

Electron scattering by triatomics: SO₂, CS₂ and OCS at intermediate energies

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Abstract. Differential, integrated elastic and momentum transfer cross sections have been calculated for the scattering of electrons by SO₂, CS₂ and OCS molecules in the energy range 100–1000 eV and total cross sections (elastic + absorption) over a wide incident energy range 100–4000 eV. A relatively simple approach, namely the independent atom model (IAM) with partial waves has been employed. In the present investigation static, polarization, exchange and absorption effects are taken into account. The present results agree fairly well with the experimental data and other theoretical calculations wherever available.

1. Introduction

A number of approximate methods are available to treat electron–atom scattering successfully over a wide intermediate energy range. However, for electron–molecule scattering no such equivalent method exists for the calculation of the scattering cross sections over a broad intermediate energy range for arbitrary molecular size and atomic composition. Generally the high-energy approximate methods are extended to study electron–molecule scattering in the intermediate energy range. One such method is the independent atom model (IAM) which assumes that each constituent atom of the molecule scatters independently, redistribution of the atomic electrons due to molecular binding is unimportant and the multiple scattering within the molecule is negligible (Massey *et al* 1969). Although it is a crude approximation, it has been employed successfully to study a number of molecules and the results were found to be quite encouraging when compared with the experimental data (Khare and Raj 1982, Raj 1993, Khare *et al* 1994 and references therein). In the present investigation we have extended this method to study the scattering of electrons by the three triatomics, namely SO₂, CS₂ and OCS, which are atmospheric pollutants.

These molecules, in spite of their practical importance (Zecca *et al* 1995), have received little theoretical attention. Out of these three molecules SO₂ has been studied more extensively. Previously, Orient *et al* (1982) measured the elastic differential cross sections (DCS) for e[−]–SO₂ scattering in the energy range 12–200 V, over scattering angles ranging from 15° to 150°. They extrapolated their data outside the range of their measurements to obtain the integrated elastic and momentum transfer cross sections. Trajmar and Shyn (1989) measured e[−]–SO₂ over a 5–50 eV energy range and 12–156° angular region. They also detected a normalization error in the data of Orient *et al* (1982) and suggested that their cross section values should be increased by about a factor of two. Recently, Iga *et al* (1995) measured the values of elastic differential cross sections for SO₂ in the energy range of 200–1000 eV over the angular region 10–120° using the relative flow technique.

Hayashi (1987) recommended momentum transfer cross sections for e^- -SO₂ in the 0.3–1000 eV energy region using available swarm and beam data and performing a consistency check on the transport coefficients based on the Boltzmann equation in a Monte Carlo simulation method. The total cross sections for e^- -SO₂ have been measured very recently by Zecca *et al* (1995) over a very wide incident energy range (90–4000 eV). OCS total cross sections were measured by Szmytkowski *et al* (1989) up to 100 eV and by Zecca *et al* (1995) over 90–4000 eV. The scattering of electrons on CS₂ molecules has been the subject of relatively few works; e^- -CS₂ total cross sections were measured by Szmytkowski (1987) over 0.4–100 eV using a linear transmission method.

No theoretical investigation, to the best of our knowledge, has been carried out for e^- -SO₂ scattering in the intermediate energy range. The theoretical studies on e^- -OCS and CS₂ elastic scattering have been performed by Lynch *et al* (1979) from 0–100 eV by employing the continuum multiple scattering method to obtain the total elastic cross sections. Szmytkowski (1989) carried out theoretical calculations of integral elastic cross sections for e^- -CS₂ scattering over the 1–100 eV energy range. He employed a two-centre, parametric optical potential for the description of the interaction between the projectile and the molecule. The resulting scattering equation was solved by using the variable phase approach. Thus theoretical work on these molecules for electron scattering in the intermediate energy range is very scarce. Hence in the present investigation we have obtained the elastic differential, integral and momentum transfer cross sections for e^- -SO₂, CS₂ and OCS scattering in the 100–1000 eV incident energy range and total cross sections in the 100–4000 eV incident energy range.

