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Total cross sections for electron scattering at 10–5000 eV by polyatomic molecules CF_4, CF_3H, C_2F_4, C_2F_6 and $C_2H_3F_3$*

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The additivity rule and complex optical potential approach have been employed to obtain the total (elastic and absorption) cross sections for electron scattering by molecules (CF_4, CF_3H, C_2F_4, C_2F_6, and $C_2H_3F_3$) over an incident energy range from 10 to 5000 eV. Compared with other calculations and experimental data wherever available, excellent agreement has been obtained. Above 1000eV, there are no experimental data for CF_3H, C_2F_4, C_2F_6 and $C_2H_3F_3$, so the present results can provide comparison and predictions for experimental research.

Keywords: total cross section, additivity rule, complex optical potential
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1. Introduction

In recent years, more and more experimental and theoretic research has focused on the total cross sections for electron scattering by molecules and atom.[1−2] The total cross sections of electron–molecule collision are important in many applied sciences. Electron–molecule scattering plays an important role in processes of great practical importance such as a variety of plasma phenomena (etching, chemical vapour deposition, etc) as well as in the understanding of the physics and chemistry of planetary atmospheres and interstellar media. Recently, increasing interest has been shown in the total cross sections of electron scattering from the halogenated hydrocarbons. These are artificial gases of wide technological interest. In particularly, carbontetrafluoride has been used as a refrigerant and in the semiconductor industry as a plasma etching gas.[3,4] The potential of these gases for greenhouse warming has been recognized.[5] Hence, cross-section data for electron scattering from fluorinated hydrocarbons are particularly urgently needed in plasma processing, material and earth science. Hexafluoroethane (C_2F_6) gas is used in laboratories and factories as an etching gas in the reactive plasma process.[6] The study of electron scattering from C_2F_6 molecules contributes the fundamental data for controlled processes in the reactive plasma. However, for some molecules, experimental data or calculations are scarce or lacking at intermediate and high energies.

Zecca and co-workers[7] have measured the total cross section of CF_4 in the 75–400eV energy range, using a modified Ramsauer setup. Szmytkowski *et al*[8] have reported absolute total cross sections for e–CF_4 scattering, using the linear transmission technique, in energy range from 0.5 to 200eV. Normalized total cross section for CF_4 have been published by Sueoka *et al*[9] for electron-impact energies from 1.0 to 400eV and total cross sections of CF_4 have been calculated by Manero *et al*[10] in the energy range of 300 to 1000eV. Total cross sections for CF_3H have been measured by Sueoka *et al*[11] for energy range from 0.1 to 600eV and by Iga *et al*[12] from 300 to 1000eV. Manero *et al*[10] have obtained the semi-empirical values of the total cross sections for CF_4 and CF_3H in the 0.5–10keV energy range by means of a formula that depends only

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on the total number of electrons and polarizability of the molecules. Total cross sections for C_2F_4 have been measured by Szmytkowski *et al*[13] in the energy range 0.6 to 370eV. To our knowledge, there are no calculational data of total electron-scattering cross sections for C_2F_4 in the literature so far. Sueoka *et al*[6] have reported the experimental data on the total cross sections for e-C_2F_6 and e-$C_2H_3F_3$ scattering for energies ranging from 0.8 to 600eV. Total cross sections for C_2F_6 have been measured by Szmytkowski *et al*[14] in the energy range 1 to 250eV. However, in spite of the scientific and technological interest of fluoromethanes, there are very few total cross-section data for these molecules, except for CF_4 in the intermediate and high energy range especially above 1000eV. This fact has prompted the present work.

It is well-known that electron–molecule scattering presents a more complex problem than corresponding electron–atom scattering due to the multi-centre nature, the lack of a centre of symmetry (in the case of polyatomic and hetero-nuclear molecules) and the nuclear motion. Many approaches have been proposed and developed. Here we are interested in the intermediate and high energy range, where almost all inelastic channels (rotational, vibrational and electronic excitation, ionization processes, etc) are open. In this energy range, a conventional close-coupling theory for electron–molecule scattering is an arduous task and almost impossible to carry out. It is, therefore, not surprising that many previous calculations on the total cross section for electron–molecule scattering have been restricted to the low-energy region. A fairly simple approach, namely application of the additivity rule,[15] has been employed to obtain the photoionization and electron impact ionization cross sections for a variety of molecules, and is regarded as a successful concept. Raj[16] made the first application of the additivity rule to obtain the elastic cross sections for electron scattering from simple molecules. Recently Joshipura and Patel[17] also gave the total cross sections for electron scattering from diatomic and polyatomic molecules by the use of the additivity rule and complex optical potential and proved the additivity rule is proper for the calculations of the total cross sections for electron–molecule scattering in the intermediate- and high-energy range. But the calculations using the additivity rule have been seldom done in the energy range above 1000eV. In this paper, we further employ the additivity rule and complex optical potential to obtain the total cross sections for electron scattering by CF_4, CF_3H, C_2F_4, C_2F_6, and $C_2H_3F_3$ at 10–5000 eV.

