

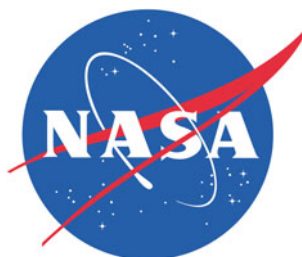
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Proceedings of the IV Advanced Ceramics and Applications Conference

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The Kinetic Energy Dependence of Association Reactions for Alkali Metal Ions with Dimethoxyethane

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Abstract In this work we select most probable reactions of alkali metal ions (Li^+ , Na^+ , K^+) 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 reaction of ions with DXE for three different pressures is studied and compared to experimental results. Calculated cross sections can be used to obtain transport parameters for Na^+ in DXE gas.

Keywords Alkali metals • DXE gas • Monte carlo simulation • Denpoh-Nanbu theory

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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 dimethoxyethane (DXE), can be produced from dimethyl ether using dielectric barrier discharge (DBD) plasmas containing water vapor [1] at atmospheric pressure. DXE is used as a part of precursors in production of ceramics [2] or as a sole compound for making other chemicals such as those used in lithium batteries production [3–6], superconductor production [7], pesticides production, nanoparticles synthesis [8–10] in etherification [11] in diesel fuel additives etc.

Since very limited information exist about processes proceeding in these or similar complex plasmas, in this study we will analyze transport properties of ions in DXE gas since ions are not only inducing reaction products but also increasing 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 [12] (DNT) 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 [13]. Nikitović et al. [14] showed how radiative association reactions (low pressure limit of three body association reactions) can be included into cross section set obtained by DNT. Approach presented in [14] is compared with existing experimental data for association cross section as a function of pressure [15] and showed good agreement at energies below few eV. Such information is necessary in plasmas at atmospheric pressures containing complex molecules such as DXE and can be highly valuable in modeling clustering in various plasmas.

In this work we applied the approach of [14] for the case of alkali ions scattering on DXE molecule since in all reactions studied experimentally [16, 17] the only product observed is the association complex $\text{Li}^+(\text{DXE})$ and similarly $\text{Na}^+(\text{DXE})$ and $\text{K}^+(\text{DXE})$.

In this paper we started with selecting the most probable reactions of alkali metal ions (Li^+ , Na^+ , K^+) with dimethoxyethane (DXE) molecule (producing neutral and ionized DXE, $\text{C}_3\text{H}_8\text{O}_2$, CH_3OCH_3 , $\text{CH}_2\text{CH}_2\text{O}$, CH_3OH , CH_2O , CH_4 , CO , H_2) for thermodynamic threshold energies below about 15 eV. Appropriate gas phase enthalpies of formation [18] 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 [12, 19]. Calculated cross sections for three body association reaction of selected ions with DXE were compared with existing experimental results for three different pressures obtained by guided ion beam tandem mass spectrometry [16].

2 Cross Section Sets

It is known that Li^+ ions in most of gases at high pressure forms clusters [1]. Association reaction responsible in this case is particularly interesting due to the fact that clusters of only one type are formed which simplifies analyses of the reaction products.

The cross-sections for scattering of alkali ions on DXE are calculated by using the DN theory [12] separating elastic from reactive collisions. DXE is known not to have dipole moment in its ground state. The dipole polarizability of $9.94 \times 10^{-30} \text{ m}^3$ [16] is used for the DXE target. Similar to our recent papers [20] 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 [12]. 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 molecular ion X^+ in DXE is commonly represented by ion capture cross-section:

$$\sigma_{\text{exo}} = \beta \sigma_{\text{L}}, \quad (1)$$

where σ_{L} is the orbiting cross-section [21] and β is the probability of a specific exothermic reaction.

Appropriate gas phase enthalpies [17] of formation for the products (Table 1) were used to calculate thermodynamic thresholds (Table 2).

In all reactions studied experimentally, the only product observed is the association complex Li^+ (DXE) and similarly in later figures complexes Na^+ (DXE) and K^+ (DXE).

