Total cross sections for electron scattering from fluoromethanes: A revised additivity rule method*

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The additivity rule for electron–molecule scattering is revised by considering the difference between the free atom and the bound atom in the molecule. The total cross sections for electron scattering from fluoromethanes (CF_4, CF_3H, CF_2H_2, and CFH_3) are calculated in an energy range from 100 eV to 1500 eV by the revised additivity rule. The present calculations are compared with the original additivity rule results and the available experimental data. Better agreement with each other is obtained.

Keywords: total cross section, electron scattering, revised additivity rule

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1. Introduction

Electron scattering by fluoromethanes is very important in some fields such as etching plasma and astrophysics.[1] For example, CF_3H is an important material for etching SiO_2.[2] CF_4 is used both as a refrigerant and as a plasma etching gas in the semiconductor industry.[3] Many prominent processes in the electron–molecule scattering can be studied from the behaviours of the total cross sections. Therefore, the total cross sections for electron scattering from fluoromethanes are indispensable in plasma processing and astrophysics. The total cross sections for electron scattering from CF_4, CF_3H, and CFH_3 molecules have been measured. For CF_4, the total cross sections of electron scattering were measured by Manero *et al.*,[4] Zecca *et al.*,[5] Sueoka *et al.*,[6] Szmytkowski *et al.*,[7] and Ariyasinghe *et al.*[8] For CF_3H, the experimental total cross sections were obtained by Sueoka *et al.*,[9] Iga *et al.*,[10] Nishimura and Nakamura.[2] The total cross sections for CFH_3 were measured only by Krzysztofowicz and Szmytkowski.[11] To the best of our knowledge, there has been no total cross section measurement of the CF_2H_2 molecule.

In theory, electron–molecule scattering presents a much more challenging problem than electron–atom scattering because of its multi-centre nature, the lack of a symmetry centre and its nuclear motion.[12,13] In order to deal with the electron scattering from molecules over a wide energy range, many approximate methods have been proposed and developed such as the R-matrix method,[14−18] the complex Kohn variational method,[19] the Schwinger variational method,[19,20] the Bethe–Born theory,[21] and the additivity rule (AR) method.[22−24] In these approaches, the AR is a relatively simple but effective one. The AR method is based on the assumption that anisotropic electron–molecule interactions do not play an important role in determining the total cross sections of the intermediate- and high-energy electron–molecule collisions. Thus, the total cross section for a molecule is the sum of the total cross sections for the constituent atoms. It is obvious that no molecule geometry is considered in the AR method, so the molecular scattering is reduced to atomic scattering. The AR method is successful for smaller molecules at high enough energies. However, for larger molecules or at lower energies, a large discrepancy between the results from the AR and the measurements still exists.[25] As is well known, the bound atoms in a molecule are different from the corresponding free atoms. The reason is that there exits an overlapping effect of electron cloud between two atoms which form a chemical bond in a molecule. Recently, considering the difference between the free atom and the bound atom in the molecule, we have revised the AR method and calcu-

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lated the total electron cross sections for some hydrocarbon molecules.[26] Our results show that the revision is very successful for calculating the total cross sections for electron scattering from these hydrocarbon molecules at lower energies. In the present paper, we shall further calculate the total cross sections for electron scattering from fluoromethanes (CF_4, CF_3H, CF_2H_2, and CFH_3) in an energy range from 100 eV to 1500 eV by the revised AR method. The present results are compared with the available experimental data.

2. Theoretical model

In the original AR model,[23] molecule orbits can be described by the sum of the valence orbitals of all atoms present in the molecule. As a result, the total cross section of electron–molecule scattering is written as the sum of the total cross sections of atoms. Thus the total cross section $Q_{\rm T}$ for molecule is given by

