# Electron Collisons with Cyclobutane

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We report integral, differential, and momentum transfer cross sections for elastic scattering of low-energy electrons by cyclobutane ($c$-$C_4H_8$), which is an isomer of the $C_4H_8$ molecule and has a closed chain. Our calculations were performed with the Schwinger multichannel method with pseudopotentials at the static-exchange level of approximation, for energies up to 50 eV. We compare the cross sections of cyclobutane with the cross sections of other three isomers of $C_4H_8$, namely, isobutene, cis-2-butene, and skew-1-butene. These isomers have open chain and were the subject of a previous study by our group [Lopes *et al.* J. Phys. B **37**, 997 (2004)]. We also show previous calculated integral and momentum transfer cross sections for isomers of $C_3H_4$, $C_3H_6$ and $C_4H_6$, which have open and closed chains. For each isomeric group we discuss the *isomer effect* focusing on the closed chain isomer. The *isomer effect* is related to differences in the isomers cross sections due to differences in their geometries.

## I. INTRODUCTION

In the last three years, motivated by some experimental works [1–4], we have been investigating electron collisions with isomers of small hydrocarbons, focusing on the *isomer effect*. This effect allows one to distinguish the different isomers of a molecule by differences in their cross sections. The main goal of this investigation was to find differences in the electron-collision cross sections due to differences in the (geometrical) structures of the isomeric groups. We calculated cross sections for electron collisions with isomers of $C_3H_4$ [5], $C_4H_6$ [6], $C_4H_8$ and $C_4H_{10}$ [7], and more recently by isomers of $C_3H_6$ [8]. In particular, for $C_4H_8$ we have not included cyclobutane ($c$-$C_4H_8$), which has a closed chain. We have noticed, however, that for the isomers of $C_4H_6$ and $C_3H_6$, the integral cross sections for the closed chain isomers, namely cyclobutene and cyclopropane, are smaller than for the other isomers. In this case the *isomer effect* is more evident for the closed chain isomers.

In this paper we report integral, differential and momentum transfer cross sections for cyclobutane, $c$-$C_4H_8$, for energies up to 50 eV. To compute the cross sections we employed the Schwinger multichannel method implemented with pseudopotentials. We compare the cross sections of $c$-$C_4H_8$ with the cross sections of isobutene, cis-2-butene and skew-1-butene, which are also isomers of $C_4H_8$ but having open chains. We also present integral and momentum transfer cross sections for isomers of $C_3H_4$, $C_4H_6$ and $C_3H_6$ and discuss the *isomer effect* on the point of view of the closed chain isomers.

In the following we briefly discuss the theoretical method and the computational procedures used in our calculations. Then we present our results and discussions. We end the paper with a brief summary of our findings.

## II. THEORY

The Schwinger multichanel (SMC) method [9–11] and its implementation with pseudopotentials [12] have been described in detail in several publications. We will only discuss the points relevant for the present calculations.

The SMC method is a variational method which results in the following expression for 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

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

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

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

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 represented by a virtual (unoccupied) orbital, and $\mathcal{A}$ is the antisymmetrizer.

## III.  COMPUTATIONAL PROCEDURES

The cross sections were obtained at the static-exchange level of approximation. The molecular geometry was optimized using the package Gaussian [13] at the MP2 (full) level of approximation with the 6-311++G(2d,p) basis set. In the remaining bound state and in the scattering calculations, the $1s$ core electrons of the carbons were replaced by the pseudopotentials of Bachelet, Hamann and Schlüter [14]. For these calculations, the basis set for the carbon atom included 6 uncontracted $s$-type functions (with exponents 12.49408, 2.470291, 0.614027, 0.184029, 0.036799, and 0.013682), 5 uncontracted $p$-type functions (with exponents 5.228869, 1.592058, 0.568612, 0.210326, and 0.072250), and 2 uncontracted $d$-type functions (with exponents 0.603592, and 0.156753), and was generated according to Ref. [15]. The basis set for the hydrogen atom was taken from Ref. [16] and is shown in Table I. We have not included in our calculations the $3s$ symmetric combination of $d$–type functions, namely $[(x^2+y^2+z^2)\exp(-\alpha r^2)]$, in order to eliminate any possible linear dependence in the basis set.

