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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.

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## 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 $1.64\ 10^{-30}$ $m^3$ 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 $F^- + F_2$ [12] we have used value $1.2611 \times 10^{-30}$ $m^3$, for polarizability of $F_2$ recommended by Spelsberg and Meyer [13].

Cross section set for $F^- + CF_4$ is calculated by taking into account value $2.8155 \times 10^{-30} m^3$ for dipole polarizability of $CF_4$.

### 2.2 Cross section set for $F^-$ scattering on $BF_3$

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 $3.3110^{-30}$ $m^3$ for $BF_3$ 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.

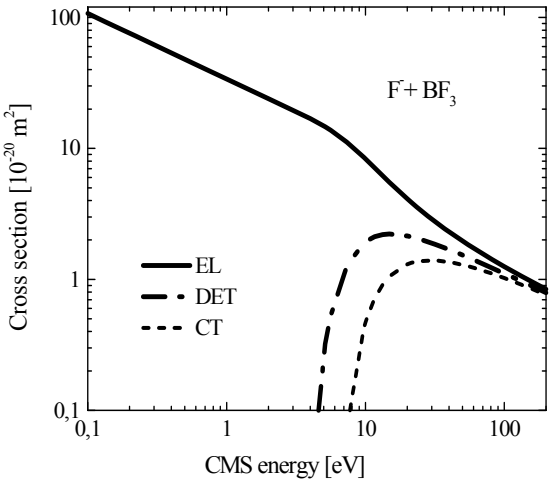


**Figure 1. Cross section set for $F^-$ scattering on $BF_3$.**

Cross section for exothermic reactions can be expressed as [19, 20] $\sigma_{exo} = f\sigma_L$, where $\sigma_L$ 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 $BF_3$ ions [20].

Thus one may account for competition between collisions of radiatively stabilized reaction (1) and elastic collisions by using elastic cross section $\sigma_{e0}$ 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 $\sigma_{e0}$ 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 $N_0 = 2.686763\text{x}10^{25}$ $m^{-3}$ 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 $E/N$.

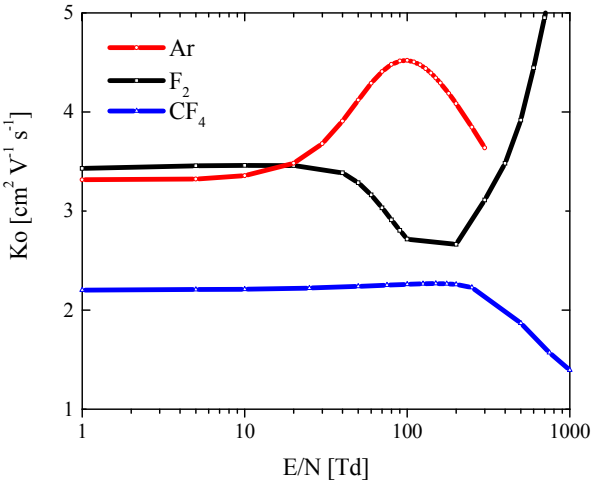


**Figure 2. Reduced mobility of $F^-$ ions in atomic and molecular gases.**

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.

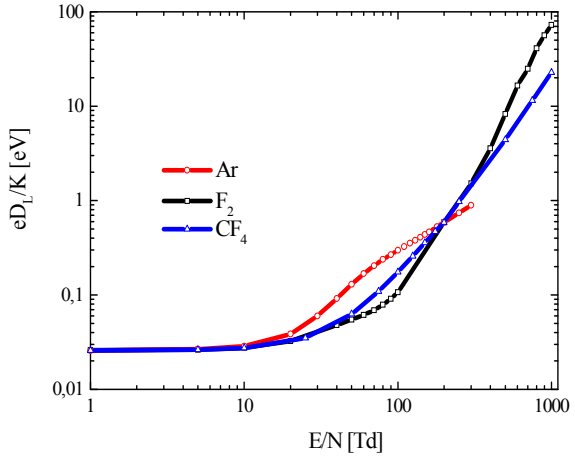


**Figure 3. Characteristic energy of $F^-$ ions in atomic and molecular gases in longitudinal direction.**

### 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.

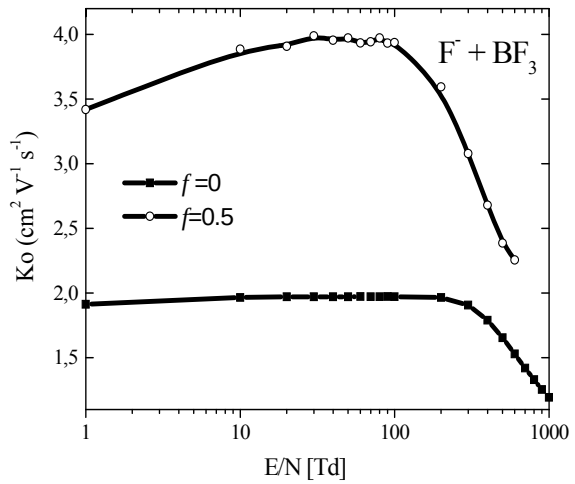


**Figure 4. Reduced mobility of F- ions in BF3.**

## 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.


## ACKNOWLEDGMENT

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## ТРАНСПОРТ F- ЈОНА КРОЗ ГАСОВЕ У ТЕХНОЛОШКИМ ПРИМЕНАМА

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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 $F_2$, $CF_4$ и $BF_3$ добијени су применом Нанбуове теорије у којој је могуће раздвојити еластичне од реактивних ударних процеса. Како би се уочили ефекти неконзервативних ударних процеса на брзине дрифта, прорачуни су рађени до високих вредности *E/N* (1000Td).