

Electron collisions with isomers of C₄H₈ and C₄H₁₀

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Received 8 December 2003

Published 17 February 2004

Online at stacks.iop.org/JPhysB/37/997 (DOI: 10.1088/0953-4075/37/5/004)

Abstract

We report integral, differential and momentum transfer cross sections for elastic scattering of low-energy electrons by several isomers of the C₄H₈ molecules, such as isobutene, trans-2-butene, cis-2-butene, skew-1-butene and syn-1-butene, and by two isomers of C₄H₁₀, the isobutane and the butane molecules. To calculate the cross sections, we use the Schwinger multichannel method with pseudopotentials (Bettega *et al* 1993 *Phys. Rev. A* **47** 1111) applied at the static exchange level of approximation for incident energies from 10 to 50 eV. Although the C₄H₈ isomers have different geometric structures, our results show that the integral cross sections for each of these isomers present a broad shape resonance around 10 eV; our results also show that for all C₄H₈ molecular targets, integral cross sections are very similar in shape and magnitude. Similarities are also found in the momentum transfer and in the differential cross sections of these isomers. The same pattern is found in the cross sections of the C₄H₁₀ isomers. Through comparison of the integral and momentum transfer cross sections of 1,3-butadiene (C₄H₆), trans-2-butene (C₄H₈) and butane (C₄H₁₀), all belonging to the C_{2h} group and having similar structures, we discuss the role of the hydrogen atoms in the scattering process by these molecules. Further we show that the integral elastic cross sections of all simple hydrocarbons present strong similarities after a scaling. We present a simple geometric model for this scaling that works quite well for a whole family of C_nH_m molecules (with combinations of $n = 1, 2, 3, 4$ and $m = 2, 4, 6, 8, 10$).

1. Introduction

Experimental studies on electron collisions with isomers of some hydrocarbons have been carried out recently. These studies dealt with measurements of elastic, vibrationally

inelastic and total cross sections for electron collisions with isomers of C_3H_4 [1–3] and C_4H_6 [4]. Nakano *et al* [1] reported elastic and vibrationally inelastic cross sections for scattering of electrons by C_3H_4 isomers, namely, allene and propine. Makochekanwa *et al* [2], and Smytkowski and Kwitnewski [3] measured total cross sections for electron scattering by these C_3H_4 isomers. Smytkowski and Kwitnewski [4] also measured total cross sections for electron collisions by isomers of C_4H_6 , namely, 1,3-butadiene and 2-butyne. We can also quote some recent experimental and theoretical studies related to other hydrocarbons such as those performed by Smytkowski and Kwitnewski on the C_3H_6 isomers [5], Merz and Linder on C_2H_6 [6] and C_3H_8 [7], Panajotovic *et al* [8], Trevisan *et al* [9] and Brescansin *et al* [10] on C_2H_4 and Curik and Gianturco on C_3H_6 [11] and C_3H_8 [12].

These experimental studies have motivated our group to perform a set of comparative studies of elastic collisions of electron with these isomers. In a first study, Lopes and Bettega [13] calculated cross sections for elastic scattering of electrons by isomers of C_3H_4 , namely, allene, propine and cyclopropene. The shape resonances found by the experimental studies were also seen in the calculated integral cross sections of allene and propine. The *isomer effect*, that is the difference in the scattering by the isomers, observed in the experimental results, was confirmed by the calculations at lower energies for the three isomers. In another study, Lopes *et al* [14] calculated elastic cross sections for electron collisions with isomers of C_4H_6 , namely, 1,3-butadiene, 2-butyne and cyclobutene. Again, the shape resonances reported by Smytkowski and Kwitnewski were found in the calculated elastic cross sections, and the *isomer effect* was also observed in these cross sections. In this work we present a comparative study of elastic cross sections for a series of isomers of C_4H_8 , namely, isobutene, trans-2-butene, cis-2-butene, skew-1-butene and syn-1-butene, and by two isomers of C_4H_{10} , namely, isobutane and butane. We also compare the cross sections for 1,3-butadiene (C_4H_6), trans-2-butene (C_4H_8) and butane (C_4H_{10}). These molecules belong to the C_{2h} group, have similar structures and a systematic increasing number of hydrogen atoms. Our calculations were performed with the Schwinger multichannel method at the static-exchange level of approximation for incident energies from 10 to 50 eV. Our interest in studying these isomers is to investigate the existence of shape resonances in their cross section, and the *isomer effect*, which allows one to distinguish different isomers by their cross sections. Besides, some of these molecules have been used as gases in processes of plasma enhanced chemical vapour deposition [16–21].

At higher energies ($E > 10$ eV), the integral cross sections of the many isomers of different hydrocarbons present similarities when a proper scaling factor is used. Thus, we also present a simple geometric model for this scaling, making the elastic integral cross sections for electron scattering by hydrocarbons coincide at energies from 10 to 40 eV. Our results show that the model works quite well for a whole family of C_nH_m molecules (with combinations of $n = 1, 2, 3, 4$ and $m = 2, 4, 6, 8, 10$).

The geometric structures of the C_4H_8 isomers are shown in figure 1 and those of the C_4H_{10} isomers are shown in figure 2. To generate these figures we used the packages GAMESS [22] and Molden [23]. The C_4H_8 isomers present a double bond between two carbons, and the C_4H_{10} isomers present only single bonds between the carbon atoms. The structures of skew-1-butene and syn-1-butene differ by the rotation of the CH_3 and CH_2 around a single bond. The structures of trans-2-butene and cis-2-butene also differ by a rotation, but around a double bond. In table 1, we show the symmetry group of the C_4H_8 and C_4H_{10} isomers along with the calculated total energies and dipole moments. The order in the stability of these isomers found in our total energy calculations agrees with the experiment and other calculations [24, 25].

