

# Total cross sections for electrons scattering from $C_2F_4$ and $SO_2$ at 30—5000 eV: considering the geometric shielding effect

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Considering the changes of the geometric shielding effect in a molecule as the incident electron energy varying, an empirical fraction, which is dependent on the incident electron energy, is presented. Using this empirical fraction, the total cross sections (TCSs) for electrons scattering from complex polyatomic molecules  $C_2F_4$  and  $SO_2$  are calculated over a wide energy range from 30 to 5000 eV together with the additivity rule model at Hartree-Fock level. In the TCS calculations, the atoms are presented by the spherical complex optical potential, which is composed of static, exchange, polarization and absorption contributions. The quantitative TCSs above 100 eV are in good agreement with those obtained by experiments and other theories. It is proved that the empirical fraction, which exhibits the TCS contributions of shielded atoms in a molecule at different energies, is reasonable.

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There has been significant progress in the development of calculation methods for total cross sections (TCSs) of electrons scattering from molecules. In the past decades, researchers have proposed many approaches, such as the Schwinger variational iterative method<sup>[1]</sup>, the distorted-wave approximation method<sup>[2]</sup>, the Schwinger multichannel method<sup>[3]</sup>, the complex Kohn variational method<sup>[4]</sup>, the Schwinger variational iterative method combined the distorted-wave approximation method<sup>[5]</sup>, the Born-closure Schwinger variational method<sup>[6]</sup>, the *R*-matrix method<sup>[7]</sup>, the *ab initio* method<sup>[8]</sup>, the close-coupling method<sup>[9]</sup> and the Glauber approximation method<sup>[10]</sup>, etc.. However, over the intermediate- and high-energy ranges, since almost all inelastic channels (rotational, vibrational, electronic excitation, and ionization process, etc.) are open, few of the above-mentioned methods can give accurate results. It is, therefore, not surprising that many previous calculations on TCSs for electron-molecule scattering have been restricted to low energies.

In order to attain the accurate TCSs for electrons scattering from molecules at higher energies, recently, a simple approach, namely, the additivity rule (AR) model<sup>[11]</sup>, wherein a molecular cross section is an incoherent sum of the cross sections of the constituent atoms, was put forward. For simple and small molecules, the AR model can give TCSs above 200—300 eV<sup>[11]</sup>. For complex molecules<sup>[12,13]</sup>, though this method can give accurate TCSs over the intermediate and high energies, larger discrepancies can still be seen at lower energies, especially below 500—800 eV.

In order to extend the AR model validity to lower energies, many investigations have been made in recent years<sup>[14–18]</sup>. Taking into account that the present widely-used absorption potential<sup>[19]</sup> overestimates the TCS values at lower energies, Raj *et al.*<sup>[14]</sup> have presented a

modification factor  $m = 1/k$ , but they only calculated the differential cross sections of electrons scattering from  $O_2$ . Baluja *et al.*<sup>[15]</sup> have presented a modification factor  $m = 1/k^{1/2}r$  and replaced the energy gap ( $\Delta$ )<sup>[20]</sup> between the target ground and the lowest excited electronic state with the positronium formation energy, but greater TCS differences between theories and experiments are still seen at lower energies for relatively larger molecules. Taking into account the polarization of target molecules, Jain<sup>[16]</sup> has employed the polarized electronic density in the absorption potential. Meanwhile, Jain<sup>[16]</sup>, Raizada<sup>[17]</sup>, and Joshipura *et al.*<sup>[18]</sup> have replaced the  $\Delta$  value with the ionization potential of the atom. However, TCS calculations on only a few molecules<sup>[14–18]</sup> are insufficient to express general behaviors. In 2003, in order to extend the AR model validity for lower energies and larger molecules, we presented the concept of bonded atom and give a modification factor<sup>[19]</sup>, which takes into account the overlapping effect of electron clouds between two atoms in a molecule. Employing this modification factor, we have obtained encouraging TCSs for electrons scattering from numerous molecules<sup>[19,21–24]</sup>. If we carefully investigate the calculated results over the whole energy range from 30 to 5000 eV, we can find that the TCSs are larger at lower energies and smaller at higher energies than the experimental results. To improve the agreement between theories and experiments, in this letter, we consider the shielding effect of atoms in a molecule and give another modification method based on the AR model, which depends on the energy of the incident electrons and the geometric structure of the molecule.

In the AR model, assuming the molecular orbitals can be described by the sum of the valence orbitals of all atoms presented in the molecule. Thus, the molecular

TCSs are given by

$$Q_{\text{AR}}(E) = \frac{4\pi}{k} \text{Im} F_m(\theta = 0) \\ \approx \frac{4\pi}{k} \text{Im} \sum_{j=1}^N f_j(\theta = 0) = \sum_{j=1}^N q_{\text{T}}^j(E), \quad (1)$$

where  $F_m(\theta = 0)$  is the electron-molecule scattering amplitude for forward direction;  $q_{\text{T}}^j(E)$  and  $f_j(\theta = 0)$  are the TCS and the complex scattering amplitude for the  $j$ th constituent atom, respectively.

