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Total cross sections for electrons scattering from simple molecules containing the larger atom sulfur at 30–5000eV*

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A complex optical model potential modified by the concept of bonded atom, which takes into consideration the overlapping effect of electron clouds, is employed to calculate the total cross sections for electrons scattering from simple molecules (SO_2, H_2S, OCS, CS_2 and SO_3) containing the larger atom, sulfur, at 30–5000eV by using the additivity rule model at Hartree–Fock level. The quantitative molecular total cross section results are compared with those obtained in experiments and other calculations wherever available, and good agreement is obtained. It is shown that the additivity rule model together with the complex optical model potential modified by the concept of bonded atom can give the results closer to the experiments than the one unmodified by it. So, the introduction of bonded-atom concept in complex optical model potential betters the accuracy of the total cross section calculations of electrons from the molecules containing the larger atom, sulfur.

Keywords: atomic and molecular collision, additivity rule, bonded atom, total cross section
PACC: 3440, 3400

1. Introduction

It is well known that electron–molecule scattering over the intermediate- and high-energy ranges plays an important role in several applications in fields of physics, such as gaseous lasers, astrophysics, plasma physics, atmospheric physics and chemical physics. Therefore it is unsurprising that both theoretical and experimental studies of electrons scattering from molecules constitute an important subject of continuously increasing interest.

There has been significant progress in the development of both theoretical and computational methods for total cross sections (TCSs) of electron–molecule scattering in the past decades. Many approaches, such as the Schwinger variational iterative method,[1] the distorted-wave approximation method,[2] the Schwinger variational iterative method combined with the distorted-wave approximation method,[3] the complex Kohn variational method,[4] the Born-closure Schwinger variational method,[5] the R-matrix method,[6] the *ab initio* method[7] and the spherical complex optical potential (SCOP) method,[8] were proposed. However, over the intermediate- and high-energy ranges, since almost all inelastic channels (rotational, vibrational, electronic excitation and ionization process, etc.) are open, most of the above-mentioned methods for electron–molecule scattering are almost impossible to give accurate TCS values. Due to the multi-centre nature (in the case of polyatomic and hetero-nuclear molecules) and its nuclear motion, acquiring the accurate single-centre molecular wavefunction is very difficult. Though the SCOP method can be used accurately to calculate the TCSs at higher energies,[8] its application is greatly restricted.

In order to avoid using the single-centre molecular wavefunction for calculations of electron–molecule scattering, recently, a simple method, namely, the Additivity Rule (AR) model, was proposed and employed by Raj[9] to obtain the elastic cross section, the momentum transfer cross section and the integral

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elastic cross section at 100–500eV. Very recently, the AR model has been widely used to calculate the total and differential cross sections.[10,11] However, large discrepancies of TCSs exit between theories and experiments at lower energies.

Two methods can improve the agreement between theories and experiments over a wide energy range. One is to establish more accurate theoretical models, but we must obtain the accurate single-centre molecular wavefunction. The other is to continue using the simple AR model, but we must modify the complex optical model potential. Obviously, the former is much more difficult than the latter. Thus, to obtain the accurate TCSs of electron–molecule scattering, we modify the potential.

In this paper, the complex optical model potential modified by the concept of bonded atom, which takes into consideration the overlapping effect of electron clouds between two atoms in a molecule, is employed to calculate the TCSs for electrons scattering from such molecules as SO_2, H_2S, OCS, CS_2 and SO_3 containing the larger atom, sulfur, at 30–5000eV by using the AR model at Hartree–Fock level. The reason of selecting molecules SO_2, H_2S, OCS, CS_2 and SO_3 as targets is two-fold. Firstly, TCS calculations for these molecules are scarce. And secondly, these molecules contain the larger atom, sulfur, and other calculation methods may be difficult to give accurate TCSs over such a wide energy range due to the lack of availability of accurate single-centre wavefunctions. In Section 2, we describe in brief the complex optical model potential modified by the concept of bonded atom, and the AR model. In Section 3, we present the TCS calculations and discussion for these molecules at 30–5000eV and compare them with those obtained by experiments and other theories. Final remarks are made in Section 4. Atomic units are employed throughout this paper if not specified.

