Elastic and total cross sections for electron–carbon disulfide collisions

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Abstract. In this work, we report on a theoretical study of electron–CS_2 collision in the low- and intermediate-energy range. More specifically, the elastic differential and integral cross sections as well as the grand total (elastic + inelastic) cross sections in the 0.05–100 eV range are reported. A complex optical potential consisting of static, exchange, correlation-polarization plus absorption contributions, derived from a fully molecular wavefunction, is used for the electron–molecule interaction. The Schwinger variational iterative method combined with the distorted-wave approximation are applied to calculate the scattering amplitudes. The comparison between the calculated results and the existing experimental and theoretical results is encouraging.

1. Introduction:

From the scientific point of view, CS_2 is a valence isoelectronic system of N_2O and CO_2. These molecules constitute a series of closely related linear triatomic systems, the simplest extension beyond diatomic molecules. The similarity of their electronic ground-state configurations may lead to resemblances in the electron impact spectra. However, CS_2 is different from N_2O and CO_2 in an important aspect. The sulfur atoms present in CS_2 with low-lying d orbitals can influence both the chemical bonding (Hehere *et al* 1986) and the ionization dynamics.

Although carbon dioxide and carbon disulfide are both important molecules for atmospheric studies, the electron scattering by CS_2 has attracted relatively little attention in the last few decades. Some early experimental investigations dealt mainly with dissociative attachment (Kraus 1961, Dorman 1966, Ziesel *et al* 1975, Dressler *et al* 1987) and electron-impact excitation processes (Hubin-Frankin *et al* 1983, Dance *et al* 1978, Wilden and Comer 1980, Ajello and Srivastava 1981) of this molecule. The only measurement of absolute differential cross sections (DCS) for vibrationally elastic and inelastic electron–CS_2 collisions in the 0.3–5.0 eV range were reported by Sohn *et al* (1987). Lately, Szmytkowski (1987) have reported absolute grand total (elastic plus inelastic) cross sections (TCS) for incident energies up to 100 eV.

On the theoretical side, the literature is even scarcer. The first theoretical investigation on electron–CS_2 scattering was carried out by Lynch *et al* (1979). These authors reported integral cross sections (ICS) for elastic electron–CS_2 scattering calculated using the continuum multiple-scattering method (CMSM), in the 0.4–100 eV incident energy range. One important finding of their study is the sharp resonance in the $k\pi_u$ scattering channel located at around 1.85 eV. Nevertheless, this resonance structure was not seen in the experiments of Sohn

et al (1987) and Szmytkowski (1987). Szmytkowski (1989) reported calculated ICS for this molecule in the 1–100 eV range using a two-centre parametric optical potential for electron–molecule interaction. His calculated ICS are in better agreement with the experimental results than those of Lynch *et al* (1979), particularly at incident energies below 2 eV. The only calculation of the DCS for elastic electron–CS_2 scattering was reported recently in the 100–4000 eV range by Raj and Tomar (1997). A very simple theoretical approach, namely the independent atom model was used in their study.

In the present investigation, we report a theoretical study on electron scattering by CS_2 in the low- and intermediate-energy range. More specifically, the calculated elastic DCS and ICS as well as the TCS are presented for electron impact energies up to 100 eV. A complex optical interaction potential, derived from a fully molecular near-Hartree–Fock SCF wavefunction, is applied to describe the electron–molecule interaction. The Lippmann–Schwinger scattering equations are solved using the Schwinger variational iterative method (SVIM, Lucchese *et al* 1982, Lee *et al* 1992) combined with the distorted-wave approximation (DWA, Lee and McKoy 1983, Lee *et al* 1990a, Michelin *et al* 1996). This ansatz has been applied recently with success by Lee and Iga (1999) to the elastic electron scattering by the nitrogen molecule over a wide (20–800 eV) energy range. Therefore, its application to the study of electron collision on CS_2 is a natural extension of the method.

This paper is organized as follows. In section 2, we describe briefly the theory used and also some details of the calculation. In section 3 we compare our calculated results with some experimental data and with some other theoretical data available in the literature.

