

Electron scattering on C₃H₆ isomers

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys. B: At. Mol. Opt. Phys. 35 2613

(<http://iopscience.iop.org/0953-4075/35/11/319>)

[The Table of Contents](#) and [more related content](#) is available

Download details:

IP Address: 153.19.42.120

The article was downloaded on 25/12/2008 at 22:15

Please note that [terms and conditions apply](#).

Electron scattering on C₃H₆ isomers

Czesław Szmytkowski and Stanisław Kwitnewski

Atomic Physics Division, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, ul. G. Narutowicza 11/12, 80-952 Gdańsk, Poland

E-mail: czsz@mif.pg.gda.pl

Received 21 March 2002, in final form 30 April 2002

Published 24 May 2002

Online at stacks.iop.org/JPhysB/35/2613

Abstract

Absolute total cross sections (TCSs) for the electron scattering from two structured isomers of C₃H₆ (propene and cyclopropane) have been determined over the energy range from 0.5 up to 370 eV in a linear electron-beam transmission experiment. The TCS for propene is generally higher than that for cyclopropane, especially around the main maximum which in both TCSs is centred near 9.5 eV. Besides this broad enhancement, already observed in earlier measurements, some additional new TCS features—specific for each target—have been noticed in the present experiment. The TCS for propene has a distinct resonant narrow peak visible at around 2.2 eV. For cyclopropane, a very weak hump at around 2.6 eV and a shoulder near 6 eV on the low-energy slope of the cross section function are distinguishable. On the descending side of the cross section energy dependence the change of the slope is located at around 40 eV. These weak cyclopropane features seem to be common for cyclic molecules.

The present results are compared with earlier C₃H₆ TCS measurements available above 4 eV and with calculations above 10 eV. A distinct difference in magnitudes is visible, especially around the main maximum. On the basis of the present propene and previous hexafluoropropene data a fluorination effect is indicated and discussed.

1. Introduction

Propene (C₃H₆) and cyclopropane (c-C₃H₆) are isomers of one another with the same number of constituent atoms but in considerably different geometrical arrangements; propene is an open-chain hydrocarbon molecule while its isomeric counterpart, cyclopropane, is a cyclic compound. Both molecules also exhibit the various forms of carbon bonds. One would, therefore, expect that such a difference in the target structure should reflect in the magnitude and the energy dependence of the electron-scattering cross sections for these molecules. To find differences in scattering processes for C₃H₆ isomers, comparative studies were carried out in some collision channels. A distinct difference was first observed in the magnitude of total ionization

cross sections for propene and cyclopropane by Lampe *et al* (1957) and then by Harrison *et al* (1966), Schram *et al* (1966), Beran and Kevan (1969) and more recently by Nishimura and Tawara (1994). However, while the experiments of Lampe *et al*, Harrison *et al* and Beran and Kevan give the total ionization cross section (at 70–75 eV) for propene lower by about 10% than that for cyclopropane, the measurements of Schramm *et al* and Nishimura and Tawara indicate the reverse relation between compared cross sections over a very wide range of impact energies. Surprisingly, very recent calculations in the Deutsch–Märk formalism (Deutsch *et al* 2000) do not reveal any difference in both single-ionization cross sections. Evidence of the isomeric effect also results from swarm experiments performed by Duncan and Walker (1974); at thermal energies, the momentum transfer cross section determined for propene is nearly an order of magnitude higher than that for cyclopropane, though above 0.2 eV the difference is less pronounced; moreover the cross section for propene has a well-marked minimum near 0.1 eV. Boesten *et al* (1993) observed, in a crossed-beam experiment, evident differences in the shape of the elastic and vibrational differential cross sections of both isomers. Experimental data of Floeder *et al* (1985) indicate that the electron-scattering total cross section (TCS) for propene is generally higher by several per cent than that for cyclopropane, though the observed difference is within the limits of experimental error. Later results of Nishimura and Tawara (1991) for C₃H₆ isomers differentiate more clearly; the discord in the magnitude of TCS for this pair exceeds 20% near the maximum at around 10 eV. The elastic calculations of Winstead *et al* (1992) at the static-exchange level of approximation provide a further indication of substantial isomer effects, which may in part account for the differences observed in TCSs.