In Eq. (1), one main effect is not considered: a close-packed molecule is not fully transparent for low-energy electrons, and the “inner” atoms are shielded by the “outer” atoms and do less contribute to the molecular TCSs at lower energies than those at higher energies. The shielding effect, which leads to negative contributions to the TCSs in the AR model, is dependent on the geometry of the molecule. Taking into account the shielding effect, Bobeldijk *et al.*<sup>[25]</sup> presented a geometric additivity rule (GAR) to calculate the ionization cross section. We notice that the GAR model, which incorporates the geometry of a molecule, is a good approach and can be applied to calculate the TCSs for electrons scattering from molecules, particularly for complex polyatomic molecules at low energies. When the GAR model is applied to calculate the TCSs, it can be expressed as

$$Q_{\text{GAR}}(E) = \frac{1}{3} Q_{\parallel}(E) + \frac{2}{3} Q_{\perp}(E), \quad (2)$$

where  $Q_{\parallel}(E)$  and  $Q_{\perp}(E)$  are the TCS for electrons approaching the molecule parallel to  $Z$  axis ( $\theta = 0$ ) and perpendicular to  $Z$  axis ( $\theta = 90^\circ$ ), respectively. For example, in the case of  $\text{C}_2\text{F}_4$  molecule,  $Q_{\parallel}$  and  $Q_{\perp}$  are equal to  $Q_{\text{CF}_2}$  and  $Q_{\text{CF}} + Q_{\text{CF}}$ <sup>[25]</sup>, respectively. And the TCSs  $Q_{\text{CF}_2}$  and  $Q_{\text{CF}} + Q_{\text{CF}}$  are obtained still by Eq. (1).

The close-packed molecule is not fully transparent for low-energy electrons, but the transparency can improve as the energy increases. That is to say, when the incident electron energy is very low, the “inner” atoms are shielded partially by the “outer” atoms, thus the GAR model can give encouraging results, but the AR model not. When the energy is very high, the molecule is fully transparent and each atom in the molecule is freely scattered. Thus the interaction effect between atoms can be neglected. Hence, the AR model is valid, but the GAR model not. Considering these factors, we have proposed the molecular TCS as

$$Q_{\text{TCS}}(E) = Q_{\text{GAR}}(E) + A(Q_{\text{AR}} - Q_{\text{GAR}}), \quad (3)$$

where  $A$ , the energy-dependent geometry parameter, is an empirical fraction that exhibits the TCS contribution of shielded atoms in a molecule at different energies. Choosing the parameter  $A$ , three factors should be considered. Firstly,  $A$  must satisfy  $Q_{\text{TCS}}(E) \approx Q_{\text{GAR}}(E)$  when the incident electron energy is low enough; and  $Q_{\text{TCS}}(E) \approx Q_{\text{AR}}(E)$  when the incident electron energy is high enough. This means that the empirical fraction  $A$  must have  $A \rightarrow 0$  if  $E \rightarrow 0$ , and  $A \rightarrow 1$  if  $E \rightarrow \infty$ . That is to say, the higher the energy is, the less the effect on the

TCSs should be. Secondly, at the same energy, the larger the size of a molecule is, the greater the discrepancies between the TCSs calculated according to Eq. (1) and the experimental values are. This implies that the larger the volume of a molecule is, the smaller the empirical fraction  $A$  should be. And the calculations also show that when molecules have same total number of electrons, the more the total number of atoms in molecules is, the smaller the empirical fraction  $A$  should be. And when molecules have the same total number of atoms, the more the total number of electrons in molecules is, the smaller the empirical fraction  $A$  should be, too. And thirdly, calculations show that Eq. (1) cannot give a correct shape of TCS curve. It can be clearly seen in log-log curves plotted by using the calculations results in Refs. [13, 19, 21–24]. The main problem is that the slopes of these log-log curves are larger than that given by the experiments. Thus, the empirical fraction  $A$  relating to  $E$  and some molecular parameters should ensure a reasonable shape for TCSs against the experimental data in the whole energy range. According to these analyses, we assume that

$$A = \frac{E}{mndC + E}, \quad (4)$$

where,  $E$  in unit of eV is the incident electron energy;  $m$  and  $n$  are the numbers of electrons and atoms in the molecule, respectively;  $d$  in unit of  $a_0$  is the molecular dimension, which can be determined by the bond length given in Ref. [26];  $C$  is a constant considering the reasonable dimension relation, which is equal to  $1 \text{ eV}/a_0$ . Such molecules as  $\text{C}_2\text{F}_4$  and  $\text{SO}_2$  can be approximated by a rodlike shape<sup>[25]</sup>.