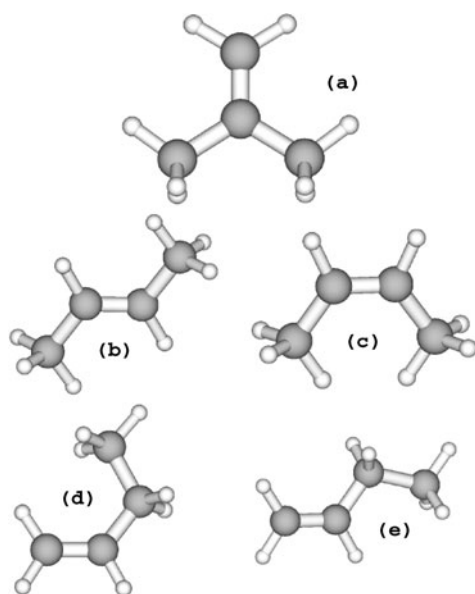


Figure 1. Structure of (a) isobutene, (b) trans-2-butene, (c) cis-2-butene, (d) syn-1-butene and (e) skew-1-butene.

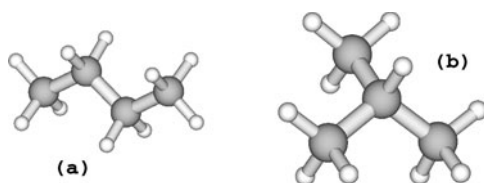


Figure 2. Structure of (a) butane and (b) isobutane.

Table 1. Symmetry groups, SCF energies (*E*) and calculated (calc) and experimental (expt) values for the dipole moments (μ) of the C₄H₈ and C₄H₁₀ isomers.

System	Group	<i>E</i> (hartrees)	μ_{calc} (D)	μ_{expt} (D)
Isobutene	C _{2v}	-26.799 058	0.552	0.503
Syn-1-butene	C _s	-26.797 310	0.436	0.438
Trans-2-butene	C _{2h}	-26.795 606	0.0	0.0
Skew-1-butene	C _s	-26.792 907	0.413	0.359
Cis-2-butene	C _{2v}	-26.791 401	0.332	0.253
Isobutane	C _{3v}	-27.984 334	0.114	0.132
Butane	C _{2h}	-27.982 392	0.0	0.0

In the next section, we present the computational procedures used in our calculations. In section 3, we present our results and discussion. A simple geometrical model for elastic integral cross sections for 10–50 eV electron scattering by hydrocarbons is presented in section 4. Section 5 concludes the paper with a brief summary of our findings.

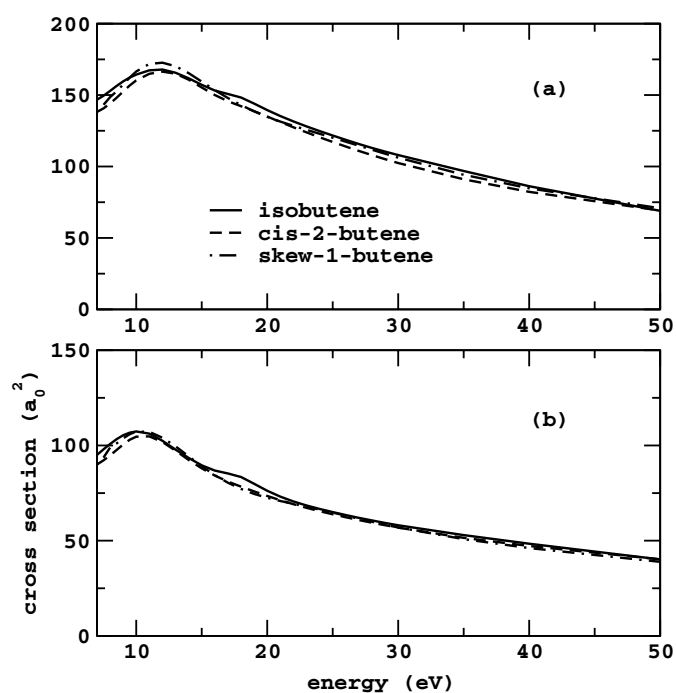


Figure 3. (a) Integral and (b) momentum transfer cross sections for C_4H_8 isomers.

2. Computational details

Our calculations employed the Schwinger multichannel (SMC) method [26, 27] with pseudopotentials of Bachelet *et al* [32]. The SMC method and its implementation with pseudopotentials have been discussed in detail in several publications. In this section, we will present only the computational detail regarding the present calculations.

The fixed-nuclei static-exchange approximation was used to compute the elastic cross sections (an average over all molecular orientations is carried out in order to allow direct comparison with experimental data). The geometries used in the ground state and scattering calculations are those from [24], for C_4H_8 , and from [31], for C_4H_{10} . The basis set for the carbon atom used in these calculations is the same used in previous studies [13, 14] and was generated according to [29]. For the hydrogen atom the basis set is from [30]. In table 1, we present the symmetry groups, the SCF energies and the calculated and experimental values for the dipole moments (μ) for the C_4H_8 and C_4H_{10} isomers. Since the values of the dipole moments are small, we have not included any correction due to the long range potential scattering.

3. Results and discussion

In this section, we will present the results of our calculations for the whole family of molecules. Although we discuss the results from 10 to 50 eV, our integral and momentum transfer cross sections are shown beginning at 7 eV in order to show the entire broad structure around 10 eV. To point out the existence (or not) of the *isomer effect*, we present the results for the C_4H_8 and C_4H_{10} in different subsections (3.1 and 3.2, respectively). In subsection 3.3, to further