Some experiments and calculations concerned only one of the isomers. For propene Bowman and Gordon (1967) evaluated the momentum transfer cross section from swarm experimental data. Close to 0.1 eV, a very deep Ramsauer minimum in the backward electron-scattering cross section, with a sharp increase towards zero energy, was recently observed for propene by Lunt *et al* (1998) in a transmission experiment. Inelastic collisions have been investigated with a trapped electron technique by Bowman and Miller (1965) and Dance and Walker (1973). Formation of negative ions in electron–propene scattering was reported by Jordan and Burrow (1980) and Rutkowsky *et al* (1980). Electronic transitions in propene induced by electrons with impact energies from 15 to 80 eV were observed by Flicker *et al* (1975). Otvos and Stevenson (1956) determined the e⁻-C₃H₆ ionization cross section at 75 eV. Recently, much more attention has been focused on the electron interaction with the cyclopropane molecule. Allan (1993) and Allan and Andric (1996) measured low-energy electron energy-loss spectra and excitation functions for vibrational transitions in cyclopropane. Very recently elastic integral and differential cross sections were computed by Čurík and Gianturco (2002a) at energies from 1 to 15 eV. Čurík and Gianturco (2002b) calculated vibrational excitation cross sections for three totally symmetric modes of cyclopropane. Hitchcock *et al* (1986) recorded and calculated inner-shell electronic excitation spectra of c-C₃H₆. Vibrational excitation of cyclopropane in thin solid films was examined by Göötz *et al* (1999). The *R*-matrix formalism was employed by Beyer *et al* (1997) to investigate elastic resonant electron scattering from cyclopropane and by Nestmann (1998) to study metastable anionic state formation. A semiempirical estimation of the electron scattering ionization cross section for cyclopropane was carried out by Bobeldijk *et al* (1994). Jiang *et al* (1997) calculated the total (elastic + inelastic) cross section for cyclopropane under the assumption that the TCS is a constitutive molecular property which can be estimated from appropriate atomic cross sections.

This work is a part of our systematic study of families of targets which can, apart from yielding accurate data, provide some stimulating insights into the role played by the physical properties of the target molecules in the scattering process and, consequently, serve as a guide

for future theoretical investigations. One of the goals of this work is to look for differences and similarities in TCSs for propene and cyclopropane over an extended energy range, from 0.5 up to 370 eV. TCS data below 10 eV are of special interest to us, since in this energy region one would expect some resonant features and, to our knowledge, no absolute results below 4 eV are available in the literature. Our motivation for making a further set of measurements above 4 eV has come from the fact that there is a significant disagreement in the TCS data reported to date. It is also of interest to compare the present TCS for propene with results obtained in our laboratory for hexafluoropropene (the perfluoro analogue of propene) to demonstrate the fluorination effect.

2. Experimental procedure

The present TCS measurements were made using a transmission method in a linear configuration. The absolute TCS $Q(E)$ for a given impact energy E was derived from the Bouguer–de Beer–Lambert relationship

$$I_p(E) = I_0(E) \exp\left[-Q(E) \frac{pl}{k\sqrt{T_m T_c}}\right],$$

where quantities measured directly in the experiment are: electron beam intensities at energy E in the presence, $I_p(E)$, or absence, $I_0(E)$, of the target gas in the scattering cell. p is the target pressure as measured with a baratron, T_m ($= 322$ K) is the temperature of the manometer head, while T_c is temperature of the scattering cell and l is the length of the scattering volume; k is the Boltzmann constant. A thermal transpiration effect is accounted for (Knudsen 1910).

The apparatus and experimental procedure used in the reported experiment was based on an electrostatic electron spectrometer extensively used in a series of experiments and described in detail elsewhere (e.g. Szmytkowski *et al* 1998). The sample in the scattering cell was irradiated with a quasi-monoenergetic electron beam with an energy spread of 80 meV (FWHM) and an intensity of about 10 pA formed by an electron optical system consisting of an electron gun coupled to an electrostatic cylinder deflector and electron lenses. The energy scale was calibrated to within ± 50 meV by reference to the well known electron-scattering oscillatory resonant structure around 2.3 eV in molecular nitrogen. Those electrons which undergo a collision with the target molecules within the reaction volume and pass through the exit aperture are energetically discriminated by the retarding field analyser and eventually collected with a Faraday cup detector with a geometrical angular acceptance of 0.6 msr.

