Cross sections for electron scattering by carbon disulfide in the low- and intermediate-energy range

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In this work, we report a theoretical study on $e^-–\text{CS}_2$ collisions in the low- and intermediate-energy ranges. Elastic differential, integral, and momentum-transfer cross sections, as well as grand total (elastic + inelastic) and absorption cross sections, are reported in the $1–1000$ eV range. A recently proposed complex optical potential composed of static, exchange, and correlation-polarization plus absorption contributions is used to describe the electron–molecule interaction. The Schwinger variational iterative method combined with the distorted-wave approximation is applied to calculate the scattering amplitudes. The comparison between our calculated results and the existing experimental and/or theoretical results is encouraging.

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I. INTRODUCTION

$\text{CS}_2$ is part of the set of linear triatomic molecules which includes $\text{CO}_2$ and OCS. It is specially interesting because these molecules have similar electronic ground-state configurations and strong dipole polarizabilities. Although this set has important applications in laser production studies and atmospheric chemical processes, electron scattering by $\text{CS}_2$ has attracted relatively little attention in recent years. An early measurement of absolute differential cross sections (DCSs) for vibrationally elastic and inelastic $e^-–\text{CS}_2$ collisions in the $0.3–5$ eV range was reported by Sohn et al. in 1987 [1]. Lately, Szymtkowski [2] reported absolute grand-total (elastic plus inelastic) cross sections (TCSs) for incident energies up to 100 eV. More recently, Jones et al. [3] measured cross sections below $0.2$ eV and very recently Bhushan et al. [4] reported measured elastic differential cross sections for energies between 30 and 500 eV.

On the theoretical side, the literature is also scarce. The first theoretical investigation on electron–$\text{CS}_2$ scattering was carried out by Lynch et al. [5]. These authors reported integral cross sections (ICSs) for elastic $e^-–\text{CS}_2$ scattering calculated using the continuum multiple-scattering method, in the $0.4–100$ eV incident energy range. They noticed the presence of a shape resonance of $\pi_u$ symmetry located at around $1.85$ eV. Nevertheless, this resonant structure was not seen in the experiments of Sohn et al. [1] and Szymtkowski [2]. Lately, Szymtkowski [6] reported calculated ICSs for this molecule in the $1–100$ eV range using a two-center parametric optical potential for electron–molecule interaction. His calculated ICSs are in better agreement with the experimental results than those of Lynch et al. [5], particularly at incident energies below $2$ eV. Early calculations of elastic DCSs were reported by Raj and Tomar in the $100–4000$ eV range [7] using the independent atom model (IAM). Lee et al. [8] calculated elastic DCSs, ICSs, and TCSs by using a combination of the iterative Schwinger variational method (ISVM) and the distorted-wave approximation (DWA). Bettega et al. [9,10] used the Schwinger multichannel method with pseudopotentials to calculate elastic cross sections for energies up to $50$ eV at the static-exchange [9] and static-exchange plus polarization [10] levels of approximation. Very recently, elastic DCSs, ICSs, and momentum-transfer cross sections (MTCSs) were calculated by Gianturco and Stoecklin [11] for energies ranging from near zero up to $100$ eV. Nevertheless, for energies above $100$ eV there are no DCS calculations beyond the IAM approximation in the literature.

In the present investigation, we report a theoretical study on electron scattering by $\text{CS}_2$ in the low- and intermediate-energy ranges. More specifically, calculated elastic DCSs, ICSs, and MTCSs, as well as TCSs and total absorption cross sections (TACSs), are presented for electron impact energies up to $1000$ eV. A complex optical interaction potential, derived from a fully molecular near-Hartree–Fock self-consistent-field (SCF) wave function, is applied to describe the electron–molecule interaction. The Lippmann–Schwinger scattering equations are solved using the ISVM combined with the DWA.

The objective of the present work is twofold: (i) to study the angular distribution of DCSs at low incident energies (up to $5$ eV) where recent calculations [10,11] exhibited significant disagreement with experiments and (ii) to evaluate the influence of absorption effects on elastic $e^-–\text{CS}_2$ scattering in the intermediate and high incident energy range where almost all inelastic channels (electronic excitations, ionization, etc.) are open. Such effects are responsible for a reduction in the electronic flux of the elastic scattering channel. To take appropriately these effects into account, several model absorption potentials have been proposed and used in a single-channel calculation framework [12,13]. In particular, version 3 of the quasi-free scattering model (QFSM3) of Staszweska et al. [12] has been widely used in $e^-–\text{molecule}$ collision calculations. Although this model potential has shown to provide, in general, quite accurate DCS, ICS, and MTCS values, most of the calculations have systematically underestimated the TCS and TACS values [14].

In a recent paper [15], our group has proposed a modified version of the QFSM3 absorption potential. In this modified model, known as the scaled quasi-free scattering model (SQFSM), an energy-dependent scaling factor is applied to the original QFSM3. Using the SQFSM, the calculated DCS, ICS, and MTCS values for elastic electron–molecule scattering do not change significantly from those calculated using the QFSM3, but the calculated TCS and TACS values...
are substantially affected. In fact, for a variety of atomic and molecular targets, the agreement between the TCS and TACS values obtained using SQFSM and the corresponding experimental values is significantly improved in comparison with those calculated using the original QFSM3. More recently, a benchmark study by Staszewska et al. [16] confirmed that the use of the scaling factor introduced by our group can improve the reliability of the calculated cross sections for electron–atom collisions.

