. Phys.* **93**, 2369 (2003).

[8] P.S. Krstić, D.R. Schultz, *J. Phys. B At. Mol. Opt. Phys.* **42**, 065207 (2009).

[9] E. Parker, F.S.M. El-Ashhab, *Int. J. Mass Spectrom. Ion. Phys.* **47**, 159 (1983).

[10] Z. Ristivojević, Z.Lj. Petrović, *Plasma Sources Sci. Technol.* **21**, 035001 (2012).

[11] Z.Lj. Petrović, Z.M. Raspopović, V.D. Stojanović, J.V. Jovanović, G. Malović, T. Makabe, J. de Urquijo, *Appl. Surf. Sci.* **253**, 6619 (2007).

[12] J. de Urquijo, J.V. Jovanović, A. Bekstein, V. Stojanović, Z.Lj. Petrović, *Plasma Sources Sci. Technol.* **22**, 025004 (2013).

[13] K.F. Ness, R.E. Robson, *Phys. Rev. A* **34**, 2185 (1986).

[14] Ž. Nikitović, Z. Raspopović, V. Stojanović, J. Jovanović, *Europhys. Lett.* **108**, 35004 (2014).

[15] Ž. Nikitović, V. Stojanović, Z. Raspopović, J. Jovanović, 10.12693/APhysPolA.126.724*Acta Phys. Pol. A* **126**, 724 (2014).

[16] R.E. Robson, *Aust. J. Phys.* **44**, 685 (1991).

[17] R.D. White, W. Tattersall, G. Boyle, R.E. Robson, S. Dujko, Z.Lj. Petrović, A. Banković, M.J. Brunger, J.P. Sullivan, S.J. Buckman, G. Garcia, *Appl. Radiat. Isot.* **83**, 77 (2014).

H$^+$ Scattering in *n*-Butanol

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In this paper we show predictions for the low energy cross-sections and transport properties for the H$^+$ in *n*-butanol gas. These data are needed for modelling in numerous technologically important applications. Appropriate gas phase enthalpies of formation for the products were used to calculate scattering cross-section as a function of kinetic energy. Calculated cross-sections can be used to obtain transport parameters as a function of E/N (E — electric field, N — gas density) for H$^+$ in *n*-butanol gas.

1. Introduction

n-Butanol (C$_4$H$_9$OH) also known as 1-butanol or bio-butanol has a 4 carbon straight-chain structure, with the –OH at the terminal carbon. It is an important chemical feedstock used to produce solvents (butyl acetate, butyl glycol ethers) [1, 2], polymers (butyl acrylate, butyl methacrylate) [3] and plastics. But the recent interest in *n*-butanol is mostly due to its application as a biofuel for use in engines, as an alternative to conventional gasoline and diesel fuels [4–7]. Biofuels are attracting great interest as transportation fuels because they are renewable, can be locally produced, less polluting, more biodegradable, and reduce net greenhouse gas emissions [8]. *n*-Butanol, like ethanol, can blend with gasoline very well and could be a future option for blending with diesel. Butanol consists more oxygen content compared with biodiesel, leading to further reduction of the soot. *n*-Butanol occurs naturally as a minor product of the fermentation of sugars and other carbohydrates and is present in many foods and beverages as well as in a wide range of consumer products. Although most volatile organic compounds can be detected by fast methods such as ion mobility spectroscopy, precise determination is possible only if reaction of specific ions with targeted compound is well known.

n-Butanol is produced by alcoholic fermentation of the biomass feedstock [9–12] which include sugar beet, sugar cane, corn, wheat, and other various plant crops containing cellulose that could not be used for food and would otherwise go waste. Recently, the use of generically enhanced bacteria has also increased the fermentation process productivity.

The goal of this work is to calculate transport parameters of fragment ions of *n*-butanol. We employ Denpoh–Nanbu's theory (DNT) [13] to calculate transport cross-section sets for H$^+$ ions scattering on *n*-butanol appropriate for low energies of H$^+$ ions. By using Monte Carlo

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technique of Ristivojević and Petrović [14] we calculated transport parameters as a function of E/N.

2. Cross-section sets

A calculation of the cross-sections would include the determination of the ion-neutral interaction potential energy surface, followed by quantum-mechanical calculations of the ion-neutral scattering processes [15]. All these tasks are tractable only if a certain level of approximation is introduced. There is another approach where it is possible to exploit some statistical theory [16] where the specific reaction rate for a unimolecular reaction may be used to obtain cross-section for each particular process [13, 17].

The scattering cross-sections of H$^+$ on *n*-butanol are calculated by using the DNT [13] separating elastic from reactive collisions. The induced dipole polarizability of 8.9×10^{-24} cm^3 [18] is used for the *n*-butanol target. In resemblance with our recent work [19] DNT has been used for separation of elastic from reactive endothermic collisions by accounting for the thermodynamical treshold energy and branching ratio according to the Rice–Rampsperger–Kassel (RRK) theory [20]. In the context of the RRK theory the internal energy is distributed among an empirical number of equivalent effective modes of the complex selected from the total number of atoms in the complex. Appropriate gas phase enthalpies of formation for the products [21] (Table I) were used to calculate thermodynamic thresholds. The cross-section for the exothermic reaction (EXO) forming a molecular ion H$^+$ in *n*-butanol is commonly represented by ion capture cross-section

$$\sigma_{exo} = \beta\sigma_L, \qquad (1)$$

where σ_L is the orbiting cross-section [15] and β is the probability of a specific exothermic reaction.

In this calculation in the absence of resonant exothermic reactions we assumed that the probability of exothermic reactions is zero ($\beta = 0$). In the low energy limit the cross-sections are similar due to dominant polarization of the target. At higher energies reactive collisions including the non-conservative collisions become efficient for various possible processes.

It is well known that swarm method [22, 23] can be used to modify the cross-section for elastic momentum transfer if transport parameters are known. Thus elastic momentum transfer cross-section can be obtained if some initial, approximate, cross-section is available. For n-butanol transport parameters are not available [17]. We have separated the endothermic and exothermic processes by using the enthalpies from Ref. [21].

In this paper there are 20 exothermic processes. Exothermic process with lowest excess energy ($H^+ + n-$butanol $\rightarrow C_3H_3OH^+ + C_3H_4 + H$) has 0.118 eV excess energy while lowest endothermic threshold ($H^+ + n-$butanol $\rightarrow C_2H_4O^+ + C_2H_2 + 2H_2 + H$) is 0.061 eV. Therefore we have assumed in this work that exothermic processes are non-resonant, and neglected their effect on transport properties. With assumed product ions (Table I) we have selected 46 endothermic processes with thermodynamic thresholds up to about 11 eV. Elastic momentum transfer (MT) cross-section representing elastic collisions with isotropic scattering together with collisions where activated complex is back to reactants, and the cross-sections for collisions where H^+ keeps on and where H^+ is lost [13] are presented in Fig. 1.
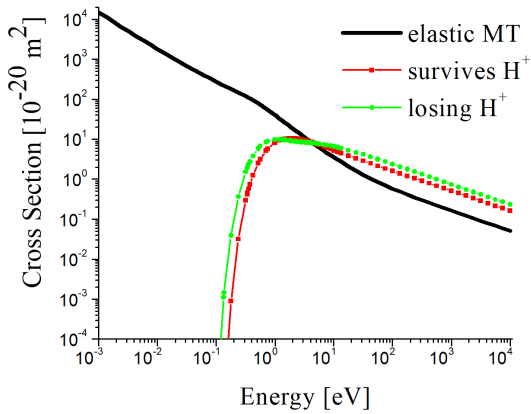
Fig. 1. Cross-sections for H^+ ions in n-butanol.

3. Transport parameters

A precise treatment to obtain transport parameters ions of higher accuracy as a function of E/N would be to follow the solutions of generalization of the Boltzmann equation [24]. The Monte Carlo simulation methods are generally built around the same initial principles as related kinetic equations. In this work we apply the Monte Carlo simulation created for swarm particles [25, 26].

Transport properties of species in gas plasmas are of great importance in understanding the nature of molecular and ionic interactions in gas mixtures [27, 28]. These properties include the mean energy, drift velocity, diffusion coefficients, ionization and chemical reaction coefficients, chemical reaction coefficients for ions and rarely excitation coefficients, and they are very useful in chemical industries for the design of many types of transport

Heats of formation $\Delta_f H^0$ at 298 K (kJ/mol)   TABLE I

Species	ΔH_f^+	ΔH_f^0
H_2	1488.3	0
CO	1241.59	−393.51
CO_2	935.4	−393.51
CH_2O	940.5	−108.7
H_2O	975.0	−241.83
CH_4	1132	−74.5
C_2H_4	1066	52.2
C_2H_6	1028	−84.0
C_3H_6	959	20.2
C_3H_8	227.5	951.5
C_4H_8	924	−0.4
C_4H_{10}	889	−126.5
CH_4O	845.3	−201.6
C_2H_6O	775.4	−234.8
C_3H_8O	731	−254.8
C_2H_2	1327.9	228.0
C_3H_4	1186.2	186.6
C_4H_6	1033	162.3
C_2H_4O	821.1	−165.8
C_3H_6O	772.9	−187.4
C_4H_8O	742	−207.5

and process equipment. Swarm parameters, which are functions of reduced electric field E/N (E — electric field, N — gas density) in DC electric fields are usually applied to plasma modeling and simulations.

In this paper we have used a Monte Carlo code that properly takes into account the thermal collisions [14, 17]. The code has passed all the tests and the benchmarks that were covered in our earlier studies [17, 29]. Calculations are performed for the gas pressure 1 Torr and gas temperature of 300 K.
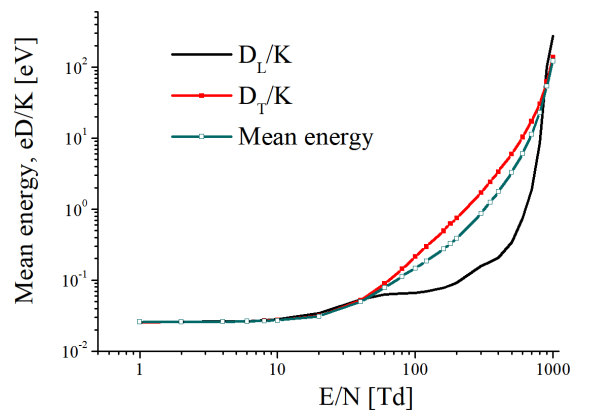

Fig. 2. Mean and characteristic energy as a function E/N for H^+ ions in n-butanol.

In Fig. 2 we show characteristic energies (diffusion coefficient normalized by mobility eD/μ in units eV) longitudinal (L) and transverse (T). We also show mean energy, which cannot be directly measured in experiments
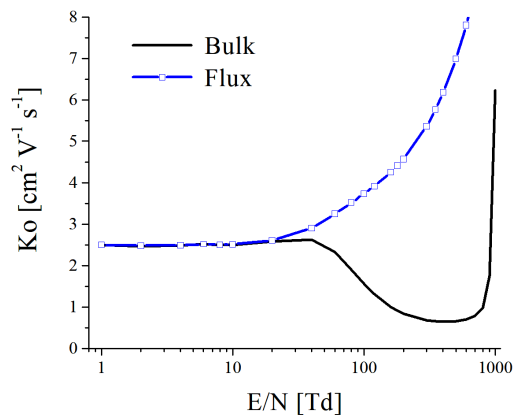
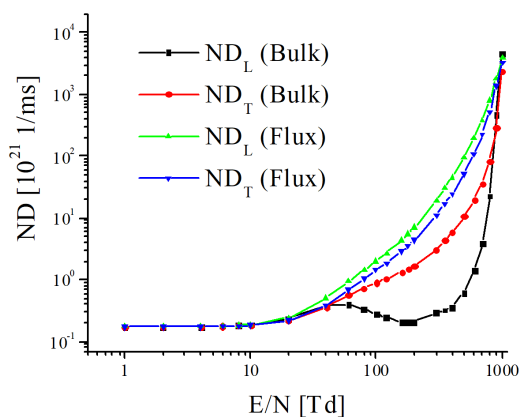Fig. 3. Reduced mobility as a function E/N for H^+ ions in n-butanol.

Fig. 4. Longitudinal and transversal diffusion coefficients as a function E/N for H^+ ions in n-butanol.

4. Conclusion

In this paper we show transport properties for the H^+ in n-butanol which do not exist in the literature. The cross-section set has been determined by extending the Denpoh–Nanbu method.

The Monte Carlo technique was applied to carry out calculations of the mean energy, characteristic energy, reduced mobility and diffusion coefficients as a function of reduced DC electric field. The results are believed to be a good base for modeling, which could be further improved when measured values of transport coefficients become available and then we could perform this analysis again.

but map of mean energy versus E/N may be used directly to provide the data in fluid models especially when local field approximation fails.

In Fig. 3 we show the results of Monte Carlo simulation for reduced mobility as a function of E/N. The mobility K of an ion is a quantity defined as the velocity attained by an ion moving through a gas under the unit electric field. One often exploits the reduced or standard mobility defined as:

$$K_0 = \frac{\nu_d}{N_0 E} N, \qquad (2)$$

where ν_d is the drift velocity of the ion, N is the gas density at elevated temperature T, $N_0 = 2.69 10^{25}$ m^{-3} and E is the electric field. Due to reactive collisions bulk and flux values of reduced mobility are separated.

Longitudinal and transversal diffusion coefficients for H^+ in n-butanol as a function of E/N are shown in Fig. 4. The peak is visible only in the behavior of longitudinal diffusion coefficients. Because of great capture of ions, we have a diminishing of NDL bulk values. However, there are no published experimental data for the longitudinal and transverse diffusion coefficients of H^+ in n-butanol so far.

References

[1] H. Xu, C. He, Sep. Purif. Technol. 56, 85 (2007).
[2] M. Johnson, S. Barnes, R. Diasio, Anal. Biochem. 182, 360 (1989).
[3] H. Jiang, S. Lu, X. Zhang, H. Peng, W. Dai, J. Qiao, Catal. Sci. Technol. 4, 2499 (2014).
[4] Z. Sahin, O. Aksu, Renew. Energy 77, 279 (2015).
[5] N. Yilmaz, F. Vigil, K. Benali, S. Davis, A. Calva, Fuel 135, 46 (2014).
[6] H. Liu, S. Li, Z. Zheng, J. Xu, M. Yao, Appl. Energy 112, 246 (2013).
[7] D. Rakopoulos, Fuel 105, 603 (2013).
[8] A. Demirbas, Prog. Energy Combust. Sci. 33, 1 (2007).
[9] A.C. Hansen, D.C. Kyritsis, C.F. Lee, Characteristics of Biofuels and Renewable Fuel Standards, Biomass to Biofuels — Strategies for Global Industries, Wiley, New York 2009.
[10] C. Togbe, G. Dayma, A. Mze-Ahmed, P. Dagaut, Energy Fuel 24, 3906 (2010).
[11] J.L. Fortman, S. Chhabra, A. Mukhopadhyay, H. Chou, T.S. Lee, E. Steen, J. Keasling, Trends Biotechnol. 26, 375 (2008).
[12] T.C. Ezejia, N. Qureshib, H.P. Blascheka, J. Biotechnol. 115, 179 (2005).
[13] K. Denpoh, K. Nanbu, J. Vac. Sci. Technol. A 16, 1201 (1998).
[14] Z. Ristivojević, Z. Lj. Petrović, Plasma Sources Sci. Technol. 21, 035001 (2012).
[15] E.W. McDaniel, V. Čermak, A. Dalgarno, E.E. Ferguson, L. Friedman, Ion-Molecule Reactions, Wiley-Interscience, 1970.
[16] P.B. Armentrout, K.M. Ervin, M.T. Rodgers, J. Phys. Chem. A 112, 10071 (2008).
[17] Z.Lj. Petrović, Z.M. Raspopović, V.D. Stojanović, J.V. Jovanović, G. Malović, T. Makabe, J. de Urquijo, J. Appl. Surf. Sci. 253, 6619 (2007).

[18] A.M. Ababneh, C.C. Large, S. Georghiou, *Biophys. J.* **85**, 1111 (2003).

[19] V. Stojanović, Z. Raspopović, J. Jovanović, Ž. Nikitović, Z.Lj. Petrović, *EuroPhys. Lett.* **101**, 45003 (2013).

[20] O.K. Rice, H.C. Ramsperger, *J. Am. Chem. Soc.* **50**, 617 (1928); L.S. Kassel, *J. Phys. Chem.* **32**, 225 (1928).

[21] S. Lias, J. Bartmess, J. Liebman, J. Holmes, R. Levin, W. Mallard, *J. Phys. Chem. Ref. Data* **17**, 1 (1988).

[22] Ž. Nikitović, V. Stojanović, Z. Raspopović, J. Jovanović, *Acta Phys. Pol. A* **126**, 724 (2014).

[23] Ž. Nikitović, Z. Raspopović, V. Stojanović, J. Jovanović, *EuroPhys. Lett.* **108**, 35004 (2014).

[24] K. Kumar, *Aust. J. Phys.* **33**, 449 (1980); L.A. Viehland, S.L. Lin, E.A. Mason, *Chem. Phys.* **54**, 341 (1981); K.F. Ness, L.A. Viehland, *Chem. Phys.* **148**, 255 (1990); L.A. Viehland, Y. Chang, *Mol. Phys.* **110**, 259 (2012).

[25] K. Kumar, H.R. Skullerud, R.E. Robson, *Aust. J. Phys.* **33**, 343 (1980).

[26] R.E. Robson, R.D. White, Z.Lj. Petrovic, *Rev. Mod. Phys.* **77**, 1303 (2005); A.M. Nolan, M.J. Brennan, K.F. Ness, A.B. Wedding, *J. Phys. D Appl. Phys.* **30**, 2865 (1997); K.F. Ness, R.E. Robson, *Phys. Rev. A* **34**, 2185 (1986).

[27] B. Todd, J.B. Young, *J. Power Sources* **110**, 186 (2002).

[28] E. Mason, *J. Chem. Phys.* **27**, 782 (1957).

[29] J. de Urquijo, J.V. Jovanović, A. Bekstein, V. Stojanović, Z.Lj. Petrović, *Plasma Sources Sci. Technol.* **22**, 025004 (2013).

THE EUROPEAN
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Regular Article

Cross sections and transport coefficients for H_3^+ ions in water vapour[*]

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Abstract. Scattering cross sections for positive H_3^+ ions in water vapour were calculated by a simple but quite general theory and then assessed by using the available data. Transport coefficients for H_3^+ ions in water vapour in DC fields were calculated by using a Monte Carlo simulation from low to moderate reduced electric fields E/N (E is electric field and N is gas number density) where the non-conservative collisions are also taken into account.

1 Introduction

Plasmas are already deeply incorporated into our everyday life either directly or indirectly within production technologies that are superior to other production methods. Plasma technologies offer treatment of various substances [1–3]. Control of reactive ion plasmas is necessary in applications related to semiconductor modifications. A cornerstone in modelling of such plasmas is precise information on the transport of ions, as the reactive ions flux and energy control the surface processes. In plasmas in collision-dominated regimes, if the negative ions dominate over the electrons, the plasmas become electronegative with properties distinctly different from the electropositive plasmas, especially in the sheath regions. In modelling and analyzing of the plasma chemistry, the cross-sections are needed (rather than interaction potentials) for all relevant species and not only concerning the momentum transfer.

In order to control increasingly complex plasmas large databases for positive and negative ion transport properties are required [4,5]. Databases should be constantly updated with new and improved data [6]. Apart from a wide range of data produced up to now in the field of ion-molecule collisions, there are still major gaps in cases of very reactive gases such as BF_3 that are not convenient to study experimentally. There are also very complex environments such as water vapor where very sophisticated methods are needed in order to obtain some information.

Sets that include cross sections for reactive processes are needed to calculate the chemical kinetics of all the species when some of the species may have low density but also have a narrow range of processes controlling their population. To remedy lack of data simpler theories have been used and in this paper we exploited so-called Denpoh and Nanbu (DN) model [7], together with other techniques to make reasonable estimates of the ion scattering cross sections. In addition to cross sections, reaction rates [8] and other transport data may be used directly in fluid and hybrid codes and in process of normalization of cross sections. An important aspect of plasma models is that a complete set of cross sections should be used. Otherwise, even if one had all perfect cross sections albeit with an incomplete set, the results would be unrealistic.

In this paper Monte Carlo technique was applied to perform calculations of transport parameters, as well as of rate coefficients in DC electric fields. We have used a Monte Carlo code that properly calculates collision probabilities for thermal collisions [9]. The code has passed all the relevant benchmarks [9] and has been tested in our work on several types of charged particles [10,11]. The choice of three seemingly different molecules with different improvements is intended as a review of the approach in supplementing the existing data with simple theories and basic calculations.

2 Cross sections

Ion-molecule reactions play a basic role in the field of gas phase reaction kinetics. They are readily studied over a wide range of collision energies and the ionic reactants in a number of cases can be prepared in defined excited

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states (see for example Ref. [12]). There is a very detailed knowledge of the ion molecule reactions in general in the literature. Nevertheless, concerning the cross sections that are necessary for modelling plasma processing there is a shortage of data even for the most pertinent processes and therefore a considerable effort in extending the existing databases is required.

At low collision energies (thermal to few electron volts) activated complex formation usually dominates the outcome of the collisions. For pressures in low temperature plasmas, related to technological applications, ranging up to atmospheric pressure average flight time between collisions is more than 4 orders of magnitudes larger than the average lifetime of activated complex [13,14]. Having that in mind the reaction can be safely assumed as infinitesimally short both in space and time. Since a large proportion of near-thermal ion-molecule reactions proceed without significant barriers, statistical theories of unimolecular decay have been successful in reproducing low-energy ion-molecule reaction rates, as well as the product state distributions [15].

Rice-Ramsperger-Kassel (RRK) theory of unimolecular reactions has proven to be not only a cornerstone for more precise theories that include quantum effects such as RRKM [16,17] but is also a sufficiently reliable method to be used to explain measurements of the rate constants (subject to selecting the required empirical parameters [18]).

Denpoh and Nanbu [7] obtained reactive cross sections for ions in collision with molecular gas by assuming their behavior close to target is affected only by the induced polarisation potential. For ions in low pressure Ar/CF_4 RF discharges they included all possible reactions with CF_4 molecule and calculated thermodynamic thresholds in the energy region about 10 times wider than the expected validity of the induced polarisation potential. They separated elastic from reactive endothermic collisions and determined branching ratio according to RRK theory which is used to calculate the scattering probability for each reaction. In their approach each reaction cross section is proportional to the scattering probability normalized to appropriate total cross section [7]. Assuming that each binary collision produces reaction with the activated complex formation, as a total cross section for reactions they used orbiting cross section [19] multiplied by cut-off value of normalized impact parameter β_∞^2 [7,20]. In terms of classical trajectory analysis [19] this means that reactions proceed within scaled orbiting distance $b_0\beta_\infty$, where the internal energy of the complex in RRK analysis is equal to the initial kinetic energy of the particles in the center of mass system. In their approach usage of normalized impact parameter allows one to calculate angles of scattering and subsequently velocities of particles after the scattering.

In this work we exploit DN model to calculate the complete cross section set for scattering of H_3^+ ions on H_2O molecules. Our basic assumption is that all trajectories appearing within orbiting distance may lead to reactions [19] while trajectories not entering the orbiting distance are leading to anisotropic elastic scattering.

We have used Monte Carlo simulations (MCS) to calculate transport parameters [8]. In order to calculate the total collision frequency in MCS we have employed the total momentum transfer cross section [21].

The basis of standard RRK theory is that critical motion leading to the chemical reaction of a molecule is vibrational. It is assumed that molecule is a collection of s classical oscillators where one of these oscillators is critical to the reactions. It is necessary to adjust number of vibrational modes by using a factor $1/n$ where the choice of n at the first instance apparently involves some degree of intuition. It is found empirically that the best agreement with experimental measurements of rate constants, for the widest range of cases is achieved for n equal to about 2 [22–24].

Number of endothermic processes that are included in DN model becomes important if possibly missing processes have threshold in the range of validity of the polarization interaction. Since consistent tables of thermochemical data are readily available [25] for large number of reactions it is possible to calculate the thermodynamic thresholds. On the other hand, we may choose to neglect processes with higher thresholds especially if ions seldom reach such energies.

Large dipole moments of gas particles significantly affect the ion-molecule interaction and increase reaction cross section. Stojanović et al. [26] used DN model for scattering O^- ions in water vapor. They calculated cross sections by using the locked dipole approximation [20]. Obtained cross section set was than corrected to fit the reduced mobility calculated by the SACM (Statistical Adiabatic Channel Model) approximation [27]. Those calculations proved to be in good agreement with the existing experimental measurements. In general DN model may be used on its own as a source of data especially when results from experiments and/or binary collision theories of a higher order are not available. We choose to combine the model with the swarm procedure to test the cross section sets. There we employ as many experimental data as available to improve the accuracy of results for cross sections and consequently for transport coefficients.

In this work we present the cross section set for $H_3^+ + H_2O$ calculated by the same method. For presented cross section set we have selected 24 endothermic reaction paths and one exothermic reaction. In calculations, we have assumed that effective number of vibrational modes is 6. Ratio between total momentum cross section and orbiting cross section is used as for the case where dipole moment of the target is neglected. Finally, exothermic reaction cross section is obtained by scaling reduced orbiting cross section according to experimentally obtained rate coefficient for the exothermic reaction. H_3^+ is in-avoidable molecule in studies of low pressure and astrophysical plasmas. It is known that H_3^+ is produced in astrophysical plasmas, in exothermic reactions of H_2^+ with H_2 [28]. Note (see Tab. 1) that the same internal energy if transferred to H_3^+ in collisions with water only increases exothermicity and cannot produce other particles than again H_3O^+ (process 2).

Table 1. H_3^+–H_2O reaction paths products and the corresponding thermodynamic threshold energies Δ.

No	Reaction products	Δ (eV)
1(EL)	$H_3^+ + H_2O$	0
1(EXO)	**$H_3O^+ + H_2$ (EXO)**	2.8097
2	$H_3O^+ + 2H$	−1.6676
3	$H_2O^+ + H + H_2$	−3.3465
4	$H_2O^+ + 3H$	−7.8238
5	$H_3^+ + H_2 + O$	−5.0587
6	$H_3^+ + 2H + O$	−9.5359
7	$H_3^+ + OH + H$	−5.1126
8	$H_2^+ + H_2O + H$	−6.1904
9	$H_2^+ + H + H_2 + O$	−11.249
10	$H_2^+ + 3H + O$	−15.726
11	$H_2^+ + 2H + OH$	−11.303
12	$H_2^+ + H_2 + OH$	−6.8257
13	$H^+ + H_2O + H_2$	−4.3632
14	$H^+ + H_2O + 2H$	−8.8405
15	$H^+ + H_2 + O + 2H$	−13.899
16	$H^+ + H_2O + 2H$	−9.4219
17	$H^+ + 4H + O$	−18.376
18	$H^+ + OH + H_2 + H$	−9.4758
19	$H^+ + OH + 3H$	−13.953
20	$O^+ + 2H_2 + H$	−9.4416
21	$O^+ + 3H + H_2$	−13.919
22	$O^+ + 5H$	−18.396
23	$OH^+ + 2H_2$	−4.4006
24	$OH^+ + 2H + H_2$	−8.8778
25	$OH^+ + 4H$	−13.355

Fig. 1. Cross section set for $H_3^+ + H_2O$ scattering: (a) without the non-conservative effect of the exothermic collisions, (b) with the non-conservative effect of the exothermic collisions. Only endothermic processes with thermodynamic thresholds lower than 6 eV are included in this figure but we have cross sections for all processes from Table 1.

3 Calculation of transport parameters

H_3^+ is not an important molecular ion in water vapor discharges but is contributing to production of H_3O^+ molecule which has been shown to be the most abundant in water vapor discharges and also in other discharges where water can be present either as a part of the mixture or as impurity. Since experimental rate coefficient for H_3O^+ production exist at thermal energies, we have used these data to normalize the reduced orbiting cross section [19] and thus improve uniqueness of the obtained cross section set. Product distributions for those reactants are found not dependent on amount of vibrational excitation of H_3^+ [29] thus only endothermic reactions may have slightly shifted thresholds towards low energy while number of reactive channels will remain the same as with H_3^+ in ground state.

Cross sections were calculated by applying DN model for scattering of H_3^+ on H_2O with the same data for polarizability and dipole moment of H_2O as used by Clary [30] and selected heats of formation from reference [25]. In Table 1 we show reaction paths products and the corresponding thermodynamic threshold energies.

Cross section set that includes differentiation of elastic and exothermic process (EXO) is shown in Figure 1. While most inelastic channels occur at high energies beyond the standard energies for gas discharges, there are some processes taking place with thresholds in the vicinity of 2–4 eV that may become relevant for most discharges.

Exothermic processes are often disregarded in their non-conservative nature, and simply added to the total elastic cross section. In any case, all channels will be accessible in the sheath of the discharge.

Regarding elastic and exothermic processes one can differentiate between two situations. In the first case one can add 1(El) and 1(EXO) processes (Fig. 1a) and treat the process as elastic. Thereby one neglects the number-changing nature of the exothermic process. If exothermic reaction with products $H_3O^+ + H_2$ is included as a non-conservative loss (Fig. 1b) then it may affect the calculated transport data greatly. We have normalized the exothermic cross section to the thermal rate at $T = 297$ K [31] and thus also scaled the total momentum transfer cross section [32].

The cross section for exothermic collisions σ_{exo} is introduced by

$$\sigma_{exo} = \beta \cdot \sigma_O \qquad (1)$$

where σ_O is the orbiting cross section and β is the scaling factor. Scaling factor can be determined if the thermal rate constant for exothermic process is available. For the case of $H_3^+ + H_2O$, rate coefficient at $T = 297$ K for exothermic reaction with products $H_3O^+ + H_2$ is measured by Betowski et al. [31] and it gives $\beta = 0.4498$ [1]. Note that
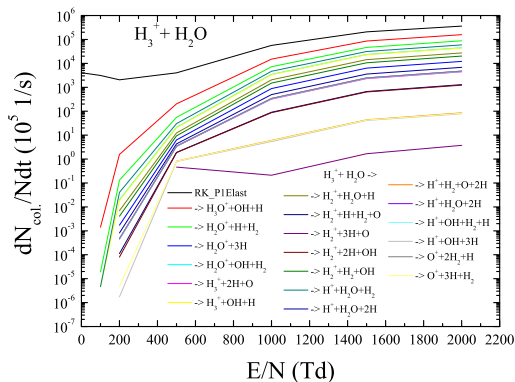
Fig. 2. Rate coefficients for reactions of H_3^+ ions with H_2O at $T = 300$ K, calculated by Monte Carlo simulations. The results were obtained without the non-conservative effect of the exothermic reaction.
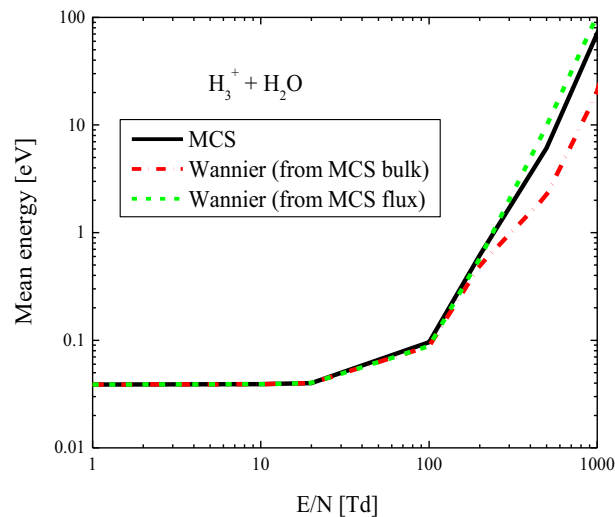

Fig. 3. Mean energy obtained from simulations and also from Wannier relations [32]. Two different drift velocities (bulk and flux see [34]) were used for Wannier relations.

our cross section for exothermic collisions has the same energy dependence as the reduced orbiting cross section obtained for the case of potential with dipole and induced polarization term.

The obtained cross section set was corrected to fit the reduced mobility calculated by SACM approximation [29], i.e. the zero field mobility of $Ko = 1.7795$ cm^2 V^{-1} s^{-1} at $T = 300$ K. We calculated rate coefficients (see Fig. 2) for reactions shown in Table 1 by using MCS. Under the same circumstances, we have obtained the mean energy and compared it with the predictions based on Wannier relations [32] using the cross sections from the MCS. Those results are shown in Figure 3. The difference between the bulk and flux drift velocities is a consequence of the energy-dependent endothermic reactions [33,34]. Strong dipole forces cause discrepancy of collisional frequency from constant value characteristic for transport of ions in the induced polarization potential [35]. In principle we are here testing the Wannier relations, but more importantly we are using in the relation the two varieties of the drift velocities (flux and bulk). The idea is to see which provides a better estimate of the mean energy, as non-conservative processes were not included explicitly in the development of these relations. Since non-conservative effect of the exothermic relation is huge, we chose to make this comparison by using only the endothermic non-conservative processes such as ionization. We can see that the predictions of Wannier relations using the flux drift velocity are in a much closer agreement with the mean energy obtained in the same simulation.

4 Transport under the influence of a strong non-conservative exothermic process

Exothermic collisions cause differences between flux and bulk drift velocities at low E/N while endothermic reactive collisions affect the swarm at high E/N. The former, however affects the transport on a much larger scale due to a larger cross section and also as it occurs in the energy region of the bulk of most gas discharges. On the other hand, if collision frequency of exothermic collisions is constant that results in equality of the bulk and flux reduced mobilities since the ions from the front and the tail are removed with an equal rate [34].

In order to indicate the importance of including the nature of all processes we have compared calculations of transport coefficients with and without the non-conservative effect of exothermic process or in other words when losses of transported ions are taken into account or when (as is usually the case in simpler models) those processes are included by their number in the total cross section. As for the isotropic scattering elastic and momentum transfer cross sections are the same this process is then effectively added to the elastic process. The calculated transport coefficients are shown in Figure 4.

At low mean energies due to energy dependence of the collision rates one has "heating" of the swarm due to preferential removal of the low energy particles. This results in a greater bulk drift velocity. When reduced electric field further increases, energy distribution of the ions becomes wider and number of slow ions that are removed by exothermic reactions reduces, so the bulk drift velocity approaches flux drift velocity. Bulk drift velocity becomes lower than flux drift velocity when endothermic collisions begin to dominate. Reactive collision frequency due to the endothermic collisions increases with respect to constant collision frequency and one has swarm "cooling" due to a preferential loss at higher energies.

In our case, bulk drift velocity appears as slowly varying function of E/N up to about 300 Td. At that point it becomes equal to the flux velocity and later on it becomes smaller. Behaviour of the diffusion coefficients is quite different due to tremendous effect of cooling and heating of the distribution function on the diffusion.

