

Elastic scattering of low-energy electrons by OCS

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We present integral and differential cross sections for elastic scattering of electrons by OCS molecules for energies between 0.1 and 10 eV. We employ the Schwinger multichannel method with pseudopotentials in the static-exchange plus polarization approximation. We compare our results with available theoretical and experimental results and find good agreement in general. Our calculated integral cross section is strongly enhanced near zero energy which is an indication of a possible existence of an s -wave virtual state.

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I. INTRODUCTION

OCS molecules have important applications in astrophysics and atmospheric studies. These molecules are also responsible for the reduction of the effective production rate of plasmas. Collisions of low-energy electrons with OCS are therefore important from both practical and fundamental points of view.

Some theoretical and experimental studies of electron collisions with OCS have been published. We may quote the calculations of Lynch *et al.* [1] using the continuum multiple-scattering model. They found a Π shape resonance at around 1.15 eV and a sharp increase in the integral cross section for energies below 1 eV in the Σ symmetry. Differential cross sections for elastic scattering and vibrational excitations were measured by Sohn *et al.* [2]. They have also observed the Π shape resonance and also a strong excitation of the bending mode overtones, which could not be explained by the Born dipole approximation. They have attributed this feature to a possible bound state of the e^- -OCS system. Szmytkowski *et al.* [3] have measured the total cross section for OCS. The Π shape resonance is also seen in this cross section at around 1.15 eV. More recently, Sueoka *et al.* [4] have measured total cross sections for electron and positron collisions with OCS, and they have also found the Π shape resonance at around 1.15 eV in the electron case. In another study, Kawada *et al.* [5] have measured vibrational excitation cross sections for OCS. Bettega *et al.* [6] have calculated elastic integral, differential, and momentum transfer cross sections for e^- -OCS collisions. The calculations were performed with the Schwinger multichannel method with pseudopotentials in the static-exchange approximation, for energies ranging from 5 to 50 eV. A joint theoretical-experimental study on e^- -OCS collisions was carried out by Michelin *et al.* [7]. To compute the cross sections they employed the Schwinger iterative method combined with the distorted-wave approximation. They have included model potentials to describe correlation, polarization, and absorption effects. Their calculated integral cross section agrees well with the results of Lynch *et al.* They also compared their differential cross sections with those measured by Sohn *et al.*

and Tanaka [8], and found good agreement. They also reported a sharp increase in the integral cross section for energies below 1 eV, but did not attribute its origin to any physical effect.

In the present paper we report elastic integral and differential cross sections for e^- -OCS collisions for energies from 0.1 to 10 eV. We employed the Schwinger multichannel method with pseudopotentials [9] in the static-exchange plus polarization approximation to compute the cross sections. The aim of our work is to further investigate the strong enhancement that appeared in the integral cross sections of Lynch *et al.* and Michelin *et al.* Although this rise is a characteristic of molecules with permanent dipole moment, it has been pointed out by Herzenberg and Saha [10] that weakly polar molecules (with dipole moment less than 1.19 D) can support a virtual state. Since OCS has a small dipole moment (the reported experimental value is 0.71 D [3]), it is a candidate to present a virtual state. Several investigators have been concerned with the existence of a virtual state in CO_2 . Some recent work on this subject can be found in Refs. [11–14]. We can also quote the work of de Carvalho *et al.* [15] on positron- C_2H_2 collisions, where the authors identified the existence of a virtual state.

In what follows we present a brief description of the Schwinger multichannel method. We then present some computational details of our calculations, focusing on the inclusion of polarization effects. We finally report our main results and discussion with a brief summary of our findings.

II. THEORY

The Schwinger multichannel (SMC) method [16–18] and its implementation with pseudopotentials [9] have been described in detail in several publications. Here we will describe only the relevant points concerning the present work.

