

Transport parameters of alkali metal ions in DXE for technological applications

Željka Nikitović

Abstract— In this paper we select most probable reactions of alkali metal ions (Li^+ , Na^+ , K^+) with dimethoxy ethane (DXE) molecule and its fragment ions are selected in order to obtain appropriate gas phase enthalpies of formation for the products. 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. The scattering cross sections set as a function of kinetic energy and transport parameters for Na^+ in DXE gas as a function of E/N (E -electric field; N -gas density) were obtained by using the Monte Carlo technique.

Key words—Monte Carlo simulations, alkali metal ions, dimethoxy ethane (DXE), Denpoh-Nanbu method

I. 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 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 dimethoxy ethane (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].

II. CROSS SECTION SETS AND TRANSPORT PARAMETERS

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 $9.94 \cdot 10^{-30} \text{ m}^3$ [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.

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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 $\text{Li}^+(\text{DXE})$ and similarly in later figures complexes $\text{Na}^+(\text{DXE})$ and $\text{K}^+(\text{DXE})$.

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. Fig. 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 ($p=0.037$ mTorr, 0.071 mTorr, 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 ($p=0.025$ mTorr, 0.053 mTorr, 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 ($p=0.026$ mTorr, 0.059 mTorr, 0.1 mTorr) for Na^+ in DXE.

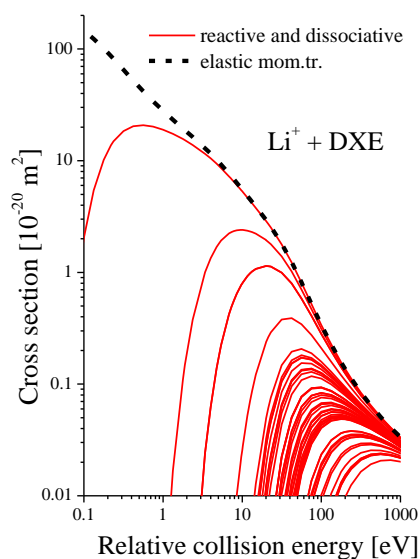


Fig.1. Cross section set for Li^+ in DXE.

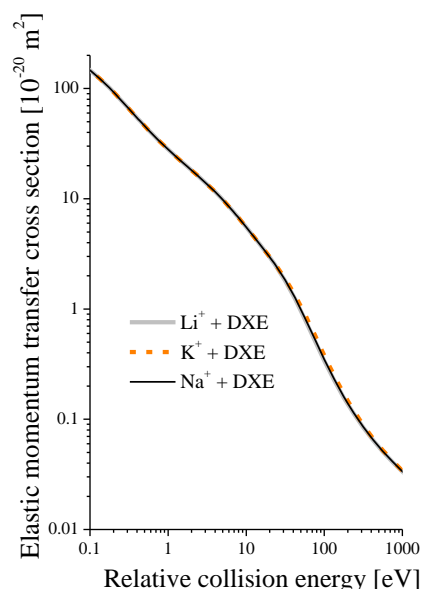
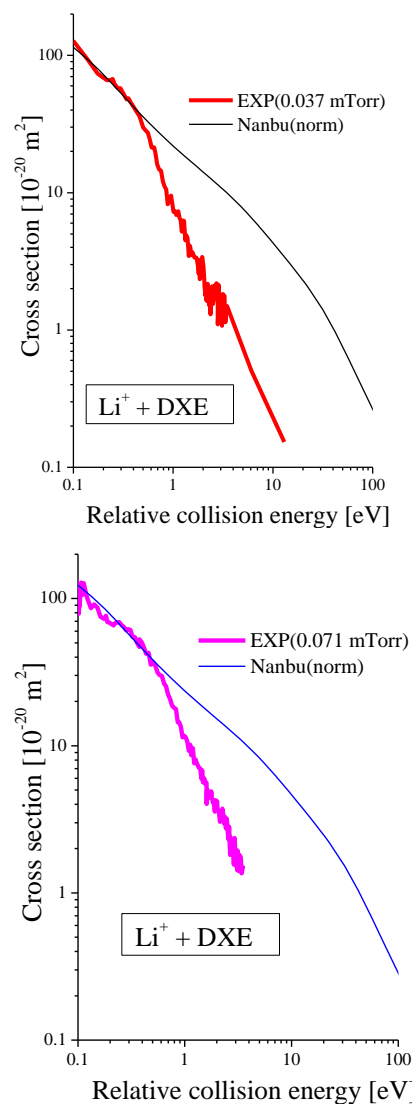


Fig.2. Cross section sets for Li^+ , K^+ and Na^+ in DXE.



