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Low-energy electron collisions with C_4H_6 isomers

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We report integral, differential, and momentum-transfer cross sections for elastic scattering of low-energy electrons by C_4H_6 isomers, namely, 1,3-butadiene, 2-butyne, and cyclobutene. We use the Schwinger multichannel method with pseudopotentials [M. H. F. Bettega, L. G. Ferreira, and M. A. P. Lima, Phys. Rev. A **47**, 1111 (1993)] at the static-exchange approximation to compute the cross sections for energies from 10 to 60 eV. In particular, we discuss the *isomer effect*, reported by experimental studies for isomers of C_3H_4 and C_4H_6. We also calculate the total ionization cross section using the binary-encounter-Bethe model for 2-butyne and 1,3-butadiene, and estimate the inelastic cross section for these two isomers.

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Recent experimental studies on electron-molecule collisions with C_3H_4 isomers, namely, propyne and allene, were done by Szmytkowski and Kwitnewski [1], Nakano *et al.* [2], and Makochekanwa *et al.* (they also measured total cross sections for positron-molecule collisions) [3]. These studies reported that the isomers cross sections (total, in the case of Refs. [1] and [3], and differential, in the case of Ref. [2]) are very similar above ~30 eV, and differ below this energy. The differences (in shape, magnitude, and resonances positions) seen in the cross sections below ~30 eV allow to distinguish between the different isomers; this is the *isomer* (or *isomeric*) *effect*. Lopes and Bettega [4] performed a theoretical study of electron collisions with C_3H_4 isomers, namely, allene, propyne, and cyclopropene. Qualitative agreement was found between their calculated integral cross sections for allene and propyne and the total cross sections of Szmytkowski and Kwitnewski and very good agreement was found between their calculated differential cross sections and the results of Nakano *et al.* They discussed the *isomer effect*, which they found to occur for the three isomers for energies below ~15 eV. They also discussed the shape resonances found in the integral cross sections of these isomers, which have also been reported by the experimental studies for allene and propyne.

More recently, Szmytkowski and Kwitnewski [5] carried out total cross-section measurements for electron collisions with C_4H_6 isomers 1,3-butadiene and 2-butyne, and also with C_4F_6 (hexafluoro-2-butyne). They discussed the *isomer effect* for these molecules, which occurs around 10 eV, and also the *halogenation effect* through the comparison of total cross sections for 2-butyne and hexafluoro-2-butyne. They reported peaks in the total cross section for the C_4H_6 isomers located around 1 eV, 3.2 eV, and 9 eV for 1,3-butadiene, and around 3.5 eV and 8 eV for 2-butyne. For 1,3-butadiene, the two peaks located at lower energies were reported to be associated with shape resonances at the A_u and B_g representations of the C_{2h} group, respectively [6]. The broad structures with peaks at higher energies were related to contributions from elastic scattering with contributions from inelastic channels open at those energies. For 2-butyne there are evidences that the low-energy peak is related to a shape resonance. In this Brief Report we report calculated elastic integral, differential, and momentum-transfer cross sections for the C_4H_6 isomers 1,3-butadiene, 2-butyne, and cyclobutene. Our calculations employed the Schwinger multichannel method with pseudopotentials at the static-exchange approximation. Our results are shown for energies from 10 to 60 eV, where target polarization can be neglected and the static-exchange approximation gives reliable cross sections [7–12]. Through the inclusion of a third isomer (cyclobutene) we made a comparative study of the elastic cross sections for these isomers and discussed the *isomer effect* reported by Szmytkowski and Kwitnewski. We also calculated the total ionization cross section using the binary-encounter-Bethe (BEB) model [13,14]. From the total, elastic, and total ionization cross sections we estimated the inelastic cross section for 2-butyne and 1,3-butadiene. The inelastic cross section is a very useful information for plasma modelers.

The structures of these isomers are very different. 2-butyne belongs to the D_{3h} group and has a triple bond between the middle carbons, 1,3-butadiene belongs to the C_{2h} group and has two double bonds between CH_2 and CH, and cyclobutene has a cyclic structure belonging to the C_{2v} group, and has a double bond between the two CH. Although their structures are very different, they present similar cross sections above a given energy, as we will show below and as shown by Szmytkowski and Kwitnewski for 1,3-butadiene and 2-butyne.