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

where $q_{\rm T}^{j}$ and f_j are the total cross section due to the j-th atom of the molecule and the complex scattering amplitude for constituent atoms of the molecule, respectively. The $q_{\rm T}^{j}$ of Eq. (1) for the j-th atom is obtained by the method of partial waves as

$$q_{\rm T}^{j} = \frac{\pi}{k^2}\sum_{l=0}^{l_{\max}} (2l+1)[|1-s_l^j|^2 + (1-|s_l^j|^2)], \tag{2}$$

where s_l^j is the l-th complex scattering matrix element of the j-th atom, which is related to the partial wave phase shift as $s_l^j = \exp(2\,{\rm i}\,\delta_{lj})$. The limit $l_{\max}$ is taken, which is enough to generate the higher partial-wave contributions until a convergence of less than 0.5% is achieved in the total cross section calculation. To obtain s_l^j we solve the following radial equation:

$$\left(\frac{{\rm d}^2}{{\rm d}r^2} + k^2 - 2V_{\rm opt} - \frac{l(l+1)}{r^2}\right)u_l(r) = 0, \tag{3}$$

under the boundary condition

$$\begin{aligned} u_l(kr) \sim\ & kr[\,{\rm j}_l(kr) - {\rm i}\,{\rm n}_l(kr)] \\ & + s_l kr[\,{\rm j}_l(kr) + {\rm i}\,{\rm n}_l(kr)], \end{aligned} \tag{4}$$

where $\rm j_l$ and $\rm n_l$ are spherical Bessel and Neumann functions separately. The atom is replaced by the complex optical potential

$$V_{\rm opt} = V_{\rm s}(r) + V_{\rm e}(r) + V_{\rm p}(r) + {\rm i}\,V_{\rm a}(r), \tag{5}$$

which incorporates all the important physical effects. Presently, the static potential $V_{\rm s}(r)$ for electron–atom system is calculated from the well-known Hartree–Fock atomic wave functions.[27] Exchange potential $V_{\rm e}(r)$ provides a semi-classical energy-dependent form given by Riley and Truhlar.[28] Zhang *et al.*[29] gives a smooth form at all values of r for polarization potential $V_{\rm p}(r)$, which has a correct asymptotic form at large r and approaches to the free-electron-gas correlation potential[30] in the near-target region. This potential model has been proved to be fairly successful to calculate the total cross sections for electron–atom scattering.[29] The imaginary part of the optical potential V is the absorption potential, which represents approximately the combined effect of all the inelastic channels. The absorption potential is derived from a quasifree-scattering model by Staszawska *et al.*[31] as

$$V_{\rm a}(r) = -\rho_0(r)\sqrt{\frac{T_{\rm L}}{2}}\bar{\sigma}_{\rm b}, \tag{6}$$

where $T_{\rm L} = k^2 - V_{\rm s} - V_{\rm e} - V_{\rm p}$ and $\rho_0(r)$ is the charge density of the corresponding free atom.

Jiang *et al.*[32] modified the absorption potential by adjusting the parameter $\bar{\sigma}_{\rm b}$ as follows:

$$\begin{aligned} \bar{\sigma}_{\rm b} =\ & \frac{32\pi^2 N_{\rm k}}{15k^2}\Big\{H(k^2-k_{\rm F}^2-W)H(2k_{\rm F}^2+2W-k^2) \\ & \times\left[\frac{5k_{\rm F}^3}{W} - \frac{k_{\rm F}^3(5k^2-3k_{\rm F}^2)}{(k^2-k_{\rm F}^2)^2}\right. \\ & \left. + H(2k_{\rm F}^2+W-k^2)\frac{2(2k_{\rm F}^2+W-k^2)^{5/2}}{(k^2-k_{\rm F}^2)^2}\right] \\ & + 4H(k^2-k_{\rm F}^2-2W)\left[\frac{5k_{\rm F}^3}{2W} - \frac{k_F^3(5k^2-3k_{\rm F}^2)}{(k^2-k_{\rm F}^2)^2}\right. \\ & + H(2k_{\rm F}^2+2W-k^2) \\ & \left.\times\frac{2(2k_{\rm F}^2+2W-k^2)^{\frac{5}{2}}}{(k^2-k_{\rm F}^2)^2}\right]\Big\}, \end{aligned} \tag{7}$$

where

$$k_{\rm F} = [3\pi^2\rho_0(r)]^{1/3}, \tag{8}$$

$$W = 2\Delta, \tag{9}$$

with k^2 being the energy of the incident electron, Δ the first excitation energy of the target atom. The absorption potential given by Jiang *et al.*[32] is used to calculate the total cross sections for electron scattering from Ar, Kr, and Xe atoms at 0.1 eV–300 eV and obtain better agreement with experimental results. Here, the absorption potential given by Jiang *et al.* is adopted. The static potential $V_{\rm s}(r)$, the exchange potential $V_{\rm e}(r)$, the polarization potential $V_{\rm p}(r)$, and

the absorption potential $V_a(r)$ are all related to the atomic charge density $\rho_0(r)$.

