Development of the electron impact cross section set for CHF₃. Monte Carlo simulation of the swarm experiments in pure CHF₃ and CHF₃/Ar mixtures

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Abstract. Trifluoromethane (CHF₃) is widely used in semiconductor processing. However, electron collision cross section set in CHF₃ is not finally completed and verified yet. Cross section sets developed before were tested only in pure CHF₃ and calculations with these sets do not describe swarm parameters in CHF₃ diluted by Ar. In this work a numerical code based on the Monte Carlo method has been developed and used to calculate swarm parameters in pure CHF₃ and Ar/CHF₃ mixtures. Calculations in CHF₃ diluted in Ar allowed us to validate the absolute value of vibration cross sections. The values and the shapes of momentum transfer, attachment and dissociation cross sections in CHF₃ were renormalized on the base of the thorough analysis of all available experimental data and quantum-mechanical calculations. As a result physically well-grounded cross section set for CHF₃ was developed and verified on various swarm experiments in CHF₃ and CHF₃/Ar mixtures.

1. Introduction

CHF₃ is widely used in semiconductor processing and plasma etching reactors. For studying plasma chemistry in such reactor it is necessary to know electron impact cross section sets for the reactor mixtures. But difficulty in constructing such cross section set for complex molecules (such as CHF₃) grows due to the absence of low-energy electron collision experimental data, for example, vibration excitation cross sections. Absolute values of vibration excitation cross sections for complex molecules are usually relatively high and excitation of vibration states is significant process of electron energy loss, which influence heavily on the electron energy distribution function (EEDF).

In the theoretical work of Morgan et al [1], quantum-mechanical calculations were carried out to get the momentum transfer cross section, shape of vibration excitation cross section, and cross sections of electron excitation states, part from which is dissociable.

In experimental work of Goto [2], ionization and dissociation cross sections were measured. Values of Goto ionization cross section are confirmed by many other experiments [3-5] and recommended for plasma processing. Dissociation cross section from work [2] is quite correct at high energies but resonance shape of cross section near threshold area, which was obtained in Morgan calculation [1] was difficult to register experimentally.

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There are other data about electron impact cross sections for CHF₃: for momentum transfer cross section – measured $\sigma_m$ for electron energy $> 1$ eV [6], recommended $\sigma_m$ [6]; for vibration excitation cross section – estimated by simulation of swarm experiments in CHF₃ [7]; for neutral dissociation cross section – measured [8], estimated by simulation of swarm experiments in CHF₃ [7]; for ionization cross section – measured [3-5]; for electron attachment cross section – experimental data [9], estimated by simulation of swarm experiments in CHF₃ [7].

There are data of swarm experiments in pure CHF₃ [10,11] and in Ar/CHF₃ mixtures [10]. Calculations with the cross section set, required for plasma processing, should describe experimental data on transport coefficients both in pure CHF₃ and its different mixtures.

Cross section sets developed before [1, 7] were tested only in pure CHF₃, and therefore it led to some uncertainty in the absolute value of the vibration excitation cross section. These sets do not describe drift velocity of the electron in Ar/CHF₃ mixture (as it seen from figure 1) in the range of reduced electric field, where vibration excitation is the main inelastic process.

Figure 1. Drift velocity in Ar/CHF₃ (99%/1%) mixture: rhombus – experimental data, squares – MC calculation with Morgan set [1], circles – MC calculation with Kushner set [7].

Figure 2. Drift velocity, calculated with TTA: rhombus – 1% CHF₃ calculation with Kushner set; triangles – 1% CHF₃, squares – 10% CHF₃ (solid symbols – experiment, open symbols – calculation with our final cross section set).

2. EEDF calculation methods

2.1. Two term approximation (TTA)
To check cross sections sets on swarm parameters the two-term approximation for determination electron energy distribution function from solution of Boltzmann equation in uniform electric fields is widely used. TTA is applicable in case of weak anisotropy of EEDF. But in case of significant inelastic collisions, like in Ar/CHF₃ mixture it is not adequate to use TTA. One can see from figure 2 that in case of 10% CHF₃, when the role of inelastic loses of energy increase, TTA leads to some mistakes in drift velocities and therefore in estimating of the cross section set.

2.2. Monte Carlo simulation
In this work Monte Carlo (MC) method was used to evaluate cross section set from swarm experiments.

In a Monte Carlo model the trajectory of the electrons is calculated according to the Newton’s laws, whereas the collisions are treated in null-collision approach, using random numbers to chose the kind of collisions, the scattering angle and velocity after scattering. The null-collision approach method was described in detail by Vahedi and Surendra [12]. In our MC calculations of swarm parameters about
10^4-10^5 probe electrons are traced in constant electric field E at constant neutral gases concentration N. Initial electron velocities are assumed isotropic with Maxwell distribution.

3. Cross section set for Ar
Cross sections for Ar are well-known [13], and as some test of the program it was made calculations of transport coefficients in pure Ar. As it seen from the figure 3 there is a good agreement between calculations and experiment in drift velocity and ionization coefficient. Note that Ar is a base component in working gas mixtures.