To compute the elastic cross sections we used the Schwinger multichannel method (SMC) with pseudopotentials. The SMC method [15–17] and its implementation with pseudopotentials [18] have been described in detail in several publications and will not review these methodologies here. Our calculations were performed at the static-exchange approximation with the ground-state equilibrium geometries given in Ref. [19] and in the C_{2v} group, for cyclobutene and 2-butyne, and in the C_{2h} group, for 1,3-butadiene. We used the *norm-conserving* pseudopotentials of Bachelet, Hamann, and Schlüter [20]. The basis set we used for the carbon and hydrogen atoms are the same given in Ref. [4], except that in the calculations for 1,3-butadiene and cyclobutene we have not used the *p*-type function for the hydrogen atom. The calculated value for the dipole moment of cyclobutene was 0.130 D, which is in agreement with the experimental value

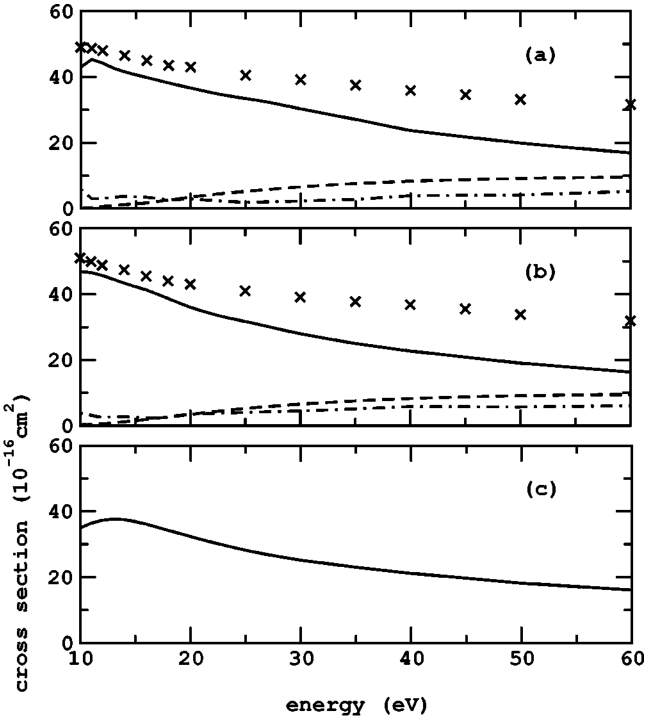

FIG. 1. Integral cross section (solid line) for (a) 2-butyne (D_{3h}), (b) 1,3-butadiene (C_{2h}), and (c) cyclobutene (C_{2v}). Total cross section (crosses) of Ref. [5], total ionization cross sections (dashed line) and inelastic cross sections (dot-dashed lines) are also shown.

of 0.132 D ([19]). Since the value of dipole moment is small, we have not carried out any special treatment (Born closure of the scattering amplitude) for the long-range part of the potential in our calculations.

To compute the total ionization cross section we used the BEB model [13,14]. The binding (U) and kinetic (T) energies needed in the BEB model were calculated using the package GAMESS [21] in a restricted Hartree-Fock calculation with a 6-311G$++(2d,1p)$ basis set at the equilibrium geometries. The BEB model gives cross sections which agree with experimental data within 5%–15% for different molecules, and for incident energies from the first ionization threshold to several keV [14].

In Fig. 1 we present our calculated elastic integral cross section (ICS) from 10 eV to 60 eV. For purposes of comparison, we also show the total cross sections measured by Szmytkowski and Kwitnewski [5].

Since the experimental results shown in Fig. 1 are related to total cross sections, they include contributions from the elastic, inelastic, and ionization channels and this explains the difference between our calculated (elastic) cross sections and the experiment. In order to estimate the inelastic cross section for 2-butyne and 1,3-butadiene, we calculated the total ionization cross section. The estimated inelastic cross section was then obtained as $\sigma_{inel}=\sigma_{tot}-(\sigma_{el}+\sigma_{ion})$. To do this subtraction we have made three assumptions: (i) the theoretical static-exchange cross sections are correct, (ii) the theoretical ionization cross sections are correct, and (iii) the measured total cross sections are correct. These results are also shown in Fig. 1. In particular, we observed that the calculated total ionization cross section for 2-butyne and 1,3-butadiene are almost identical in the energy range considered, which agrees with the observations reported for the C_3H_6 isomers [22]. The same type of similarity is seen in the inelastic cross section for the two isomers.