$q_{\text{T}}^j(E)$  in Eq. (1) is obtained by the method of partial waves

$$q_{\text{T}}^j(E) = q_{\text{e}}^j(E) + q_{\text{a}}^j(E) \\ = \frac{\pi}{k^2} \sum_{l=0}^{l_{\text{MAX}}} (2l+1) \times [ |1 - S_l^j|^2 + (1 - |S_l^j|^2) ], \quad (5)$$

where  $q_{\text{e}}^j$  and  $q_{\text{a}}^j$  are elastic and absorption cross sections, respectively;  $S_l^j$  is the  $l$ th complex scattering matrix element of the  $j$ th atom, which is related to the partial wave phase shift as  $S_l^j = \exp(2i\delta_{lj})$ . To obtain  $S_l^j$ , we solve the following radial equation

$$\left( \frac{d^2}{dr^2} + k^2 - V_{\text{opt}} - \frac{l(l+1)}{r^2} \right) u_l(r) = 0, \quad (6)$$

under the boundary condition ( $r \sim \infty$ )

$$u_l(kr) \sim kr [j_l(kr) - in_l(kr)] \\ + S_l^j kr [j_l(kr) + in_l(kr)], \quad (7)$$

where  $j_l$  and  $n_l$  are spherical Bessel and Neumann functions, respectively. The limit  $l$  is taken large enough to generate the higher partial-wave contributions until again a convergence of less than 0.5% is achieved in the TCSs.  $V_{\text{opt}}$  is the spherical complex optical potential which incorporates all the important physical effects and is given by

$$V_{\text{opt}}(r) = V_{\text{s}}(r) + V_{\text{p}}(r) + V_{\text{e}}(r) + iV_{\text{a}}(r). \quad (8)$$

In detail, the static potential  $V_s(r)$  for electron-atom system is calculated by using the atomic charge density, determined from the well-known Hartree-Fock atomic wave function<sup>[27]</sup>. The exchange potential  $V_e(r)$  is provided by Riley *et al.*<sup>[28]</sup>. Polarization potential  $V_p(r)$  is given by our group<sup>[29]</sup>. And the absorption potential  $V_a(r)$  is presented by Staszewska *et al.*<sup>[20]</sup>.

Using the present spherical complex optical potential, we have calculated the TCSs for electrons scattering from atoms He, Ne, Ar, Kr, Xe, and Na. Compared with the experimental data, the calculated TCS results are encouraging at the involved energies within experimental error. It shows that the electron-atom potential used in this letter appears to be satisfactory, at least for the calculation of the TCSs for electron-atom scattering over the present energy range.

Employing the Eq. (3) together with the spherical complex optical potential, we have obtained the TCSs for electrons scattering from complex molecules  $C_2F_4$  and  $SO_2$  at 30–5000 eV. Our calculated results obtained by Eq. (3) (modified AR calculations), the AR results obtained by Eq. (1) (unmodified AR calculations) together with those obtained by experiments<sup>[30–33]</sup> and other theories<sup>[21,18,34]</sup> are given in Figs. 1 and 2, respectively.

The experimental results about electrons scattering from  $C_2F_4$  are very scarce at intermediate and high energies, and no other theoretical calculations can be found. The only group of experiments was reported by Szymtkowski *et al.*<sup>[30]</sup> at 0.6–370 eV. The modified AR calculations, the unmodified AR calculations together with the experimental data in Ref. [30] and the theoretical results calculated by the concept of bonded atom in Ref. [21] (CBA results) are shown in Fig. 1. From it, we can see that the modified AR calculations are in excellent accord with the only experiments above 50 eV. The differences between the modified AR calculations and the experiments in Ref. [30] are about 11.6% at 50 eV and 8.1% at 100 eV, respectively. But the ones between the CBA results and the experiments in Ref. [30] are about 33.4% at 50 eV and 24.2% at 100 eV, respectively.

Figure 2 shows the modified and unmodified AR calculations for electrons scattering from  $SO_2$  together with

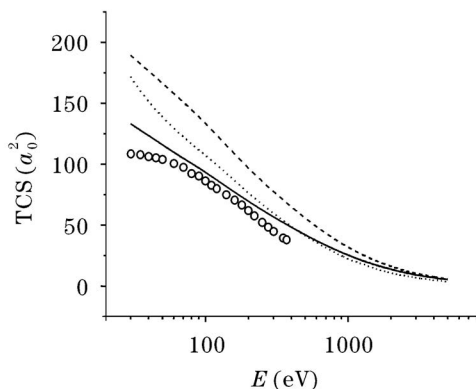


Fig. 1. Total cross sections for e- $C_2F_4$  scattering. Theoretical results: present modified AR calculations (solid line), present unmodified AR calculations (dashed line), results given by the concept of bonded atom<sup>[21]</sup> (dotted line). Experimental results: Szymtkowski *et al.*<sup>[30]</sup> (circles).