![Figure 3](image_url)

**Figure 3.** Drift velocities and ionization coefficient in Ar. Experimental results and MC calculations.

4. Cross section set for CHF₃

4.1. Vibration excitation cross section
There are six different vibration modes of molecule CHF₃ (without taking into account vibration modes degeneration). Cross sections of initial modes excitation were grouped into four vibration excitation cross section (with threshold 0.06, 0.14, 0.18, 0.37 eV). The shape of cross sections corresponds to quantum-mechanical calculations in first Born approximation, which were made in [1].

As it seen from figure 4, vibration excitation cross sections of molecule CHF₃ are in the area of Ramsauer minimum of momentum transfer cross section of Ar. Vibration excitation of the CHF₃ molecule is the main inelastic process in the electron energy range up to 10 eV. The absolute values of vibration excitation cross section were varied and adjusted to fit the electron drift velocity in CHF₃ heavily diluted by Ar; in such mixture elastic losses of energy are determined by Ar, and inelastic loses are determined by CHF₃.

![Figure 4](image_url)

**Figure 4.** Ar momentum transfer cross section, CHF₃ vibration excitation cross sections.

**Figure 5.** Drift velocities in Ar/CHF₃ mixtures: circles – 0.1% CHF₃, triangles – 1% CHF₃, squares – 10% CHF₃, solid symbols - experimental results, open symbols - MC calculations.
Drift velocities in different Ar/CHF₃ mixture after final estimation of absolute values of vibration excitation cross section are shown in figure 5.

4.2. Momentum transfer cross section
Now we can start numerical experiments in pure CHF₃ having the vibration excitation cross sections. The shape of momentum transfer cross section of CHF₃ was taken from the quantum-mechanical calculations [1]. By modifying low energy part of this cross section, where accuracy of quantum calculations was the lowest we describe drift velocity in pure CHF₃ [10], and so it was estimated the absolute value of momentum transfer cross section. (see figure 6)

4.3. Ionization cross section
The total and partial ionization cross sections are studied experimentally [2-5,8,9], both in the range of high electron energies [2-4] and near threshold range [5]. Analysis of these investigations can be found in article of Christophorou’s group [14]. In this work Kim total ionization cross section [15] was used (see figure 9) in order to fit the absolute dissociation cross section measured by Winters [16]. This absolute total dissociation cross section was confirmed by the recent report [17].
Partial ionization cross sections correspond to work [2], and thresholds were taken from work [3].

![Figure 6. Drift velocity in pure CHF₃, experimental results [9] and MC calculations.](image)

![Figure 7. Electron attachment cross section for molecule CHF₃.](image)

4.4. Neutral dissociation cross section
The dissociation cross section is studied experimentally for high electron energies [2], but there is some uncertainty in the near threshold range. Resonance shape of the cross section was taken in this range; such shape was obtained from the Morgan’s quantum-mechanical calculations of CHF₃ electron excited states [1].

Note that in the swarm and different discharge conditions experiments electron temperature range is about 2-5 eV and the near threshold behavior of the dissociation (and ionization) cross sections is extremely important. In these conditions, dissociation rates are defined mainly by near threshold values of dissociation cross section. A simple scaling by large factor (such calculations were made, for example, in [1]) of dissociation cross sections affects strongly the high energy part (“tail”) of electron energy distribution function and leads to significant difference in dissociation and ionization rate constants values.

In Morgan’s work [1] quantum mechanical calculations were carried out to study the cross sections of 3A₁, 1A₁, 3E and 1E states excitation in CHF₃. The calculations indicated that the 3A₁ state dissociates to CF₃ + H, the 1A₁ dissociates to CHF₂ +F and both the 3E and 1E states dissociate to CHF + 2F. Experimental data of [3] indicates that the 3E and 1E states are not dissociated. Thus, near threshold resonance behavior in our dissociation cross section is connected with dissociation into CF₃.
and CHF$_2$ channels. The excitation of the $^3$E and $^1$E states corresponds to indirect vibration excitation. And cross section of this process was introduced with the threshold 13.42 eV and energy loss 0.4 eV. Note that same results about the existence of indirect vibration excitation were observed in CF$_4$.

Including resonance part in dissociation cross section allowed us to keep the experimental values for high energy part of this cross section and avoid unjustified scaling of cross section (like in work [7], where this cross section value exceeds the experimental one [2] at 110 eV more than 4 times!)

Partial cross sections in non-resonance part of total dissociation cross section correspond to [2]. Rate constants of dissociation into different channels were calculated and can be used in plasma-chemistry research. The absolute value of the resonance part of dissociation cross section was varied and adjusted to fit the net ionization coefficient in pure CHF$_3$ (see figure 8).

4.5. Electron attachment cross section

The shape of electron attachment cross section was taken from the experimental data [9], and its absolute value was estimated by describing the net ionization coefficient (ionization coefficient minus attachment coefficient) in the low values of reduced electric field E/N

Note that correct values of vibration cross sections allowed us to use experimental shape of attachment cross section [9] without unobserved low energy “foot” which was introduced in [7] (see figure 7).