Measurements at a given energy E were carried out in a series of runs using a range of target pressures (0.08–0.12 Pa) and different sets of electron-beam-controlling parameters. To lessen the influence of gas effusing from the scattering chamber on the intensity of the primary electron beam and in consequence on the measured TCS, the experiment was carried out at the constant background pressure of the target gas (0.2 mPa) in the electron optics region. The final TCS value at each particular energy is a weighted mean of data obtained in an independent series of individual runs. The statistical uncertainty (one standard deviation of the weighted mean value) of the measured TCS reaches 2% below 1 eV and is less than 1% for other applied energies. Systematic errors in the present experiment are mainly related to:

- (i) the uncertainty of capacitance manometer calibration ($\sim 1\%$);
- (ii) the inability to correctly determine the length of the interaction region within a target of inhomogeneous density ($\sim 2\%$);
- (iii) the incomplete discrimination by the detector system of electrons which are scattered through small angles in the forward direction: the possible reduction in the measured TCS was estimated to be about 3% at 2 eV, 2–3% at 10 eV and 4–6% near 350 eV,

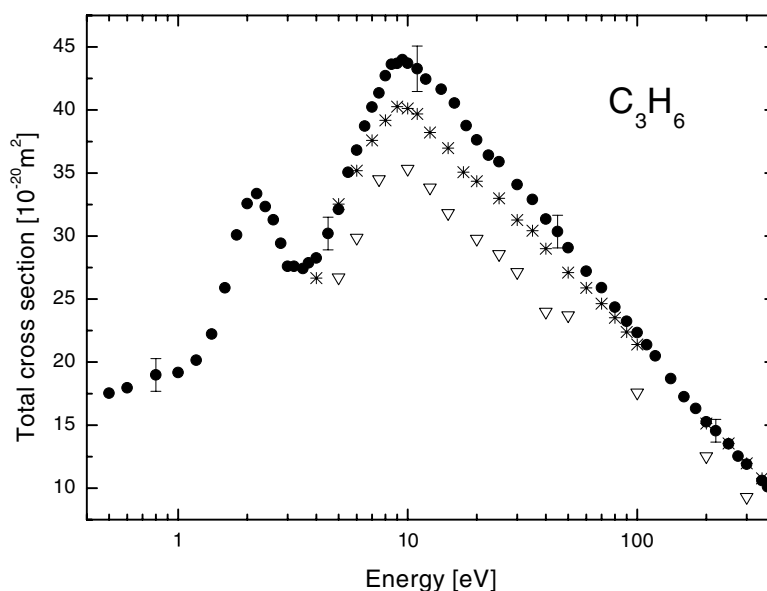


Figure 1. Experimental electron–propene scattering TCSs: (●), present; the error bars at selected points represent the overall (systematic plus statistical) experimental uncertainties; (▽), Floeder *et al* (1985); (*), Nishimura and Tawara (1991).

by using the available calculated elastic low-energy differential cross section (Winstead *et al* 1992, Beyer *et al* 1997, Čurík and Gianturco 2002a) and intermediate-energy elastic computations (Możejko and Szmytkowski 2002);

- (iv) the uncertainties in the measurements of the electron beam intensity: up to 3–4% below 2 eV and less than 1% above 10 eV. Systematic errors related to other quantities (e.g. temperature, energy, gas purity) do not exceed 1%. A quadrature sum of all relevant individual potential systematic uncertainties is estimated to be about 6% below 2 eV, decreasing to 4% between 10 and 100 eV and increasing again to 6–7% at the highest applied energies. The samples of propene and cyclopropane of 99+ % purity (Sigma–Aldrich) were used without further purification.

3. Results and discussion

3.1. Propene

The absolute electron-scattering TCS for propene measured in this work for impact energies from 0.5 to 370 eV is shown in figure 1. Previous experimental results of Floeder *et al* (1985) and Nishimura and Tawara (1991) in the overlapping energy range are included for comparison. The numerical cross sections are listed in table 1.

As can be seen from figure 1, the measured TCS has two distinct maxima, the smaller one ($34 \times 10^{-20} \text{ m}^2$) with a width of $\sim 0.9 \text{ eV}$ is located at about 2.2 eV, while the much higher, very broad enhancement of the maximum value $44 \times 10^{-20} \text{ m}^2$ is centred close to 9.5 eV. The low-energy feature at around 2.2 eV can likewise be related to vibrational excitation of the target molecule, which between 1.7 and 3 eV effectively proceeds via formation of the transient C_3H_6^- ion when the extra electron is captured by low-lying unoccupied orbitals for a long time interval compared with the collision time. Some indications on the resonant character

Table 1. Absolute TCSs measured for electron impact on C₃H₆ (propene) in units of 10⁻²⁰ m².