2. Theory

In the independent atom model (Massey *et al* 1969), the DCS averaged over all orientations of the molecular axis is given by (we express length in units of a_0 and energy in Rydberg)

$$\bar{I}_m(\theta) = \sum_{l,j=1}^N f_j(\theta) f_l^*(\theta) \sin Kr_{lj} / Kr_{lj} \quad (1)$$

where N represents the number of atoms within the molecule and $f_j(\theta)$ is the scattering amplitude due to the j th atom of the molecule. K ($= 2k \sin \theta/2$) is the magnitude of the momentum transfer during the collision by the incident particle. r_{lj} is the distance between the l th and j th atom.

The atomic scattering amplitude $f_j(\theta)$ for the constituent atoms of the molecules, namely C, O and S, was calculated in the partial waves given by

$$f_j(\theta) = \frac{1}{k} \sum_{l=0}^{L_{\max}} (2l+1) (e^{i\delta_{lj}} \sin \delta_{lj} - \delta_{lj}^B) P_l(\cos \theta) + f_{\text{dp}}^B(\theta). \quad (2)$$

To obtain δ_{lj} , the l th partial-wave phase shift for the j th atom of the molecule, the appropriate scattering equation was solved numerically under proper boundary conditions (equation (4) of Khare *et al* (1994)). The constituent atoms were replaced by an equivalent local, spherically symmetric and energy-dependent complex potential known as an optical potential. The static, dynamic polarization and exchange potential constitute the real part and the absorption potential is the imaginary part of the optical potential. The details of these potentials are given elsewhere (Khare *et al* 1994).

In equation (2) the contribution of the first $L_{\max} + 1$ partial waves is taken into account exactly, whereas the contribution of the remaining partial waves is included through the

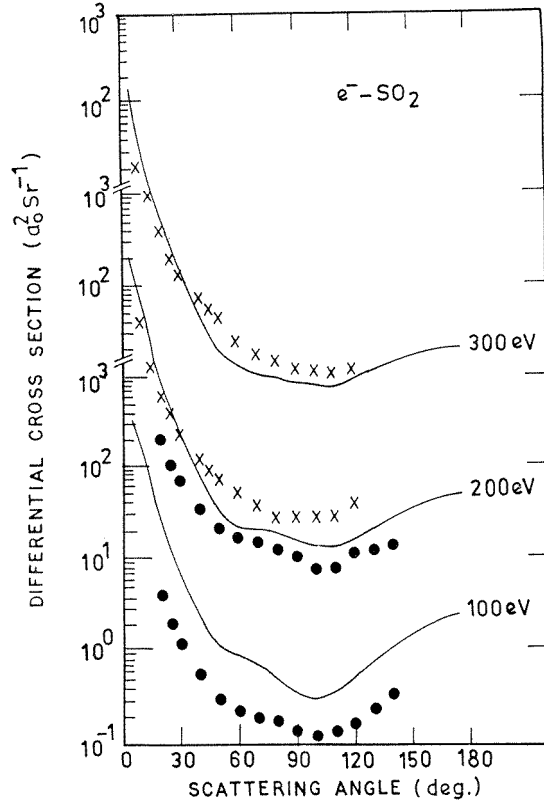


Figure 1. Elastic differential cross section for e^- -SO₂ collisions at incident energies between 100 and 300 eV. Theory: —, present work; experimental data: ×, Iga *et al* (1995), ●, Orient *et al* (1982).

first Born approximation along with the approximation that $e^{i\delta_l} \sin \delta_l \cong \delta_l^B$ for $l > L_{\max}$. The value of L_{\max} is chosen so that at $l = L_{\max}$ the relative difference between the real part of δ_{lj} and $\delta_{lj}^B \leq 2\%$. If the condition is not satisfied at any energy the maximum value of L_{\max} is taken to be 30.

