Determination of the Vibrational Excitation Cross-section for the F₂ Molecule in a Plasma Discharge Simulation

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The electron collision cross-section for a fluorine molecular gas, which is necessary for modeling electron diffusion in a plasma reactor, has been determined included. This cross-section includes the vibrational excitation cross-section for F₂ molecule. We have calculated the electron drift velocities in two F₂-He mixtures (with 0.2% and 1% fluorine) and in pure F₂ by using the determined cross-sections and a two-term approximation of the Boltzmann equation for the energies. The results agree well with available experimental data for the electron drift velocity over a wide range of E/N (ratio of the electric field, E, to the neutral number density N). The present cross-sections may be important for quantitatively modeling plasma discharges for processing procedures with materials containing fluorine molecules.

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1. INTRODUCTION

The Kyoto Protocol has listed the greenhouse gases as CO₂, CH₄, N₂O, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and SF₆, and we need to regulate the emissions and the utilizations of those gases in the many industries [1]. On the other hand, with the higher electron affinity of a molecule, the isolated performance and theoretical materials possessing a higher electronegativity are possible [2]. Concurrently, we have the fluorine molecular gas (F₂) with a higher electron affinity than other gases (3.0, 2.5, 2.23, and 2.0 eV for F₂, Cl₂, Br₂, and I₂ molecules, respectively) [2]. In recent years, F₂ has been intensively used in plasma-etching processes for semiconductors because it has not only a global warming potential of zero but also a high etching selectivity [3]. F₂ is an element of the halogen family and is present in significant quantities in the oceans, the atmosphere and Earth’s crust [4]. F₂ is a highly toxic, pale-yellow gas at atmospheric temperature and pressure [5].

Because of its physical and industrial importance, there were three published attempts at gathering a complete cross-section set for the F₂ molecule [6–8]. These used a combination of experiments and theoretical cross-sections for elastic scattering, momentum transfer, vibrational excitation, electronic excitation, dissociative electron attachment and ionization. Hayashi and Nimura [6] and Morgan [7] combined the electron collision cross-section set but neglected all processes at energies above about 6.5 - 7.5 eV and the Rydberg-valence-ionic electronic states. Jón [8] also combined the electron collision cross-sections of Hayashi and Nimura [6], but they did not consider the experimental data for the dissociation excitations of F₂(a¹Πₜ) and F₂ (A¹Πₜ) determined by Morgan and Szöke [9]. None have presented the electron drift velocity for F₂ in binary mixtures with other gases even though published measurements are available. Furthermore, in recent years, there has been a growing interest in determining the vibrational excitation cross-section [10], the electronic states [11,12] and the ionization cross-sections of the F₂ molecule by using theoretical method [13,14]. Therefore, the electron collision cross-sections for the F₂ molecule need to be re-determined for a plasma discharge simulation.

In the present study, one complete set of vibrational excitation cross-sections for the F₂ molecule were determined successfully. The electron drift velocities were calculated using the determined set in two F₂-He mixtures (with 0.2% and 1% fluorine) over the E/N (ratio of the electric field, E, to the neutral number density N) range from about 2 - 20 Td (1 Td = 10⁻¹⁷ V cm²) and in pure F₂ over the wide E/N range from 0.02 to 320 Td at 1 Torr by using a two-term approximation of the Boltzmann equation for the energy. The present set should be important for quantitative modeling of related plasmas. We also determined a set of electron collision cross-sections for the F₂ molecule, which may be consid-
ered to be the best available for quantitative modeling of
a plasma discharge for processing procedures with materials containing F₂ molecules.

II. A SET OF ELECTRON COLLISION CROSS-SECTIONS FOR THE F₂ MOLECULE

The set of electron collision cross-sections for the F₂ molecule consists of cross sections for momentum transfer, excitations of vibrational and electronic states and ionization and dissociative attachment. These cross-sections are discussed separately below.

Elastic scattering cross-sections were computed and shape resonances at 1.8 eV and 2.2 eV, respectively, were shown by Schneider and Hay [15] and Rescigno et al. [16]. Since no experimental data are available for elastic scattering and momentum transfer cross-sections, the momentum transfer cross-section, Qₘₜ, for molecular F₂ is chosen from Hayashi and Nimura [6] who based it on the theoretical estimate of the elastic scattering of an electron by a F₂ molecule given by Schneider and Hay [15].