2. Theory and calculation

Since details of the SVIM and the DWA have already been presented elsewhere (Lucchese *et al* 1982, Lee and McKoy 1983), here we will only outline briefly the theory used. After carrying out the average of the molecular orientation, the j_t basis representation (Fano and Dill 1972) of the laboratory-frame (LF) DCS for elastic electron–CS_2 scattering is given by

$$\frac{d\sigma}{d\Omega} = \frac{\pi}{k^2} \sum_{j_t m_t m_t'} \frac{1}{(2j_t + 1)} |B_{m_t m_t'}^{j_t}|^2 \tag{1}$$

where k is the linear momentum of the incoming electron, $\vec{j}_t = \vec{l}' - \vec{l}$ is the transferred angular momentum during the collision, with projections m_t' and m_t along the laboratory and molecular axis, respectively. In equation (1), the $B_{m_t m_t'}^{j_t}$ is the coefficient of the j_t-basis expansion of the LF scattering amplitudes and is given by

$$B_{m_t m_t'}^{j_t}(\Omega') = \sum_{l'lm'm} (-1)^m a_{ll'mm'} (ll'0m_t | j_t m_t)(ll'mm' | j_t m_t') Y_{lm_l}(\Omega') \tag{2}$$

where the dynamical coefficients $a_{ll'mm'}$ are related to the partial-wave components of the elastic T-matrix as

$$a_{ll'mm'} = -\tfrac{1}{2}\pi [4\pi(2l' + 1)]^{1/2} i^{l'-l} \langle k_n lm, n|T|k_0 l' - m, 0\rangle. \tag{3}$$

The elastic scattering T-matrix is calculated using a complex optical potential, given by

$$V_{\text{opt}}(\vec{r}) = V^{\text{SEP}}(\vec{r}) + iV_{\text{ab}}(\vec{r}) \tag{4}$$

where V^{SEP} is the real part of the interaction potential formed by the static, the exchange and the correlation-polarization contributions as

$$V^{\text{SEP}}(\vec{r}) = V_{\text{st}}(\vec{r}) + V_{\text{ex}}(\vec{r}) + V_{\text{cp}}(\vec{r}) \tag{5}$$

and V_{ab} is the absorption potential. In our calculation, V_{st} and V_{ex} are treated exactly, while V_{cp} is obtained within the framework of the free-electron-gas (FEG) model derived from a parameter-free local density, as prescribed by Padial and Norcross (1984). The dipole polarizabilities $\alpha_0 = 59.04$ au and $\alpha_2 = 43.233$ au (Böttcher *et al* 1973) were used to calculate the asymptotic form of V_{cp}. The absorption potential V_{ab} in equation (4) is given by (Staszewska *et al* 1984)

$$V_{ab}(\vec{r}) = -\rho(\vec{r})(T_L/2)^{1/2}(8\pi/5k^2 k_F^3)H(\alpha + \beta - k_F^2)(A + B + C) \qquad (6)$$

where

$$T_L = k^2 - V^{SEP} \qquad (7)$$
$$A = 5k_F^3/(\alpha - k_F^2) \qquad (8)$$
$$B = -k_F^3(5(k^2 - \beta) + 2k_F^2)/(k^2 - \beta)^2 \qquad (9)$$

and

$$C = 2H(\alpha + \beta - k^2)\frac{(\alpha + \beta - k^2)^{5/2}}{(k^2 - \beta)^2}. \qquad (10)$$

In equations (6)–(10), k^2 is the energy (in Rydbergs) of the incident electron, k_F the Fermi momentum and $\rho(\vec{r})$ the local electronic density of the target. $H(x)$ is a Heaviside function defined by $H(x) = 1$ for $x \geqslant 0$ and $H(x) = 0$ for $x < 0$. According to the quasi-free-scattering model version 3 of Staszewska *et al* (1984),

$$\alpha(\vec{r}, E) = k_F^2 + 2(2\Delta - I) - V^{SEP} \qquad (11)$$

and

$$\beta(\vec{r}, E) = k_F^2 + 2(I - \Delta) - V^{SEP} \qquad (12)$$

where Δ is the mean excitation energy and I is the ionization potential. In this study, the published ionization potential $I = 0.370$ Hartree (Herzberg 1966) is used and the mean excitation energy to the target is assumed to be the same as I as suggested by Jain and Baluja (1992), since the calculated values of Δ and I are very close to each other for a variety of molecules.