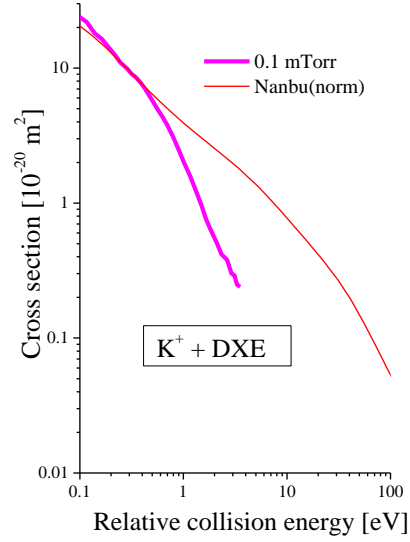
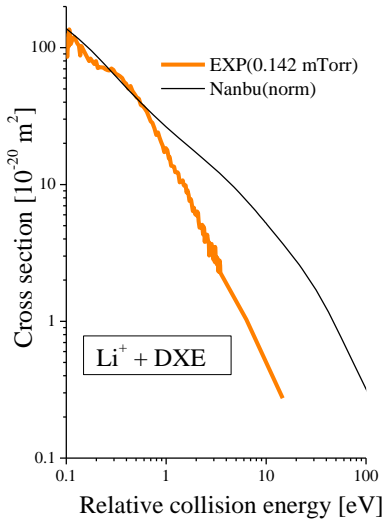
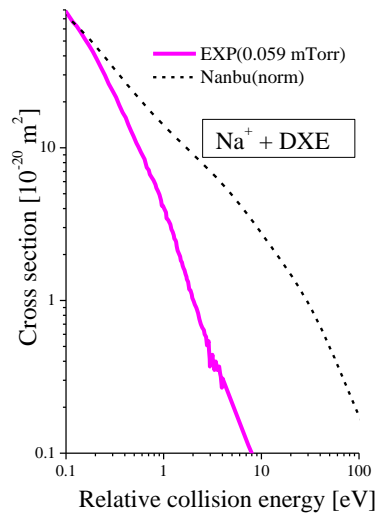
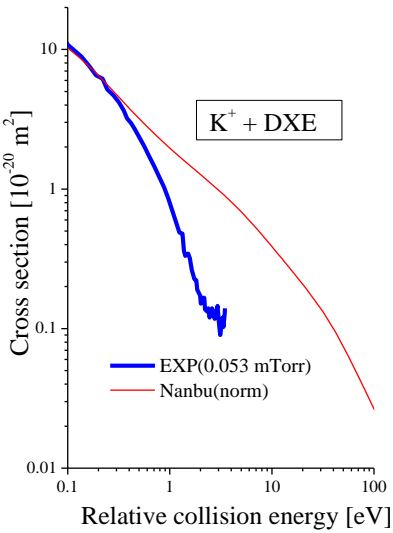
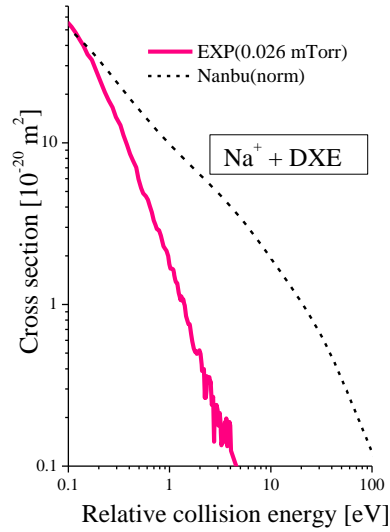
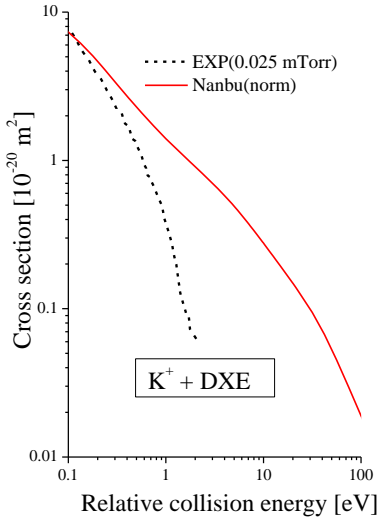


