Zoran M. Raspopović
Associate Research professor
University of Belgrade
Institute of Physics, Zemun

Vladimir D. Stojanović
Associate Research professor
University of Belgrade
Institute of Physics, Zemun

Uroš Cvelbar
Research Professor
Jozef Stefan Institute
Ljubljana,
Slovenia

Željka D. Nikitović
Research Professor
University of Belgrade
Institute of Physics, Zemun

Jasmina V. Jovanović
Full Professor
University of Belgrade
Faculty of Mechanical Engineering

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 nowadays 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

Received: November 2014, Accepted: December 2014
Correspondence to: Jasmina Jovanović
Faculty of Mechanical Engineering,
Kraljice Marije 16, 11120 Belgrade 35, Serbia
E-mail: jjovanovic@mas.bg.ac.rs
doi:10.5937/fmet1502168R

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 Et =5.6 eV, electron detachment (DET) with Et =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.

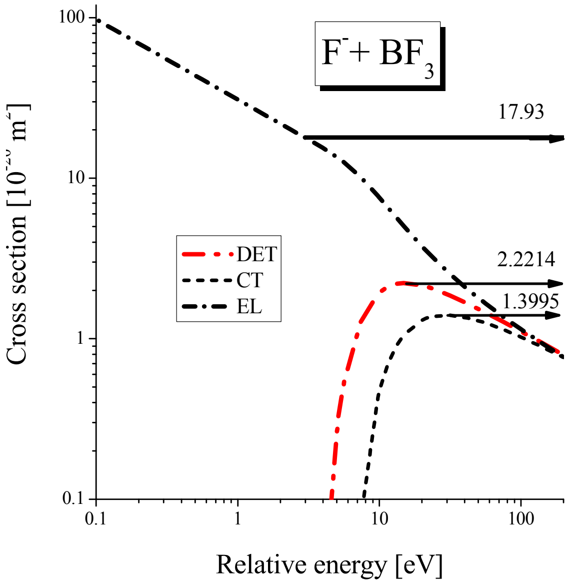

Figure 1. Cross sections for F^- scattering on BF_3.

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.

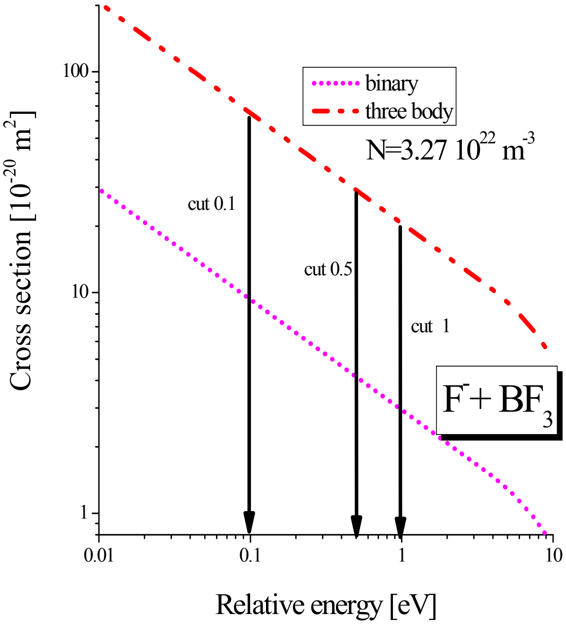

Figure 2. Cross sections for exothermic reactions for F^- scattering on BF_3 for at pressure 1 Torr and T=295 K.

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.

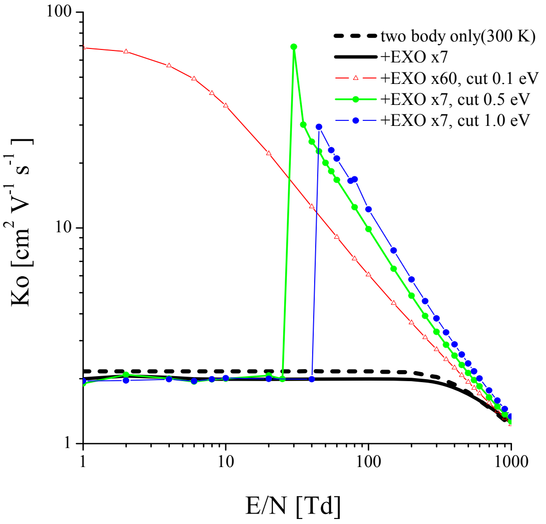

Figure 3. Reduced mobility of F^- ions in BF_3.

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.

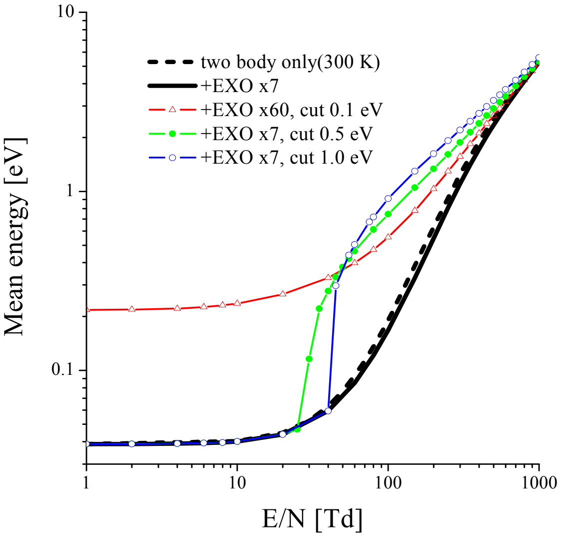

Figure 4. Mean energy of F^- ions in BF_3 in longitudinal direction.

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.

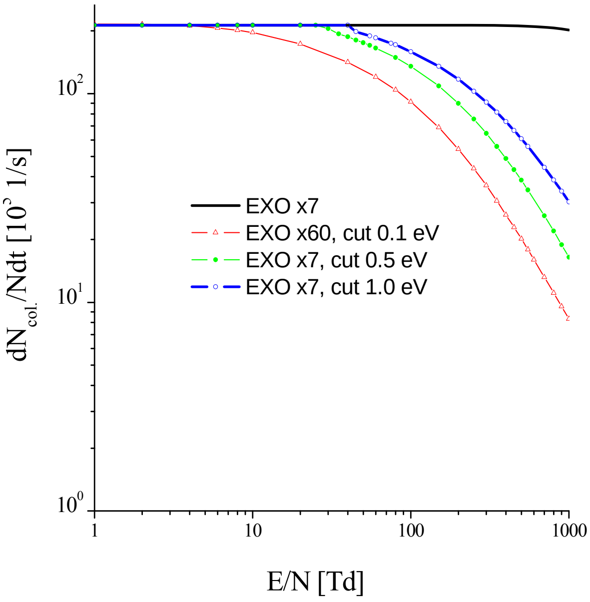

Figure 5. Rate coefficient for association reaction of F^- ions in BF_3.

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

This work was supported by MNRS Projects ON171037 and III 410011.

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УЛОГА ПРИТИСКА У ТРАНСПОРТУ F$^-$ ЈОНА У ГАСУ БОР-ТРИФЛУОРИДА У ТЕХНОЛОШКИМ ПРИМЕНАМА

Зоран М. Распоповић, Владимир Д. Стојановић, Урош Цвелбар, Жељка Д. Никитовић, Јасмина В. Јовановић

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).