To proceed, the interaction potential is split as

$$V_{opt} = U_1 + U_2 \qquad (13)$$

where U_1 is taken as the real part of the complex optical potential, whereas U_2 is the imaginary absorption potential. The corresponding distorted wavefunctions satisfy the following scattering equation:

$$(H_0 + U_1 - E)\chi = 0 \qquad (14)$$

which is solved using the SVIM (Lucchese *et al* 1982). Furthermore, the absorption part of the T-matrix is calculated via DWA as

$$T_{ab} = i\langle \chi_f^- | V_{ab} | \chi_i^+ \rangle. \qquad (15)$$

In the SVIM calculations, the continuum wavefunctions are single-centre expanded as:

$$\chi_{\vec{k}}(\vec{r}) = (2/\pi)^{1/2} \sum_{lm} \frac{(i)^l}{k} \chi_{klm}(\vec{r}) Y_{lm}(\hat{k}) \qquad (16)$$

where $Y_{lm}(\hat{k})$ are the usual spherical harmonics.

The calculation of $\chi_{\vec{k}}(\vec{r})$ starts with the expansion of the trial functions in a set R_0 of L^2-basis functions $\alpha_i(\vec{r})$ as follows:

$$\tilde{\chi}_{k,lm}(\vec{r}) = \sum_{i=1}^{N} a_{i,lm}(k)\,\alpha_i(\vec{r}). \tag{17}$$

Using this basis set, the reactance K-matrix elements can be derived as

$$K_{k,ll'm}^{(R_0)} = \sum_{i,j=1}^{N} \langle \Phi_{k,l'm}|U_1|\alpha_i\rangle [D^{-1}]_{ij}\langle \alpha_j|U_1|\Phi_{k,lm}\rangle \tag{18}$$

where $\Phi_{k,lm}$ are the partial-wave free-particle wavefunctions and

$$D_{ij} = \langle \alpha_i|U_1 - U_1 G_0^{(P)} U_1|\alpha_j\rangle. \tag{19}$$

Here $G_0^{(P)}$ is the principal value of the free-particle Green's operator and the zeroth-iteration wavefunction $\chi_{k,lm}^{R_0}$ is calculated using equation (17) with appropriately calculated coefficients $a_{i,lm}$. As demonstrated by Lucchese *et al* (1982), the converged scattering solutions can be obtained via an iterative procedure. This procedure consists in augmenting the basis set R_0 by the set

$$S_0 = \{\chi_{k,l_1m_1}^{(P)(R_0)}(\vec{r}), \chi_{k,l_2m_2}^{(P)(R_0)}(\vec{r}), \ldots, \chi_{k,l_cm_c}^{(P)(R_0)}(\vec{r})\} \tag{20}$$

where l_c is the maximum value of l for which the expansion of the scattering solution (16) is truncated, and $m_c \leqslant l_c$. A new set of partial-wave scattering solutions can now be obtained from

$$\chi_{k,lm}^{(P)(R_1)}(\vec{r}) = \Phi_{k,lm}(\vec{r}) + \sum_{i,j=1}^{M} \langle \vec{r}|G^{(P)}U_1|\eta_i^{(R_1)}\rangle [D^{-1}]_{ij}\langle \eta_j^{(R_1)}|U_1|\Phi_{k,lm}\rangle \tag{21}$$

where $\eta_i^{(R_1)}(\vec{r})$ is any function in the set $R_1 = R_0 \cup S_0$ and M is the number of functions in R_1. This iterative procedure continues until a converged $\chi_{k,lm}^{(P)(R_n)}(\vec{r})$ is achieved. In the present calculations, three iterations are needed to obtain the converged scattering functions.

The electronic configuration of the ground-state CS_2 is $1\sigma_u^2 1\sigma_g^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 4\sigma_g^2 1\pi_g^4$ $1\pi_u^4 5\sigma_g^2 4\sigma_u^2 6\sigma_g^2 5\sigma_u^2 2\pi_u^4 2\pi_g^4$, X $^1\Sigma_g^+$. The SCF wavefunctions are derived from a standard [10s6p/5s3p] basis set (Dunning 1971) augmented by three s ($\alpha = 0.0453, 0.0157$ and 0.00537), two p ($\alpha = 0.032\,37$ and 0.934) and one d ($\alpha = 1.673$) uncontracted functions on the carbon centre and from a standard [9s5p/6s4p] basis set (Huzinaga 1965) augmented by two s ($\alpha = 0.0459$ and 0.0178), two p ($\alpha = 0.0502$ and 0.0153) and one d ($\alpha = 1.533$) uncontracted functions on the sulfur centres. With this basis set, the calculated SCF energy, at the experimental equilibrium geometry of the ground-state CS_2 ($R_{C-S} = 2.937\,62$ au) is -832.85 au. This result compares well with the corresponding RHF value of -832.8841 au and MCSCF value of -832.9207 au (Tseng and Poshuta 1994).