Energy (eV)	TCSs	Energy (eV)	TCSs	Energy (eV)	TCSs	Energy (eV)	TCSs
0.5	17.5	3.5	27.4	11	43.3	80	24.4
0.6	18.0	3.7	27.9	12	42.4	90	23.2
0.8	19.0	4.0	28.2	14	41.6	100	22.3
1.0	19.2	4.5	30.2	16	40.6	110	21.4
1.2	20.1	5.0	32.1	18	38.8	120	20.5
1.4	22.2	5.5	35.1	20	37.6	140	18.7
1.6	25.9	6.0	36.8	22.5	36.4	160	17.2
1.8	30.1	6.5	38.7	25	35.9	180	16.3
2.0	32.6	7.0	40.4	30	34.1	200	15.2
2.2	33.4	7.5	41.4	35	32.9	220	14.6
2.4	32.3	8.0	42.7	40	31.3	250	13.5
2.6	31.3	8.5	43.6	45	30.4	275	12.5
2.8	29.4	9.0	43.7	50	29.1	300	11.9
3.0	27.6	9.5	44.0	60	27.2	350	10.6
3.2	27.6	10.0	43.7	70	25.9	370	10.1

of the scattering in this electron energy range come from the excitation spectra of Bowman and Miller (1965) and Dance and Walker (1973) and the derivative transmission spectra of Jordan and Burrow (1980). The existence of the low-energy π^* shape-resonance was also suggested by Winstead *et al* (1992) although it was not directly revealed in their elastic calculations. The clear evidence for this shape resonance comes from the crossed-beam experiment of Boesten *et al* (1993) as a sharp maximum in the excitation function of ν_3 vibration near 2 eV. Calculations (Winstead *et al* 1992) indicate that the broad enhancement centred near 9.5 eV can be associated mainly with elastic scattering, although the measurements of Bowman and Miller (1965), Dance and Walker (1973), Rutkowsky *et al* (1980) and Boesten *et al* (1993) clearly demonstrate that numerous inelastic (including resonant) processes can significantly contribute to the scattering in this energy regime.

On the whole, the shape of the compared experimental TCS functions (figure 1) is similar over the energy range where overlap in the data occurs, though they distinctly differ in magnitude, mostly around the 9.5 eV maximum. Results of Floeder *et al* (1985), obtained using a transmission TOF experiment with the use of a magnetic guiding field, are on average 20% lower than the present data over the whole energy range investigated. TCSs of Nishimura and Tawara (1991) obtained in the linear transmission experiment agree quite well with the present data at the lowest common energy range and at intermediate energies above 100 eV, while close to the maximum at 9.5 eV they are 10% lower. The reason for this difference is somewhat unclear, as results from both laboratories (Nishimura and Tawara 1991, Szmytkowski and Krzysztofowicz 1995) for another hydrocarbon molecule, C₂H₆, show a quite opposite relation around the maximum than that mentioned above for C₃H₆. On the other hand, the difference is well within the limits of the declared overall experimental uncertainties. In addition, it is worth noting that the shape of the present TCS function around 2.2 eV is quite similar to the relative backscattering cross section of Lunt *et al* (1998).

3.2. Cyclopropane

Figure 2 displays our TCSs, collected in table 2, for electron scattering from cyclopropane over the energy from 0.5 to 370 eV together with earlier experimental data of Floeder *et al* (1985)