5 Conclusion

In this work we present details of how Denpoh-Nanbu model is used to calculate cross sections for reactive scattering of H_3^+ ions with H_2O target for energies in the range
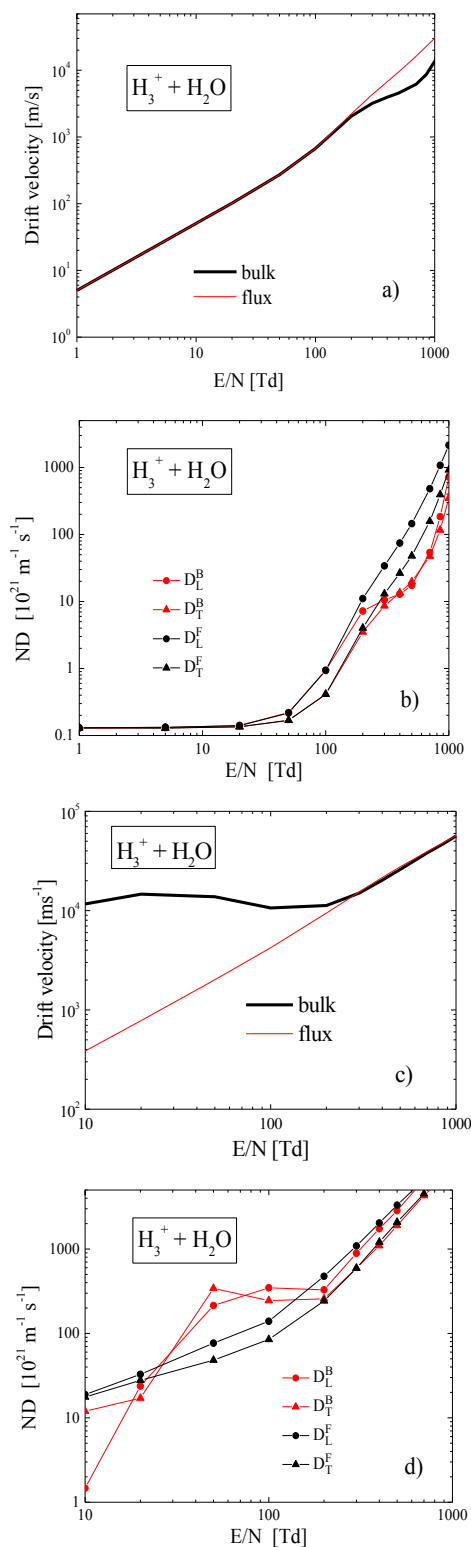
from 0.01 eV to 200 eV. The role of these ions in water vapour containing discharges is essential especially in the chain of reactions leading to formation of the dominant H_3O^+ ions.

Cross section set and transport parameters presented in this work were not available up to now. Accuracy of exothermic cross section is $\pm 25\%$ that comes from accuracy of the experimental rate constant and having in mind successful description of exothermic reactions by capture theories. Langevin Hasse model provides a good low energy total cross section that may be successfully extrapolated to higher energies. Having in mind the uncertainty of the polarizabilities available in the literature and the tests made for other ions by the same technique the total cross section at lower energies is uncertain to $\pm 20\%$. Although accuracy of the particular endothermic cross sections may vary significantly, approximate accuracy of data is about $\pm 50\%$ with an uncertainty of the total effect of endothermic inelastic processes being established more accurately.

The Monte Carlo technique was applied to carry out calculations of transport parameters as a function of reduced electric field. Due to the lack of experimental transport data, such calculations for H_3^+ ions in H_2O are the best data that are available. The information on all the reactants is an important part of the kinetic models for discharges in mixtures with water vapour, in the interface between liquid water and air and in the discharges in liquids [36–43].

Author contribution statement

Fig. 4. Transport parameters as a function of E/N for H_3^+ in H_2O, exothermic losses not included: (a) drift velocity, (b) diffusion coefficients; exothermic losses included, (c) drift velocity, and (d) diffusion coefficients.

References

1. M.A. Lieberman, A.J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, 2nd ed. (Wiley, 2005)

2. T. Makabe, Z. Petrović, *Plasma Electronics: Applications in Microelectronic Device Fabrication* (Taylor and Francis, CRC Press, New York, 2006)

3. Z.Lj. Petrović, P. Maguire, M. Radmilović-Radjenović, M. Radetić, N. Puač, D. Marić, C. Mahony, G. Malović, in *Nanotechnology for Electronics, Photonics and Renewable Energy*, edited by A. Korkin et al. (Springer, 2010), Vol. 85

4. S. Samukawa, M. Hori, S. Rauf, K. Tachibana, P. Bruggeman, G. Kroesen, J.C. Whitehead, A.B. Murphy, A.F. Gutsol, S. Starikovskaia, U. Kortshagen, J.-P. Boeuf, T.J. Sommerer, M.J. Kushner, U. Czarnetzki, N. Mason, J. Phys. D: Appl. Phys. **45**, 253001 (2012)

5. I. Adamovich, S. Baalrud, A. Bogaerts, P.J. Bruggeman, M. Cappelli, V. Colombo, U. Czarnetzki, U. Ebert, J.G. Eden, P. Favia, D.B. Graves, S. Hamaguchi, G. Hieftje, M. Hori, I.D. Kaganovich, U. Kortshagen, M.J. Kushner, N.J. Mason, S. Mazouffre, S. Mededovic Thagard, H.-R. Metelmann, A. Mizuno, E. Moreau, A.B. Murphy, B.A. Niemira, G.S. Oehrlein, Z. Lj. Petrović, L.C. Pitchford, Y.-K. Pu, S. Rauf, O. Sakai, S. Samukawa, S. Starikovskaia, J. Tennyson, K. Terashima, M.M. Turner, M.C.M. van de Sanden, A. Vardelle, J. Phys. D: Appl. Phys. **50**, 323001 (2017)

6. http://mail.ipb.ac.rs/~cep/ipb-cnp/ionsweb/database.htm; www.lxcat.net, see for example Phelps or Viehland database, retrieved on: 2017/04/05

7. K. Denpoh, K. Nanbu, J. Vac. Sci. Technol. A **16**, 1201 (1998)

8. J. Tennyson, S. Rahimi, C. Hill, L. Tse, A. Vibhakar, D. Akello-Egwel, D.B. Brown, A. Dzarasova, J.R. Hamilton, D. Jaksch, S. Mohr, K. Wren-Little, J. Bruckmeier, A. Agarwal, K. Bartschat, A. Bogaerts, J.-P. Booth, M.J. Goeckner, K. Hassouni, Y. Itikawa, B.J. Braams, E. Krishnakumar, A. Laricchiuta, N.J. Mason, S. Pandey, Z.Lj. Petrovic, Y.-K. Pu, A. Ranjan, S. Rauf, J. Schulze, M.M. Turner, P. Ventzek, J.C. Whitehead, J.-S. Yoon, Plasma Sources Sci. Technol. **26**, 055014 (2017)

9. Z. Ristivojević, Z.Lj. Petrović, Plasma Sources Sci. Technol. **21**, 035001 (2012)

10. Z.Lj. Petrović, Z.M. Raspopović, V.D. Stojanović, J.V. Jovanović, G. Malović, T. Makabe, J. de Urquijo, Appl. Surf. Sci. **253**, 6619 (2007)

11. J. de Urquijo, J.V. Jovanović, A. Bekstein, V. Stojanović, Z.Lj. Petrović, Plasma Sources Sci. Technol. **22**, 025004 (2013)

12. C.L. Liao, C.X. Liao, C.Y. Ng, J. Chem. Phys. **81**, 5672 (1984)

13. Y. Xu, B. Xiong, Y.C. Chang, C.Y. Ng, J. Chem. Phys. **139**, 024203 (2013)

14. D.K. Bohme, D.B. Dunkin, F.C. Fehsenfeld, E.E. Ferguson, J. Chem. Phys. **51**, 863 (1969)

15. H.F. Davis, H.U. Stauffer, in *Encyclopedia of Physical Science and Technology*, 3rd ed., edited by R.A. Meyers (Academic Press, 2000), Vol. 4, p. 697

16. R.A. Marcus, J. Chem. Phys. **20**, 359 (1952)

17. H.O. Pritchard, *The Quantum Theory of Unimolecular Reactions* (Cambridge University Press, 1984)

18. D.W. Placzek, B.S. Rabinovitch, G.Z. Whitten, E. Tschuikow-Roux, J. Chem. Phys. **43**, 4071 (1965)

19. E.W. McDaniel, V. Čermak, A. Dalgarno, E.E. Ferguson, L. Friedman, *Ion-Molecule Reactions* (Wiley-Interscience, 1970)

20. J.V. Dugan, J.L. Magee, J. Chem. Phys. **47**, 3103 (1967)

21. Z.Lj. Petrović, V.D. Stojanović, J. Vac. Sci. Technol. A **16**, 329 (1998)

22. D.W. Placzek, B.S. Rabinovitch, G.Z. Whitten, J. Chem. Phys. **43**, 4071 (1965)

23. G.B. Skinner, B.S. Rabinovitch, J. Phys. Chem. **76**, 2418 (1972)

24. H.W. Schranz, S. Nordholm, N.D. Hamer, Int. J. Chem. Kinet. **14**, 543 (1982)

25. S.G. Lias, J.E. Bartmess, J.F. Xebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data **17**, 1 (1988)

26. V. Stojanović, Z. Raspopović, D. Marić, Z.Lj. Petrović, Eur. Phys. J. D **69**, 6 (2015)

27. J.A. de Gouw, M. Krishnamurthy, S.R. Leone, J. Chem. Phys. **106**, 5937 (1997)

28. A.V. Phelps, Phys. Rev. E **79**, 066401 (2009)

29. J.K. Kim, I.P. Theard, W.T. Huntress, Int. J. Mass Spectrosc. Ion Phys. **15**, 223 (1974)

30. D.C. Clary, Chem. Phys. Lett. **232**, 267 (1995)

31. D. Betowski, J.D. Payzant, G.I. Mackay, D.K. Bohme, Chem. Phys. Lett. **31**, 321 (1975)

32. G.H. Wannier, Bell Syst. Tech. J. **32**, 170 (1953)

33. Z.Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž.D. Nikitović, O. Šašić, J. Jovanović, V. Stojanović, M. Radmilović-Rađenović, J. Phys. D: Appl. Phys. **42**, 194002 (2009)

34. R.E. Robson, Aust. J. Phys. **44**, 685 (1991)

35. Z. Raspopović, V. Stojanović, Ž. Nikitović, EPL **111**, 45001 (2015)

36. P.J. Bruggeman, M.J. Kushner, B.R. Locke, J.G.E. Gardeniers, W.G. Graham, D.B. Graves, R.C.H.M. Hofman-Caris, D. Marić, J.P. Reid, E. Ceriani, D. Fernandez Rivas, J.E. Foster, S.C. Garrick, Y. Gorbanev, S. Hamaguchi, F. Iza, H. Jablonowski, E. Klimova, J. Kolb, F. Krcma, P. Lukes, Z. Machala, I. Marinov, D. Mariotti, S. Mededovic Thagard, D. Minakata, E.C. Neyts, J. Pawlat, Z.Lj. Petrović, R. Pflieger, S. Reuter, D.C. Schram, S. Schröter, M. Shiraiwa, B. Tarabová, P.A. Tsai, J.R.R. Verlet, T. von Woedtke, K.R. Wilson, K. Yasui, G. Zvereva, Plasma Sources Sci. Technol. **25**, 053002 (2016)

37. S.A. Norberg, E. Johnsen, M.J. Kushner, Plasma Sources Sci. Technol. **24**, 035026 (2015)

38. D.X. Liu, P. Bruggeman, F. Iza, M.Z. Rong, M.G. Kong, Plasma Sources Sci. Technol. **19**, 025018 (2010)

39. T. Murakami, K. Niemi, T. Gans, D. O'Connell, W.G. Graham, Plasma Sources Sci. Technol. **22**, 015003 (2013)

40. F. Taccogna, G. Dilecce, Eur. Phys. J. D **70**, 251 (2016)

41. E.R. Adhikari, S. Ptasinska, Eur. Phys. J. D **70**, 180 (2016)

42. S. Lazović, D. Maletić, A. Leskovac, J. Filipović, N. Puač, G. Malović, G. Joksić, Z.Lj. Petrović, Appl. Phys. Lett. **105**, 124101 (2014)

43. A. Hurlbatt, A.R. Gibson, S. Schroter, J. Bredin, A.P.S. Foote, P. Grondein, D. O'Connell, T. Gans, Plasma Process. Polym. **14**, 1600138 (2017)

FME TRANSACTIONS

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Transport of F⁻ Ions in Gaseous Environment for Technological Applications

In this work we present swarm data obtained for F- ions in atomic and molecular gases necessary to form the global models for the complex collisional plasmas. We also present the new results for the simple scattering cross section set and proposed transport coefficients for F- ions in BF3 that can be used in such models. Nanbu's theory based on thermodynamic threshold energies and separating elastic and reactive collisions is used to calculate cross sections for binary collisions of ions with atoms and molecules. For the cases in which the measured transport coefficients were available Momentum Transfer theory (MTT) was applied in order to unfold the cross sections from the measured transport data. Direct Monte Carlo method is applied to obtain swarm parameters at the temperature of T=300 K.

Keywords: Negative ions, F- ion, transport coefficients, Global model, Monte Carlo, cross sections.

1. INTRODUCTION

The goal of this work is to present data for modeling of complex low temperature collisional plasmas containing F⁻ ions by using a global [1-3] and other plasma models.

The electronegativity of the F atom is the largest of all atoms. The F⁻ ion is also a highly reactive nucleophilic reagent and generally forms strong bonds with many Lewis acids in the gas phase [4].

The negative halogen ions are abundant in various forms of nonequilibrium plasmas relevant to applications such as excimer lasers [5] and electrical discharges, biomedical devices, nanotechnologies and in radiation chemistry in the atmosphere. For example, it is experimentaly found that negative ions are effective for increasing the etch rate and improving the etch profile [6]. F⁻ ions are also inavoidable part of production of cubic boron nitride (c-BN) films [7]. It is thus important to understand plasma chemistry and the behavior of negative ions for the control of etching characteristics.

Additionally, the recent progress of discharge modeling and simulation have made contributions to a deeper understanding of the discharge phenomena and to the optimization of reactor design or operating conditions.

The transport coefficients include drift velocity, diffusion coefficients, ionization and attachment coefficients and chemical reaction coefficients for ions [8]. Excitation coefficients are also measured but seldom used in modeling. Ion transport coefficients are used in both fluid and hybrid models of plasmas. Indirectly, transport coefficients are used to verify validity of the cross sections in the sets used in computer modelling.

2. ION ATOM/MOLECULE COLLISION MODEL

In plasma modeling ion-atom/molecule collisions have been usually simplified for the lack of detailed collision data. In this work instead of very often cited Langevin's theory to determine effective cross section for collision and reaction rate we used Nanbu's theory [9, 10] that may distinguish between reactive and nonreactive collisions of collision partners.

Depending of available experimental data we also applied procedure [10] to unfold the cross sections from the measured transport coefficients and thermochemical data in a separate drift tube experiment.

2.1 Calculation of cross section sets

The cross sections for scattering of F- ions on several atoms and molecules are calculated by using Nanbu's theory [9,10]. According to Nanbu's theory elastic and reactive endothermic collision are separated and treated by accounting for thermodynamic threshold energy and branching ratio according to the Rice–Rampsperger–Kassel (RRK) theory [9]. Within the RRK theory excited molecular complex is treated as excited activated complex where internal energy is distributed among s equivalent oscillators–vibrational modes of the complex. For example, in such a way we used s = 3 for F- + BF3 system.

For F⁻ + Ar initial cross section set is calculated by using Nanbu's theory with polarizability of $1.64 \ 10^{-30}$ m³ and extended [9] by measured values of detachment cross section. Then MTT theory is used to unfold momentum transfer cross section from available experimental data for reduced mobility [11].

For calculation of cross section set for F⁻ + F₂ [12] we have used value 1.2611×10^{-30} m³, for polarizability of F₂ recommended by Spelsberg and Meyer [13].

Cross section set for F⁻ + CF₄ is calculated by taking into account value 2.8155×10^{-30} m³ for dipole polarizability of CF₄.

2.2 Cross section set for F⁻ scattering on BF₃

Thus we have decided to use Nanbu's procedure that was shown to give very good results for a number of ions relevant to plasma processing [14,15]. Elastic scattering in the low energy limit is controlled by polarization force and thus for the same target, the cross-sections as a function of relative energy are almost identical.

If we apply Nanbu's theory by assuming elastic collisions (EL), charge transfer collisions (CT) producing $F_2^- + BF_2$ [16] with threshold energy $E_t = 5.6$ eV, electron detachment (DET) with $E_t = 3.4012$ eV thus initially omitting exothermic reaction [17]:

$$F^- + BF_3 \rightarrow BF_4^-, \qquad (1)$$
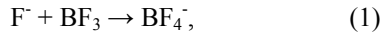
we obtain resulting cross section set as shown in Figure 1. In these calculations we used polarizability of $3.31 \, 10^{-30}$ m³ for BF₃ from [18].

In the low energy limit the cross sections are similar due to dominant polarization of the target. At higher energies reactive collisions including the non conservative collisions become efficient with different possible processes.
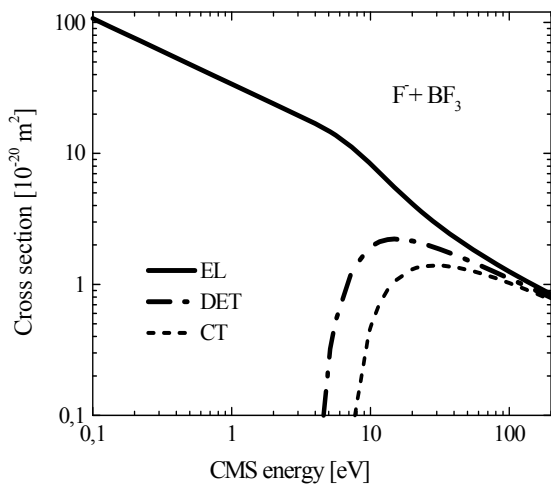

Figure 1. Cross section set for F⁻ scattering on BF₃.

Cross section for exothermic reactions can be expressed as [19, 20] $\sigma_{exo} = f\sigma_L$, where σ_L is orbiting cross section [21] and f the probability of exothermic reaction. It is also known [20] that during reaction (1) stabilization must proceed either radiatively or collisionally [22]. Very similar situation appears in the case where BF_4^- emerges from the surface sputtering of the cluster BF₃ ions [20].

Thus one may account for competition between collisions of radiatively stabilized reaction (1) and elastic collisions by using elastic cross section σ_{e0} from Nanbu's theory as an orbiting cross section. Now the cross section for exothermic reaction is $\sigma_{exo} = f\sigma_{e0}$, where f is selected to define elastic cross section as $\sigma_e = (1-f)\sigma_{e0}$, where σ_{e0} is the elastic cross section (EL) shown in Fig. 1.

3. MONTE CARLO METHOD

The swarm is an ensemble of charged particles travelling through the neutral gas and balancing

between the energy and momentum gained from the external (electric) field and dissipating the energy and momentum in collisions with the background gas [24].

Assuming that probability of collisions of swarm particles with collisions products can be neglected a swarm of particles is not affected by other charged particles so one may assume that external voltage defines the field.

Swarm parameters are generally applied to plasma modeling and simulations. At the same time, the nonequilibrium regime in discharges is well represented under a broad range of conditions by using the Boltzmann equation with collisional operator representing only binary collisions.

In this work the Monte Carlo simulation technique for ion transport that accounts for finite gas temperature of the background gas particles [25] is used to calculate swarm parameters of F⁻ ions in gas at temperature T=300 K.

4. TRANSPORT PARAMETERS OF THE F⁻ IONS

The critical review of experimentally obtained transport properties of gaseous halogen ions is presented in [26].

The mobility K of an ion is the quantity defined as the velocity attained by an ion moving through a gas under unit electric field. One often exploits the reduced or standard mobility defined as:

$$K_0 = \frac{v_d}{N_0} NE \qquad (2)$$

where v_d is the drift velocity of the ion, N is the gas density, at elevated temperature T, E is the electric field and $N_0 = 2.686763 \times 10^{25}$ m⁻³ is the standard gas density (of an ideal gas at T=273K and p=101 325 kPa).

In Figure 2 we show the results obtained for reduced mobility as a function of E/N.

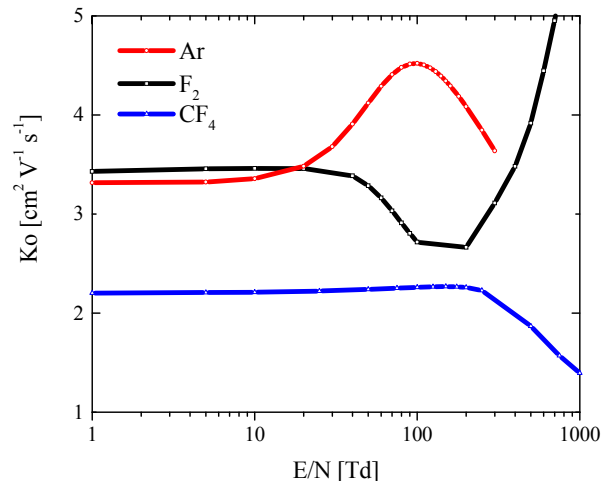**Figure 2. Reduced mobility of F⁻ ions in atomic and molecular gases.**

One had to be aware of non-conservative effects [24] on the drift velocities that are observable at higher E/N. Reduced mobilities shown in Figs. 2 and 4. at higher E/N are represented by so called bulk drift velocities [24]. Diffusion coefficient is a tensor having components that refer to the directions parallel and

perpendicular to the electric field named longitudinal and transverse diffusion coefficients respectively.

In Figure 3 we show characteristic energies (longitudinal diffusion coefficient normalized by mobility eD_L/K in units eV. These data can be directly used in global models for discharges for F^- ions.
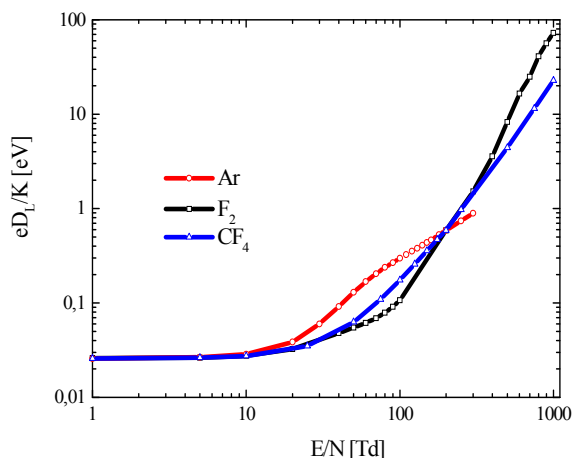

Figure 3. Characteristic energy of F^- ions in atomic and molecular gases in longitudinal direction.

4.1 Transport of F in BF$_3$

In Fig. 4. we show results for reduced mobility as a function of E/N for F^- ions in BF$_3$ distinctive by inclusion of reaction (1). Results for reduced mobility obtained by Monte Carlo simulation for the cross-section set shown in Fig. 1 ($f=0$) are shown in Fig. 4 (connected full circles). Results for reduced mobility obtained when exothermic reaction is present ($f=0.5$) are almost twice larger (connected open circles) with respect to results without exothermic reaction.
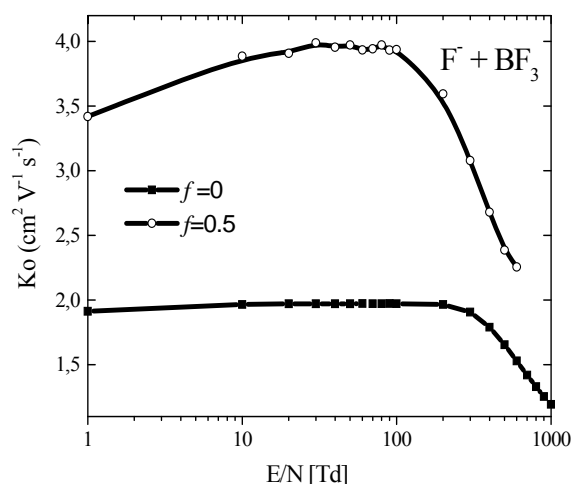

Figure 4. Reduced mobility of F- ions in BF3.

5. REMARKS

The cross sections for scattering of F^- ions on molecule are calculated by using Nanbu's theory [9] separating elastic from reactive collisions.

Monte Carlo technique was applied to perform calculations of the mean energy per particle and drift velocity as a function of reduced electric field in DC electric fields.

The cross-sections and transport data for technologically very important gas BF$_3$ have been determined by using simple theory. While it is a good basis for modeling it would be much better to add a data base of measured transport coefficients and then to perform the analysis again.

REFERENCES

[1] Lieberman, M.A. and Lichtenberg, A.J.: *Principles of Plasma Discharge and Materials Processing*, Wiley Hoboken, 2005.

[2] Lee, C. and Lieberman, M.A.: Global model of Ar, O$_2$, Cl$_2$, and Ar/O$_2$ high-density plasma discharges, Journal of Vacuum Science and Technology A, Vol. 13, pp. 308-380, 1995.

[3] Gudmundsson, J.T and Lieberman, M.A.: Model and measurements for a planar inductive oxygen discharge, Plasma Sources Science and Technology, Vol. 7, pp. 1-12, 1998.

[4] Hiraoka, K., Nasu, M., Katsuragawa, J, Sugiyama, T., Ignacio, E.W. and Yamabe, S. : How is the Fluoride Ion Bound to O$_2$, N$_2$, and CO Molecules, The Journal of Physical Chemistry A, Vol. 102, pp.6916-6920, 1998.

[5] Takahashi, M., Maeda, K., Kitamura,T., Takasaki, M. and Horiguchi, S.: Experimental study of formation kinetics in a discharge-pumped F$_2$ laser, Optics Communications, Vol. 116, pp. 269-278, 1995.

[6] Matsui, J., Nakano, N., Petrović, Z. Lj. and Makabe, T.: The effect of topographical local charging on the etching of deep- submicron structures in SiO$_2$ as a function of aspect ratio, Applied Physics Letters, Vol. 78, pp. 883-885, 2001.

[7] Yamamoto, H., Matsumoto, S., Okada, K., Yu, J. and Hirakuri, K.: Synthesis of c-BN films by using a low-pressure inductively coupled BF$_3$–He–N$_2$–H$_2$ plasma, Diamond and Related Materials, Vol. 15, pp.1357 – 1361, 2006.

[8] Petrović, Z.Lj, Dujko, S., Marić, D., Malović, G., Nikitović, Ž., Šašić, O., Jovanović, J., Stojanović, V. and Radmilović-Rađenović, M.: Measurement and interpretation of swarm parameters and their application in plasma modelling, Journal of Physics D: Applied Physics, Vol. 42, 194002, 2009.

[9] Denpoh, K. and Nanbu, K.: Self-consistent particle simulation of radio-frequency CF$_4$ discharge with implementation of all ion–neutral reactive collisions, Journal of Vacuum Science & Technology A, Vol. 16, pp. 1201-1207, 1998.

[10] Petrović, Z.Lj., Raspopović, Z.M., Stojanović, V.D., Jovanović, J.V., Malović, G., Makabe, T. and Urquijo J.De: Data and modeling of negative ion transport in gases of interest for production of integrated circuits and nanotechnologies, Applied Surface Science, Vol. 253, pp. 6619–6640, 2007.

[11] Jovanović, J.V. and Petrović, Z.Lj.: Cross sections and transport properties of negative ions in rare gases, Journal of Physics: Conference Series, Vol. 162, 012004, 2009.

[12] Stojanović, V., Raspopović, Z., Jovanović, J., Nikitović, Ž. And Petrović, Z. Lj.: Transport of F⁻ ions in F₂, Europhysics Letters, to be published 2013.

[13] Spelsberg, D. and Meyer, W.: Static dipole polarizabilities of N₂, O₂, F₂ and H₂O, Journal of Chemical Physics, Vol. 101(2), pp.1282-1288, 1994.

[14] Georgieva, V., Bogaerts, A. and Gijbels, R.: Numerical study of Ar/CF4/N2 discharges in single- and dual-frequency coupled plasma reactors, Journal of Applied Physics, Vol. 94, pp.3748-3757, 2003.

[15] Georgieva, V., Bogaerts, A. and Gijbels, R.: Numerical investigation of ion-energy-distribution functions in single and dual frequency capacitively coupled plasma reactors, Physical Review E, Vol. 69, 026406, 2004.

[16] MacNeil, K.A.G. and Thynne, J.C.J.: Negative Ion formation by boron trifluoride and phosphorus trifluoride, The Journal of Physical Chemistry A, Vol. 74, (1970) pp. 2257-2262.

[17] Veljković, M., Nešković, O, Zmbov, K.F,. Borshchevsky, A.Y., Vaisberg, V.E. and Sidorov, L.N.: Heats of Formation of BF, ions and the fluorine anion affinity of BF₃ molecules, Rapid Communications in Mass Spectrometry, Vol. 5, pp.37-39, 1991.

[18] Szmytkowski, C., Piotrowicz, M., Domaracka, A., Klosowski, L., Ptasinska-Denga, E. and Kasperski, G.: Electron collisions with trifluorides: BF₃ and PF₃ molecules, Journal of Chemical Physics Vol. 121, pp. 1790-1795, 2004.

[19] Sakimoto, K.: Ion-molecule reactions at extremely low energies: H⁻ + H→H₂ + e, Chemical Physics Letters - Journal, Vol. 164, pp.294-298, 1989.

[20] Babcock, L.M. and Streit, G.E.: Third-body effects in termolecular reactions. halide ion addition to boron trifluoride and boron trichloride, The Journal of Physical Chemistry, Vol. 88, pp.5025-5031, 1984.

[21] McDaniel, E.W., Cermak, V., Dalgarno, A., Ferguson, E.E. and Friedman, L.: *Ion-Molecule Reactions,* Wiiey-lnterscience, New York, 1970.

[22] Herd, C.R. and Babcock, L.M.: Radiative stabilization in the addition of F⁻ to BF, The Journal of Physical Chemistry, Vol. 91, pp. 2372-2376, 1987.

[23] Zhao, X.L. and Litherland, A.E.: The anions of the Li, Be and B fluorides: The super-halogens and AMS, Nuclear Instruments and Methods in Physics Research Section B, Vol. 259, pp. 224-229, 2007.

[24] Makabe, T. and Petrović, Z.: *Plasma Electronics: Applications in Microelectronic Device Fabrication* Taylor and Francis, CRC Press, New York, 2006.

[25] Ristivojević, Z. and Petrović, Z.: A Monte Carlo simulation of ion transport at finite temperatures, Plasma Sources Science and Technology, Vol. 21, 035001, 2012.

[26] Viehland, L.A. and Mason, E.A.: Transport properties of gaseous ions over a wide energy range, Atomic Data and Nuclear Data Tables, Vol. 60, pp. 37-95, 1995.

ТРАНСПОРТ F- ЈОНА КРОЗ ГАСОВЕ У ТЕХНОЛОШКИМ ПРИМЕНАМА

Јасмина В. Јовановић, Зоран М. Распоповић, Владимир Д. Стојановић, Жељка Д. Никитовић

Негативни халогени јони су заступљени у различитим неравнотежним плазмама које су заступљене у биомедицинским уређајима, нанотехнологијама, електричним пражњењима и хемији атмосфере. Приказани су подаци за моделовање нискотемпературних плазми које садрже F⁻ јоне применом глобалних и других плазма модела. Овај јон је изабран због своје изузетно велике електронегативности, веома је јак нуклеофилни реагент и формира веома јаке везе са Луисовим киселинама у гасној фази. Са друге стране, неизбежан је у производњи c-BN филмова. Ефикасни пресеци за расејање F⁻ јона на атомима Ar и молекулима F₂, CF₄ и BF₃ добијени су применом Нанбуове теорије у којој је могуће раздвојити еластичне од реактивних сударних процеса. Како би се уочили ефекти неконзервативних сударних процеса на брзине дрифта, прорачуни су рађени до високих вредности *E/N* (1000Td).

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Role of Pressure in Transport of F- Ions in BF$_3$ Gas For Technological Applications

In this work we present swarm data obtained for F- ions in molecular gas BF3 necessary to form the global models for the complex collisional plasmas. The new results for scattering cross section set and proposed transport coefficients for F- ions in BF$_3$ that can be used in such models are presented. First we used Nanbu's theory based on thermodynamic threshold energies to calculate cross sections for binary collisions of F- ions with BF$_3$ molecules. Cross section for three body association reaction is included by using exothermic cross section for binary reaction normalized at selected pressure. Monte Carlo method is used to obtain swarm parameters at temperature of T=295 K and pressure of 133.32 Pa (1 Torr).

Keywords: Negative ions, three body rate coefficient,association reaction, F- ion, transport coefficients, Global model, Monte Carlo, cross section set, BF$_3$ gas.

1. INTRODUCTION

Plasma technologies are nowadys almost inavoidable step in all branches of engineering with primary goal to improve various materials properies. In order to control reactive processes related to semiconductor properties present knowledge stil have to be extended. Thus goal of this work is to extend database for modeling of complex low temperature collisional plasmas containing F- ions by using a global [1,2,3] and other plasma models. Recent progress in plasma modeling have made contributions to a deeper understanding of the discharge phenomena and to the optimization of reactor design or operating conditions.

The electronegativity of the F atom is the largest of all atoms and F- ion is highly reactive nucleophilic reagent and generally forms strong bonds with many Lewis acids in the gas phase [4]. Association reaction of F- with BF$_3$ produces very stable BF$_4$- ion. This reaction proceeds either with radiative or collisional stabilisation both with similar intensities at pressures of about 100 Pa and temperatures near room temperature [5]. Immediately follows that production of BF$_4$- in three body association process needs to be included in all existing plasma models [6,7,8] for cases with similar pressures and temperatures.

The negative halogen ions are abundant in various forms of nonequilibrium plasmas relevant to applications such as excimer lasers [9] and electrical discharges, biomedical devices, nanotechnologies and in radiation chemistry in the atmosphere. For example, it is experimentaly found that negative ions are able to taylor

increase of the etch rate and to improve the etch profile [10]. F- ions are involved in the production of cubic boron nitride (c-BN) films [11] used in various engineering projects. It is thus necessary to understand plasma chemistry and the behavior of negative ions not only for the control of plasma processing devices but also for understanding properties of produced materials.

In this work our focus will be to study effect of three body association reaction to transport parameters of F- ions in BF$_3$ gas.

The transport parameters include mean energy, drift velocity, diffusion coefficients, ionization and attachment coefficients and chemical reaction coefficients for F- ion [12,13]. Ion transport coefficients are used in both fluid and hybrid models of plasmas. Indirectly, transport coefficients are used to check validity of the cross sections in the sets used in computer modelling.