For the long-range dynamic polarization potential used in the present investigation, the l th Born phase shift may be obtained from the relation (Jhanwar *et al* 1978)

$$\delta_l^B = \frac{\pi}{2} \left[-\alpha_d \frac{\partial}{\partial x} - \frac{\alpha_d x - \alpha_q}{2} \frac{\partial^2}{\partial x^2} + \frac{\alpha_q x}{3} \frac{\partial^3}{\partial x^3} + \frac{\alpha_q x^2}{24} \frac{\partial^4}{\partial x^4} \right] I_{l+1/2}(kd) K_{l+1/2}(kd) \quad (3)$$

where $x = d^2$ with $d = 0.75k/\Delta$: k is the wavenumber of the incident particle, α_d and α_q are, respectively, the dipole and quadrupole polarizabilities of the constituent atom and Δ represents the mean excitation energy, which may be calculated from the ground state properties of the atom. $I_n(z)$ and $K_n(z)$ are the modified Bessel functions. It has been found (Raj 1981) that the values of the Born phase shifts are almost identical to the corresponding semiclassical phase shifts for various incident energies and targets for the polarization potential used here. Hence, in equation (2) we have replaced the Born phase shifts by the semiclassical phase shifts. Furthermore, the evaluation of the Born phase shifts for higher partial waves is equally time consuming as the numerical integration of the

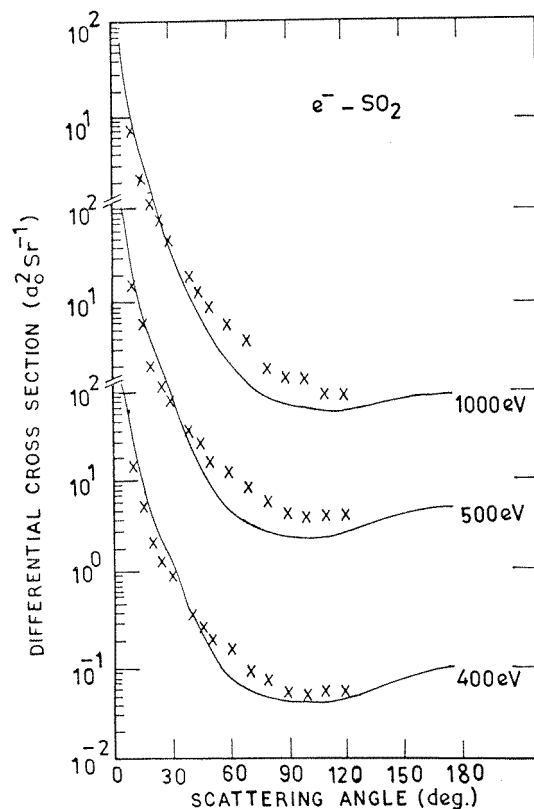


Figure 2. Elastic differential cross section for e^- - SO_2 collisions at incident energies between 400 and 1000 eV. Theory, —, present work; experimental data: \times , Iga *et al* (1995).

scattering equation. However, the semiclassical phase shifts need negligible computer time for their evaluation.

For the same polarization potential one obtains in the first Born approximation,

$$f_{dp}^B(\theta) = \frac{\pi}{4d} \left[\frac{1}{4} \alpha_d (3 - Kd) + \frac{5\alpha_q}{64d^2} (1 + Kd - \frac{2}{3} K^2 d^2 + \frac{1}{15} K^3 d^3) \right] e^{-Kd}. \quad (4)$$

Finally, $\bar{I}_m(\theta)$ is calculated from equation (1). The integrated elastic cross section $Q_I(E)$ and the momentum transfer cross section, $Q_M(E)$ were obtained by integrating $\bar{I}_m(\theta)$ with appropriate weighting factors given by, respectively,

$$Q_I(E) = \int \bar{I}_m(\theta) d\Omega \quad (5)$$

$$Q_M(E) = \int \bar{I}_m(\theta) (1 - \cos \theta) d\Omega. \quad (6)$$

The total cross section $Q_T(E)$ (elastic + absorption) of the molecule was obtained using the optical theorem

