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Total cross section of electron scattering by fluorocarbon molecules

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Abstract
A compact linear electron transmission apparatus was used for the measurement of the total electron scattering cross section at 4–500 eV. Total cross sections of chlorofluorocarbon (CCl_2F_2), hydrochlorofluorocarbon ($CHClF_2$), perfluoropropane (C_3F_8), perfluoro-n-pentane (C_5F_{12}), perfluoro-n-hexane (C_6F_{14}) and perfluoro-n-octane (C_8F_{18}) were obtained experimentally and compared with the values obtained from a theoretical calculation and semi-empirical model calculation.

1. Introduction

Global warming is a serious problem. It is largely the result of emissions of carbon dioxide and other greenhouse gases such as chlorofluorocarbon and fluorocarbon. These halogen-containing compounds are widely used in homes and in industry as a refrigerant, plasma processing gas [1], solvent, insulator and coolant. Sometimes fluorocarbons are decomposed to eliminate the negative effects on the environment. There are many reports on decomposition under nonequilibrium oxidizing plasma conditions, such as a high-voltage gliding arc discharge, surface discharge and corona discharge, and under a plasma torch using high-pressure and high-frequency discharge [2–8]. Progress in the development of these systems requires the understanding of collision processes in gaseous discharges and plasma. Electron interaction studies are of fundamental importance in the development of a basic understanding of the kinetics and dynamics of processes in which electrons are involved. Halogen-containing electronegative gases are employed for dry etching of semiconductor materials in submicron technology using radio-frequency plasma [1]. Plasma yields active species such as ions, atoms and radicals via electron collisions. They play very important roles in dry etching processes. The investigation of the collision process, which is the fundamental for dry etching technology is particular important. On the other hand, a series of fluorocarbon compounds provides specific opportunities for the investigation of the molecular size effect on the mechanism of the scattering process. The total electron scattering cross section (TCS) is the sum of the integral cross sections for all scattering channels and can be obtained in absolute values experimentally. TCS may also be used as a standard value for the estimation of the upper limit for cross sections obtained in arbitrary units. We measured the total electron scattering cross sections of CCl_2F_2, $CHClF_2$, C_3F_8, C_5F_{12}, C_6F_{14} and C_8F_{18}.

2. Experimental method

We used a linear electron transmission system designed by Nishimura [9]. The experimental apparatus and procedure were the same as those used in TCS measurements reported by Nishimura *et al* [9–12] and will here only be briefly described. The TCS σ is described by the Beer–Lambert relation,

$$I = I_0 \exp(N\sigma l), \tag{1}$$

where I is the transmitted current, I_0 is the incident current, l is the electron scattering length, the length l used was 29.5 mm, and N is the number density of the target gas with $p = NkT$ (p stands for the gas pressure of the gas cell, T for the gas temperature and k for Boltzmann's constant.). The pressure p used varied between 0.15 and 0.7 Pa. The target gas pressure was measured using a MKS Baratron capacitance manometer. The magnetic field in the electron optics volume is reduced to a value below 10 mG with a double-layered μ-metal shielding. Measurements at a given energy were typically carried out in

Table 1. Total cross section of CCl_2F_2, $CHClF_2$, C_3F_8, C_5F_{12}, C_6F_{14} and C_8F_{18}. (10^{-20} m^2).