Table 1 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
$\text{C}_3\text{H}_8\text{O}_2$	-364	$\text{C}_3\text{H}_8\text{O}_2^+$	562
$\text{C}_2\text{H}_6\text{O}$	793.1	$\text{C}_2\text{H}_6\text{O}^+$	775.4
$\text{C}_2\text{H}_4\text{O}$	821.1	$\text{C}_2\text{H}_4\text{O}^+$	-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

Table 2 X^+ —DXE reaction paths ($X = \text{Li}, \text{Na}, \text{K}$) showing reaction products and the corresponding thermodynamic threshold energies Δ

No	Products	Δ (eV)		
		Li^+	Na^+	K^+
1	$X^+ + \text{DXE}$	0	0	0
2	$X + \text{C}_4\text{H}_{10}\text{O}_2^+$	3.905	4.158	4.9561
3	$X^+ + \text{C}_3\text{H}_8\text{O}_2 + \text{CH}_2$	3.793	3.793	3.793
4	$X + \text{C}_3\text{H}_8\text{O}_2^+ + \text{CH}_2$	7.999	8.252	9.050
5	$X + \text{C}_3\text{H}_8\text{O}_2 + \text{CH}_2^+$	8.724	8.977	9.775
6	$X^+ + \text{C}_2\text{H}_6\text{O} + \text{CH}_2 + \text{CO}$	4.513	4.513	4.513
7	$X + \text{C}_2\text{H}_6\text{O}^+ + \text{CH}_2 + \text{CO}$	9.147	9.400	10.198
8	$X + \text{C}_2\text{H}_6\text{O} + \text{CH}_2^+ + \text{CO}$	9.444	9.697	10.495
9	$X + \text{C}_2\text{H}_6\text{O} + \text{CH}_2 + \text{CO}^+$	13.135	13.388	14.186
10 _(EXO1)	$X^+ + \text{C}_2\text{H}_4\text{O} + \text{C}_2\text{H}_6\text{O}$	−0.1016	−0.1016	−0.1016
11	$X + \text{C}_2\text{H}_4\text{O}^+ + \text{C}_2\text{H}_6\text{O}$	4.7353	4.9882	5.7862
12	$X + \text{C}_2\text{H}_4\text{O} + \text{C}_2\text{H}_6\text{O}^+$	4.5322	4.7851	5.5831
13 _(EXO2)	$X^+ + \text{C}_3\text{H}_8\text{O} + \text{CO}$	−0.2625	−0.2625	−0.2625
14	$X^+ + \text{CH}_2\text{O} + \text{C}_2\text{H}_6 + \text{CO}$	0.3811	0.3811	0.3811
15	$X + \text{CH}_2\text{O}^+ + \text{C}_2\text{H}_6 + \text{CO}$	5.8636	6.1165	6.9145
16	$X + \text{CH}_2\text{O} + \text{C}_2\text{H}_6^+ + \text{CO}$	6.5145	6.7674	7.5654
17	$X + \text{CH}_2\text{O} + \text{C}_2\text{H}_6 + \text{CO}^+$	9.0031	9.256	10.054
18	$X^+ + \text{CH}_4\text{O} + \text{C}_3\text{H}_4 + \text{H}_2\text{O}$	0.8620	0.8620	0.8620
19	$X + \text{CH}_4\text{O}^+ + \text{C}_3\text{H}_4 + \text{H}_2\text{O}$	6.3207	6.5736	7.3716
20	$X + \text{CH}_4\text{O} + \text{C}_3\text{H}_4^+ + \text{H}_2\text{O}$	5.8305	6.0834	6.8814
21	$X + \text{CH}_4\text{O} + \text{C}_3\text{H}_4 + \text{H}_2\text{O}^+$	8.0818	8.3347	9.1328
22	$X^+ + \text{C}_4\text{H}_6 + 2\text{H}_2 + \text{O}_2$	5.0307	5.0307	5.0307
23	$X + \text{C}_4\text{H}_6^+ + 2\text{H}_2 + \text{O}_2$	9.2012	9.454	10.2521
24	$X + \text{C}_4\text{H}_6 + 2\text{H}_2 + \text{O}_2^+$	15.064	15.317	16.115
25	$X + \text{C}_4\text{H}_6 + \text{H}_2^+ + \text{H}_2 + \text{O}_2$	11.716	11.969	12.7674
26 _(EXO3)	$X + \text{CH}_4 + \text{C}_3\text{H}_6^+ + \text{O}_2$	−2.4304	−2.1775	−1.3794
27 _(EXO4)	$X + \text{C}_4\text{H}_8^+ + \text{H}_2 + \text{O}_2$	−1.8717	−1.6189	−0.8208
28 _(EXO5)	$X^+ + \text{C}_3\text{H}_8 + \text{H}_2 + \text{CO}_2$	−1.6376	−1.6376	−1.6376
29 _(EXO6)	$X + \text{C}_3\text{H}_6^+ + 2\text{H}_2 + \text{CO}_2$	−5.7366	−5.4837	−4.6857