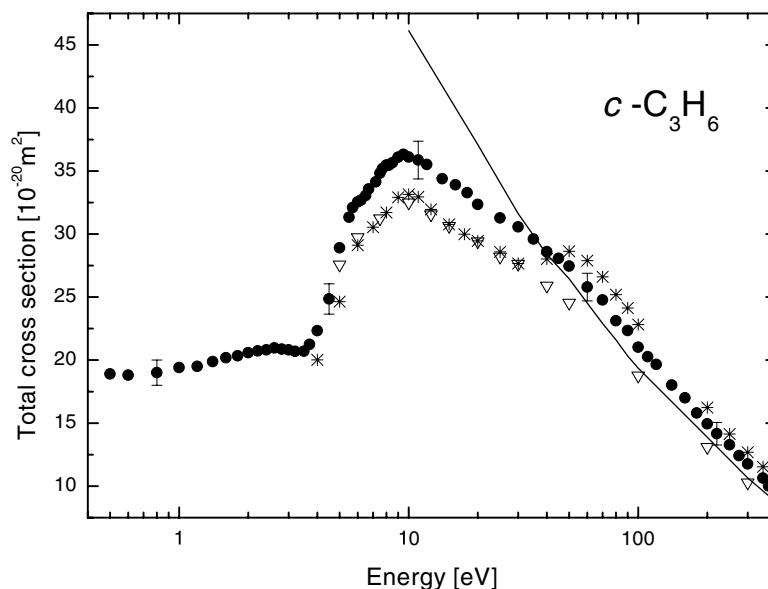


Figure 2. Total electron–cyclopropane scattering cross sections. Experimental: (●), present; the error bars at selected points represent the overall (systematic plus statistical) experimental uncertainties; (▽), Floeder *et al* (1985); (*), Nishimura and Tawara (1991). Theoretical: (—), energy-dependent geometric additivity rule (EGAR), Jiang *et al* (1997).

Table 2. Absolute TCSs measured for electron impact on c-C₃H₆ (cyclopropane) molecules in units of 10^{−20} m².

Energy (eV)	TCSs	Energy (eV)	TCSs	Energy (eV)	TCSs	Energy (eV)	TCSs
0.5	18.9	4.0	22.3	9.0	36.1	70	24.8
0.6	18.8	4.5	24.8	9.5	36.3	80	23.1
0.8	19.0	5.0	28.9	10	36.1	90	22.3
1.0	19.4	5.5	31.3	11	35.9	100	21.0
1.2	19.5	5.7	32.1	12	35.5	110	20.3
1.4	19.8	6.0	32.5	14	34.4	120	19.6
1.6	20.2	6.2	32.7	16	33.9	140	18.0
1.8	20.3	6.5	33.0	18	33.3	160	17.0
2.0	20.6	6.7	33.6	20	32.3	180	15.8
2.2	20.7	7.0	33.9	25	31.3	200	14.9
2.4	20.8	7.2	34.1	30	30.6	220	14.2
2.6	21.0	7.5	34.8	35	29.6	250	13.3
2.8	20.9	7.7	35.2	40	28.6	275	12.4
3.0	20.8	8.0	35.4	45	28.1	300	11.8
3.2	20.7	8.2	35.5	50	27.4	350	10.6
3.5	20.7	8.5	35.7	60	25.8	370	10.0
3.7	21.2						

and Nishimura and Tawara (1991). The calculations of Jiang *et al* (1997) are also included for completeness.

The present TCS function shows, in the range of applied energies, one very distinct broad enhancement with the maximum value of $36 \times 10^{-20} \text{ m}^2$ located at 9.5 eV. Closer inspection of the TCS energy dependence enables one to distinguish some very weak but repetitive features

located on both the low-energy and high-energy slopes. A small flat hump is visible around 2.8 eV, just at the foot of the main enhancement. Near 6 eV a weak shoulder, of width ~ 1 eV, is noticeable on the steep low-energy slope of the curve while a distinct change of the curve inclination is located at higher energies between 30 and 50 eV.

The calculations of Winstead *et al* (1992) indicate that the principal component of the observed TCS enhancement comes from the elastic scattering, direct and resonant. Extensive studies of vibrational processes (Allan 1993, Boesten *et al* 1993, Allan and Andric 1996) indicate that at low energies, where the above-mentioned TCS features occur, numerous resonant processes are possible. A weak structure near 2.6 eV was noticed in vibrational (ν_1 and ν_2 modes) excitation functions and was assigned to the formation of σ^* resonance associated with the a_2'' virtual orbital of cyclopropane. It is interesting that the *R*-matrix calculations of Beyer *et al* (1997) and Nestmann (1998) did not reveal this resonance. Some broad structure appears around 2–3 eV in the A_1' partial component of elastic scattering computed by Čurík and Gianturco (2002a). However, the effect is so weak that no feature due to this structure is perceptible in their integral total elastic cross section. It is also interesting that their computations give, at low energies, the elastic results slightly above the present TCS. During their research Čurík and Gianturco (2002b) observed a fairly weak structure (less than $0.1 \times 10^{-20} \text{ m}^2$) centred near 3.7 eV in the vibrationally inelastic integral cross section for the CH₂ scissoring (ν_2) mode, related to the resonant A_1' contribution.