$$Q_T(E) = (4\pi/k) \text{Im } F_m(\theta = 0) \quad (7)$$

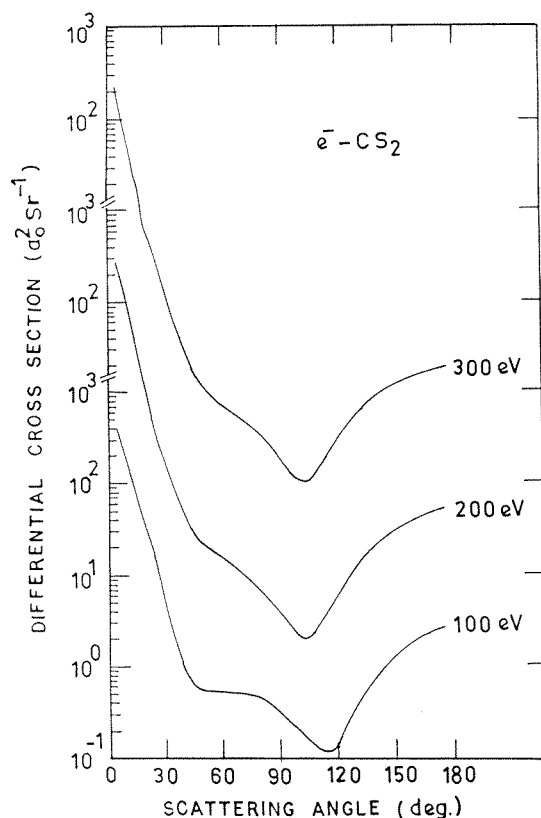


Figure 3. Elastic differential cross section for e^- -CS₂ collisions at incident energies between 100 and 300 eV.

where $F_m(\theta)$ is the molecular scattering amplitude which in IAM is given by the relation

$$F_m(\theta) = \sum_{j=1}^N f_j(\theta) e^{i\mathbf{K} \cdot \mathbf{r}_j} \quad (8)$$

The present results of DCS over the incident energy range 100–1000 eV along with available experimental data are presented in figures 1–6. Our values of the integrated elastic, momentum transfer and the total cross section are given in tables 1 and 2 for e^- scattering by SO₂, CS₂ and OCS.

3. Results and discussion

We start by discussing differential cross sections for e^- -SO₂ scattering. Figures 1 and 2 show the e^- -SO₂ differential scattering cross sections along with the available experimental data of Orient *et al* (circles) and Iga *et al* (crosses). Orient *et al* (1982) measured the elastic differential cross sections (DCS) for e^- -SO₂ scattering in the energy range 12–200 eV and over scattering angles ranging from 15–150°. They extrapolated their data outside the range of their measurements to obtain the integrated elastic and momentum transfer cross sections. Recently, Trajmar and Shyn (1989) have measured the values of

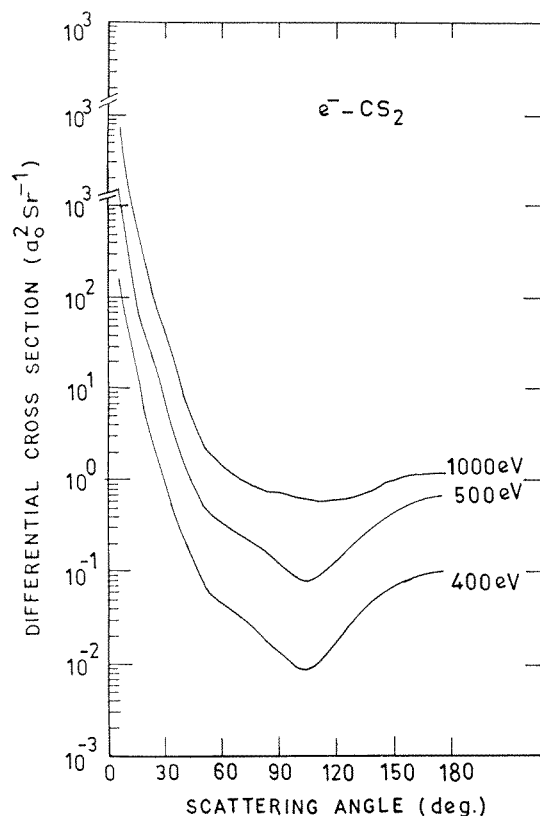


Figure 4. Elastic differential cross section for e^- -CS₂ collisions at incident energies between 400 and 1000 eV.

