

Cross sections for electron scattering by carbon disulfide in the low- and intermediate-energy rangeL. M. Brescansin,¹ I. Iga,² L. E. Machado,³ S. E. Michelin,⁴ and M.-T. Lee²¹*Instituto de Física “Gleb Wataghin,” UNICAMP, 13083-970 Campinas, SP, Brazil*²*Departamento de Química, UFSCar, 13565-905 São Carlos, SP, Brazil*³*Departamento de Física, UFSCar, 13565-905, São Carlos, SP, Brazil*⁴*Departamento de Física, UFSC, 88040-900, Florianópolis, SC, Brazil*

(Received 30 October 2009; published 27 January 2010)

In this work, we report a theoretical study on e^- -CS₂ 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.

DOI: [10.1103/PhysRevA.81.012709](https://doi.org/10.1103/PhysRevA.81.012709)

PACS number(s): 34.80.Bm

I. INTRODUCTION

CS₂ is part of the set of linear triatomic molecules which includes CO₂ 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 CS₂ has attracted relatively little attention in recent years. An early measurement of absolute differential cross sections (DCSs) for vibrationally elastic and inelastic e^- -CS₂ collisions in the 0.3–5 eV range was reported by Sohn *et al.* in 1987 [1]. Lately, Szmytkowski [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-CS₂ scattering was carried out by Lynch *et al.* [5]. These authors reported integral cross sections (ICSs) for elastic e^- -CS₂ 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 π_u symmetry located at around 1.85 eV. Nevertheless, this resonant structure was not seen in the experiments of Sohn *et al.* [1] and Szmytkowski [2]. Lately, Szmytkowski [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 CS₂ 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^- -CS₂ 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 Staszewska *et al.* [12] has been widely used in e^- -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

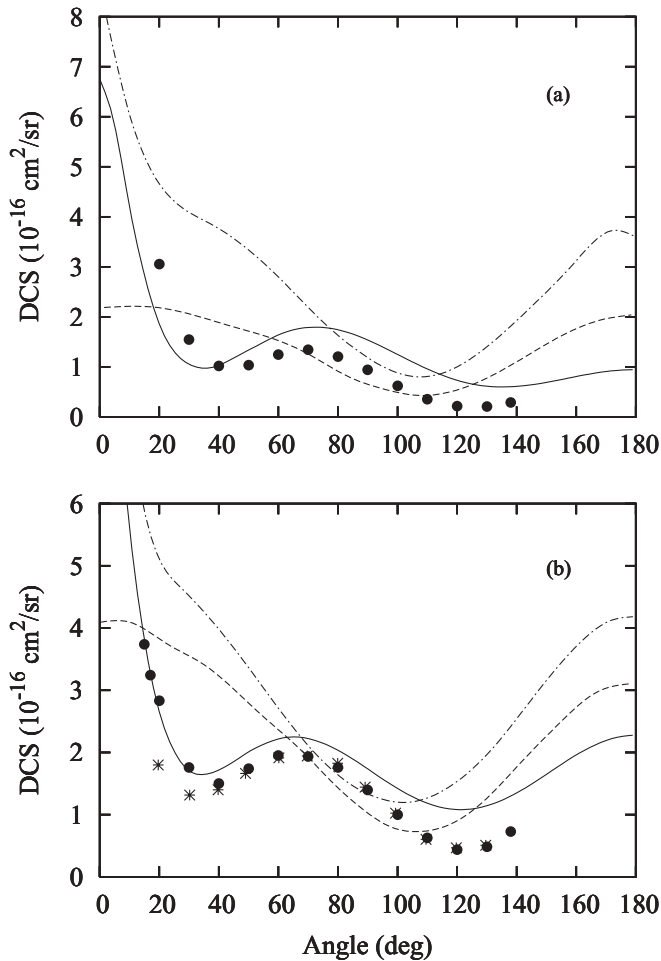


FIG. 1. DCS for e^- -CS₂ scattering at incident energies of (a) 1 eV and (b) 1.5 eV. Solid line, present calculated results; dashed line, theoretical results of Bettega *et al.* [10]; dashed-dotted line, theoretical results of Gianturco and Stoecklin [11]; full circles, experimental data of Sohn *et al.* [1]; asterisks, measured data of Kitajima, as quoted in Ref. [11]. The results of Gianturco and Stoecklin in Fig. 1(a) are calculated at 1.2 eV.

