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Mobility of positive ions in CF_4

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Abstract. Cross-section sets for transport of positive ions in CF_4 that fit the available experimental data for mobility are assessed by normalizing the available experimental and theoretical cross-sections within the framework of the swarm method. Transport parameters for positive ions in CF_4 in DC fields at a gas temperature of T = 300 K are calculated as a function of the reduced electric fields E/N (N being the gas density) by using Monte Carlo simulation.

1. Introduction

Control of reactive ion plasmas is necessary in applications related to semiconductor modifications. A cornerstone in the modelling of such plasmas is precise information on the transport of ions, as the reactive ions' flux and energy control the surface processes. In plasmas in collision-dominated regimes, if the negative ions dominate over the electrons, the plasmas become electronegative with properties distinctly different from the electropositive plasmas, especially in the sheath region. In modelling and analyzing the plasma chemistry, the cross-sections are needed for all relevant species and not only concerning the momentum transfer. We focused our attention on the transport of positive ions originating from CF_4 by using the swarm method [1] and attempted also to compile a comprehensive cross-section set based on the available thermochemical data and on a simple procedure. This paper is a preliminary publication of such a set.

The CF_3^+ ion is the most abundant positive ion in pure CF_4 plasmas and its mixtures. It is also known that F^+ ions are produced due to the F atom's significant ionization potential with respect to that of other radicals. In (intensive) exothermic charge-transfer collisions of F^+ ions with CF_4, CF_3^+ ions are mainly produced [2]. No tested cross-section sets for these two ions in a CF_4 gas can be found in the literature.

Many authors [3, 4, 5, 6] have used collisional models for ions in CF_4 or its mixtures taking into account the long-range effects of ion-induced dipole interaction. Although based on a simple theory, a very wide range of possible reactions of ions with a CF_4 target have been considered [4, 5] in a consistent way. Taking into account a large number of reactions may lead to a selection of numerous processes with a scattering probability higher [4, 5] than that observed in the existing crossed-beam experiments [7].

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The aim of this study was to compile cross-section sets for F^+ and CF_3^+ ions and use Monte Carlo (MC) simulation to test them by comparing the calculated mobility data with the available experimental results. Input cross-sections were prepared over a wide collision-energy range, from 0.01 eV up to 500 eV. The results for the higher energies in this interval were obtained by extrapolation. However, the energy range of swarm studies used to normalize them is quite narrow and close to the thermal energies.

2. Cross section sets

2.1. CF_3^+ on CF_4

The cross-section set for scattering of CF_3^+ on the CF_4 molecule has been calculated recently by using available data and a simple procedure known as Nanbu's theory [4, 5]. It groups reactions scaled by their scattering probability according to reaction rate coefficients allowing separation of elastic from reactive endothermic collisions. The thermodynamic threshold energy and the branching ratio are accounted for following the Rice-Ramsperger–Kassel (RRK) theory [5]. A wide range of ion-molecule reactions were included in the cross-section set presented in [4] covering endothermic reactions only.

In this work, as a basis of the calculation of cross-section sets for F^+ and CF_3^+ ions in CF_4, we focused our efforts only on the processes observed in the experiment conducted by Peko *et al.* [7] rather than taking into account all processes listed by Nanbu [4, 5]. These reactions, with the thermodynamic threshold energies based on the existing thermochemical data [9], are shown in table 1.

Table 1. List of reactions and the corresponding thermodynamic threshold energies Δ [7] for CF_3^+ (a) and F^+ (b). Endothermicities are in eV and the underlined products have the same laboratory velocity as the reaction ion in the model.