2. ION MOLECULE COLLISION MODEL

In plasma modeling ion-molecule collisions have been usually simplified for lack of detailed collision data. In this work instead of very often cited Langevin's theory to determine effective cross section for collision and reaction rate we used Nanbu's theory [14, 15] that may succesfully distinguish between reactive and nonreactive collisions of collision partners.

2.1 Nanbu's theory

The cross sections for scattering of F- ions on several molecules are calculated by using Nanbu's theory [14, 15, 16]. According to Nanbu's theory elastic and reactive endothermic collision are separated and treated by accounting for thermodynamic threshold energy and branching ratio according to the Rice–Rampsperger–Kassel (RRK) theory [14]. Within the RRK theory

excited molecular complex is treated as excited activated complex where internal energy is distributed among s equivalent oscillators–vibrational modes of the complex. For example, in such a way we used $s = 3$ for $F^- + BF_3$ system.

2.2 Cross section set for F^- scattering on BF_3

In this work we used cross sections assembled by using Nanbu's procedure that was shown to give useful results for a number of ions relevant to plasma processing [17,18]. Elastic scattering in the low energy limit is controlled by polarization force and thus for the same target, the cross sections as a function of relative energy have almost identical shape.

Nanbu's theory by assuming elastic collisions (EL), charge transfer collisions (CT) producing $F2^- + BF2$ [19] with threshold energy $E_t = 5.6$ eV, electron detachment (DET) with $E_t = 3.4012$ eV is applied [8] (See Fig. 1). In the low energy limit the cross sections are similar due to dominant polarization of the target while at higher energies reactive collisions become efficient and it is common to represent cross sections at these energies by hard sphere cross sections (see arrows in Fig. 1). The total momentum transfer cross section at high energies is distributed between elastic and reactive processes as shown in Fig 1.
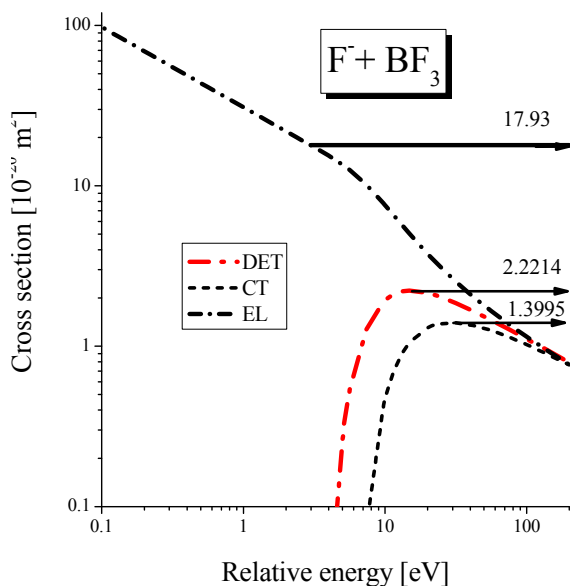

Figure 1. Cross sections for F^- scattering on BF_3.

Exothermic reaction [17]:

$$F^- + BF_3 \rightarrow BF_4^-, \qquad (1)$$

is included in the cross section set [8] and its cross section is shown in Figure 2. Competition between radiatively stabilized reaction (1) and elastic collisions is included in the cross section set.

Cross section representing three body association reactions at elevated pressure can be expressed with the same relation used for binary exothermic reaction [8]. Cross section and its pressure dependence comes from the rate coefficient for three body reaction that is reduced to two body rate coefficient [21] with BF_3 gas density $[N_{BF3}]$ at elevated pressure

$$\sigma_{3B} = \sigma_{exo} \frac{k_3}{k_2} [N_{BF3}], \qquad (2)$$

where σ_{exo} is the cross section for binary exothermic reactions (see EXO in Fig. 2) and k_3 (20 cm^6/s/s/molec^2) and k_2 are the rate coefficients for three body and two body association reactions respectively. Cross sections for exothermic reactions are shown in Fig. 2. Since one may expect slow fall off of the exothermic cross section at highest energies (see for example ref. [22]) we studied this effect by cutting off cross section for three body reaction at energies 0.1 eV (cut 0.1), 0.5 eV (cut 0.5) and 1 eV (cut 1) (see Fig. 2) and calculating transport parameters.
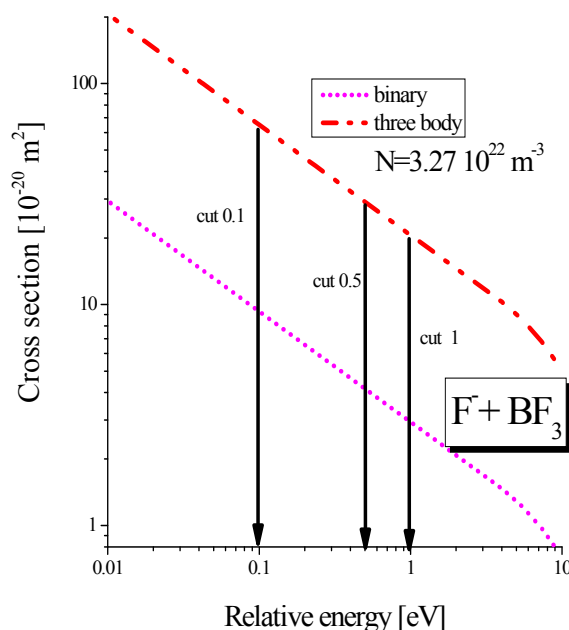

Figure 2. Cross sections for exothermic reactions for F^- scattering on BF_3 for at pressure 1 Torr and T=295 K.

3. MONTE CARLO METHOD

The swarm is ensemble of charged particles travelling through the neutral gas and balancing between the energy and momentum gained from the external (electric) field and dissipating the energy and momentum in collisions with the background gas [13].

Assuming that probability of collisions of swarm particles with collisions products can be neglected swarm of particles is not affected by other charged particles so one may assume that external voltage defines the field.

Swarm parameters are generally applied to plasma modeling and simulations. At the same time, the nonequilibrium regime in discharges is well represented under a broad range of conditions by using the Boltzmann equation with collisional operator representing only binary collisions.

In this work the Monte Carlo simulation technique for ion transport that accounts for finite gas temperature of the background gas particles [23] is used to calculate swarm parameters of F^- ions in gas at temperature T=295 K and pressure p=133.3 Pa.

4. TRANSPORT PARAMETERS OF THE F- IONS

Experimental data for transport coefficients of F- in BF$_3$ does not exist in the literature. The critical review of experimentally obtained transport properties of F- and other halogen ions in various gases is presented in [24].

The mobility K of an ion is the quantity defined as the velocity attained by an ion moving through a gas under unit electric field. One often exploits the reduced or standard mobility defined as:

$$K_0 = \frac{v_d}{N_0} NE \qquad (2)$$

where v_d is the drift velocity of the ion, N is the gas density, at elevated temperature T, E is the electric field and $N_0 = 2.686763\ 10^{25}\ m^{-3}$ is the standard gas density (of an ideal gas at T=273 K and pressure p=101 325 kPa).

In following we show the Monte Carlo results obtained for T=295 K and pressure 133.3 Pa. For all cases in Fig. 2 cross sections for exothermic reaction is scaled in such a way that all obtained exothermic rate coefficients have the same value at lowest E/N value.

In Figure 3 we show the results obtained for reduced mobility as a function of *E/N*. One had to be aware of non-conservative effects [13] on the drift velocities that are observable at higher *E/N*. Values of the reduced mobility shown in Figs. 3 at higher *E/N* are represented by so called bulk drift velocities [13].

Due to the discrepancy from constant collision frequency reduced mobility at low E/N's shows deviations from plateau obtained for case of uncut exothermic cross section (dashed and thick line; see also ref. [8]). Widest discrepancy with respect to E/N is related to lowest energies cut off of exothermic process (cut 0.1). Electrons passing exothermic process above 0.1 eV increase reduced mobility orders of magnitudes higher. Note that reduced mobility for case cut01 is obtained for exothermic process multiplied by factor of 10 with respect to other cases in order to keep constant rate coefficient for association reaction.
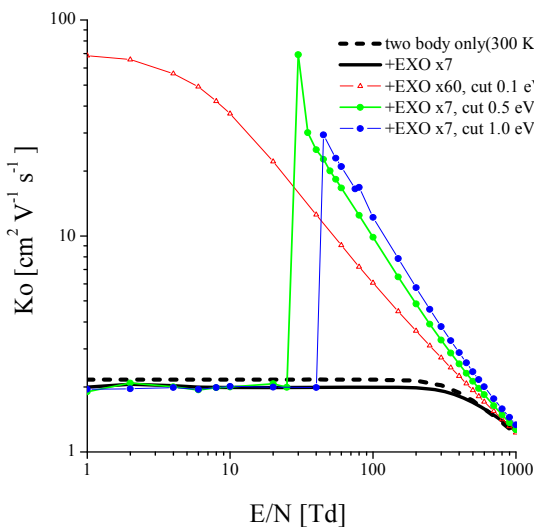
One had to be aware of non-conservative effects [13] on the drift velocities that are observable at higher E/N. The reduced mobility shown in Figs. 3 at higher E/N are represented by so called bulk drift velocities [13].

In Figure 4 we show mean energies as a function of reduced electric field. These data can be directly used in global models for discharges for F- ions. Significant increase of mean energy for the case cut0.1 is due to the high energy electrons that passed without association reaction. As cut off is shifted towards higher energies groups of higher energy ions are passing without association thus increasing mean energy. Such behaviour is clearly shown for all curves for E/N > 50 Td.
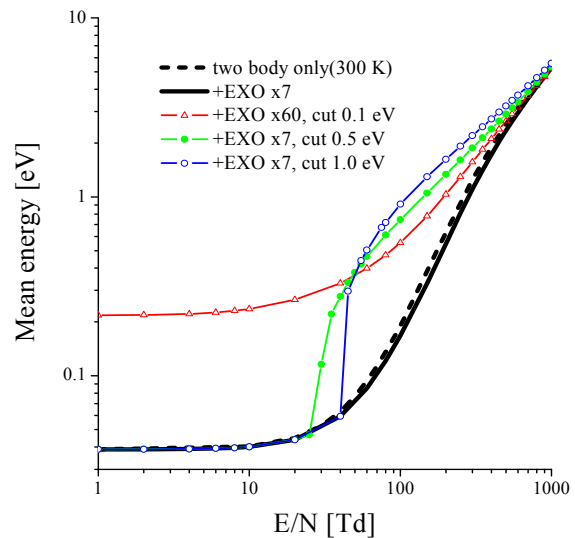
Figure 4. Mean energy of F$^-$ ions in BF$_3$ in longitudinal direction.

In Figure 5 we show the rate coefficient for association reaction as a function of E/N. As assumed, all the rate coefficients are the same at lowest E/N while fall of the rate coefficient at high E/N is proportional to the cut off of the cross section for exothermic reaction.

Figure 5. Rate coefficient for association reaction of F$^-$ ions in BF$_3$.

Figure 3. Reduced mobility of F$^-$ ions in BF$_3$.

5. REMARKS

The existing cross sections for scattering of F^- ions on BF_3 molecule are extended by adding the cross section for three body association that is depending on elevated pressure. For three variations of three body cross section transport parameters are obtained and discussed.
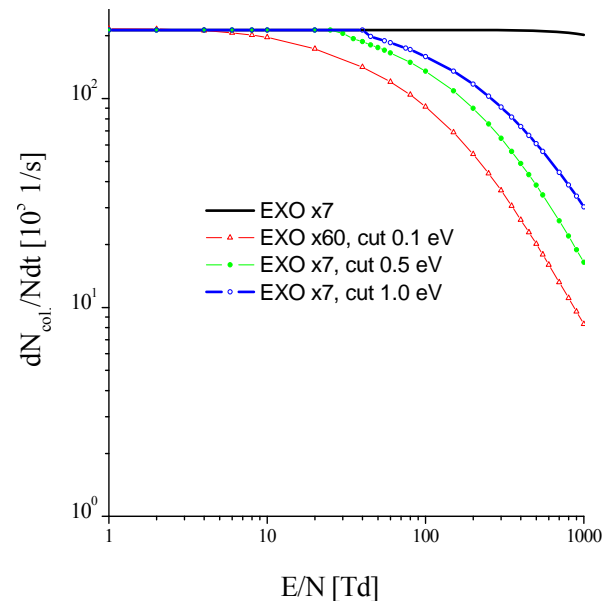Monte Carlo technique was applied to perform calculations of the mean energy per particle and drift velocity as a function of reduced electric field in DC electric fields. Similar study from the point of view of transport theory where effects of three body electron attachment on transport coefficients are studied is presented in Ref. [25].

The cross sections and transport data for technologically significant gas BF_3 have been assesed by using simple theory and facts. This cross section set is a good basis for modeling. It would be reliable to add a data base of measured transport coefficients and then to perform the analysis again.

ACKNOWLEDGMENT

REFERENCES

[1] Lieberman, M.A., Lichtenberg, A.J., Principles of Plasma Discharge and Materials Processing, Wiley Hoboken, 2005.

[2] Lee, C. and Lieberman, M.A.: Global model of Ar, O2, Cl2, and Ar/O2 high-density plasma discharges, J. Vac. Sci.Technol. A 13, pp. 308-380, 1995.

[3] Gudmundsson, J. T and Lieberman, M. A.: Model and measurements for a planar inductive oxygen discharge, Plasma Sources Sci. Technol. 7, pp. 1-12, 1998.

[4] Hiraoka, K., Nasu, M., Katsuragawa, J, Sugiyama, T., Ignacio, E.W., Yamabe, S. : How is the Fluoride Ion Bound to O2, N2, and CO Molecules?, J. Phys. Chem. A 102, pp.6916-6920,1998.

[5] Herd, C. R and Babcock, L. M.: Radiative Stabilization in the Addition of F- to BF, J. Phys. Chem 91, pp. 2372-2376, 1987.

[6] Jovanović J.V, Raspopović, Z.M., Stojanović V.D., Nikitović Ž.D.: Transport of F- Ions in Gaseous Environment for Technological Applications, FME Transactions 41, pp.163-166, 2013.

[7] Stojanović, V.D. Raspopović, Z.M., Jovanović, J.V., Radovanov, S.B., Nikitović Ž.D., Petrović Z.Lj.: Cross sections and transport properties of positive ions in BF3 plasmas, Nucl. Instrum. Meth. Phys. Res. B 279, pp.151-154, 2012.

[8] Nikitović, Ž.D., Raspopović, Z. M., Stojanović, V.D., Jovanović, J.V.: Transport parameters of F- ions in Ar/BF3 mixtures, accepted for publication in Europhys. Letters 2014.

[9] Takahashi, M., Maeda, K., Kitamura,T., Takasaki, M. and Horiguchi, S.: Experimental study of formation kinetics in a discharge-pumped F2 laser, Opt. Comm. 116, pp. 269-278, 1995.

[10] Matsui, J., Nakano, N., Petrović, Z. Lj. and Makabe, T.: The effect of topographical local charging on the etching of deep- submicron structures in SiO2 as a function of aspect ratio, Appl. Phys.Lett, 78, pp. 883-885, 2001.

[11] Yamamoto, H., Matsumoto, S., Okada, K., Yu, J., Hirakuri, K.: Synthesis of c-BN films by using a low-pressure inductively coupled BF3–He–N2–H2 plasma, Diamond & Related Materials 15, pp.1357 – 1361, 2006.

[12] Petrović, Z. Lj, Dujko, S., Marić, D., Malović, G., Nikitović, Ž., Šašić, O., Jovanović, J., Stojanović, V. and Radmilović-Rađenović, M.: Measurement and interpretation of swarm parameters and their application in plasma modelling, J. Phys. D: Appl. Phys. 42, 194002, 2009.

[13] Makabe, T., Petrović, Z.: Plasma Electronics: Applications in Microelectronic Device Fabrication Taylor and Francis, CRC Press, New York, 2006.

[14] Denpoh, K., Nanbu, K.: Self-consistent particle simulation of radio-frequency CF4 discharge with implementation of all ion–neutral reactive collisions, J. Vac. Sci. Technol. A 16, pp. 1201-1207, 1998.

[15] Petrović Z. Lj., Raspopović Z. M., Stojanović V. D., Jovanović J.V., Malović, G., Makabe T., Urquijo J. De: Data and Modeling of Negative Ion Transport in Gases of Interest for Production of Integrated Circuits and Nanotechnologies, Applied Surface Science 253, pp. 6619–6640, 2007.

[16] Stojanović, V., Raspopović, Z., Jovanović, J.B., de Urquijo, J., Petrović, Z. Lj., Collision cross section set and transport properties of CF3+ in CF4, J. Phys.: Conf. Series, 514, 012059,2014.

[17] Georgieva, V., Bogaerts, A., Gijbels R.: Numerical study of Ar/CF4/N2 discharges in single- and dual-frequency coupled plasma reactors, J. Appl. Phys. 94, pp.3748-3757, 2003.

[18] Georgieva, V., Bogaerts, A., Gijbels, R.:Numerical investigation of ion-energy-distribution functions in single and dual frequency capacitively coupled plasma reactors, Phys. Rev. E 69, 026406, 2004.

[19] MacNeil, K. A. G. and Thynne, J. C. J.: Negative Ion Formation by Boron Trifluoride and Phosphorus Trifluoride, J. Phys. Chem., Vol. 74, pp. 2257-2262, 1970.

[20] Veljković, M. , Nešković, O. and Zmbov, K. F. A. Ya. Borshchevsky, V. E. Vaisberg and L. N. Sidorov,: Heats of Formation of BF, Ions and the Fluorine Anion Affinity of BF3 Molecules, Rapid Comm. Mass. Spectrom., 5, pp.37-39,1991.

[21] Babcock, L.M. and Smith,G.E., Third-Body Effects in Termolecular Reactions. Halide Ion Addition to Boron Trifluoride and Boron Trichloride, J. Phys. Chem. , 88, pp.5025-5031,1984.

[22] Koizumi, H., Armentrout, P.B., J.Chem.Phys., 119, p.12819, 2003.

[23] istivojević, Z. and Petrović, Z.: A Monte Carlo simulation of ion transport at finite temperatures, Plasma Sources Sci. Technol. 21, 035001, 2012.

[24] Viehland, L. A. and Mason, E. A.: Transport properties of gaseous ions over a wide energy range, At. Data. Nucl. Data Tables. 60, pp. 37-95, 1995.

[25] Dujko,S., Ebert, U., White, R.D. and Petrović, Z.Lj.: Boltzmann Equation Analysis of Electron Transport in a N2–O2 Streamer Discharge, Jap. J. of Appl. Phys. 50, 08JC01, 2011.

УЛОГА ПРИТИСКА У ТРАНСПОРТУ F⁻ ЈОНА У ГАСУ БОР-ТРИФЛУОРИДА У ТЕХНОЛОШКИМ ПРИМЕНАМА

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У овом раду представили смо транспортне параметре добијене за F⁻ јоне у молекуларном гасу BF_3 неопходне за формирање глобалних модела за комплексне сударне плазме. Нови резултати за сет пресека и добијени транспортни коефицијенти за F⁻ јоне у BF_3 који се могу користити у таквим моделима су представљени. Прво смо користили Нанбу теорију за одређивање пресека бинарних судара F⁻ јона са молекулима BF_3. Пресек за судар три тела укључује егзотермни бинарни пресек нормиран на изабрани притисак. Користили смо Монте Карло методу за добијање транспортних параметара на температури од T = 295 K и притисаку од 133.32 Pa (1 Torr).

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Modeling of the Effect of Radicals on Plasmas Used for Etching in Microelectronics

Plasma etching represents one of the critical steps in manufacturing of integrated circuits. Further optimization of plasma equipment is needed since new generations in technology require different plasma chemistry. In this paper, we will study the influence of radicals on the plasma characteristics, since it was often neglected in plasma models. The radicals dominate attachment of electrons as the basic etching mixture is weakly electronegative and they also affect the drift velocity through modified momentum balance. We have used numerical solutions to the Boltzmann equation and Monte Carlo simulations (MCS) to determine the transport coefficients of electrons.

Keywords: CF_4, transport coefficients, Global model, Monte Carlo code

1. INTRODUCTION

The CF_4 has an important role in technological applications such as discharge switches [1], in gaseous detector technology [2] and for the development of particle detectors [3, 4]. The CF_4 belongs to Freon group of gases that unfortunately significantly affect the global warming of our planet. Its atmospheric lifetime is estimated at over 50 000 years and it has one of the largest potentials to global warming. Because of this it is important to continue research related to removal of this Freon from the atmosphere. One technique proposed to achieve this by applying plasma which could be induced by focused microwave radiation [5].

Carbon tetrafluoride is commonly used in today's semiconductor industry for etching of dielectric materials, such as SiO_2 [6, 7] and also for deposition of fluorinated polymer films.

2. CROSS SECTION SETS

In order to achieve further improvements of the high resolution plasma processing for future generations of integrated circuits, empirical development of plasma processing tools has to be replaced by exact modeling of the physics and chemistry of plasmas in real geometries.

A description of electron kinetics in non-equilibrium plasma modeling necessarily includes, either directly or indirectly the calculation of transport coefficients. Such calculations are usually based on compilations of cross sections from various sources [8]. Requirement to establish reliable transport coefficients for CF_4 plasmas is especially demanding since practical conditions include many reac–tive species. The reactive radicals have often been neglec–

ted in plasma models. Free radical species, such as CF_y (y=1-3) and fluorine atoms, play important but complex roles in plasma processing. Electron transport coefficients were calculated for pure CF_4 and in X/CF_4 mixtures (X= F, F_2, CF, CF_2 and CF_3) for the conditions overlapping with those used in plasma technologies for semiconductor production. In this paper we shall only consider CF. Set of cross sections for CF, CF_2 and CF_3 is based on work of Rozum *et al.* [9]. Set of cross sections for F_2 is from [10] and for F is according to Gudsmundsson [11].

Attachment and ionization rate coefficients were calculated for 0.01%, 0.1%, 1% and 10% of the radical species X in CF_4. Transport coefficients are obtained by using numerical solution of Two Term approximation to Boltzmann equation [12].

3. RESULTS AND DISCUSSION

The basic cross sections of pure CF_4 were used from [8] with a modification made in [13, 14] in order to include production of CF_3^- ions. Complete cross section set is shown in Figure 1.
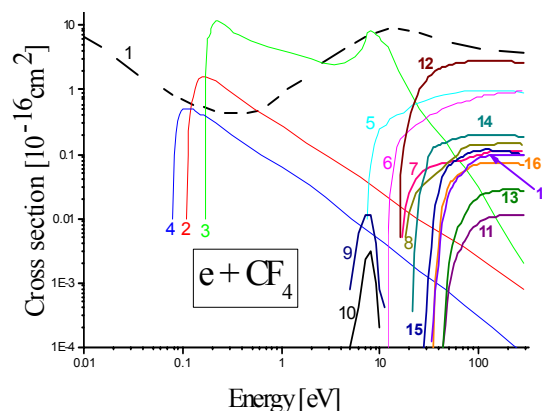

Figure 1. Electron impact cross sections for scattering on CF₄ (1- el. mom. transfer, 2- vib.exc. v=1, 3-vib.exc. v=3, 4 - excitation v=4, 5-electronic excitation, 6-dissociation to products CF₃, 7- dissociation to products CF₂, 8- dissociation to products CF, 9-diss.el.at. (F), 10-diss.el.at (CF₃⁻), 11-ionization CF₃⁺ + F + 2e, 12-17 -other channels of ionization.

In Figure 2 we show the input data for the cross sections for e-CF scattering.
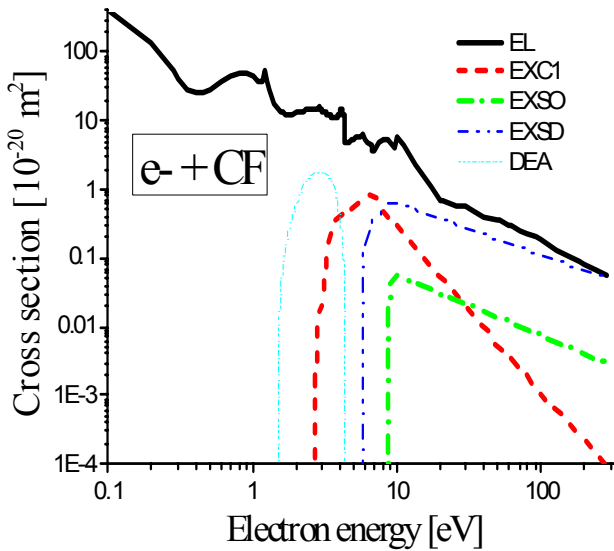

Figure 2. Electron impact cross sections for scattering on CF (EL-elastic momentum transfer. EXC1, EXCM-excitation to first exc.state, EXSB-exc.to bound and radiative state, EXSO-exc.to other dissociative states, EXSD-exc to dissociative A and B states,DEA-dissociative attachment).
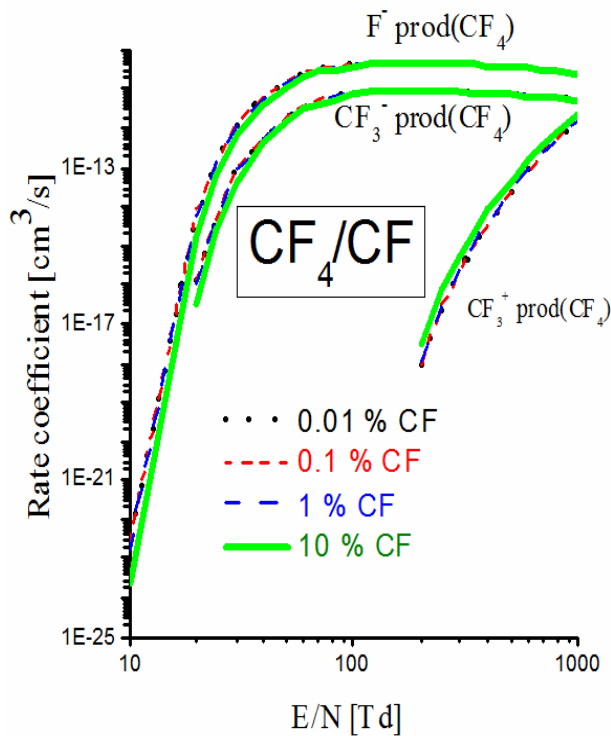

Figure 3. Total rate coefficients for attachment in CF₄/ CF mixture.

We present transport coefficients for electrons in mixtures of CF_4 with its radicals (specifically CF) for ratios of the electric field to the gas number density *E/N* from 1 Td to 1000 Td (1 Td=10^{-21} Vm^2).

The rate coefficients for the formation of F⁻, CF_3^- and CF_3^+ ions calculated for the CF_4/CF mixture are presented in Figure3. In principle almost negligible differences between low and higher abundance data indicate a very small perturbations of the EEDF as those

ions are produced in collisions of electrons with CF_4 molecule.

In the Figure 4. we show the Electron Energy Distribution Function (EEDF) in mixtures of CF_4/ CF.

Even the large attachment introduced by CF for electron energies around 1 eV only causes minor differences in the EEDF shape for energies below 0.5 eV and insignificant changes at higher energies.

The electron mean energy and electron drift velocity in mixtures of CF_4/ CF as a function of *E/N* is shown in Figure5 and Figure6. Adding 1% or less of CF did not significantly change the mean energy, although the effect on the momentum balance is significant as can be observed in the disappearance of the high velocity peak (enhanced drift velocity) and of the negative differential conductivity (NDC). This change on its own is sufficient to warrant taking into account radicals when one models realistic plasma devices.
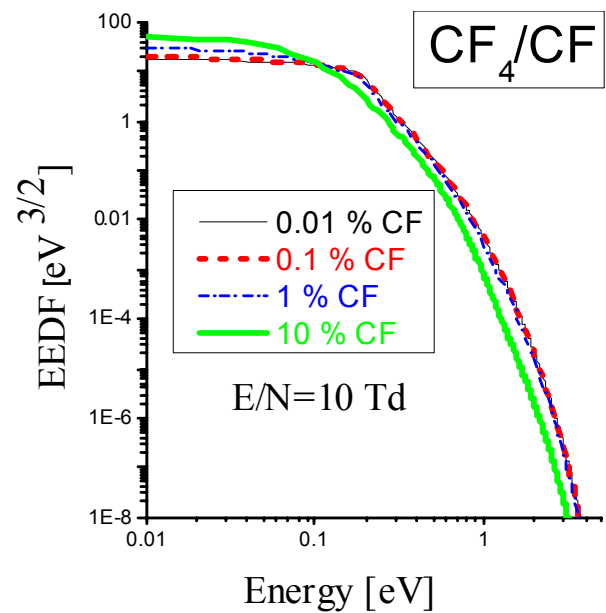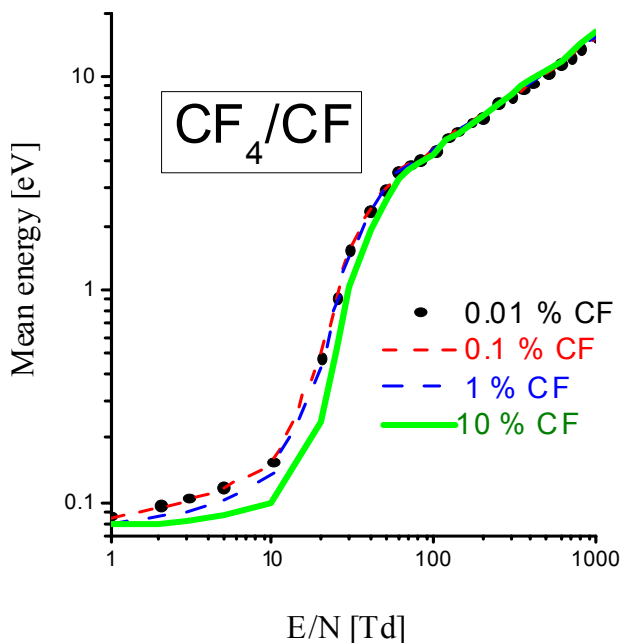

Figure 4. EEDF in CF_4/ CF mixture.

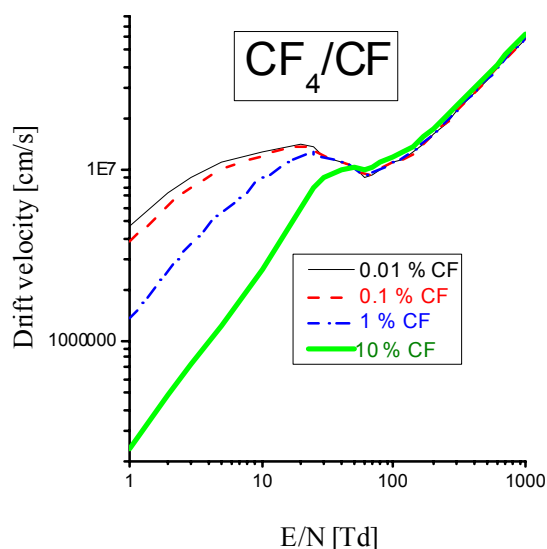**Figure 5. Mean energy in CF4/ CF mixture.**

Figure 6. Drift velocity in CF$_4$/ CF mixture.

4. REMARKS

It was shown in this paper that even at small abundances some rate and transport coefficients may change drastically and the best example is the attachment rate. The most abundant radical in plasmas containing CF$_4$ is CF [15, 16] and it can be found even at abundances of the order of several %. As CF have attachment at low energies with thresholds considerably smaller than that of the dissociative electron attachment for electrons in CF$_4$ the overall attachment rate is enhanced and extended to lower energies. Attachment rate at low mean energies increases many orders of magnitude, even the peak value is considerably increased. Also it was found that even a small amount of radicals affects the plasma and makes it more electronegative.

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REFERENCES

[1] Hunter S. R., J. G. Carter and Christophorou L.G.: Electron transport studies of gas mixtures for use in e-beam controlled diffuse discharge switches, *J. Appl. Phys.* **58,** pp. 3001-3015, 1985.

[2] James D. R., Christophorou L. G. and Mathis R. A.: New unitary and multicomponent gaseous dielectrics *in Gaseous Dielectrics II* (ed. Christophorou L.G.), Pergamom, New York, p.115, 1980.

[3] Kopp M. K., Valentine K. H., Christophorou L. G. and Carter J. G.: New gas mixture improves performance of ^{3}He neutron counters, *Nucl. Instrum. Methods* **201**, pp.395-401, 1982.

[4] Yamashita T., Kurashige H., Morii M. M., Nakamura T. T., Nomura T., Sasao N., Shibata K., Fukushima Y., Ikegami Y., Kobayashi H. and Taniguchi T.: Measurements of electron drift velocities and positive ion mobilities for gases containing CF$_4$ II, "*Nucl. Instrum. Methods Phys. Res. A* **317**, pp.213-220, 1992.

[5] Bzenić S., Manola S. S. and Petrović Z. Lj.: The influence of frequency on the efficiency of dissociation of freons by microwave discharges, Proceedings *of the 25th European Microwave Conference*, Swanley Nexus, Bologna, Italy, p.856, 1995.

[6] Makabe T. and Petrovic Z. Lj.: Plasma Electronics, Taylor and Francis New York , 2006.

[7] Lieberman and Lichtenberg, "Plasma processing of Materials", 1994.

[8] Kurihara M., Petrović Z. Lj. and Makabe T.: Transport coefficients and scattering cross-sections for plasma modelling in CF$_4$-Ar mixtures: a swarm analysis, *J. Phys. D: Appl. Phys.* **33,** pp. 2146-2153, 2000.

[9] Rozum I., Limao-Vieira P., Eden S. and Tennyson J.: Electron Interaction Cross Sections for CF$_3$I, C$_2$F$_4$ and CFx (x=1-3) Radicals, *J. Phys. Chem. Ref. Data,* Vol. **35**, No.**1**, pp. 267-284, 2006.

[10] Morgan W. L. :A critical evaluation of low-energy electron impact cross sections for plasma processing modeling. I: Cl$_2$, F$_2$ and HCl, *Plasma Chemistry and Plasma Processing* **12**, pp. 449-476, 1992.

[11] Gudmundsson J. T.: Global model of plasma chemistry in a low-pressure O$_2$/F$_2$ discharge, *J. Phys. D: Appl. Phys.* **35**, pp. 328-341, 2002.

[12] Morgan W. L. and Penetrante B. M.: ELENDIF: A time-dependent Boltzmann solver for partially ionized plasmas, *Computer Physics Communications* **58**, pp. 127-152, 1990.

[13] Donko Z. and Petrović Z. Lj.: Analysis of a Capacitively Coupled Dual-Frequency CF$_4$ Discharge, *J. Journal of Applied. Phys.* **45**, pp. 8151-8156, 2006.

[14] Donko Z.: personal communication 2006.

[15] Georgieva V. Bogaerts A. and Gejbels R.: Particle-in-cell/Monte Carlo simulation of a capacitively coupled radio frequency Ar/CF$_4$ discharge: Effect of gas composition, *Journal of Applied Physics* **93**, pp. 2369-2379, 2003.