In the SMC method the scattering amplitude is given by

$$f(\vec{k}_f, \vec{k}_i) = -\frac{1}{2\pi} \sum_{m,n} \langle S_{k_f}^- | V | \chi_m \rangle (d^{-1})_{mn} \langle \chi_n | V | S_{k_i}^- \rangle, \quad (1)$$

where

$$d_{mn} = \langle \chi_m | A^{(+)} | \chi_n \rangle \quad (2)$$

and

$$A^{(+)} = \frac{\hat{H}}{N+1} - \frac{(\hat{H}P + P\hat{H})}{2} + \frac{(VP + PV)}{2} - VG_P^{(+)}V. \quad (3)$$

In the above equations, $|S_{k_i, f}^{\pm}\rangle$ is a solution of the unperturbed Hamiltonian H_0 and is a product of a target state and a plane wave, V is the interaction potential between the incident electron and the electrons and nuclei of the target, $|\chi_m\rangle$ is a set of $(N+1)$ -electron Slater determinants [configuration state functions (CSF's)] used in the expansion of the trial scattering wave function, $\hat{H} = E - H$ is the total energy of the collision minus the full Hamiltonian of the system, with $H = H_0 + V$, P is a projection operator onto the open-channel space defined by the target eigenfunctions, and $G_P^{(+)}$ is the free-particle Green's function projected on the P space. The direct configuration space is constructed as follows:

$$\{|\chi_i\rangle\} = \{\mathcal{A}(|\Phi_1\rangle \otimes |\varphi_i\rangle)\} \quad (4)$$

where $|\Phi_1\rangle$ is the single-configuration Hartree-Fock wave function which describes the ground state of the molecular target, $|\varphi_i\rangle$ is a one-electron function represented by an unoccupied (virtual) orbital, and \mathcal{A} is the antisymmetrizer. To take polarization into account, the configuration space is enlarged by including CSF's of the type:

$$\{|\chi_i\rangle\} = \{\mathcal{A}(|\Phi_j\rangle \otimes |\varphi_u\rangle)\}, \quad j \geq 2, \quad (5)$$

where $|\Phi_j\rangle$ are virtual states of the target which are obtained from the ground state by performing single excitations, and $|\varphi_u\rangle$, as before, is a one-electron function.

III. COMPUTATIONAL DETAILS

The ground state of the molecule is described by a single-configuration wave function at the Hartree-Fock level of approximation. Our calculations were carried out in the fixed-nuclei approximation, with the nuclei fixed at the equilibrium geometry of the target ground state [19]. We have employed the pseudopotentials of Bachelet, Hamann, and Schlüter to describe the atomic cores [20]. The basis functions used in the description of the target ground state and of the scattering orbitals are the same used in Ref. [6], and were obtained through a variational method as described in Ref. [21]. We have not included in our calculations the combination $[(x^2 + y^2 + z^2)\exp(-ar^2)]$ in order to avoid linear dependency in the basis set. We used the sum-over-states method [22] to compute the average electric polarizability for OCS, and obtained $6.45 \times 10^{-24} \text{ cm}^3$, which compares well with the experimental value of $5.71 \times 10^{-24} \text{ cm}^3$ [19]. Our calculated dipole moment is 0.74 D, which compares well with the experimental value of 0.71 D reported by Szymtkowski *et al.* [3].

Our calculations were performed within the C_{2v} group. The A_1 symmetry of this group includes the Σ symmetry and one component of the Δ symmetry ($\Delta_{x^2-y^2}$) of the $C_{\infty v}$ group. The two components of the Π symmetry, Π_x and Π_y , of the

$C_{\infty v}$ split into B_1 (Π_x) and B_2 (Π_y) symmetries of the C_{2v} group. The other component of the Δ symmetry (Δ_{xy}) corresponds to the A_2 symmetry of the C_{2v} group.

