Total cross sections for electron scattering from sulfur compounds*

Tan Xiao-Ming(谭晓明)[a)†] and Wang Yan-Wen(王艳文)[b)]

[a)] School of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, China
[b)] Department of Life Science and Technology, Xinxiang Medical University, Xinxiang 453003, China

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The original additivity rule method cannot give good results for electron scattering from SO, SO_2, SO_2Cl_2, SO_2ClF, and SO_2F_2 molecules at low energy, because the electron–molecule scattering is simply reduced to electron–atom scattering. Considering the difference between the bound atom in a molecule and the corresponding free atom, the original additivity rule is revised. With the revised additivity rule, the total cross sections for electron scattering from these molecules are calculated over a wide energy range below 3000 eV and compared with the available experimental and theoretical data. A better agreement between them is obtained.

Keywords: the revised additivity rule, total cross sections, electron scattering

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1. Introduction

Electron scattering from atoms and molecules has long been a very important subject for the requirements in many scientific areas.[1–3] SO, SO_2, SO_2Cl_2, SO_2ClF, and SO_2F_2 are very important molecules in industry, plasma processing, environmental and atmospheric physics, and astrophysics.[4] For example, SO is an abundant component in the plasma processing containing SO_2.[5] The SO_2 molecule is the fatal pollutant of the Earth's atmosphere and plays an important role in forming acid rain.[6] SO_2 is also abundant in the Venus atmosphere and in the atmosphere of satellite Io of Jupiter.[4,6] Total cross sections for electron scattering from the SO_2 molecule are indispensable in the designing of electrical-discharge-based devices for removing SO_2 pollutant from industrial fumes.[6] SO_2Cl_2 is used as a constituent of the catholyte system in batteries,[7] and is also used as a chlorinating and sulfonating reagent.[8,9] In addition, SO_2Cl_2 may play a catalytic role as the minor component in the Venus atmosphere.[10] SO_2F_2 is a decomposition product[11] in the SF_6/O_2 plasma which may greatly increase etching anisotropy.[12] In spite of the importance of these molecules, the total cross sections for electron scattering from these molecules (except SO_2) are relatively scarce; there is no experimental total cross section for electron scattering to our knowledge, and the theoretical total cross sections have only been calculated recently in a range from 10 eV to 2000 eV.[4] The total cross section measurements for electron scattering from SO_2 were made first by Szmytkowski and Maciag[13] in an energy range from 1.5 eV to 70 eV. Recently, Szmytkowski *et al.*[14] further measured the total cross sections for SO_2 using the modified electron spectrometer working in a linear transmission mode in an energy range from 0.5 eV to 370 eV. The total cross sections of SO_2 have also been obtained through attenuation measurements in a Ramsauer-type apparatus by Zecca *et al.*[6] in an energy range from 90 eV to 4000 eV. Joshipura and Gangopadhyay[4] have calculated the total cross sections for electron scattering from SO_2 in an energy range from 15 eV to 2000 eV using the complex potential formalism and the complex scattering potential-ionization contribution approximation method. Szmytkowski *et al.*[15] have measured the total cross sections for electron scattering by SO_2Cl_2 in an energy range from 0.5 eV to 150 eV. Above 150 eV, no experimental data are available on SO_2Cl_2. Joshipura and Gangopadhyay[4] presented the theoretical results for electron scattering from SO_2Cl_2 in an energy range from 10 eV to 2000 eV. For SO_2ClF, the total electron scattering cross sections were measured by Szmytkowski *et al.*[16] in an energy range from 0.6 eV to 370 eV and calculated by Joshipura and Gangopadhyay[4] in an energy range from 15 eV to 2000 eV. Above 370 eV, there are no experimental total cross sections for electron scattering from the SO_2ClF molecule. The total cross section measurements for electron scattering from SO_2F_2 have been made by Wan *et al.*[17] of electron energy only below 12 eV. Recently, the total cross sections for electron scattering by SO_2F_2 have been calculated theoretically by Szmytkowski *et al.*[15] and Joshipura and Gangopadhyay[4] for electron energies ranging from 40 eV to 4000 eV and from 20 eV to 2000 eV, respectively.