The vibrational excitation cross-sections, Qₑₓ, for the F₂ molecule have been calculated [10, 17–20]. Hall’s cross-sections [17] are nearly an order of magnitude larger than those computed by Bardsley and Wadehra [18]. Wong and Light’s results [19] have the same threshold behavior as Hall’s results. Kalin and Kazansky’s results [20] were computed by using the semi-classical non-local theory, and these results agreed well with other results [18]. The shapes and the intensities of the vibrational excitation spectra presented by Brems et al. [10] are very different from the model study results published recently [18]. To the best of our knowledge, two measurements of Qₑₓ by slow electrons were carried out; one by Hoshiba et al. [21] at 11.62, 11.75, 11.86, and 11.99 eV and the other by Fujita et al. [22] at impact energies of 0.55 - 1.75 eV. The results of Fujita et al. [22] agreed well with Bardsley and Wadehra’s prediction [18]. Since no experimental data are available for vibrational excitation cross-section, the initial total vibrational cross-section for molecular F₂ is chosen from Hall [17]. The threshold energy for the vibrational excitation is 0.11 eV.

The two lowest excited electronic states are the dissociative a₃Πₙ and A¹Πₙ states calculated theoretically by Cartwright and Hay [23] on the ground state X¹Σ⁺ and the 11 excited electronic states of F₂, and by Lengsfield III and Rescigno [24] with those results being about 2.5 times larger than other theoretical values and experimental values. These excited electronic states were also measured [9,25]. Nishimura et al. [26] determined the integral cross-section for F₂ (a₃Πₙ, A¹Πₙ, C¹Σ⁺, 3Σ⁺, H¹Π₆). The integral cross-section for excitations of the five one-electron excited valence states (a₃Πₙ, A¹Πₙ, 3Π₉, ¹Π₉) and the Rydberg-valence-ionic electronic states of ¹Σ⁺ symmetry in F₂ have also been estimated [27,28]. Furthermore, Hazi [29] calculated the integrated cross-sections for the X¹Σ⁺ → C¹Σ⁺ and X¹Σ⁺ → H¹Π₆ transitions in the F₂ molecule. In recent years, there were some theoretical calculations of the differential cross-sections in the F₂ molecule for the C¹Σ⁺ state at 300 - 500 eV and the I¹Σ⁺ state at 400 and 500 eV [11], and of the threshold energies of the excited states in the F₂ molecule [12]. In the present study, therefore, the lowest electron excitation levels (a₃Πₙ (Qₑₓ₁) and A¹Πₙ (Qₑₓ₂) with threshold energies of 3.16 and 4.34 eV, respectively) are chosen from the experimental results of Morgan and Szöke [9]. The three one-electron excited valence states (3Π₉ (Qₑₓ₃), 3Σ⁺ (Qₑₓ₄), and ¹Π₉ (Qₑₓ₅) with threshold energies of 7.0, 7.5, and 7.6 eV, respectively) and the Rydberg-valence-ionic electronic states (Qₓ₆) at 12.87 eV are chosen from theoretical results of Cartwright et al. [28]. The two levels C¹Σ⁺ (Qₑₓ₆) and H¹Π₆ (Qₑₓ₇) with threshold energies of 11.57 and 13.08 eV, respectively, are chosen from Hazi [29].

The dissociative attachment cross-section, Qₐ, of the F₂ molecule measured by Chantry [30] exhibited the full shape in the energy range of about 0 - 9 eV. This cross section is reasonably consistent with electron swarm measurements. For electron energies above 0.3 eV, the agreement with the theoretical results of Hall was very good [17]. The dissociative attachment cross-sections were also measured by McCorkle et al. [31] at ambient (298 K) temperature and had a peak at 0.0 eV and by Chutjian and Alajajian [32] in the energy range 0 to 0.14 eV, but this cross-section has a total statistical uncertainty of 25%. The dissociative attachment cross-sections calculated by Hazi et al. [33] by using an ab-initio theoretical study was about 1.5 - 2 times larger than the data of Chantry [30] in the energy range 0.15 - 1.5 eV. These authors could not account for the cross-section shape at energies below 0.15 eV. The dissociative attachment cross-sections calculated by Bardsley and Wadehra [18] for the ground state agreed with those of Chantry [30] and Hazi et al. [33] at energies above 0.2 eV, but did not show a peak at zero energy. In recent years, Brems et al. [10] also calculated the dissociative attachment cross-section by using an ab-initio theoretical study. That approximation was good and matched the exact results for energies larger than 1 eV. Moreover, the dissociative attachment rate coefficients for F₂ in Ar, N₂, Kr, and He buffer gases were determined by many authors by measurements [31,32] and calculations [17,30,31]. The dissociative attachment cross-sections (Qₐ) at electron energies below 0.15 eV and the dissociative attachment rate coefficients at electron mean energies below about 0.15 eV of different authors differ significantly. Therefore, the dissociative attachment cross-section of F₂ is chosen from Chantry [30].