To take polarization effects into account, we have considered the resonant and the nonresonant symmetries, separately. To construct the $|\Phi_j\rangle$ states for the nonresonant symmetries (in the present case the Σ symmetry) we have proceeded as follows: we have considered only single excitations from the occupied orbitals to a small set of polarized orbitals [14,23] given by

$$|\varphi_{i,\mu}\rangle = \sum_{j \in \text{virtuals}} \frac{\langle \varphi_j | x_{\mu} | \varphi_i \rangle}{E_j - E_i} |\varphi_j\rangle \quad (6)$$

where $|\varphi_i\rangle$ is an occupied orbital, x_{μ} is a component of the dipole moment operator, and j runs over the Hartree-Fock virtual orbitals. An orthonormal set of orbitals is constructed using the Schmidt orthogonalization procedure, from the polarizing orbitals and the residual scattering orbitals. All unoccupied orbitals (polarized and virtual orbitals) are then used as scattering orbitals.

In the construction of the $|\Phi_j\rangle$ states for the resonant symmetry (in the present case the Π symmetry) we have considered only single excitations from the occupied orbitals to the virtual orbitals which preserve the spatial and spin symmetries of the target ground state. We have then used a set of virtual orbitals of the Π symmetry which reproduced the static-exchange cross section of this symmetry as scattering orbitals. This procedure is different from those used by Rescigno *et al.* [14] and Winstead and McKoy [23] in their calculations on electron-molecule collisions. Rescigno *et al.* have considered excitations from the occupied orbitals to the polarized orbitals that preserved spatial and spin symmetries of the ground state of the molecule and used all polarized and virtual orbitals of the resonant symmetry as scattering orbitals. Winstead and McKoy have considered all possible excitations from the occupied orbitals to the virtual orbitals that preserved spatial and spin symmetries of the ground state of the molecule and used just one orbital of the resonant symmetry, a valencelike virtual orbital (a modified virtual orbital), as scattering orbital. These two procedures describe the target and the temporary-anion states in a balanced way, thus avoiding overcorrelation. We have also used both procedures and the resonance was located too high in energy: at 1.48 eV using the polarized orbitals and at 1.65 eV using the modified virtual orbital.

In our calculations we have considered the Σ symmetry and the component $\Delta_{x^2-y^2}$ of the Δ symmetry together, and obtained 2272 CSF's. For the Π symmetry we used 3152 CSF's. The other component of the Δ symmetry, Δ_{xy} , was computed in the static-exchange approximation with nine CSF's. In the whole calculation we have used 5433 CSF's.

IV. RESULTS AND DISCUSSION

In Fig. 1 we present our calculated integral cross section obtained with the static-exchange plus polarization approximation with and without including the correction due to the dipole interaction, using a Born closure of the scattering am-

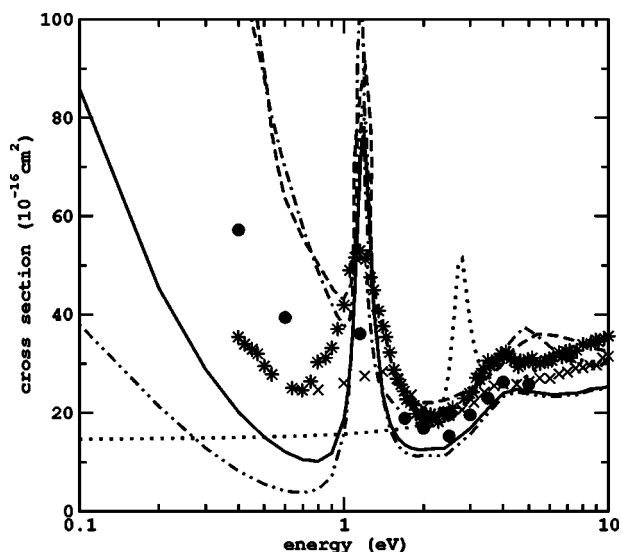


FIG. 1. Integral cross-section section for OCS. Solid line present results including polarization effects with Born closure; dash-dot-dotted line, present results including polarization effects without Born closure; dotted line, results at the static-exchange approximation; dot-dashed line, theoretical results of Ref. [1]; dashed line, theoretical results of Ref. [7]; circles, experimental elastic cross section of Ref. [2]; stars, experimental total cross section of Ref. [3]; crosses, experimental total cross section of Ref. [4].