This paper is organized as follows. In Sec. II we describe briefly the theory used and give some details of the calculation. In Sec. III we compare our calculated results with the existing experimental data and with some other theoretical data available in the literature.

II. THEORY AND CALCULATION

In this study, a complex optical potential is used to represent the electron–molecule interaction, whereas a combination of the ISVM [17] and the DWA [18,19] is used to solve the Lippmann–Schwinger scattering equations. The details of the basic theory used in this work were already presented elsewhere [17–19], and therefore they will only be briefly outlined.

The Schrödinger equation for the scattering electron, in atomic units, is given by

\[ (-\frac{1}{2}\nabla^2 + V_{\text{opt}}(\vec{r}) - \frac{1}{2}k^2)\Psi(\vec{r}, \vec{k}) = 0. \]  

The complex optical potential is given by

\[ V_{\text{opt}}(\vec{r}) = V_{\text{SEP}}(\vec{r}) + iV_{\text{abs}}(\vec{r}), \]  

where \( V_{\text{SEP}} \) is the real part of the interaction potential composed of static (\( V_{\text{st}} \)), exchange (\( V_{\text{ex}} \)), and correlation-polarization (\( V_{\text{cp}} \)) contributions, whereas \( V_{\text{abs}} \) is an absorption potential. In our calculation, \( V_{\text{st}} \) and \( V_{\text{ex}} \) are derived exactly from a Hartree–Fock SCF target wave function. A parameter-free model potential introduced by Padial and Norcross [20] is used to account for the correlation-polarization contributions.

In this model, a short-range correlation potential between the scattering electron and the target electrons is defined in an inner interaction region, and a long-range polarization potential in an outer region. The first crossing of the correlation and polarization potential curves defines the inner and the outer regions. The correlation potential is calculated in a
free-electron-gas model, derived using the target electronic density according to Eq. (9) of Padial and Norcross [20]. An asymptotic form of the polarization potential is needed to treat the long-range electron–target interaction. Dipole polarizabilities are needed to generate the asymptotic form of \( V_{cp} \). No additional parameters are used in the calculation of \( V_{cp} \).

In principle, the scattering equations for elastic electron–molecule collisions should be solved using the full complex optical potential. Nevertheless, a tremendous computational effort would be required, particularly due to the large number of coupled equations involved, which makes such calculations practically prohibitive. On the other hand, our calculation has revealed that the magnitude of the imaginary part (absorption) of the optical potential is considerably smaller than its real counterpart. Therefore, it can be treated as a perturbation and the scattering equations can be solved by ISVM using only the real part of the optical potential (\( V_{SEP} \)). The absorption potential appearing in Eq. (3) is our modified SQFSM version [15].

In ISVM calculations, the continuum wave functions are single-center expanded as

\[
\chi_k^{\pm}(\vec{r}) = \sqrt{\frac{2}{\pi}} \sum_{lm} \left( \frac{i^l}{k} \right) \chi_{l,m}^{\pm}(\vec{r}) Y_{lm}(\hat{k}),
\]

where the superscripts \((-\) and \((+)\) denote the incoming- and outgoing-wave boundary conditions, respectively, and \( Y_{lm}(\hat{k}) \) are the usual spherical harmonics.

Moreover, the TCSs for electron–molecule scattering are obtained by using the optical theorem, namely

\[
\sigma_{tot} = \frac{4\pi}{k} \text{Im} f_{el}(\theta = 0).
\]

All matrix elements appearing in our calculations are computed using a single-center expansion technique with radial integrals being evaluated using a Simpson quadrature.
The contributions from the direct and exchange parts of the interaction potential are truncated at $l_{\text{max}} = 58$. In ISVM calculations, the partial-wave expansion of the scattering wave functions is limited to $l_{\text{max}} = 58$ and $m_{\text{max}} = 17$.

In the present study, a standard [10s6p/6s4p] basis set of Dunning [21] augmented by three $s$ ($\alpha = 0.032, 0.0157,$ and $0.00537$), one $p$ ($\alpha = 0.934$ and $0.0178$), and three $d$ ($\alpha = 1.5, 0.75$, and $0.3$) uncontracted functions for the carbon atom and a [13s9p/6s4p] basis set of McLean and Chandler [22] augmented by three $s$ ($\alpha = 0.085, 0.032$, and $0.012$), two $p$ ($\alpha = 0.055$ and $0.0153$), and three $d$ ($\alpha = 2.35, 1.10$, and $0.45$) uncontracted functions for the sulfur atom are used for the calculation of the target wave function. With these basis sets, the SCF energy calculated at the experimental geometry of the ground state of CS$_2$ ($R_{C-S} = 2.9376$ a.u.) is $-832.94514$ a.u. This value is considerably lower than the corresponding restricted-Hartree–Fock value of $-832.8841$ a.u. of Tseng and Poshusta [23]. This difference is probably due to the larger basis set used in the present calculation, since in their work the basis set used is the standard 6-31G*.

