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Elastic scattering of low-energy electrons by C_3H_4 isomers

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We report integral, differential, and momentum-transfer cross sections for elastic scattering of low-energy electrons by the C_3H_4 isomers allene, propyne, and cyclopropene, which belong to the D_{2d}, C_{3v}, and C_{2v} groups, respectively. We use the Schwinger multichannel method with pseudopotentials [Bettega *et al.*, Phys. Rev. A **47**, 1111 (1993)] at the static-exchange approximation to compute the cross sections for energies up to 40 eV. We compare our results with available experimental results and find very good agreement. Our results confirm the existence of the shape resonances in the cross sections of allene and propyne, and the *isomer effect*, both reported by the experimental studies.

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I. INTRODUCTION

Recent experimental studies on electron-molecule collisions have focused their attention on hydrocarbons, specially the C_3H_4 isomers [1,2]. Szmytkowski and Kwitnewski measured total cross sections (TCS) for scattering of electrons by the C_3H_4 isomers allene and propyne, and for C_3H_8 (propane). They found that the shapes of the TCS for the isomers are very similar, specially at high energies, and that both present shape resonances centered around 2.3 eV for allene, and around 3.4 eV for propyne. They also reported a very broad structure around 10 eV for allene, and around 8.5 eV for propyne. Although the shapes of the TCS are very similar, they present some features at low energies that allow to distinguish the two TCS, which is the *isomeric effect*. They also made a comparison of the TCS for the open-chain C_3 hydrocarbons with different number of C-C bonds, namely, C_3H_4 (propyne), with a triple bond; C_3H_6 (propene), with a double bond; and C_3H_8 (propane), with a single bond. Another experimental study on the C_3H_4 isomers allene and propyne has been done by Nakano *et al.* They measured elastic differential cross sections and vibration excitations for energies from 1.5 eV to 100 eV. They also calculated the differential cross sections (DCS) using the continuum multiple-scattering method, and found good agreement between their calculated and measured results. They found in the DCS for allene and propyne some resonant characteristics below 4 eV. The *isomer effect* (or *isomeric effect*) was discussed for different energies through direct comparison of the DCS for allene and propyne, which is most evident at low energies, where the DCS showed to be very different. These results agree with the observations of Szmytkowski and Kwitnewski. Nakano *et al.* also discussed the bonding effect through the comparison of the DCS of allene with the DCS of C_2H_2, which have a double bond, and of the DCS of propyne with the DCS of C_2H_4, which have a triple bond.

In the present work we calculated elastic integral, differential, and momentum-transfer cross sections for the C_3H_4 isomers allene, propyne, and cyclopropene for energies up to 40 eV. The isomers allene, propyne, and cyclopropene belong to the D_{2d}, C_{3v}, and C_{2v} groups, respectively. These calculations employed the Schwinger multichannel method (SMC) with pseudopotentials (SMCPP) [6] at the static-exchange approximation. Our goal in the present work is to carry out a comparative study of the elastic cross sections for electron collisions with allene, propyne, and cyclopropene, and then extend the experimental studies of Szmytkowski and Kwitnewski, and Nakano *et al.* We can further explore the shape resonances found in the cross sections for allene and propyne, and also discuss the *isomer effect* through the inclusion of a third isomer, cyclopropene.

In the rest of this paper we present a brief description of the theoretical formulation of our method, the computational procedures used in our calculations, and our results and discussion. We end this paper with a brief summary of our findings.

II. THEORY

The SMC method [3–5] and its implementation with pseudopotentials (SMCPP) [6] have been described in detail in several publications. Here we will describe only the relevant points concerning the present work.

The SMC method is a variational method that results in the following expression of the scattering amplitude:

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

where

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

and

TABLE I. Cartesian Gaussian functions for H.

Type	Exp.	Coef.
s	13.3615	0.130844
	2.0133	0.921539
	0.4538	1.0
	0.1233	1.0
p	0.7500	1.0

TABLE II. Dipole moments (D) for the C_3H_4 isomers.