plitude [24,25], together with the calculated cross sections of Lynch *et al.* and Michelin *et al.*, and with the experimental total cross sections of Szmytkowski *et al.* and Sueoka *et al.* and the experimental elastic cross section of Sun *et al.* We also show for purposes of comparison our calculated integral cross section obtained in the static-exchange (SE) approximation. This figure clearly shows the importance played by polarization effects, especially in the description of the resonance position and in the strong enhancement in the integral cross section near zero energy. It also shows that the long-range interaction increases the magnitude of the integral cross section mainly for energies below 1 eV. The shape of our calculated integral cross section agrees with the shape of the results of Lynch *et al.* and Michelin *et al.*, except for the sharp increase in their cross sections, which is stronger than ours. This point will be discussed below. Good agreement is also found between the shape of our cross section with the shape of the experimental data, especially with the total cross sections of Szmytkowski *et al.* at low energy. In particular, all calculations and experiments locate the Π shape resonance at the same position. In our calculations the resonance is located at 1.190 eV and has a width of 0.195 eV.

In Fig. 2 we present the symmetry decomposition of the integral cross section of Fig. 1. The results shown in this figure were obtained without including the correction for the long-range dipole interaction. The symmetry decomposition shows, as reported by the previous studies, that the shape resonance belongs to the Π symmetry, and that the cross section of the Δ symmetry (in fact of the Δ_{xy} component of this symmetry), which was obtained at the SE approximation, is very small in the energy range considered. In addition to the shape resonance, the most prominent feature seen in

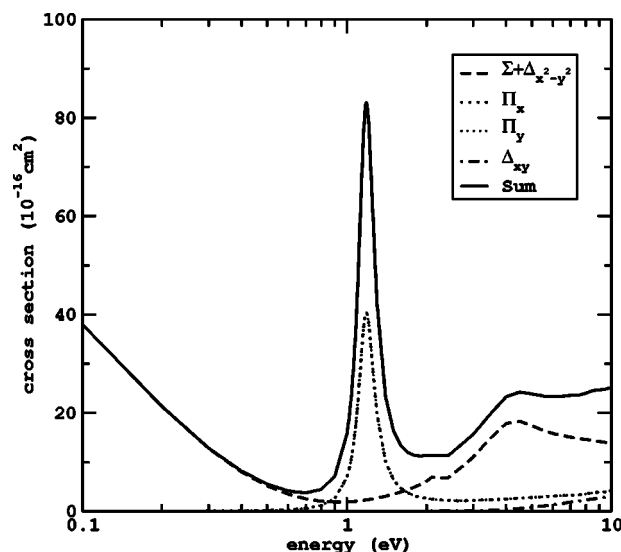


FIG. 2. Symmetry decomposition of the integral cross section for OCS (obtained without Born closure).

our calculated integral cross section is the strong enhancement near zero energy which appears in the Σ symmetry. This rise in the s -wave cross section is a characteristic of a virtual state. The virtual state is not a true bound state, and is related to a zero of the s -wave Jost function on the negative imaginary k axis [26]. It appears when the potential is nearly strong enough to support an s -wave bound state. The corresponding scattering length (a), which can be computed from the s -wave eigenphase, is large and negative (in potential scattering $a \rightarrow -\infty$ as $k \rightarrow 0$). In order to calculate a for OCS we have followed the procedure described by Morrison [11], and obtained the value of $-4.73a_0$. For CO_2 , Morrison obtained $-6.17a_0$ and Winstead and McKoy obtained $-4.51a_0$. These values are small if compared with the value of $-229a_0$, which has been obtained by Carvalho *et al.* for positron- C_2H_2 collisions.