The spherical ($\alpha_0$) and nonspherical ($\alpha_2$) parts of the dipole polarizability used to calculate the asymptotic form of $V_{\text{ep}}$ are 59.04 and 43.233 a.u., respectively [24].

In the present study, the ground-state wave function of CS$_2$ is calculated using the PC GAMESS/FIRELY QC package [25], which is partially based on the GAMESS source code [26]. The original ISVM code was written by Lucchese et al. [17] from the California Institute of Technology and modified by our group. Moreover, the codes for calculation of absorption effects were developed by our group.

### III. Results and Discussion

In Figs. 1–3 we show our calculated DCSs for elastic $e^-$–CS$_2$ scattering in the 1–10 eV energy range, along with the theoretical results of Bettega et al. [9,10] and Gianturco and Stoecklin [11]. Experimental absolute elastic DCS values of Sohn et al. [1] and Kitajima (as quoted by Gianturco and Stoecklin [11]) are also shown for comparison. For these energies, the absorption effects are either nonexistent or negligible; therefore, they were not included in calculations. Particularly for incident energies up to 3 eV, our calculated data reproduce well the shape of the experimental DCSs. The quantitative agreement between our results and those measured data is also fair. Such good agreement is not seen in the other calculations [9–11].

In Figs. 4–6 we present our DCSs, calculated both with and without the inclusion of absorption effects, in the 30–500 eV energy range.
range. The absolute DCSs of Bhushan et al. [4] are also included for comparison. In this energy range, the influence of absorption effects is evident: Our DCS values calculated including those effects are consistently lower than those not accounting for them. Qualitatively, all theoretical results are in very good agreement with each other and with the experimental DCSs of Kitajima. Quantitatively, our calculated DCSs including the absorption effects are in better agreement with the experimental data of Kitajima than all other theoretical results. It is interesting to notice a qualitative disagreement with the experimental data of Kitajima than all other theoretical results. Also, it is surprising to notice the good agreement between the ICSs of Bettega et al. [1] and Bhushan et al. [4] at 30 and 100 eV. Also, the magnitude of the DCS values of Bhushan et al. [4] are significantly larger than those of Kitajima. For energies of 100 eV and above, the experimental data of Bhushan et al. [4] are in general larger than our calculated results with absorption, particularly at small scattering angles.

In Figs. 7(a) and 7(b) we show our calculated ICS and MTCS values, respectively, for energies up to 1000 eV, along with the experimental results of Sohn et al. [1] and Bhushan et al. [4] and the theoretical results of Gianturco and Stoecklin [11] and Bettega et al. [9,10]. For energies above 20 eV, absorption effects were taken into account in our calculations. Our ICSs are in good quantitative agreement with the other two calculated results for energies above 3 eV, although some discrepancies between the results are seen below this energy. Moreover, all theoretical results exhibit a Ramsauer–Townsend minimum at energies below 1 eV. Particularly, our calculated minimum is located at about 0.3 eV, which is shifted to lower energies in comparison with the experimental results of Sohn et al. [1] and other calculated results. Also, it is surprising to notice the good agreement between the ICSs of Bettega et al. [10] and the experimental ICSs [1] at energies below 3 eV, despite the observed significant discrepancy between their calculated DCSs and the corresponding experimental data in this energy region. The measured ICSs of Bhushan et al. [4] are systematically larger than all calculated results, wherever the comparison is possible. This observation is consistent with the fact that their DCSs are systematically overestimated, particularly at small scattering angles. As it can be seen from Fig. 7(b), our calculated MTCSs are generally in good agreement with the experimental

![Graphs showing ICS and MTCS for e⁻–CS₂ collisions.](image-url)
MTCSs of Bhushan et al. [4] and with the calculated MTCSs of Bettega et al. [9]. Nevertheless, although the MTCSs of Gianturco and Stoecklin are in good qualitative agreement with ours, quantitatively, they are much larger than all theoretical and experimental data. Since their DCSs have similar shape and magnitude to ours, we may speculate that their MTCSs are in error, possibly due to the use of Eq. (22) in their article [11].

In particular, the two broad maxima are well reproduced in the present calculation, although our data are slightly shifted toward higher energies. Quantitatively, our TACSs also agree reasonably well with the experimental TICSs of Rao and Srivastava [29] for energies above 50 eV. The agreement with the calculated TICs using the BEB model [27] is also good. Nevertheless, the TICSs of Freund et al. [28] lie significantly below our results for energies above 30 eV. From Fig. 8(b) it can be seen that our TCSs calculated using both the SQFSM and QFSM3 models are in very good agreement with the experimental results of Szmytkowski [2], at energies above 1 eV.

In summary, we have presented a theoretical study of electron scattering by CS$_2$ molecules in a wide energy range. The comparison between our calculated cross sections and the available experimental data is encouraging. For energies above 20 eV, the importance of absorption effects is evident. The disagreement between the experimental results of Bhushan et al. with the available theoretical and experimental data suggests that further experimental investigations on electron scattering by this system are needed.

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