[16] Nikitović Ž., Stojanović V., Booth J. P. and Petrović Z. Lj.: Electron transport coefficients in mixtures of CF$_4$ and CF$_2$ radicals, *Plasma Sources Sci. Technol.* **18,** 035008, 2009.

ЕФЕКТИ РАДИКАЛА У МОДЕЛИРАЊУ ПЛАЗМИ КОРИШЋЕНИХ ЗА НАГРИЗАЊЕ У МИКРОЕЛЕКТРОНИЦИ

Жељка Д. Никитовић, Јасмина В. Јовановић, Урош Цвелбар, Миран Мозетич, Владимир Д. Стојановић

Плазма нагризање представља један од критичних корака у изради интегрисаних кола. Даља оптими– зација плазма уређаја је потребна јер нове генерације у технологији захтевају различиту плазма хемију. У овом раду бавимо се утицајем радикала на плазма карактеристике, што је често занемаривано у плазма моделима. Радикали доминирају захватом електрона чинећи да је базна смеша за нагризање слабо електронегативна, а они такође модификују брзину дрифта преко модификованог баланса момента. Ми смо користили нумеричка решења Болцманове једначине и Монте Карло симулације (МЦС) за одређивање транспортних коефицијената електрона.

Development of Fast Neutral Etching for Integrated Circuits and Nanotechnologies
Fast Neutrals in Gas

Z.Lj. Petrović, V. Stojanović, N. Škoro, Ž. Nikitović, G. Malović, J. Sivoš, D. Marić

Abstract - In this paper we attempt to correlate the recently developed procedure to use fast neutrals as a replacement to fast positive ions in charging free plasma etching with the development in gas discharge, atomic and molecular collision and swarm physics. It is shown how ideas in the gas discharges progressed and how, when it became well known that charging is one of the primary problems in integrated circuit manufacture , it became possible to transfer the ides directly to the processing technology. Our ability to describe sources of fast neutrals as well as possible future developments and applications are also discussed.

I. INTRODUCTION

In the past decade fast neutral etching has become a principal etching mechanism for many of the plasma induced processes in integrated electronics [1]. One could be led to believe that it is not such a recent paradigm change from ion induced to neutral induced etching. In this paper we shall follow the development of the idea of fast neutral etching, the reasons why it was introduced and mostly we shall review the pertinent atomic collision and transport physics that is involved and that still opens room for new fundamental studies and even possible applications. On the other hand, we shall pursue the observation of very fast neutrals in gas discharges with energies close to the largest available energy (energy equal to the total voltage drop times electron charge).

Most importantly we shall summarize our present ability to model the processes due to fast neutrals both in the gas phase and at the surface. That would be the basis for exact representation of fast neutral etching and the next stage in nano-sized integrated electronics. In addition, we shall discuss some possible fields where knowledge of fast neutrals produced in gas discharges may lead to better understanding or control of processing of nano structures.

II. FAST NEUTRALS IN GAS DISCHARGES

Doppler broadened profiles have been used for many years to obtain the kinetic temperature of the background gas. In those studies it has been established that structured

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wings often indicate the existence of some high energy groups. Those have been associated with dissociative processes in plasmas such as dissociative excitation and recombination [2]. Explanation was founded on independently observed profiles in binary collision experiments [3-5]. In principle, if one excites a molecule to a repulsive curve the molecule will slide down the intra-molecular potential leading to dissociation and a large kinetic energy of fragments (depending on the profile of the molecular potential). As a result, structures in the wings of Doppler broadened lines appear and may actually provide information on potentials [3,4].

The dissociative processes may produce fast neutrals only up to around 15 eV which is defined by the Frank Condon overlap of the ground state and repulsive curve. In addition, the release of the resulting fragments appears to be isotropic. On the other hand, a strong anisotropy was observed in profiles of DC discharges with energies even slightly in excess of the limit defined by the potential diagrams [6]. The alternative explanation was that due to acceleration of the positive ions, their momentum was imparted onto the target molecules and the excited fragments after dissociative excitation. However, it was then difficult to explain the wing corresponding to the motion towards the anode. Some degree of anisotropy was even noticed in RF discharges, especially the asymmetric systems and along the line of the external field, while it is absent in the side-on observations [7].

At the same time due to the efforts of Art Phelps [8-10] studies have begun of the spatial profiles of emission from discharges at high E/N (electric field normalized by the gas number density). By the virtue of the Paschen curves [11, 12], the high *E/N* may be achieved at lower pressures (left hand side of the Paschen curve) typically under conditions when electrons have only a few collisions, barely sufficient to sustain the discharge [11, 12]. When operated in the Townsend regime, the profiles mostly depart from the typical exponential growth towards the anode (due to an avalanche of electrons and an increase of their density). It was found that profiles become flat and even peak close to the cathode [8-10, 13]. One explanation was that electrons never achieve equilibrium with the local field due to a small number of collisions. Thus, a beam like component develops and the profile merely represents the shape of the collision cross section against the spatially distributed (i.e. increasing) beam energy. Under those

conditions ions gain high energies, so another way to explain the cathode peak was to invoke excitation by heavy particles.

As a matter of fact, the latter explanation proved to be the valid one albeit with one caveat: the excitation is actually performed by the fast neutrals produced from fast ions in the process of charge transfer collisions [14]. The only exception was the first negative band of nitrogen, where spatial profile peaking close to but not right against the cathode is due to the beam like electron energy distribution convoluting the cross section for this process. This is presently the only known example of a weak excitation by heavy particles [14]. While not entirely impossible, the excitation by ions has a much higher onset and may eventually enter the kinetics but perhaps at energies above 1 keV [15].

Quantitative comparisons were used to prove that the excitation in low current Townsend discharges at very high E/N is due to fast neutral collisions [14,16]. In addition, one experiment was developed as well, providing a direct and a very clear proof. It is a system where cathode is a grid with transparency of around 50% and in the region behind the grid the field is such that it prevents passage of ions and electrons [17]. Yet, unperturbed by the field, the fast neutrals penetrate this region and excitation profile is extended almost exactly according to the transparency of the grid. This experiment was modeled in [18] achieving an almost perfect agreement without any adjustments to the cross sections. This system also provides a blueprint for a source of a beam of fast neutrals, neutrals that may have energies in excess of 1 keV.
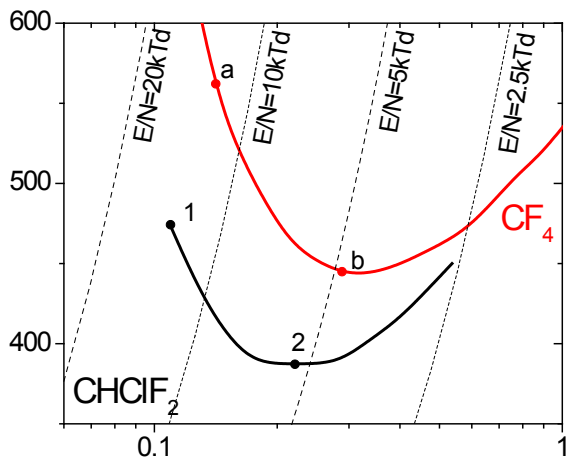

Fig. 1. Paschen curves of CHClF$_2$ and CF$_4$. Labels correspond to profiles shown in Fig. 2 [21].

Thus it was well established that a profile of emission in parallel plate low current diffuse Townsend discharge is an indication of the fast neutrals being present and even being dominant in excitation kinetics. The effect has been observed and analyzed in a number of gases and mostly the molecules containing hydrogen are prone to the effect but not exclusively. The list includes (in addition to the nitrogen, argon and hydrogen that were originally observed by Phelps), methane [19], water vapour [20], fluorocarbons [21], all rare gases and many more [22]. In Figure 1 we show Paschen curves for CF$_4$ and for CHClF$_2$ [23].

It was found that the hydrogen containing molecule has a much stronger effect due to fast neutrals. Presumably the reason is dissociation followed by formation of a fast atomic H which efficiently excites other molecules due to being much lighter and more able to transfer energy to inelastic processes. In Figure 2 we show spatial emission profiles for the two gases shown in Figure 1. For CHClF$_2$ a strong peak close to the cathode is observed even at around 5 kTd (1 Td = 10^{-17} Vcm^2) that equals electron peak at the anode. For 12 kTd the cathode peak is much higher. At the same time, for CF$_4$ the peak at 12 kTd close to the cathode is observable and may have some fast neutral excitation but it is much smaller than the anode peak.
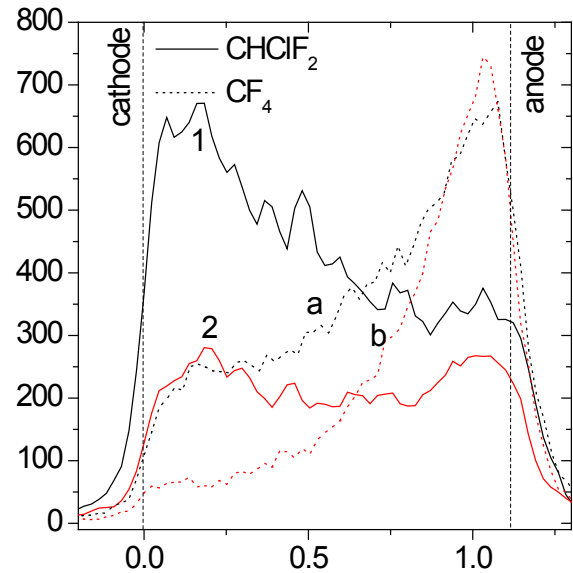
Fig. 2. Solid line CHClF$_2$ profiles at 1: pd=0.11Torrcm, E/N=13.2kTd, 2: pd=0.22Torrcm, E/N=5.3kTd, dotted line CF$_4$ profiles at a: pd=0.14Torrcm, E/N=12.2kTd, b: pd=0.29Torrcm, E/N=4.7kTd [23].

Particularly strong effects of the fast neutrals, as evidenced by the peaks against the cathode, were found in mixtures of rare gases with hydrogen containing molecules (H$_2$, CH$_4$, etc.) [24]. The reason for this was that the threshold for excitation by fast neutrals proved to be much lower than that in pure gases and thus effects became more visible [15].

It is important to note that all these observations of the spatial profiles are for the low current limit of the Townsend diffuse discharge where one expects exponential growth of emission towards the anode (due to electron

excitation and avalanche). Still, observations of the previously mentioned anomalous Doppler broadening were also made in higher current discharges since a much larger current was required to measure line profiles.

III. ANOMALOUS DOPPLER BROADENING DUE TO FAST NEUTRALS AND THEIR DETECTION IN HIGHER CURRENT DENSITY DISCHARGES

Returning to anomalously broadened Doppler profiles, an explanation that combines effect of fast neutrals with processes at the cathode surface [25] could be offered only when a single experiment under swarm-Townsend discharge conditions was made. Before that, however, it is worth noting that Z. Šternberg [26] has proposed an explanation of the profiles considering ion acceleration towards the cathode and reflection of fast ions neutralized at the cathode. Thus, fast neutrals would originate at the surface and subsequently be excited by electron collisions in the negative glow of the DC discharge.
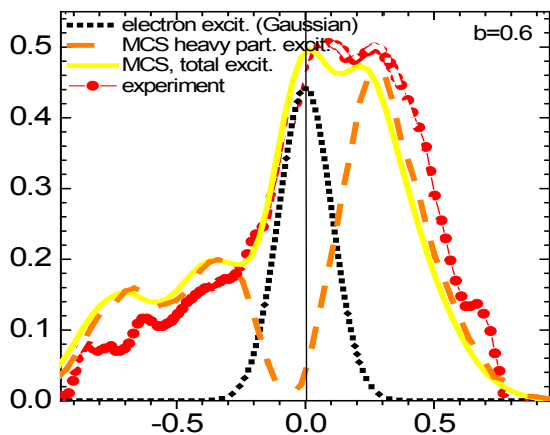

Fig 3. Doppler profile of Hα line in hydrogen discharge at 10 kTd. Line with (red) dots is experimental, dashed (orange) line are simulated wings due to heavy particle (fast neutral) excitation, dotted (black) line is simulated electron induced excitation including dissociative processes and instrumental resolution and solid (yellow) line is the total simulated profile.

The validity of this proposal was disproved by testing the current dependence of the signal in the low current experiment [25]. Nevertheless, it opened a possibility that neutralized ions reflected from the cathode may produce the wing of the Doppler profile that is the opposite to the acceleration of positive ions by the electric field. Combining this effect due to the surface neutralization/reflection and excitation by the fast neutrals originating from fast ions provided an explanation that could fit both qualitatively and quantitatively all the observations [25, 27]. Thus the experiment under swarm

conditions (the only one carried out so far, consisting of profiles of both spatial emission and Doppler broadened lines) proved to be essential in establishing the explanation of both wings and the basic process. It also allows us to normalize the cross sections and test the set of cross sections. In Figure 3 we show measured and simulated (Monte Carlo procedure for all particles) Doppler profiles of the Hα line in hydrogen at very high E/N of 10 kTd.

The component of the far wings, consistent with the acceleration of ions by the field, is mostly produced by the fast neutrals which were generated in charge transfer collisions of fast ions. This component was found to be consistent with the explanation for the spatial profiles peaking close to the cathode and it extends all the way to the maximum available energy at lower pressures. In case of H_2 discharge at 10 kTd, the maximum energy is beyond 1 keV. Fast neutrals hitting the cathode may also be reflected which leads to a component with a motion against the acceleration of the ions by the field. This wing is augmented by the neutralization/reflection at the surface of the fluxes of different positive ions (in hydrogen those would be H^+, H_2^+ and H_3^+) but some energy is lost at the surface. Molecular ions break up upon hitting the surface and are reflected mostly as fast neutral atomic hydrogen. It was also found that atomic hydrogen dominates direct excitation although fast H_2 also contributes. The distinction between normal (i.e. expected) Doppler profiles (due to kinetic energy resulting from the temperature of the gas), hyper-thermal fast neutrals (resulting from dissociative processes and limited to energies below 20 eV) and high energy particles that produce the anomalously Doppler broadened lines (due to the explained mechanisms) is in the magnitude of the energy and in the opportunity to observe the velocity of particles. At higher pressures, fast heavy particles dissipate their momentum very rapidly so low pressures are more favourable. In addition, a region of a high electric field is required to provide energy to the ions preferably with as few collisions as possible. A very good agreement of the simulated profiles with experiment is achieved without any fitting and it provides an important test of both phenomenology, model and data. One should bear in mind that the right wing, which is due to reflected particles, is greater in magnitude as it also contains the neutralized ion flux. At the same time, if we use non reflecting graphite cathode, the right wing is almost completely removed as in [25].

Anomalous Doppler broadening has only been observed for hydrogen and hydrogen containing molecules, with distinct chances that such profiles may still be found for deuterium and helium. The reason is that energy translates into greater velocity for lighter particles, and having atomic excited hydrogen is a perfect way to detect the activity of fast neutrals and their energy distribution. On the other hand, when effect of fast neutrals is observed at lower available energies (i.e. somewhat lower E/N and higher pressures) it is almost impossible to see the Doppler broadening in a swarm experiment. It is due to the need to

reduce the resolution since the intensity at few µA currents is too low. At the same time at higher current discharges it is possible to observe these effects in a number of gases but in that case the boundary between dissociative and kinetic mechanisms becomes blurred.

Several groups have probed Doppler profiles in a number of gases and gas mixtures at higher powers. Most notably the group in Belgrade from the department of Physics and also the Institute of Physics has covered different sources, and different conditions as well as gases in a large number of papers [28-30]. In all those cases all that was observed is consistent with the three proposed mechanisms.

Thus it is worth noting that apart from the cathode peak in the Townsend (and even in the glow regime) the anomalous Doppler profile is another way of detecting fast neutrals albeit only when one of the neutrals has a low mass. Other techniques include a version of spatial profiles with selection by using a grid to prevent passage of ions [17,18] and also mass analysis. Mass analysis did not prove to be very effective as it is very difficult to achieve high efficiency of ionization of fast neutrals as they pass through the ionizer of the mass analyzer. However, Bochum group managed to provide direct evidence of fast neutrals by using their conversion to negative ions inside the discharge [31].

It should be mentioned, however, that observation of fast neutrals have led to one of the most controversial series of publications where these were linked to cold fusion and new atomic states inconsistent with standard quantum mechanics and observations of the stable universe. Unfortunately, numerous reputable scientific groups jumped on that bandwagon only to regret that decision later. The hype has been laid to rest by the efforts of A. V. Phelps [32] and J. Lawler [33]. We shall not cite the literature that we believe is erroneous because we do not wish to give credit to bad practices in science. One can however notice that the prescribers to the "alternative" view have almost completely avoided to address the swarm Doppler broadening experiment and to perform quantitative comparisons based on the model proposed there [25, 27].

IV. APPLICATION OF FAST NEUTRALS IN PLASMA ETCHING

To our knowledge the first mention of the fast neutral came from Giapis and coworkers [34] who discussed hyper thermal neutrals with energies of several eV, most likely products of dissociative processes. These authors later used the term hyper thermal for very large energy ions accelerated to several hundred eV. At ICRP conference in 1991 [24] it was discussed by one of the coauthors that one cannot assume that etching is only due to the flux of ions reaching the substrate and that fast neutrals may contribute significantly. That issue was inspired by the observation that the efficiency of etching in plasma equaled that of the pure beam with maximum

energy. It was postulated that due to a broad energy distribution and variability of the etching rate on energy, the contribution of ions is only partial and the rest of the etching is provided by fast neutrals. This suggestion was not widely noticed. However, when it became apparent that charging of dielectric layers is one of the biggest problems in manufacturing, one of the present authors has proposed fast neutral etching as a solution for the charging free process [18] at ICRP conference in 1997. The proposal focused on the source of fast neutrals from the Scott-Phelps experiment [17] but it was quite general. The grid served the purpose to block the passage of fast ions and also some of the ions could be neutralized at the grids surface. However, as it was shown that the loss of fast neutral excitation corresponds well to the absorption by the grid, the surface neutralization was neglected for this case. It was also pointed out that the grid enables application of DC discharges as a source of fast neutrals.

The principle of fast neutral etching has been demonstrated several years later [35-41] in 2001. It was however assumed that dominant process was surface neutralization and thus narrow and long nanotubes were used to maximize the production of fast neutrals. The fast neutral beams have been implemented in a large number of procedures in manufacturing of integrated circuits and other aspects of nanotechnologies. It is worth stressing that the technique has been implemented with a resolution of several nm that matches excellent result in bottom-up procedures and yet it is applicable in mass production [40]. In addition, this study showed that fast neutral etching has a much smaller roughness almost an order of magnitude than the ion etching. In the latter case the roughness is typically around 2 nm. The requirement that the roughness must be less than 10% of the critical dimension may lead to the need to employ almost exclusively the fast neutral etching for structures below 20 nm.

The principal developers of this technique focused however on neutralization on surface employing narrow large aspect ratio tubes in the grid. This, on the other hand, may reduce the flux of both fast neutrals and radicals considerably. This system would have a relatively small transparency with a possible shadowing (thereby scanning of the surface may be required). We have, however, performed a detailed modeling of the sources as used in [35, 36] and came to conclusion [42-44] that gas phase production of fast neutrals under conditions of those experiments may be dominant at somewhat larger pressures but is still significant at the lowest pressures. In the process we have also shown that for all practical purposes 100% efficiency may be assumed for the grazing incidence neutralization on metallic surfaces.

It is unfortunate that the developers of the fast neutral etching did not address any of the gas discharge and swarm papers dealing with the issue of fast neutrals. This paper attempts to make that connection.

V. OUR ABILITY TO PREDICT THE PROPERTIES OF FAST NEUTRAL SOURCES

Tools developed to model swarm physics and gas discharges may be used very well to model the origin of the fast neutrals. In addition to the already mentioned theoretical and modeling papers, mainly aimed at swarm experiments [10,11,14,16,18,27], one should also mention other reviews presenting mainly preliminary versions of our Monte Carlo simulations covering electrons, ions and fast neutrals as well all relevant processes at surfaces [45, 46]. Similar models have been employed in Monte Carlo simulations [47], and hybrid codes [48, 49]. In particular, it is important to note an excellent agreement between the model and experimental data without any adjustment for normal and abnormal glow discharges [49] and also for the breakdown data with the effect of fast neutrals included [11].
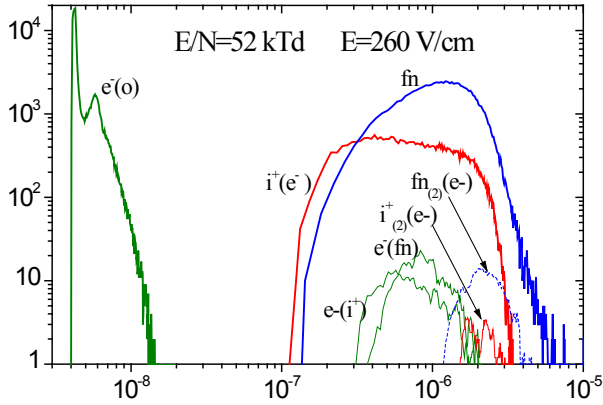
Fig. 4. Arrival time spectrum a) for particles in a Townsend N_2 discharge, b) for groups of fast neutrals born after the secondary electron emission in heavy particle collisions [50].

To illustrate the quality of the models we shall first include a prediction of the arrival time spectra of a pulse of electrons released at the cathode (see Figure 4). The result is relevant for setting up the relaxation times for electrons and fast heavy particles as the two occur at very different time scales [51] and fast neutrals require times longer that μs to develop.

As for the discharges in argon we may predict the fluxes (Figure 5) and energy distribution of fast neutrals and ions. One can see that even in a discharge with a rather low *E/N*, corresponding to the minimum of Paschen curve, the flux of fast neutrals exceeds by almost an order of magnitude the flux of ions. The overall effect of the fast neutrals will be proportional to their energy. At a much higher energy and *E/N*=150 kTd (see Figure 6) one has energies of the fast neutral that cover the entire range to the highest available energy. One must admit that ions have a distinct advantage as they peak at the maximum energy and also at these low pressures fluxes of ions and fast neutrals are similar.

Finally we shall show in Figure 7 a prediction of the angular and spatial dependence of the velocity components for fast H atoms in a Townsend hydrogen discharge [52]. These velocity components directly translate to the different wings of the anomalously Doppler broadened profile.
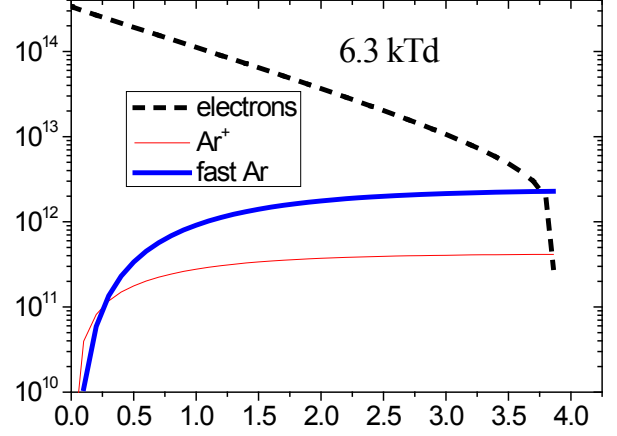
Fig. 5. Fluxes of ions and fast neutrals compared to the flux of electrons in a self sustained Townsend discharge in Ar at high E/N (E/N=6.3 kTd) [18].
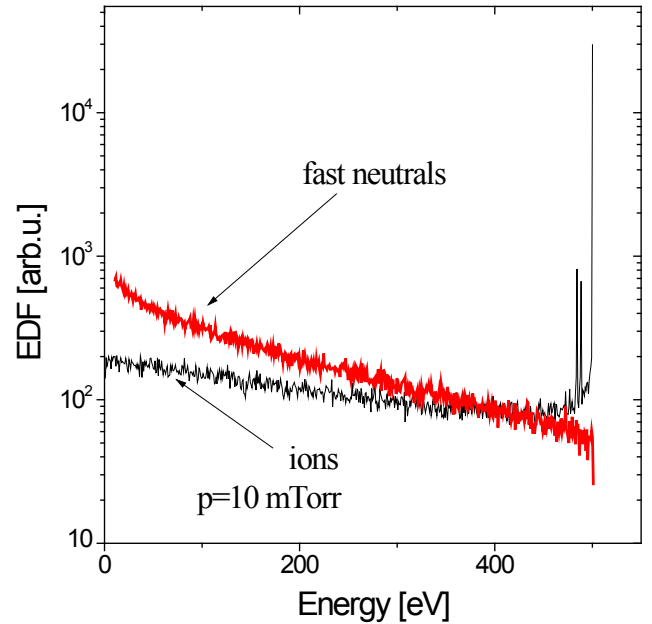
Fig.6. Energy distribution function of fast neutrals (with energies greater than 10 eV) produced by ions at the cathode, in uniform field discharge in Ar (E/N=152 kTd) [18].

VI. CONCLUSION

We can conclude that it is possible to predict quantitatively all the properties of gas discharges relevant

for prediction of the properties of fast neutral fluxes and energy distributions at surfaces of the reactor chamber. First comparisons should be made and models tested for the swarms or Townsend regime low current diffuse discharges. It is also possible to obtain excellent results for the higher current glow discharges. Thus, one may be able to develop predictive models for fast neutral etching devices. In doing so a particular attention should be made for the processes on surfaces (see as an example [11, 53]). Therefore, as far as making models of the fast neutral etchers for integrated circuit production goes, it is mainly an issue in refining the available data and models of surface interactions.

At the same time, it has not been studied sufficiently whether fast neutrals make any contribution to development of other nanostructures. In particular, the role of fluxes of different particles in creating nanostructures that may be unlikely under thermodynamic conditions may very well depend on fluxes of ions and fast neutrals. For example, etching of graphite in graphene nanotube production may depend on these fluxes. Presently, we have

enough knowledge to modify these fluxes and control the desired effects in the manufacture of nano particles. In particular, one would want to connect the energy distributions of particles impinging on the surface and simulations of the dynamics of the nanostructure upon the collision [54].

Fast neutral etching may prove to be the dominant strategy for charging free etching in production of integrated circuits and it has been expected that it will lead to a reduced roughness thus allowing sub 20 nm etching to be executed. At the same time, it allows functionalization of the surface, certain surface alloys and selective etching of some materials such as graphite carbon material. It is an excellent example how knowledge of elementary processes (charge transfer collisions and surface collisions) together with the theoretical and experimental experience in plasma surface interaction and in transport of particles as well as the ability to integrate the knowledge into predictive models for plasma devices may merge fundamental science with applied science and solving of the critical technological issues.
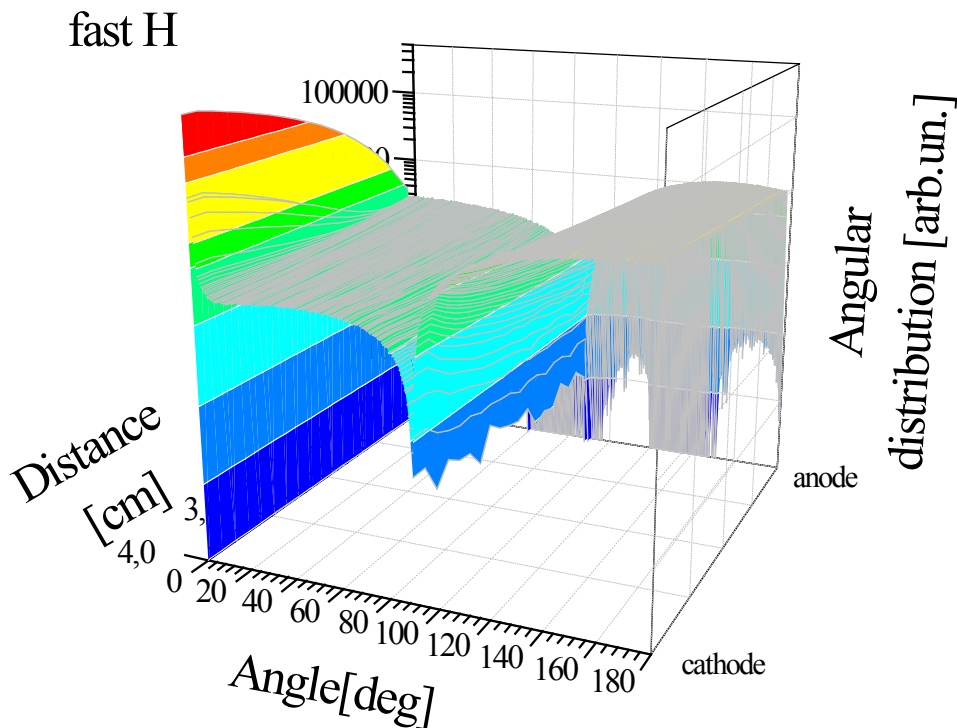
Fig.7. Angular distribution of the fast neutral H atom flux in H_2 discharge at 10 kTd. [52].

REFERENCES

[1] K. Kumar, "Challenges in the Plasma Etch Process Development in the sub-20nm Technology Nodes", Invited lecture at GEC 2013, *Bull. of the American Phys. Soc.*, vol. 58, no. 8, LW1 1 (70pp), 2013.

[2] A.I. Capelli, R.A. Gottscho, and T.A. Miller, "Doppler-broadened line shapes of atomic hydrogen in parallel-plate

radio frequency discharge", *Plasma Chem. Plasma Process.*, vol. 5, no. 4, pp. 317-331, 1985.

[3] T. Ogawa and M. Higo, "Analysis of the translational energy distribution of H* produced in the e-H$_2$ collisions", *Chem. Phys. Lett.*, vol. 65, no. 3, pp. 610–612, 1979.

[4] K. Ito, N. Oda, Y. Hatano, and T. Tsuboi, "Doppler profile measurements of balmer-α radiation by electron impact on H$_2$" *Chem Phys.*, vol. 17, no. 1, pp. 35–43, 1976.

[5] J Loureiro and J Amorim, "Non-Maxwellian velocity distributions and non-Gaussian profiles of H atoms in low-pressure hydrogen discharges", *Plasma Sources Sci. Technol.*, vol. 22, p. 015016, 2013.

[6] W. Benesch and E. Li, "Line shapes of atomic hydrogen in hollow cathode discharges", *Opt. Lett.*, vol. 9, no. 8, pp. 338–340, 1984.

[7] S.B. Vrhovac, S.B. Radovanov, S.A. Bzenić, Z. Lj. Petrović, and B.M. Jelenković, "Dissociative excitation of hydrogen in rf and dc glow discharges through H$_2$," *Chem. Phys.*, vol. 153, no. 1-2, pp. 233-245, 1979.

[8] B. M. Jelenković and A. V. Phelps, „Excitation of N$_2$ in dc electrical discharges at very high E/N", *Phys. Rev .A*, vol.36, no.11, pp.5310, 1987.

[9] A. V. Phelps and B. M. Jelenković, "Excitation and breakdown of Ar at very high ratios of electric field to gas density", *Phys. Rev. A,* vol.38, no.6, pp.2975, 1988.

[10] Z. Lj. Petrović and A. V. Phelps, "Energetic ion, atom, and molecule reactions and excitation in low-current H$_2$ discharges: Spatial distributions of emissions," *Phys. Rev. E*, vol. 80, no. 6, p. 016408, 2009.

[11] A. V. Phelps and Z. Lj. Petrović "Cold cathode discharges and breakdown in argon: surface and gas phase production of secondary electrons", *Plasma Sources Sci. Technol.*, vol.8, pp. R21-44, 1999.

[12] D Marić, M Savić, J Sivoš, N Škoro, M Radmilović-Radjenović, G Malović and Z Lj Petrović, ″Gas breakdown and secondary electron yields″, *Submitted to European Phys. J. D*, 2014.

[13] G. Malović, A. Strinić, S. Živanov, D. Marić, and Z. Lj. Petrović, "Measurements and analysis of excitation coefficients and secondary electron yields in Townsend dark discharges", *Plasma Sources Sci. Technol.*, vol. 12, pp. S1-S7, 2003.

[14] V. D. Stojanović, B. M. Jelenković, and Z. Lj. Petrović, "Excitation by electrons and fast neutrals in nitrogen discharges at very high electric field to gas number density ratios", *J. Appl. Phys.*, vol. 81, no. 3, pp. 1601-1603., 1997.

[15] A.V. Phelps, "Collisions of H$^+$, H$_2^+$, H$_3^+$, ArH$^+$,H$^-$, H, and H$_2$ with Ar and of Ar$^+$ and ArH$^+$ with H$_2$ for Energies from 0.1 eV to 10 keV", *J. Phys. Chem. Ref. Data*, vol. 21, no. 4, pp. 883-897, 1992.

[16] A. V. Phelps, "Energetic ion, atom, and molecule reactions and excitation in low-current H$_2$ discharges: Model", *Phys. Rev. E,* vol. 79, no. 6, p. 066 401, 2009.

[17] D. A. Scott and A. V. Phelps, "Excitation by fast atoms at very high electric field to gas-density ratios in argon," *Phys. Rev. A*, vol. 43, no. 6, pp. 3043-3056, 1991.

[18] Z. Lj. Petrović and V. D. Stojanović, "The role of heavy particles in kinetics of low current discharges in argon at high electric field to gas number density ratio," *J. Vac. Sci. Technol. A, Vac. Surf. Films*, vol. 16, no. 1, pp. 329–336, 1998.

[19] Ž. D. Nikitović, A. I. Strinić, G. N. Malović, V. D. Stojanović, and Z. Lj. Petrović, "Modeling of absolute spatial emission profiles of Townsend discharges at high *E/N* in methane by a

Monte Carlo technique", *Czech. J. Phys.,* vol. 56, Suppl. B, pp. B958-B963, 2006.

[20] N. Škoro, D. Marić, G. Malović, W. G. Graham and Z. Lj. Petrović, "Electrical Breakdown in Water Vapor", *Phys. Rev E*, vol.84, pp. 055401(R), 2011.

[21] N. Škoro, "Breakdown and discharge regimes in standard and micrometer size dc discharges", *J. Phys.: Conf. Ser.*, vol. 399, 012017, 2012.

[22] J. Sivoš, N. Škoro, G. Malović, Z. Lj. Petrović, and D Marić, in preparation.

[23] N. Škoro, G. Malović, Z.Lj.Petrović, and D. Marić, to be published.

[24] Z. Lj. Petrović and A.V. Phelps, "Heavy particle excitation and ionization in low pressure discharges", *Proc.of the International Seminar on Reactive Plasmas*, Nagoya, vol. E3, p.351-360, 1991.

[25] Z. Lj. Petrović, B. M. Jelenković, and A. V. Phelps, "Excitation by and surface reflection of fast hydrogen atoms in low pressure hydrogen discharges", *Phys. Rev. Lett.*, vol. 68, no. 3, pp. 325–328, 1992.

[26] Z. Šternberg, personal communication, 1988.