As shown in Fig. 1, our static-exchange integral cross section is flat for energies below ~ 2 eV. With the inclusion of polarization effects, our integral cross section shows the strong enhancement below 0.7 eV. Sohn *et al.* have presented a small discussion about this when they reported their results for vibrational excitations and attributed the behavior seen in their cross sections, which could not be explained by the Born dipole approximation, to the existence of a possible bound state of the e^- -OCS system. Lynch *et al.* attributed the sharp increase seen in their calculated cross section to the permanent dipole moment of the molecule, although they have not included the dipole in their calculations. Michelin *et al.* obtained their integral cross section from a truncated T matrix and did not discuss the rise that appeared in the calculated cross section below 1 eV on any physical grounds. Our integral cross section was obtained with and without the incorporation of the correction due to the long-range dipole potential, and the strong enhancement is also present in both results. We may conclude that the strong enhancement seen in our integral cross section is not related to the dipole moment of the molecule and that indicates the existence of a virtual state.

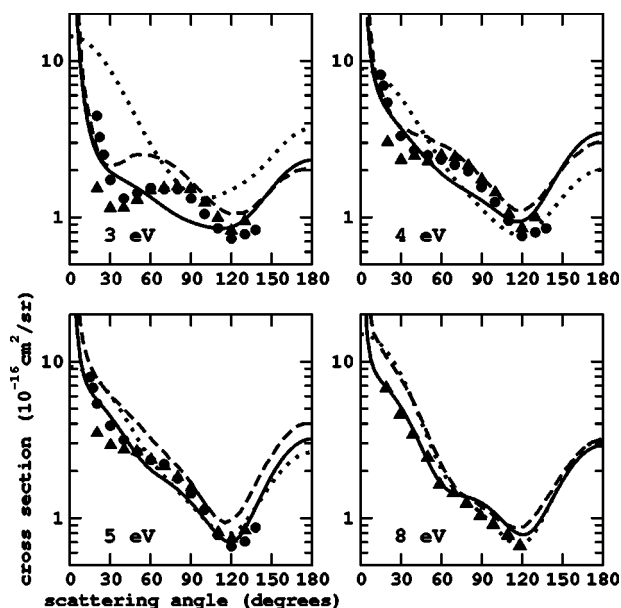


FIG. 3. Differential cross section for OCS at 3, 4, 5, and 8 eV. Solid line, present results including polarization effects; dotted line, results obtained at the static-exchange approximation; dashed line, theoretical results of Ref. [7]; circles, experimental results from Ref. [2]; triangles, experimental results from Ref. [8].

Figures 3 and 4 compare our calculated differential cross sections (DCSs) with the experimental data of Sohn *et al.* and Tanaka *et al.* and with the theoretical results of Michelin *et al.* at 3, 4, 5, 8, and 10 eV. The agreement between the calculated DCS's is good, except at 3 eV. There is also good agreement between theory and experiment. We have also shown in these two figures our results in the static-exchange approximation for purposes of comparison.

In summary, we have presented elastic cross sections for e^- -OCS collisions. Our calculations have included polarization effects. Good agreement was found between our results

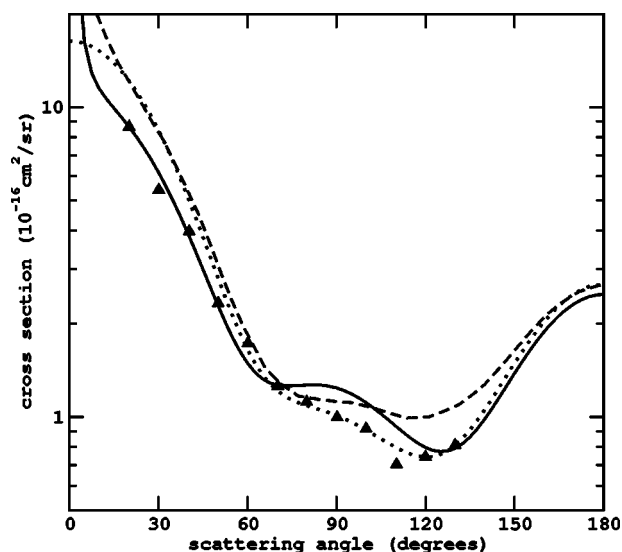


FIG. 4. As in Fig. 3 at 10 eV.

and other results available. In particular, the behavior of our calculated integral cross section indicates the presence of an s -wave virtual state.

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