Rate Coefficients of Ar^+ Ions in Ar/CF_4 Mixtures

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In this paper we present a cross-section set for Ar^+ in Ar/ CF_4 mixtures where existing experimentally obtained data are selected and extrapolated. The Monte Carlo simulation method is applied to accurately calculate transport coefficients in hydrodynamic regime. We discuss new data for Ar^+ ions in Ar/CF_4 mixtures where mean energy, flux and bulk velocity and rate coefficients are given as a function of E/N (E — electric field, N — gas density).

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1. Introduction

Transport of Ar^+ plays significant role in various etching and deposition processes [1], in dark matter detection [2] and many more applications. Transport parameters in the presence of exothermic reactions (recombination energy of the ion is higher than the ionization potential of the gas particles) are generally less studied than the other. In our selected case reason is a large rate coefficient for exothermic reactions (resonant [3]) that limits number of ions necessary for determination of mobility. By using Monte Carlo simulations one may calculate transport parameters for the cases that are out of the reach of experimental efforts provided complete cross-section set is known. Transport parameters of Ar^+ in Ar/CF_4 are shown [4] to be significantly affected by exothermic collisions. Mean energy as a function of E/N, both flux and bulk velocity are expected to be significantly affected by the presence of exothermic reactions in the case of Ar^+ transport in the Ar/CF_4 mixtures. These processes in the study of ion molecule reactions are of fundamental interest [5].

2. Monte Carlo simulation

Cross-section sets for ion transport are scarce in spite of a broad range of specific methods relevant for quantification of particular cross-sections. The main problem in heavy particle scattering, precisely selecting the state of the projectile and target before the collision, is still very complicated so databases for ion scattering [6, 7] are still devoid of such data. Phelps established the first worldwide accessible database with cross-section sets [6] tested for each particular case either for swarm conditions of spatially resolved measurements of emission or ion mobility values. Another range of cross-section sets was established by measurements of ionic transport coefficients [7] and this work is ongoing. In all cases only the most important cross-sections may be established from the transport data. In the following section we will establish a complete cross-section set for Ar^+ scattering on Ar and CF_4 from 0.1 meV to 1000 eV [8] which will be used to calculate transport properties. Generally one may distinguish three characteristic energy ranges: low energy regime where polarization scattering is dominant, medium energy regime where polarization scattering is gradually replaced by hard sphere repulsion, and high energy approximation regime.

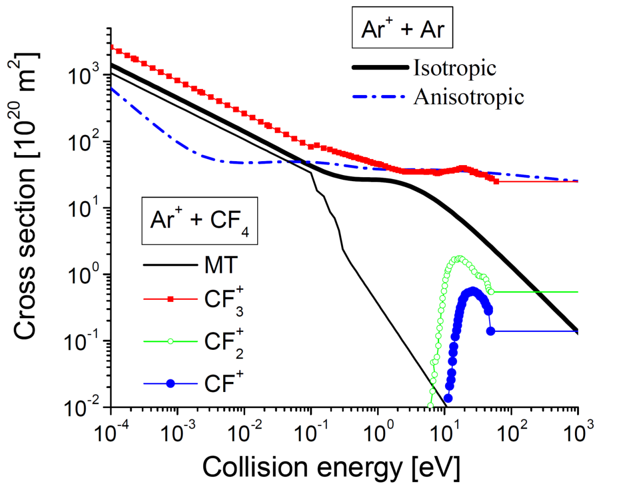

Fig. 1. Cross-section sets for Ar^++ Ar [14] and Ar^++ CF_4 [4, 9] as a function of collision energy.