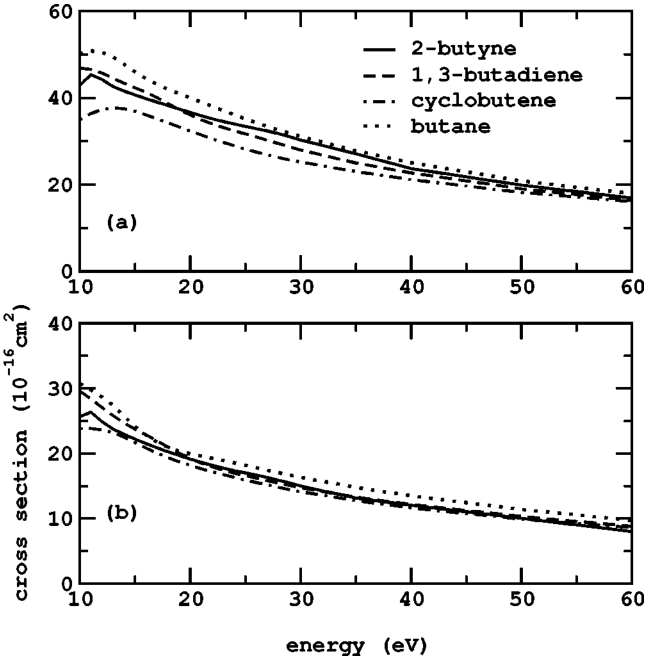

FIG. 2. (a) Integral cross section and (b) momentum-transfer cross section for C_4H_6 isomers. We also show cross sections for butane (C_4H_{10}).

Figure 2 shows the integral and momentum-transfer cross sections for the three C_4H_6 isomers. The integral cross section for 1,3-butadiene and 2-butyne become very close around 10 eV, which agrees with the results of Szmytkowski and Kwitnewski. This explains the similarity in the inelastic cross section of 2-butyne and 1,3-butadiene seen in Fig. 1. The ICS for cyclobutene lies below the ICS of the other two isomers and becomes similar to them above 45 eV. Considering now the three isomers, the *isomer effect* occurs for energies below ~45 eV. The momentum-transfer cross sections of the C_4H_6 isomers are close for energies above 20 eV.

In Figs. 3 and 4 we present the calculated differential

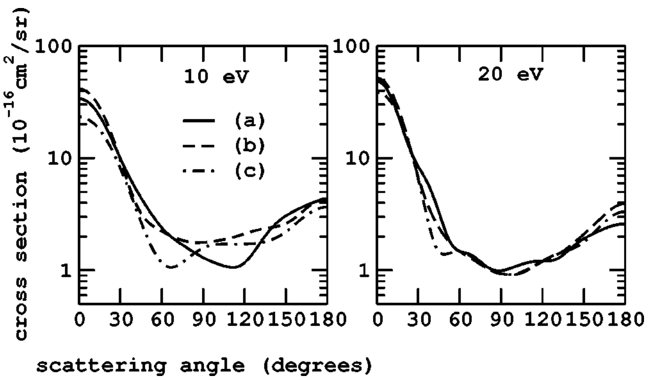

FIG. 3. Differential cross section for (a) 2-butyne (D_{3h}), (b) 1,3-butadiene (C_{2h}), and (c) cyclobutene (C_{2v}), at 10 and 20 eV.

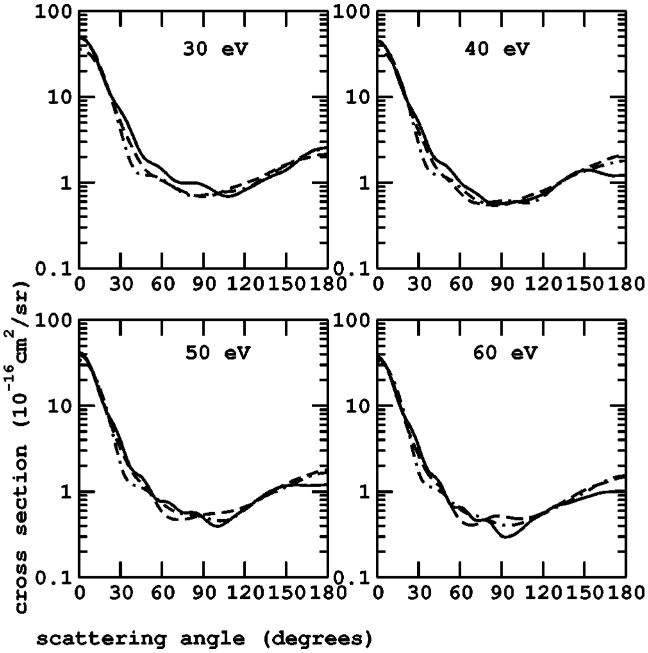

FIG. 4. As in Fig. 3 at 30, 40, 50, and 60 eV.