Three sets of cross sections were calculated with help of the Denpoh-Nanbu theory. The Fig. 1 shows a set of cross sections for Li^+ ion on DXE while the other two sets are similar. Figure 2 provides the elastic momentum transfer cross section for all three gases and it is clear that there are no essential differences between them.

In the Fig. 3 we show experimental cross section sets and ones obtained with DNT for three different pressures ($p = 0.037, 0.071, 0.142$ mTorr) for Li^+ in DXE.

In the Fig. 4 we present experimental and cross section sets obtain with DNT for three different pressures ($p = 0.025, 0.053, 0.1$ mTorr) for K^+ in DXE.

In the Fig. 5 we show experimental and cross section sets obtain with DNT for three different pressures ($p = 0.026, 0.059, 0.1$ mTorr) for Na^+ in DXE.

Fig. 1 Cross section set for Li^+ in DXE

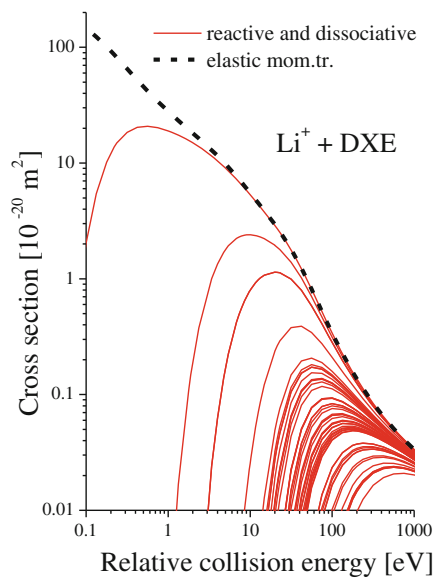
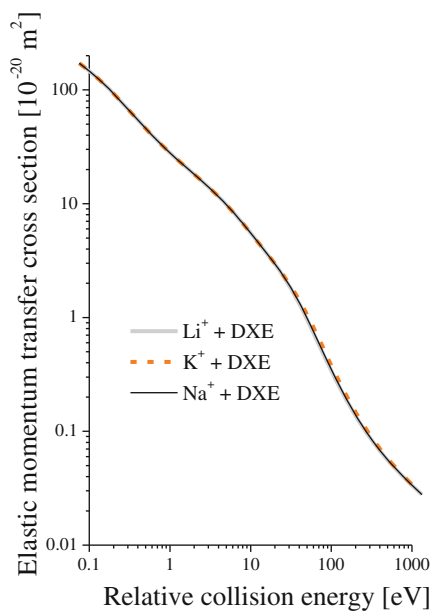