System	Calc.	Expt.
propyne	0.807	0.784 (Ref. [8])
allene	0.000	0.200 (Ref. [2])
cyclopropene	0.509	0.450 (Ref. [8])

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

In the above equations, $|S_{\vec{k}_{i,f}}\rangle$ 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) 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

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

where $|\Phi_1\rangle$ is the target ground-state wave function, described at the Hartree-Fock level of approximation, $|\varphi_i\rangle$ is a one-electron function, and $\mathcal{A}$ is the antisymmetrizer.

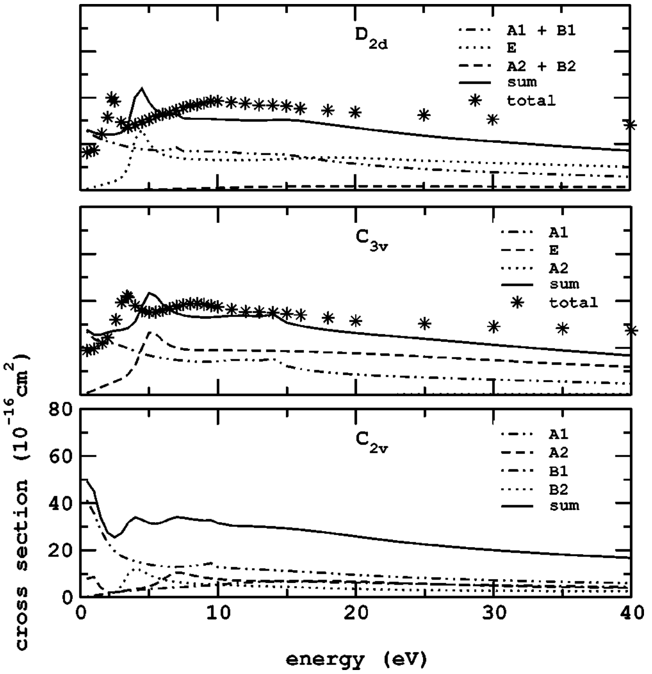

FIG. 1. Integral cross section for C_3H_4 isomers. The total cross sections of Ref. [1] are also shown.

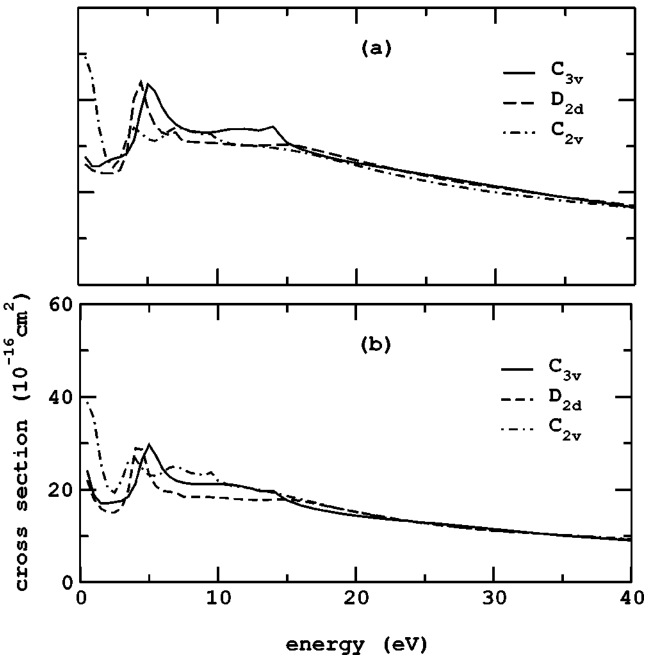

FIG. 2. (a) Integral cross section and (b) momentum transfer cross section for C_3H_4 isomers.