eV	CCl_2F_2	$CHClF_2$	C_3F_8	C_5F_{12}	C_6F_{14}	C_8F_{18}
4	41.1	23.6				
5	42.5	24.5				
6	43.6	31.3				
7	46.2	29.5				
8	47.8	31.5	40.2	62.1	71.1	
9	48	28.5	40.8	61.4	68.2	
10	49.2	24.2	40.2	60.4	68.2	
11		23.1				
12	47.1	23	38.9	59.8	67.4	
13		26.1				
14		29				
15	43.6	31.4	38	60.4	68.5	
16		29.3				
17	42.1	30.6	38.5	62.2	70	83.6
20	39.5	29.7	41	64.5	71.7	83.5
25	37.4	29.8	42.9	65.2	73.2	84.1
30	34.8	29.1	43.2	65.6	72.9	83.2
34		28.3				
40	32.6	25.2	45.5	64.1	71.2	83.3
50	29.6	24.7	44.3	65.6	72.9	80.4
60	29.5	22.2	44.1	63.9	71	78
70	27.4	22.9	41.9	62.46	69.4	77.9
80	26.5	20.1	41	58.95	66.5	74.9
90			39.9	59.31	65.9	72.8
100	24	19	39.5	58.05	64.5	72.1
120	23.2	17.5	38	54.81	60.9	69
150	20.6	16.7	34.1	50.76	56.4	66
200	19.1	13.2	29	44.28	52.2	59.5
250	17	12.5	25.5	39.96	47.1	56.3
300	14.2	11.1	23.1	36.18	43.2	53
400	13.8	9.2	19.4	30.2	35.1	44.8
500	12.4	8.2	17.3	27.9	33	41.2

five times. They showed scattering of about ±5% on average. The systematic uncertainties were introduced by the drift of gas pressure for target gases of large mass number, and the decrease of I_0 and I in the region of low electron energy owing to difficulties in electron optics adjustment probably caused by the residual magnetic field. The overall systematic uncertainty is estimated to be less than 15% in the low-energy measurements and does not exceed 6% in the experiments from the intermediate-energy to the highest-energy region.

3. Result and discussion

The obtained TCSs are listed in table 1. Our present data are compared with the theoretical values reported by Jiang *et al* [13] that were obtained using the additivity rule (AR) and the values determined using the semi-empirical model of Karwasz *et al* [14].

The additivity rule is based on the hypothesis that integral cross sections for molecules can be obtained as an arithmetic sum of atomic contributions. The AR is a successful approach for simple and small molecules in the intermediate- and high-energy regions [13, 15–18]. However, the AR results for some complex molecules (such as C_nH_m) showed large discrepancies from experimental results, especially below 50 eV. Jiang *et al* [18] presented a new modified additivity rule in which the change of the shielding effect in molecules as the energy of the incident electrons is varied is considered. This energy-dependent geometry additivity rule (EGAR) was employed in the calculation of TCSs of C_2F_6, C_3F_8 and C_6F_6.

Zecca *et al* reported that the TCS of gases can be well approximated by a 'semi-empirical model' with the formula

$$\sigma(E) = \frac{\sigma_z}{1 + \sigma_z E/b}, \tag{2}$$

where σ_z and b are two adjustable values for each target [14, 19–21]. We refer to σ_z as a low-energy parameter of TCS and to b as a high-energy parameter showing the high-energy asymptotic slopes of TCSs. It is known that equation (2) has the same energy dependence of the Born approximation. Karwase *et al* [14] showed that the σ_z parameter can be approximated by

$$\sigma_z = 20(\sqrt{\alpha} - 1), \tag{3}$$

by considering the correlation between the molecular dipole polarizability α (in an arbitrary unit) and asymptotic 'low-energy' cross section parameter σ_z for 20 molecular targets measured in their laboratory. They obtained the parameter b by fitting equation (2) to the experimental results of TCS and introduced the additivity relation on b:

$$b(X_nY_m) = nb(X) + mb(Y), \tag{4}$$

where X_nY_m is a molecular formula, and $b(X)$ is the atomic b parameter for atom X. They showed that this semi-empirical model has been successfully verified for halomethanes including CF_4 and CF_2Cl_2.

AR and SEM in figures stand for the values obtained using the additivity rule of Jiang *et al* [13] in the range of 10–500 eV and using the semi-empirical model presented by Karwase *et al* [14] in the range of 50–500 eV, respectively. The set of atomic cross sections given by Jiang *et al* [13] has been used here to evaluate values of the AR model. We need to know the molecular dipole polarizability α in the calculation of the semi-empirical model. The dipole polarizability of n-hydrocarbon compounds (C_nH_{2n+2}) is proportional to the number of carbon atoms in the compound [22]. We assumed the same relation for the dipole polarizability of n-fluorocarbon compounds (C_nF_{2n+2}), because the two types compounds have the same molecular structure. By linear extrapolation of the values of polarizability 3.86, 6.82 and 9.4 (in the units of 10^{-24} cm^3) for CF_4 [22], C_2F_6 [22] and C_3F_8 [23], respectively, we obtained dipole polarizabilities of 12.14, 14.79, 17.61 and 23.53 for C_4F_{10}, C_5F_{12}, C_6F_{14} and C_8F_{18}, respectively. We used semi-empirical values of the atomic cross section parameter b derived by Karwase *et al* [14] in the calculation of equations (2) and (4).