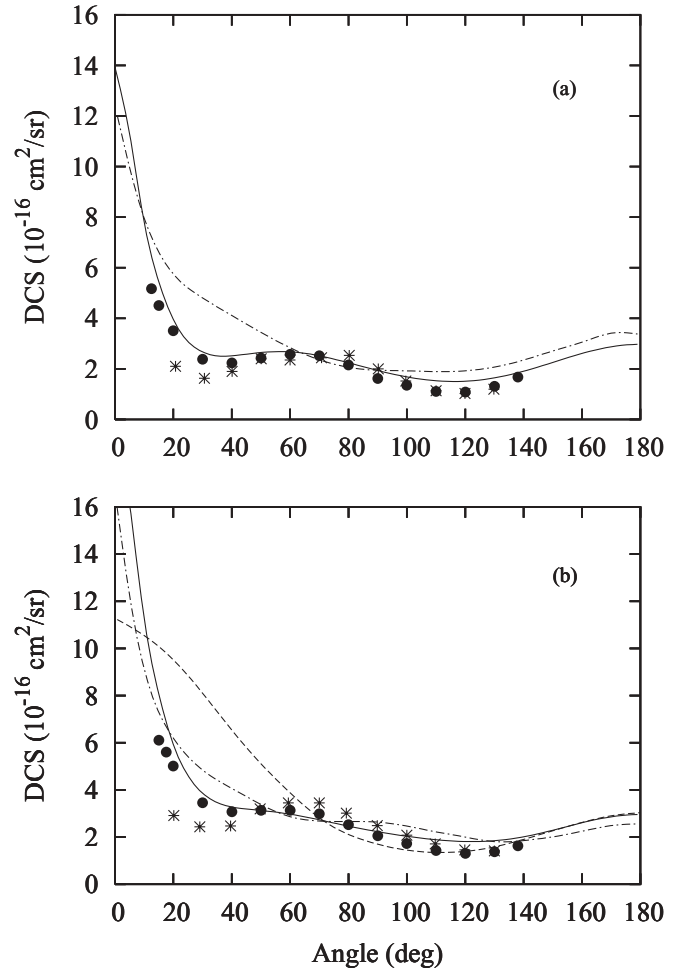


FIG. 2. Same as Fig. 1 but for (a) 2.2 eV and (b) 3 eV.

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

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{opt}}(\vec{r}) - \frac{1}{2}k^2\right)\Psi(\vec{r}, \vec{k}) = 0. \quad (1)$$

The complex optical potential is given by

$$V_{\text{opt}}(\vec{r}) = V_{\text{SEP}}(\vec{r}) + iV_{\text{ab}}(\vec{r}), \quad (2)$$

where V_{SEP} is the real part of the interaction potential composed of static (V_{st}), exchange (V_{ex}), and correlation-polarization (V_{cp}) contributions, whereas V_{ab} is an absorption potential. In our calculation, V_{st} and V_{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 used 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. In our work, the DWA [18,19] is used to calculate the absorption part of T matrix, which is given as

$$T_{\text{abs}} = i \langle \chi_f^- | V_{\text{ab}} | \chi_i^+ \rangle, \quad (3)$$

where χ 's represent the continuum wave functions which are the solutions of the Lippmann-Schwinger equation with

