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High-Pressure Study of Ion–Molecule Reactions in the Mixture of Carbon Tetrafluoride and Argon

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Charge-exchange ion–molecule reactions of Ar^+ ions with CF_4 have been studied in the pressure range 1.33–39.99 Pa. A quadrupole mass spectrometer with a high-pressure ion source has been used for measuring gaseous ion–molecule reactions in the mixture of 1% CF_4 and 99% Ar. The fractional abundance $I_i/\sum I_i$ of the observed CF_3^+, CF_2^+ and argon ions has been determined as a function of the gas mixture pressure (at the values of the repeller electrode potentials V_R ranging from 2 to 10 V).

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1. Introduction

Dissociative charge-exchange processes in the ion–molecule reactions of rare gas ions with the polyatomic molecules have been studied extensively using several methods [1–12].

These processes in the study of ion–molecule reactions are of fundamental interest. The mechanism in these reactions presents important questions concerning, first, the means by which energy is deposited in the produced ion and the, second, problem of the distribution of energy within the molecule which can lead to molecular fragmentation. From the applied point of view, knowledge of both the product fractional abundance and the reaction rate coefficient is fundamental for the modeling and optimization of plasmas for industrial applications [7].

CF_4 is a commonly used gas in radiofrequency (rf) plasmas for etching SiO_2 (typically, mixtures of fluorocarbons and argon are used in plasma etching), depositing silicon oxide and silicon nitride layers and for plasma chamber cleaning processes [1, 13–17].

The ion–molecule reactions of argon ions with CF_4 have been described in papers [6, 8, 14, 16, 18, 19].

In the present paper, the charge-exchange reactions of argon ions with carbon tetrafluoride molecules have been studied by observing fractional abundance mass spectra in a quadrupole mass spectrometer with a high-pressure ion source. The data are presented as the fractional ratio of the particular reaction product ions and the sum of all product ions $I_i/\sum I_i$.

2. Experimental

The measurements were performed by using of a quadrupole mass spectrometer with a high pressure ion source constructed by the authors [20–23]. The primary ions were produced in the ion source by an electron beam. A gas or a gaseous mixture has been introduced into the ion source ionization chamber, where the gas pressure (controlled by a MKS Baratron capacitance manometer) can be changed from 0.133 to 133 Pa. The positive (relative to the ionization chamber) potential V_R is applied to the ion repeller electrode. The vacuum system of the mass spectrometer is of a differential type and independently evacuates the ion source region (the pumping speed 2000 l/s) and the analyzer region (the pumping speed 800 l/s). The quadrupole mass spectrometer is able to perform ion analyses in the mass range of 400 a.m.u. The ions are detected by the Balzers electron multiplier. The mass spectrometer was controlled by a computer.

For the experiments performed in this work, the electron energy was 300 eV, the ion accelerating voltage 20 V, the gas temperature 297 K, ion repeller electrode potential was changed between 2 and 10 V. The mixture pressure of 1% CF_4/99% Ar was varied from 1.33 to 39.99 Pa.

3. Results and discussion

In the present experiment the charge-exchange reactions of argon ions with carbon tetrafluoride have been studied at low ion energy in the pressure range 1.33–39.99 Pa. The primary Ar^+ ions are produced in the mixture of 1% CF_4 and 99% Ar by the electron impact. The fractional abundance of the secondary CF_3^+, CF_2^+ and argon ions have been determined as a function of gas mixture pressure for nine (2–10 V) repeller electrode potentials.

The charge-exchange reaction between A^+ ions and molecules XY can be written as follows:

$$A^+ + XY \rightarrow XY^+ + A. \quad (1)$$

The simple energy balance equation for the charge-exchange reaction (1) is given by [24]:

$$RE(A^+) - IE(XY) = I_{nt}E(XY^+) + KE, \quad (2)$$

where $RE(A^+)$ is the recombination energy of A^+, IE(XY) is the ionization energy of XY, I_{nt} $E(XY^+)$ is the product ion internal energy, and KE is the kinetic energy release.

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If the charge-exchange reaction is dissociative:

$$A^{+} + XY \rightarrow X^{+} + Y + A, \quad (3)$$

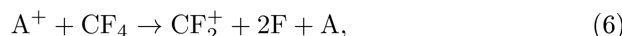
then

$$RE(A^{+}) - AE(X^{+}) =$$

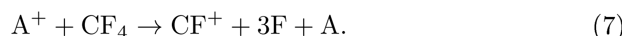
$$I_{nt}E(X^{+}, Y) + KE(A, X^{+}, Y). \quad (4)$$

The dissociative charge-exchange reactions of rare-gas ions with CF_4 from thermal energy to 50 eV have been studied by Fisher et al. [6]. They found out the following ion–molecule reactions:

$$A^{+} + CF_4 \rightarrow CF_3^{+} + F + A, \quad (5)$$



$$A^{+} + CF_4 \rightarrow CF_2^{+} + 2F + A, \quad (6)$$



$$A^{+} + CF_4 \rightarrow CF^{+} + 3F + A. \quad (7)$$

A^{+} — the rare-gas ions (Ar^{+}, Ne^{+}, He^{+}).

The present study results for the reaction $Ar^{+} + CF_4$ are shown in Fig. 1. The figure shows that the Ar^{+}/CF_4 reaction yields CF_3^{+} and CF_2^{+} fragments.

CF_3^{+} ions are produced by reaction (5) which is exothermic by 1.07 ± 0.05 eV [15].