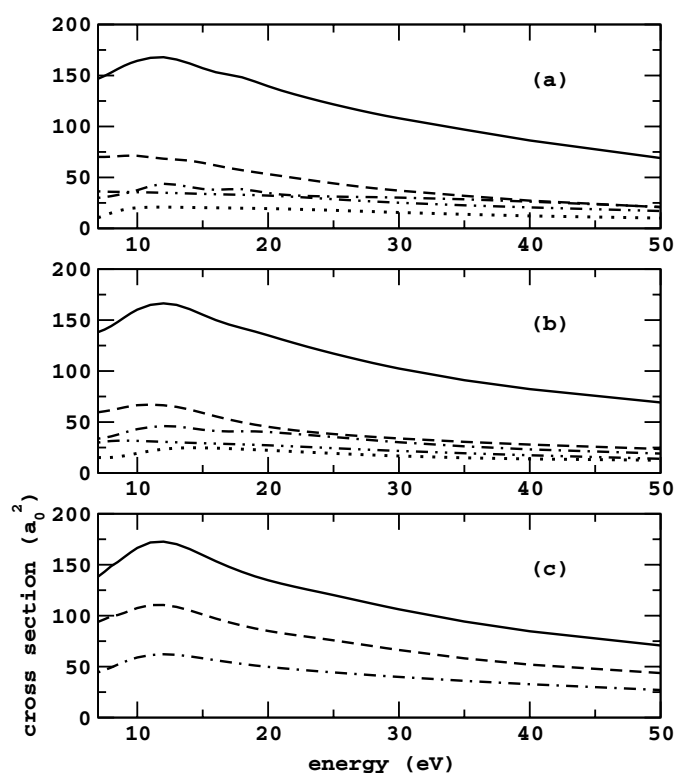


Figure 4. Symmetry decomposition of the integral cross sections for C_4H_8 isomers. (a) isobutene (C_{2v} group): solid line, integral cross section; dashed line, cross section for the A_1 representation; dotted-dashed line, cross section for the B_1 representation; dotted-dotted-dashed line, cross section for the B_2 representation; dotted line, cross section for the A_2 representation. (b) cis-2-butene (C_{2v} group): solid line, integral cross section; dashed line, cross section for the A_1 representation; dotted-dashed line, cross section for the B_1 representation; dotted-dotted-dashed line, cross section for the B_2 representation; dotted line, cross section for the A_2 representation. (c) skew-1-butene (C_s group): dashed line, cross section for the A' representation; dotted-dashed line, cross section for the A'' representation.

exploit similarities among cross sections of electron-hydrocarbon molecule scattering, we present results of a comparative study for 1,3-butadiene (C_4H_6), trans-2-butene (C_4H_8) and butane (C_4H_{10}), all belonging to the C_{2h} group. Similar illustrative comparison is done in subsection 3.4 for CH_4 , C_2H_6 , C_3H_8 and C_4H_{10} molecules.

3.1. C_4H_8

In figure 3, we show the calculated integral cross sections (ICS) and momentum transfer cross sections (MTCS) for isobutene, cis-2-butene and skew-1-butene for energies from 10 to 50 eV. A comparison of the calculated ICS of these isomers shows that they are very similar, having the same shape and same magnitude in the energy range considered. Some similarities are seen for MTCS. In particular, the energy-dependent cross sections of figure 3 show a broad structure around 10 eV.

In order to further explore the shape resonances shown in figure 3, we obtained the symmetry decomposition of the ICS for these isomers, and show the results in figure 4. For

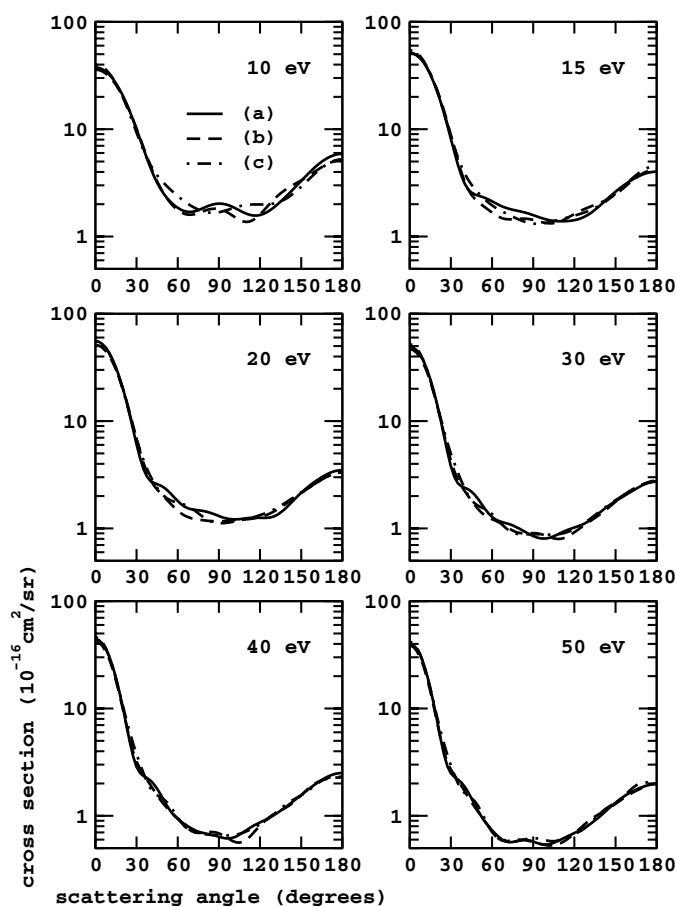


Figure 5. Differential cross sections for the C_4H_8 isomers at 10, 15, 20, 30, 40 and 50 eV: (a) isobutene, (b) cis-2-butene and (c) skew-1-butene.

isobutene, which belongs to the C_{2v} group, the broad structure around 10 eV is due mostly from a superposition of shape resonances from B_1 and A_2 representations. For cis-2-butene, also belonging to the C_{2v} group, the broad structure around 10 eV is a superposition of shape resonances belonging to the A_1 and B_1 representations. The next isomer is skew-1-butene, which belongs to the C_s group. For this isomer, the structure around 10 eV is a superposition of broad shape resonances from the A' and A'' representations.

In figure 5, we present the differential cross sections (DCS) at 10, 15, 20, 30, 40 and 50 eV for isobutene, cis-2-butene and skew-1-butene. At 10 eV the DCS for isobutene shows two minima, which is a characteristic of a d-wave. The same occurs for the DCS of cis-2-butene at 10 eV. At 15 eV the DCS for the three isomers become similar. This similarity becomes more evident at higher energies.

Comparisons of the ICS and MTCS for cis-2-butene and trans-2-butene are shown in figure 6. The cross sections for these two isomers are very similar to each other. The DCS for these molecules at 10, 15, 30 and 50 eV are shown in figure 7. Again similarities are found in the DCS. We also compare the ICS and MTCS for skew-1-butene and syn-1-butene. The results are shown in figure 8. The DCS at 10, 15, 30 and 50 eV are shown in figure 9.

