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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.*

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:

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

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	Δ_fH^0	Species	Δ_fH^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.

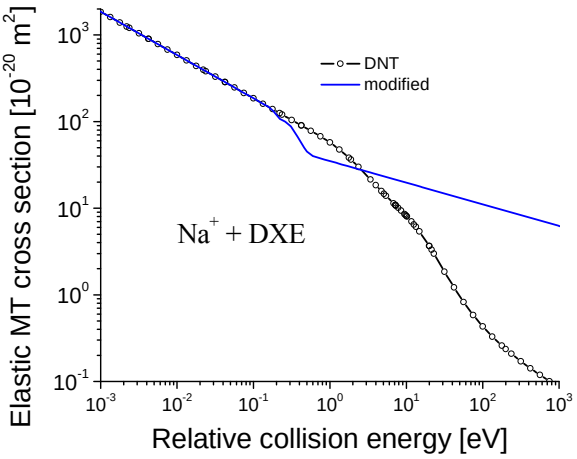

Fig. 1. Elastic momentum transfer cross section as a function of collision energy for Na^+ and DXE.

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.

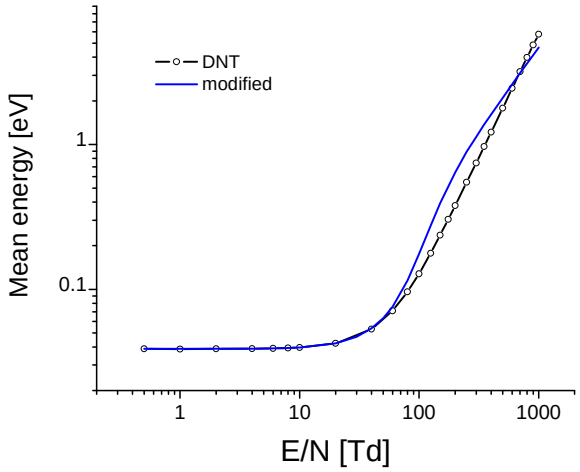

Fig. 2. Mean energy as a function E/N for Na^+ ions in DXE gas.

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.

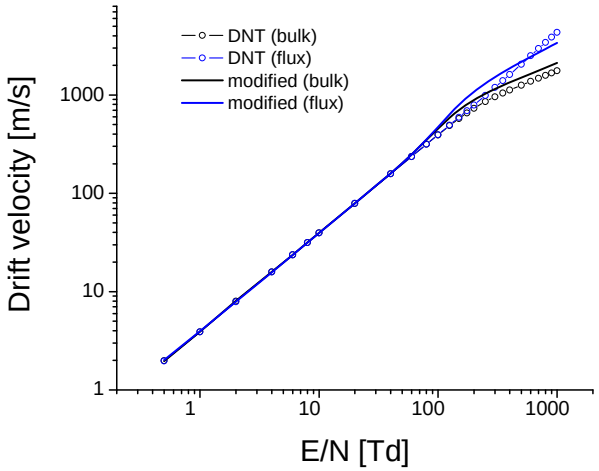

Fig. 3. Flux and bulk drift velocity as a function E/N for Na^+ ions in DXE gas.

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.

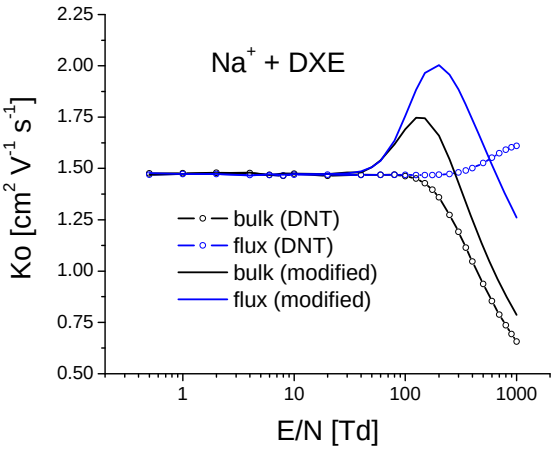

Fig. 4. Reduced mobility as a function E/N for Na^+ ions in DXE gas.

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.

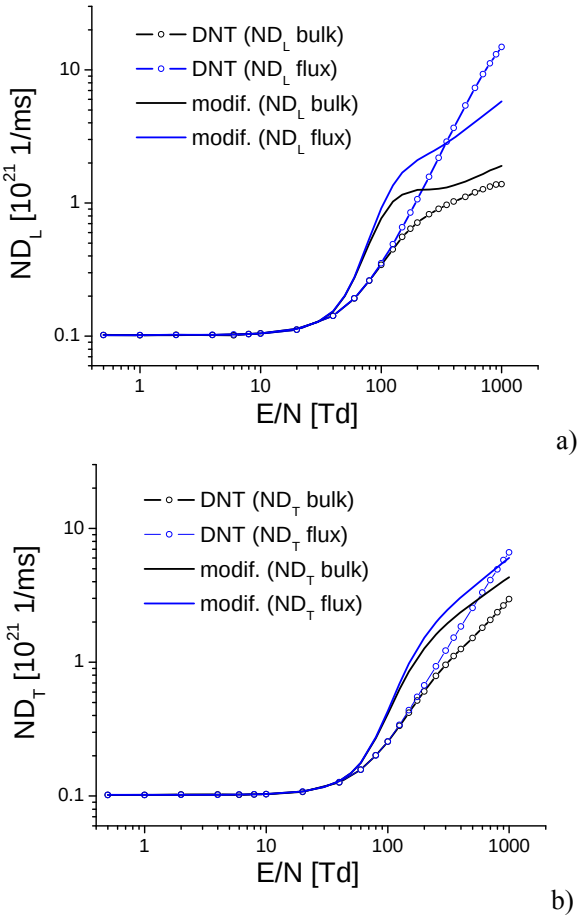

Fig. 5. a) Longitudinal and b) transversal diffusion coefficients as a function E/N for Na^+ ions in DXE gas.

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.

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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 судare 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*