III. COMPUTATIONAL DETAILS

Our cross-section calculations were performed with the Schwinger multichannel method along with the pseudopotentials of Bachelet, Hamann, and Schlüter [7], at the static-exchange approximation. We used the ground-state equilibrium geometries of allene, propyne, and cyclopropene given in Ref. [8]. The basis set for the carbon atom is formed by

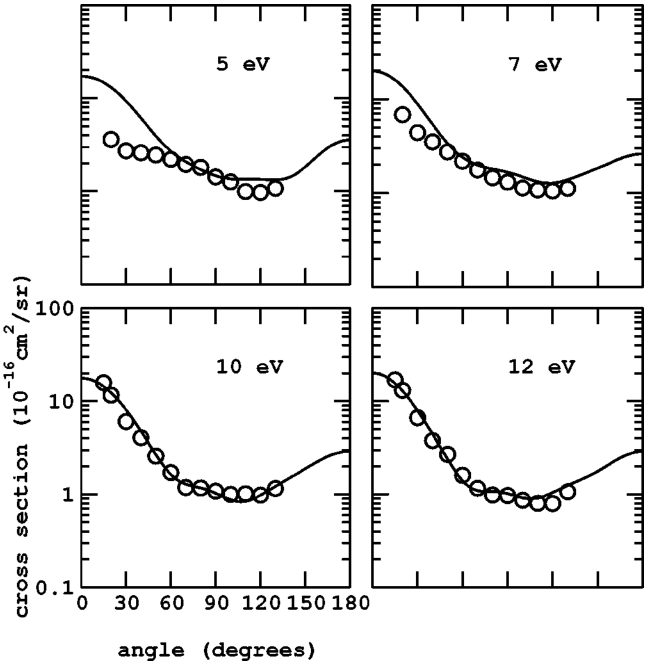

FIG. 3. Differential cross section for allene (D_{2d} group) at 5, 7, 10, and 12 eV. Solid line, our calculated results; circles, experimental data from Ref. [2].

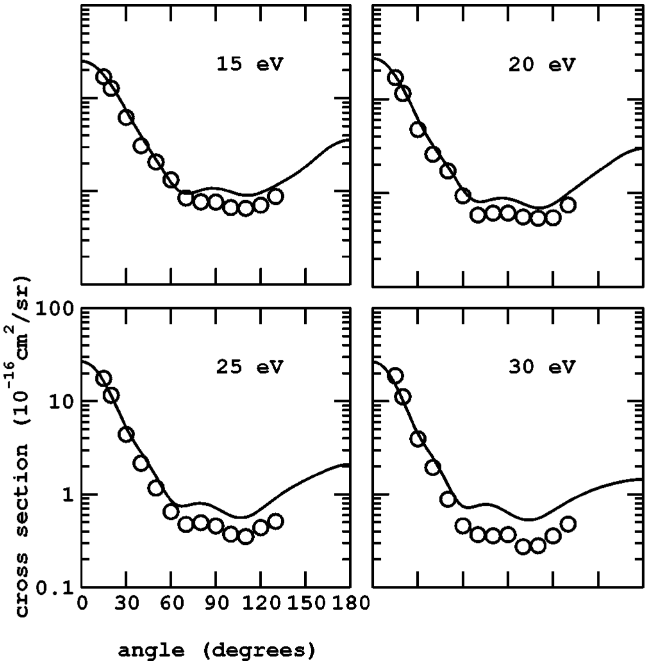

FIG. 4. As in Fig. 3, but at 15, 20, 25, and 30 eV.