At the lowest presented energies polarization scattering is dominant as also observed in guided beam experiment [9]. Thus one may use simple scattering models [1, 10] if a reliable value of the average polarizability of CF_4 is provided [11, 12]. Stojanović et al. [11] found excellent agreement for mobility of CF_3^+ ions in CF_4 by using value of 3.86 Å^3 [12] as an acceptable value for average polarizability of CF_4. A similar value was previously found appropriate by Jarvis et al. [13]. It is also generally accepted that dipole and quadruple moments are negligible (see for example [9]) in the analyses with CF_4. Fisher et al. [9] by measuring fast charge transfer reaction for CF_3^+ production proved that internal states of the target which are populated, are those closest to the recombina-

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tion energy of the projectile [3, 13]. Accounting for all details of Ar$^+$ scattering on CF$_4$ in Ref. [4] a complete cross-section set is presented that is also used in this work. Extensive discussion about transport properties of Ar$^+$ ions scattering in Ar gas applied to plasma physics problems was presented by Phelps [14] and Petrović and Stojanović [15]. Analytical expressions were offered in [14] to express apparently isotropic and anisotropic components of the cross-section set (see Fig. 1). In order to focus on effects of reactive processes introduced by CF$_4$ we neglected all but these two components of the Ar$^+$+ Ar cross-section set. Complete cross-section sets used in this work are shown in Fig. 1.

3. Transport coefficients

The Monte Carlo simulations (MCS) have many applications for analysis of the transport of charged particles in plasmas. MCS provide swarm data with the only the uncertainty due to statistical fluctuations and uncertainties in the cross-sections. In addition, MCS is the basis of hybrid models of plasmas allowing easy and accurate representation of the end effects and of the non-local high energy groups of particles which are essential in production of plasmas and treatment of surfaces. The MC code used in our analysis is based on the null collisions method.

Monte Carlo simulation code appropriate to calculate transport parameters [16, 17] of Ar$^+$ ions in Ar/CF$_4$ mixtures at non-zero temperature [18] has been used. In the Monte Carlo simulations exothermic reactive collisions are followed in a similar way as all non-conservative collisions i.e. the swarm particle dissappears from the ensemble after exothermic collisions. This results in changes of the swarm particle number in the entire energy range introducing nonconserving effects in kinetic equations and thus division of transport parameters to flux and bulk ones [16].

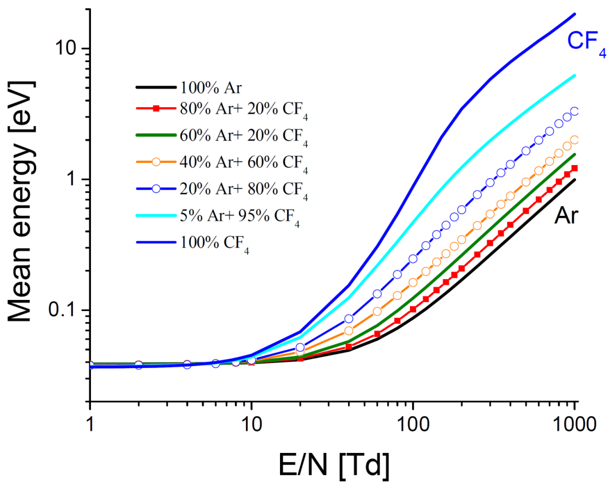

Fig. 2. Mean and characteristic energies of Ar$^+$ ions in Ar/CF$_4$ mixtures as a function of E/N.

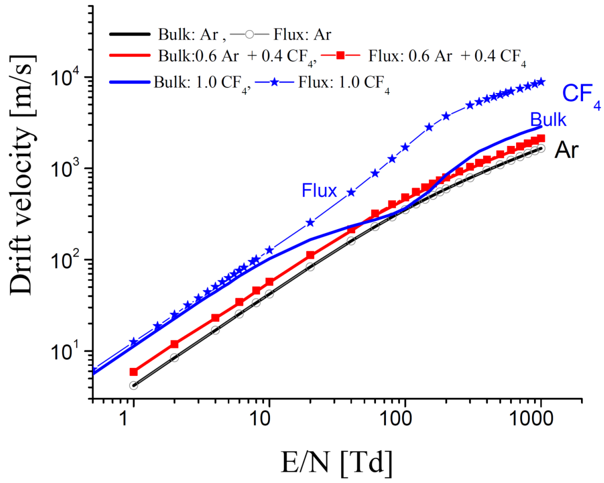

Fig. 3. Drift velocity as a function of E/N for Ar$^+$ in Ar/CF$_4$ mixtures at 300 K.