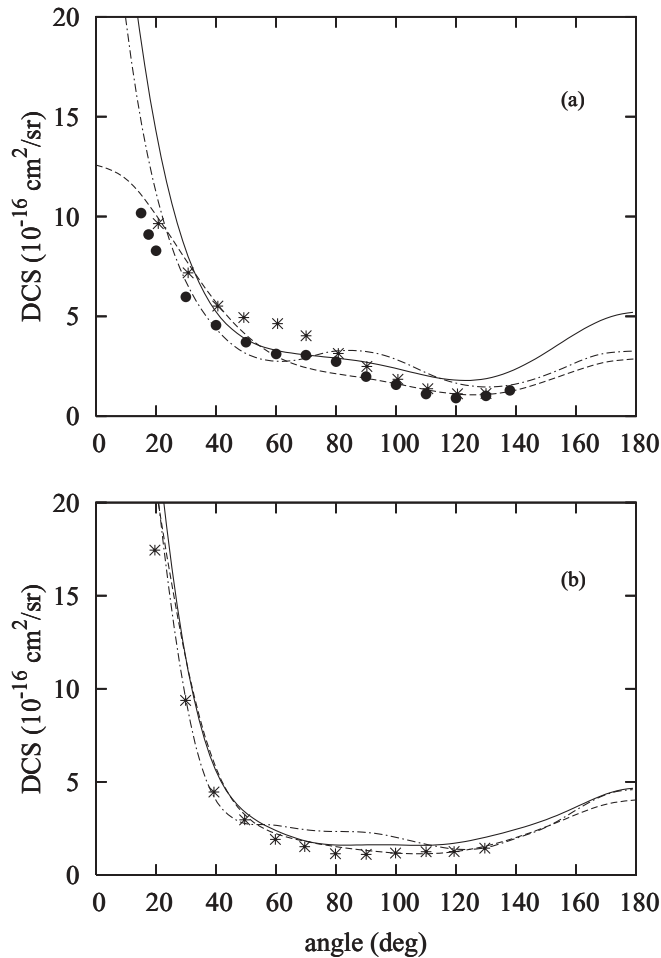


FIG. 3. Same as Fig. 1 but for (a) 5 eV and (b) 10 eV. The symbols are the same as in Fig. 1, except the dashed line gives the theoretical results of Bettega *et al.* [9].

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

$$\chi_{\vec{k}}^{\pm,S}(\vec{r}) = \sqrt{\frac{2}{\pi}} \sum_{lm} \frac{(i)^l}{k} \chi_{klm}^{\pm,S}(\vec{r}) Y_{lm}(\hat{k}), \quad (4)$$

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

$$\sigma_{\text{tot}} = \frac{4\pi}{k} \text{Im} f_{\text{el}}(\theta = 0). \quad (5)$$

All matrix elements appearing in our calculations are computed using a single-center expansion technique with radial integrals being evaluated using a Simpson quadrature.

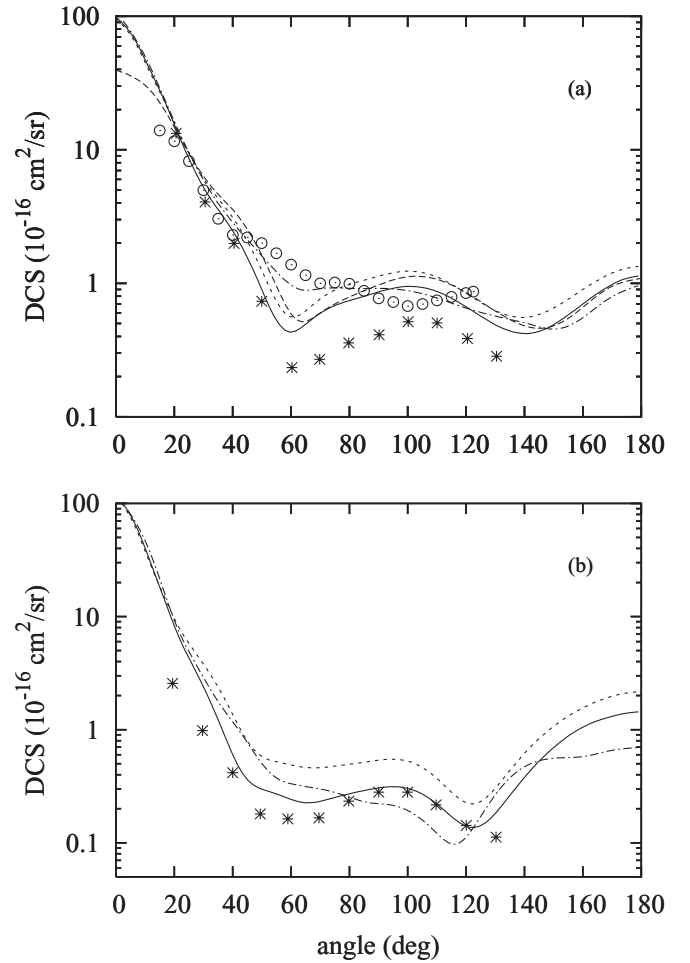


FIG. 4. Same as Fig. 3 but for (a) 30 eV and (b) 60 eV. Solid line, present results calculated using the SQFSM; short-dashed line, present theoretical results without absorption effects; dashed line, theoretical results of Bettega *et al.* [9]; dashed-dotted line, theoretical results of Gianturco and Stoecklin [11]; open circles, experimental data of Bhushan *et al.* [4]; asterisks, measured data of Kitajima, as quoted in Ref. [11].