From the above equations, we can see that the electron–molecule scattering is reduced to electron–atom scattering by the original AR. Considering the formation of the chemical bond and the overlapping of electron clouds between two atoms in a molecule, we present

$$\rho(r) = f \cdot \rho_0(r). \tag{10}$$

Here, $\rho(r)$ is the charge density of the bound atom in the molecule and $\rho_0(r)$ is the charge density of the corresponding free atom. f is a revised factor for a bound atom in the molecule. To obtain factor f, two points should be considered as follows.

(i) The total cross sections calculated from the optical potential with the AR are much higher than the experimental results at lower energies. So, to obtain the accurate total cross sections for electron scattering from molecules, the effect of the optical potential should decrease at lower energies.

(ii) The bound atoms in a molecule are different from the corresponding free atoms. The reason is that there exits the overlapping effect of electron cloud between two atoms which form a chemical bond in a molecule. This shows that the revision should be related to the radii of the constituent atoms and the bond length between the two atoms. Between the two atoms which form a chemical bond in a molecule, the more the electron number of the constituent atoms, the smaller the influence from the overlapping effect of electron cloud is. This indicates that the revision should also have relation with the electron number of the constituent atoms.

From the above two points, many f factors are tested and good agreement between the revised results and the experimental data are obtained by using the following formula:

$$f = 1 - \frac{R}{R+d}\frac{N-Z}{N}, \tag{11}$$

where d is the bond length between two bound atoms in the molecule and R is the sum of the radii corresponding to two free atoms. Z is the number of electrons in the atom and N is the sum of the numbers of electrons of the two atoms which form the chemical bond. Thus, the original AR is revised with Eqs. (10) and (11). Obviously, the revised AR is related to molecular structure.

3. Results and discussion

With the revised AR considering the difference between the free atom and the bound atom in a molecule, the total cross sections for electron scattering from fluoromethanes (CF_4, CF_3H, CF_2H_2, and CFH_3) are calculated in an energy range from 100 eV to 1500 eV. The present results along with the available experimental data are compared in Figs. 1–4.

In Fig. 1, the present total cross sections for electron scattering from CF_4 are compared with the measurements given by Zecca *et al.*,[5] Manero *et al.*,[4] Sueoka *et al.*,[6] Szmytkowski *et al.*,[7] and Ariyasinghe[8] at energies ranging from 100 eV to 1500 eV. From Fig. 1, we can see that the present results are in better agreement with the experimental data than the original AR results in the whole energy range. For example, the difference between the original AR result and the experimental datum of Zecca *et al.* reaches 26.28% at 400 eV, while the difference between the present result and the Zecca *et al*'s datum is only 6.18%. The differences between the present results and the experimental values of Manero *et al.* and Sueoka *et al.* are only 13.75% and 25.44% at 300 eV, respectively, while the differences between the original AR results and the experimental values of Manero *et al.* and Sueoka *et al.* reach 34.11% and 47.89%, respectively. The original AR result deviates from the Szmytkowski *et al.*'s measurement by 28.25% at 200 eV, while the present result deviates only by 9.42%. The original AR result is 35.91% higher than the Ariyasinghe *et al.*'s measurement at 1000 eV, while the present result is only 10.58% higher than the measurement.

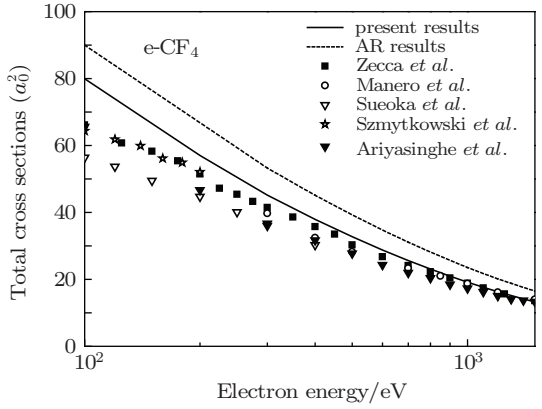


Fig. 1. Total cross sections for electron scattering from CF_3H.