All matrix elements appearing in these calculations were computed by a single-centre expansion technique with the radial integral evaluated using a Simpson quadrature. The contributions from the direct and exchange parts were truncated at $l = 119$ and 40, respectively. In the SVIM calculations, the partial-wave expansion of the scattering wavefunctions is limited to $l_{max} = 40$ and $m_{max} = 7$. Furthermore, contributions from the higher partial waves were accounted for via the Born-closure procedure, where the $B_{m_tm'_t}^{j_t}$ is given by

$$B_{m_tm'_t}^{j_t}(\hat{k}') = B_{m_tm'_t}^{\mathrm{Born},j_t}(\hat{k}') + \sum_{l'lmm'}(-1)^m(\mathrm{i})^{l-l'}(2l+1)^{-1}(T_{ll'mm'}^S - T_{ll'mm'}^{\mathrm{Born}})$$

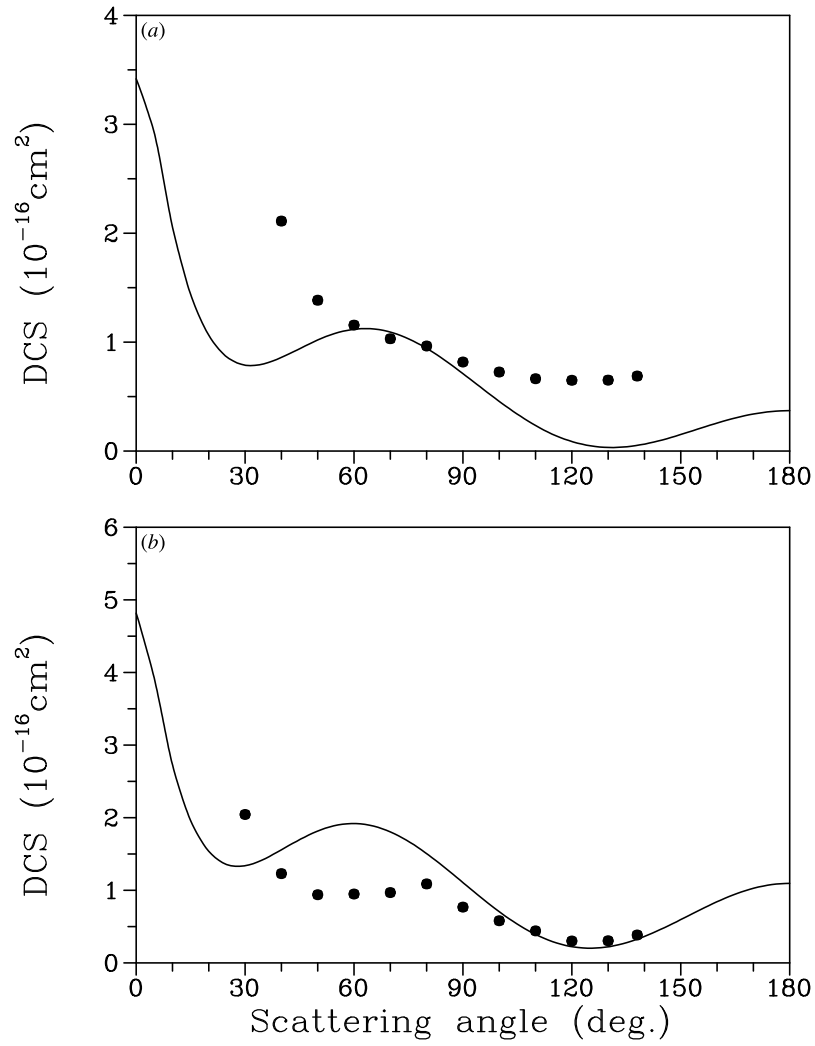$$\times (l-m, l'm'|j_t'm_t')(l0, l'm_t|j_tm_t)Y_{l'm_t}(\hat{k}'). \tag{22}$$

Figure 1. Elastic differential cross sections for e⁻–CS₂ scattering at (*a*) 0.5 eV, (*b*) 0.8 eV. Full curve, present SVIM results; full circles, experimental data of Sohn *et al* (1987).