2. Theory and method

Over the intermediate- and high-energy ranges, the TCS of the AR model[9] for a molecule containing N atoms is given by

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

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

$q_{\mathrm{T}}^j(E)$ in term of partial wave is given by

$$\begin{aligned} q_{\mathrm{T}}^j(E) =& q_{\mathrm{e}}^j(E) + q_{\mathrm{a}}^j(E) \\ =& \frac{\pi}{k^2}\sum_{l=0}^{l_{\mathrm{MAX}}} (2l+1)\times[|1-S_l^j|^2 + (1-|S_l^j|^2)], \end{aligned} \tag{2}$$

where $q_{\mathrm{e}}^j(E)$ and $q_{\mathrm{a}}^j(E)$ are the elastic cross section and the absorption cross section of the jth constituent atom, respectively. The limit l_{MAX} is taken to be large enough to generate the higher partial-wave contributions until a convergence of less than 0.5% is again achieved in the TCS. S_l^j is the lth complex scattering matrix element of the jth constituent atom, which is related with the partial wave shift as $S_l^j = \exp(2\mathrm{i}\delta_{mj})$. To obtain S_l^j, we solve the following radial equation,

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

Under the boundary condition $r \to \infty$,

$$\begin{aligned} u_l(r) \sim& kr[j_l(kr) - \mathrm{i}n_l(kr)] \\ &+ S_l kr[j_l(kr) + \mathrm{i}n_l(kr)], \end{aligned} \tag{4}$$

where j_l and n_l are spherical Bessel and Neumann functions, respectively. k is the momentum of the incident electron. V_{opt} is the complex optical model potential of an atom and is given by

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

In Eq.(5), the static potential $V_{\mathrm{s}}(r)$ for electron–atom scattering is calculated by using the atomic charge density determined from the Hartree–Fock atomic wavefunction.[12] The exchange potential $V_{\mathrm{e}}(r)$ provides a semiclassical energy-dependent form presented by Riley and Truhlar.[13] The polarization potential $V_{\mathrm{p}}(r)$ is given by our group.[14] The absorption potential $V_{\mathrm{a}}(r)$ represents the combined effect of all the inelastic channels and is given by Staszewska *et al.*[15]

In Eq.(1), the TCS of electron–molecule scattering simply equals sum of TCSs of electrons scattering from each constituent atom. Obviously, there is no consideration about interferences between atoms. Here, to reduce the differences between theories and experiments, we introduce the concept of bonded atom and take into consideration the overlapping effect of electron clouds between two atoms. That is to say, in

Eq.(5), electron charge density $\rho(r)$ may be modified as follows:

$$\rho'(r) = f\rho(r), \tag{6}$$

where f is a structural factor. To obtain the factor f, the following three points are considered:

1) The potential described by Eq.(5) overestimates the TCS of electron–molecule scattering at 30–5000eV using the AR model (see dashed lines in Figs.1–4). Thus, to get accurate TCSs of electron–molecule scattering, the effect of the potential described by Eq.(5) should decrease.

2) Numerous calculations using Eq.(5) show that the more the electron number of the outmost shell in the constituent atom is, the more the TCS differences between theories and experiments are. When we investigate the target molecules resembling each other in structure, calculations also show that the more the total electron number of the constituent atom is, the more the TCS differences between theories and experiments are. These indicate that the modification should have relations with the electron number of the outmost shell and the total electron number of the constituent atom.

3) The atoms in molecules are quite different from the ones in the free states. The reason is that the atoms in molecules are bonded atoms whereas the ones in the free states are not. Thus there exists the overlapping effect of electron clouds between two atoms in a molecule, but it does not exist between two free ones. This indicates that the modification should have relations with the radius of the constituent atom and the bond length between two atoms in a molecule.

Keeping these in mind, a number of f factors are tried and the best agreement in theories and experiments are obtained for

$$f = 1 - \frac{r}{R}\frac{Z}{N}. \tag{7}$$

In Eq.(7), r is the bond length between two atoms and R is the sum of the radii of the two atoms. Z and N are the number of electrons in the outmost shell and the total number of electrons in the atom, respectively.