## IV.  RESULTS AND DISCUSSION

Figure 1 shows our calculated integral and momentum transfer cross sections for cyclobutane. Unfortunately there are no experimental data nor theoretical results available for this molecule for comparison. The most prominent feature seen in these cross sections is the broad structure located around 12 eV. In Fig. 2 we show the symmetry decomposition of the integral cross section according to the $D_{2d}$ group. We chose to present the two components of the $E$ symmetry separately, in order to show that they are equivalent. This asserts that our results are converged with respect to the numerical quadratures employed in our calculations. The main contribution to the structure seen in Fig. 1 comes from the $B_2$ ad E symmetries. We also found another interesting feature that was hidden in the cross sections shown in Fig. 1: a shape resonance located around 10 eV and belonging to the $A_2$ symmetry. In their study concerning electron collisions with the isomers of $C_3H_6$, Winstead *et al.* [17] found a shape resonance in the cross section of cyclopropane belonging to the $A_2'$ symmetry. They commented that cyclobutane could present a shape resonance analogous to that of cyclopropane.

Differential cross sections (DCSs) at selected energies are shown in Fig. 3. A very pronounced minimum is seen in the DCSs from 5 to 10 eV at around 75°. Another minimum is visible at around 150°. These features disappear for energies above 10 eV.

Figure 4 compares the integral and momentum transfer cross sections of cyclobutane with the cross sections of other
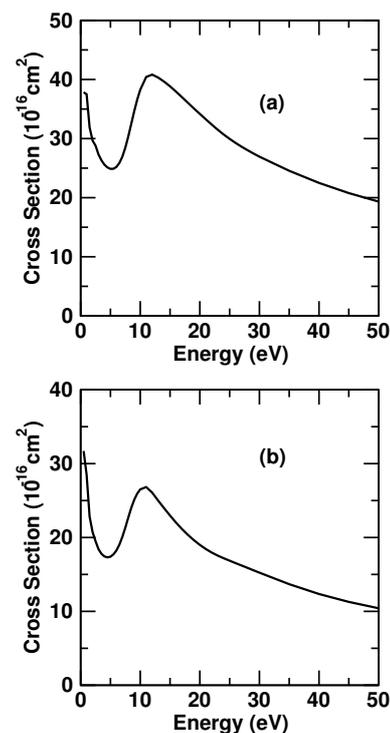


FIG. 1: (a) Integral and (b) momentum transfer cross sections for cyclobutane.
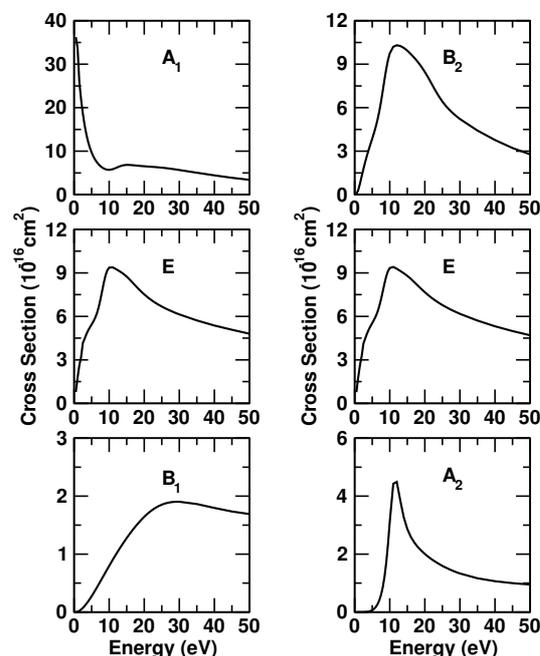


FIG. 2: Symmetry decomposition of the integral cross section of cyclobutane.

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 |
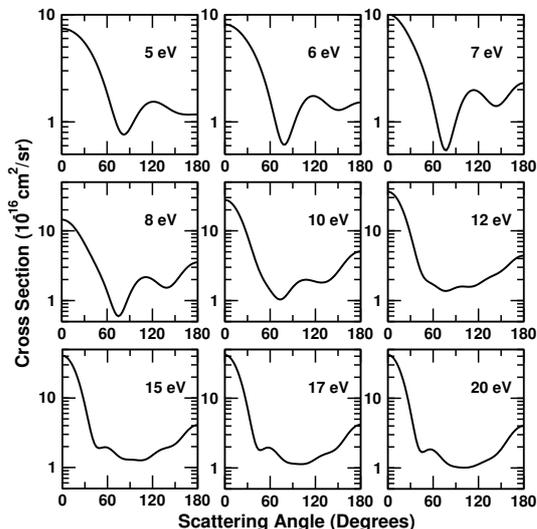


FIG. 3: Differential cross sections for cyclobutane at selected energies.



FIG. 4: (a) Integral and (b) momentum transfer cross sections for isobutene, cis-2-butene, skew-1-butene and cyclobutane.

three isomers of $C_4H_8$, isobutane, cis-2-butene, and skew-1-butene. From this comparison one may notice that the cross sections for cyclobutane lie below the cross sections of the other isomers. The cross sections match at 50 eV; the *isomer effect* being more evident for cyclobutane, which is the closed chain isomer.