On the theoretical side, the additivity rule[18–20] is a relatively simple but effective method, especially for smaller molecules or at high enough energies. However, for larger

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†Corresponding author. E-mail: scu_txm@163.com

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molecules or at lower energies, great disagreement between the experimental data and the additivity rule results still exists even at an electron energy of several hundreds of eV. This is because electron–molecule scattering is reduced to electron–atom scattering in the additivity rule. Considering the difference between the bound atom in the molecule and the corresponding free atom, the additivity rule method has been revised.[21,22] With the revised additivity rule, the total cross sections for electron scattering from some hydrocarbon molecules and fluoromethanes were obtained and a better agreement with the experimental data was achieved.[21,22] In the present paper, we further use the revised additivity rule to calculate the total cross sections for electron scattering from SO, SO_2, SO_2Cl_2, SO_2ClF, and SO_2F_2 molecules. The information about electron scattering for these molecules is scarce in spite of their importance.

2. Theory

The additivity rule[18–20] is based on the assumption that anisotropic interactions between electrons and molecules are negligible in the calculation of total cross sections for intermediate and high energies. As a result, the total cross sections of electron–molecule scattering are written as the sum of the total cross sections of the constituent atoms in the molecule. Here, it is obvious that no molecular geometry is involved, so electron–molecule scattering problem is reduced to an electron–atom scattering problem which is easier to handle. The electron–atom interactions are represented by the optical potential

$$V_{\rm opt} = V_{\rm s}(r) + V_{\rm e}(r) + V_{\rm p}(r) + iV_{\rm a}(r), \tag{1}$$

which incorporates all the important physical effects. Presently the static potential $V_{\rm s}(r)$ for an electron–atom system is calculated from the well-known Hartree–Fock atomic wave function.[23] Exchange potential $V_{\rm e}(r)$ provides a semi-classical energy-dependent form of Riley and Truhlar.[24] Zhang *et al*.[25] gave a smooth form for polarization potential $V_{\rm p}(r)$ at values of all r's, which has a correct asymptotic form at large value of r and approaches to the free-electron–gas correlation potential[26] in the near-target region. This potential model has been proved to be fairly successful in obtaining total cross sections for electron–atom scattering.[24] The imaginary part of the optical potential $V_{\rm a}(r)$ is the absorption potential, which represents approximately the combined effect of all the inelastic channels. Here, the absorption potential of Jiang *et al*.[27] is adopted as the following form

$$V_{\rm a}(r) = -\rho_0(r)\sqrt{\frac{T_{\rm L}}{2}}\overline{\sigma_{\rm b}}, \tag{2}$$

$$T_{\rm L} = k^2 - V_{\rm s} - V_{\rm e} - V_{\rm p}. \tag{3}$$

In Eq. (2), $\rho_0(r)$ is the charge density of the corresponding free atom, and

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

where

$$k_{\rm F} = [3\pi^2\rho_0(r)]^{1/3}, \tag{5}$$

$$W = 2\Delta, \tag{6}$$

k^2 is the energy of the incident electron, with Δ being the first excitation energy of the target atom. Static potential $V_{\rm s}(r)$, exchange potential $V_{\rm e}(r)$, polarization potential $V_{\rm p}(r)$, and the absorption potential $V_{\rm a}(r)$ are all relevant to the atomic charge density $\rho_0(r)$.

According to the additivity rule, the total cross section $Q_{\rm T}$ for a molecule is given by

$$\begin{aligned}Q_{\rm T} &= \frac{4\pi}{k}\,{\rm Im}\,f_M(\theta=0)\\ &= \frac{4\pi}{k}\,{\rm Im}\sum_{j=1}^{N} f_j(\theta=0)\\ &= \sum_{j=1}^{N} q_{\rm T}^j(E),\end{aligned} \tag{7}$$

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. (7) for the j-th atom is obtained by the partial wave method as

$$q_{\rm T}^j = \frac{\pi}{k^2}\sum_{l=0}^{l_{\max}}(2l+1)[|1-s_l^j|^2 + (1-|s_l^j|^2)], \tag{8}$$

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:

$$\left(\frac{{\rm d}^2}{{\rm d}r^2} + k^2 - 2V_{\rm opt} - \frac{l(l+1)}{r^2}\right)u_l(r) = 0. \tag{9}$$

Under the boundary condition

$$u_l(kr) \sim kr[{\rm j}_l(kr) - {\rm in}_l(kr)] + s_l kr[{\rm j}_l(kr) + {\rm in}_l(kr)], \tag{10}$$

where j_l and n_l are spherical Bessel and Neumann functions separately.