In equation (22), $B^{\mathrm{Born},\,j_\mathrm{t}}_{m_\mathrm{t}m'_\mathrm{t}}(\hat{k}')$ is the j_t-basis representation of the Born scattering amplitude, defined as

$$B^{\mathrm{Born},\,j_\mathrm{t}}_{m_\mathrm{t}m'_\mathrm{t}}(\hat{k}') = \frac{(2j_\mathrm{t}+1)}{8\pi^2}\frac{k}{\mathrm{i}\pi^{(1/2)}}\int \mathrm{d}\hat{R}'\, f^{\mathrm{Born}}(\hat{R}';\hat{k}')\, D^{j_\mathrm{t}*}_{m_\mathrm{t}m'_\mathrm{t}}(\hat{R}') \tag{23}$$

where $D^{j_\mathrm{t}*}_{m_\mathrm{t}m'_\mathrm{t}}(\hat{R}')$ are the usual rotation matrices and $T^{\mathrm{Born}}_{ll'mm'}$ is the partial-wave Born T-matrix element given by

$$T^{\mathrm{Born}}_{ll'mm'} = \langle \Phi_{klm}|U_{\mathrm{st}}|\Phi_{kl'm'}\rangle. \tag{24}$$
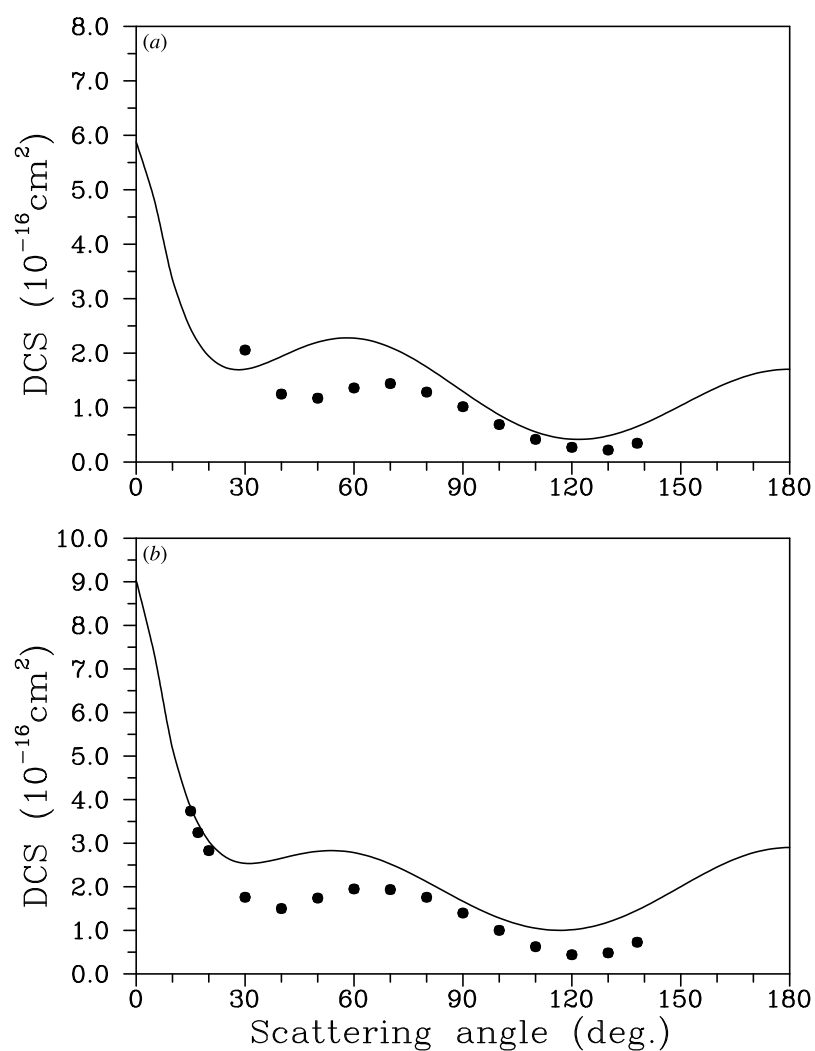
Figure 2. Same as figure 1 at (*a*) 1.0 eV, (*b*) 1.5 eV.

Moreover, the total cross sections (TCS) for electron–molecule scattering are obtained using the optical theorem, namely

$$\sigma_{\text{tot}} = \frac{4\pi}{k} \, \text{Im} \, f_{\text{el}}(\theta = 0^\circ) \tag{25}$$

where f_{el} is the scattering amplitude for elastic electron–molecule collisions.