The integral and momentum transfer cross sections of all isomers present a broad maximum located at the same energy (at around 12 eV). However, the cross sections of cyclobutane do not show the low-energy sharp structure seen in the cross sections of the other three isomers. This sharp structure is a $\pi^*$ shape resonance and is a characteristic of hydrocarbons with double carbon-carbon bonds; cyclobutane has only single carbon-carbon bonds. Fig. 5 shows the cross sections for the resonant symmetries of isobutane ($C_{2v}$ group), cis-2-butene ($C_{2v}$ group), and skew-1-butene ($C_s$ group).

Comparison of the DCSs at 5, 7, 10, 15, 20, 30, 40 and 50 eV for cyclobutane, isobutane, cis-2-butene, and skew-1-butene are shown in Figs. 6 and 7. The DCSs for cyclobutane differ most from the DCSs of the other three isomers for energies below 15 eV. At 15 eV the differences in the DCSs become smaller, but at 15 eV and above the DCSs of cyclobutane are still distinguishable from the DCSs of the other isomers by the minima located at around $30°$ and $120°$.

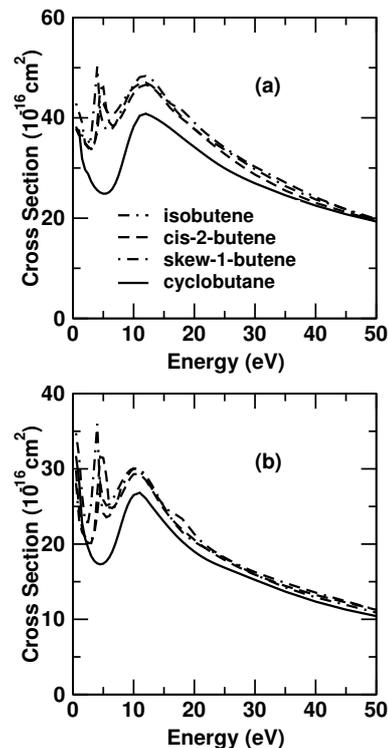In Figs. 8, 9, and 10 we show the integral and momentum transfer cross section for the isomers of $C_3H_4$, $C_3H_6$
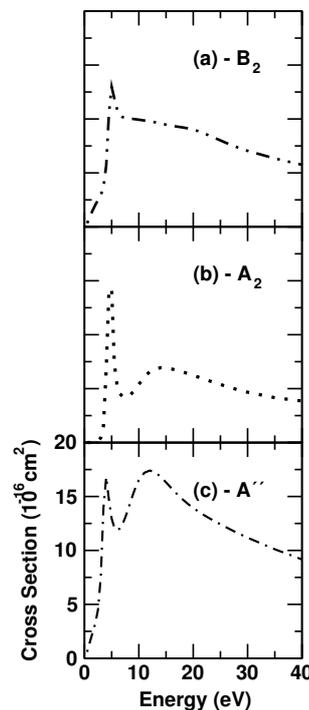


FIG. 5: Integral cross sections for (a) isobutene ($C_{2v}$ group), (b) cis-2-butene ($C_{2v}$ group) and (c) skew-1-butene ($C_s$ group).
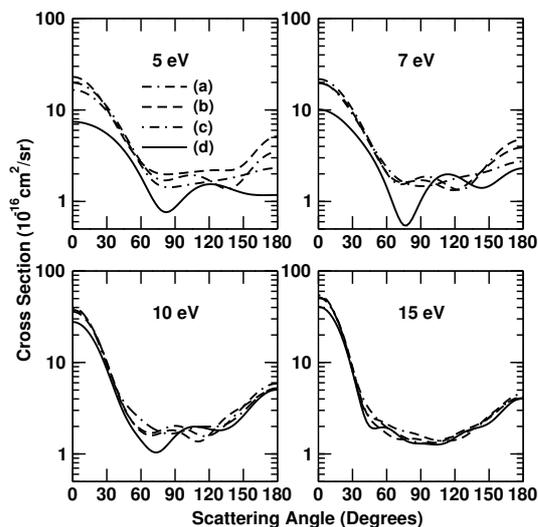
FIG. 6: Differential cross section for (a) isobutene, (b) cis-2-butene, (c) skew-1-butene and (d) cyclobutane at 5, 7, 10 and 15 eV.
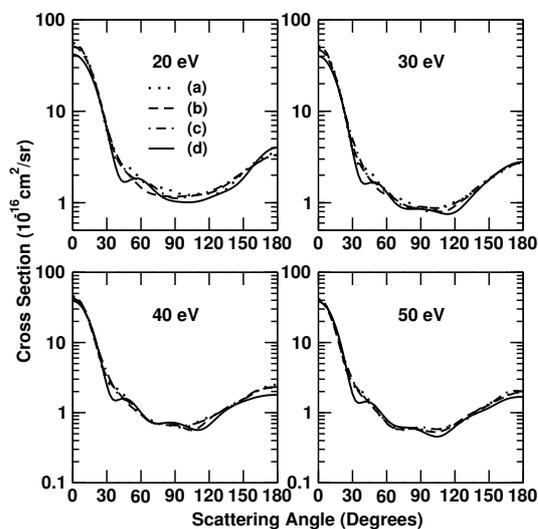


FIG. 7: Same as Fig. 5 at 20, 30, 40 and 50 eV.