2. Theoretical model

We deal with the problem using the additivity rule. The basic philosophy of the additivity rule is based on the assumption that anisotropic electron–molecule interactions do not play a significant role in shaping the total cross section of the intermediate- and high-energy electron–molecule collisions. According to the additivity rule and optical theorem, the total cross section (elastic and inelastic) $Q_{\rm T}(E)$ of the molecules is given by

$$\begin{aligned} Q_{\rm T}(E) =& \frac{4\pi}{k}{\rm Im} f_M(\theta=0) \\ =& \frac{4\pi}{k}{\rm Im}\sum_{j=1}^{N} f_j(\theta=0) \\ =& \sum_{j=1}^{N} q_{\rm T}^j(E), \end{aligned} \tag{1}$$

where $q_{\rm T}^j(E)$ and f_j are the total cross section due to the jth atom of the molecule and the complex scattering amplitude of constituent atoms of the molecule, respectively. Here it is obvious that no molecular geometry is involved, so the molecular scattering problem is reduced to the atomic scattering problem which is easier to handle.

In the present investigation the atoms of molecule are replaced by the appropriate complex optical potential

$$V_{\rm opt}(r) = V_{\rm s}(r) + V_{\rm e}(r) + V_{\rm p}(r) + {\rm i}V_{\rm a}(r). \tag{2}$$

Thus $V_{\rm opt}(r)$ incorporates all the important physical effects. Presently the static potential $V_{\rm S}(r)$ for e–atom systems is calculated by using the atomic charge density, determined from the well-known Hartree–Fock atomic wavefunctions.[18] The exchange potential $V_{\rm e}(r)$ takes the semi-empirical energy-dependent form of Truhlar and co-workers.[19] $V_{\rm p}(r)$ and $V_{\rm a}(r)$ are polarization[20] and absorption potentials[21] of the jth atom of the molecule, respectively. This potential model has been proved fairly successful in electron–atom scattering.[20] The $q_{\rm T}^j(E)$ is obtain by the method of partial waves,[22]

$$\begin{aligned} q_{\rm T}^j(E) =& q_{\rm e}^j(E) + q_{\rm a}^j(E) \\ =& \frac{\pi}{k^2}\sum_{l=0}^{l_{\max}} [\left|1 - s_l^j\right|^2 + (1 - \left|s_l^j\right|^2)]. \end{aligned} \tag{3}$$

Here $q_e^j(E)$ and $q_a^j(E)$ are elastic and absorption cross sections, respectively, s_l^j is lth complex scattering matrix element of jth atom, which is related to the partial wave phase shift by $s_l^j = \exp(2i\delta)$. To obtain s_l^j, we solve the following radial equation:

$$\left(\frac{d^2}{dr^2} + k^2 - 2V_{opt} - \frac{l(l+1)}{r^2}\right) u_l(r) = 0 \qquad (4)$$

under the boundary condition

$$u_l(kr) \backsim kr\,[j_l(kr) - in_l(kr)] + s_l kr\,[j_j(kr) + in_l(kr)]\,. \qquad (5)$$

Here k^2 is energy of the incident electron, j_l and n_l are spherical Bessel and Neumann functions, respectively. The limit l_{max} of Eq.(4) is taken to be 50.

An effective-range formula

$$\tan\delta_l = \frac{\pi\alpha k^2}{(2l+1)(2l+3)(2l-1)} \qquad (6)$$

where α is polarizability)

is used to generate the higher partial wave contributions until a convergence of less than 0.5% is achieved in the total cross section. Eq.(4) is applicable to all cases of electron–atom scattering.

3. Results and discussion

Using the present optical potential, we have obtained qualitatively good total cross sections results for electron scattering by He,[20] Ar, Kr, Xe[23] compared with some experimental data. At intermediate and high energies, our results are within experimental error. The e–atom potentials employed in this work appear to be satisfactory, at least for the calculation in the present energy range. In this paper, employing the additivity rule (Eq.(1)) along with the optical potential model, we have obtained the total cross sections for e–molecules (CF_4, CF_3H, C_2F_4, C_2F_6 and $C_2H_3F_3$) at 10–5000 eV. The values obtained by us are listed in Table 1. The results have been compared with available experimental and calculated data.