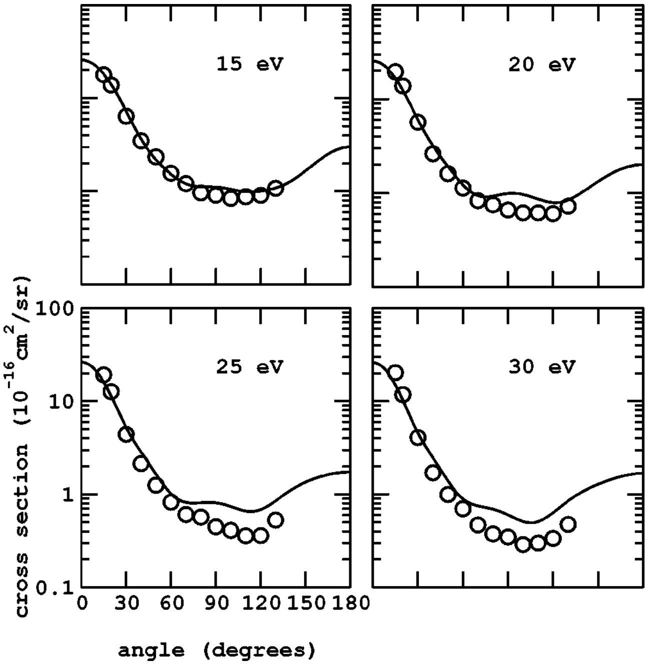

FIG. 6. As in Fig. 4, but for propyne.

six uncontracted *s*-type functions (with exponents 12.49 408, 2.470 291, 0.614 027, 0.184 029, 0.036 799, and 0.013 682), five uncontracted *p*-type functions (with exponents 5.228 869, 1.592 058, 0.568 612, 0.210 326, and 0.072 250), and two uncontracted *d*-type functions (with exponents 0.603 592 and 0.156 753), and was generated according to Ref. [9]. The basis set for the hydrogen atom is shown in Table I. The calculated and experimental dipole moments for the C_3H_4 isomers are shown in Table II. Due to the small value of the dipole moments we have not included the long-range potential due to the dipole interaction in our calculations.

IV. RESULTS AND DISCUSSION

As discussed at the end of the preceding section, we have not included in our cross-section calculations the correction due to the long-range dipole interaction, since the values of the dipole moments are small, as shown in Table II. This is usually done by combining the scattering amplitude obtained

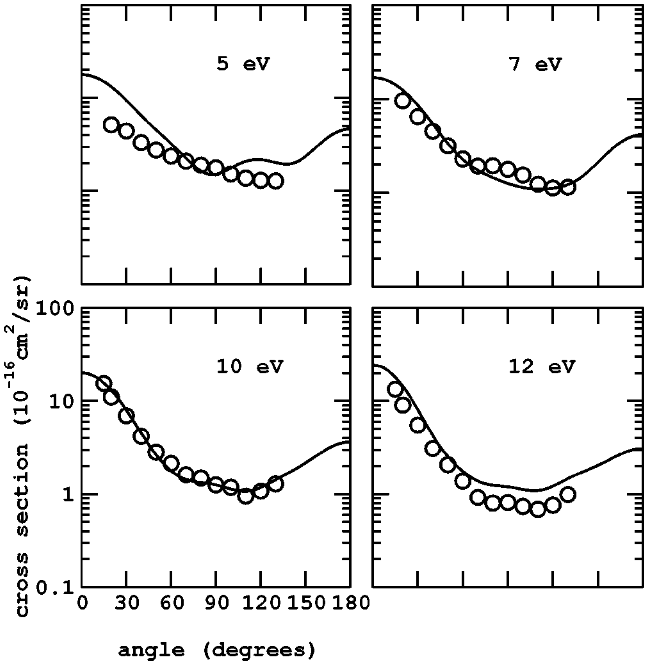

FIG. 5. As in Fig. 3, but for propyne (C_{3v} group).