3. Results and discussion

In figures 1–4 we show our calculated DCS for elastic electron–CS_2 scattering in the 0.5–5 eV energy range along with the measured absolute data of Sohn *et al* (1987). In contrast with the data reported by Sohn *et al*, our calculated results are vibrationally unresolved. Therefore, the comparison is made with the sum of their vibrationally elastic DCS and the cross sections for
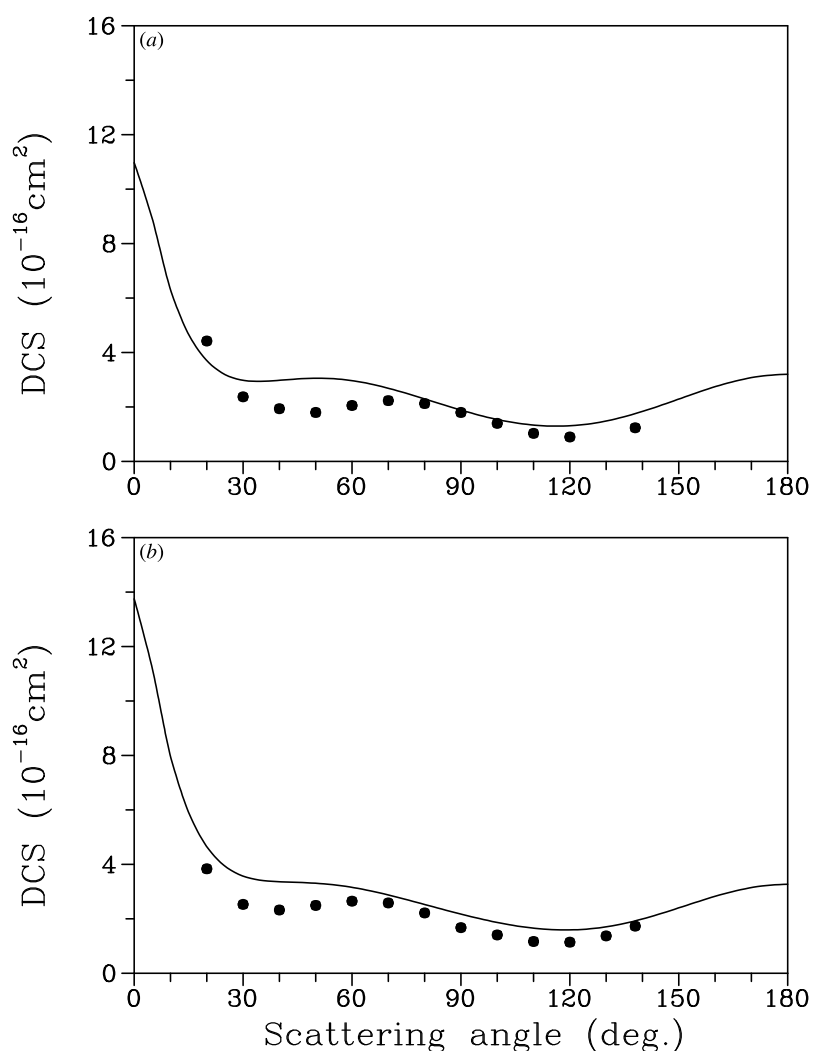
Figure 3. Same as figure 1 at (*a*) 1.8 eV, (*b*) 2.2 eV.

the $v = 0 \rightarrow v' = 1$ vibrational excitations, including both the stretching and bending modes. DCS for excitation to higher vibrational levels are small and are then neglected. In general, there is a good qualitative agreement between the calculated and measured data in this energy range except for 0.5 eV. At that energy, the calculation has shown two minima at around 60° and 120°, not seen in the experimental data. Quantitatively, the agreement between the calculated and measured data is fair, but improving with increasing incident energies. Unfortunately, there are no available experimental results reported for incident energies above 5 eV, which seriously limits the discussion.