Table 1. Total cross sections for electron scattering from CF_4, CF_3H, C_2F_4, C_2F_6, and $C_2H_3F_3$ in units of ($10^{-20}m^2$).

E/eV	CF_4	CF_3H	C_2F_2	C_2F_6	$C_2H_3F_3$
100	25.17543	22.0654	32.28174	41.3163	31.9862
300	14.8905	12.66315	18.79702	24.28901	17.60695
500	10.98373	9.20645	13.63542	17.80144	12.4696
800	7.86905	6.51703	9.60934	12.67372	8.61766
1000	6.58738	5.42758	7.98348	10.57911	7.09972
1500	4.62205	3.77731	5.53397	7.38903	4.85482
2000	3.51032	2.85547	4.17526	5.59795	3.63339
2500	2.80032	2.27132	3.31846	4.45955	2.87257
3000	2.31212	1.87174	2.7342	3.67922	2.35808
3500	1.95842	1.58326	2.31321	3.11503	1.98953
4000	1.69156	1.36615	1.99678	2.68995	1.71371
4500	1.48372	1.19737	1.75099	2.35921	1.50018
5000	1.31778	1.06283	1.55511	2.09534	1.33046

For CF_4 molecule, the experimental results are showed in Fig.1. We notice that the present results of the total cross section by the use of the additivity rule are in good agreement with the measurements of Zecca *et al*[7] at higher energies and the calculations of Manero *et al*[10] by a semi-empirical formula at whole overlapped energies. As the energy of the incident electron increases, the interactions among the atoms of a molecule have a smaller effect on the total cross sections. The additivity rule ignores the interactions. So, we see, from Fig.1, that the present approach is in fairly good agreement with the available experimental data at higher energies. However, at lower energies, our results are not as good. The larger differences between the experimental data are also shown in Fig.1.

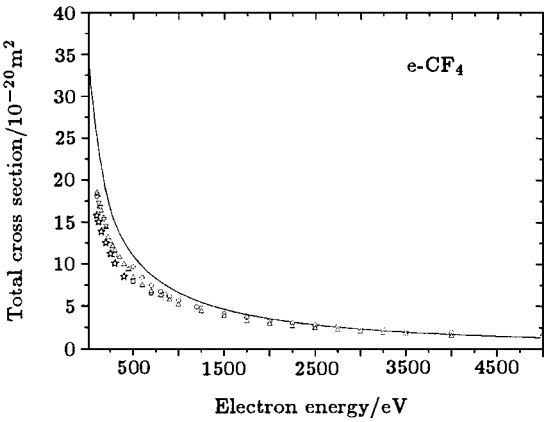

Fig.1. Total cross section for CF_4: solid line, present result; ◯, Ref.[10]. Experiment data: △, Ref.[7]; □, Ref.[10]; ▽, Ref.[8]; ☆, Ref.[9].

In Figs.2–5, we report the total cross sections on CF_3H, C_2F_4, C_2F_6, and $C_2H_3F_3$ molecules in the present energy range. There are no experimental data for C_2F_4, C_2F_6, and $C_2H_3F_3$ in the energies above 1000eV, so our results are not compared with the experimental data at higher energies. From Fig.2, we can see that the present results are much higher than the experimental data at energies below 500eV. For example, our results are about 45.9% and 36.5% higher than the experimental data of Sueoka *et al* at 400eV and Iga *et al* at 300eV, respectively. At the same time, it must be noticed that the experimental data of Iga *et al* are 6.7–25.4% higher than that of Sueoka *et al* at overlapping energies. The calculations of Manero *et al* using a semi-empirical formula are in good agreement with our results. For C_2F_4, there are only experimental data below 370eV. Our results are higher than these data. For C_2F_6 and $C_2H_3F_3$, there are also experimental data below 600eV. Our results are also higher than these data.

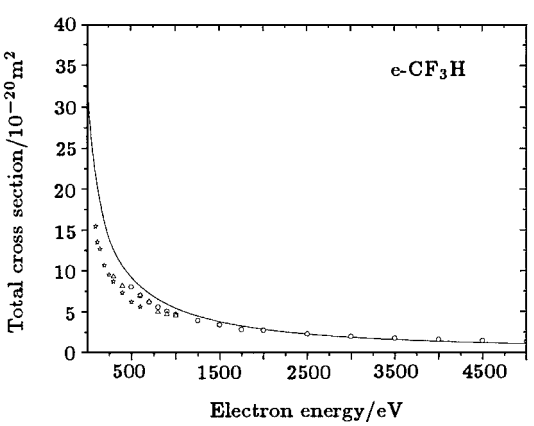

Fig.2. Total cross section for CF_3H: solid line, present result; ◯, Ref.[10]. Experiment data: △, Ref.[12]; ☆, Ref.[11].