[27] Z. Lj. Petrović and A. V. Phelps, "Energetic ion, atom, and molecule reactions and excitation in low-current H$_2$ discharges: Hα Doppler profiles", *Phys. Rev. E*, vol. 80, no. 6, p. 066 401, 2009.

[28] I. R. Videnović, N. Konjević, M. M. Kuraica,"Spectroscopic investigations of a cathode fall region of the Grimm-type glow discharge", *Spectrochim. Acta B*, vol.51, p. 1707-1731, 1996.

[29] S. Jovicević, N. Sakan, M. Ivković, N. Konjević, "Spectroscopic study of hydrogen Balmer lines in a microwave-induced discharge", *J. Appl. Phys.*, vol.105, 013306, 2009.

[30] S. B. Radovanov, K. Dzierzega, J. R. Roberts, and J. K. Olthoff, "Time-resolved Balmer-alpha emission from fast hydrogen atoms in low pressure, radio-frequency discharges in hydrogen", *Appl. Phys. Lett.*, vol. 66, no. 20, p.2637-2639, 1995.

[31] T. Babkina, T. Gans, and U. Czarnetzki, "Energy analysis of hyperthermal hydrogen atoms generated through surface neutralisation of ions", *Europhys. Lett.,* vol. 72, pp. 235, 2005.

[32] A. V. Phelps and J. Clementson, "Interpretation of EUV emissions observed by Mills et al.", *Eur. Phys. J. D.*, vol. 66, pp.120, 2012.

[33] J. Lawler and C.J. Goebel, "Comment on "Time-resolved hydrino continuum transitions with cutoffs at 22.8 nm and 10.1 nm" by R.L. Mills and Y. Lu", *Eur. Phys. J. D*, vol.64, pp. 65-72, 2011.

[34] K. P. Giapis, T. A. Moore, and T.K. Minton, „Hyperthermal neutral beam etching", *J. Vac. Sci. Technol. A*, vol.13, pp. 959-965, 1995.

[35] S. Samukawa, K. Sakamoto, and K. Ichiki, "Generating high-efficiency neutral beams by using negative ions in an inductively coupled plasma source", *J. Vacuum Sci. and Technol. A,* vol.20, pp.1566-1573, 2002.

[36] S. Panda and D.J. Economou, "Anisotropic etching of polymer films by high energy (100s of eV) oxygen atom neutral beams", *J. Vac. Sci. Technol. A*, vol. 19, pp. 398-404, 2001.

[37] S.Samukawa, K. Sakamoto, and K. Ichiki, „High-Efficiency Neutral-Beam Generation by Combination of Inductively Coupled Plasma and Parallel Plate DC Bias", *Jpn. J. Appl. Phys.*, vol.40, pp. L779–L782, 2001.

[38] K. Ichiki and M. Hatakeyama, "Characterization of neutral beam source using dc cold cathode discharge and its

application processes," *J. Phys. D: Appl. Phys.*, vol. 41, p. 024003, 2008.

[39] G. Kokkoris, A. Tserepi, and E. Gogolides, "The potential of neutral beams for deep silicon nanostructure etching*", J. Phys. D: Appl. Phys.,* vol. 41, p. 024004, 2008.

[40] T. Kubota, T. Baba, S. Samukawa, H. Kawashima, Y. Uraoka, T. Fuyuki, and I. Yamashita, "A 7-nm nanocolumn structure fabricated by using a ferritin iron-core mask and low-energy Cl neutral beams", *Appl. Phys. Lett.*, vol. 84, p.9, 2004.

[41] D. J. Economou, "Fast (tens to hundreds of eV) neutral beams for materials processing", *J. Phys. D: Appl. Phys.*, vol. 41, p. 024001, 2008.

[42] M. Radmilović-Radjenović, A. Stojković, A. Strinić, V. Stojanović, Ž. Nikitović, G.N. Malović, and Z.Lj. Petrović, "Modeling of a Plasma Etcher for Charging Free Processing of Nanoscale Structures," *Mat. Sci. Forum*, vol. 518, pp. 57-62, 2006.

[43] M. Radmilović-Radjenović, A. Stojković, A. Strinić, V. Stojanović, Ž. Nikitović, G. N. Malović, and Z. Lj. Petrović, "Particle-in-cell Modelling of a Neutral Beam Source for Material Processing in Nanoscale Structures Fabrication", *Mat. Sci. Forum,* vol. 555, pp. 47-52, 2007.

[44] A.Stojković, M.Radmilović-Radjenović, and Z.Lj. Petrović, "Neutralization of Ion Beams for Reduction of Charging Damage in Plasma Etching", *Mat. Sci. Forum,* vol. 494, pp. 297-302, 2005.

[45] Z. Lj. Petrović, V. D. Stojanović, and Ž. D. Nikitović, "Electron, Ion and Atom Collisions Leading to Anomalous Doppler Broadening in Hydrogen," *AIP Conf. Proc.*, vol. 938, p. 237, 2007.

[46] Z. Petrović and V. Stojanović, „Anomalous Doppler broadening of Hydrogen lines due to excitation by fast neutrals in low pressure Townsend discharges", *Mem. S.A.It.*, vol. 7, p. 172, 2005.

[47] N. Cvetanović, B. M. Obradović, M. M Kuraica, "Monte Carlo simulation for excessive Balmer line broadening generated by transport of fast H atoms in an abnormal glow discharge", *J. Appl. Phys.,* vol. 105, no. 4, p. 043306, 2009.

[48] A. Bogaerts and R. Gijbels, "Effects of adding hydrogen to an argon glow discharge: Overview of some relevant processes and some quantitative explanations", *J. Anal. At. Spectrom.,* vol. 15, pp. 441-449, 2000.

[49] D Marić, P Hartmann, G Malović, Z Donkó and Z Lj Petrović, "Measurements and modelling of axial emission profiles in abnormal glow discharges in argon: heavy-particle processes", *J. Phys. D: Appl. Phys.*, vol.36, pp.2639-2648, 2003.

[50] Z. Lj. Petrović and V. D. Stojanović, "Arrival time spectra and ionization kinetics of high E/N discharges in N_2", in preparation.

[51] N. Nakano, N. Shimura, Z. Lj. Petrović, and T. Makabe, "Simulations of RF glow discharges in SF6 by the relaxation continuum model: Physical model and function of the narrow gap reactive-ion plasma etcher," *Phys. Rev. E*, vol. 49, no. 5b, pp. 4455–4465, 1994.

[52] V. Stojanović, Ž Nikitović, and Z.Lj Petrović, "On Anisotropy and Spatial Dependence of Doppler-Induced Broadening Due to Heavy-Particle Excitation", *IEEE Trans. Plasma Sci.*, vol. 39, p. 2592 – 2593, 2011.

[53] Z. Lj. Petrović and V. D. Stojanović, "The role of heavy particles in kinetics of low current discharges in argon at high electric field to gas number density ratio", *J. Vac. Sci. Technol A*, vol.16, p. 329-336, 1998.

[54] Z.Lj. Petrović, P. Maguire, M. Radmilović-Radjenović, M-Radetić, N. Puač, D. Marić, C. Mahony, G. Malović, " On application of plasmas in nanotechnologies" in "Nanotechnology for Electronics, Photonics, and Renewable Energy", Editors A. Korkin, P.S. Krstic and J.C. Wells, *Springer Series Nanostructure Science and Technology, Springer* (New York), p.85 2010.

Kinetic Phenomena in Transport of Electrons and Positrons in Gases caused by the

Properties of Scattering Cross Sections

Kinetic Phenomena in Transport of Electrons and Positrons in Gases caused by the Properties of Scattering Cross Sections

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Abstract. Collisions of electrons, atoms, molecules, photons and ions are the basic processes in plasmas and ionized gases in general. This is especially valid for low temperature collisional plasmas. Kinetic phenomena in transport are very sensititive to the shape of the cross sections and may at the same time affect the macroscopic applications. We will show how transport theory or simulation codes, phenomenology, kinetic phenomena and transport data may be used to improve our knowledge of the cross sections, our understanding of the plasma models, application of the swarm physics in ionized gases and similar applications to model and improve gas filled traps of positrons. Swarm techniques could also be a starting point in applying atomic and molecular data in models of electron or positron therapy/ diagnostics in radiation related medicine..

1. Introduction

In this paper we present a survey of some of the recent results of the physics of swarms of charged particles (we will confine our interest to electrons and positrons). Our first and necessary point is to illustrate some of the recent results obtained by the group(s) at the Institute of Physics in Belgrade (together with our collaborators). We also wish to illustrate

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how swarm physics connects on one side to atomic and molecular collisions (and thus to overall atomic and molecular physics) and on the other to non-equilibrium plasmas and their numerous applications. As the topic of swarms has not been addressed frequently at ICPEAC (although one of its satellites, Electron-molecule Collisions and Swarms, covers the topic very well) this presentation will necessarily be rather broad but not very detailed.

Collisions of electrons, atoms, molecules, photons and ions are the elementary processes occurring in plasmas. It may be argued that the level of individual collisions is the most fundamental level of phenomenology required to describe non-equilibrium collisional plasmas. That is so for two principal reasons: the first being that the duration of the collisions is many orders of magnitude shorter than the mean free time between the collisions. Thus we may bury all the quantum mechanics into the cross sections and basic properties of the energy levels and molecules. As a result, we may even use classical trajectories for charged particles and thus the Monte Carlo technique has had so much success. The second reason is related to the first and it is that the De Broglie's wavelength of particles is usually small compared to the mean volume per particle in the gas, at least until we reach very high densities (e.g. as in liquids). Thus electrons collide with only one target per collision.

A reductionist view of the science which dominated in the past declared that the more basic the phenomena were, the more fundamental they were. In that view of the world, the field theory and mathematics on their own may explain the psychological states of humans! A more realistic view which, luckily, prevails today is that there are layers of phenomenology, each with its own rules and foundations and each providing its accomplishments that are not trivially predicted at the more basic levels. In this way we may construct a path between atomic and molecular physics and the numerous modern applications of low temperature plasmas. As previously mentioned, there is no need to go deeper than the physics of collisional processes (including a range of collisions with surfaces). The next stage is the physics of swarms where collisions join the statistical physics and kinetic theory in addition to the surface processes. More detailed presentations of this realm of physics have been given in earlier texts [1,2], while more recent reviews have been given in references [3-5]. It is possible to say that little in the papers presenting the cross section data prepares us for the complex kinetic phenomena that evolve in the swarm physics, such as negative differential conductivity or negative absolute mobility [6,7].

The next layer of phenomenology is that of low temperature or more accurately non-equilibrium plasmas (NEP). It brings in space charge and other plasma effects, chemistry and many more different inputs. Swarm physics, represented by its kinetic phenomena, together with atomic collision data are the building blocks of the NEPs but little prepares us for the phenomena such as the spewing of the plasma bullet (ionization front) from the glass tube where an atmospheric pressure plasma jet (APPJ) is formed [8,9]. This device often produces a plasma bullet (ionization front) that actually moves faster, and is bigger and brighter, in the supposedly hostile world of atmospheric gases once it leaves the region of high field between the electrodes wrapped around the tube where more favourable gases for its formation dominate. But even at this level one cannot really envisage why and how such plasmas may induce, for example, preferential differentiation of human (periodontal ligament mesenchymal) stem cells into one out of four possible types of the cells [10].

Finally, one should welcome another change in the attitude that happened recently. It has been slightly over 100 years since the discovery of electron. Its discoverer J.J. Thompson toasted at Christmas receptions: ˝To the electron and may nobody find its application.˝. Needless to say, the previous century being labeled as the century of the electron means that some applications were eventually found. The attitude that applied is not fundamental has, however, changed. Luckily non-equilibrium plasmas offer one of the quickest and most abundant fronts of development of new applications and each application brings in requirements for new phenomena to be included. For example, attempting to apply NEPs to

medicine requires an understanding of a large part of the relevant medical knowledge. Following publication of a major review by David Graves, of the mechanisms coupling reactive species from the plasmas with biological triggers [11], there is now no room for plasma and atomic physicists to claim that medical processes need not be understood from their viewpoint, they simply have to learn them (Latin terms and all). Nevertheless one could claim that at the deepest relevant level leading to such applications, one may find atomic and molecular collisions however remote from the final outcome those may be [10].

2. Electron swarms in gases, cross section data sets and kinetic phenomena

Swarms may be simply defined as ensembles of particles (in this case electrons and positrons) moving in the background gas under the influence of external fields (if charged), limited by the walls of the vessel. These particles do not suffer effects of any significance due to interactions between themselves (Coulomb force, shielding of the external field) and also have negligible chances of colliding with the remnants of previous collisions. In other words, they move in the external fields affected mainly by the collisions with the pristine background gas.

Swarms bring transport theory and other aspects of statistical physics to the table, and often effects of surfaces may be needed albeit only in specific situations (e.g. a Steady State Townsend experiment). The transport may be well represented by a single particle distribution function, so the standard Boltzmann equation (BE) is appropriate. However, due to 7 degrees of freedom, a complex theoretical treatment is required for solving the BE. Due to the complexity of the cross sections (the dependence on the energy that can only be tabulated) and hence collision operator, the final result has to be obtained numerically. The resulting energy distribution function is however not something that can be measured, and the swarm physics focuses on averaged properties such as transport coefficients (drift velocity, diffusion tensor, ionization coefficients) or rates for specific processes (excitation or chemical).

Initially swarm physics was developed when techniques of electrochemistry were applied to study properties of charged particles in gases, especially when their elementary nature became obvious. However, they quickly proved to be a very good source of data for cross sections for the dominant processes especially after numerical solutions to the BE became available. The advantage of the technique was originally significant, as it provided good absolute calibration, and results for He were only matched by theory and beam techniques some ten to twenty years later [1]. Most importantly, if a full set of swarm facilities is used the resulting cross section set provides good number, momentum and energy balances for the charged particles in the gas and is thus directly applicable in the modeling of plasmas.
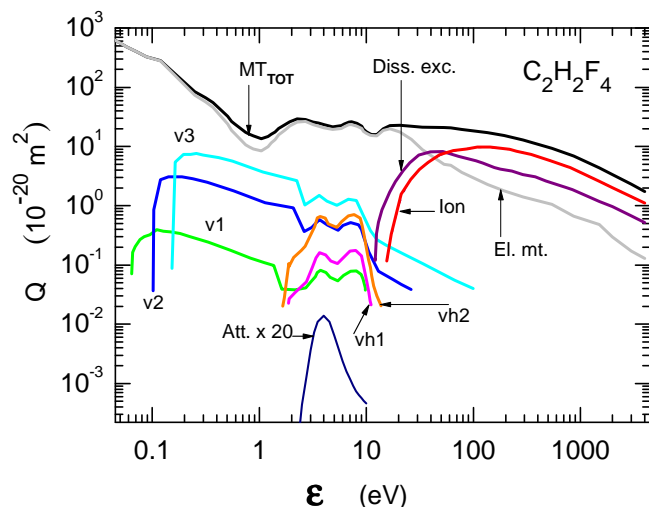
Recent swarm derived cross section sets cover many gases so we shall give only one example, for the 1,1,1,2-tetrafluoroethane ($C_2H_2F_4$) molecule [12]. Transport coefficients measured by a Pulsed Townsend technique were converted to cross sections, based on an initial set that was available in the literature due to S. Biagi. Results are shown in Figure 1.

A disadvantage of the swarm technique is that it is indirect i.e. it involves guessing of the cross section set and then comparing the calculated transport coefficients to the experimental data until agreement is

Figure 1. The cross section set for $C_2H_2F_4$ [12], MT- total momentum transfer, v-vibrational modes, Att-attachment, ion-ionization, El mt elastic momentum transfer, Diss. Exc. Dissociative excitation..

reached. In addition its resolution is poor, especially at higher energies, and the results potentially suffer from non-uniqueness.

Reliable results are usually obtained from drift velocities and characteristic energies (diffusion coefficient divided by mobility) for energies up to $1 - 2$ eV, while typical electron energies in relevant plasmas are higher. If the ionization coefficient is used in the analysis one may extend the energy range of the set. Assuming that the measured ionization cross sections are very accurate we can fit the ionization rate by adjusting the middle range electronic excitation cross sections or dissociation to the ground state (which are often incomplete).

The accuracy of the resulting cross sections depends very much on the accuracy of the transport theory (or the corresponding Monte Carlo simulation (MCS). Numerous tests need to be made to check the codes against specially designed benchmarks, for various aspects of the transport or properties of the processes [13]. On the other hand one needs to reopen, in a systematic fashion, the issue of anisotropic scattering. At low energies, due to the randomizing effect of frequent collisions, isotropic scattering is a good approximation provided that the momentum transfer cross section was obtained with that approximation. It has been shown, however, that for mean energies in excess of 20 eV or even for smaller energies when inelastic processes are very strong, one needs to include differential cross sections i.e. a full anisotropic model.

A plethora of atomic and molecular processes acting at the same time, that use up the energy gained from the field, leads to the formation of the shape of the electron energy distribution function (EEDF), and furthermore, but less obviously to the dependencies of the averaged properties, i.e. the transport and rate coefficients. Those processes finally lead to the functionality of low temperature plasmas and their many applications. From the viewpoint of fundamental physics the most interesting aspect of the swarm physics are the so-called kinetic phenomena [3,5]. Those represent an often counter intuitive behaviour of the collective properties, that cannot be predicted from the individual trajectories or from the shape of the cross sections (at least not without some experience). Those may be loosely classified according to the primary source of their existence (although the cross section magnitudes, shapes and properties are generally relevant) :

- **Dependence on the rates of momentum transfer and inelastic processes:** anisotropic diffusion; diffusion heating/cooling; enhanced mobility; negative differential conductivity (NDC); spatial separation of fast and slow particles-i.e the energy gradient, ...
- **Non conservative transport:** attachment heating/cooling; negative absolute mobility; difference between flux and bulk transport coefficients; positron NDC for bulk drift; skewed Gaussians, …
- **Magnetic field induced:** magnetic field cooling; ExB drift; ExB anisotropy of diffusion,...
- **NDC for positrons in liquids**
- **Time dependent fields:** anomalous diffusion; limited relaxation; phase delays at high frequencies; time resolved NDC; transient negative diffusivity, heating of electrons due to cyclotron-resonance effects,,..
- **Non-hydrodynamic:** Frank Hertz oscillations and Holst Oosterhuis structures; runaway ions; runaway electrons; thermalization/equilibration (non-local transport); increasing mean energies close to the boundaries; back-diffusion.

The fundamental reasons for these effects lie in the interplay between the times or spatial scales required for relaxation of number, momentum and energy, and in the interplay between the source of energy and momentum (i.e. the external field) and the processes that dissipate those properties. One example of kinetic phenomena is particularly important for the world of Atomic and Molecular physics. Absolute negative mobility has been predicted by several authors. The phenomenological explanation requires a group of electrons to be released with energy of 2 eV in a mixture of argon with 0.5% of F_2 (or any other gas with a large thermal attachment). The majority of the electrons would be accelerated by the field and would have an increasing chance to collide. If scattering is isotropic then 50% of the electrons will scatter backwards and join the smaller group of electrons that move against the field. Although those lose energy, the decreasing cross section will reduce their chances of

redirection until they thermalize in the region of the Ramsauer Townsend (RT) minimum. There, the electric field would again accelerate the majority of the electrons in the expected direction. Thus, for a while, electrons would on average move against the field and current – mobility would be negative. If one adds small amount of F_2 the thermal attachment will eat up the thermalized electrons not allowing them to accelerate and the current would be negative perpetually [14,15]. Of course it has been shown that this does not mean that we have a source of free energy although entropy is in principle reduced. However we pay the price by producing a lot of negative ions which contribute to an even greater growth of entropy [16]. The importance of this example is that it provides a situation where atomic processes may be used to tailor the distribution function, and in essence act as Maxwell's demon (in this case the thermal attachment). It is also not a man made device. Requirement to maintain the second law of thermodynamics requires us to separate at least two kinds of transport coefficients. For drift velocities we may have an average over all electrons in all of the space (the flux drift velocity), while we may also follow the center of the mass of electrons and determine its velocity (the bulk drift velocity). The distinction between these two is due to the changing number of particles (non-conservative processes; attachment, postronium (Ps) formation for positrons or ionization for electrons) and the difference may be associated with the vailidity of the second law of thermodynamics [16].
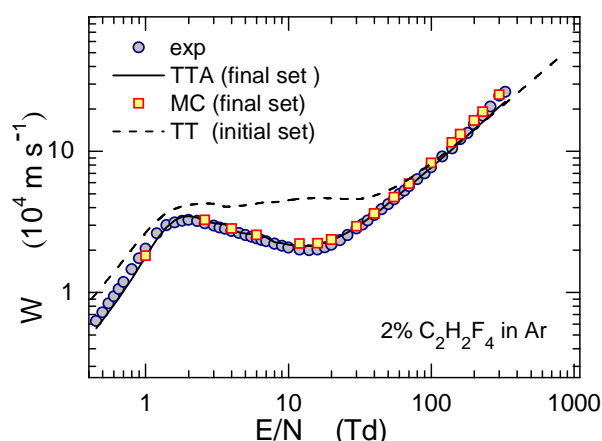

Figure 2. Fit of the experimental drift velocities (open circles) in $C_2H_2F_4$ with cross sections from figure 1 [12] (solid circles and line) and with an older set that was previously in use (see [12]). NDC is well developed between 2 Td and 20 Td.

We shall also show one example of the related phenomenon of negative differential conductivity (NDC), where drift velocity is reduced as the field increases and the mean energy increases due to the reduced control of the energy by inelastic process and increased randomization of directions in momentum transfer collisions. This example also shows how the structure in the drift velocity may be used to improve the uniqueness of the cross sections, as the calculations with another, similar, set does not show the experimentally observed NDC [12].

Kinetic phenomena, being shaped by the cross sections, provide an opportunity to strengthen the ability to normalize the cross section sets and also to modify and even define some of the applications or plasma properties. Thus those effects should be recognized and their implications understood when one wants to model collisional NEP.

3. Direct application of swarm data and models in the physics of ionized gases
In some cases when space charge is not excessive, swarms may be used as a direct representation of the ionized gas (often under those conditions, however, all conditions are not met to call such systems a plasma). The first example is the physics of Townsend discharges. The fact that swarm models are exact for such circumstances (in the limit of vanishingly small currents), makes them perfect to determine atomic and molecular processes in gas phase [17] and on surfaces and to study gas breakdown as well sometimes even revealing new phenomena in experimental observations [18]. Further direct application of swarm data and theory is in attempts to optimize gaseous dielectrics. In principle, two directions of research are dominant. The first is replacing SF_6 by more ecologically acceptable gases and the second is to produce mixtures of such gases that would allow their operation without the need for expensive high pressure vessels.

Another direction of research where swarm models and data are used abundantly (albeit that field has almost severed its connections with the swarm community) is that of the gas filled particle

detectors, including the nowadays most popular Resistive Plate Chambers (RPC)[19]. Using the Monte Carlo code developed to study swarms and obtain cross sections, and the newly established cross section set, we were able to calculate the time response of such devices [20] that agrees well with experiments. These results may nowbe used to optimize gas mixtures, operating conditions, chemistry and control the degree of ionization to speed up the counting rate. Other types of gas filled detectors may be modeled in a similar fashion.

The most important aspect in application of swarm physics, is in so called low temperature plasmas (we prefer to call them non equilibrium plasmas-NEP). We could spend much space on this issue, but it is only covered here as a brief introduction with more being found in reference [21]. The kinetic theory and the transport data all enter fluid models and together with the solution for the field distribution are the foundation of the theory. The hybrid models use the same data together with the cross section sets **that have to be complete** and thus be tested by the swarm technique, as do the kinetic codes. As one example we can describe capacitively coupled RF plasmas, which have sheaths close to the electrodes and with high fields that increase on one side and decrease on the other. During the reduction of the field electrons diffuse into that region and get accelerated into the plasma when the field starts increasing again. The diffusion flux of electrons is defined by the longitudinal diffusion coefficient, the one that shows anomalous behavior due to inability of the electron energy to respond the changes in the fields. This inability follows from the finite relaxation time of the electron energy which is strongly affected by the shape of the elastic cross section. On the other hand, for inductively coupled RF plasmas the ExB drift opens new channels to feed energy into the plasma [3]. Most models however assume constant (in space and time) transport coefficients, and neglect additional components of drift velocity and diffusion when magnetic fields are present. Nevertheless it has been difficult to impress upon the plasma modeling community that their models, when applied to simple low space charge limit benchmark situations, **should be able to replicate the swarm benchmarks**. Completing this exercise, however, would open many issues on the available cross sections and would forge a stronger link between atomic and molecular collision physics and the plasma modeling community. At the same time it would make binary collision experts aware of the data needs for the numerous plasma applications,

Another issue is that of the pertinent theory. As mentioned above, most frequently spatial and temporal uniformity are assumed in modeling. This is seriously wrong in cases of sharp gradients, in the profiles of plasma properties when hydrodynamic expansion of the theory is not an option (and is still being used in almost all cases). One such example is that of the streamers. Streamers are the basis for most high pressure discharges and recently a theory has been developed that includes proper treatment of transport across strong gradients in various streamer properties. Although the space charge made the final profile very robust, the improved theory produced results that had a significant change in the speed of propagation [22]. Streamers are an essential component of a number of atmospheric plasmas including lightning, sprite discharges in the upper atmosphere and atmospheric pressure plasma jets, which are being championed for novel medical procedures while having some intriguing physics on their own [8]. Other atmospheric discharges like aurora are often modeled [23] by using measured distribution functions from the atmosphere, in a procedure that resembles swarm models. It seems possible that a similar analysis should be made with distribution functions calculated having in mind all the available data and conditions at high altitudes.

4. Positrons in gases: swarms and (swarms in) traps
The absence of swarm experiments for positrons, with two exceptions [24], made us adopt a strategy that we do not advise for electrons. That is to collect the available cross sections, which are now generally available for several of the most important gases [25-27], and calculate the transport coefficients hoping to identify new kinetic phenomena that would justify building new swarm experiments. It was found that for gases with a strong positronium formation cross section, skewing of the positron swarm occurs due to preferential loss at the front of the group leading to a major reduction (NDC) for the bulk drift velocity. One such example is water vapour [28], which is critically

important for applications of positrons in medicine. Assuming that a set of cross sections is sufficiently complete, we may proceed to model tracks of positrons in water vapour allowing also for assessment of nanodosimetry [29].

One should be aware that some of the critical devices in positron physics contain gas to reduce the energy of positrons, below the threshold for Ps formation, and then to further cool them so that the outgoing beams might have a very narrow energy spread. the Penning-Malmberg-Surko trap is usually separated to three stages, with pressures ranging from 10^{-3} Torr to 10^{-5} Torr, with pure N_2 at the front and mixture of N_2 and CF_4 in the last stage [30,31]. We have been able to apply the code originally developed for electron swarms (and tested against all known benchmarks) to model the Surko trap [32]. In figure 3 one can see the development of the distribution function from a single beam, through to multiple beams (due to inelastic collisions with electronic excitations), and to gradual development of the low energy distribution which becomes dominant and eventually decays to the Maxwell Boltzmann distribution at room temperature [33]. This is fully analogous to the equilibration of electron swarms with initial beam, followed by Frank Hertz like effects during the first collisions and subsequent development of a broad energy distribution function demonstrating also that interpretation of the experiment using swarm phenomenology is appropriate (including of course a good set of cross sections). Having this tool it became possible to determine other aspects of trap operation: losses, optimum choice of potential drops and geometry. It led to some new proposals such as the idea of S. Marjanović for the inversion of the gases, whereby CF_4 would be used at the trap front and with the mixture still at the last stage, with lower potential drops that would help avoid Ps formation and allow efficiencies of up to 90%.
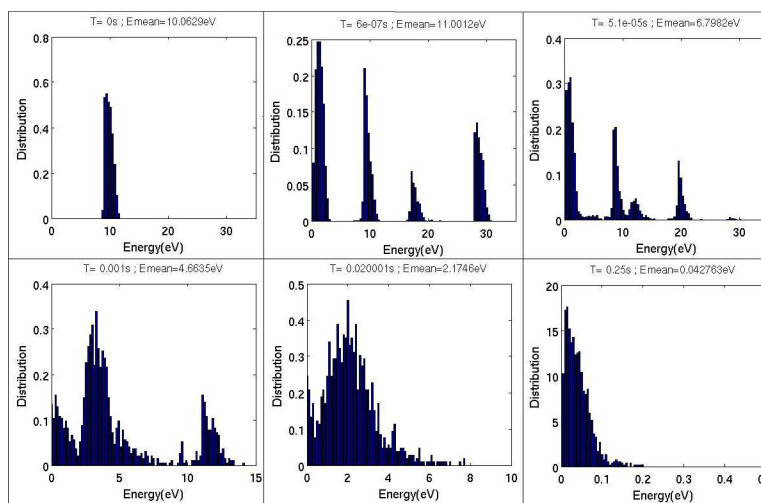

Figure 3. Temporal development of the energy distribution function in a positron trap [33].

A large number of elastic collisions, which happen during thermalization, leads to an expansion of the positron swarm in the trap. For many applications, however, increased density is required and thus additional narrowing in the final stage may be required. For this purpose a rotating wall stage has been developed that may operate in two regimes: single particle [34,35] and plasma regimes. A theory of the former has been provided in reference [36] where viscosity was added to a simple transport equation allowing the experiments to be fitted. In our approach a swarm based Monte Carlo codes has been used with realistic sets for the cross sections [37]. The role of each of the processes has been elucidated, and it is possible to characterise all the salient features of the rotating wall trap. As the system develops with an entire ensemble, it appears that the term single particle rotating wall should be replaced by the swarm regime of the rotating wall.

5. Conclusion

The realm of the physics of ionized gases controlled by collisions without a significant effect of the Coulomb interaction between charged constituents, is known as swarm physics. It is in this area that the kinetic phenomena are observed most directly. The tools of swarm physics allow us to cross the path from the elementary microscopic collisional processes all the way to the macroscopic properties of swarms, plasmas and other forms of charged particle ensembles and their applications. It appears that for gas filled systems the phenomenology, tools and data of swarm physics provide the best way

to understand and even optimize the devices and their applications, while crossing the gap between microscopic cross sections and the large scale practical devices.

References

[1]   Huxley LGH and Crompton RW The drift and diffusion of electrons in gases, John Wiley, New Yourk (1974).
[2]   Kumar K, Skullerud H R and Robson R E 1980 *Aust. J. Phys.* **33** 343
[3]   Petrović Z Lj, Dujko S, Marić D, Malović G, Nikitović Ž, Šašić O, Jovanović J, Stojanović V and Radmilović-Rađenović M 2009 *J. Phys.* D: *Appl. Phys.* **42** 194002
[4]   Robson RE 2006 *Introductory transport theory for charged particles in gases* (World Scientific: Singapore)
[5]   Robson RE, White RD and Petrović Z Lj 2005 *Rev. Modern Phys.* **77** 1303
[6]   Petrović ZLj, Haddad G and Crompton RW1984 *Aust J Phys* **37** 23
[7]   Robson RE, Petrović ZLj, Raspopović ZM and Loffhagen D 2003 *J. Chem. Phys.* **119** 11249
[8]   Puač N, Maletić D, Lazović S, Malović G, Đorđević A and Petrović ZLj 2012 *Appl. Phys. Lett.* **101**, 024103
[9]   Zhongmin Xiong and Kushner M. 2012 *Plasma Sources Sci. Technol.* **21** 034001
[10] Miletić M, Mojsilović S, Okić Đorđević I, Maletić D, Puač N, Lazović S, Malović G, Milenković P, Petrović Z Lj and Bugarski D 2013 *J. Phys. D: Appl. Phys* accepted
[11] Graves D B 2012 *J. Phys. D: Appl. Phys.* **45** 263001 (42pp)
[12] Šašić O, Dupljanin S, De Urquijo J and Petrović Z Lj 2013 *J. Phys.* D: *Appl. Phys.* **46** 325201
[13] Dujko S, White R D, Petrović Z Lj and Robson R E 2010 *Phys. Rev. E* **81** 046403
[14] Dyatko N A, Napartovich A P, Petrović Z Lj, Raspopović Z R and Sakadžić S 2000 *J. Phys. D: Appl Phys.* **33** 375
[15] Šuvakov M, Ristivojević Z, Petrović ZLj, Dujko S, Raspopović ZM, Dyatko NA, Napartovich AP 2005 *IEEE Trans. Plasma Sci.* **31** 532
[16] Robson RE, Petrović ZLj, Raspopović ZM and Loffhagen D 2003 *J. Chem. Phys.* **119** 11249
[17] Phelps A V and Petrović Z Lj 1999 *Plasma Sources Sci. Technol.***8** R21
       Phelps AV Petrović ZLj and Jelenković B M 1993 *Phys. Rev.* E **47** 2825
[18] Marić D, Malović G and Petrović Z.Lj. Plasma *Sources Sci. Technol.* **18** (2009) 034009
[19] Riegler W and Lippmann C. 2004 *Nucl. Instr. Meth. A* **518** 86
[20] Bošnjaković D, Petrović ZLj and Dujko S, in Proceedings of XVIII International Symposium on Electron-Molecule Collisions and Swarms, 19-21 July 2013, Kanazawa, Japan, p. 44
[21] Makabe T and Petrović Z Lj 2006 *Plasma Electronics* (New York: Taylor and Francis)
[22] Dujko S, Markosyan A, White R D and Ebert U 2013 *J. Phys. D: Appl. Phys*. Submitted
[23] Campbell L and Brunger M J 2013 *Plasma Sources Sci. Technol.* **22** 013002
[24] Charlton M 2009 *J. Phys.: Conf. Ser.* **162** 012003
[25] Marler J. P., Surko C. M., 2005 *Phys Rev* A **72** 062713
[26] Surko C M, Gribakin G F and Buckman S J 2005 *Journal of Physics B* **38** R57-R126
[27] Makochekanwa C, Banković A, Tattersall W, Jones A, Caradonna P, Slaughter D S, Sullivan J P, Nixon K, Brunger M J, Petrović Z Lj, Buckman S J, 2009 *New J. Phys.***11** 103036
[28] Banković A, Dujko S, White R D, Marler J P, Buckman S J, Marjanović S, Malović G, García G, Petrović Z Lj, 2012 *New Journal of Physics* **14** 035003
[29] Petrović Z Lj, Marjanović S, Dujko S, Banković A, Malović G, Buckman S, Garcia G, White R, Brunger M 2013 *Appl. Radiat. Isotopes* Available online doi: 10.1016/j. apradiso.2013.01.010
[30] Greaves R G and Surko C M 2002 *Nuc. Inst. Meth. in Phys. Res. B* **192** 90
[31] Sullivan J P, Jones A, Caradonna P, Makochekanwa C and Buckman S J 2008 *Rev. Sci. Instrum.***79** 113105
[32] Marjanović S, Šuvakov M, Banković A , Savić M, Malović G, Buckman S J and Petrović Z Lj 2011 *IEEE Trans. Plasma Sci.* **39** 2614

[33]   Marjanović S, Šuvakov M, Banković A and Petrović Z Lj 2011 unpublished

[34]   Cassidy D B, Deng S H M, Greaves R G and Mills Jr A P 2006 *Rev. Sci. Instrum.***77** 073106

[35]   Greaves R G and Moxom J M 2008 *Phys. Plasmas* **15** 072304

[36]   Isaac C A, Baker C J, Mortensen T, van der Werf D P and Charlton M 2011 *Phys. Rev. Lett.* **107** 03320

[37]   Marjanović S *et al.* 2012 unpublished

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Heavy-particle collisions in water vapour discharges at low pressures

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We present results of research on basic processes governing low-current liquid vapour discharges. Experimental measurements of breakdown properties, spectrum and spatial emission profiles of Townsend regime in low pressure water vapour are used for comparison with the data obtained from a Monte Carlo simulation. The realistic simulation includes both reactions with electrons and heavy particles in the discharge volume with borders. Thus, by attaining good agreement between experimental and modeling data we can obtain cross sections for processes between heavy particles and provide detailed description of the discharge.