Fig.3. Cross section sets of Li^+ in DXE - experimental and obtained with DN theory for three different pressures: a) 0.037 mTorr; b) 0.071 mTorr; c) 0.142 mTorr

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



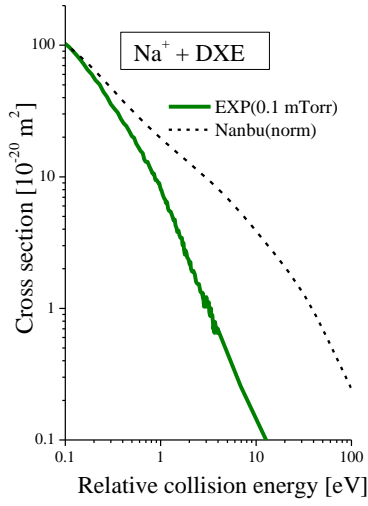


Fig.5. Cross section sets of Na^+ in DXE - experimental and obtained with DN theory for three different pressures: a) 0.026 mTorr; b) 0.059 mTorr; c) 0.1 mTorr

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.

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:

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

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

In Fig. 8 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.

Longitudinal (a) and transversal (b) diffusion coefficients for Na^+ in DXE as a function of E/N are shown in Fig. 9. 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.

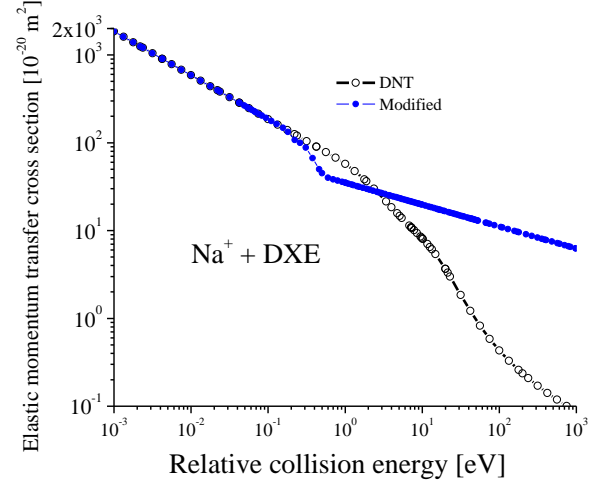


Fig.6. Elastic momentum transfer cross section as a function of collision energy.

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 ($X=Li, Na, K$) 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

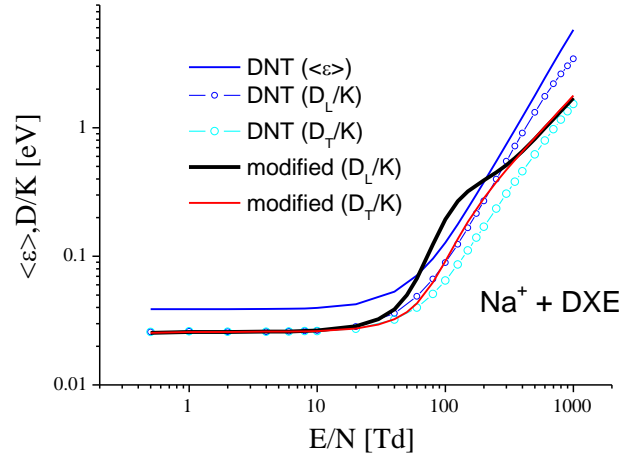


Fig.7. Mean energy and characteristic energy for Na^+ in DXE.