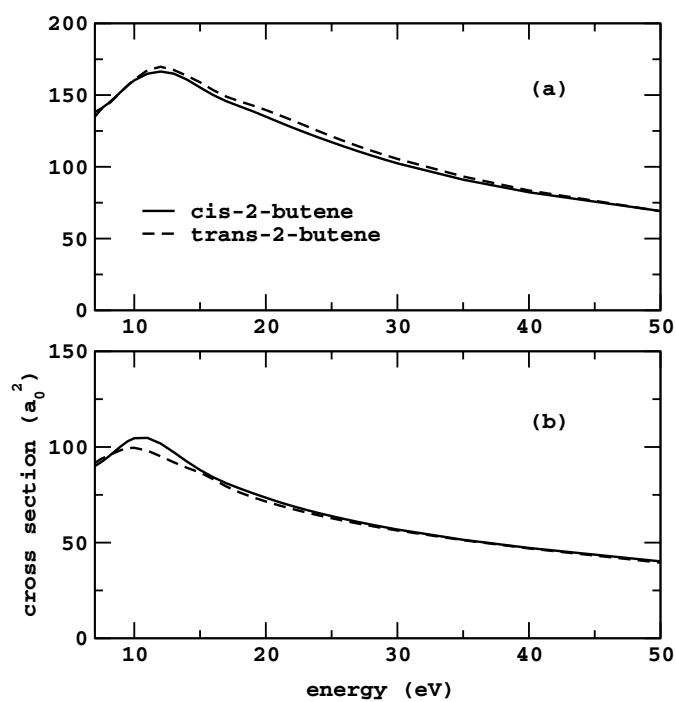


Figure 6. (a) Integral and (b) momentum transfer cross sections for the C_4H_8 isomers trans-2-butene and cis-2-butene.

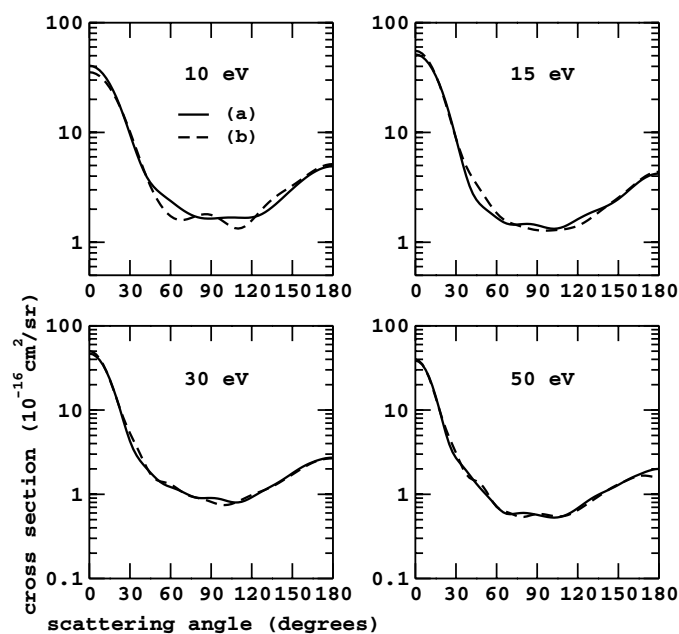


Figure 7. Differential cross sections for the C_4H_8 isomers at 10, 15, 30 and 50 eV: (a) trans-2-butene and (b) cis-2-butene.

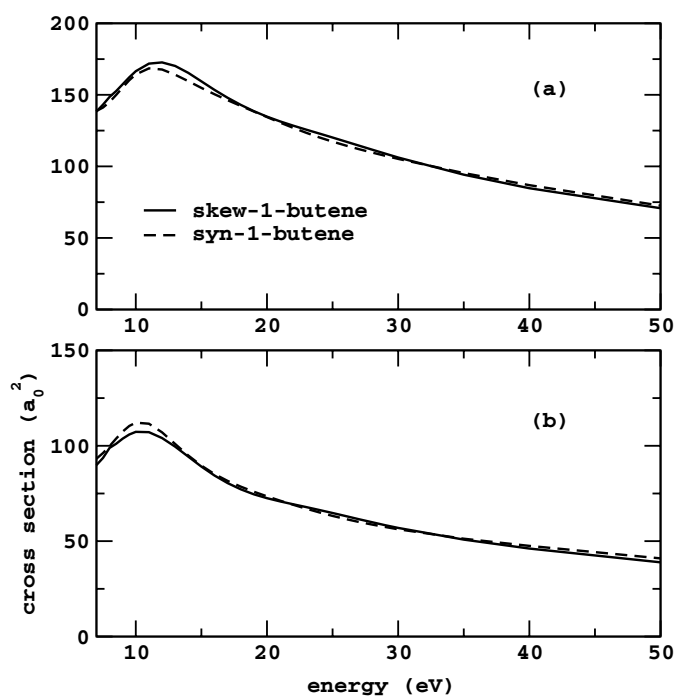


Figure 8. (a) Integral and (b) momentum transfer cross sections for the C_4H_8 isomers syn-1-butene and skew-1-butene.

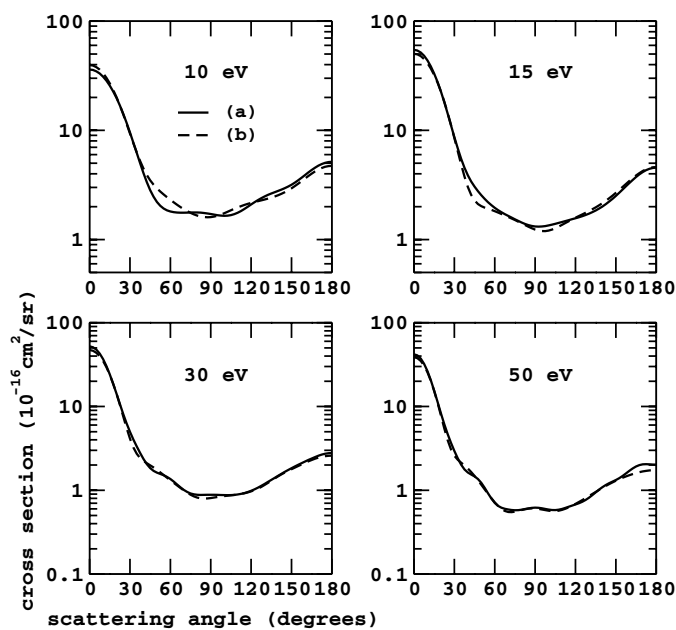


Figure 9. Differential cross sections for the C_4H_8 isomers at 10, 15, 30 and 50 eV: (a) syn-1-butene and (b) skew-1-butene.