Statistical errors are shown in the figures for each target gas. The present results for CCl_2F_2 and C_3F_8 are compared with other experimental TCS data together with the AR and SEM data. The present data for $CHClF_2$, C_5F_{12}, C_6F_{14} and C_8F_{18}, are shown with the AR and SEM data, since no other experimental data were found for them.

The TSC of CF_2Cl_2 is shown in figure 1. Zecca *et al* [20] and Karwase *et al* [14] obtained the TSC of CF_2Cl_2 in the 75–4000 eV range, and Jones [24] obtained values in the 0.6–50 eV range. Jiang *et al* reported values calculated by

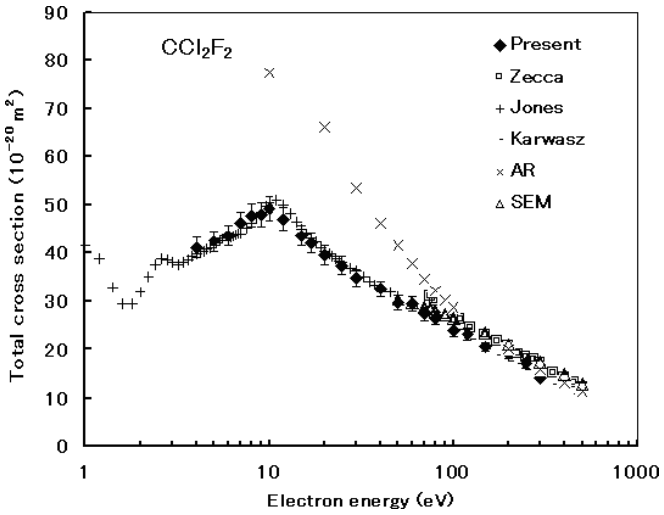

Figure 1. Total cross sections for e-CCl_2F_2. Experimental data: our data, Zecca *et al* [20], Karwase *et al* [14] and Jones [24]. Calculated results: AR model [13] and SEM model.

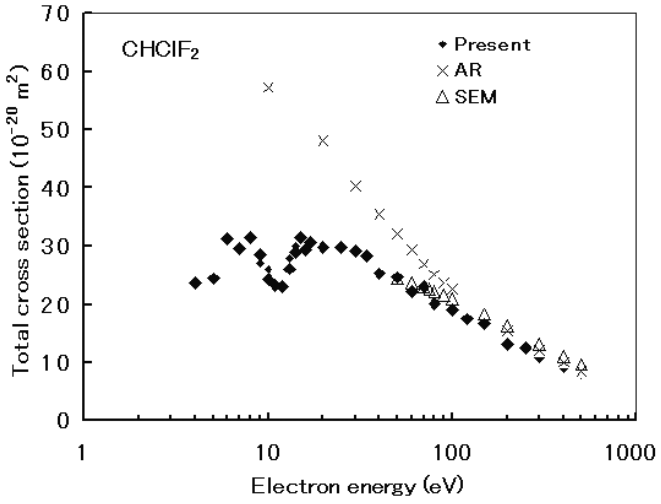

Figure 2. Total cross sections for e-$CHClF_2$. Experimental data: our data. Calculated results: AR model and SEM model.

using the AR model together with experimental results in the 10–1000 eV range [13]. Christophorou *et al* [25] compiled the above results, and showed the recommended values of TCS as well as rate coefficients. Below 50 eV, our results are in fair agreement with those of Jones [24] and Karwase *et al* [14]. In the range of 75–500 eV, our results are 10% smaller than those of Zecca *et al* [20]. Results obtained using the SEM model show good agreement with those of Zecca *et al* [20] in the entire overlap of energies. Results obtained using the AR model agree well with our data and those of Karwase *et al* [14] above 100 eV.