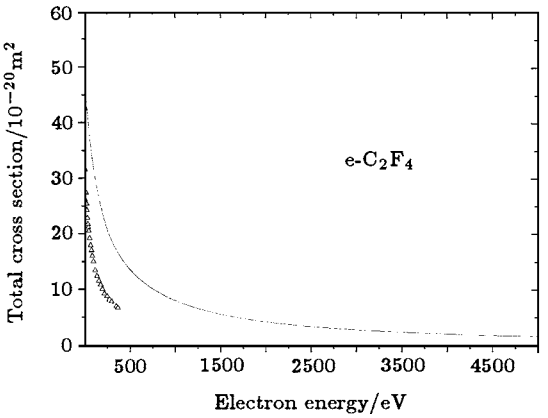

Fig.3. Total cross section for C_2F_4: solid line, present result. Experiment data: △, Ref.[13].

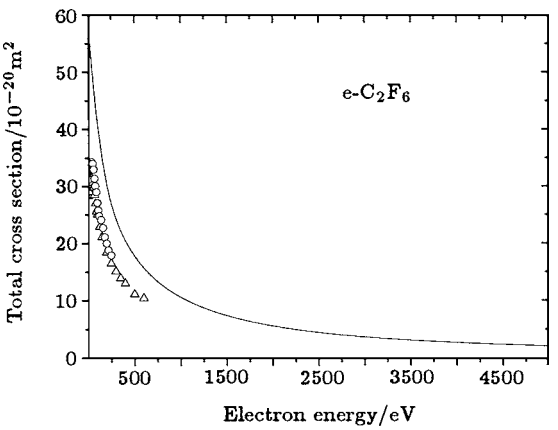

Fig.4. Total cross section for C_2F_4: solid line, present result. Experiment data: △, Ref.[6]; ◯, Ref.[14].

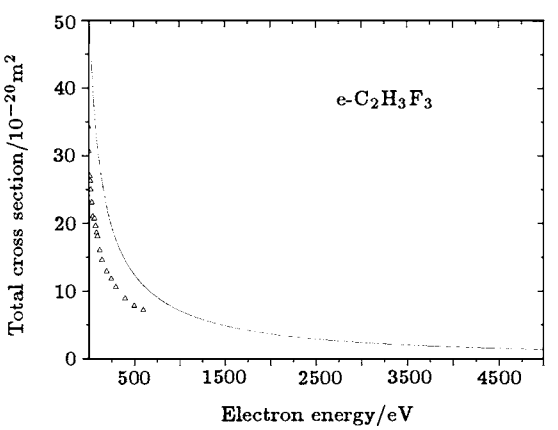

Fig.5. Total cross section for $C_3H_3F_3$: solid line, present result. Experiment data: △, Ref.[6].

At lower energies, as evidenced from Figs.1–5, the present results substantially exceed the measurements because we have ignored the multi-centre scattering and the valence-bond effect in the additivity rule. In addition, a close-packed molecule is not fully transparent for low energy electrons and the inner atoms

are shielded by the outer atoms, which does not contribute to the total cross sections. As the energy of incident electron increases, the interactions of atoms and shielding effect have a smaller effect on the total cross section. Therefore, we assume the errors are caused mostly by the additivity rule at lower energies. At higher energies, the additivity rule and optical potential are a good approach and the errors by them are within the experimental errors. For example, for CF_4, the present results are about 34% and 0.9% higher than the measurements of Manero *et al* at 300eV and 3000eV respectively.

4. Conclusion

In this paper, we have calculated the total cross section of many molecules using the additivity rule and complex optical potential approach. We found that no previous data, including experimental or theoretical ones except the calculations of Manero *et al*[10] could be found for the total cross sections for electron scattering by CF_4, CF_3H, C_2F_4, C_2F_6, and $C_2H_3F_3$ at 10–5000 eV. There are very few total cross-section data for these molecules, except for CF_4, in the intermediate and high energy range especially above 1000eV. However, in this paper, we employ the additivity rule to obtain the total cross sections on CF_4, CF_3H, C_2F_4, C_2F_6 and $C_2H_3F_3$ molecules at 10–5000 eV and obtain quite encouraging the results for a series of molecules. The experimental and theoretical data for these molecules are very scarce, so we hope that more experiments for them can be performed in the future. Since the contributions from the interference occurring between the scattering amplitudes originating from the different constituent atoms of the molecule and molecular shielding effect are not included in the additivity rule, the results of the total cross section using the additivity rule show larger discrepancies at lower energy range. We will consider the overlapping between atoms and mutual shielding between two atoms in molecules in the future. We hope that the results will provide qualitatively good predictions for experimental research.

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