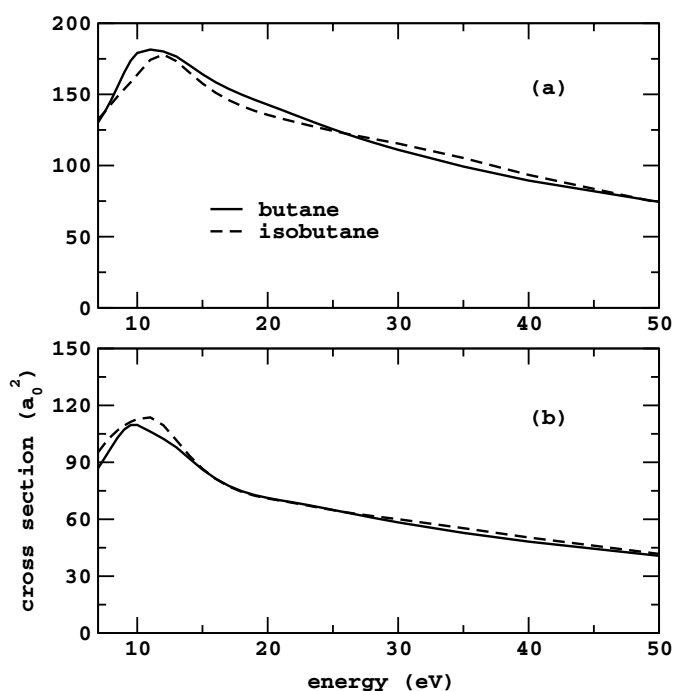


Figure 10. (a) Integral and (b) momentum transfer cross sections for the C_4H_{10} isomers.

In general, the ICS and MTCS for the C_4H_8 isomers considered in this study are very similar, and it becomes difficult to distinguish these isomers by their cross sections. Based on the results shown above, we may conclude that the *isomer effect*, which is related to differences in the isomer cross sections, is not so evident for the C_4H_8 isomers.

3.2. C_4H_{10}

The ICS and MTCS for butane and isobutane are shown in figure 10. The cross sections for both isomers are very similar, following the pattern observed in the ICS and MTCS for the C_4H_8 isomers. The symmetry decomposition of the ICS is shown in figure 11 according to the C_{2h} group, for butane, and according to the C_{3v} group, for isobutane. The structure seen in the ICS of butane is a superposition of structures from B_g , A_u and B_u representations of the C_{2h} group. For isobutane, the contribution for its structure comes mostly from the E representation of the C_{3v} group with a small contribution from the structure belonging to the A_1 representation of this group.

The DCS for butane and isobutane are shown in figure 12 at 10, 15, 20, 30, 40 and 50 eV. For isobutane, a d-wave behaviour is seen at 10 eV. At 15 eV the DCS for these isomers become similar, except for the oscillations around 30° . As for the C_4H_8 isomers, the *isomer effect* is not so evident for the C_4H_{10} isomers.

3.3. C_4H_6 , C_4H_8 and C_4H_{10}

In figure 13, we compare the ICS and MTCS of 1,3-butadiene (C_4H_6), trans-2-butene (C_4H_8) and butane (C_4H_{10}). We chose these molecules because they belong to the C_{2h} group and

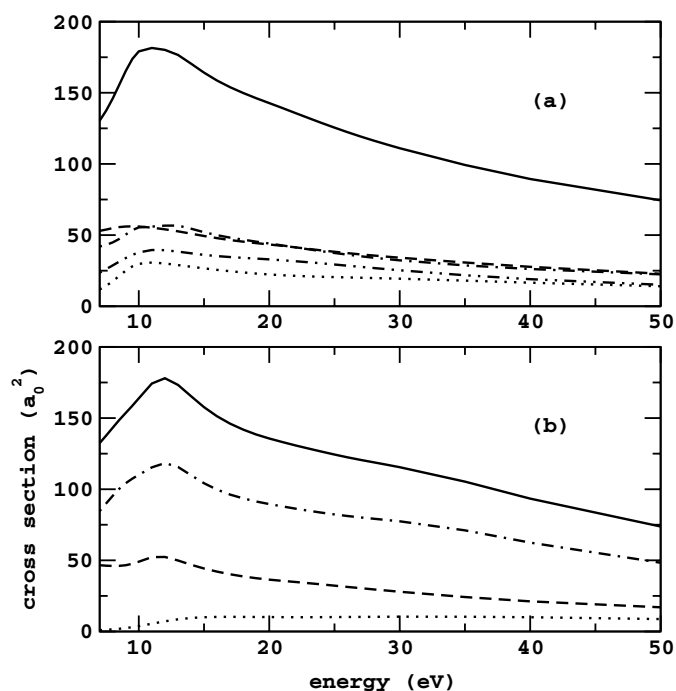


Figure 11. Symmetry decomposition of the integral cross sections for the C_4H_{10} isomers. (a) butane (C_{2h} group): solid line, integral cross section; dashed line, cross section for the A_g representation; dotted-dashed line, cross section for the B_u representation; dotted-dotted-dashed line, cross section for the A_u representation; dotted line, cross section for the B_g representation. (b) isobutane (C_{3v} group): solid line, integral cross section; dashed line, cross section for the A_1 representation; dotted-dashed line, cross section for the E representation; dotted line, cross section for the A_2 representation.

therefore have similar structures, but they differ in the number of hydrogens and in the bond lengths and angles. Above 12.5 eV, the order in magnitude of the integral cross sections follows the increase in the number of hydrogen. However, the difference in magnitude is very small. For energies below 12.5 eV these molecules present shape resonances that are located at different energies. The MTCS follow the same pattern of the ICS. Small differences in the DCS for these molecules are shown in figure 14 for 10, 15, 30 and 50 eV electron impact energies.