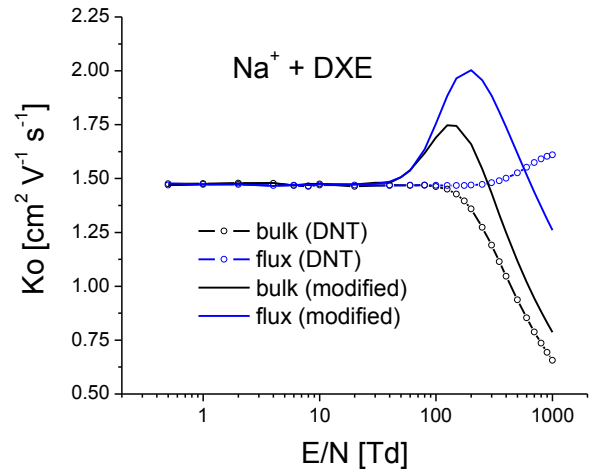
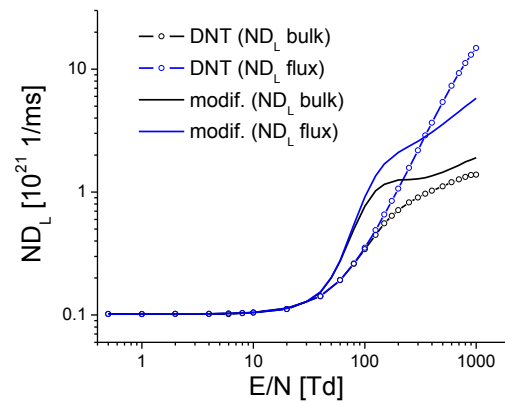
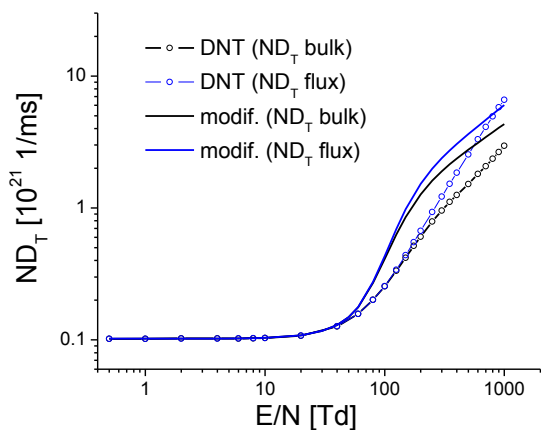


Fig.8. Reduced mobility for Na^+ in DXE.

a)





b)

Fig.9. a) Longitudinal and b) transversal diffusion coefficients as a function E/N for Na^+ ions in DXE gas.

III. CONCLUSION

In this work we present most probable reactions of alkali metal ions with dimethoxy ethane (DXE) molecule. In calculating the scattering cross section as a function of the kinetic energy with the Denpoh-Nanbu 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 and characteristic energy, reduced mobility and diffusion coefficients) for Na^+ ion in DXE gas.