The CF_2^{+} ions are produced in reaction (6) at higher energies of primary Ar^{+} ions. It is so because the CF_2^{+} fragment ions are formed in an endothermic process, where for CF_2^{+} production, the reaction threshold is at 6.55 ± 0.14 eV [6].

The CF^{+} ions are not detected in the mass spectrum because reaction (7) is highly endothermic (ion repeller electrode potential in the present study was increased up to 10 V).

In general, it can be seen in Fig. 1 that CF_3^{+} is the main ionic product of ion–molecule reaction (1). This ion shows increase in the fractional abundance at higher values of the gas mixture pressure ($I_i/\sum I_i = 0.659$ at $p = 39.99$ Pa and $V_R = 2$ V). CF_2^{+} shows also small increase with the increasing pressure. Due to an endothermic reaction (2) these ions are detected in the mass spectrum when the repeller potential $V_R \geq 8$ V. For the product ion CF_2^{+} there was observed fractional abundance $I_i/\sum I_i = 0.0597$ (with the pressure 39.99 Pa and the repeller electrode potential $V_R = 10$ V).

Further experimental and theoretical studies are required in order to compare these results of charge-exchange reactions with those presented in the literature. Very interesting study was performed by Kato and his co-workers [25]. In that study, a computational method of the kinetic model of carbon tetrafluoride (CF_4) in wet argon gas under the electron beam irradiation was developed.

The results of several other mass-spectrometric studies of ion–molecule reactions carried out in our research group using a high-pressure mass spectrometer are presented in [23, 26–30].

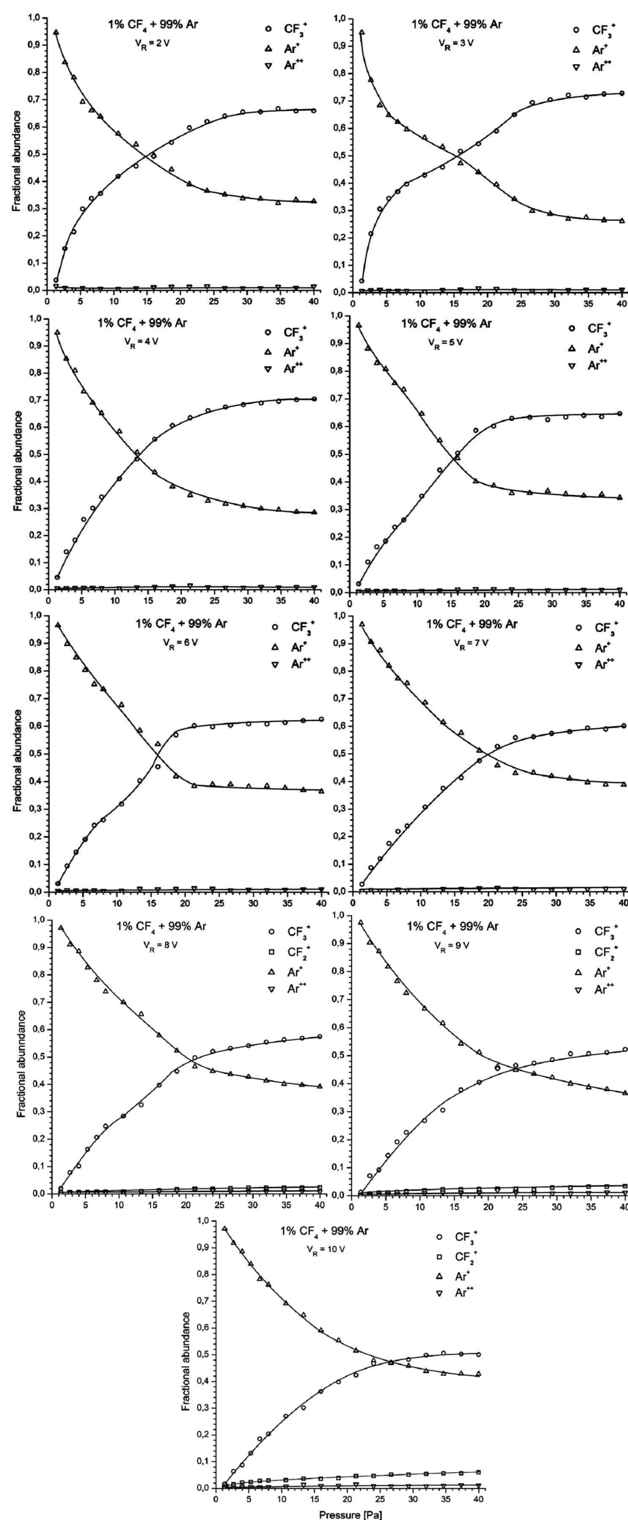


Fig. 1. Fractional abundance of observed ions as a function of pressure in the $1\%CF_4 + 99\%Ar$ mixture (the repeller electrode potential $V_R = 2, 3, 4, 5, 6, 7, 8, 9$, and 10 V).

4. Conclusions

Dissociative charge-exchange reactions of Ar^+ ions with CF_4 have been investigated using a quadrupole mass spectrometer with a high pressure ion source.

The main purpose of the study was to determine fractional abundance of ions produced in the charge-exchange reactions in the carbon tetrafluoride and argon mixture.

The fractional abundance $I_i/\sum I_i$ of the observed CF_3^+, CF_2^+ and argon ions has been determined as a function of the 1% CF_4 and 99% Ar gas mixture pressure (in the range 1.33–39.99 Pa). The repeller electrode potential was varied over the range 2–10 V. The results obtained in the present study are useful for modeling plasma etching processes and fundamental studies of plasma control.

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