3.4. CH_4 , C_2H_6 , C_3H_8 and C_4H_{10}

Winstead *et al* [33] pointed out that the hydrocarbons C_nH_{2n+2} (CH_4 , C_2H_6 and C_3H_8) present a very broad shape resonance located around the same position. In this study we repeated this comparison including an additional molecule, C_4H_{10} (butane). This comparison is shown in figure 15. This figure shows that butane also has a broad shape resonance, and that is located at the same position of the resonances of the other molecules. Besides, the C–H bond length of butane is 1.2 Å, which is very similar to the C–H bond length of the other molecules (1.09 Å, for CH_4 , 1.11 Å, for C_2H_6 and 1.09 Å, for C_3H_8). The large difference in magnitude of the integral cross sections of electron scattering against these molecules is notable.

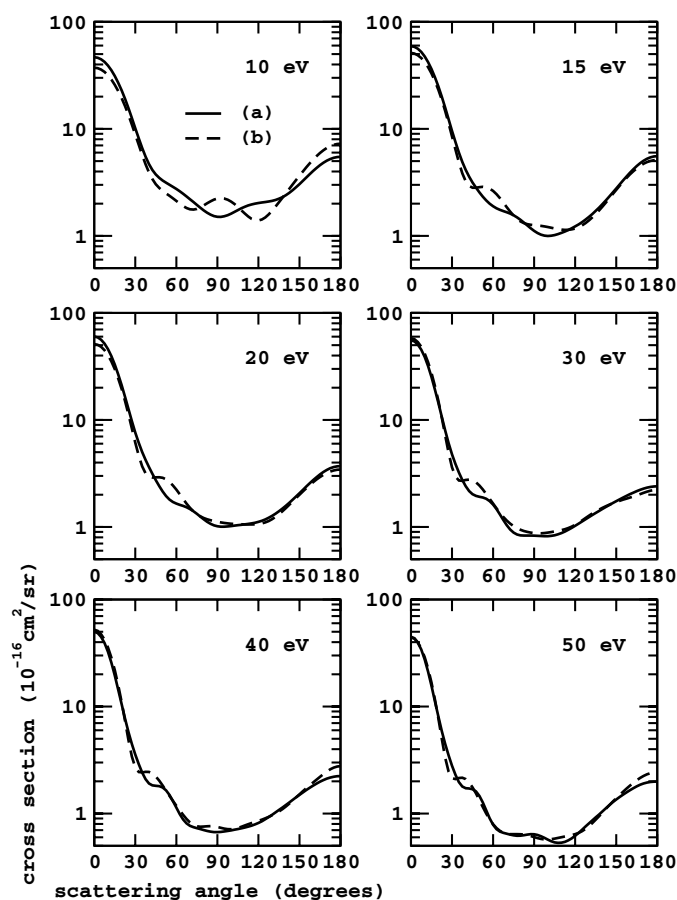


Figure 12. Differential cross sections for the C_4H_{10} isomers at 10, 15, 20, 30, 40 and 50 eV: (a) butane, and (b) isobutane.

4. Geometric model of the integral elastic cross section of hydrocarbons

One surprising feature seen in the hydrocarbon cross sections presented in the last section is their similarity at energies above 10 eV. First, comparing hydrocarbons that have different number of hydrogens, or different geometries, but the same number of carbons, one is led to conclude that hydrogens do not matter for electron scattering and geometry has a very small effect (as shown in figure 13). Second, comparing hydrocarbons with different numbers of carbons, one cannot fail to note that their cross sections seem to differ only by a scale that depends on the energy of electron beam (as shown in figure 15).

We consider spheres of radii R centred at the molecular carbon sites. We distinguish three carbon types: those with four neighbours ($C^{(4)}$), those with three neighbours ($C^{(3)}$) and those with two neighbours ($C^{(2)}$). Of course, the less neighbours a carbon atom has the more π binding orbitals it has. Thus it is natural to assume that the sphere radii depend on the number of neighbours. On this molecule of spheres we impinge randomly oriented light rays and calculate the area of the shadow on a screen behind the molecule. The calculation of the shadow area is made with the Monte Carlo technique because of the confusing intersections

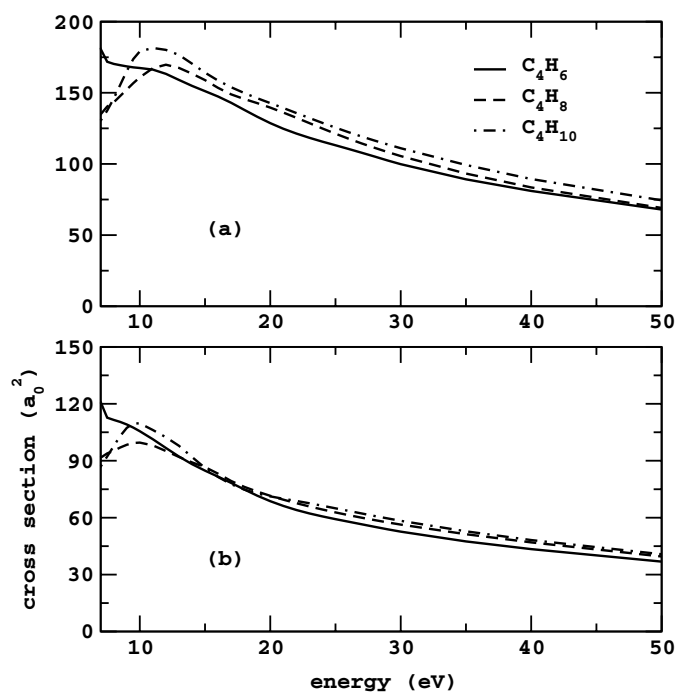


Figure 13. (a) Integral and (b) momentum transfer cross sections for 1,3-butadiene (C_4H_6), trans-2-butene (C_4H_8) and butane (C_4H_{10}). These three molecules belong to the C_{2h} group.