Table 1. Parameters for EEDF calculation for each cross section in pure CHF$_3$.

| Cross section                  | Threshold (eV) | Energy loss (eV) |
|-------------------------------|----------------|-----------------|
| Elastic Momentum, $\sigma_{\text{m}}(\varepsilon)$ | 0.0001         | 0.0             |
| Direct Vibration Excitation, $\sigma_{\text{vib}_1}(\varepsilon)$ | 0.066          | 0.066           |
| Direct Vibration Excitation, $\sigma_{\text{vib}_2}(\varepsilon)$ | 0.14           | 0.14            |
| Direct Vibration Excitation, $\sigma_{\text{vib}_3}(\varepsilon)$ | 0.18           | 0.18            |
| Direct Vibration Excitation, $\sigma_{\text{vib}_4}(\varepsilon)$ | 0.37           | 0.37            |
| Indirect Vibration Excitation, $\sigma_{\text{ind-vib}}(\varepsilon)$ | 13.42          | 0.4             |
| Ionization, $\sigma_{\text{ion}_1}(\varepsilon)$, CF$_3$(+) | 14.41          | 14.41           |
| Ionization, $\sigma_{\text{ion}_2}(\varepsilon)$, CF$_2$(+) | 15.23          | 15.23           |
| Ionization, $\sigma_{\text{ion}_3}(\varepsilon)$, CHF$_2$(+) | 15.26          | 15.26           |
| Ionization, $\sigma_{\text{ion}_4}(\varepsilon)$, CF$(^*)$ | 17.8           | 17.8            |
| Ionization, $\sigma_{\text{ion}_5}(\varepsilon)$, CHF$(^*)$ | 19.8           | 19.8            |
| Ionization, $\sigma_{\text{ion}_6}(\varepsilon)$, CH$(^*)$ | 28.29          | 28.29           |
| Ionization, $\sigma_{\text{ion}_7}(\varepsilon)$, F$(^*)$ | 34.9           | 34.9            |
| Attachment, $\sigma_{\text{att}}(\varepsilon)$ | 0.066          | -               |
| Dissociation into Neutrals, $\sigma_{\text{diss}_1}(\varepsilon)$, CF$_3$ | 12.2           | 12.2            |
| Dissociation into Neutrals, $\sigma_{\text{diss}_2}(\varepsilon)$, CHF$_2$ | 13.0           | 13.0            |
| Dissociation into Neutrals, $\sigma_{\text{diss}_3}(\varepsilon)$, CF | 19.0           | 19.0            |
| Dissociation into Neutrals, $\sigma_{\text{diss}_4}(\varepsilon)$, CF$_2$ | 25.0           | 25.0            |
| Dissociation into Neutrals, $\sigma_{\text{diss}_5}(\varepsilon)$, CHF | 37.0           | 37.0            |
5. Conclusion
Physically well grounded electron impact cross section set for CHF$_3$ was developed. This set describes
swarm parameters both in pure CHF$_3$ and different Ar/CHF$_3$ mixtures. Absolute values of vibration
excitation cross sections were obtained. Initial vibration modes of molecule CHF$_3$ are represented
much better than in previous works. Total dissociation cross section of molecule CHF$_3$ were obtained
with the resonance behavior near threshold.

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References
[1] Morgan L, Winstead C and McKoy V 2001 J. Appl. Phys. 90 2009
[2] Goto M, Nakamura K, Toyoda H and Sugai H 1994 Jpn. J. Appl. Phys. 33 3602-7
[3] Fiegele T, Hanel G, Torres I, Lezius M and Mark T D 2000 J. Phys. B: At.Mol.Opt. 33 4263-83
[4] Poll H U and Meichsner J 1987 Contrib.Plasma Phys. 27 359
[5] Jiao C Q, Nagpal R and Haaland P D 1997 Chem.Phys.Lett. 269 117
[6] Sueoka O, Takaki H, Hamada A, Sato H and Kimura M 1998 Chem.Phys.Lett. 288 124
[7] Kushner M J and Zhang Da 2000 J. Appl. Phys. 88 3231
[8] Motlagh S and Moore J H 1998 J.Chem.Phys. 109 432-8
[9] Scheunemann H U, Henri M, Illenberger E and Baumgartel H 1982 Ber. Bunsenges. Phys.
Chem. 86 321-6
[10] Wang Y, Christophorou L G, Olthoff J K and Verbrugge J K 1999 Chem. Phys. Lett 304 303
[11] Urquijo J, Alvarez I and Cisneros C 1999 Phys. Rev. E 60 4990
[12] Vahedi V and Surendra M 1995 Comput. Phys. Commun. 87 179
[13] Phelps A V 1985 JILA Information Center Report vol 28
[14] Christophorou I G, Olthoff J K and Rao M V V S 1997 J. Phys. Chem. Ref. Data 26 1
[15] Kim Y K, Hwang W, Ali M A and Rudd M E Proc. 20th Int. Conf. on the Physics of Electronic
and Atomic Collisions July 1997 Vienna Austria vol II p WE103
[16] Winters H F and Inokuti M 1982 Phys. Rev. A 25 1420
[17] Flaherty D W, Kasper M A, Baio J E, Graves D B and Winters H F Proc. 27th Int. Conf. on
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