Total ionization cross-sections, Qᵢ, for the impact of intermediate- and high-energy electrons on the F₂ molecule were measured [34–36]. The relative shapes of
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III. RESULTS AND DISCUSSION

The method for the present analysis was almost the same as that used by Jeon [37,38] to derive a set of electron collision cross-sections for the oxygen molecule and for the perfluoropropane molecule by using the Boltzmann equation. The initial electron collision cross-sections with the F\(_2\) molecule will be used to simulate the electron drift velocity in binary mixtures with He gas in modeling a plasma discharge for processing procedures with materials containing F\(_2\) molecules. The accuracy of the cross-sections set for the He atom is suggested [39] and is that determined by Itoh and Musha [40].

1. Electron Drift Velocity in the F\(_2\)-He Mixtures

The electron drift velocities, W, were measured in two F\(_2\)-He mixtures (with 0.2% and 1% fluorine) by Nygaard et al. [41] with experimental errors of 12 - 15%. The results for the electron drift velocity as a function of E/N in both F\(_2\)-He mixtures calculated using the set of initial cross-sections for the F\(_2\) molecule are shown in Fig. 2. There were deviations exceeding the experimental error limit for both F\(_2\)-He mixtures. The calculated results for W in the 1% F\(_2\)-He mixture deviated significantly from the measurements over the entire E/N range, but the calculated results for the W in the 0.2% F\(_2\)-He mixture did not. The corresponding mean electron energy range is about 0.111 - 7.0 eV.

Figure 2 shows clearly that the W values in the 0.2% F\(_2\)-He mixture were higher than those in the 1% F\(_2\)-He mixture over the entire E/N range. The W values in both F\(_2\)-He mixtures, however, were analysed and increase with increasing fluorine concentration [41]. The initial calculated results for W in the two F\(_2\)-He mixtures, therefore, were not accurate. In fact, the electron drift velocity enhancement in these mixtures depends mainly on the magnitude and the energy of the vibrational excitation cross-sections for the F\(_2\) molecule because this phenomenon has been observed and was suggested in some published cases with several mixtures in dilute molecular gas - rare gas mixtures [37,38].

2. Vibrational Excitation Cross-section for the F\(_2\) Molecule

Both the elastic momentum transfer cross-section for the helium gas and the vibrational excitation cross-section for the F\(_2\) molecule mainly cause the prominent
E/N dependencies in the electron drift velocities in both the present mixtures at low E/N in Fig. 3. The mix ratio of the F$_2$ molecule in the two F$_2$-He mixtures is low. Moreover, the energy loss of electrons in pure F$_2$ through the momentum transfer cross-section with the F$_2$ molecule is small. The momentum transfer cross-section for the F$_2$ molecule, therefore, has a very weak contribution to the electron drift velocities in the mixtures.

The electron drift velocities were analyzed by using a two-term approximation of the Boltzmann equation. To agree with the measurements over the whole E/N range, we modified the magnitude of the vibrational excitation cross-section for F$_2$ molecule in a trial-and-error manner by using the electron swarm method. The corresponding mean electron energy ranges were below 0.5 eV, 0.5 - 4.0 eV, and above 4.0 eV, respectively.

The present vibrational excitation cross-section for the F$_2$ molecule is shown in Fig. 1 by the full curve and is tabulated in Table 1. In this figure, there are considerable differences from the vibrational excitation cross-section of Hall [17] (dashed line and initial choice) over the entire electron energy ranges. In Fig. 3, the present vibrational cross-section set appears to reproduce the measured electron drift velocities in the two F$_2$-He mixtures within the maximum error limit.