More attention is attracted by the structure located near 6 eV, visible as a shoulder in the present TCS and hardly distinguishable as a slight change of the slope in the Nishimura and Tawara (1991) measurements. The presence of a resonant structure in this energy regime, though shifted to 8.5 eV, was predicted in static-exchange elastic calculations of Winstead *et al* (1992); due to the absence of the polarization–correlation component of interaction, one would expect this shift to move shape resonances by some electronvolts towards higher energies. The exceptionally narrow feature was observed at lower energy, around 5.5 eV, in the elastic as well as the vibrationally inelastic channel by Allan (1993), Boesten *et al* (1993) and Allan and Andric (1996). On the basis of these observations, the 5.5 eV structure was unambiguously interpreted in terms of the formation of a relatively long-lived negative ion leading to selective excitation of the C–C (ring) stretching vibrational (ν_3 mode) motion. These observations were then reproduced in the elastic calculations of Beyer *et al* (1997), Nestmann (1998) and very recently by Čurík and Gianturco (2002a). Vibrationally inelastic calculations of Čurík and Gianturco (2002b) locate this resonance at 6.4 eV.

In the range of the TCS maximum, between 8 and 10 eV, a fairly broad resonant band was observed in elastic and in vibrationally inelastic experiments and calculations. Computational studies of Čurík and Gianturco (2002b) resolved this structure and related it to overlapping contributions from three symmetric vibrational modes (ν_1 , ν_2 and ν_3). Calculated resonant features are usually centred about 1 eV below the experimental findings of Allan (1993) and Allan and Andric (1996).

It is worth noting that the qualitative behaviour of the TCS in the low-energy part of energy dependence for cyclopropane resembles that for another cyclic hydrocarbon benzene (Mozejko *et al* 1996) and, to some extent, that for hexafluorobenzene (cf Kasperski *et al* 1997).

An interesting feature in the TCS function (visible as the change of the slope) arises around 40 eV. It looks like a weak ($\sim 2 \times 10^{-20} \text{ m}^2$) and very broad hump, centred near 40 eV, superimposed on the main TCS enhancement. In view of the apparent absence of more detailed experiments or calculations in this energy range one can only speculate on the possible processes which contribute to the observed feature. The ionization TCS, one of the main components of the scattering at intermediate energies, does not reach its maximum value ($\sim 9 \times 10^{-20} \text{ m}^2$) until 90 eV (Nishimura and Tawara 1994). As the effectiveness of other

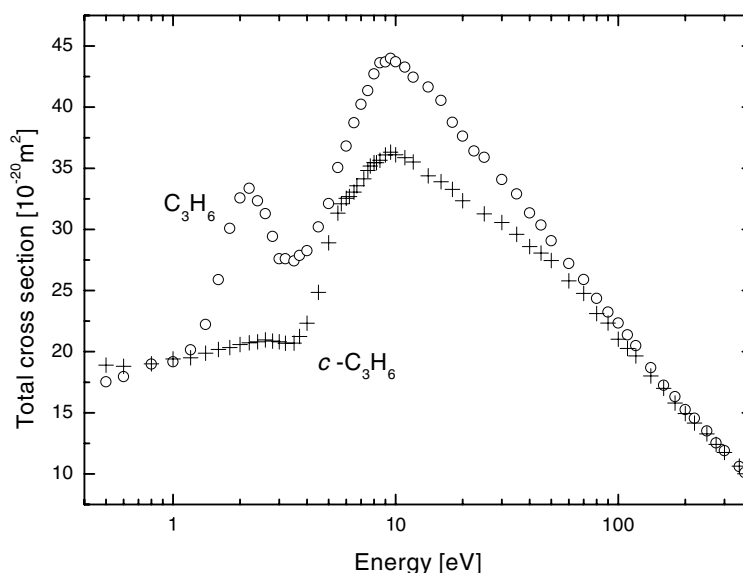


Figure 3. Comparison of present TCSs for electron scattering from propene and cyclopropane molecules: (○), C_3H_6 ; (+), $c-C_3H_6$.

partial direct inelastic processes is relatively low at low–intermediate energies, the observed feature may thus result from a superposition of numerous weak contributions associated with core-excited shape resonances.