a)			b)		
No	*reaction* $CF_3^+ + CF_4 \rightarrow$	Δ (eV)	*No*	*reaction* $F^+ + CF_4 \rightarrow$	Δ (eV)
R1	$\mathbf{CF_3}^+ + F + \underline{CF_3}$ (DCT)[a]	-5.7	P1	$\mathbf{CF_3}^+ + F + \underline{F}$ (DCT)[a]	+2.7
R2	$\mathbf{CF_2}^+ + F_2 + \underline{CF_3}$ (DCT)[a]	-10.3	P2	$\mathbf{CF_2}^+ + F_2 + \underline{F}$ (DCT)[a]	-1.9
R3	$\mathbf{CF}^+ + F + F_2 + \underline{CF_3}$ (DCT)[a]	-13.1	P3	$\mathbf{CF}^+ + F + F_2 + \underline{F}$ (DCT)[a]	-4.7
R4	$\mathbf{C}^+ + 2F_2 + \underline{CF_3^-}$ (DCT)[a]	-19.2	P4	$\mathbf{C}^+ + 2F_2 + \underline{F}$ (DCT)[a]	-10.79
R5	$\underline{\mathbf{CF_2}}^+ + F + CF_4$ (CID)[b]	-6.2	P5	$\mathbf{F}^+ + CF_3 + \underline{F}$ (CID)[b]	-10.8
R6	$\underline{\mathbf{CF}^+} + \underline{F_2} + CF_4$ (CID)[b]	-7.4	P6	$\mathbf{CF_3}^{++} + F + \underline{F^-}$ (DCT)[a]	-21
R7	$\underline{\mathbf{F}^+} + \underline{CF_2} + CF_4$ (CID)[b]	-12.3	P7	$\mathbf{CF_2}^{++} + F_2 + \underline{F^-}$ (DCT)[a]	-21.1
R8	$\underline{\mathbf{C}^+} + \underline{F} + \underline{F_2} + CF_4$ (CID)[b]	-15.1			

[a] Dissociative charge transfer; [b] Collision-induced dissociation.

We used the polarizability value of 3.86×10^{-30} m^3 [10] for the CF_4 molecule. When this value is substituted in Langevin's formula [11] for the zero-field mobility of CF_3^+ ions in CF_4, the value of 1.13375 cm^2 V^{-1} s^{-1} is obtained, which is close to the low-field mobility measured of 0.96 cm^2 V^{-1} s^{-1} [8].

The ionization potentials of CF_3 and CF_4 and the bond values between ions/atoms were taken from [4, 9]. We than applied a simple semi-analytic momentum transfer theory (MTT) to obtain the integral momentum-transfer cross-section. The cross-sections obtained were modified in such a way that the MC results agree perfectly with the experimental results for the reduced mobility (see figure 2 (a)). A more detailed explanation of the procedure applied can be found in our earlier papers [12, 13]. The lack of reactivity at low collision energies has also been found by other authors [2].

The inelastic and reactive cross-sections obtained using the Nanbu theory were scaled in the threshold region in order to fit the experimental cross-sections obtained by Peko *et al.* [7]. Finally, in order to provide data for modelling plasma sheaths and plasma etching applications, the cross-sections were extrapolated up to 500 eV following the trends in the experimental measurements. A complete set of cross-sections is shown in figure 1 (a).

2.2. F^+ on CF_4

Because of the small endothermicity (2.7 eV), the exothermic reaction of F^+ with CF_4 produces mainly CF_3^+ ions at lower energies (reaction P1 in table 1(b)). The careful extrapolation of the measurements [7] towards the lower energies for reaction P1 leads to a low-energy capture process curve that is positioned approximately at β *tot (β = 0.12), which is the low energy part of the exothermic cross-section for CF_3^+ production. The total cross-section is the sum of the elastic and capture (exothermic reaction) cross-sections; these are shown in figure 1(b).

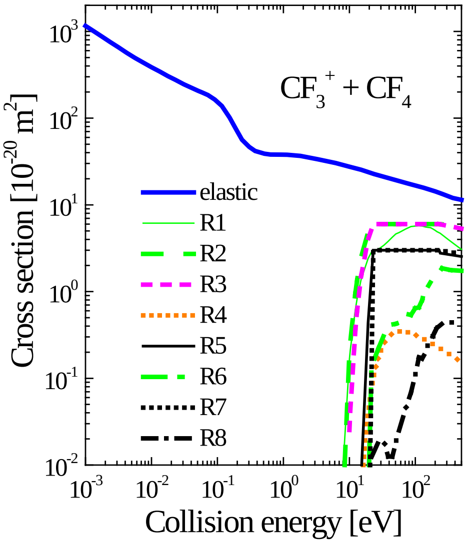

Figure 1(a). Cross-section set for CF_3^+ ions in CF_4 as a function of the collision energy.

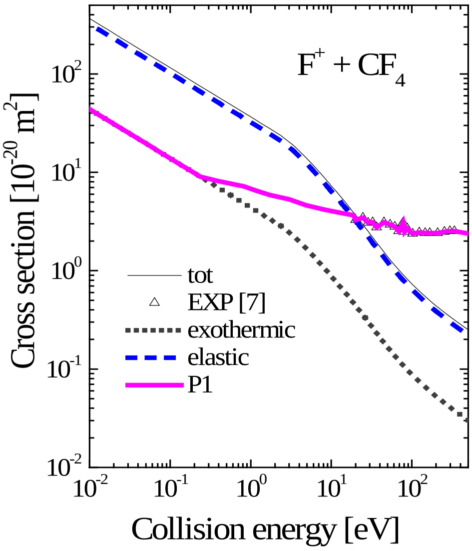

Figure 1(b). Cross-sections for elastic scattering and exothermic reaction for F^+ scattering on CF_4.