FIG. 8: (a) Integral and (b) momentum transfer cross sections for isomers of $C_3H_4$.



FIG. 9: Same as Fig. 8 for isomers of $C_3H_6$.

and $C_4H_6$. Except for $C_3H_4$, the isomers of $C_3H_6$ and $C_4H_6$ present the same behavior as that shown by the isomers of $C_4H_8$. The integral and momentum transfer cross sections of the isomers with closed chain, namely cyclopropane, of $C_3H_6$, and cyclobutene, of $C_4H_6$, also lie below the cross sections of the open chain isomers. Cyclopropane has only single carbon-carbon bonds, and its cross sections do not present the low-energy sharp structure, which is seen in the cross section of propane, which is an open chain isomer with a carbon-carbon double bond. The cross sections of cyclobutene also present a low-energy sharp structure. This isomer has a carbon-carbon double bond.

Figure 11 compares the integral and momentum transfer cross sections for the closed chain isomers of $C_4H_8$ (cyclobu-
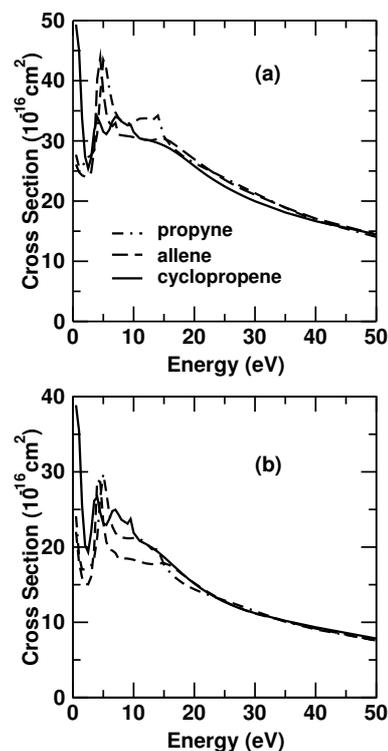
FIG. 10: Same as Fig. 8 for isomers of $C_4H_6$.



FIG. 11: (a) Integral and (b) momentum transfer cross sections for cyclobutane, cyclobutene and cyclopropane.

tane), $C_4H_6$ (cyclobutene) and $C_3H_6$ (cyclopropane). The magnitude of the cross sections follows the molecular size, except by the $\pi^*$ shape resonance that appears in the cross sections of cyclobutene.

## V. SUMMARY

We presented integral, differential and momentum transfer cross sections for cyclobutane, which is one of the isomers of $C_4H_8$. We found a shape resonance located around 10 eV and belonging to the $A_2$ symmetry of the $D_{2d}$ group. Through the comparison of the integral and momentum transfer cross sections of cyclobutane with those of isobutane, cis-2-butene and skew-1-butene, we concluded that the *isomer effect* is more 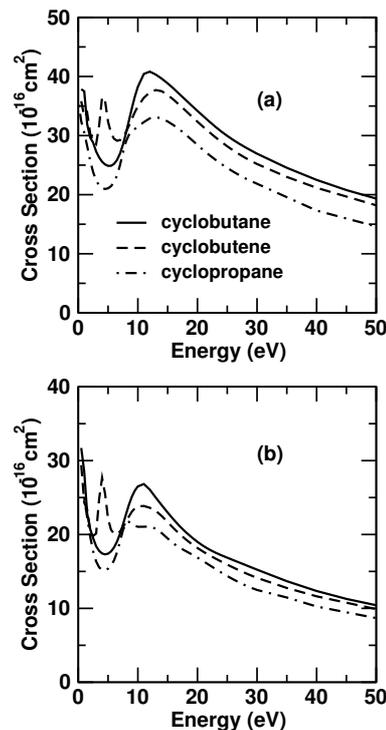evident for cyclobutane, which has a closed chain. The *iso-mer effect* is also more evident for closed chain isomers of other molecules. In particular, for cyclopropane, an isomer of $C_3H_6$, and cyclobutene, an isomer of $C_4H_6$.

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