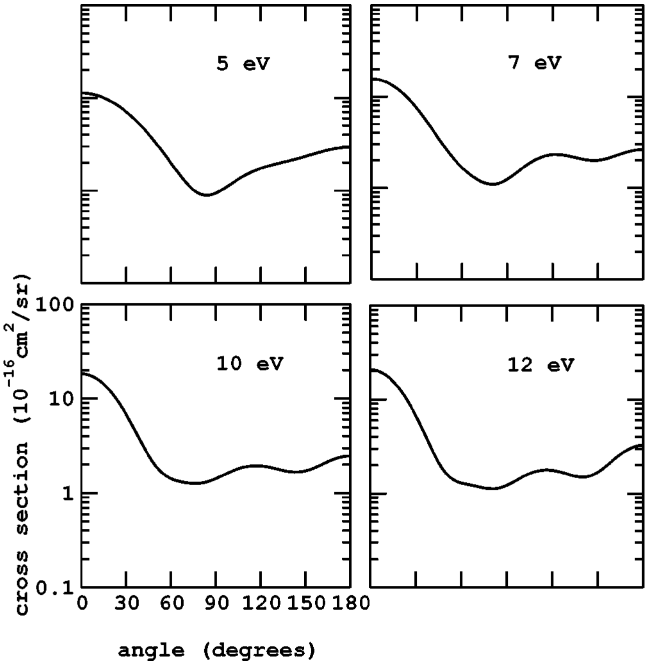

FIG. 7. As in Fig. 3, but for cyclopropene (C_{2v} group).

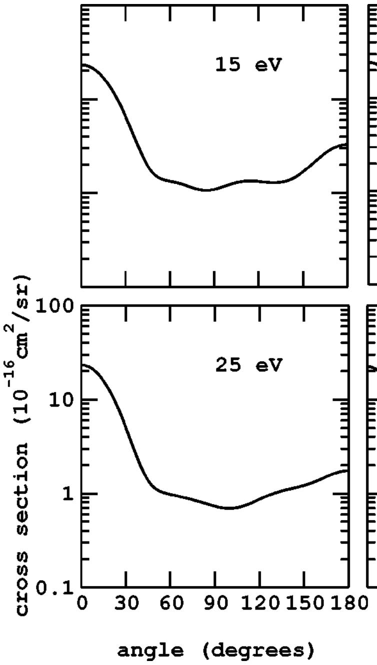

FIG. 8. As in Fig. 4, but for cyclopropene.

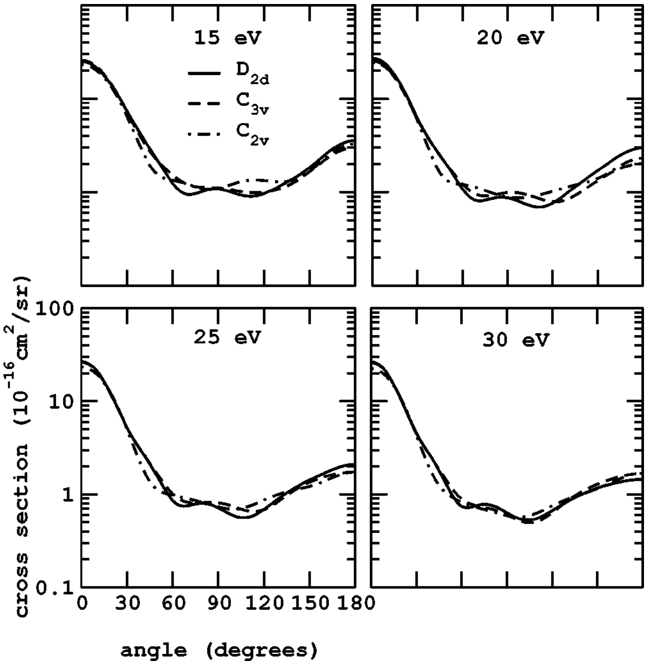

FIG. 9. Differential cross sections at 15, 20, 25, and 30 eV for allene, propyne, and cyclopropene.

with the SMC method with the scattering amplitude obtained with the first Born approximation of the dipole potential. For the values of the dipole moments of the C_3H_3 isomers, this correction would increase the integral cross sections in a small amount, and would retain the shape resonances at the same location. It would correct the differential cross sections at low scattering angles, and would cause no effect in the momentum transfer cross sections (due to the weight factor $1-\cos\theta$ in the integral).