Our data of the TSC of CF_2Cl_2 are shown in figure 2 together with results calculated using AR and SEM models. Results obtained using the SEM model show good agreement with our data at the entire overlap of energies. Results obtained using the AR model agree well with our data above 100 eV.

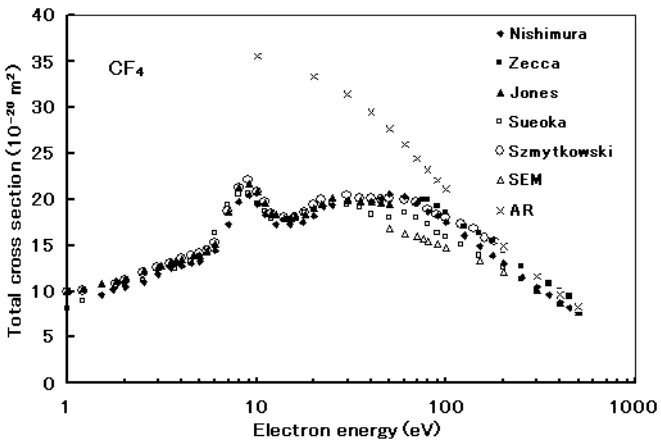

Figure 3. Total cross sections for e-CF_4. Experimental data: Nishimura [11], Jones [24], Sueoka [26], Szmytkowski [31]and Zecca [20]. Calculated results: AR model and SEM model.

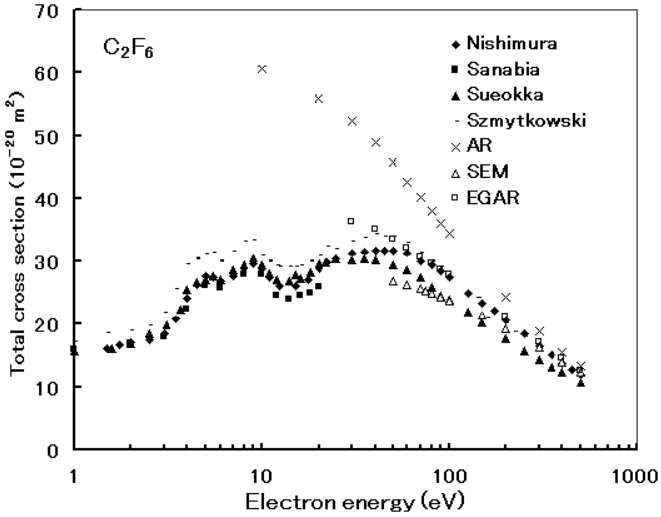

Figure 4. Total cross section for e-C_2F_6. Experimental data: Nishimura [11], Sueoka [28], Szmytkowski [27] and Sanabia [29]. Calculated results: AR model, SEM model and EGAR [18].

It has been reported that AR model results for C_nH_m molecules had large discrepancies from the experimental results at the same energies [18]. In order to confirm the limitation of the validity of the AR model and the SEM model for an increasing number of carbon atoms in n-perfluorocabon compounds, the TCS values of a series of n-perfluorocabon are shown in figures 3–8. Figures 3–5 show the experimental results for CF_4, C_2F_6 and C_3F_8, respectively, published by others. In the case of CF_4, SEM results show good agreement with experimental results of Sueoka *et al* [26] above 90 eV and those of Nisimura *et al* [11] above 200 eV. The AR model results show that discrepancies from the experimental results decrease as energy increases, and they agree with the experimental ones of Szmytkowski *et al* [31] and Zecca *et al* [20] above 140 eV. The experimental results of TCS for C_2F_6 obtained by Nishimura *et al* [11], Szmytkowski *et al* [27], Sueoka *et al* [28] and Sanabia *et al* [29] are shown in figure 4. The EGAR results calculated by Jiang *et al* [18] for C_2F_6 are in perfect agreement with the experimental data obtained