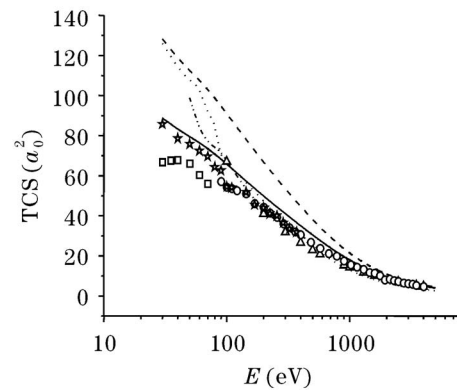


Fig. 2. Total cross sections for e- $SO_2$  scattering. Theoretical results: present modified AR results (solid line), present unmodified AR results (dashed line), Shi *et al.*<sup>[21]</sup> (dotted line), Joshipura *et al.*<sup>[18]</sup> (dash-dotted line), Raj *et al.*<sup>[34]</sup> (triangles). Experimental results: Zecca *et al.*<sup>[31]</sup> (circles), Szymtkowski *et al.*<sup>[32]</sup> (squares), Szymtkowski *et al.*<sup>[33]</sup> (stars).

the experimental data obtained by Zecca *et al.*<sup>[31]</sup> at 90–4000 eV, Szymtkowski *et al.*<sup>[32]</sup> at 30–70 eV, and Szymtkowski *et al.*<sup>[33]</sup> at 30–370 eV, and the theoretical calculations obtained by Joshipura *et al.*<sup>[18]</sup> at 30–5000 eV, Shi *et al.*<sup>[21]</sup> at 30–5000 eV, and Raj *et al.*<sup>[34]</sup> at 100–4000 eV. From it, we can easily see that the modified AR calculations are in good agreement with the experimental results obtained by Zecca *et al.*<sup>[31]</sup> at the whole overlapping energy range and by Szymtkowski *et al.*<sup>[33]</sup> above 100 eV, but are in slightly poor agreement with those obtained by Szymtkowski *et al.*<sup>[32]</sup> at 30–70 eV and by Szymtkowski *et al.*<sup>[33]</sup> below 100 eV. Compared with the unmodified AR calculations and the CBA results<sup>[21]</sup>, we clearly see that our modified AR calculations are much closer to the experimental data<sup>[32]</sup> at low energies.

Only Fig. 2 contains the experimental data at high energies. From it, we can easily see that the CBA results<sup>[21]</sup> are higher at lower energies and lower at higher energies than the experimental ones in Ref. [31], for example, higher by 21.4% at 100 eV, 6.9% at 200 eV, and lower by 29.5% at 3000 eV and 31.2% at 4000 eV, respectively. And the similar analyses are suitable for the theoretical results obtained by Raj *et al.*<sup>[34]</sup> within 100–1000 eV. Whereas the higher the energy is, the closer to the experimental data<sup>[31]</sup> the modified AR calculation result are. For example, the modified AR calculations are higher than the experiments<sup>[31]</sup> by 21.1% at 100 eV, 11.9% at 200 eV, 5.6% at 3000 eV, and 3.6% at 4000 eV, respectively.

At lower energies, as seen from Figs. 1 and 2, the modified AR calculation results are still much higher than all the experimental data because we have ignored the multicenter scattering and the valence-bond distortion effect<sup>[34]</sup> in the present investigation. At lower energies, the de Broglie wavelength associated with the incident particle becomes comparable to or larger than the bond length of the molecule which will increase the possibility of multiple scattering effects. It is expected that the inclusion of multiple scattering effects at lower energies will reduce the TCSs by a significant amount<sup>[35]</sup>. So, though we have taken into account the shielding effect in

molecules, TCS differences still exist at lower energies between present modified AR calculations and the experimental findings.

With the energy increasing, the wavelength of the incident electrons becomes smaller and smaller compared with the bond length of the molecule. Then the valence-bond distortion effect contributes less and less. Therefore, the higher the energy is, the better the modified AR calculations are, as shown in Figs. 1 and 2.

In summary, the AR model neglects the molecular geometry and its nuclear motion, so the electron-molecule scattering is reduced to the electron-atom scattering problem. The modified AR calculations are encouraging, even though we ignore the molecular geometry and its nuclear motion. As further investigation, we will concentrate our attention on the multicenter scattering and the valence-bond distortion effect so that we can successfully calculate the TCSs of electron-molecule scattering at both lower and higher energies.

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