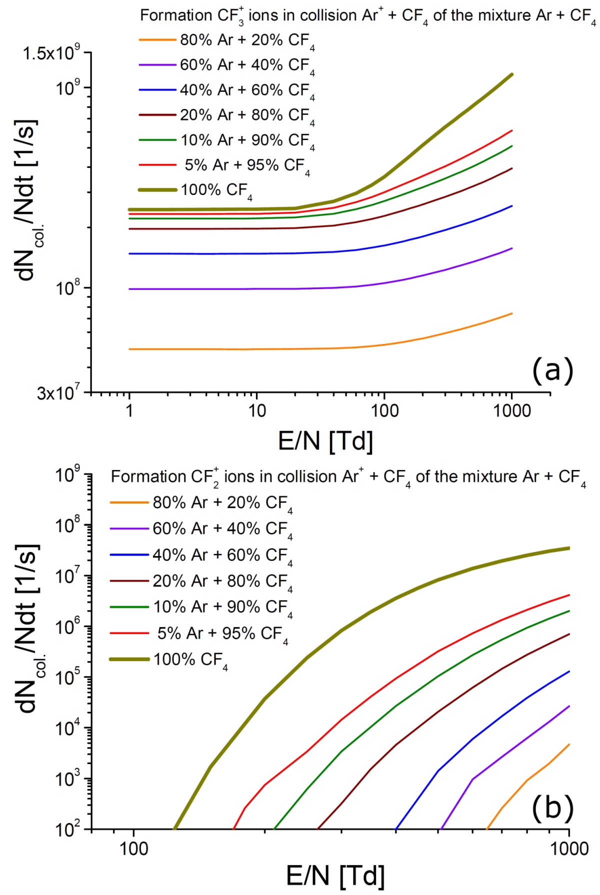

Fig. 4. Rate coefficients of Ar$^+$ in Ar/CF$_4$ mixtures.

In Fig. 2 we show results for mean energy as a function of E/N (E — electric field and N — gas density). Significant reduction and uniform control of mean energy of Ar$^+$ is obtained for argon content below 90%. For Ar content below 10% largest variations of mean energy are obtained for $E/N > 100$ Td (1 Td= 10^{-21} V m^2).

These variations are the consequence of a reduced momentum transfer cross-section for Ar^+ scattering with CF_4 (see Fig. 1) as compared to the scattering with Ar. At a high content of Ar charge transfer collisions dominate and make variation of mean energy with Ar content more uniform. Note that for transport coefficients of Ar^+ in pure Ar one may find benchmark data presented in tabular form by Ristivojević and Petrović [18].

The flux and bulk drift velocities [19] for Ar^+ in Ar/CF_4 as a function of E/N are given in Fig. 3. The drift velocities obtained by the Monte Carlo simulation are calculated in real space (bulk) and in velocity space (flux) values which are obtained as $\langle v \rangle$ and $\mathrm{d}\langle x \rangle/\mathrm{d}t$, respectively. Up to 40% CF_4 has no difference between bulk and flux values. Since the growth of the collision frequency with the energy of the reactive processes decreases the bulk drift velocity.

In Fig. 4 we show rate coefficients for reactions of Ar^+ ions with Ar/CF_4 mixtures at $T = 300$ K, calculated by the Monte Carlo simulations. Rate coefficients are important for applications of the global model to Ar/CF_4 mixtures. We are presenting formation (a) CF_3^+ ions in collision Ar^+ of the mixtures Ar/CF_4 and (b) CF_2^+ ions in collision Ar^+ of the mixtures Ar/CF_4 for different percent Ar and CF_4.

4. Conclusion

In this paper we show transport parameters for the Ar^+ in Ar/CF_4 mixtures which do not exist in the literature. In addition to presenting the data we show here the effects of non-conservative collisions to ion transport. Due to exothermic cross-sections that are dominant at low energies, for small abundances of Ar ($< 10\%$) exothermic process may be larger than the elastic scattering cross-section.

The Monte Carlo technique was applied to carry out calculations of the mean energy, drift velocity, and rate coefficients as a function of reduced DC electric field. Data for swarm parameters for ions are needed for hybrid and fluid codes and the current focus on liquids or liquids in the mixtures with rare gases dictates the need to produce data compatible with those models.

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