The contributions from the direct and exchange parts of the interaction potential are truncated at $l_{\max} = 58$. In ISVM calculations, the partial-wave expansion of the scattering wave functions is limited to $l_{\max} = 58$ and $m_{\max} = 17$.

In the present study, a standard $[10s6p/6s4p]$ basis set of Dunning [21] augmented by three s ($\alpha = 0.032, 0.0157, \text{ and } 0.00537$), one p ($\alpha = 0.934 \text{ and } 0.0178$), and three d ($\alpha = 1.5, 0.75, \text{ and } 0.3$) uncontracted functions for the carbon atom and a $[13s9p/6s4p]$ basis set of McLean and Chandler [22] augmented by three s ($\alpha = 0.085, 0.032, \text{ and } 0.012$), two p ($\alpha = 0.055 \text{ and } 0.0153$), and three d ($\alpha = 2.35, 1.10, \text{ and } 0.45$) 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 ($R_{\text{C-S}} = 2.9376 \text{ a.u.}$) 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 (α_0) and nonspherical (α_2) parts of the dipole polarizability used to calculate the asymptotic form of V_{cp} 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/FIREFLY 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

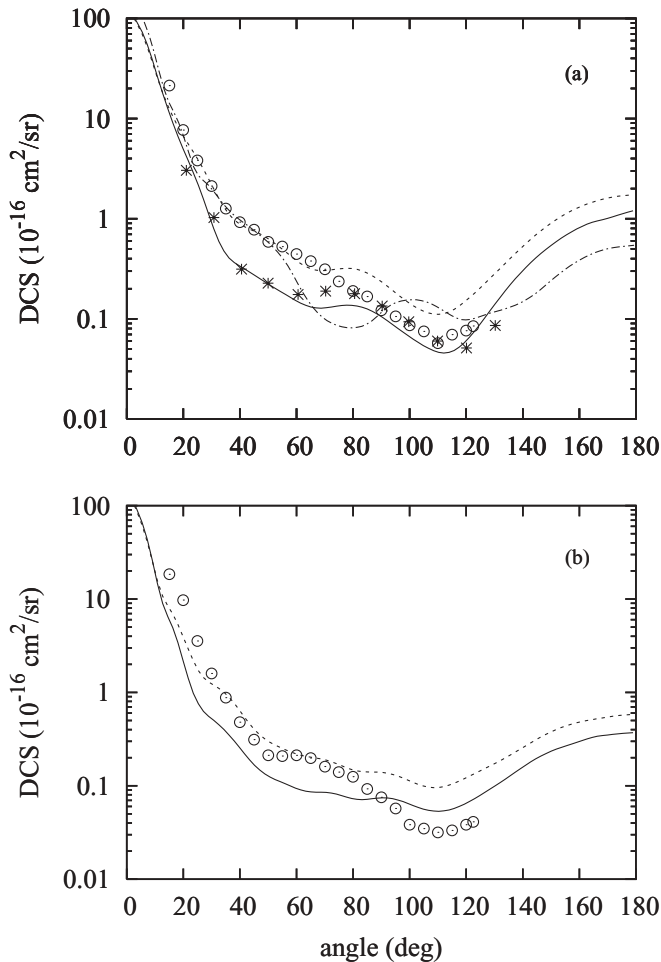


FIG. 5. Same as Fig. 4 but (a) 100 eV and (b) 200 eV.