Obviously, the additivity rule model does not distinguish the free atom from the bound atom in the molecule. Considering this, we present[21,22]

$$\rho(r) = f \cdot \rho_0(r), \tag{11}$$

where

$$f = 1 - \frac{R}{R+d}\frac{N-Z}{N}, \tag{12}$$

$\rho(r)$ 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. Thus, the additivity rule is revised with Eqs. (11) and ((12).

3. Results and discussion

The total cross sections for electron scattering from SO, SO_2, SO_2Cl_2, SO_2ClF, and SO_2F_2 are calculated with the revised additivity rule method. The present results are compared with the available experimental and theoretical data shown in Figs. 1–5.

There are no experimental total cross sections for electron scattering from SO to our knowledge, so the present results for electron scattering from SO in an energy range from 10 eV to 3000 eV are compared with the theoretical data of Joshipura and Gangopadhyay[4] as shown in Fig. 1. The present results are in better agreement with the theoretical data[4] than the original additivity rule results above 300 eV. Below this, the present results and the original additivity rule results are both much higher than the theoretical data,[4] so experimental data are needed to elucidate our results.

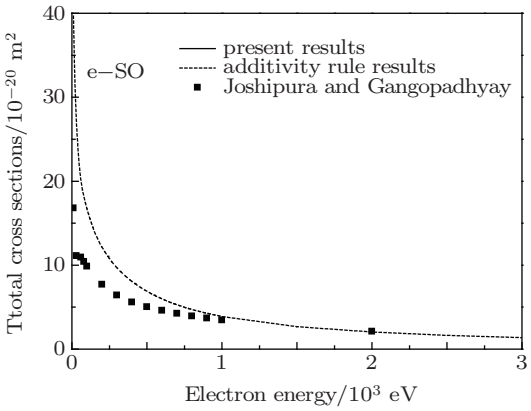


Fig. 1. Total cross sections for SO. Solid line: present results, dashed line: additivity rule results. Theoretical results: Joshipura and Gangopadhyay.[4]

Figure 2 shows the present total cross sections for electron scattering from SO_2 in an energy range from 20 eV to 3000 eV and the available experimental and theoretical results. From Fig. 2, we can see that the present results are in better agreement with the experimental data than the additivity rule results in the whole energy range. For example, the difference between the preset result and the measurement of Szmytkowski *et al.*[14] is only 11.65% at 50 eV, while the difference between the additivity rule result and the measurement of Szmytkowski *et al.*[14] reaches 31.19%. The additivity rule result deviates from the experimental result of Zecca *et al.*[6] by 27.95%, while the present result deviates only by 4.09% at 400 eV. At the same time, we also notice that larger differences exist between the measurements of Szmytkowski *et al.*[14] and those of Szmytkowski and Maciag[13] in an energy range between 20 eV and 70 eV. This may be due to the improvement made in the new experimental setup.[14] The difference between the present result and the theoretical datum of Joshipura and Gangopadhyay[4] is 27.95% at 100 eV, while the difference for the additivity rule is 39.37%. The present result deviates from the semiemprical datum of Zecca *et al.*[6] by about 3.4% at 800 eV, while the additivity rule result deviates by 23.02%.

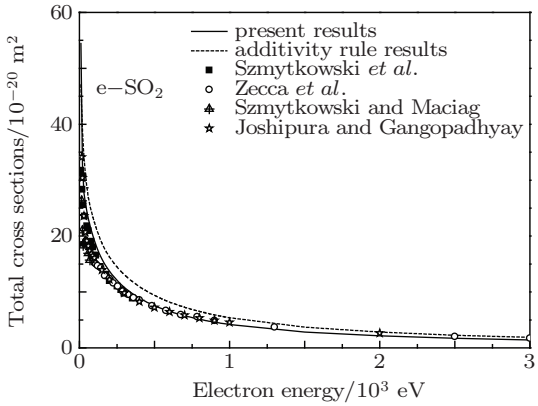


Fig. 2. Total cross sections for SO_2. Solid line: present results, dashed line: additivity rule results. Experimental results: Szmytkowski *et al.*,[14] Zecca *et al.*,[6] Szmytkowski and Maciag.[13] Theoretical results: Joshipura and Gangopadhyay,[4] semiempirical data of Zecca *et al.*[6]