Fig. 2 Cross section sets for Li^+ , K^+ and Na^+ in DXE



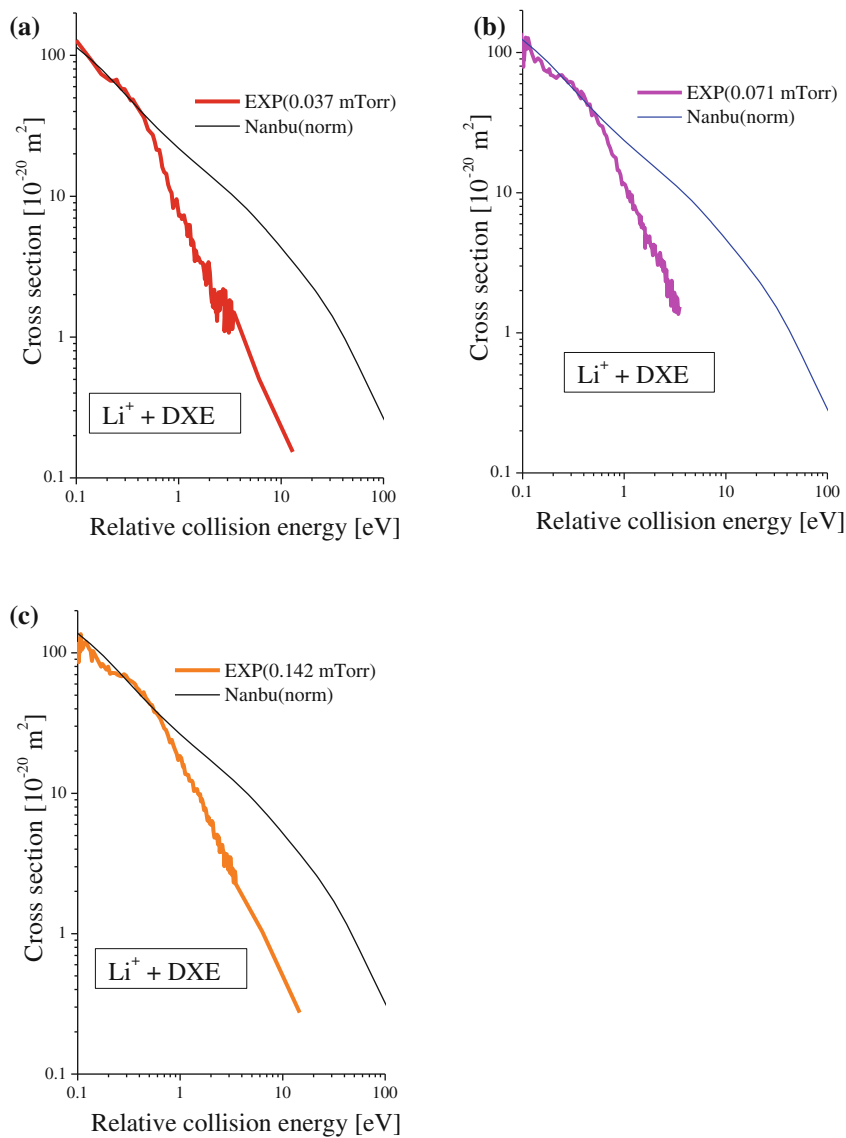


Fig. 3 Cross section sets of Li^+ in DXE—experimental and obtained with DN theory for three different pressures: **a** 0.037 mTorr; **b** 0.071 mTorr; **c** 0.142 mTorr