DCS for e^- -SO₂ elastic scattering for incident energies 5–50 eV over the angular region 12–156°. Trajmar and Shyn (1989) have detected the normalization error in the data of Orient *et al* (1982) and suggested that the cross section values of Orient *et al* should be increased by about a factor of two. The present investigation is consistent with this observation of Trajmar and Shyn as is evident from figure 1. It may be noted that present values of EDCS at 100 and 200 eV are almost double the values of Orient *et al* (1982). However, the qualitative behaviour of the present results is almost similar to that of Orient *et al* (●). The minor variations in the data are reproduced by the theoretical curve. We have also included the relative data of Iga *et al* (×) for comparison in the 200–1000 eV energy range and over the 10–120° angular region. It is evident from figures 1 and 2 that our values are slightly higher than the experimental data of Iga *et al* (1995) for the scattering angles $\theta \leq 30^\circ$ and slightly lower for $\theta > 30^\circ$. There is no other theoretical investigation, to our knowledge, for e^- -SO₂ elastic scattering in the intermediate energy range.

Figures 3 and 4 show the elastic differential cross sections (DCS) for the e^- -CS₂ molecule. Figures 5 and 6 show the DCS for the e^- -OCS molecule. No theoretical or experimental work seems to be available on the elastic differential cross sections for these two molecules in the present energy range. Since the present approach has yielded quite encouraging results for the SO₂ molecule, it is expected that the present values of the

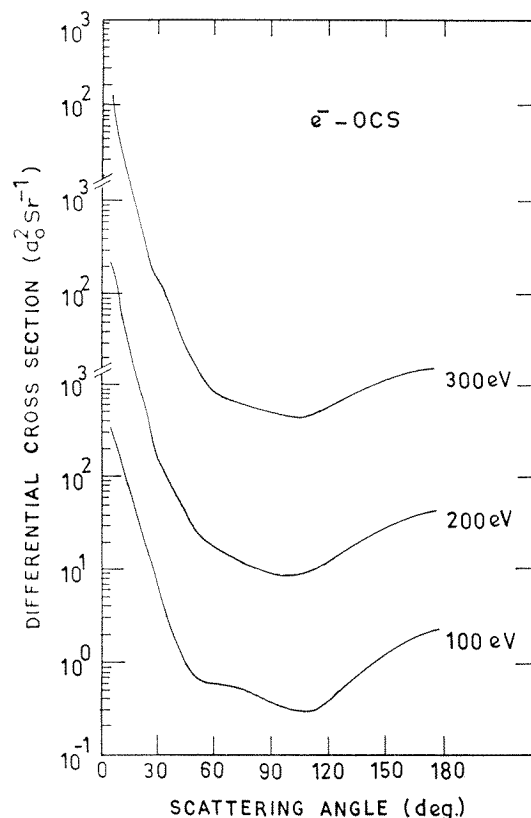


Figure 5. Elastic differential cross section for e^- -OCS collisions at incident energies between 100 and 300 eV.

differential cross section for electron scattering by CS_2 and OCS molecules may also be fairly reliable.

Table 1 shows the integrated elastic (Q_1) and the momentum transfer (Q_M) cross sections for e^- - SO_2 , CS_2 and OCS molecules in the energy range 100–1000 eV. For integrated elastic cross sections of SO_2 we have included the data of Orient *et al* (1982) and Zecca *et al* (1995) which are available only at 100 and 200 eV. It may be noted that although Zecca *et al* (1995) have measured the total cross sections, they have also derived elastic cross sections by subtracting averaged ionization cross sections from their total cross section value at 100 and 200 eV. They have assumed that ionization contributes about 40–45% of the total cross section at 100 and 200 eV for SO_2 . Present values of Q_1 are closer to the derived values of Q_1 by Zecca *et al* (1995) than the data of Orient *et al* at 100 and 200 eV. The agreement of our value at 200 eV with the value of Zecca *et al* is quite satisfactory. However, at 100 eV the present value is much higher than their value. 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 100 eV will reduce the cross section (Hayashi and Kuchitsu 1976) by a significant amount. The likely effect of the