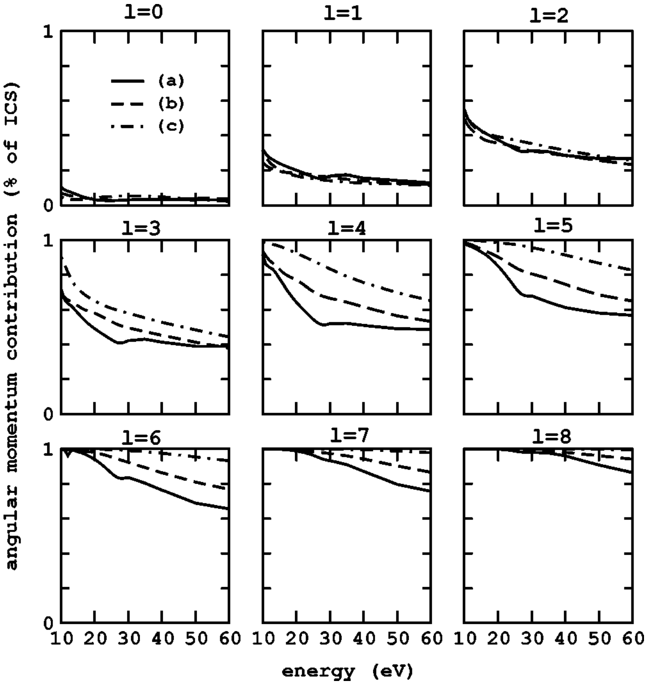

FIG. 5. Angular-momentum contribution for the integral cross section. (a) 2-butyne (D_{3h}), (b) 1,3-butadiene (C_{2h}), and (c) cyclobutene (C_{2v}).

cross sections (DCS) for the C_4H_6 isomers at 10, 20, 30, 40, 50, and 60 eV. The DCS for 1,3-butadiene and 2-butyne are similar for energies above 10 eV (the *isomer effect* for these two isomers occurs for energies below 10 eV). At energies below 40 eV the DCS of cyclobutene differ from the DCS of the other two isomers, and become similar to them at higher energies. Although, in general, the DCS are quite similar for the C_4H_6 isomers, they present some differences in shape for energies below 20 eV. For 20 eV and above, apart from slightly different oscillation patterns, the isomers could be hardly distinguished by their DCS.

In order to investigate the oscillatory behavior of these DCS, we follow the procedure used by da Costa *et al.* [23] and defined the ratio $f^{(l)}$ as follows:

$$f^{(l)}=\frac{\sum_{l'=0}^{l}\sum_{m=-l'}^{l'}\int d\hat{k}_i|f^{LAB}(\vec{k}_i,l'm')|^2}{\sum_{l'=0}^{10}\sum_{m=-l'}^{l'}\int d\hat{k}_i|f^{LAB}(\vec{k}_i,l'm')|^2}. \qquad (1)$$

The partial-wave cross sections used in this analysis were obtained for scattering processes of incoming electrons in a plane wave with momentum $\vec{k}_i$ to outgoing electrons in a sum of partial waves (l',m_l') averaged in all molecular orientations. Although we have included in our calculations partial waves up to $l=10$, we present in Fig. 5 the partial-wave contribution of the $f^{(l)}$ up to $l=8$. The value of l shown above each plot in Fig. 5 tells that the numerator of Eq. (1) is summed up to this value. According to this figure, high partial waves seem to be more important for 2-butyne, followed by 1,3-butadiene and then by cyclobutene.

It has been observed in previous studies concerning electron collisions with XH_4 (X=C, Si, Ge, Sn, Pb) [24], XH_3 (X=N, As, P, Sb) [25], and XH_2 (X=O, S, Se, Te) [26] that the hydrogens are not good scatterers and that the cross sections for the above families are mainly determined by the heavier atom. In the case of the present study, although the investigated isomers have very different structures, we have found that their cross sections are similar in the 10–60 eV energy range. Since we average over all incident directions to take into account the random molecular orientations in order to compare our results with the experiment, this procedure may explain why molecules with different structures have similar cross sections in a given energy range. To further investigate this point, we also show in Fig. 2 the integral and momentum-transfer cross sections for butane, which is one of the C_4H_{10} isomers and has a similar structure to 1,3-butadiene (butane also belongs to the C_{2h} group). One can observe from Fig. 2 that the cross sections of butane are similar to the cross sections of the C_4H_6 isomers. These results are in agreement with the above discussion.

In summary, we presented elastic integral, differential, and momentum-transfer cross sections for elastic scattering of electrons by C_4H_6 isomers. We found that the integral cross sections for these isomers are different below ~45 eV and that the differences in their differential cross sections are more evident at 10 eV. These results are in agreement with observations reported by Szmytkowski and Kwitnewski for 2-butyne and 1,3-butadiene. We estimated the inelastic cross section for 2-butyne and 1,3-butadiene from the calculated elastic and total ionization (calculated using the BEB model) cross sections and from the measured total cross sections. We also compared the cross sections of the C_4H_6 isomers with the cross sections of butane, which is one of the C_4H_{10} isomers, and found that they are similar.

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