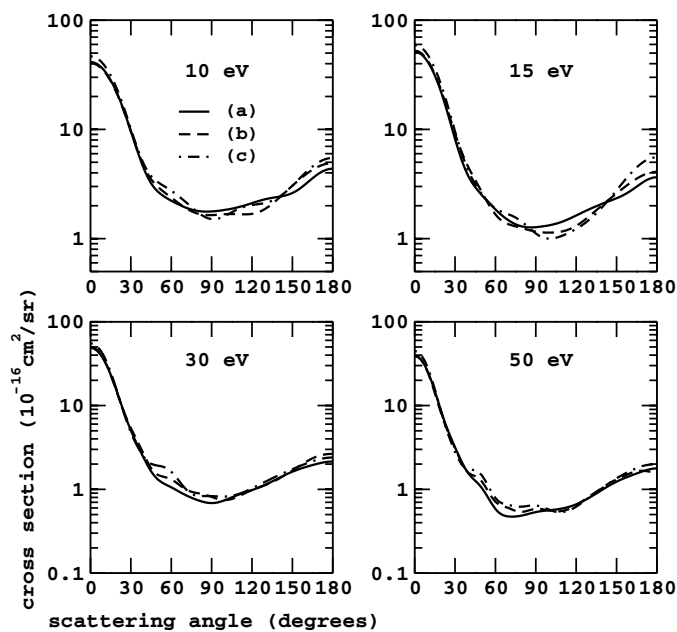


Figure 14. Differential cross sections for (a) 1,3-butadiene (C_4H_6), (b) trans-2-butene (C_4H_8) and (c) butane (C_4H_{10}) 10, 15, 30 and 50 eV.

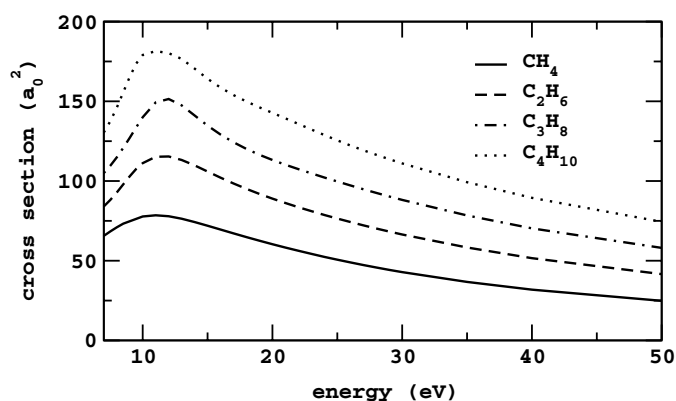


Figure 15. Integral cross sections for CH₄, C₂H₆, C₃H₈ and C₄H₁₀.

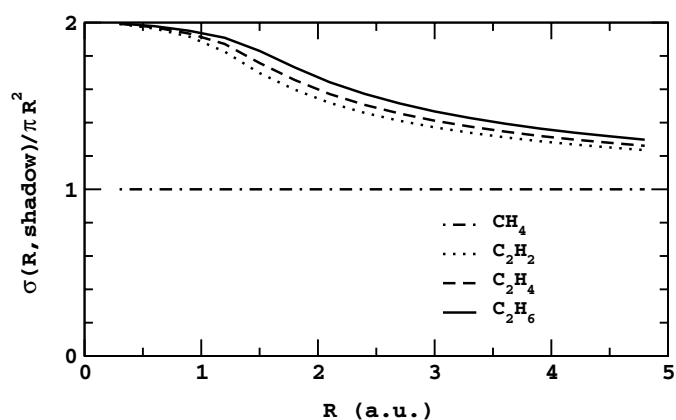


Figure 16. Shadow areas (divided by shadow of single sphere) as function of the sphere radius R for simple hydrocarbons.

of the many sphere projections on the screen. Thus, for a given randomly oriented ray hitting at random point of a sphere, we check whether the ray also hit another sphere, in which case the ray is eliminated from the count if it was reckoned previously. For the hydrocarbons that we calculate we used up to 83 million randomly oriented rays to calculate the average shadow (geometric cross section). Figure 16 shows the shadow areas of simple molecules divided by the shadow area of a single sphere. If the radius tends to zero naturally the ratio tends to the number of carbons. If the radius tends to infinity, the distances between centres become relatively negligible and the shadow tends to that of a single sphere. In this case, the ratio tends to 1.

For a generic hydrocarbon, the calculation of the average shadow only requires knowledge of the carbon atomic positions and the sphere radii $R^{(4)}$, $R^{(3)}$, $R^{(2)}$, corresponding to the carbons with four, three and two neighbours, respectively³. The radii are assumed to depend on the incident electron energy. We determined the radii as follows. First we equate the ratios

$$\frac{\sigma(E, \text{CH}_4, \text{SMC})}{\sigma(R^{(4)}, \text{CH}_4, \text{shadow})} = \frac{\sigma(E, \text{C}_2\text{H}_6, \text{SMC})}{\sigma(R^{(4)}, \text{C}_2\text{H}_6, \text{shadow})}$$

³ Though the H atoms do not contribute to the cross section or shadow, they must be counted as neighbours of the carbons.

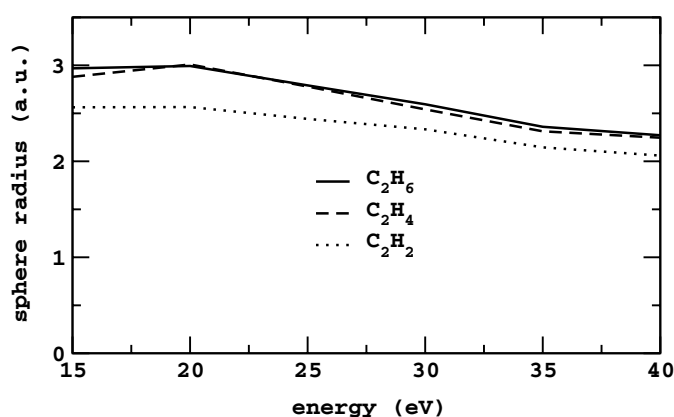


Figure 17. Radii $R^{(4)}$, $R^{(3)}$ and $R^{(2)}$ as functions of energy. The radii are determined by equating the ratios of $\sigma(\text{SMC})/\sigma(\text{shadow})$ for the molecules C_2H_6 , C_2H_4 , C_2H_2 with that of methane.