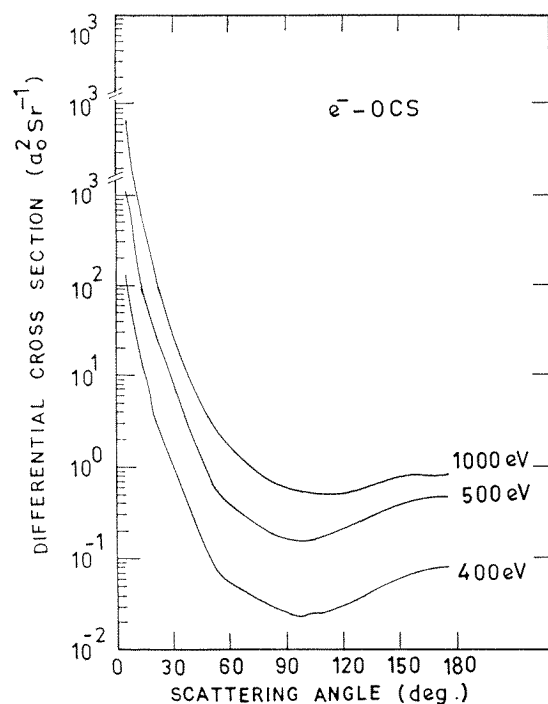


Figure 6. Elastic differential cross section for e^- -OCS collisions at incident energies between 400 and 1000 eV.

Table 1. Calculated and measured values of the integrated elastic (Q_I) and momentum transfer (Q_M) cross sections (in units of a_0^2) for electron scattering by SO_2 , CS_2 and OCS molecules at various impact energies.

E (eV)	SO ₂				CS ₂		OCS	
	Q_I		Q_M		Q_I	Q_M	Q_I	Q_M
	Theory present	Expt	Theory present	Expt				
100	67.4	9.2 ^a 30.4 ^b	13.3	3.8 ^a 9.3 ^c	73.5	9.8	64.7	10.8
200	29.4	4.5 ^a 25.0 ^b	3.9	1.9 ^a 5.4 ^c	54.7 ^d , 53.6 ^e 33.8	2.5	46.3 ^d 29.2	3.0
300	19.8	—	2.0	3.4 ^c	23.3	1.2	19.8	1.5
400	15.4	—	1.2	2.5 ^c	18.2	0.8	15.4	0.9
500	12.7	—	0.8	2.0 ^c	15.0	0.6	12.7	0.6
1000	7.1	—	0.3	1.0 ^c	8.3	0.3	6.9	0.23

^a Orient *et al* (1982).

^b Zecca *et al* (1995).

^c Hayashi (1987).

^d Lynch *et al* (1979).

^e Szmytkowski (1989).

valence bond distortion is also to reduce the cross section (Bonham and Iijima 1963). In the present approach IAM also ignores the effect of molecular permanent dipole moments.

Table 2. Calculated and measured values of the total cross section (elastic + absorption) (in units of a_0^2) for electron scattering by SO₂, CS₂ and OCS molecules at various energies.

E (eV)	SO ₂		OCS		CS ₂	
	Theory present	Expt Zecca <i>et al</i> (1995)	Theory present	Expt Zecca <i>et al</i> (1995)	Theory present	Expt
100	67.0	54.3	71.6	71.1 72.1 ^a	88.4	83.2 ^b
200	40.9	44.3	44.7	48.6	56.1	—
300	31.8	37.5	34.6	41.1	43.5	—
400	26.5	30.6	28.8	33.6	36.3	—
500	22.9	26.4	24.8	27.1	31.4	—
576	20.8	23.8	22.5	24.9	28.6	—
900	15.3	17.5	16.4	18.1	21.0	—
1000	14.2	—	15.2	15.8	19.5	—
1300	11.7	13.3	12.5	13.1	16.1	—
1600	10.0	11.3	10.6	10.9	13.8	—
2500	7.0	7.2	7.4	7.0	9.7	—
3500	5.3	5.3	5.5	5.3	7.3	—
4000	4.7	4.7	4.9	4.6	6.5	—

^a Szmytkowski *et al* (1989).^b Szmytkowski (1987).