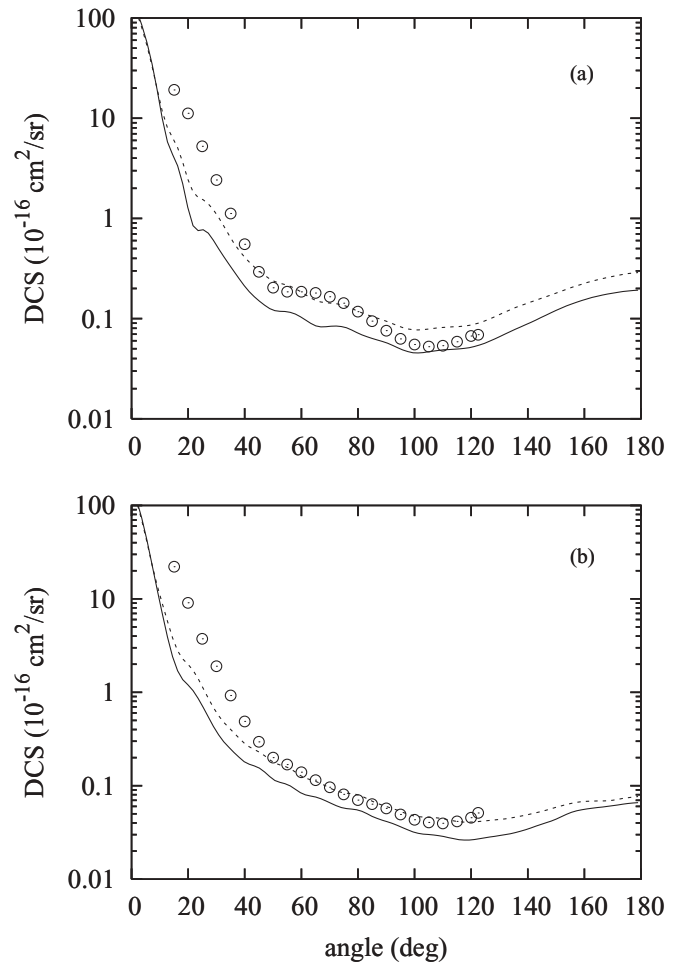


FIG. 6. Same as Fig. 4 but (a) 300 eV and (b) 500 eV.

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 between the measured DCS values of Kitajima 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

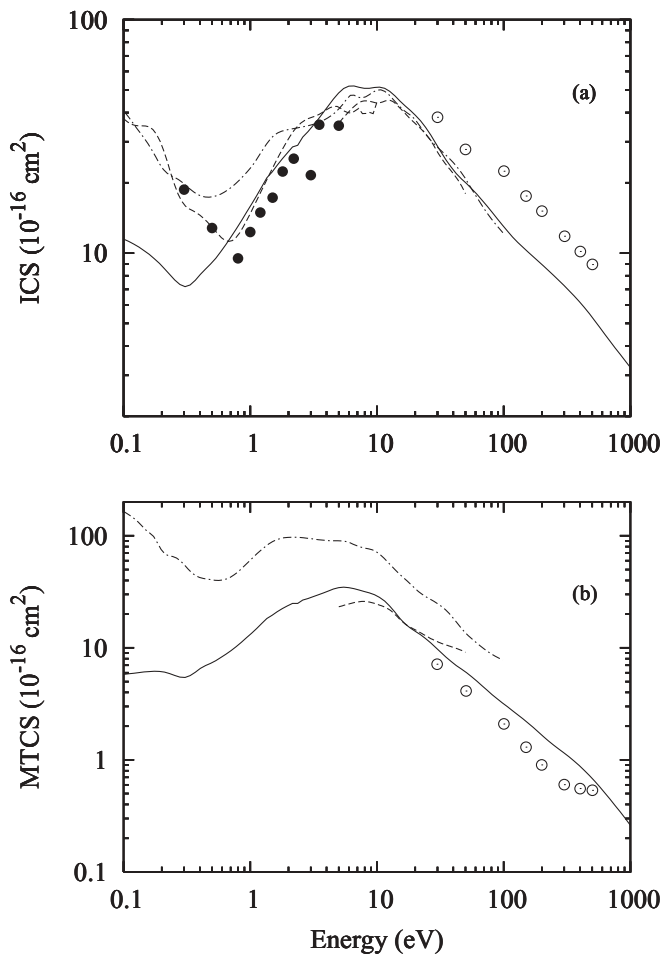


FIG. 7. (a) ICS and (b) MTCS for e^- -CS₂ collisions. Solid line, present results calculated with SQFSM; dashed-line, calculated results of Bettega *et al.* [9,10]; dashed-dotted line, theoretical results of Gianturco and Stoecklin [11]; open circles, experimental data of Bhushan *et al.* [4]; full circles, experimental data of Sohn *et al.* [1].