Since the static potential $V_{\rm s}(r)$,[12] exchange potential $V_{\rm e}(r)$[13] and absorption potential $V_{\rm a}(r)$[15] apparently contain electron charge density $\rho(r)$, thus having introduced the concept of bonded atom and considered the overlapping effect of electron clouds, $V_{\rm opt}$ can be expressed as follows:

$$V_{\rm opt}(r) = fV_{\rm s}(r) + V_{\rm p}(r) + V_{\rm e}(r) + {\rm i}fV_{\rm a}(r) \tag{8}$$

with

$$V_{\rm e} = -\frac{1}{4}\{\sqrt{[k^2 - 2(fV_{\rm s} + V_{\rm p})]^2 + 16\pi f\rho} - [k^2 - 2(fV_{\rm s} + V_{\rm p})]\}. \tag{9}$$

Values of the parameter R in target molecules are achieved by using the atomic charge density, determined from the Hartree–Fock atomic wavefunctions.[12]

The structural factor f reflects the overlapping effect of electron clouds between two atoms in a molecule. It is very simple, but we find that the calculated TCS values are very encouraging.

3. Calculations and discussion

Employing the AR model together with the potential modified and unmodified by the concept of bonded atom, we have calculated the TCSs for electrons scattering from molecules SO_2, H_2S, OCS, CS_2 and SO_3, which contain the larger atom, sulfur, at 30–5000eV. The modified and unmodified TCS results together with those obtained by experiments and other theories[8,16–20] are given in Figs.1–5, respectively. At the same time, the present modified calculations are also shown in Table 1.

As far as the TCSs of e-H_2S scattering are concerned, for comparison the modified calculations, the measurements obtained by Zecca *et al*[16] at 75–4000eV and the calculations obtained by Jain and Baluja[8] are all shown in Fig.1. From Fig.1, we notice that there is excellent agreement between the calculations and the measurements. It shows that the complex optical model potential modified by the concept of bonded atom is completely suitable for the calculation of e-H_2S scattering over the corresponding energy range.

As seen from Fig.1, the present modified calculations are obviously closer to the measurements than the unmodified ones over a wide energy range, especially at lower energies. The reason is that the modified potential takes into consideration the overlapping effect of electron clouds between two atoms but the unmodified potential does not. For the AR model with the unmodified potential, the shielded or overlapped clouds in polyatomic molecules are still used to calculate the TCS of the constituent atom, but in fact they have no contributions to the molecular TCS. So, the unmodified potential gives worse calculations.

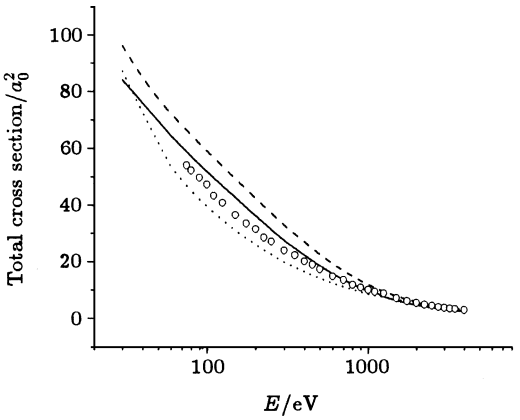


Fig.1. Total cross section for e-H_2S scattering. Theoretical results: solid line presents modified results; dashed line presents unmodified results; dotted line presents Jain and Baluja[8] calculations. Experimental results: circle presents Zecca *et al*'s[16] measurements.

For the e-SO_2 and e-OCS scatterings, present calculations, measurements[18–20] and calculations from other theories[17] are shown in Figs.2 and 3 for comparison. Obviously, the present modified calculations are in good accord with the measurements[18–20] and calculations from other theories[17] at the corresponding energy range, and are much closer to the measurements[18–20] and the calculations from theories[17] than the unmodified ones at lower energies ($E < 1000$eV).