In Fig. 2, the present results for CF_3H are compared with the experimental data and the original AR

results. From Fig. 2, we can see that the present results are in better agreement with the available experimental data than the original AR results. For example, the differences between the original AR results and the experimental data of Sueoka *et al.*[9] and Iga *et al.*[10] are 45.70% at 300 eV and 15.56% at 600 eV, respectively, while the differences for the present results are only 20.34% and 6.38%, respectively. The original AR results deviate from the experimental data of Nishimura and Nakamura[2] by 34.92% at 400 eV and 29.09% at 1500 eV, while the present results deviate only by 10.66% at 400 eV and 1.70% at 1500 eV.

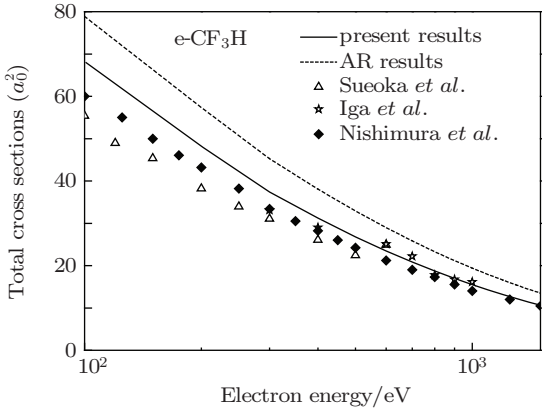


Fig. 2. Total cross sections for electron scattering from CF_4.

For CF_2H_2, there are no experimental results available at present. The present calculations are compared with the semi-empirical data of Manero *et al.*[4] in Fig. 3. From Fig. 3, we can see that the semi-empirical and our theoretical curves are very close to each other, while the present results are systematically lower than the semi-empirical data of Manero *et al.* We hope that further experimental results can be presented to elucidate our results.

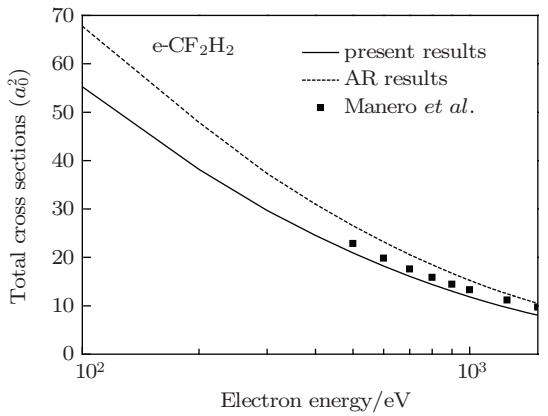


Fig. 3. Total cross sections for electron scattering from CF_2H_2.

Figure 4 shows the total cross sections of the present calculations for CFH_3 together with the experimental data of Krzysztofowicz and Szmytkowski.[11] From Fig. 4, we can see that the present results are in very good accordance with the experimental data. For example, the differences between the original AR results and the experimental data of Krzysztofowicz and Szmytkowski[11] are 34.40% and 33.40% at 100 eV and 200 eV, respectively, while the differences between the present results and the experimental data of Krzysztofowicz and Szmytkowski[11] are only 1.90% at 100 eV and 0.09% at 200 eV. Above 250 eV, there are no experimental total cross sections for electron scattering from CFH_3 molecule. So, the present calculations can give a reference for further experimental investigations of electron scattering from CFH_3 molecule above 250 eV.

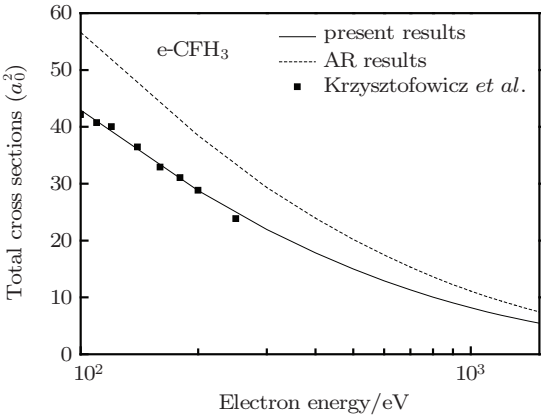


Fig. 4. Total cross sections for electron scattering from CFH_3.

From our studies, we can see that the revised AR with considering the difference between the bound atom and the free atom is more successful than the original AR for calculating the total cross sections of electron scattering from CF_4, CF_3H, CF_2H_2, and CFH_3 in the present energy range. At the same time, we also notice that larger discrepancies exist at low energy range, especially below 200 eV. As is well known, a 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 shielding effect becomes smaller and smaller and has an insignificant influence on total cross section. Since the shielding effect is not included in the present calculations, the differences may be caused by it at low energies. Of course, more experimental and theoretical investigations of electron scattering from CF_4, CF_3H, CF_2H_2, and CFH_3 are needed to elucidate our calculations.