3. Results and discussion

The Monte Carlo technique was applied to calculations of the transport parameters in DC electric fields. In this work we used a Monte Carlo code that takes properly into account the thermal collisions [12, 14]. The code has passed all the tests and the benchmarks that were covered in our earlier studies [12, 15].

Figure 2 presents the reduced mobility of CF_3^+ ions (a) and F^+ ions (b) colliding with CF_4 as a function of the reduced electric field at room gas temperature (T = 300 K). The low-field mobility measured (0.96 $cm^2\ V^{-1}\ s^{-1}$) is in a good agreement with the value measured for the CF_3^- ion in CF_4 of 0.99 $cm^2\ V^{-1}s^{-1}$ [16]. The mobility curve of CF_3^+ in CF_4 shows a well-defined maximum for 200 Td <E/N <300 Td (1 Townsend = 10^{-17} V cm^2), followed by a decrease due to the predominance of the repulsive part of the interaction potential. The agreement of the experimental values for the reduced mobility of CF_3^+ ions in CF_4 with the MC results in the polarization limit also helped in determining the F^+ mobility at low electric fields. The presence of exothermic CF_3^+ formation of unknown intensity complicates the experimental observation of the F^+ mobility in CF_4 at low electric fields. Thus lack of experimental values for the reduced mobility of F^+ ions in CF_4 forced us to look for an agreement between the MC results and the experimental data in [16] for the mobility of F^- ions drifting through CF_4. The difference of around 15 % is not as good as that in CF_3^+,but is of the same order as the negative ion scatterring data; we thus can claim that a consistency of the MC results and the experimental values in [16] was achieved. More experimental data are needed to establish the effects of the exothermic process observed in the transport of F^+ ions in CF_4 so that the cross-section sets could be improved further.

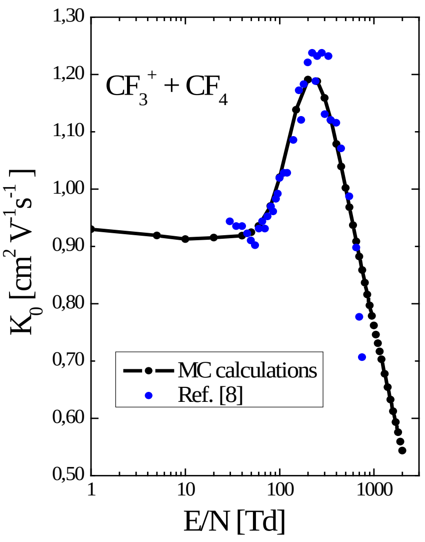

Figure 2(a). Mobility of CF_3^+ ions in CF_4 as a function of *E/N*.

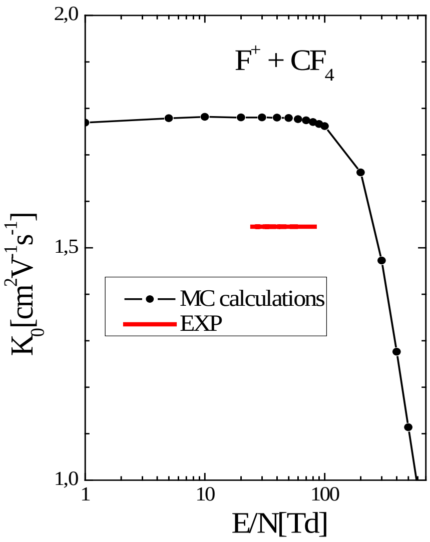

Figure 2(b). Mobility of F^+ ions in CF_4, as a function of *E/N*. EXP denotes averaged results of [12].

4. Conclusions

We present preliminary reults on the complete cross-section sets for the F^+ and CF_3^+ ions in CF_4 gas tested in a wide energy range. These sets were compiled by using simple theories covering both endothermic and exothermic reactions and the existing theoretical and experimental data for both binary collisions and swarms. The data for CF_3^+ were determined with sufficient accuracy thanks mainly to the available swarm data, while the data for F^+ are of lesser quality but still allowing proper plasma modelling.

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