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References

- [1] Y. Wang, C. Liu, Y. Zhang "Conversion from Dimethyl Ether to Dimethoxymethane and Dimethoxyethane Using Dielectric-Barrier Discharge Plasma", *Plasma Sci. & Technology* Vol. 7, No. 3, pp. 2839-2841, Jun 2005.
- [2] N. Kumar, Y. Yang, W. Noh, G. S. Girolami, and J. R. Abelson, "Titanium Diboride Thin Films by Low-Temperature Chemical Vapor Deposition from the Single Source Precursor $\text{Ti}(\text{BH}_4)_3(1,2\text{-dimethoxyethane})$ ", *Chem. Mater.* Vol. 19, 15, pp. 3802-3807, July 2007.
- [3] B. D. McCloskey, C. M. Burke, J. E. Nichols and S. E. Renfrew, "Mechanistic insights for the development of Li-O₂ battery materials: addressing Li₂O₂ conductivity limitations and electrolyte and cathode instabilities," *Chem. Commun.* Vol. 51, pp. 12701-12715, 2015.
- [4] Y. Cheng, R. M. Stolley, K. S. Han, Y. Shao, B. W. Arey, N. M. Washon, K. T. Mueller, M. L. Helm, V. L. Sprenkle, J. Liu and G. Li, "Highly active electrolytes for rechargeable Mg batteries based on a $[\text{Mg}_2(\mu\text{-Cl})_2]^{2+}$ cation complex in dimethoxyethane," *Phys. Chem. Chem. Phys.* Vol. 17 pp. 13307-14, 2015.
- [5] S.-H. Chung and A. Manthiram, "High-performance Li-S Batteries with an Ultra-lightweight MWCNT-coated Separator," *J. Phys. Chem. Lett.* Vol. 5, pp. 1978-1983, 2014.
- [6] J.-L. Shui, N. K. Karan, M. Balasubramanian, S.-Y. Li and D.-J. Liu, "Fe/N/C Composite in Li-O₂ Battery: Studies of Catalytic Structure and Activity toward Oxygen Evolution Reaction," *J. Am. Chem. Soc.* Vol.134, pp. 16654-16661, 2012.
- [7] W. D. Buchanan, M. A. Guino-o, and K. Ruhlandt-Senge, "Highly volatile alkaline earth metal fluoroalkoxides," *Inorg.Chem.* Vol.49, pp. 7144-7155, 2010.
- [8] R. K. Baldwin, K. A. Pettigrew, E. Ratai, M. P. Augustine, S. M. Kaulzarich, "A Nanoparticle Approach towards Morphology Controlled Organic Photovoltaics (OPV)," *Chem. Commun.* pp. 1822-1823, 2002.
- [9] A. L. Pickering, C. Mitterbauer, N. D. Browning, S. M. Kaulzarich, and P. P. Power, "Room temperature synthesis of surface-functionalised boron nanoparticles", *Chem. Commun.* pp. 580-582, 2007.
- [10] T. Hawa and M. R. Zachariah, "Understanding the Effect of Hydrogen Surface Passivation and Etching on the Shape of Silicon Nanocrystals", *J. Phys. Chem. C* Vol. 112, pp. 14796-14800, 2008.
- [11] P. Che, F. Lu, X. Si and J. Xu, "Catalytic etherification of hydroxyl compounds to methyl ethers with 1,2-dimethoxyethane," *RSC Adv.* Vol. 5, pp.24139- 24143, 2015.
- [12] K. Denpoh and K. Nanbu, "Self-consistent particle simulation of radio-frequency CF₄ discharge with implementation of all ion-neutral reactive collisions," *J. Vac. Sci. Technol. A* Vol. 16, pp.1201-1207, 1998.
- [13] V. Georgieva, A. Bogaerts and R. Gijbels, "Numerical study of Ar/CF₄/N₂ discharges in single-and dual-frequency capacitively coupled plasma reactors," *J. Appl. Phys.* Vol. 93 pp. 2369-2379, 2003.
- [14] Ž. Nikitović, V. Stojanović, Z. Raspopović and J. Jovanović, "Transport Parameters of F⁻ Ions in BF₃", *Acta Phys. Pol. A* No. 3, Vol. 126, pp. 724-726, 2014.
- [15] Nebojša Romčević, Milica Petrović, Martina Gilić, Vladimir Stojanović, Željka Nikitović and Zoran Raspopović, "Advanced ceramics and applications IV," Belgrade, Serbia, , P, p.74, September 21-23, 2015.
- [16] H. Koizumi, P. B. Armentrout, "The Kinetic Energy Dependence of Association Reactions. A New Thermokinetic Method for Large Systems," *J. Chem. Phys.* Vol.119, pp. 12819-12829, 2003.
- [17] Y. Satoh, M. Takebe, K. Inuma, "Measurements of mobilities and longitudinal diffusion coefficients for Li⁺ ions in some molecular gases," *J. Chem. Phys.* Vol. 87, pp. 6250, 1987.
- [18] S. G. Lias, J. E. Bartmess, J. F. Xebman and J. L. Holmes, R. D. Levin and W. G. Mallard, "Gas-phase ion and neutral thermochemistry," *J. Phys. Chem. Ref. Data*, Supl. 1 Vol. 17, 1, 1988.
- [19] 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," *Appl. Surf. Science* Vol. 253, pp. 6619-6640, 2007.
- [20] V. Stojanović, Z. Raspopović, J. Jovanović, Ž. Nikitović and Z. Lj. Petrović, "Transport of F⁻ ions in F₂", *EPL*, Vol.101, pp. 45003, 2013.
- [21] McDaniel E. W., Čermak V., Dalgarno A., Ferguson E. E. and Friedman L., *Ion-Molecule Reactions* (Wiley-Interscience) 1970.
- [22] Z. Ristivojević and Z. Lj. Petrović, "A Monte Carlo simulation of ion transport at finite temperatures", *Plasma Sources Sci. Technol.* Vol. 21, 035001, 2012.
- [23] Ž. Nikitović, V. Stojanović, O. Šašić, Z. Raspopović and Z. Petrović, "Određivanje transportnih koeficijenata u smeši BF₃ i F₂", *Zbornik radova 52. konferencije ETRAN, Palić, NM 1.8. ,8-12. juna ,2008.*
- [24] Ž. Nikitović, Z. Raspopović, V. Stojanović and J. Jovanović, "Transport parameters of F⁻ ions in Ar/BF₃ mixtures", *EPL*, Vol. 108, 35004, 2014.
- [25] L. A. Viehland and E. A. Mason, "Transport Properties of Gaseous Ions over a Wide Energy Range," *At. Data. Nucl. Data Tables*, Vol. 60, pp. 37-95, 1995.
- [26] Viehland database, www.lxcat.net, retrieved on 2016.