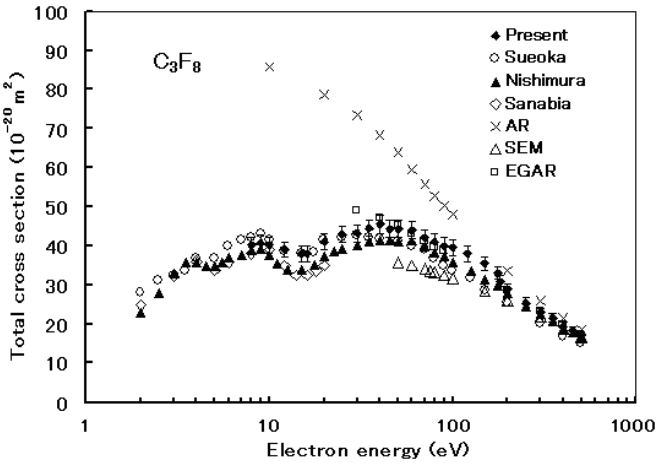

Figure 5. Total cross section for e-C_3F_8. Experimental data: our data, Nishimura [11], Sanabia [29], Tanaka [30]. Calculated results: AR model, SEM model and EGAR [18].

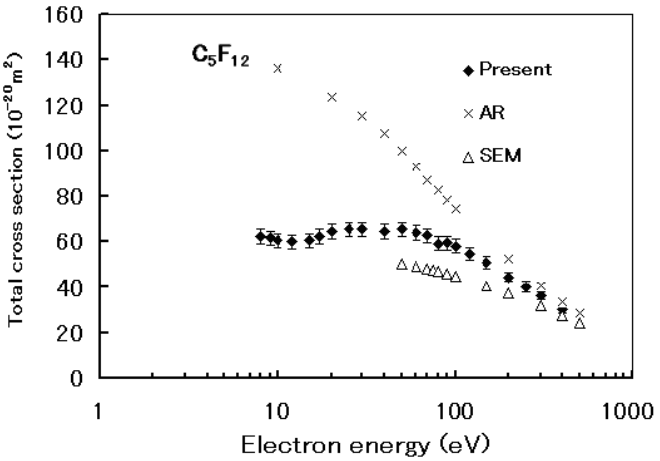

Figure 6. Total cross section for e-C_5F_{12}. Experimental data: our data. Calculated results: AR model and SEM model.

by Nishimura *et al* [11] and Szmytkowski *et al* [27] in the entire overlap of energies. SEM results for C_2F_6 show good agreement with the experimental results, except the results of Sueoka *et al* [28] above 200 eV. AR results for C_2F_6 show the same tendency as the results of CF_4.

The TCS of C_3F_8 is shown in figure 5. The present data agree well with those of Tanaka *et al* [30] below 30 eV, and are about 10% larger than those reported by Nishimura *et al* [11] and Tanaka *et al* [30] from 30 eV to 200 eV. The EGAR results calculated by Jiang *et al* [21] are in perfect agreement with the experimental data obtained by Nishimura *et al* [11] above 40 eV. SEM results agree with the present data and those of Nishimura *et al* [11] above 250 eV. AR results converge to the present data and those of Nishimura *et al* [11] above 300 eV. Figures 6–8 show TCS obtained in the present experiments and by the calculations using the AR model and the SEM model for C_5F_{12}, C_6F_{12} and C_8F_{18}, respectively. There are large discrepancies between experimental and calculated results. Values calculated using the SEM model are smaller than the experimental results, and those obtained using the AR model are larger than the experimental results, below 450 eV for all