In Fig. 1 we present the integral cross section (ICS) for the C_3H_4 isomers allene, propyne, and cyclopropene. For allene and propyne we also include the TCS of Szmytkowski and Kwitnewski. In this figure we also show the symmetry decomposition of the ICS for each isomer. Allene and propyne present a shape resonance for energies around 5 eV, which belongs to the E representation of the D_{2d} group for allene, and to the E representation of the C_{3v} group for propyne. These shape resonances for allene and propyne are seen in the TCS of Szmytkowski and Kwitnewski, and are also supported by the results of Nakano *et al.* For the other isomer, cyclopropene, we find two resonances, one around 4 eV, and the other around 7 eV, which belong to the B_2 and A_2 representations of the C_{2v} group, respectively. The ICS's for these molecules also present some spurious structures, due to numerical problems, in the sum of A_1 and B_1 representations of D_{2d} group for allene, in the A_1 representation of C_{3v} group for propyne, and in the A_1 representation of the C_{2v} group for cyclopropene. Since our calculations do not include polarization effects, we expect that the positions of the shape resonances are placed at higher energies. The lack of polarization explains the shift in energy seen in the position of the shape resonaces in the measured TCS and in the calculated ICS.

In Fig. 2 we present the ICS and the momentum-transfer cross section (MTCS) for the C_3H_4 isomers. For energies above 15 eV, the ICS's for the three isomers are identical, the same occurring with the MTCS. For energies between 20 and 40 eV the molecules are no longer distinguishable by their ICS and MTCS. For energies below 15 eV the ICS's for these isomers present different features, the same occurring with the MTCS. Below 15 eV the C_3H_4 isomers can then be distinguished by their cross sections. This result is in agreement with the *isomer effect* (or *isomeric effect*), which has been pointed out by Szmytkowski and Kwitnewski, and Nakano *et al.*

In Figs. 3–8 we present the DCS for allene, propyne, and cyclopropene at 5, 7, 10, 12, 15, 20, 25, and 30 eV. The calculated DCS for allene and propyne are compared with the results of Nakano *et al.* In both cases our calculated DCS agree very well with experiment, except at 5 and 7 eV. Since our calculations do not include polarization effects, this discrepancy is not a surprise. At higher energies, our calculated DCS lie above of the experimental data of Nakano *et al.* for angles above ~40°. This type of discrepancy was already seen for other molecules, and may be attributed to the lack of open inelastic channels. The use of a complex potential allows the flux to leak into other channels but the elastic one, lowering the elastic cross section [10].

Figure 9 shows a comparison between our calculated DCS for allene, propyne, and cyclopropene at 15, 20, 25, and 30 eV. At these energies, the differential cross section for these isomers show very small differences, the DCS for cyclopropene being more distinguishable from the other two molecules. At 30 eV, the DCS for these molecules are almost identical, confirming again the results of Szmytkowski and Kwitnewski, and Nakano *et al.* (the *isomer effect*).

V. SUMMARY

We presented elastic integral, differential, and momentum-transfer cross sections for elastic scattering of electrons by C_3H_4 isomers allene, propyne, and cyclopropyne. Our calculated ICS's show shape resonances for energies below 5 eV. The existence of these shape resonances in the cross sections of allene and propyne is supported by the results of Szmytkowski and Kwitnewski, and Nakano *et al.* The calculated DCS for allene and propyne agree very well with the experiment, except at 5 and 7 eV. We compared our calculated ICS's for the three isomers, and found that they become identical for energies above 15 eV. The same behavior was found in the MTCS. This is the confirmation of the *isomer effect*, which has been reported by Szmytkowski and Kwitnewski, and Nakano *et al.*

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