In Fig. 3, the present results for SO_2Cl_2 are compared with the measurements of Szmytkowski *et al.*[15] and the theoretical values.[4,15] The present results give better agreement with the measurements of Szmytkowski *et al.*[15] than the additivity rule results in the whole overlapping energy range. For example, the difference between the present result and the experimental result of Szmytkowski *et al.*[15] is 28.74% at 70 eV, while the difference between the additivity rule result and the measurement of Szmytkowski *et al.*[15] reaches 52.75%. Above 150 eV, there are no experimental data for SO_2Cl_2, so the present results are compared with the theoretical data.[4,15] Above 400 eV, the present results are in better agreement with the theoretical data of Joshipura and Gangopadhyay[4] than the additivity rule results. Below 400 eV, the theoretical data of Joshipura and Gangopadhyay[4] are much lower than the present data and the additivity rule results. The present results are in good agreement with the theoretical results of

Szmytkowski *et al.*[15] in the overlapping energy range. For example, the present results deviate from the theoretical data of Szmytkowski *et al.*[15] only by 4.7% at 500 eV. Of course, more experimental data are needed to elucidate the present results and the other theoretical data.

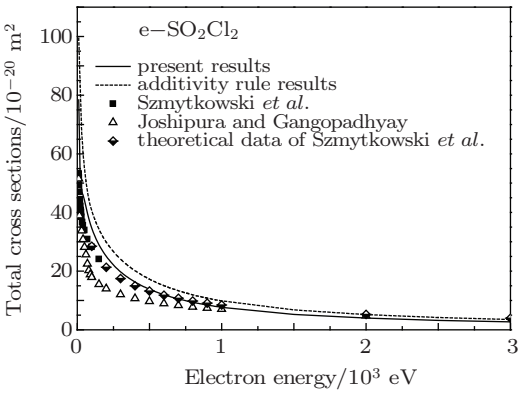


Fig. 3. Total cross sections for SO_2Cl_2. Solid line: present results, dashed line: additivity rule results. Experimental results: Szmytkowski *et al.*[15] Theoretical results: Joshipura and Gangopadhyay,[4] and Szmytkowski *et al.*[15]

The present total cross sections for electron scattering from SO_2ClF are shown in Fig. 4 with the experimental data of Szmytkowski *et al.*[16] and the theoretical results of Joshipura and Gangopadhyay[4] and Szmytkowski *et al.*[16] The present results are in better agreement with the measurements of Szmytkowski *et al.*[16] than the additivity rule results in the whole overlapping energy range. Above 370 eV, there are no experimental data for the comparison, so the present results are compared with the other theoretical results.[4,16] The difference between the present result and the theoretical datum of Joshipura and Gangopadhyay is 15.67% at 700 eV, while the difference between the present result and the theoretical result of Szmytkowski *et al.* is only 2.83% at 600 eV.

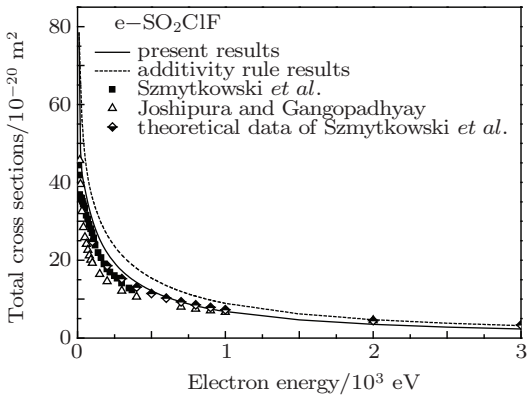


Fig. 4. Total cross sections for SO_2ClF. Solid line: present results, dashed line: additivity rule results. Experimental results: Szmytkowski *et al.*[16] Theoretical results: Joshipura and Gangopadhyay,[4] and Szmytkowski *et al.*[16]

Figure 5 shows all the total cross sections for electron scattering from SO_2F_2. The only available experimental data are the measurements by Wan *et al.*[17] in an energy range from 0.2 eV to 12 eV. From this figure, we can see that the measurements of Wan *et al.*[17] are much lower than all the theoretical results. From a comparison between the total cross section behaviors for fluorinated targets, Christophorou and Olthoff[28] concluded that the experimental data of Wan *et al.*[17] are significantly underestimated. In general, the present results are in fair agreement with the theoretical data of Szmytkowski *et al.*[15] in the whole overlapping energy range. Above 400 eV, the present results are also in better agreement with the theoretical results of Joshipura and Gangopadhyay[4] than the additivity rule results. Below 400 eV, the theoretical results of Joshipura and Gangopadhyay[4] are much lower than the other theoretical data, so further experimental and theoretical studies are needed in this energy range.