Intense investigation of discharges in liquids or liquid vapours have been present for more than a decade initiating a new realm in non-equilibrium discharge field. Motivation for the investigation comes both from scientific and technological interests to unravel and explain complex systems that intertwine vapours, liquids and electrical discharges. On one hand, these complex systems have found many applications such as novel environmentally friendly light sources, plasma sterilization and modifications of different kind of surfaces, biomedical applications and many other [1-3]. They all necessitate basic research in order to explain processes important for particular application and to enhance the device itself. On the other hand, there is a scientific interest in liquid/vapour discharges so as to provide relevant information about this non-equilibrium system. Since there is variety of discharge configurations employed there are many different approaches of investigation, both experimental and modeling [4-7]. Investigation of basic processes in these discharges can be successfully accomplished only as a joint effort between experimental measurements and modeling. Prerequisite for a complete set of reliable experimental results is well controlled conditions in a wide range of experimental parameters, which can sometimes be difficult to achieve. Afterwards, experimental data can be used either as input data for models or for comparison with the modeling results. However, complexity of systems investigated requires a step-by-step modeling approach, i.e. separating the liquid/vapour discharge system into parts and running a separate model for every subsystem.

Vapour environment is a feature shared by many vapour/liquid discharge systems and therefore is an important system to investigate. Hence, we aim to investigate elementary processes taking place inside vapour discharge at low-pressures, at breakdown conditions and low currents. Here we will present results of experimental measurements and simulation obtained in a water vapour discharge.

Our experiment consists of parallel flat electrodes, copper cathode and platinum film coated anode, separated at 1.1 cm. Electrodes are placed in a quartz cylinder that allows side-on observation to the discharge and at the same time prevents long-path breakdown. Chamber construction, capacitive manometer and gas pumping system allow precise pressure control and measurement at minimal gas flow rate intended only for slow purging of the discharge volume. Electrical system in the experiment enables control of the working point of the discharge in a wide range of discharge currents. Electrical signals from the discharge are monitored and registered on an oscilloscope providing an insight to time-dependent waveforms. Therefore, a special attention is devoted to produce stable discharge parameters and carefully control them, resulting in reproducible measurements.

Water vapour for the measurements was produced by evaporation of a liquid sample of bidestilled deionized water at low pressure, which was previously made devoid of all volatile constituents (such as dissolved oxygen) by a prolonged pumping of the sample. Although we have shown that the influence of minerals and other dissolved content of tap water is not significant for breakdown [8] we chose processed water sample in order to keep the pumping system clean. The ambient temperature during measurements was kept at 300 K.

Emission was recorded either by an ICCD camera with a photographic objective – a setup suitable for recording spatial emission profiles of the discharge, or a spectrometer equipped with the ICCD camera as detector to record spatially integrated spectrum of the discharge. Spatial profiles can be recorded as 2D images of entire discharge emission, i.e. emission integrated in visible spectral range, or they can be spectrally resolved by inserting a band-pass filter (Hα line at 656 nm). Details about the experimental setup can be found elsewhere [8,9].

A Monte Carlo simulation (MCS) was employed to realistically model the discharge with parameters used in the experiment and take into account boundary conditions, spatially dependent transport coefficients for electrons and heavy particles as well as distribution functions that may include a runaway component. Monte Carlo code for electron transport was coupled with similar particle codes involving ions and neutrals, all based on the null collision technique. Details about the MCS technique have previously been published [10]. Cross sections for electron collisions were taken from the literature [11,12]. For heavy-particle processes we modified initial collisions cross sections from the data reviewed by Phelps [13,14] and Miller and Green [15] assuming the dominant role of fast H atoms in excitation. Electrons reflected from electrodes were also included in the simulation. As an output of the model we observed Hα emission coming from excitation processes induced by electrons and in heavy particle collisions.

Fig. 1 shows measurement of spatially-integrated emission spectrum of water vapour discharge at $pd = 0.2$ Torrcm for wavelengths in wide interval from 300 nm to 880 nm. In the visible part of the spectrum H atom emission at 656.3 nm (Hα), 486.1 nm (Hβ) and 434.1 nm (Hγ) are present. Moreover, strong lines of OH band (306-309 nm) are visible as well as atomic O lines at 777.4 nm and 844.6 nm.
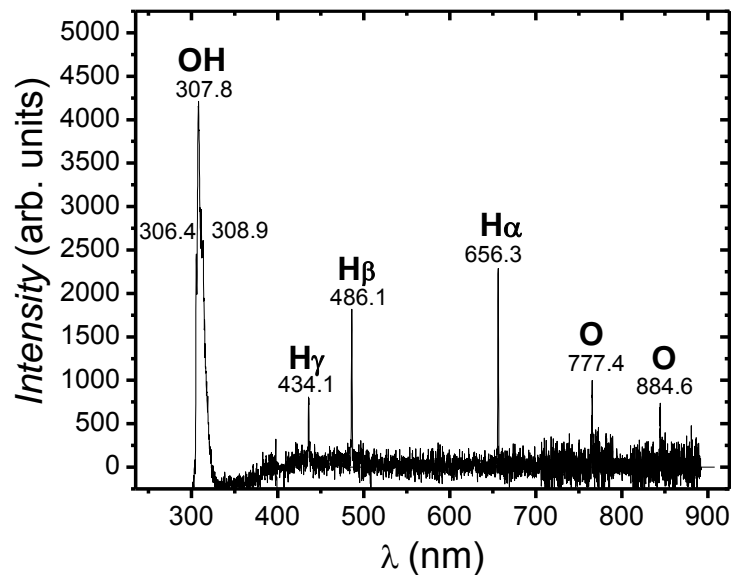

Fig. 1: Emission spectrum of Townsend discharge in water vapour at pd = 0.2 Torrcm and d = 1.1 cm with characteristic lines designated in the plot.

In Fig. 2 axial emission profiles from H_2O vapour discharge running in low-current limit are shown. Total emission in visual spectral range is plotted using full lines while filtered emission is represented by dashed lines. At low pressures (high *E/N*), small pressure variations in different measurement sets change significantly the breakdown point and therefore presented total emission and Hα profiles are acquired at two comparable *E/N* values. The profiles are obtained at two disparate pressures, i.e. *E/N* values. The profiles recorded at higher *E/N* field (lower pressures) corresponds to breakdown conditions in the left-hand side of the Paschen curve, while the profiles at *E/N* = 3 kTd are recorded around minimum of the breakdown curve [5].
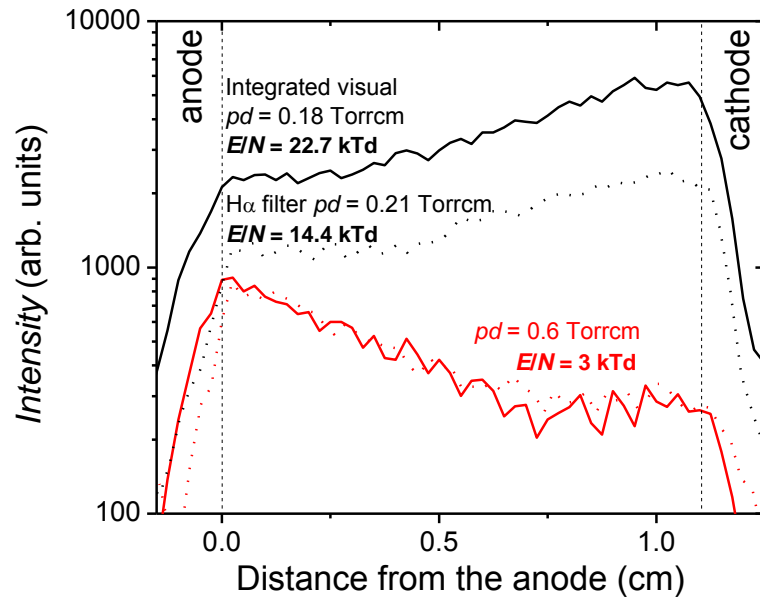
Fig. 2: Axial profiles of emission from water vapour discharge at around $pd = 0.2$ Torrcm and $pd = 0.6$ Torrcm. Intesity of profiles obtained with Hα filter (dotted line) is multiplied by a factor of 60 to facilitate the comparison. (1 Td = 10^{-21} V·m^2)

The lower E/N profile peaks at the anode due to excitation of particles induced in collisions with electrons. At such conditions, while discharge running in the low-current limit, the emission slope of the discharge rises from the cathode towards anode reflecting electron multiplication in the volume and allowing determination of the effective ionization coefficient [16]. Flattened part of the profile in front of the cathode belongs to the non-hydrodynamic region [16].

Contrary to this, in the case of high *E/N* field, the slope of the profile has a maximum at the cathode. This suggest that the dominant particle excitations are induced by collisions with energetic heavier particles, most likely fast H, present in the discharge [9]. Obviously, at high *E/N* heavy-particle processes dominate over electron processes. Between these two *E/N* values there is a continuous transition between dominant processes in different regimes, i.e. electron-dominated excitation gradually declines with *E/N* increment as heavy-particle excitation emerges and prevails at high *E/N*.

Spatial discharge profiles recorded with Hα filter have the same shape as the profiles of emission integrated in visual spectra (Fig. 2). This indicates that major contribution to overall emission comes from excited hydrogen atoms, both in the regime where electrons play crucial part in excitation and also in the case of heavy-particle excitation. However, in order to clarify a particular role of H atoms and all possible heavy-particles involved, we have performed further investigation.

To quantify the role of heavy-particle processes in low-current limit discharge we employed our comprehensive MCS and compared Hα emission from the simulation to the experimentally obtained data. In Fig. 3 we show the comparison of results at *E/N* = 14.4 kTd, presenting separately calculated contributions due to electron excitation and fast H atom excitation. The MCS data and experimental results agree quite well with almost identical shapes of emission profiles. On the other hand, intensity of the simulated profile of Hα emission is somewhat higher than the experimental. Discrepancy in front of the anode (a narrow anode peak) may come from an overestimated reflection of electrons. Additionally, spatial resolution of the optical detection system will broadened the anode peak due to reflection. Adjusting the reflection and the magnitude of the excitation cross section will produce an excellent agreement with experimental data.
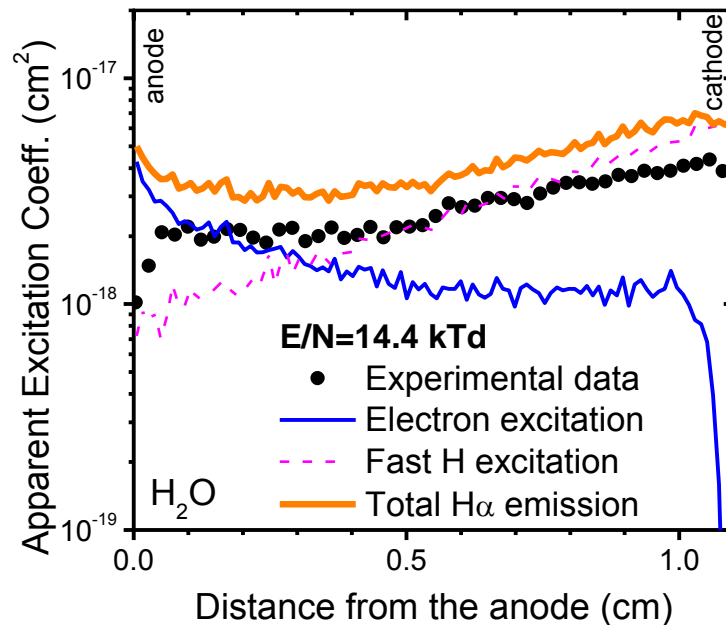
Fig. 3: Townsend discharge Hα emission obtained from MCS at *E/N* = 14.4 kTd (*pd* = 0.2 Torrcm). Thin and dashed lines show individual contribution of electron and fast H excitations respectively.

Extensive experimental investigation of low-pressure water vapour discharges yielded complete sets of data for different operating regimes. We used the data obtained from Townsend discharge, the breakdown data and optical emission profiles, to compare to the MCS results in order to obtain quantitative information regarding heavy-particle processes. Specifically, cross sections for processes between heavy particles assumed in the simulation returned a good agreement between calculated and measured emission data, and therefore proved to describe the heavy-particle processes well. The cross sections obtained here can be further used for modeling different discharge systems in water vapour environment that involve heavy particle processes.

References

[1] M. Laroussi, *IEEE Trans. Plasma Sci.* **30** (2002) 1409.

[2] J. Vasiljevic, M. Gorjanc, R. Zaplotnik, A. Vesel, M. Mozetic, B. Simoncic, *Mat. Tech.* **47** (2013) 379–384.

[3] M. Miletić, D. Vuković, I. Živanović, I. Dakić, I. Soldatović, D. Maletić, S. Lazović, G. Malović, Z. Lj. Petrović, N. Puač, N. *Cent. Europ. J. Phys.* **12** (2014) 160-167.

[4] Y. Lu, S. F. Xu, X. X. Zhong, K. Ostrikov, U. Cvelbar, D. Mariotti *EPL* **102** (2013) 15002.

[5] J. Sivoš, N. Škoro, D. Marić, G. Malović, Z. Lj. Petrović *J. Phys. D: Appl. Phys.* **48** (2015) 424011

[6] M. Klas, S. Matejčik, M. Radmilović-Radjenović, B. Radjenović *EPL* **99** (2012) 57001.

[7] W. Tian, M. J. Kushner *J. Phys. D: Appl. Phys* **47** (2014) 165201.

[8] N. Skoro, D. Maric, G. Malovic, W. G. Graham, Z. Lj. Petrovic Phys. Rev. E **84** (2011) 055401(R)

[9] D. Marić, P. Hartmann, G. Malović, Z. Donko, Z. Lj. Petrović, *J. Phys. D: Appl. Phys.* **36** (2003) 2639.

[10] V. Stojanović, B. Jelenković, Z. Lj. Petrović *J. Appl. Phys.* **81** (1997) 1601-1603.

[11] A.V. Phelps *http://www.lxcat.laplace.univ-tlse.fr* retrieved June 4, 2013.

[12] Y. Itikawa, N. Mason *J. Phys. Chem. Ref. Data* **34** (2005) 1.

[13] A. V. Phelps *J. Phys. Chem. Ref. Data* **19** (1990) 653-675.

[14] A. V. Phelps *Phys. Rev. E* **79** (2009) 066401.

[15] J. H. Miller, A. E. S. Green *Rad. Res.* **54** (1973) 343.

[16] G. Malović, A. Strinić, S. Živanov, D. Marić, Z. Lj. Petrović *Plasma Sources Sci. Technol.* 12 (2003) S1–7.

27th Summer School and International Symposium on the Physics of Ionized Gases

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CROSS SECTIONS AND TRANSPORT PARAMETERS OF O⁻ IONS IN WATER WAPOUR

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Abstract. The transport properties of O⁻ ions in water wapour in DC fields were obtained by using Monte Carlo simulation technique with the scattering cross section sets assembled on the basis of Nanbu's technique and available experimental data. In this work we present the mean energy and the reduced mobility for the conditions of low to moderate reduced electric fields E/N (N-gas density) accounting for the non-conservative collisions.

1. INTRODUCTION

Interest in application of plasmas in medicine, nanotechnologies and environmental remediation [1-5] has drawn attention to studies of discharges in water and in proximity to water [6]. Current studies show that in such systems, discharge is produced in water vapour either from evaporating liquid electrode or in bubbles created by an induced phase transition within the liquid. More generally, all atmospheric discharges contain some degree of water vapour. It is therefore of increased interest to determine how discharges are created in water [7–9]. Until recently it has been thought that discharges can only be formed in water vapor resulting from an induced phase transition. Therefore an initial point must be to have accurate knowledge of the electrical properties of water vapor and in particular its breakdown potential [10,11]. Complicated chemistry and poor data for a range of processes of particles interacting with gas and surface require further insights and more data. In this work our intention is to study energy dependent scattering probabilities of O⁻ ions in H_2O gas and to explore effects of non- conservative processes on transport properties of the O⁻ ions.

2. CROSS SECTION SETS

The scattering cross sections of O⁻ on H_2O molecule, measured by Hasted and Smith [12] for electron detachment (DET) and Lifshitz [13] for other low energy processes, are presented in Fig. 1.a) (thick lines) and listed in Table 1. A simple cross section set (S1) is completed based on these experimental data and applying appropriate linear extrapolations [see thin lines in Fig. 1.a)]. Note that in our extrapolations we have taken into account that polarisation and dipole

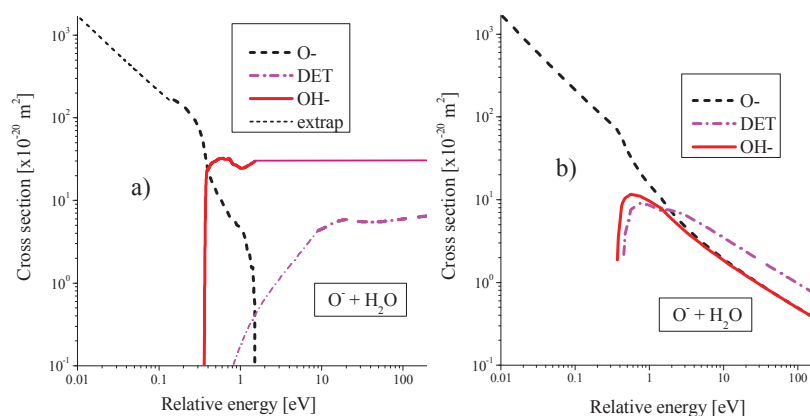forces are expected to be important over the energy range from 20 meV to few eV.

Figure 1. Cross section set of O$^-$ ions in H$_2$O based on a) available experimental data (S1) with extrapolations, b) Nanbu theory (S2).

We have also calculated a cross section set by using Nanbu's theory [14-15] (S2) which is modified to treat endothermic reactions with polar molecules by the locked dipole model [16]. In Nanbu's theory reactive collision is treated by selecting the thermodynamic threshold energy and branching ratio according to the Rice-Rampsperger–Kassel (RRK) theory [14]. Obtained cross sections were corrected to fit reduced mobility obtained by SACM (Statistical Adiabatic Channel Model) approximation [Fig. 1.b].

We have used data for polarizability and dipole moment of H$_2$O as used by Clary [17] and selected heats of formation and electron affinities from Ref. [18]. Threshold for electron detachment (DET) has been taken from Ref. [19].

The most probable reaction paths are shown in Table 1. We found them relevant for the selected domain of low O$^-$ energies in water vapour.

Table 1. The list of products and the corresponding thermodynamic threshold energies Δ for reaction O$^-$ + H$_2$O.

No	Reaction products	Δ (eV)
1	O$^-$ + H$_2$O (EL)	0.0
2	OH$^-$ + OH	-0.36
3	H$_2$O$_2$ + e-(DET)	-0.43
	O + H$_2$O + e$^-$	-1.46

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Moreover the usually applied procedure would be to unfold the cross sections from the measured transport coefficients and thermo-chemical data in a separate drift tube experiment but to our knowledge no such data are available.

Monte Carlo technique was applied to perform calculations of transport parameters as well as rate coefficients in DC electric fields. In this paper we have used a Monte Carlo code that properly takes into account the thermal collisions [20].

3.   RESULTS AND DISCUSSION

Bulk values of drift velocity [15] are used to obtain the reduced mobility for two selected cross section sets as shown in Fig. 2.a) for a range of reduced electric fields E/N (E-electric field, N-gas density) including the range where the effects of the charge transfer collisions take place. As expected, excellent agreement is achieved for the lowest field reduced mobility where the same trend for both cross section sets exists. Reactive processes with low thresholds gradually split the two curves. At the end of our E/N scale the difference appears as a consequence of very different total cross sections at highest energies. We also show the mean energy, a parameter which cannot be directly measured in experiments but a mean energy as a function of E/N may be used directly to provide the input data in fluid models especially when the local field approximation fails. The mean energies for two cross section sets overlap up to 100 Td where slow rise of energy is obtained due to the disappearance of the O^- in the process of producing OH^-. As shown in Figure 2.b) mean energy increase with E/N from about 20 Td at room temperature. Significant increase of mean energy with E/N for the S2 with respect to the S1 is due to a significant fall of the reactive cross section with energy for S2.
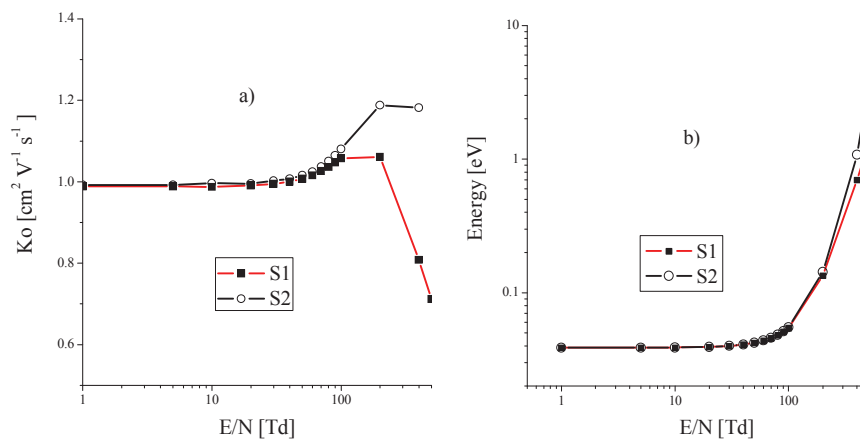

Figure 2. a) Reduced mobility, and b) mean energy, for O^- ions in water vapour as a function of E/N obtained by Monte Carlo simulation at T=300 K.

Acknowledgements

REFERENCES

[1]   K. R. Stalder, G. Nersisyan and W. G. Graham, J. Phys. D: Appl. Phys. **39** 3457 (2006).

[2]   T. Makabe and Z. Petrović *Plasma Electrinics: Applications in Microelectronic Device Fabrication* (Boca Raton, FL: Taylor&Francis, 2006)

[3]   M. Laroussi, Plasma Process. Polym. **2**, 391 (2005).

[4]   S. Lazović, N. Puač, M. Miletić, D. Pavlica, M. Jovanović, D. Bugarski, S. Mojsilović, D. Maletić, G. Malović,P. Milenković, and Z. Lj. Petrović, New J. Phys. **12**, 083037 (2010).

[5]   K. Kutasi and J. Loureiro, J. Phys. D **40**, 5612 (2007).

[6]   P. Bruggeman, D. Schram, M. Á. González, R. Rego, M. G. Kong, and C. Leys, Plasma Sources Sci. Technol. **18**, 025017 (2009); P. Bruggeman and C. Leys, J. Phys. D: Appl. Phys. **42** 053001 (2009).

[7]   G. Ruíz-Vargas, M. Yousfi, and J. de Urquijo, J. Phys. D **43**, 455201 (2010).

[8]   Y. Itikawa and N. Mason, J. Phys. Chem. Ref. Data **34**, 1 (2005).

[9]   R. E. Robson, R. D. White, and K. F. Ness, J. Chem. Phys. **134**, 064319 (2011).

[10] N. Škoro, D. Marić, G. Malović, W. G. Graham, and Z. Lj. Petrović, Phys.Rev. E **84**, 055401(R) (2011).

[11] M. Radmilović-Rađenović, B. Rađenović, Ž. Nikitović, Š. Matejčik and M. Klas, Nucl. Instr.Meth. in Phys.Res. B **279** 103 (2012).

[12] J.B. Hasted, R.A. Smith, Proc. Roy. Soc. Lond. A , Vol. 235, No.1202 349 (1956).

[13] C. Lifshitz, J. Phys. Chem. **86,** 3634 (1982).

[14] K. Denpoh and K. Nanbu, J. Vac. Sci. Technol. A **16** 1201 (1998).

[15] Z.Lj. Petrović , Z.M. Raspopović , V.D. Stojanović , J.V. Jovanović , G. Malović, T. Makabe, J. De Urquijo, Appl. Surf. Sci. **253** 6619 (2007).

[16] J.V. Dugan and J.L. Magee, J. Chem. Phys. **47** 3103 (1967).

[17] D.C. Clary, Chem. Phys. Lett. **232** 267 (1995).

[18] UMIST RATE12 astrochemistry.net \ape.jb.man.ac.uk\.

[19] F. C. Fehsenfeld and E. E. Ferguson, J. Chem. Phys., **61** 3181 (1974).

[20] Z. Ristivojević and Z.Lj. Petrović, Plasma Sources Sci. Technol. **21** 035001 (2012).

MODELING OF F- IONS IN Ar/BF3 MIXTURES

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Abstract. Transport parameters of F^- ions in mixtures Ar/BF_3 in DC fields were calculated using Monte Carlo simulation technique assuming the scattering cross section set assembled on the basis of Nanbu's technique separating elastic from reactive collisions. In this work we present characteristic energy and drift velocity for low and moderate reduced electric fields E/N (*N*-gas density) and accounting for the non-conservative collisions.

1. INTRODUCTION

Negative ions are abundant in plasmas in fluor containing molecules that are also relevant for a wide range of applications. One should bear in mind that electron affinity of F atom is the largest of all atoms and also that electronegative plasmas containing F^- ions are highly reactive. Knowledge of the plasma chemistry and behavior of negative ions in plasmas is thus necessary in order to model plasma processing devices. Additionally, recent progress of discharge modeling and simulation have made contributions to a deeper understanding of the discharge phenomena and to the optimization of reactor design or finding operating conditions. One such example is plasma implantation where Boron dopant penetration in silicon is achieved by a pulsed DC plasma system (PLAD) most widely employing BF_3 gas [1, 2].

Uniform plasma and implantation with normal ion incidence are the main goals in this technological process. Control over the number density of negative ions, in this case F^- and BF_4^-, increase efficiency of implantation. Modeling of such plasmas requires knowledge of transport parameters of all abundant particles [3].

2. EQUATIONS

The cross sections for scattering of BF_4^- ions on Ar and BF_3, and for F^- ions on BF_3 are calculated by using Nanbu's theory [4, 5] separating elastic from detachment collisions. The cross sections for F^- on Ar [5] were used to calculate

rate coefficients for detachment. The dipole polarizability of $3.31 \cdot 10^{-30}$ m^3 [6] and $1.64 \cdot 10^{-30}$ m^3 [7] is used for BF$_3$ and Ar target respectively. Monte Carlo technique of Ristivojević and Petrović [8] was used to calculate transport parameters as a function of E/N.

According to the Nanbu's theory, elastic and reactive endothermic collisions are separated and treated by accounting for the thermodynamic threshold energy and branching ratios according to the Rice–Rampsperger–Kassel (RRK) theory [4]. Within the RRK theory an excited molecular complex is treated as an excited activated complex where the internal energy is distributed among s equivalent vibrational modes of the complex.

The cross section for exothermic reaction (EXO) forming a super halogen molecular ion BF$_4^-$ is commonly represented by ion capture cross section:

$$\sigma_{exo} = \beta \sigma_L \tag{1}$$

where σ_L is the orbiting cross- section [9] and β is is the probability of a specific exothermic reaction.

3. DISCUSSION AND RESULTS

The transport coefficients include drift velocity, diffusion coefficients, ionization and attachment coefficients and chemical reaction coefficients for ions [3]. Excitation coefficients are also measured but seldom used in modeling.

Swarm parameters are generally applied in plasma modeling and simulations. At the same time, the non-equilibrium regime in discharges is well represented under a broad range of conditions by using Monte Carlo simulation scheme.

In this work we use Monte Carlo technique that accounts for a finite gas temperature of the background gas particles [5] to calculate swarm parameters of F$^-$ ions in gas for temperature T=300 K.

In Figure 1 we show the characteristic energies (diffusion coefficient normalized to mobility eD/K in units of eV) based on longitudinal (D$_L$) diffusion coefficients. We also show the mean energy, a parameter which cannot be directly measured in experiments but a map of mean energy versus E/N may be used directly to provide the data in fluid models especially when the local field approximation fails. As seen in Figure 1, the mean energy increases from about 10 Td. The Monte Carlo code [8] gives good results in which for all mixtures Ar/ BF$_3$ the mean energy converges to the thermal mean energy 3/2 kT = 0.038778 eV, while the thermal eD/K = kT converges to 0.025852 eV (longitudinal (DL) and transverse (DT) diffusion coefficients).
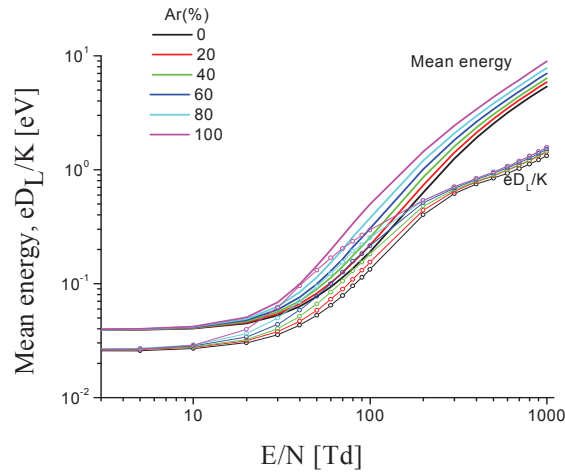
Figure 1. Mean and characteristic energy of F⁻ ions in BF$_3$ gas as a function of *E/N* at *T* = 300 K.

The bulk and flux drift velocities for F- in Ar/BF3 as a function of E/N are given in Figure 2. The drift velocities obtained by Monte Carlo simulation are calculated in real space (bulk) and in velocity space (flux) values and are obtained as <v> and dx/dt, respectively. The bulk and flux values of the drift velocity begin to differ above 100 Td but very little.
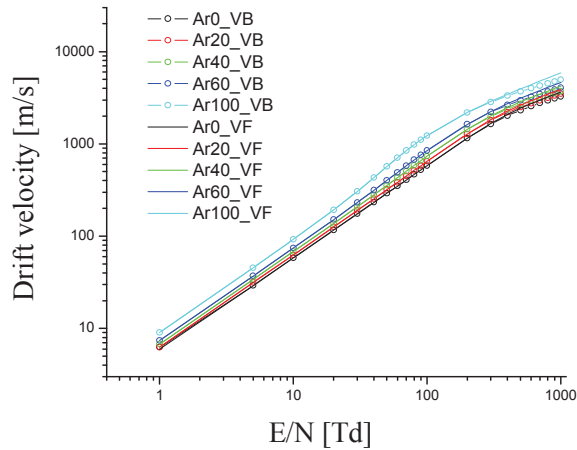

Figure 2. The bulk and flux drift velocity of F- ions in Ar/BF3 as a function of E/N at T=300 K.

4. CONCLUSION

In this paper we show transport properties for the F- in mixtures Ar/BF3 which do not exist in the literature. The complete cross section set has been determined by extending Nanbu's theory.

The results are believed to be a good base for modeling, which could be further improved when measured values of transport coefficients become available and then perform the analysis again.

Acknowledgements

REFERENCES

[1] B.-W Koo, Z. Fang, L. Godet, S. B. Radovanov, C. Cardinaud, G. Cartry, A. Grouillet and D. Lenoble, IEEE Trans. Plasma Sci., 32, 456 (2004).

[2] Ž. Nikitović, S. Radovanov, L. Godet, Z. Raspopović, O. Šašić, V. Stojanović and Z. Lj. Petrović, EPL 95, 45003 (2011).

[3] Z. Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, V. Stojanović and M. Radmilović-Rađenović, J. Phys.D: Appl. Phys. 42, 194002 (2009).

[4] K. Denpoh and K. Nanbu, J. Vac. Sci. Technol. A16, 1201(1998).

[5] Z. Lj. Petrović, Z. M. Raspopović, V. D. Stojanović, J. V. Jovanović, G. Malović, T. Makabe and J. De Urquijo, Appl. Surf. Sci. 253, 6619 (2007)

[6] C. Szmytkowski, M. Piotrowicz, A. Domaracka, L. Klosowski, E. Ptasinska-Denga and G. Kasperski, J. Chem. Phys. 121, 1790 (2004).

[7] E.W Mc Daniel, Atomic Collisions : Electron and Photon Projectiles, John Willey & Sons, Inc. 655 (1989).

[8] Z. Ristivojević and Z. Petrović, Plasma Sources Sci. Technol., 21, 035001 (2012).

[9] E. W. McDaniel, V. Čermak, A. Dalgarno, E. E. Ferguson and L. Friedman, Ion-Molecule reactions, Willey-Interscience (1970).

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CROSS SECTION AND TRANSPORT PARAMETERS FOR K$^+$ IN DIMETHOXY ETHANE

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Abstract. In this work we present most probable reactions of alkali metal ion K$^+$ with dimethoxy ethane (DXE) molecule. Appropriate gas phase enthalpies of formation for the products were used to calculate scattering cross section as a function of kinetic energy. Three body association reaction of ion with DXE is studied and compared to experimental results. Calculated cross sections were used to obtain transport parameters for K$^+$ in DXE gas.

1. INTRODUCTION

Cold plasmas are often used in new technologies where they offer methods for nonintrusive production or modification of specific substances. Main characteristics of these plasmas are their high electron temperature and low gas temperature. Dimethoxy-containing compounds, such as dimethoxy ethane (DXE), can be produced from dimethyl ether by using dielectric barrier discharge (DBD) plasmas containing water vapor at atmospheric pressure [1]. As clear and colorless liquid at room temperature and atmospheric pressure, DXE is used as a precursor in production of ceramics or as a sole compound to make other chemicals such as those used in lithium batteries production, superconductor production and nanoparticles synthesis.

In this paper we firstly selected the most probable reactions of alkali metal ion K$^+$ with DXE molecule (and its most probable products) for thermodynamic threshold energies below about 15 eV. Appropriate gas phase enthalpies of formation [2] for the products were used to calculate thermodynamic thresholds.