### Table 1. Vibrational excitation cross-sections for the F$_2$ molecule in units of $10^{-16}$ cm$^2$.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$Q_{vib}$ (eV)</th>
<th>Energy (eV)</th>
<th>$Q_{vib}$ (eV)</th>
<th>Energy (eV)</th>
<th>$Q_{vib}$ (eV)</th>
</tr>
</thead>
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<tr>
<td>0.11</td>
<td>0.00000</td>
<td>0.4</td>
<td>20.00000</td>
<td>0.9</td>
<td>34.95097</td>
</tr>
<tr>
<td>0.111</td>
<td>0.00001</td>
<td>0.435</td>
<td>40.18300</td>
<td>1.2952</td>
<td>13.97800</td>
</tr>
<tr>
<td>0.25956</td>
<td>0.00100</td>
<td>0.4756</td>
<td>64.09850</td>
<td>2</td>
<td>4.03454</td>
</tr>
<tr>
<td>0.3</td>
<td>0.05000</td>
<td>0.5</td>
<td>70.63000</td>
<td>3</td>
<td>0.69779</td>
</tr>
<tr>
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<td>0.13262</td>
</tr>
<tr>
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<td>0.63083</td>
<td>72.80000</td>
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<td>0.05000</td>
</tr>
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<td>0.7</td>
<td>64.09850</td>
<td>7</td>
<td>0.01000</td>
</tr>
</tbody>
</table>

Fig. 3. Electron drift velocity, W, as functions of E/N for the two F$_2$-He mixtures (with 0.2% and 1% fluorine). The solid line and the symbols (■, ▲) show values calculated using a two-term approximation of the Boltzmann equation with the present cross-sections set for the F$_2$-He mixture and for the 0.2% F$_2$-He mixture, respectively, for a F$_2$ molecule. The solid curve shows the W values for the pure He atom. The other lines and symbols are the same as those used in Fig. 2.

### 3. Electron Drift Velocity in the Pure F$_2$ Molecule

The results for the electron drift velocity, W, in pure F$_2$ calculated using the present electron collision cross-section set for the F$_2$ molecule is shown in Fig. 4 (solid circles) by using a two-term approximation of the Boltzmann equation over the E/N range from 0.02 to 320 Td at 1 Torr. The calculated results in pure F$_2$ for 25 Td < E/N < 70 Td were sensitive to the vibrational excitation cross-section. The corresponding mean electron energy ranges are from about 0.21 eV to 0.26 eV. These

$$W(\text{cm/s}) = \frac{\text{Energy}}{\text{Cross-section}} \times \text{Electron density}$$
values could not be calculated. To the best of our knowledge, there are no experimental data to compare with those results. Therefore, it is very difficult to suggest the accuracy of the electron drift velocity for the pure F\(_2\) molecule.

Hayashi and Nimura [6] calculated the electron drift velocity in pure F\(_2\) over the E/N range from 100 to 2000 Td; these data are shown in the same figure for comparison. The present results for W agreed with the values calculated by Hayashi and Nimura [6] for E/N > 70 Td. The velocity-field curve exhibits a negative differential mobility with a peak electron drift velocity W at a critical field E\(_c\) = 1.72 kV/cm. The present electron drift velocity indicates a region of negative differential conductivity (NDC), that is, decreasing electron drift velocity with increasing electric fields strength [42], corresponding to the E/N range 2 < E/N < 20 Td.

IV. CONCLUSIONS

The electron drift velocities of electrons in two F\(_2\)-He mixtures (with 0.2% and 1% fluorine) and in pure F\(_2\) were calculated by using a two-term approximation of the Boltzmann equation in the E/N ranges of 2 - 20 Td and 0.02 - 320 Td, respectively. The measured electron drift velocities in the two F\(_2\)-He mixtures were used with an electron swarm method to determine the vibrational excitation cross-sections for the F\(_2\) molecule. The agreement between the results calculated by using the determined electron collision cross-sections and the measurements was satisfactory.

We have succeeded in determining one complete set of vibrational excitation cross-section that is consistent with various electron drift velocities over wide E/N ranges by using a two-term approximation of the Boltzmann equation. The NDC phenomenon can occur in the molecular F\(_2\) gas. The present electron collision cross-section set for the F\(_2\) molecule may be considered to be the best available for a quantitative numerical modeling of a plasma discharge for processing procedures with materials containing F\(_2\) molecules.

REFERENCES