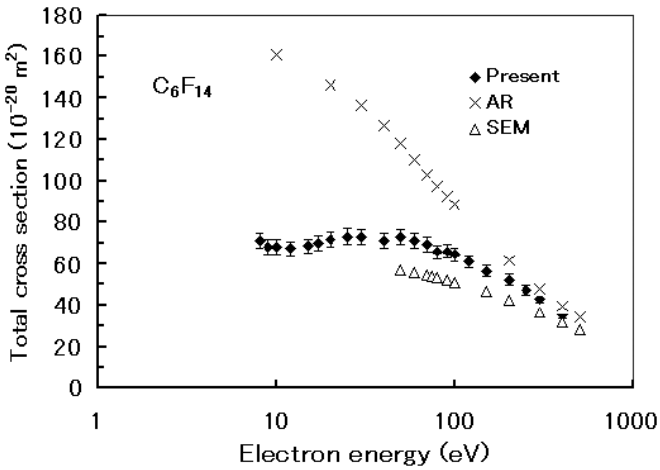

Figure 7. Total cross section for e-C_6F_{14}. Experimental data: our data. Calculated results: AR model and SEM model.

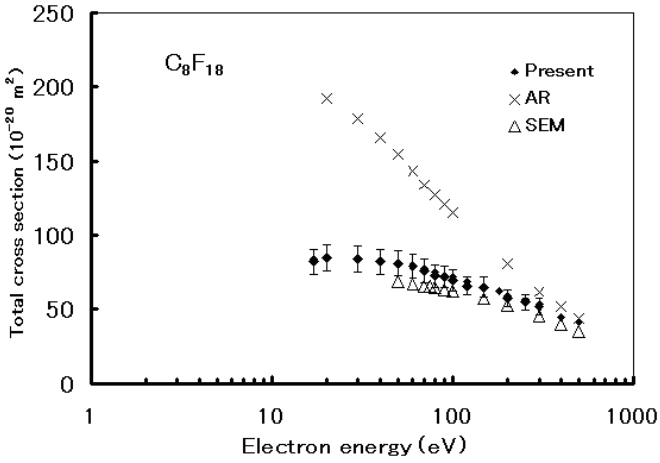

Figure 8. Total cross section for e-C_8F_{18}. Experimental data: our data. Calculated results: AR model and SEM model.

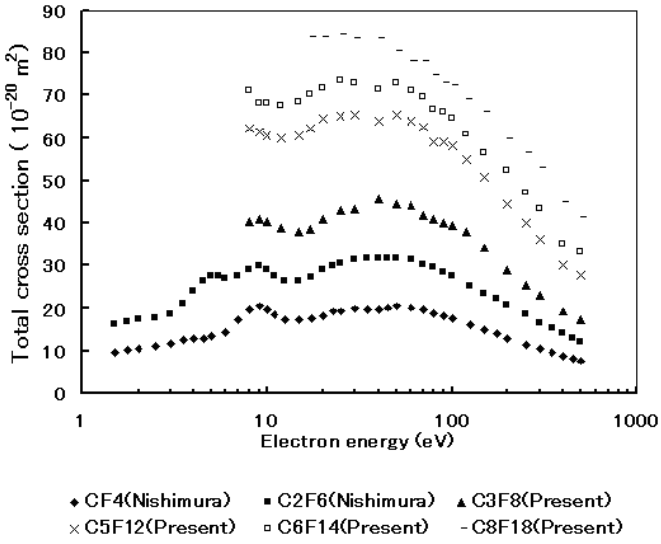

Figure 9. Total cross section of a series of n-perfluorocabon as a function of the number of carbon atoms.

molecules. Both sets of calculated results converge to the experimental ones above 450 eV.

The TCS data for a series of n-perfluorocabon are shown in figure 9 with the parameter of a number of carbon atoms in molecules. TCS obtained by Nishimura *et al* [11] for CF_4 and C_2F_6, and in the present experiments for C_3F_8, C_5F_{12}, C_6F_{14} and C_8F_{18} are used. TCS values of a series of n-perfluorocabon are proportional to the number of carbon atoms in molecules.

4. Conclusion

A compact linear electron transmission apparatus was used for the measurement of the total electron scattering cross section at 4–500 eV. Total cross sections of chlorofluorocarbon (CCl_2F_2), hydrochlorofluorocarbon ($CHClF_2$) and fluorocarbons (C_3F_8, C_5F_{12}, C_6F_{14} and C_8F_{18}) were obtained experimentally and compared with the values obtained from a theoretical calculation and semi-empirical model calculation.

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