2. CROSS SECTION SET

The scattering cross section of alkali ion K$^+$ on DXE are calculated by using the Denpoh-Nanbu (DN) theory [3] separating elastic from reactive collisions. DXE is known not to have dipole moment in its ground state. The dipole polarizability of 9.94×10^{-30} m^3 [4] is used for the DXE target. Similar to

our recent papers [5] DN method is used to separate elastic from reactive endothermic collisions by accounting the thermodynamic threshold energy and branching ratio according to the Rice-Rampsperger-Kassel (RRK) theory [3]. Within the RRK theory the internal energy is being distributed among an empirical number of *s* equivalent effective modes of the complex selected from the total number of atoms involved in the complex.
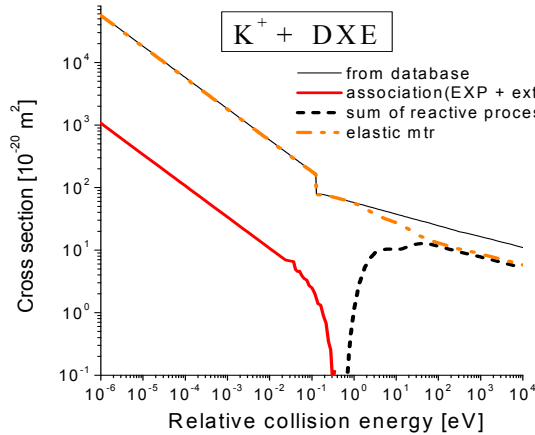

Figure 1. Cross section sets for K$^+$in DXE.

Elastic momentum transfer cross section is modified in order to fit approximate mobility peak characteristic for presented systems. Swarm method [5, 6] is exploited to modify the cross section for elastic momentum transfer where for reduced mobility in the peak region (experimental [7] or theoretical values [8]) similarity with ions of equal or similar reduced mass is targeted. Elastic momentum transfer cross section for elastic collisions of K$^+$ with DXE is presented in Figure 1.

3. DISCUSSION AND RESULTS

Swarm parameters as a function of reduced electric field *E/N* in DC electric fields are generally applied to plasma modeling and simulations.

We have used a Monte Carlo code that properly takes into account thermal collisions [9]. The code has passed all the relevant benchmarks and has been tested in our work on several types of charged particles.

In Figure 2. we show the mean energy, which cannot be directly measured in experiments but a map of the mean energy versus *E/N* may be used

directly to provide the data in fluid models especially when the local field approximation fails.
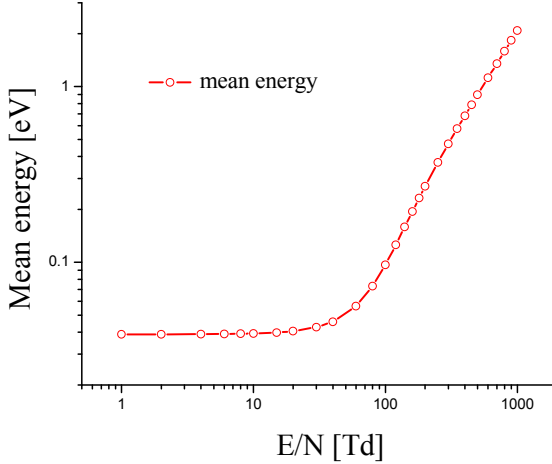

Figure 2. Mean energy of K^+ ions in DXE gas as a function of *E/N* at *T* = 300 K.

In Figure 3. we show the results of Monte Carlo simulation for reduced mobility as a function of *E/N*. Due to reactive collisions bulk and flux values of reduced mobility are separated.
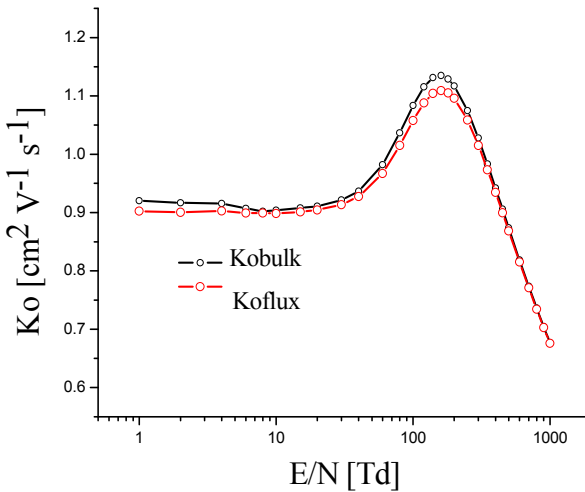

Figure 3. Reduced mobility of K^+ ions in DXE as a function of *E/N* at *T*=300 K.

The mobility K of an ion is the quantity defined as the velocity attained by an ion moving through a gas under the unit electric field. One often exploits the reduced or standard mobility defined as:

$$K_0 = \frac{v_d}{N_0 E} N \,, \tag{1}$$

where v_d is the drift velocity of the ion, N is the gas density at elevated temperature T and is the electric field.

4. CONCLUSION

Calculated cross sections are used to obtain transport parameters for alkali metal ion K^+ in DXE gas.

The cross sections and transport data for technologically very important gas DXE have been determined by using simple theory. While it is a good basis for modeling it would be much better to add a data base of measured transport coefficients and then to perform the analysis again.

Acknowledgements

REFERENCES

[1] Y. Wang, C. Liu, Y. Zhang, Plasma Sci. & Technology 7, No. 3, 2839 (2005).
[2] S. G. Lias, J. E. Bartmess, J. F. Xebman and J. L. Holmes, R. D. Levin and W. G. Mallard, J. Phys. Chem. Ref. Data, Supl. 1 Vol. 17, 1 (1988).
[3] K. Denpoh and K. Nanbu, J. Vac. Sci. Technol. A 16 (3), 1201 (1998).
[4] H. Koizumi, P. B. Armentrout, J. Chem. Phys. 119, 12819 (2003).
[5] V. Stojanović, Z. Raspopović, J. Jovanović, Ž. Nikitović and Z. Lj. Petrović, EPL 101, 45003 (2013).
[6] Ž. Nikitović, Z. Raspopović, V. Stojanović and J. Jovanović, EPL 108, 35004 (2014).
[7] L. A. Viehland and E. A. Mason, At. Data. Nucl. Data Tables 60, 37 (1995).
[8] http://nl.lxcat.net/data/set type.php.
[9] Z. Ristivojević and Z. Lj. Petrović, Plasma Sources Sci. Technol. 21, 035001 (2012).

TRANSPORT PROPERTIES OF He$^+$ IN CF$_4$

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Abstract. In this paper we are presenting cross section set for scattering He$^+$ ions in CF$_4$ that is assessed by using available experimental data for charge transfer cross sections. Monte Carlo method is used to calculate mean energy and drift velocity as a function of *E/N* and discussed as a consequence of non-conservative reactions at temperature T=300 K.

1. INTRODUCTION

Charge transfer reactions of ions with molecules are inavoidable elementary processes in modeling kinetics in terrestrial, industrial and astrophysical plasmas. In selected cases charge transfer reactions are known to represent the most significant part of a cross section set. Line spectra of excited atoms obtained in spectrometric measurements in CF$_4$ indicate that the charge transfer reaction is dominant process in collisions with inert gas ions. Thus, in this work we assessed cross section set for He$^+$ in CF$_4$ by using existing experimental data [1] for charge transfer collisions producing radical ions of CF$_4$. Since no direct information is found in the literature how mobility of high recombination energy ions such as He$^+$ ions behaves in CF$_4$ gas we also calculated transport parameters by using Monte Carlo simulation technique [2].

2. MONTE CARLO TECHNIQUE

The cross sections measured by Fisher *et al.* [1] were used to deduce elastic momentum transfer cross section (Figure 1) assuming total momentum transfer cross section σ_{mt} is known. At very low energies we assumed that σ_{mt} behaves as Langevin's cross section and elastic momentum transfer cross section is determined by deducing all reactive cross sections i.e productions of CF$_2^+$ and CF$_3^+$ ions. In the absence of association reaction [1] these were only processes that may affect mobility of He$^+$ ions. Accordingly for average polarizability of CF$_4$ we adopted value of 3.86 A^3 used by Stojanović *et al.* [3] who found excellent agreement between experimental and calculated mobility of CF$_3^+$ ions in CF$_4$.
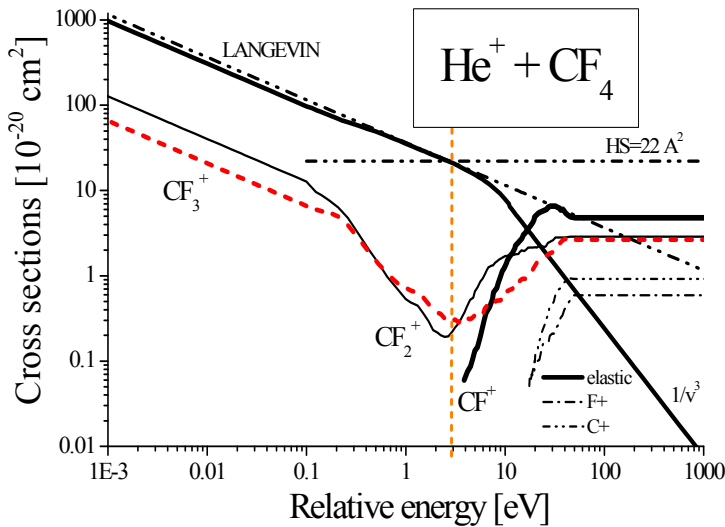
Figure 1. Cross section set for He$^+$ in CF$_4$.

Further, extrapolation of elastic momentum transfer cross section trend beyond crossing point of Langevin's and hard sphere (HS) cross section [1] is done by smoothly connecting to $1/v^3$ trend [4, 5] where v is the center-of-mass velocity (see Figure 1).

At all ion kinetic energies above 50 eV reactive cross sections are extrapolated by constant values.

Effect of various extrapolations (short dot-dashed or dashed line in Figure 1) of unusual behavior at low energy, observed with measurements of the cross section leading to formation of CF$_2^+$ (where irrespective of the He$^+$ spin state exothermic behavior of reaction is expected) is found negligible on mobility.

3. DISCUSSION AND RESULTS

The transport coefficients include drift velocity, diffusion coefficients, ionization and attachment coefficients and chemical reaction coefficients for ions [2]. Excitation coefficients are also measured but seldom used in modeling.

Swarm parameters are generally applied in plasma modeling and simulations. At the same time, the non-equilibrium regime in discharges is well represented under a broad range of conditions by using Monte Carlo simulation scheme.

        In this work we use Monte Carlo technique that accounts for a finite gas temperature of the background gas particles [6] to calculate swarm parameters of He$^+$ ions in CF$_4$ gas for temperature T=300 K.

        In Figure 2 we show the characteristic energies (diffusion coefficient normalized to mobility eD/K in units of eV) based on longitudinal (D$_L$) and transversal (D$_T$) diffusion coefficients.
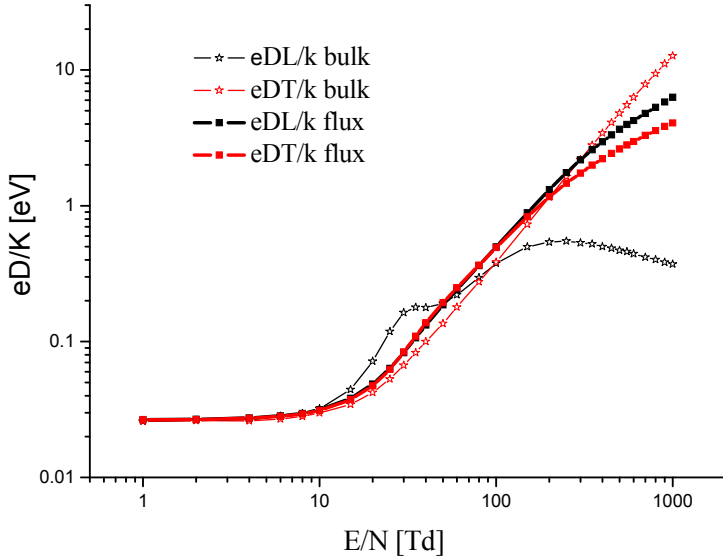

Figure 2. Characteristic energy of He$^+$ ions in CF$_4$ gas as a function of *E/N* at *T* = 300 K.

        The bulk and flux drift velocities for He$^+$ in CF$_4$ as a function of *E/N* are given in Figure 3. The drift velocities obtained by Monte Carlo simulation are calculated in real space (bulk) and in velocity space (flux) values and are obtained as <*v*> and d*x*/d*t*, respectively. The bulk and flux values of the drift velocity begin to differ above 20 Td.
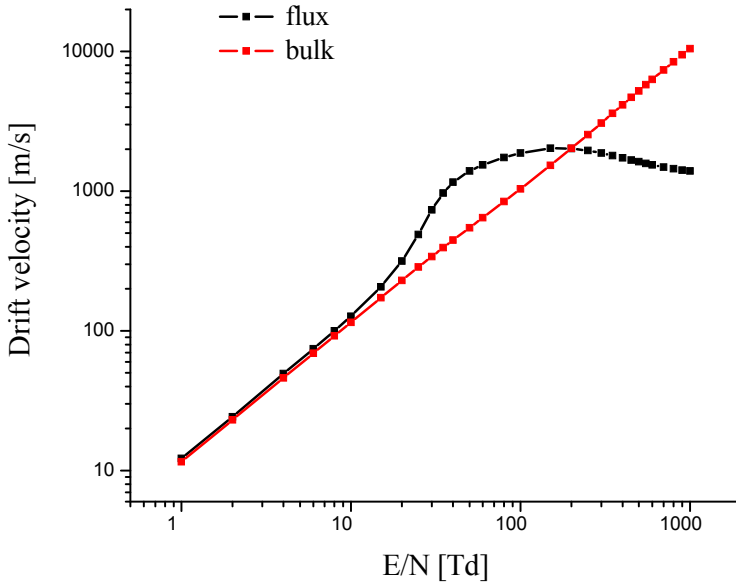
Figure 3. The bulk and flux drift velocity of He$^+$ ions in CF$_4$ as a function of *E/N* at *T*=300 K.

Acknowledgements

REFERENCES

[1] E. R. Fisher, M. E. Weber and P. B. Armentrout, J. Chem. Phys. 92, 2296 (1990).
[2] Z. Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, V. Stojanović and M. Radmilović-Rađenović, J. Phys. D: Appl. Phys. 42, 194002 (2009).
[3] V. Stojanović, Z. Raspopović, J. V. Jovanović, J. de Urquijo and Z. Lj. Petrović, J. Phys. Conf. Ser. 514, 012059 (2014).
[4] P. S. Krstić and D. R. Schultz, J. Phys. B: At. Mol. Opt. Phys. 42, 065207 (2009).
[5] Z. Raspopović, V. Stojanović and Ž. Nikitović, EPL 111, 45001 (2015).
[6] Z. Lj. Petrović, Z. M. Raspopović, V. D. Stojanović, J. V. Jovanović, G. Malović, T. Makabe and J. de Urquijo, Appl. Surf. Sci. 253, 6619 (2007).

CROSS SECTIONS FOR SCATTERING AND MOBILITY OF OH⁻ AND H₃O⁺ IONS IN H₂O

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Abstract. In an attempt to provide the data that are not yet available, we present cross sections sets and reduced mobility for OH⁻ and H_3O^+ ions. Denpoh-Nanbu procedure (DNT) has been applied to calculate cross section sets for collisions of OH⁻ and H_3O^+ ions with H_2O molecule. Reduced mobility for OH⁻ and H_3O^+ ions in H_2O are calculated by using a Monte Carlo code over a wide range of *E/N* (*E*-electric field, *N*-gas density) at temperature *T*=295 K, in the low pressure limit.

1. INTRODUCTION

The interest in application of plasmas in medicine, some nanotechnologies and environmental remediation [1] has drawn the attention to studies of discharges in water and in proximity to water [2] although other liquids are of interest as well. More generally, all atmospheric discharges contain some degree of water vapour [3]. It is therefore of interest to determine how discharges are created in water vapour and to provide elementary transport data for the charged particles [1, 4].

We applied Denpoh-Nanbu [5] procedure to calculate cross section sets for collisions of OH⁻ and H_3O^+ ions with H_2O molecule. Induced polarization and permanent dipole interaction in reactions of these ions with H_2O are taken into account. The OH⁻ set includes production of anions (OH⁻, H⁻,O⁻,O_2^-, HO_2^-) and electrons released in ion induced electron detachment, while the H_3O^+ set includes production of cations (H⁺, H_2^+, H_3^+, H_2O^+, O⁺, O_2^+, O_2H^+, OH⁺). Reduced mobility for OH⁻ and H_3O^+ ions in H_2O are calculated by using a well tested Monte Carlo code over a range of *E/N* from 1 Td to 1200 Td at temperature *T* = 295 K, in the low pressure limit.

The data are valid for low pressure water vapour or small amounts in mixtures. These data will provide a solid basis for calculation of ion-water molecule clusters properties that are most commonly found at higher pressures, and for modelling of discharges in liquids.

2. CALCULATION OF THE CROSS SECTIONS AND REDUCED MOBILITY

The scattering cross section sets for OH$^-$ and H$_3$O$^+$ ions on H$_2$O molecule, are presented in Fig. 1 and Fig. 2, respectively. Cross section sets are initially calculated by applying Denpoh-Nanbu theory [5, 6] where we have taken into account that polarisation and dipole forces are expected to be important over the energy range from 20 meV to few eV. Since range of polarisation potential is a few eV, only processes with low threshold energies are taken into account.

For both ions we have used data for polarizability ($\alpha=1.45\cdot10^{-30}$ m^3) and dipole moment of H$_2$O as suggested by Clary [7]. Selected heats of formation and electron affinities are taken from from Ref. [8].

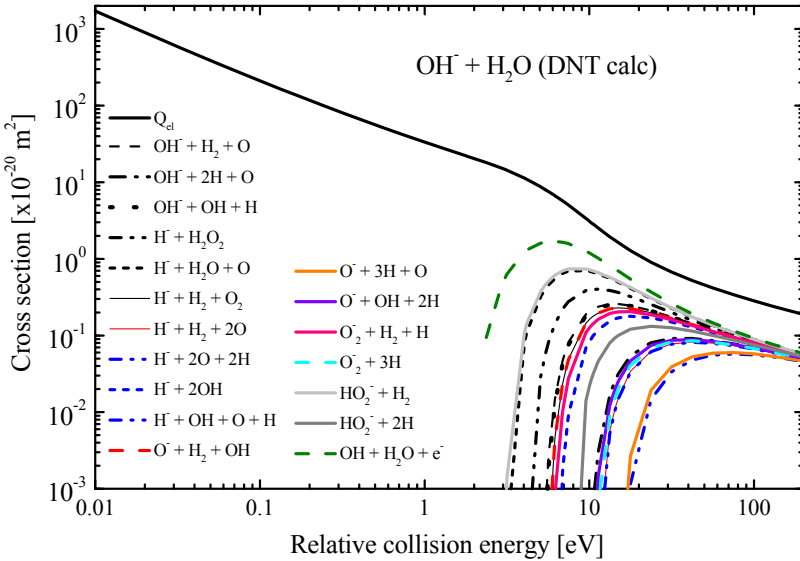**Figure 1.** Cross section set for OH$^-$ scattering on H$_2$O.

In Fig. 1 and Fig.2 we have shown cross section set for scattering of OH$^-$ ion and H$_3$O$^+$ ions, respectively. Considering H$_3$O$^+$ ions obtained cross section set was used as initial in swarm procedure in which elastic momentum transfer cross section was further improved by assuring a good agreement between our Monte Carlo (MC) calculated reduced mobility and the available experimental results [9].

Reduced mobilities for OH$^-$ and H$_3$O$^+$ ions in H$_2$O as a function of *E/N* are shown in Fig. 3. Reduced mobilities for OH$^-$ and H$_3$O$^+$ ions in H$_2$O are calculated as a function of *E/N* at temperature *T* = 295 K, for conditions where pressure effects can be assumed to be negligible. A Monte Carlo simulation method appropriate to calculate transport parameters [10, 11] for ions in gases at

elevated temperature [11] was used. In Monte Carlo simulations exothermic reactive collisions are followed in a similar way as all non-conservative collisions, i.e. followed swarm particle dissappear from the swarm after the exothermic collision.
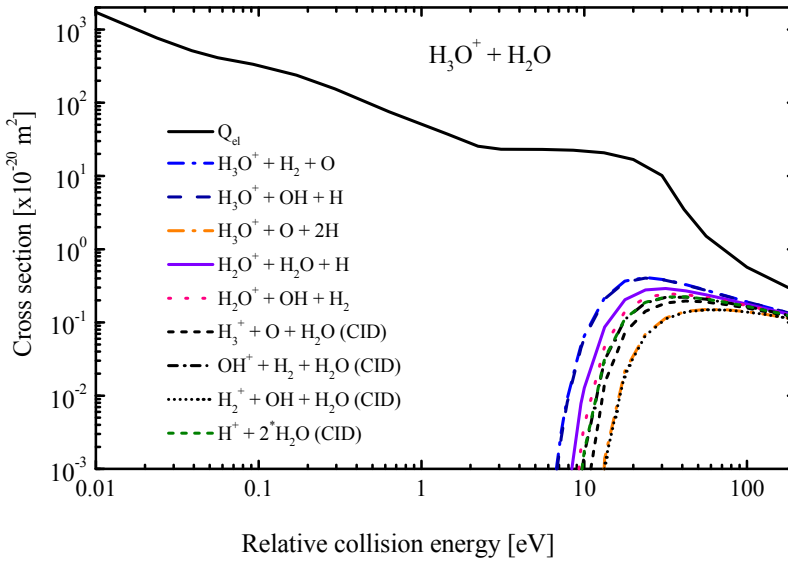

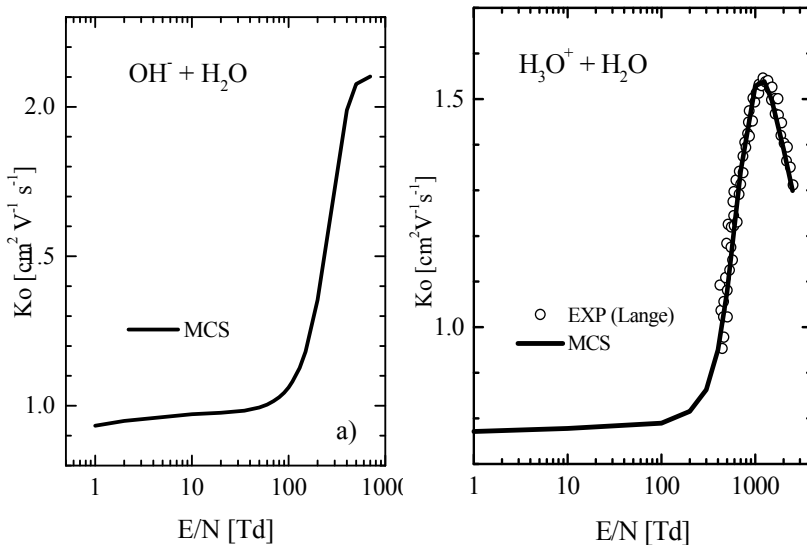**Figure 2.** Cross section set for H_3O^+ scattering on H_2O.

Figure 3. Reduced mobility as a function of E/N for a) OH^- ion and b) H_3O^+ ion.

3. CONCLUSION

In this paper the cross-section set has been obtained by using a simple theory. The Monte Carlo technique was applied to carry out calculations of reduced mobility as a function of reduced electric field. Due to the lack of experimental data, we were not able to test the accuracy of derived cross sections set for OH⁻ ions in H_2O. However, considering H_3O+ ions it is noteworthy saying that the agreement between calculated and measured reduced mobility is very good and for these ions the derived cross section set is more accurate but for further validation some additional experimental data such as diffusion coefficients are needed. Anyway, the obtained results are a good base for modelling, which could be further improved by adding a data base of the measured values of transport coefficients and then performing the analysis again.

Acknowledgment

REFERENCES

[1] J. de Urquijo, E. Basurto, A.M. Juarez, K.F. Ness, R.E. Robson, M.J. Brunger, R.D.White, J. Chem. Phys. 141, 014308 (2014).

[2] P. Bruggeman, D. Schram, M. Á. González, R. Rego, M. G. Kong, and C. Leys, Plasma Sources Sci. Technol. 18, 025017 (2009); P. Bruggeman and C. Leys, J. Phys. D: Appl. Phys. 42 053001 (2009).

[3] T. Murakami, K. Niemi, T. Gans, D. O'Connell, W.G.Graham, Plasma Sources Sci. Technol. 22, 015003 (2013); W. Van Gaens, A. Bogaerts, J. Phys. D 46, 275201 (2013);

[4] G. Ruíz-Vargas, M. Yousfi, and J. de Urquijo, J. Phys. D 43, 455201 (2010); R.D. White, W. Tattersall, G. Boyle, R.E. Robson, S. Dujko, Z.Lj. Petrović, A. Banković, M.J. Brunger, J.P. Sullivan, S.J. Buckman, G. Garcia, Appl. Radia. Isotopes 83, 77 (2014).

[5] K. Denpoh and K. Nanbu, *J. Vac. Sci. Technol.* A **16** (1998) 1201

[6]   Z.Lj. Petrović , Z.M. Raspopović , V.D. Stojanović , J.V. Jovanović , G. Malović, T. Makabe, J. De Urquijo, Appl. Surf. Sci. 253 6619 (2007).

[7] D.C. Clary, Chem. Phys. Lett. 232 267 (1995).

[8] S.G. Lias,J.E. Bartmess, J.F. Liebman, J.L. Holmes. R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data, 17, supplement 1,1 (1988) .

[9] F.D. Lange, Int.J.Mass.Spectrosc.Ion.Proc, 37 341-354 (1981).

[10] R.E. Robson, R.D. White and Z. Lj.Petrović, *Rev. Mod. Phys*. **77** (2005) 1303; Robson R. E., Aust. J. Phys., 44 (1991) 685.

[11] Z. Ristivojević and Z.Lj. Petrović, Plasma Sources Sci. Technol. 21 035001 (2012).

MASS SPECTRA ANALYSIS OF RF NITROGEN PLASMA FOR FUNCTIONALIZATION OF CARBON NANOSTRUCTURES

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Abstract. Low pressure (0.1 - 0.2 mbar) capacitively-coupled RF nitrogen plasma is used for plasma functionalization of carbon nanotubes. To optimize the functionalization, the samples are exposed at different distances (0 - 93 mm) from plasma source. To analyze the active species, the mass spectrometry is done at same positions. On short distances the majority of ion flux consists of N_2^+ ions. However, the large flux of N_2H^+, H_2O^+ and H_3O^+ is detected too, which originate from relatively small amount of impurities. The possible ion-molecule reactions responsible for the detected ion fluxes are analyzed.

1. INTRODUCTION

The functionalized carbon nanotubes (CNTs) are used in biotechnology for creating bio-nanocomposits [1], in particular for fabricating components for biosensors [2]. The functionalization of CNTs with nitrogen containing functional groups is used to create chemical (covalent) binding with polymers [1]. Low-temperature nitrogen plasmas provide an important alternative way to functionalize CNTs with nitrogen [3].

In order to get the optimal parameters for low-temperature plasma polymerization the diagnosis and control of plasma properties is necessary [4]. Recently, it is shown for radiofrequency (RF) oxygen plasma that significant amount of impurity ions, especially water cluster, contribute to the total ion flux upon the distance of the mass spectrometer sampling orifice and plasma source [5]. The presence of impurity ions can, in some cases, help to improve functionalization of CNTs. Here, we will present the results of ion mass spectra of RF nitrogen plasma upon the different distances to plasma source. By

analyzing ion -molecule reactions in the reactor it is possible to explain the change of ion spectra form "nitrogen dominated" (near to the plasma source) to the "impurity dominated" (far away from the plasma source). These results will be correlated with the material analysis of CNTs functionalized at the same positions.

2. EXPERIMENT

Experimental set-up consists of discharge chamber equipped with vacuum system, providing the basic pressure of $5 - 7 \times 10^{-8}$ mbar. The system of mass flow controllers and valves ensures the continuous flow of gas mixture and the working pressure. RF power in the range of 3 W to 15 W is capacitively coupled to the discharge by using matching network. Plasma properties can be monitored with different diagnostic techniques, including infrared absorption spectroscopy, microwave interferometry, emission spectroscopy and electric probe. Here, we use mass spectrometer equipped with energy analyzer that is mounted on the mechanical rail and can be traveled to and from the plasma. The mass spectrometer is mounted perpendicular to the discharge axis and supplies the information about different neutral and ionic species, as well as ion energy distributions at different distances from the plasma source. The details on experimental set-up and procedure can be found in the literature [5].

3. EXPERIMENTAL RESULTS

Table 1. Total ion fluxes for different ions for two distances between the plasma and the sampling orifice. Discharge conditions are: pressure $p = 0.1$ mbar, electric power $P = 4$ W, working gas N_2, flow - rate 50 sccm.

distance (cm)	N_2^+ (c/s)	H_2O^+ (c/s)	$H(H_2O)^+$ (c/s)
0	$3.40 \cdot 10^7$	$2.93 \cdot 10^7$	$3.40 \cdot 10^7$
9.3	1340	$1.33 \cdot 10^6$	$1.59 \cdot 10^5$

Energy resolved ion distributions of some relevant positive ions are measured for different distances between sampling orifice of mass spectrometer and plasma. Energy resolved ion fluxes of specific ions are integrated over measured energy range to obtain the total ion fluxes, which are listed in Table 1. In addition, fluxes of N^+, N_3^+, N_4^+, N_2H^+, NO^+, OH^+, and ion clusters of water molecules $H^+(H2O)_n$, $(n = 2, 3)$ are also detected (not presented here).

As expected, close to the plasma the most prominent ion is N_2^+. Nevertheless, even the abundance of water impurities are very low in comparison to the working gas (nitrogen) the flux of water ions and protonized water ions $H^+(H_2O)$ is very high and close to the flux of N_2^+ ion.

The relative ion contributions are dramatically changed with the distance. At 9.3 cm distance, the molecular nitrogen ions disappear, leaving the H_2O^+ as the most dominant constituent of the positive ion flux.

4. CHARGED PARTICLES TRANSPORT

It is obvious that change of mass spectra is induced by various ion reactions that occur during the travel of ions between plasma and the sampling orifice. It is why is necessary to analyze the ion transport processes in the presence of impurities. The first step is to select the proper set of cross sections for N_2^+, N_2H^+, H_2O^+, H_3O^+ and NO^+ scattering on H_2O molecule. In this work we present assessed cross section set for scattering of N_2^+ on H_2O as probably most relevant for production of N_2H^+ impurity ions detected in our system.

Since only a few measurements of the cross sections exist for selected system we used Denpoh-Nanbu theory [6] to resolve between elastic and reactive cross sections assuming induced and permanent dipole interaction [7-9]. In Table 2 we show most probable reactions, based on thermo chemical values [10]. At hyperthermal collision energies, intermediate collision complex become too short-lived and thus measurements of Dressler *et al.*[6] (EXP, see Fig. 1) were included to cover that energy range. Rate constant for charge transfer reaction selected in Ref. [11] (k=1.8 10^{-9} cm^3/s at 300 K) is in agreement with value calculated from charge transfer cross section presented in Fig. 1. If cross section for N_2H^+ production is extrapolated to low energies with the same trend as charge transfer cross section we obtained about 2.3 times lower rate constant at 300 K than suggested in Ref. [11].

Our preliminary Monte Carlo calculations [12] of transport parameters show that non conservative collisions strongly affect transport of N_2^+ in H_2O not only by producing N_2H^+ but also in significant variation of transport parameters in whole range of reduced electric field values [13].

Table 2. N_2^+-H_2O reaction products and the corresponding thermodynamic threshold energies Δ.

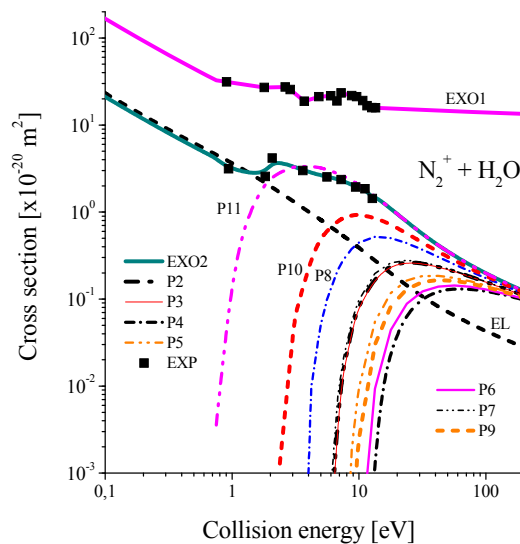| No	products	Δ (eV)
P1	$N_2^+ + H_2O$ (EL)	0
EXO1	**$H_2O^+ + N_2$**	2.999
EXO2	**$N_2H^+ + OH$**	1.974
P2	$N_2^+ + H_2 + O$	-5.059
P3	$N_2^+ + OH + H$	-5.113
P4	$N_2^+ + O + 2H$	-9.536
P5	$H_2O^+ + 2N$	-6.799
P6	$N^+ + N + H_2O$	-8.751
P7	$H_2^+ + O + N_2$	-4.903
P8	$O^+ + H_2 + N_2$	-3.096
P9	$H+ + H + O + N_2$	-7.553
P10	$NO^+ + H_2 + N$	-1.999
P11	$N_2O^+ + H_2$	-10.58

Figure 1. Cross section set for $N_2^+ + H_2O$ reaction as a function of collision energy. EL-the elastic momentum transfer cross section, EXOx- xth exothermic and Py-yth endothermic cross section (see Table 2).

Acknowledgements

REFERENCES

[1]   L. Nagy, *et al*, Current Protein and Peptide Science, 15, 363 (2014).
[2]   A. Matsumoto and Y. Miyahara, Nanoscale, 5, 10702 (2013).
[3]   B. Khare, P. Wilhite, B. Tran, *et al*, J. Phys. Chem. B, 109, 23466 (2005).
[4]   K. Spasić, N. Škoro, *et al*, 32nd ICPIG P. 2.51 (2015) ; K. Spasić, N. Škoro, *et al*, 42nd IEEE Conf. Plasma Sci.(ICOPS) P. 2B-4 (2015).
[5]   I. Stefanović, V. Stojanović *et al* J. Phys. D: Appl. Phys. 49 265202 (2016).
[6]   K. Denpoh and K. Nanbu, J. Vac. Sci. Technol. A 16 (3), 1201(1998).
[7]   D.C. Clary, Chem. Phys. Lett. 232 267 (1995).
[8]   S. G. Lias *et al* J. Phys. Chem. Ref. Data, Supl. 1 Vol. 17, 1 (1988).
[9]   V. Stojanović, Z. Raspopović, *et al* , Eur. Phys. J. D 69, 63 (2015).
[10] R.A. Dressler *et al* J.Chem.Phys., 92, 1117-1125 (1990).
[11] L. W. Sieck *et al*, Plasma Chem. and Plasma Proc., 20, 235 (2000).
[12] Z. Ristivojević and Z. Lj. Petrović, PSST 21, 035001 (2012).
[13] R.E. Robson, R.D. White and Z. Lj.Petrović, *Rev. Mod. Phys*. **77** (2005) 1303.