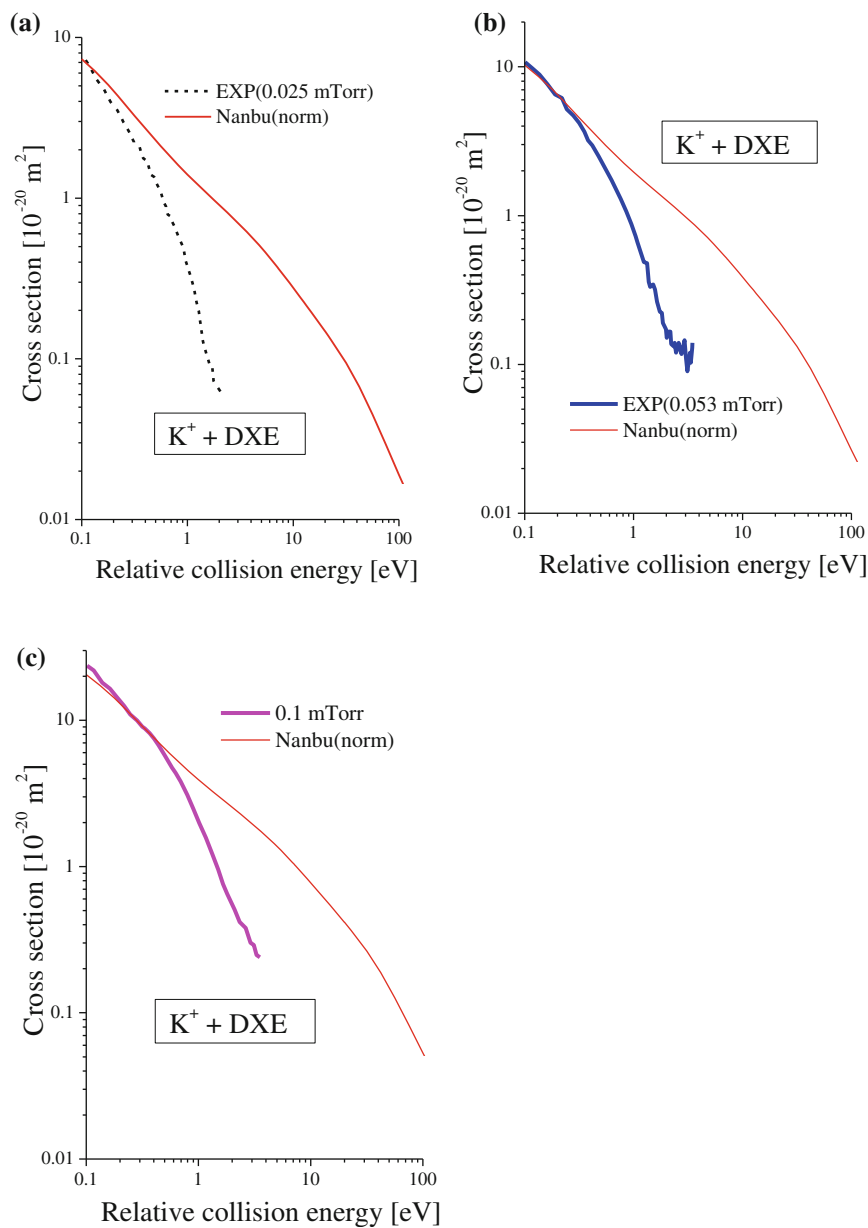


Fig. 4 Cross section sets of K^+ in DXE—experimental and obtained with DN theory for three different pressures: **a** 0.025 mTorr; **b** 0.053 mTorr; **c** 0.1 mTorr