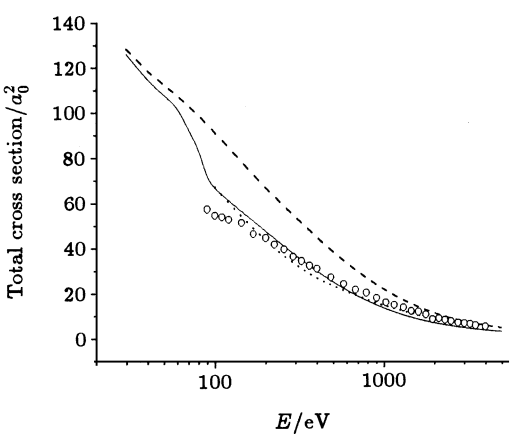


Fig.2. Total cross section for e-SO_2 scattering. Theoretical results: solid line presents modified results; dashed line presents unmodified results; dotted line presents Raj and Tomar[17] calculations. Experimental results: circle presents Zecca *et al*'s[18] measurements.

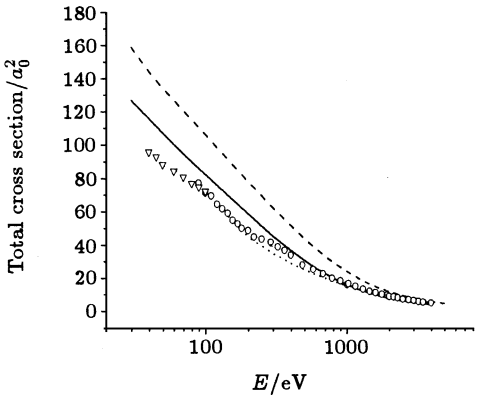


Fig.3. Total cross section for e-OCS scattering. Theoretical results: solid line presents modified results; dashed line presents unmodified results; dotted line presents Raj and Tomar[17] calculations. Experimental results: circle presents Zecca *et al*'s[18] measurements; triangle presents Szmytkowski *et al*'s[19] measurements.

From Figs.1-3, we easily see that the present modified calculations are higher than all measurements at lower energies. The reason might be the multiple scattering and the valence bond distortion which have been neglected in the present investigation. At lower incident energies, the de Broglie wavelength associated with the incident particle will become comparable to or larger than the internuclear distance which will increase the possibility of multiple scattering. It is expected that the inclusion of multiple scattering effects at lower energies will reduce the TCS by a significant amount.[21,22] The likely effect of the valence bond distortion is also to reduce the TCS at lower energies, especially below 100eV.[21,22]

For the e-CS_2 and e-SO_3 scatterings, the measurements and the calculations are both scarce. we give present calculations together with the only measurements obtained by Szmytkowski[20] at 30–80eV and the calculations obtained by Raj and Tomar[17] at 100–4000eV in Figs.4 and 5. Though there is slightly poorer agreement between the modified calculations and the measurements[20], as shown from the modified calculations, measurements and calculations from other theories in Figs.1–3, we come to the conclusion that the TCSs given in Figs.4 and 5 are also accurate above 100eV.

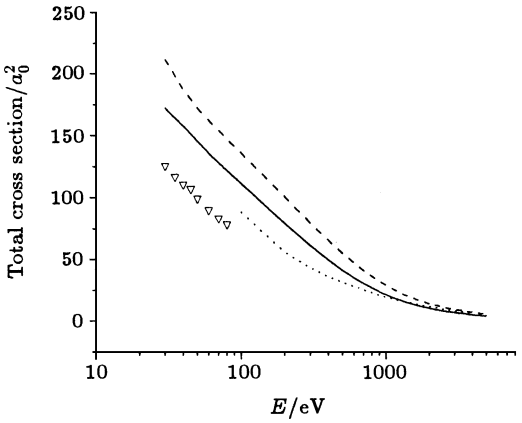


Fig.4. Total cross section for e-CS_2 scattering. Theoretical results: solid line presents modified results; dashed line presents unmodified results; dotted line presents Raj *et al*'s[17] calculations. Experimental results: triangle presents Szmytkowski *et al*'s[20] measurements.