The discrepancy at lower energies is probably due to electronic correlation effects of the target, not taken into account in the present study. Indeed, the inclusion of the influences of target correlation on electron–molecule scattering cross sections is a difficult task. To date, very few investigations on this subject have been reported in the literature (McCurdy 1992, Lee *et al* 1990b, Tanaka *et al* 1998). Recently, we have also investigated the target correlation
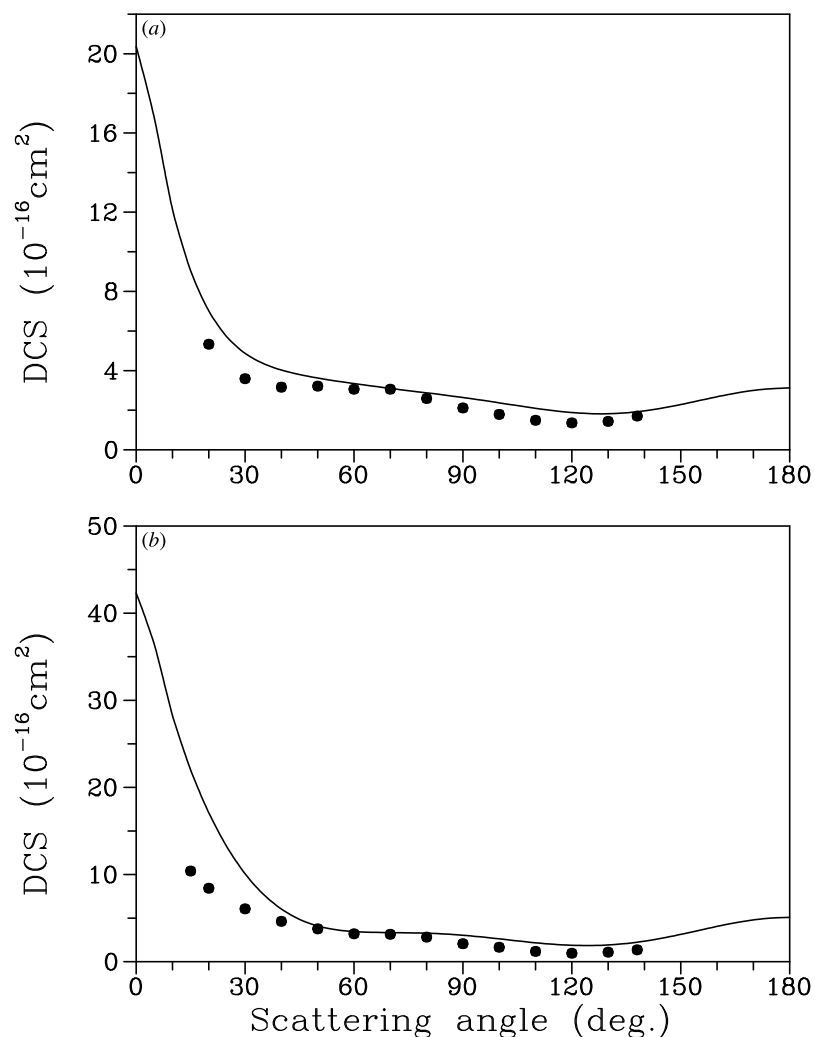
Figure 4. Same as figure 1 at (*a*) 3.0 eV, (*b*) 5.0 eV.

effects on vibrationally elastic and inelastic electron–H_2 scattering in the 1–60 eV range (Lee and Fujiwara 1998). Our studies have revealed that the electronic correlation of the target influences the calculated cross sections significantly at energies below 2 eV. Nevertheless, it is not important for high incident energies.