Since SO₂ has an appreciable permanent dipole moment, its inclusion is expected to increase the values of the cross sections at low incident energies (Gulley and Buckman 1994). Hence the present value of Q_1 at 100 eV is not expected to be reliable. No theoretical calculations for the integrated elastic cross section for e[−]–SO₂ are available in the present energy range.

Lynch *et al* (1979) and Szmytkowski (1989) carried out the theoretical calculations of the integrated elastic cross section for electron scattering by the CS₂ molecule over an incident energy range of 0–100 eV. However, for e[−]–OCS scattering the only theoretical investigation, to our knowledge, is that of Lynch *et al* (1979) over the same incident energy range. It may be noted (table 1) that the present values of the integrated elastic cross section at 100 eV are much higher than their values for both the molecules. The reason again may be the neglect of the multiple scattering and valence bond distortion in the present investigation which have been found to be significant at low incident energies and are expected to reduce the cross sections. Furthermore, OCS has a permanent dipole moment and its inclusion is expected to increase its cross sections at low incident energies. Table 1 also shows the momentum transfer cross sections for the three molecules investigated along with the available experimental data. In comparing the values of momentum transfer cross section for e[−]–SO₂ scattering with those of Orient *et al* (1982) the same remarks apply as for the differential cross section and the integrated elastic cross section. Hayashi (1987) recommended momentum transfer cross sections for e[−]–SO₂ in the 0.3–1000 eV energy range using available swarm and beam data and performing a consistency check on transport coefficients based on the Boltzmann equation in a Monte Carlo simulation method. Our values of Q_M are much smaller than the values recommended by Hayashi (1987) at all the incident energies investigated except at 100 eV. Furthermore, the difference between the two values increases with the increase of incident energy. The reason remains obscure. No theoretical or experimental data are available for the

momentum transfer cross section Q_M for the CS_2 and OCS molecules in the present energy range.

Table 2 shows the present total cross section results (elastic + absorption) along with the experimental data available for e^- - SO_2 , CS_2 and OCS scattering over a very wide incident energy range 100–4000 eV. It is evident from table 2 that the present values of TCS for e^- - SO_2 and OCS are in very good agreement with the experimental data of Zecca *et al* (1995) throughout the whole incident energy range investigated. For OCS there is good consistency between the two experimental values (Zecca *et al* 1995, Szmytkowski *et al* 1989) at 100 eV which is in excellent agreement with the present value. For CS_2 the present value of TCS also agrees fairly well with the experimental data of Szmytkowski (1987) which is available for 100 eV only within the energy range of the present investigation. In the present energy range, no other theoretical work seems to be available on these molecules for the total cross section.

The present approach (IAM) along with the partial waves has yielded the values of elastic DCS for e^- - SO_2 scattering in very good qualitative and to a lesser extent in quantitative agreement with the absolute data of Orient *et al* (1982) and the relative data of Iga *et al* (1995). The present values of EDCS for e^- - SO_2 also confirm the observation of Trajmar and Shyn (1989) who detected a normalization error in the data of Orient *et al* and suggested that their values of DCS should be multiplied by about a factor of two. It is evident from figure 1 that if the data of Orient *et al* at 100 and 200 eV are multiplied by a factor of two the agreement with the present values will be fairly good. However, the situation in the case of the integrated cross sections is less clear because no absolute direct measurements or other theoretical work are available for comparison over a wide incident energy range for either of the molecules investigated. The agreement of our values of TCS (elastic + absorption) for e^- - SO_2 and OCS with the experimental data (Zecca *et al* 1995, Szmytkowski *et al* 1989) is excellent over the entire energy range of the present investigation. However, for better understanding of the phenomena and to arrive at a definite conclusion, we stress the need for more theoretical and experimental work on these molecules.

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