At low energies, especially below 100eV, as evidenced in Figs.1–4, the modified calculations substantially exceed the measurements because we have ignored the multicentre scattering and the valence-bond effect in the AR model. In addition, a close-packed molecule is not fully transparent for low energy electrons, and the 'inner' atoms are shielded by the 'outer' atoms and do not contribute to the molecular TCS.[21,22] Generally, if the target molecule contains more electrons, the TCS calculations may show worse agreement with measurements because the valence-bond effect and shielding effect of the molecule containing more electrons yield more contributions to the TCS of electron–molecule scattering than those of the molecules containing fewer electrons, as shown in Figs.1–4.

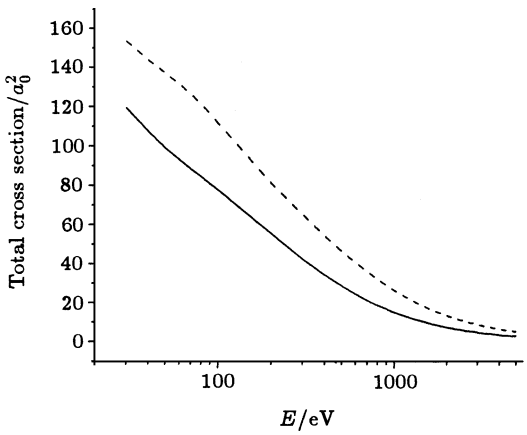


Fig.5. Total cross section for e-SO_3 scattering. Theoretical results: solid line presents modified results; dashed line presents unmodified results.

With the increase of the incident energy, the wavelength of the incident electron becomes smaller and smaller than the bond length of the molecule, and then the valence-bond effect and shielding effect contribute less and less. Therefore, at 100–300eV, present modified calculations become better and better. And above 300eV, the contributions of molecular structure and shielding effect to the TCSs may be neglected. So, the AR model together with the potential modified by the concept of bonded atom can obtain excellent calculations, as verified in Figs.1–3.

Table 1. Total cross sections for electron scattering from molecules H_2S, SO_2, OCS, CS_2 and SO_3 with the modified potential in units of a_0^2.

Energy/eV	H_2S	SO_2	OCS	CS_2	SO_3	Energy/eV	H_2S	SO_2	OCS	CS_2	SO_3
30.0	84.03	125.9	126.7	172.2	119.3	700.0	13.65	18.33	22.38	30.73	21.53
40.0	76.13	114.4	115.9	157.7	107.5	800.0	12.01	16.18	19.69	27.04	19.02
50.0	69.41	107.7	107.1	145.2	99.16	900.0	10.69	14.45	17.54	24.08	16.99
60.0	64.41	102.6	100.3	135.8	93.20	1000.0	9.62	13.04	15.78	21.67	15.33
70.0	60.45	92.17	94.69	128.2	88.50	1500.0	6.36	8.67	10.35	14.28	10.19
80.0	57.12	84.20	89.97	121.9	84.50	2000.0	4.75	6.47	7.63	10.64	7.58
100.0	42.89	65.92	82.27	111.5	77.82	2500.0	3.82	5.16	6.04	8.52	6.02
200.0	30.98	47.37	58.32	79.46	55.85	3000.0	3.22	4.30	5.00	7.15	4.99
300.0	24.18	36.44	44.94	61.57	42.81	3500.0	2.79	3.70	4.28	6.19	4.27
400.0	19.66	29.49	36.31	49.84	34.62	4000.0	2.48	3.25	3.74	5.47	3.73
500.0	16.44	24.64	30.26	41.56	28.92	4500.0	2.23	2.89	3.32	4.91	3.31
600.0	14.05	21.06	25.79	35.43	24.73	5000.0	2.03	2.61	2.99	4.46	2.98

4. Conclusion

Obviously, the AR model together with the present complex optical model potential modified by the concept of bonded atom, which takes into consideration the overlapping effect of electron clouds between two atoms in a molecule, can successfully calculate the TCSs of electron–molecule scattering over a wide energy range, even though we ignore the molecular geometry and its nuclear motion. The contributions from the interference occurring between the scattering amplitudes originating from the different constituent atoms of the molecule are not included in the AR model, so, even taking into consideration the overlapping effect of electron clouds in the modified potential, the results of TCS using the AR model show large discrepancies at lower energies, especially below 100eV.

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