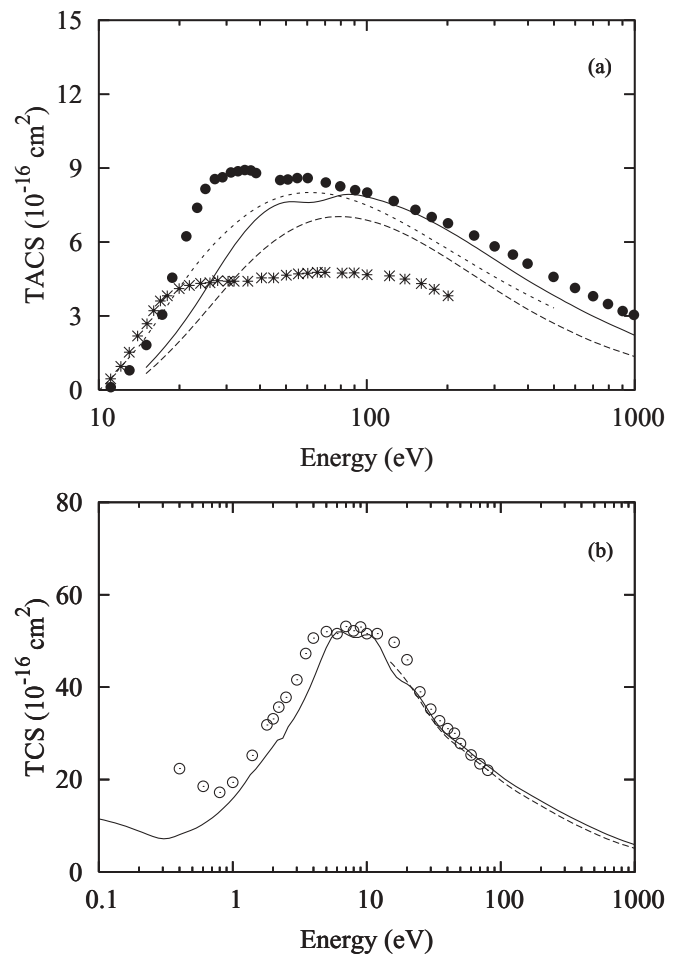


FIG. 8. (a) TACS and (b) TCS for e^- -CS₂ collisions. Solid line, present results calculated with SQFSM; dashed line, present results calculated with QFSM-3; short-dashed line: BEB TICS of Kim *et al.* [27]; full circles, experimental TICS of Rao and Srivastava [29]; asterisks, experimental TICS of Freund *et al.* [28]; open circles, experimental TCS of Szymkowski [2].

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 Figs. 8(a) and 8(b) we present our TACS and TCS values, respectively, calculated using both the SQFSM and QFSM3 absorption potentials for the e^- -CS₂ collisions at incident energies up to 1000 eV, along with the total ionization cross sections (TICSs) of Kim *et al.* [27], calculated using the binary-encounter-Bethe (BEB) model. Experimental TICSs of Freund *et al.* [28] and of Rao and Srivastava [29] and measured TCSs of Szmytkowski [2] are also presented. In principle, our calculated TACSs account for all inelastic scattering channels including both excitation and ionization processes. Josphipura *et al.* [30] have observed that for a set of molecules ionization dominates the inelastic processes, the values of the TICS being about 80% of the TACS values at energies around 100 eV and about 100% for energies above 300 eV. Thus, the comparison of our TACSs with the experimental TICSs is meaningful. From Fig. 8(a), it can be seen that our calculated SQFSM TACS values agree qualitatively well with the experimental TICS values of Rao and Srivastava [29].

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 TICSs 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 CS₂ 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.

ACKNOWLEDGMENTS

This work was partially supported by the Brazilian agencies CNPq and FAPESP.