MODELING EMISSION FROM WATER VAPOR DC DISCHARGE AT LOW PRESSURE

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Abstract. We follow transport of electrons, positive ions and fast H atoms in H_2O in high DC fields by using Monte Carlo simulation technique. Cross section sets for scattering of electrons, positive ions (H^+, H_2^+, OH^+, H_2O^+, H_3O^+) and fast hydrogen atoms on H_2O were assessed and used as an input in Monte Carlo simulations. In this paper we show results of our Monte Carlo simulations (MCS) for spatially resolved Hα emission for the conditions of high reduced electric fields *E/N* (*N*-gas density). Cross section for Hα excitation of H_2O by fast H atoms is modified in order to obtain agreement with a range of experimental results for Hα emission from moderate to high *E/N*.

1. INTRODUCTION

Interest in application of plasmas in medicine, nanotechnologies and environmental applications [1-5] has motivated studies of discharges in water and with water vapour as well as the water boundaries [6]. Current studies show that in such systems, discharge is produced in water vapour either from evaporating liquid electrode or in bubbles created by an induced phase transition within the liquid. Since all atmospheric discharges contain some degree of water vapour it is of an increased interest to determine how discharges are created in water [7–9] both liquid, at the interface betwene liquid and gas and in water vapour. Accurate knowledge of the electrical properties of water vapor and in particular its breakdown potential [10,11] are the basic information for modelling in various situations. Complicated chemistry and poor understanding for range of processes of particles interacting with gas and surface forced to further insights of such discharges. In this work our aim is to model spatially resolved Hα emission in water vapor gas by using assembled cross sections for positive ions (H^+, H_2^+, OH^+, H_2O^+, H_3O^+) and fast H neutrals scattered on H_2O and to explore effects of heavy particles.

2. MONTE CARLO SIMULATION

A Monte Carlo simulation (MCS) was employed to model the Townsend discharge with parameters used in the experiment and take into account boundary conditions, spatially dependent transport coefficients for electrons and heavy particles as well as distribution functions that may include a runaway component. Monte Carlo code for electron transport was coupled with similar particle codes involving ions and neutrals [12]. Cross sections for electron collisions were taken from the literature [13,14]. For heavy-particle processes we modified collision cross sections from the data reviewed by Phelps [15,16] and Miller and Green [17] assuming the dominant role of fast H atoms in excitation. For ions other than H^+ we exploited Denpoh-Nanbu theory [18,19] to calculate cross sections for elastic and reactive processes which where extrapolated towards high energy by a hard sphere cross section. Energy partition of ions dissociated at the cathode is according to data for pure H_2 discharge as well as integrated probability of escape [16]. Electrons reflected from the electrodes were also included in the simulation. As an output of the model we observed H emission coming from excitation induced by electrons and in heavy particle collisions.

3. RESULTS

Spatial discharge profiles recorded with Hα filter have the same shape as the profiles of emission integrated in visual spectra [10]. This indicates that major contribution to overall emission comes from excited hydrogen atoms, both in the regime where electrons play a crucial part in excitation and also in the case of heavy-particle excitation. In order to clarify a particular role of H atoms and all possible heavy-particles involved, we have modified cross section for fast H [16] (dashed-dot-dot line in Fig. 1) by fitting Monte Carlo results for spatial emission to experimental emission data from moderate(not shown) to very high *E/N*.

Modified cross section for Hα excitation by fast H atoms is presented by connected solid line in Fig.1. Energy distribution function (EDF) of fast H atoms at the cathode is shown in Fig. 1 for 6.1 kTd and 14.4 kTd (1 Td=10^{-21} Vm^2).
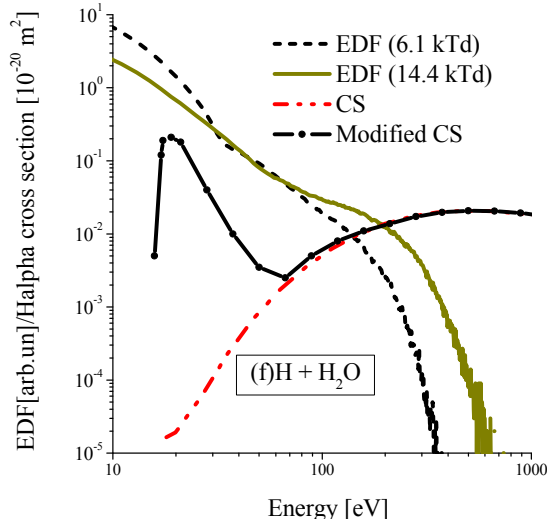
Figure 1. Cross sections for Hα emission/EDF as a function of energy. Energy distribution function (EDF) of fast H particles 0.05 cm from the cathode.

In Fig. 2 we show comparison of Monte Carlo simulation (MCS) results with experimental data (EXP) at very high E/N. The experimental results are
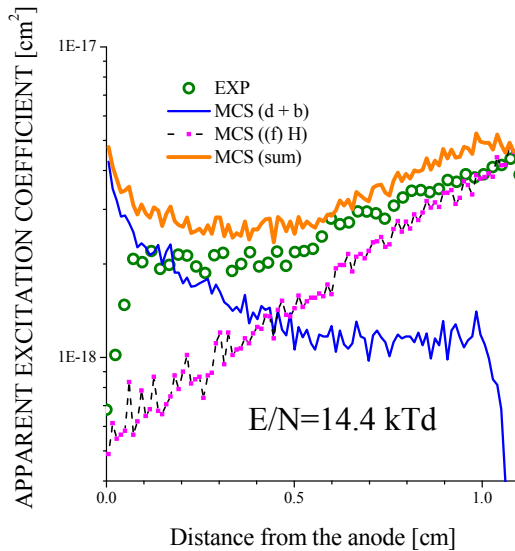

Figure 2. Comparison of the experimental and Monte Carlo simulation results for the apparent excitation coefficient as a function of the distance from the anode in pure water vapor discharge at E/N=14.4 Td.

normalized to the apparent (electron induced) excitation coefficient [16] at the anode. Total Hα emission signal obtained from MCS (sum) consists of a sum of electron component (d + b) including backscattered electrons (b), and fast H component [(f) H] which accounts also for all fast H reflected back from the cathode.

Acknowledgements

REFERENCES

[1]   K. R. Stalder, G. Nersisyan and W. G. Graham, J. Phys. D: Appl. Phys. **39** 3457 (2006).
[2]   T. Makabe and Z. Petrović *Plasma Electrinics: Applications in Microelectronic Device Fabrication* (Boca Raton, FL: Taylor&Francis, 2006)
[3]   M. Laroussi, Plasma Process. Polym. **2**, 391 (2005).
[4]   Long and short term effects of plasma treatment on meristematic plant cells N. Puač, S. Živković, N. Selaković, M. Milutinović, J. Boljević, G. Malović, and Z. Lj. Petrović Applied Physics Letters **104**, 214106 (2014).
[5]   K. Kutasi and J. Loureiro, J. Phys. D **40**, 5612 (2007).
[6]   P. Bruggeman, D. Schram, M. Á. González, R. Rego, M. G. Kong, and C. Leys, Plasma Sources Sci. Technol. **18**, 025017 (2009); P. Bruggeman and C. Leys, J. Phys. D: Appl. Phys. **42** 053001 (2009).
[7]   G. Ruíz-Vargas, M. Yousfi, and J. de Urquijo, J. Phys. D **43**,455201 (2010).
[8]   Y. Itikawa and N. Mason, J. Phys. Chem. Ref. Data **34**, 1 (2005).
[9]   R. E. Robson, R. D. White, and K. F. Ness, J. Chem. Phys. **134**,_064319 (2011).
[10] N. Škoro, D. Marić, G. Malović, W. G. Graham, and Z. Lj. Petrović, Phys.Rev. E **84**, 055401(R) (2011).
[11] M. Radmilović-Rađenović, B. Rađenović, Ž. Nikitović, Š. Matejčik and M. Klas, Nucl. Instr.Meth. in Phys.Res. B **279** pp.103-105 (2012).
[12] V. Stojanović, B. Jelenković, Z. Lj. Petrović J. Appl. Phys. **81** 1601-1603 (1997).
[13] A.V. Phelps *http://www.lxcat.laplace.univ-tlse.fr* retrieved June 4, (2013).
[14] Y. Itikawa, N. Mason J. Phys. Chem. Ref. Data **34** 1 (2005).
[15] A. V. Phelps J. Phys. Chem. Ref. Data **19** 653-675 (1990).
[16] A. V. Phelps Phys. Rev. E **79** 066401 (2009).
[17] J. H. Miller, A. E. S. Green Rad. Res. **54** 343 (1973).
[18] K. Denpoh and K. Nanbu, J. Vac. Sci. Technol. A **16** 1201 (1998).
[19] V. Stojanović, Z. Raspopović, *et al* , Eur. Phys. J. D **69**, 63 (2015).

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Cross section set and transport properties of Ne$^+$ in CF$_4$

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Cross section set and transport properties of Ne$^+$ in CF$_4$

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Synopsis Cross section set for scattering Ne$^+$ ions in CF$_4$ is assessed by using available experimental data for charge transfer cross sections. Monte Carlo method is used to calculate transport properties of Ne$^+$ ions in CF$_4$.

Charge transfer reactions of ions with molecules are unavoidable elementary processes in modeling kinetics in terrestrial, industrial, and astrophysical plasmas. In selected cases charge transfer reactions are known to represent the most significant part of a cross section set. Line spectra of excited atoms obtained in spectrometric measurements in CF$_4$ indicate that the charge transfer reaction is dominant process in collisions with inert gas ions. Thus, in this work we assessed cross section set for Ne$^+$ in CF$_4$ by using existing experimental data [1] for charge transfer collisions producing radical ions of CF$_4$.

Since no direct information is found in the literature how mobility of high recombination energy ions such as Ne$^+$ ions behaves in CF$_4$ we also calculated transport parameters by using Monte Carlo simulation technique [2].

The cross sections presented by Fisher *et al* [1] were used to determine the elastic momentum transfer cross section ("elastic" in Fig. 1) assuming the total momentum transfer cross section σ_{mt} is known. At low energies we assumed that σ_{mt} is Langevin's cross section and elastic momentum transfer cross section is determined by deducing all reactive cross sections.

Average polarizability of CF$_4$ is not well established [1] and may produce discrepancy for calculated mobility of ions in CF$_4$ [3] and thus affect plasma parameters prediction in modeling. We adopted value of 3.86 A^3 used by Stojanović *et al* [3] who found excellent agreement between experimental and calculated mobility of CF$_3^+$ ions in CF$_4$.
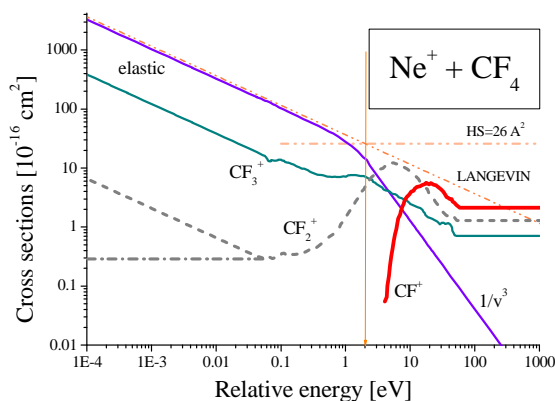
Further, extrapolation of elastic momentum transfer cross section trend beyond crossing point of Langevin's and hard sphere (HS) cross section [1] is done by smoothly connecting to $1/v^3$ trend [4] where v is the center-of-mass velocity (see Fig. 1).

At all ion kinetic energies above 50 eV reactive cross sections are extrapolated by constant values.

Effect of various extrapolations (short dot-dashed or dashed line in Fig. 1) of unusual behavior at low energy, observed with measurements of the cross section leading to formation of CF$_2^+$ (where irrespective of the Ne$^+$ spin state exothermic behavior of reaction is expected) is found negligible on mobility. Reduced mobility for Ne$^+$ ions as a function of E/N (E-electric field, N-gas density) compared with Langevin's value is shown in Fig. 2.
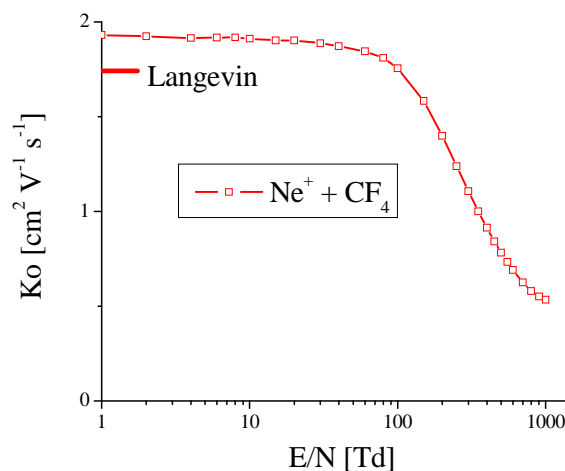

Figure 2. Reduced mobility for Ne$^+$ in CF$_4$ at 300 K.

References

[1] E R Fisher *et al*. 1990, *J.Chem.Phys.* **92** **2296**

[2] Z Lj. Petrović Z. Lj *et al.* 2009 *J. Phys. D: Appl. Phys.* **42** 194002.

[3] V Stojanović *et al.* 2014 *J. Phys. Conf. Ser.* **514** 012059

[4] P S Krstić and D R Schultz 2009 *J. Phys. B: At. Mol. Opt. Phys.* **42** 065207

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Figure 1. Cross section set for Ne$^+$ + CF$_4$.

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Cross sections and transport parameters for F⁻ ions in BF₃

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We presented results for reduced mobility as a function of *E/N* for F⁻ ions in BF₃ gas. Results were obtained by using the Monte Carlo technique for cross section set determined on the basis of Nanbu's theory.

1. Introduction

Negative halogen ions are abundant in plasmas relevant for wide range of applications. Since electron affinity of F atom is largest of all atoms electronegative plasmas containing F⁻ ions are highly reactive. Knowledge of the plasma chemistry and behaviour of the negative ions in the plasmas is thus a key to control plasma processing devices.

Boron dopant penetration in silicon is technologically achieved by DC pulsed plasma system (PLAD) most widely applying BF₃ gas [1]. Uniform plasma and implantation with normal ion incidence are main goals in this technological process. Control over the number density of negative ions, in such a case being F⁻ and BF₄⁻, increase efficiency of implantation. Modelling of such plasmas requires knowledge of transport parameters of all abundant particles [2].

In this work, we employ Nanbu theory [3] to calculate transport cross section set for F⁻ ions scattering on BF₃ molecule appropriate for low energies of F⁻ ions. By using Monte Carlo technique of Ristivojević and Petrović [4] we calculated transport parameters as a function of *E/N*.

2. Results and discussion
2.1. Calculation of the cross section set

According to Nanbu's theory elastic and reactive endothermic collision are separated and treated by accounting for thermodynamic threshold energy and branching ratio according to the Rice–Rampsperger–Kassel (RRK) theory [3]. Within the RRK theory excited molecular complex is treated as excited activated complex where internal energy is distributed among *s* equivalent vibrational modes of the complex. We used polarizability of $3.31 \ 10^{-30} \ m^3$ for BF₃ from [5]. For F⁻ + BF₃ system characteristic low energy reactive channels are shown in Table 1.

Table1. F⁻ - BF₃ reaction paths considered in and the corresponding thermodynamic threshold energies Δ.

No	reaction	Δ (eV)
1	$F_2^- + BF_2$ (CT)	-5.6 [12]
2	$F+BF_3+e^-$ (DET)	-3.4012 [13]
3	BF_4^- (EXO)	+3.58 [11]

Cross section for exothermic reaction (EXO) forming super halogen BF₄⁻ can be expressed as:

$$\sigma_{exo} = \beta \sigma_L \qquad (1)$$

where σ_L is orbiting cross section [6] and β the probability of exothermic reaction. It is also known that stabilization proceed either radiatively or collisionally [7] for reaction EXO in Table 1. at room temperatures and pressures of about 0.5 Torr. Similar situation appears in case where BF₄⁻ emerges from the surface sputtering of cluster BF₃ ions [8]. Herd and Babcock (1987) further concluded that magnitudes of collisional stabilization, radiative stabilization, and unimolecular decomposition back to initial reactants are comparable in these conditions. Since non-associative reactions are shearing the same collisional complex we may account cross section for exothermic reaction as $\sigma_{exo} = \beta \sigma_{e0}$, where β is selected to define elastic cross section contribution as $\sigma_e = (1 - \beta)\sigma_{e0}$. σ_{e0} is the elastic cross section (EL) obtained by Nanbu theory.

Fig.1. Cross section set for F$^-$ ions in BF$_3$.
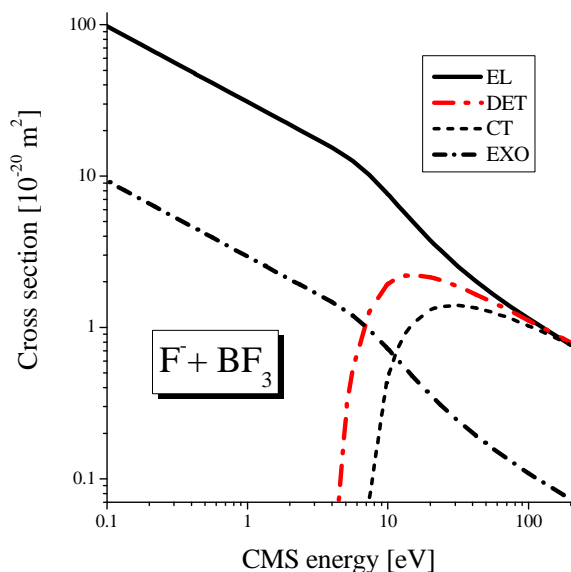
Fig.2. Reduced mobility of F$^-$ ions in BF$_3$.

Thermal rate coefficient for association reaction 3 (Table 1) is determined by Babcock and Streit [9] and has a value $9.4 \cdot 10^{-11}$ cm^3/ molecule/ s for T=300 K. By combining the relation (1) and thermal rate coefficient we determined probability of exothermic reaction and thus contribution of association cross section (EXO) and elastic cross section (EL) (Fig.1).
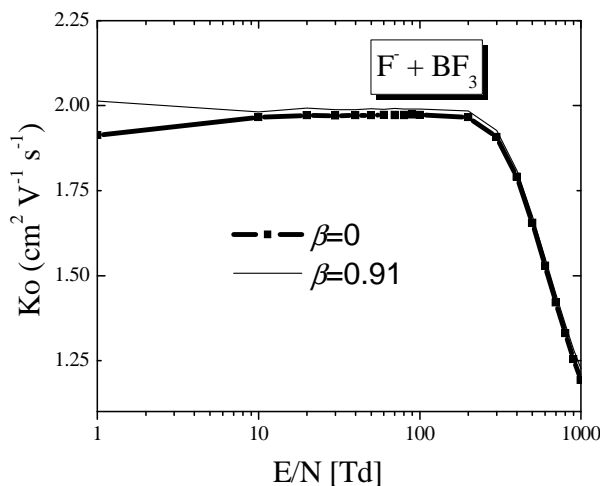
2.2. Transport parameters

The critical review of experimentally obtained transport properties of gaseous halogen ions is presented in [10].

The mobility K of an ion is the quantity defined as the velocity attained by an ion moving through a gas under unit electric field. One often exploits the reduced or standard mobility defined as:

$$K_0 = \frac{v_d}{N_0} NE \qquad (2)$$

where v_d is the drift velocity of the ion, N is the gas density, at elevated temperature T, E is the electric field and $N_0 = 2.686763 \cdot 10^{25}$ m^{-3} is the standard gas density (of an ideal gas at T=273K and pressure p= 101 325 kPa).

In Figure 2 we show the results of Monte Carlo simulation for reduced mobility as a function of E/N. Non-conservative collisions of F$^-$ ions producing BF$_4^-$ ions are only slightly modifying mobility curve obtained for the case of inclusion of only endothermic processes ($\beta = 0$).

3. Acknowledgment

4. References

[1] B. Koo –Z. W. Fang, L. Godet, S. B. Radovanov, C. Cardinaud, G. Cartry, A. Grouillet and D. Lenoble, IEEE Trans. Plasma Sci. **32** (2004) 456.
[2] Z. Lj. Petrović, S. Dujko, D. Marić, G. Malović, Ž. Nikitović, O. Šašić, J. Jovanović, V. Stojanović, and M. Radmilović-Rađenović, J. Phys. D: Appl. Phys. **42** (2009) 194002.
[3] K. Denpoh, K. Nanbu, J. Vac. Sci. Technol. A **16** (1998) 1201.
[4] Z. Ristivojević and Z. Petrović, Plasma Sources Sci. Technol. **21,** (2012) 035001.
[5] C. Szmytkowski, M. Piotrowicz, A. Domaracka, L. Klosowski, E. Ptasinska-Denga, G. Kasperski, J. Chem. Phys. **121** (2004) 1790.
[6] E. W. Mc. Daniel, V. Čermak, A. Dalgarno, E. E.Ferguson and L. Friedman, Ion-Molecule reactions, Willey-Interscience (1970).
[7] C. R. Herd and L. M. Babcock, J. Phys. Chem **91** (1987) 2372.
[8]X. L. Zhao and A.E. Litherland, Nucl. Instr. Meth. Phys. Res. B **259** (2007) 224.
[9] L. M. Babcock and G.E. Streit, J. Phys. Chem. **88** (1984) 5025.
[10] L. A. Viehland and E.A. Mason, At. Data. Nucl. Data Tables. **60** (1995) 37.
[11] G. L. Gutsev, P. Jena, R. J. Bartlett, Chemical Physics Letters **292** (1998) 289.
[12] K.A.G. MacNeil and J.C.J. Thynne, J. Phys. Chem., Vol. **74** (1970) 2257.

[13] E.W. McDaniel, Atomic Collisions: Electron and Photon projectiles, John Wiley&Sons (1989)

[13] E.W. McDaniel, Atomic Collisions: Electron and Photon projectiles, John Wiley&Sons (1989)

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Cross section set and transport properties for Ar$^+$ in CF$_4$

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Cross section set for scattering Ar$^+$ ions in CF$_4$ is developed by using and extrapolating the available experimental data for charge transfer cross sections. Monte Carlo simulation is employed to calculate transport properties of Ar$^+$ ions in CF$_4$.

1. Introduction

In often applied mixtures of argon (dominant gas) and CF$_4$ (minority gas- 5-10% in the abundance) often overlooked collisions are those of argon ions on minority constituent in the mixture since their transport is dominated by the resonant charge exchange collisions with the parent gas argon. Still one believes that completing the set of data would be welcome and provide more accurate foundation for modelling. In addition, taking in account Ar$^+$ collisions on CF$_4$, reactive collisions may provide new channels for some ionic species and alter their kinetics.

Charge transfer reactions of ions with molecules are unavoidable elementary processes in modelling kinetics in terrestrial, industrial, and astrophysical plasmas. In the selected case, charge transfer reactions are known to represent the most significant part of a cross section set. Line spectra of excited atoms obtained in spectrometric measurements in CF$_4$ [1] indicate that the charge transfer reaction is the dominant process in collisions with inert gas ions. Thus, in this work we assessed cross section set for Ar$^+$ in CF$_4$ by using existing experimental data [2] for charge transfer collisions producing radical ions of CF$_4$.

Since no direct information is found in the literature how mobility of inert ions such as Ar$^+$ ions behaves in CF$_4$ we also calculated transport parameters by using Monte Carlo simulations.

2. Cross section set

The cross sections presented by Fisher *et al* [2] were used to determine the elastic momentum transfer cross section ("elastic" in Fig. 1) assuming the total momentum transfer cross section σ_{mt} is known. At low energies we assumed that σ_{mt} is Langevin's cross section and elastic momentum transfer cross section is determined by deducting all reactive cross sections.

Average polarizability of CF$_4$ is not well established [2] and may produce discrepancy for calculated

mobility of ions in CF$_4$ [3] and thus affect plasma parameters prediction in modelling. We adopted value of 3.86 A^3 used by Stojanović *et al* [3] who found excellent agreement between experimental and calculated mobility of CF$_3^+$ ions in CF$_4$. Note that usage of this polarizability increases Langevin's cross section above reaction cross sections of Fisher *et al.* (1990) at least in the region of the validity of polarization potential approximation.
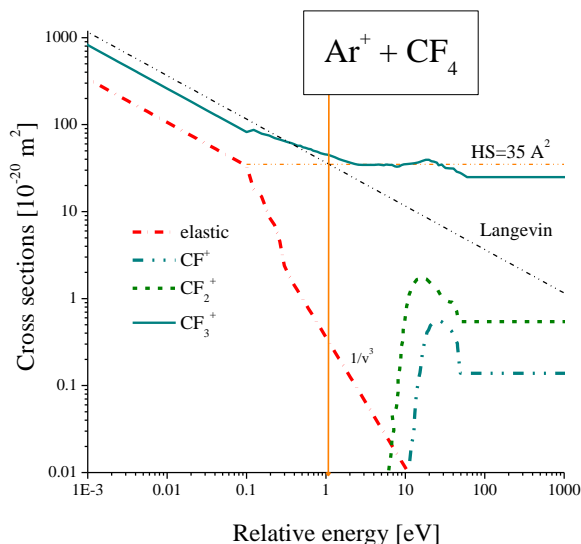

Figure 1. Cross section set for Ar$^+$ + CF$_4$.

Further, extrapolation of elastic momentum transfer cross section trend approximately beyond the crossing point of Langevin's and hard sphere (HS) cross section [2] is done by smoothly connecting to $1/v^3$ trend [4] where v is the center-of-mass velocity (see Fig. 1).

Reactive cross sections for ions are extrapolated by constant values for kinetic energies above 50 eV following measurements of emission cross section by Motohashi *et al.* [1] where slow oscillatory behaviour of the emission cross sections was found at high projectile energies and almost constant reaction probability was found over a wide energy range.

3. Transport parameters

In this paper Monte Carlo technique was applied to perform calculations of transport parameters. We have used a code that properly takes into account thermal collisions [5]. The code has passed all the relevant benchmarks [6] and has been tested in our work on several types of charged particles [6,7].

Results of Monte Carlo simulations are shown in Figs. 2-5. Note that these transport parameters are the only information present in the literature up to now, there are no published experimental data for the transport coefficients of Ar$^+$ in CF$_4$.

The reactive collisions which are spread over the entire energy range affect the drift velocity (as well as other transport coefficients) at all *E/N* values (Fig. 2). Since the total collision frequency for endothermic reactions increases with energy at high *E/N*, the dominant loss of the fast ions happens at the front of the swarm. This shifts the swarm's centre of mass towards the lower values. Thus, the bulk values (real space drift velocity d<x>/dt) are lower than the flux values (velocity space drift velocity <v>).
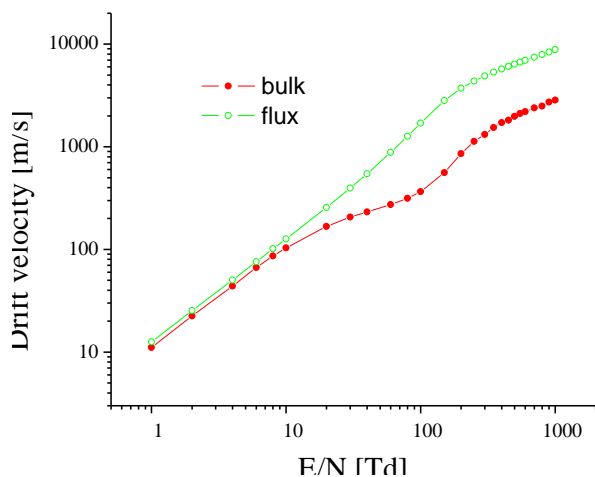

Figure 2. Drift velocities of Ar$^+$ ions in CF$_4$ as a function of *E/N*.

Reduced mobility for Ar$^+$ ions as a function of *E/N*(*E*-electric field, *N*-gas density) compared with Langevin's value K$_{pol}$ is shown in Fig. 3. Values of the reduced mobility as a function of *E/N* shown are obtained by using bulk drift velocities, as those are measured in most experiments, though proper quantities should be applied according to the source of experimental data [8,9]. A significant increase of mobility at low E/N is the result of non-conservative

charge exchange at low energy. At about 300 Td another mobility peak appears, representing a significant increase of reactive collisions.
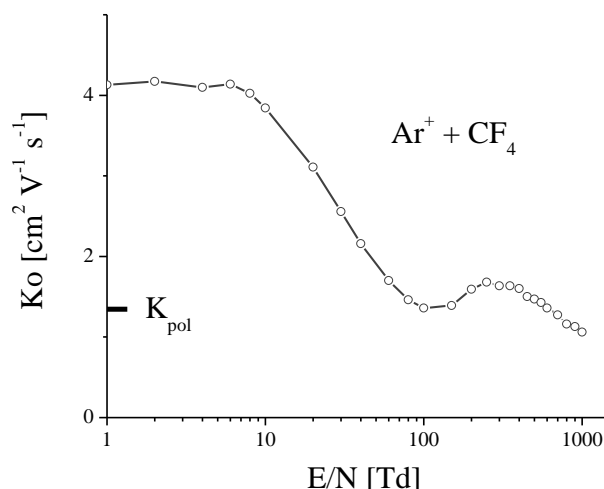

Figure 3. Reduced mobility for Ar$^+$ in CF$_4$ at 300 K.

Characteristic energies (longitudinal L and transverse T) and the mean energy, as a function of *E/N*, are shown in Fig. 4. To calculate the longitudinal component properly here and also in the case of diffusion coefficients, one would need a better and more complete information on the anisotropy of scattering.
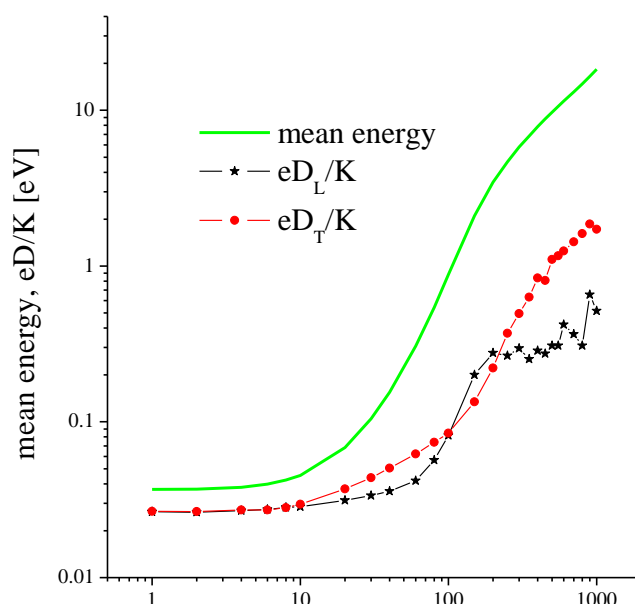

Figure 4. Mean and characteristic energy for Ar$^+$ in CF$_4$ at 300 K.

Diffusion coefficients are given in Fig. 5 and one should also notice very large non-conservative effects almost as large as in positron transport [10,11]. Similarly to the results for drift velocity flux diffusion coefficients are significantly larger than the bulk values.
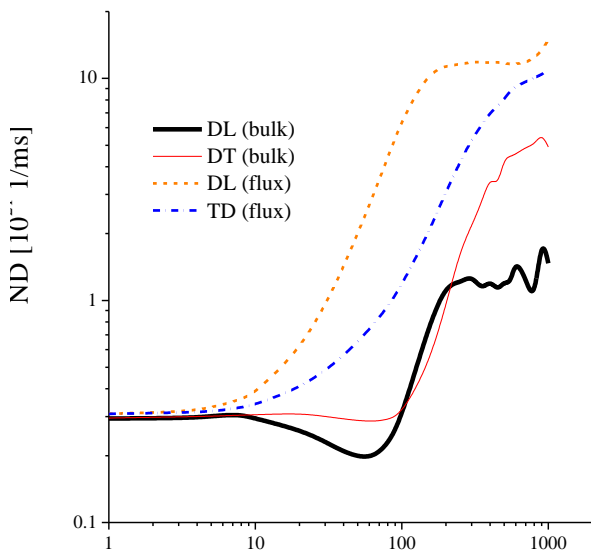

Figure 5. Diffusion coefficients as a function of E/N for Ar$^+$ in CF$_4$ at 300 K.

4. Conclusion

In addition to presenting the data we show here effects of non-conservative collisions on ion transport. Due to non-conservative cross sections that are larger than the elastic scattering cross section differences between flux and bulk transport coefficients are quite large - comparable to the strongest cases observed for electrons, even positrons.

Data for swarm parameters for ions are needed for hybrid and fluid codes and the current focus on discharges in liquids or possibly liquids in mixtures with rare gases dictates the need to produce similar data for ions stemming from the liquid vapour .

4. Acknowledgment

5. References

[1] K. Motohashi, T. Takahashi1, N. Takahashi, and S. Tsurubuchi *J. Phys. B: At. Mol. Opt. Phys.* **38** (2005) 3339–3348.

[2] E. R. Fisher, M.E. Weber and P.B. Armentrout, *J.Chem.Phys.* **92** (1990) 2296.

[3] V. Stojanović, Z. Raspopović, J.V. Jovanović, J. de Urquijo, and Z. Lj. Petrović *J. Phys. Conf. Ser.* **514** (2014) 012059.

[4] P. S. Krstić and D. R. Schultz *J. Phys. B: At. Mol. Opt. Phys.* **42 (**2009) 065207.

[**5**] Z. Ristivojević and Z.Lj. Petrović, *Plasma Sources Sci. Technol.* **21** (2012) 035001.

[6] Z.Lj. Petrović, Z.M. Raspopović, V.D. Stojanović, J.V. Jovanović, G. Malović, T. Makabe, J. De Urquijo, *Appl. Surf. Sci.* **253** (2007) 6619.

[7] J.de Urquijo, J.V. Jovanović, A. Bekstein, V. Stojanović and Z.Lj. Petrović, *Plasma Sources Sci. Technol.* **22** (2013) 025004.

[8] R.E. Robson, *Aust.J. Phys*. **44** (1991) 685.

[9] Z. Lj. Petrović *et al. J. Phys. D: Appl. Phys.* **42 (**2009) 194002.

[10] R. D. White, W. Tattersall, G. Boyle, R.E. Robson, S. Dujko, Z.Lj. Petrović, A. Banković, M.J. Brunger, J.P. Sullivan, S.J. Buckman and G.Garcia, *Applied Radiation and Isotopes* **83** (2014) 77.

[11] A. Banković, S. Dujko, R. D. White, J. P. Marler, S. J. Buckman, S. Marjanović, G. Malović, G. Garcıa and Z. Lj. Petrović**,** *New Journal of Physics* 14 (2012) 035003.