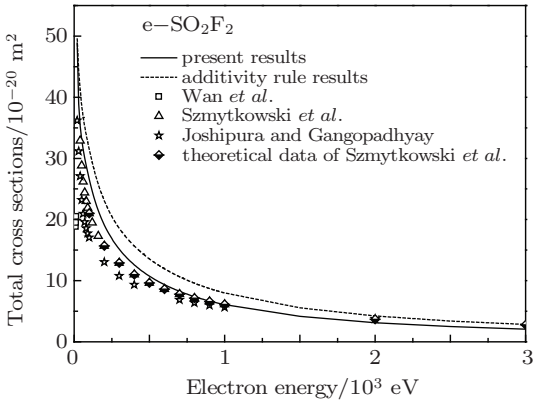


Fig. 5. Total cross sections for SO_2F_2. Solid line: present results, dashed line: additivity rule results. Experimental results: Wan *et al.*[17] Theoretical results: Szmytkowski *et al.*,[15] and Joshipura and Gangopadhyay.[4]

In general, as shown in Figs. 1–5, the present revised additivity rule results which consider the difference between the bound atom in a molecule and the corresponding free atom can give better agreement with the available experimental and theoretical data than the original additivity rule results over a wide energy range. At low energies, the present results exceed the experimental values, since the geometry shielding effect is not included in the present calculations. This effect may be important at low energies, because 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.

4. Conclusions

In this paper, the revised additivity rule approach is employed to calculate the total cross sections for electron scattering by five molecules SO, SO_2, SO_2Cl_2, SO_2ClF, and SO_2F_2 in the energy range from 10 eV to 3000 eV. From our studies, we can draw some conclusions as follows.

(i) Generally, the original additivity rule method cannot give reasonable results for these molecules especially below

1000 eV, because the electron–molecule scattering is simply reduced to electron–atom scattering in this method.

(ii) The revised additivity rule method is effective in generating the total cross sections of electron scattering from these molecules in the present energy range, and therefore can be used to predict the total electron scattering cross sections for larger or more complex molecules over a wide energy range. At the same time, we also notice that the experimental results of electron scattering for SO, SO_2Cl_2, SO_2ClF, and SO_2F_2 molecules are very scarce in the present energy range, so the present results can give a reference for further experiments.

References

[1] Cheng Y J, Zhou Y J and Jiao L G 2012 *Chin. Phys.* B **21** 013405

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

[3] 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)

[4] Joshipura K N and Gangopadhyay S 2008 *J. Phys.* B **41** 215205

[5] Tarnovski V, Levin A, Deutsch H and Becker K 1995 *J. Chem. Phys.* **102** 770

[6] Zecca Z, Nogueira J C, Karwasz G P and Brusa R S 1995 *J. Phys.* B **28** 477

[7] Boyle T J, Andrews N L, Alam T M, Tallant D R, Rodrigues M A and Ingersoll D 2005 *Inorg. Chem.* **44** 5934

[8] Yu G, Mason H J, Wu X, Endo M, Douglas J and Macor J E 2001 *Tetrahedron Lett.* **42** 3247

[9] Alonso M and Riera A 2005 *Tetrahedron: Asymmetry* **16** 3908

[10] Demore W B, Leu M T, Smith R H and Yung Y L 1985 *Icarus* **63** 347

[11] Turban G and Rapeaux M 1983 *J. Electrochem. Soc.* **130** 2231

[12] Manenschijn A, Janssen G C A M, Drift E V D and Radelaz S 1989 *J. Appl. Phys.* **65** 3226

[13] Szmytkowski C and Maciag K 1986 *Chem. Phys. Lett.* **124** 463

[14] Szmytkowski C, Mozejko P and Krzysztofowicz A 2003 *Rad. Phys. Chem.* **68** 307

[15] Szmytkowski C, Mozejko P, Kwitnewski S, Domaracka A and Denga E P 2006 *J. Phys.* B **39** 2571

[16] Szmytkowski C, Mozejko P, Kwitnewski S, Denga E P and Domaracka A 2005 *J. Phys.* B **38** 2945

[17] Wan H X, Moore J H, Olthoff J K and Van Brunt R J 1993 *Plasma Chem. Plasma Process* **13** 1

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

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

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

[21] Tan X M, Liu Z J and Tian X H 2010 *Nucl. Instrum. Methods* B **268** 1535

[22] Tan X M and Zhao G 2012 *Chin. Phys.* B **21** 063402

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

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

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

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

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

[28] Christophorou L G and Olthoff J K 2004 *Fundamental Electron Interactions with Plasma Processing Gases* (New York: Kluwer/Plenum)