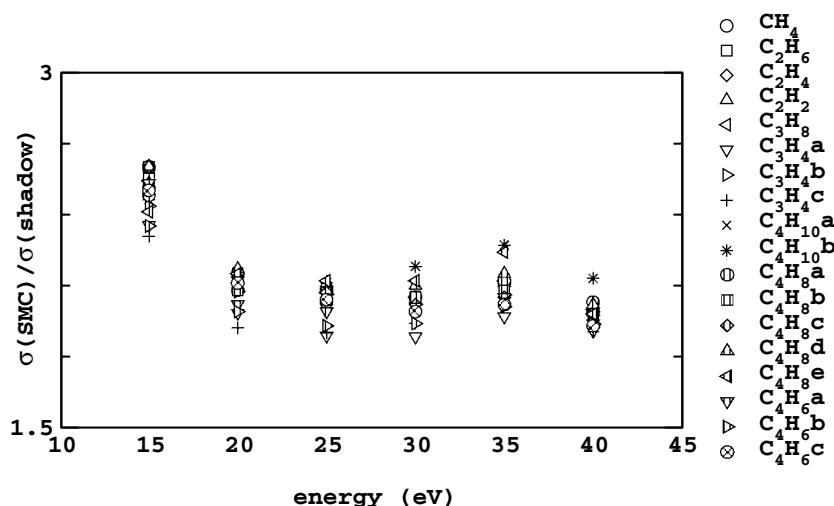


Figure 18. Cross section ratios for 18 hydrocarbons: CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , propane (C_3H_8), cyclopropane ($\text{C}_3\text{H}_4\text{a}$), propyne ($\text{C}_3\text{H}_4\text{b}$), alene ($\text{C}_3\text{H}_4\text{c}$), butane ($\text{C}_4\text{H}_{10}\text{a}$), isobutane ($\text{C}_4\text{H}_{10}\text{b}$), syn-1-butene ($\text{C}_4\text{H}_8\text{a}$), skew-1-butene ($\text{C}_4\text{H}_8\text{b}$), trans-2-butene ($\text{C}_4\text{H}_8\text{c}$), isobutene ($\text{C}_4\text{H}_8\text{d}$), cis-2-butene ($\text{C}_4\text{H}_8\text{e}$), 2-butyne ($\text{C}_4\text{H}_6\text{a}$), 1,3-butadiene ($\text{C}_4\text{H}_6\text{b}$) and cyclobutene ($\text{C}_4\text{H}_6\text{c}$).

of the SMC-calculated cross section and shadow for the molecules CH_4 and C_2H_6 , both having carbons with four neighbours, to determine $R^{(4)}$ as function of energy. Then we use the equations

$$\frac{\sigma(E, \text{CH}_4, \text{SMC})}{\sigma(R^{(4)}, \text{CH}_4, \text{shadow})} = \frac{\sigma(E, \text{C}_2\text{H}_4, \text{SMC})}{\sigma(R^{(3)}, \text{C}_2\text{H}_4, \text{shadow})} = \frac{\sigma(E, \text{C}_2\text{H}_2, \text{SMC})}{\sigma(R^{(2)}, \text{C}_2\text{H}_2, \text{shadow})}$$

to determine $R^{(3)}$ and $R^{(2)}$. The results of this preliminary calculation are in figure 17.

After finding the radii, we calculated the shadow cross sections for several hydrocarbons: propane (C_3H_8), cyclopropane ($\text{C}_3\text{H}_4\text{a}$), propyne ($\text{C}_3\text{H}_4\text{b}$), alene ($\text{C}_3\text{H}_4\text{c}$), butane ($\text{C}_4\text{H}_{10}\text{a}$), isobutane ($\text{C}_4\text{H}_{10}\text{b}$), syn-1-butene ($\text{C}_4\text{H}_8\text{a}$), skew-1-butene ($\text{C}_4\text{H}_8\text{b}$), trans-2-butene ($\text{C}_4\text{H}_8\text{c}$), isobutene ($\text{C}_4\text{H}_8\text{d}$), cis-2-butene ($\text{C}_4\text{H}_8\text{e}$), 2-butyne ($\text{C}_4\text{H}_6\text{a}$), 1,3-butadiene ($\text{C}_4\text{H}_6\text{b}$) and

cyclobutene (C₄H_{6c}). We show our results in figure 18, where we plot the ratio $\sigma(\text{SMC})/\sigma(\text{shadow})$ for the above hydrocarbons. We note that the dispersion is very small ($\simeq 5\%$) and that curiously the ratio is around 2.0.

5. Summary and conclusions

We presented elastic cross sections for scattering of electrons by isomers of C₄H₈ and C₄H₁₀ for energies between 10 and 50 eV. Our results show that the cross sections for the C₄H₈ isomers are very similar and present a very broad structure around 10 eV. The same pattern is found for the C₄H₁₀ isomers. Comparing the cross sections of C₄H₆ and all hydrocarbons with four carbon atoms, but with different number of hydrogens, we again found that they are similar. Further, comparing the cross sections of hydrocarbons with different number of carbon atoms, we again found the same behaviour, *as long as the cross sections are scaled*. Then what is the *isomer effect*? As a manifestation of the isomer individualities, it is only observable at lower energies when resonances are likely to occur.

Acknowledgments

ARL acknowledges scholarship from Brazilian agency Coordenação de Aperfeiçoamento de Pessoal de Nível superior (CAPES). MHFB, MAPL and LGF acknowledge support from Brazilian agency Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). MHFB also acknowledges support from the Paraná state agency Fundação Araucária and from FUNPAR. The authors acknowledge computational support from Professor Carlos M de Carvalho at DF-UFPR, from CENAPAD-SP and also from Centro de Computação Científica e Software Livre (C³SL) at DINF-UFPR.

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