In figures 5(*a*) and (*b*) we show the calculated ICS and TCS in the 0.05–100 eV range along with the experimental ICS of Sohn *et al* and the measured TCS of Szmytkowski (1987), respectively. The calculated ICS of Lynch *et al* (1979) using the CMSM and Szmytkowski (1989) are also shown for comparison. Our ICS are in reasonable agreement with the measured data of Sohn *et al* in the 0.5–5 eV energy range. In addition, the calculated TCS up to 100 eV are in very good agreement with the experimental data of Szmytkowski (1987, 1989). Nevertheless, the Ramsauer minimum seen in the experimental ICS and TCS at around 0.8 eV is shifted to 0.2 eV in the present study. This shift is probably also due to the neglect of the electronic correlation of the target. Comparing with other theoretical studies, our ICS are in
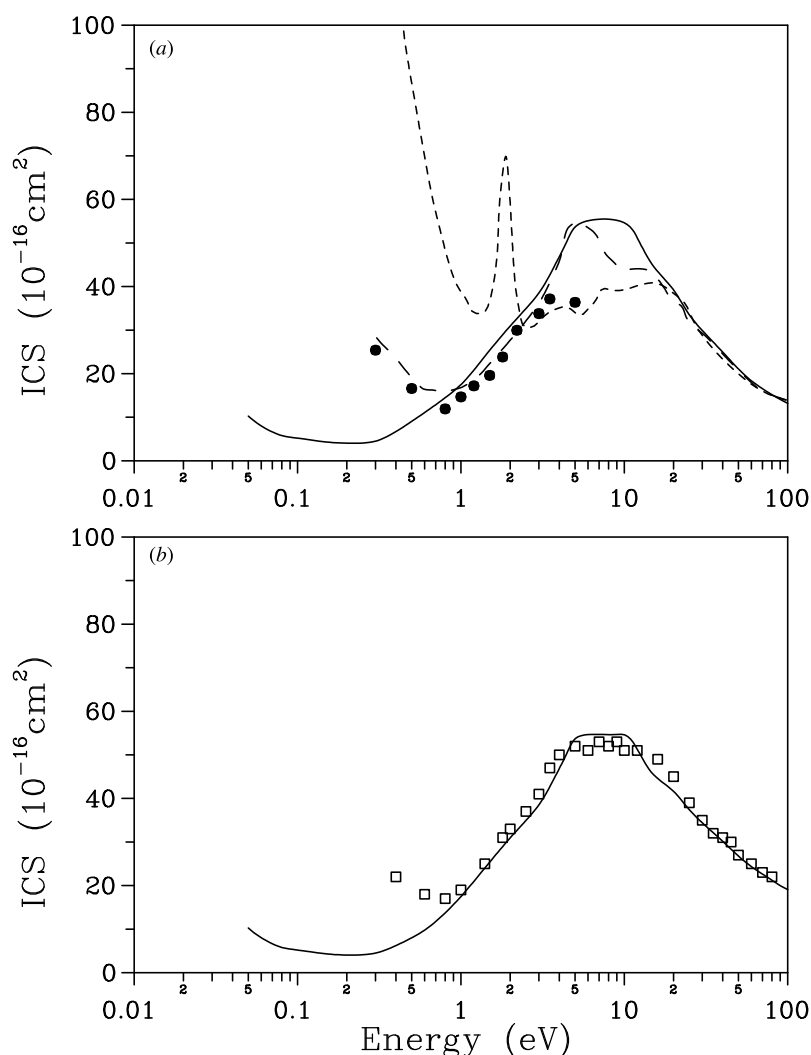
Figure 5. (*a*) Elastic ICS and (*b*) TCS for electron–CS_2 collisions. Full curve, present calculated results; short-broken curve, calculated results of Lynch *et al* (1979); broken curve, calculated results of Szmytkowski (1989); full circles, experimental data of Sohn *et al* (1987); open squares, experimental data for TCS of Szmytkowski (1987).

general good agreement with the calculated ICS of Szmytkowski (1989). The position of the Ramsauer minimum in their calculation is in better agreement with experiment than ours. It is not surprising since in their calculation, they have employed parameter-dependent interaction potentials. On the other hand, the CMSM results of Lynch *et al* (1979) disagree significantly with our calculated ICS and TCS. In particular, the sharp resonance at around 1.8 eV in their study does not show up in our investigation.

For the sake of completeness, in table 1 we show the calculated DCS and ICS for incident energies $E_0 \geqslant 10$ eV.

In summary, we present a theoretical study of elastic electron scattering by CS_2 molecules in the low- and intermediate-energy range. The calculated elastic DCS in the 0.5–100 eV

Table 1. DCS and ICS (in 10^{-16} cm^2) for elastic e$^-$–CS$_2$ scattering.

Angle (deg)	E_0 (eV)				
	10	12	20	50	100
0	70.31	73.33	90.08	106.98	116.22
10	47.81	49.33	52.10	42.90	30.61
20	26.71	26.80	22.01	10.39	4.93
30	12.69	12.06	8.25	3.15	1.04
40	5.89	5.53	4.15	0.95	0.40
50	3.63	3.70	2.37	0.53	0.27
60	2.82	2.83	1.14	0.38	0.21
70	2.16	1.90	0.92	0.30	0.17
80	1.75	1.43	1.24	0.22	0.17
90	1.65	1.52	1.39	0.19	0.11
100	1.65	1.71	1.27	0.19	0.06
110	1.69	1.66	1.06	0.29	0.05
120	1.79	1.46	0.87	0.50	0.08
130	1.98	1.31	0.73	0.77	0.18
140	2.18	1.29	0.65	1.08	0.37
150	2.44	1.47	0.63	1.39	0.62
160	2.89	1.95	0.69	1.67	0.88
170	3.43	2.55	0.81	1.90	1.07
180	3.68	2.83	0.89	1.95	1.15
ICS	54.68	51.21	39.24	21.07	13.19

range are reported for the first time. The comparison between the calculated cross sections and the available experimental data is encouraging. In this energy range, the importance of the polarization and absorption effects in calculations is evident. The discrepancies seen for very low energies are attributed to the neglect of electron correlation of the target.

Acknowledgments

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