4. Conclusion

The total cross sections of electron–molecule scattering, calculated from the original AR, deviate from the experimental data at lower energies because the molecular structure is not considered in the original additivity rule. Considering the difference between the free atom and the bound atom in the molecule, the original AR is revised. With the revised AR, the total cross sections of electron scattering from CF_4, CF_3H, CF_2H_2, and CFH_3 are calculated in an energy range from 100 eV to 1500 eV. The present results are compared with the available experimental data and the original AR results. From our study, we can see that the revised AR is more successful than the original AR. Of course, our calculations should be elucidated by further experiments.

References

[1] Marcio T N V, Winstead C, Mckoy V, Kitajima M and Tanaka H 2002 *Phys. Rev.* A **65** 022702

[2] Nishimura H and Nakamura Y 2005 *J. Phys. Soc. Jpn.* **74** 1160

[3] Scheer H C 1992 *Rev. Sci. Instrum.* **63** 3050

[4] Manero F, Blanco F and Garcia G 2002 *Phys. Rev.* A **66** 032713

[5] Zecca A, Karwasz G P and Brusa R S 1992 *Phys. Rev.* A **46** 3877

[6] Sueoka O, Mori S and Hamada A 1994 *J. Phys.* B **27** 1453

[7] Szmytkowski C, Krzysztofowicz A M, Janicki P and Rosenthal L 1992 *Chem. Phys. Lett.* **199** 191

[8] Ariyasinghe W M 2003 *Radiat. Phys. Chem.* **68** 79

[9] Sueoka O, Takaki H, Hamada A, Sato H and Kimura M 1998 *Chem. Phys. Lett.* **288** 124

[10] Iga I, Pinto P R and Homem M G 1999 *International Symposium on Electron–Molecule Collisions and Swarms* Tokyo, Japan, July 18–20, 1999 p. 123

[11] Krzysztofowicz A M and Szmytkowski C 1995 *J. Phys.* B **28** 1593

[12] Kothari H N and Joshipura K N 2010 *Chin. Phys.* B **19** 103402

[13] Wang X L, Feng H, Sun W G, Fan Q C, Wang B and Zeng Y Y 2011 *Acta Phys. Sin.* **60** 023401 (in Chinese)

[14] Schneider B I 1975 *Chem. Phys. Lett.* **31** 237

[15] Schneider B I 1975 *Phys. Rev.* A **11** 1957

[16] Schneider B I and Hay P J 1976 *Phys. Rev.* A **13** 2049

[17] Burke P G, Mackey I and Shimamura I 1977 *J. Phys.* B **10** 2497

[18] Burke P G and Tennyson J 2005 *Mol. Phys.* **103** 2537

[19] Rescigno T N, Mccurdy C W, Orel and Lengsfield B H 1995 *Computational Methods for Electron–Molecule Collisions* (New York: Plenum Press)

[20] Jorge L S L 2009 *Phys. Scr.* **79** 025303

[21] Bethe H 1930 *Ann. Physik* **5** 3250

[22] Otvos J W and Stevenson D P 1956 *J. Am. Chem. Soc.* **78** 546

[23] Raj D 1991 *Phys. Lett.* A **160** 571

[24] Joshipura K N and Patel P M 1994 *Z. Phys.* D **29** 269

[25] Sun J F, Xu B, Liu Y F and Shi D H 2005 *Chin. Phys.* **14** 1125

[26] Tan X M, Liu Z J and Tian X H 2010 *Nucl. Insturm. Method* B **268** 1535

[27] Clementi E and Roetti C 1974 *Atom. Data Nucl. Data Tables* **14** 177

[28] Riley M E and Truhlar D G 1975 *J. Chem. Phys.* **63** 2182

[29] Zhang X Z, Sun J F and Liu Y F 1992 *J. Phys.* B **25** 1893

[30] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048

[31] Staszewska G, Schwenke D G, Thirumalai D and Truhlar D G 1983 *Phys. Rev.* A **28** 2740

[32] Jiang Y H, Sun J F and Wan L D 1994 *Chin. J. At. Mol. Phys.* **11** 418 (in Chinese)