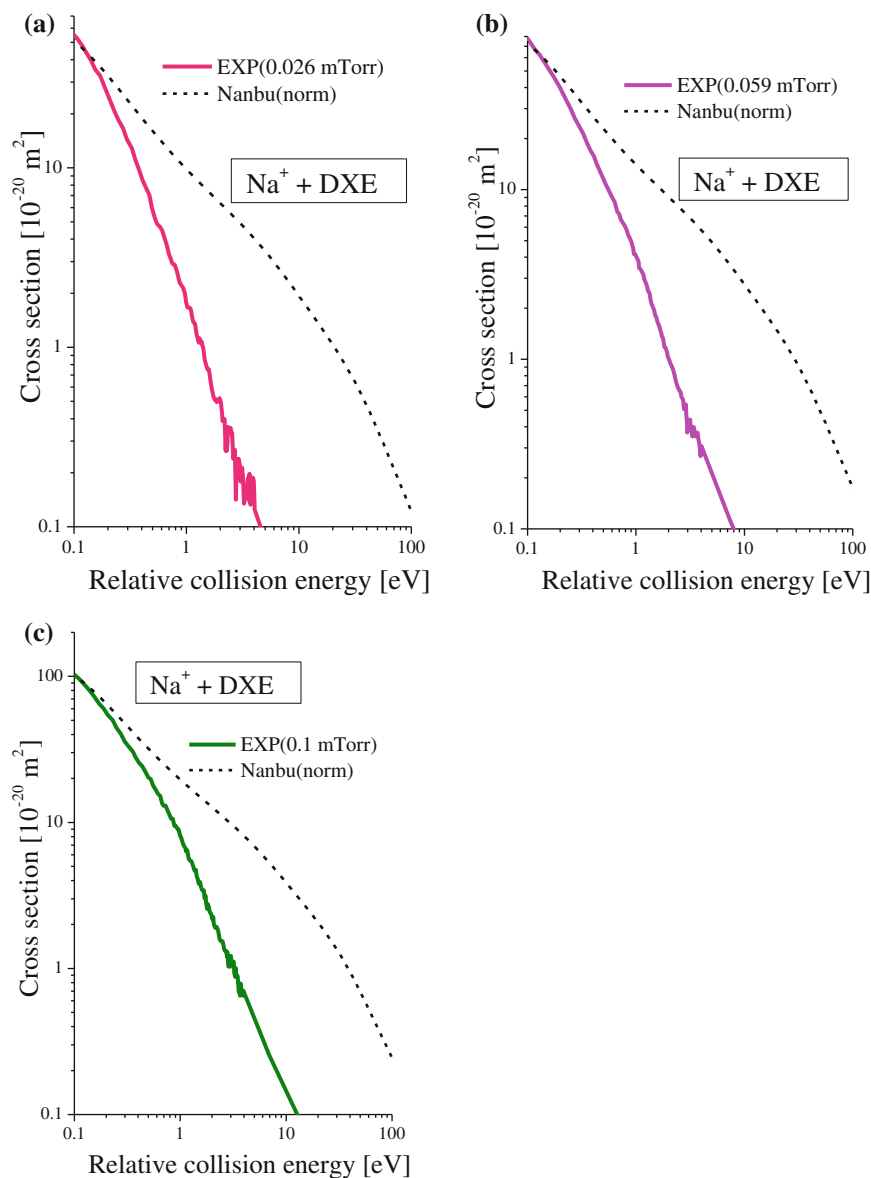


Fig. 5 Cross section sets of Na^+ in DXE—experimental and obtained with DN theory for three different pressures: **a** 0.026 mTorr; **b** 0.059 mTorr; **c** 0.1 mTorr

3 Transport Parameters

Transport parameters accounting for two body reactions (low pressure limit) are calculated by using Monte Carlo technique [22].

We have used a Monte Carlo code that properly takes into account thermal collisions [22]. The code has passed all the relevant benchmarks and has been tested in our work on several types of charged particles.

Swarm method [23, 24] is exploited to modify the cross section for elastic momentum transfer where for reduced mobility in the peak region (experimental [25] or theoretical values [26]) similarity with ions of equal or similar reduced mass is targeted (for example $\text{Ne}^+ + \text{CF}_4$). Elastic momentum transfer cross section is modified in order to fit approximate mobility peak characteristic for presented systems (Fig. 6).

In Fig. 7 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 for Na^+ in DXE. 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 on Fig. 7 the mean energy and the characteristic energies increase from ~ 20 Td.

Fig. 6 Elastic momentum transfer cross section as a function of collision energy

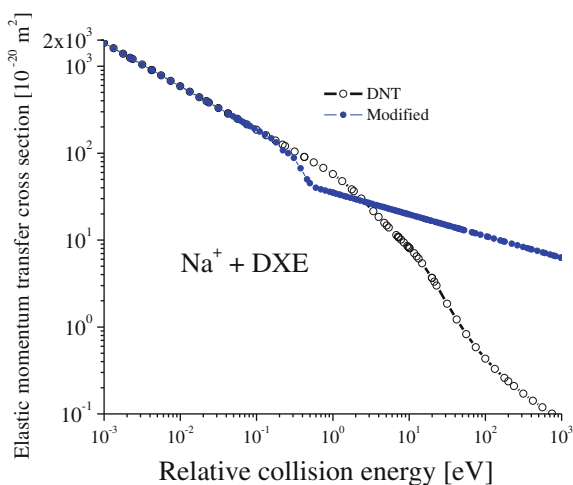
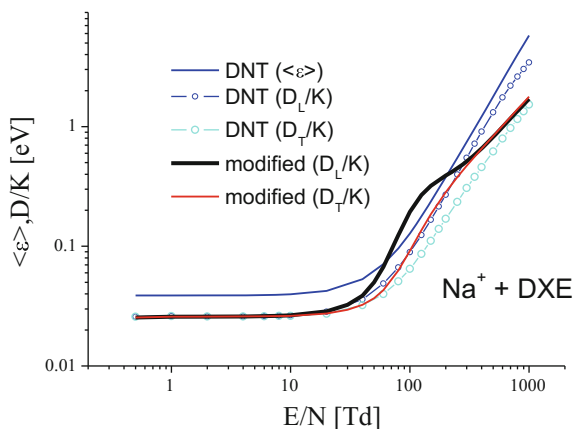


Fig. 7 Mean energy and characteristic energy for Na^+ in DXE



4 Conclusion

In this work we present most probable reactions of alkali metal ions with dimethoxyethane (DXE) molecule. In calculating the scattering cross section as a function of the kinetic energy with the Denpoh-Nambu theory we have used the appropriate gas phase enthalpies of formation for the products. Three body association reaction of ions with DXE is studied and compared to experimental results. Calculated cross sections were used to obtain transport parameters (mean energy and characteristic energy) for Na^+ ion in DXE gas.

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