-
- [1] W. Sohn, K.-H. Kochem, K.-M. Sheuerleim, K. Jung, and H. Ehrhardt, *J. Phys. B* **20**, 3217 (1987).
- [2] Cz. Szmytkowski, *J. Phys. B* **20**, 6613 (1987).
- [3] N. C. Jones, D. Field, J.-P. Ziesel, and T. A. Field, *Phys. Rev. Lett.* **89**, 093201 (2002).
- [4] K. G. Bhushan, K. C. Rao, S. C. Gadkari, J. V. Yakhmi, and S. K. Gupta, *Phys. Rev. A* **79**, 012702 (2009).
- [5] M. G. Lynch, D. Dill, J. Spiegel, and J. L. Dehmer, *J. Chem. Phys.* **71**, 4249 (1979).
- [6] Cz. Szmytkowski, *Fizika* **21**, 325 (1989).
- [7] D. Raj and S. Tomar, *J. Phys. B* **30**, 1989 (1997).
- [8] M.-T. Lee, S. E. Michelin, T. Kroin, and E. Veitenheimer, *J. Phys. B* **32**, 3043 (1999).
- [9] M. H. F. Bettega, A. P. P. Natalense, M. A. P. Lima, and L. G. Ferreira, *Braz. J. Phys.* **30**, 189 (2000).
- [10] M. H. F. Bettega, M. A. P. Lima, and L. G. Ferreira, *J. Phys. B* **38**, 2087 (2005).
- [11] F. A. Gianturco and T. Stoecklin, *Eur. Phys. J. D* **42**, 85 (2007).
- [12] G. Staszewska, D. W. Schwenke, and D. G. Truhlar, *Phys. Rev. A* **29**, 3078 (1984).
- [13] F. Blanco and G. García, *Phys. Lett.* **A255**, 147 (1999); **A295**, 178 (2002).
- [14] M.-T. Lee, I. Iga, M. G. P. Homem, L. E. Machado, and L. M. Bescansin, *Phys. Rev. A* **65**, 062702 (2002).
- [15] M.-T. Lee, I. Iga, L. E. Machado, L. M. Bescansin, E. A. y. Castro, I. P. Sanches, and G. L. C. de Souza, *J. Electron Spectrosc. Relat. Phenom.* **155**, 14 (2007).
- [16] G. Staszewska, P. Staszewski, and K. Zebrowski, *J. Electron Spectrosc. Relat. Phenom.* **168**, 40 (2008).
- [17] R. R. Lucchese, G. Raseev, and V. McKoy, *Phys. Rev. A* **25**, 2572 (1982).
- [18] A. W. Fliflet and V. McKoy, *Phys. Rev. A* **21**, 1863 (1980).
- [19] M.-T. Lee, I. Iga, M. G. P. Homem, L. E. Machado, and L. M. Bescansin, *Phys. Rev. A* **65**, 062702 (2002).
- [20] N. T. Padiál and D. W. Norcross, *Phys. Rev. A* **29**, 1742 (1984).
- [21] T. H. Dunning, *J. Chem. Phys.* **55**, 716 (1971).
- [22] A. D. McLean and G. S. Chandler, *J. Chem. Phys.* **72**, 5639 (1980).
- [23] D. C. Tseng and R. D. Poshusta, *J. Chem. Phys.* **100**, 7481 (1994).
- [24] C. J. F. Böttcher, O. C. Van Belle, P. Bordewijk, and A. Rip, *Theory of Electric Polarization*, 2nd ed. (Elsevier, Amsterdam 1973), p. 332.
- [25] A. A. Granovsky, PC GAMESS/FIREFLY version 7.1.F, <http://classic.chem.msu.su/gran/gamess/index.html>.
- [26] M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1993).
- [27] Y.-K. Kim, W. Hwang, M. N. Weinberger, M. A. Ali, and M. E. Rudd, *J. Chem. Phys.* **106**, 1026 (1997).
- [28] R. S. Freund, R. C. Wetzel, and R. J. Shul, *Phys. Rev. A* **41**, 5861 (1990).
- [29] M. V. V. S. Rao and S. K. Srivastava, *J. Geophys. Res.* **96**, 17563 (1991).
- [30] K. N. Josphipura, M. Vinodkumar, and P. M. Patel, *J. Phys. B* **34**, 509 (2000).