The present TCS function is in general quite similar in shape to earlier measurements; however, the difference in magnitude is evident. The data of Nishimura and Tawara (1991) are between 4 and 40 eV systematically lower than the present results. The difference amounts to almost 13% at the lowest energies, decreasing to 8% around the TCS maximum and increasing again to 11% near 30 eV. The data of Floeder *et al* are somewhat lower than the results of Nishimura and Tawara. Between 30 and 50 eV the TCS curve of Nishimura and Tawara indicates additional enhancement with a well-marked maximum near 45 eV. Such a maximum is not visible in either the present or the Floeder *et al* results, although in both curves near 40 eV the change of the slope is appreciable. The presence of the distinct maximum near 50 eV is somewhat unexpected because the TCS data obtained hitherto for other perhydrogenated targets do not exhibit such features in this energy regime. Reaching the maximum at 45 eV the data of Nishimura and Tawara remain a few per cent higher at intermediate energies than the present results. TCSs calculated by Jiang *et al* (1997), with the assumption of additivity of constituent atomic cross sections regarding the energy-dependent shielding correction (EGAR approximation), are above 40 eV and thus in quite satisfactory agreement with the existing experimental data. However, at around 10 eV the calculations exceed the experimental values by more than 30% which clearly demonstrates that the additivity rule breaks down at such low energies.

3.3. Isomeric effect

Figure 3 compares the variation of the electron impact TCSs versus energy for the investigated pair of C_3H_6 isomers. Substantial differences resulting from various structures of both isomers are visible, especially at low impact energies. In particular, the difference in the shape of the compared TCS functions is evident. The cross section for propene has two very distinct

enhancements, one weak but narrow near 2.2 eV and the second one much higher and broader located at around 9.5 eV. In the TCS function for cyclopropane, apart from a remarkable enhancement centred at 9.5 eV, one can distinguish some less pronounced features: there is a small hump at 2.6 eV, a weak shoulder around 6 eV and a change of the slope close to 40 eV. The presence and location of these structures, resonant in character, is closely associated with particular atom groups and is therefore very sensitive to structural changes leading to different forms of bonds.

Another discernible difference concerns the magnitude of compared TCSs: that for propene is distinctly higher—between 1 and 100 eV—than that for cyclopropane. Such a relation could be connected with diversity in the general distribution of electric charge in both molecules which is manifested in different electrical properties of the targets under study: propene has a small electric dipole moment ($\mu = 0.366$ D) while for cyclopropane $\mu = 0$. Both isomers also differ in the response on the electric charge of the probe electron: the polarizability, α , for propene and cyclopropane has values of 6.26×10^{-30} m³ and 5.66×10^{-30} m³, respectively. As a result there is a clear difference in longer-range (electron–permanent dipole moment) interaction and, to a lower degree, in the shorter-range (due to induced dipole moment) interaction of both target molecules with the impinging electron, which is reflected in the magnitude of TCSs.

It is also worth mentioning some similarities in the TCS for both isomers. In both cases the main broad enhancement is centred near 9.5 eV; however this feature seems to be rather common for all hydrocarbons. At the highest applied energies TCSs for both molecules converge although, as one would expect from the larger geometrical size of the propene molecule, propene should have a higher cross section. The practical unsensitivity of the total electron-scattering cross section on the geometry of the molecule, appreciable at higher energies, serves as a ground for the additivity concept.

3.4. Fluorination effect

As we have now in hand TCSs for propene (C₃H₆) and data for hexafluoropropene (C₃F₆) measured at the same laboratory (Szmytkowski *et al* 2002a, 2002b) it would be interesting to inspect how the perfluorination of propene is reflected in the shape and magnitude of respective TCSs. Some differences are easily discernible (figure 4):

- (i) at the lowest applied energies the TCS for hexafluoropropene is nearly twice as high as that for propene and while this latter descends towards lower energies the cross section for C₃F₆ rises slowly;
- (ii) the resonant structure located at around 2.2 eV for propene is, for hexafluoropropene, less pronounced and shifted to 3.2 eV;
- (iii) the TCS for hexafluoropropene, the larger molecule, is clearly lower (~20%) than for propene around the main maximum near 10 eV;
- (iv) above 10 eV the TCS for propene monotonically decreases with the energy increase, while for hexafluoropropene—after only an initial decrease—the cross section has a very broad enhancement spanning 20 and 70 eV, and is significantly higher than that for C₃H₆.

As was already demonstrated for other perhydrogenated and perfluorinated molecules (Szmytkowski and Ptasińska-Denga 2001) this effect arises mainly from different contributions of the elastic and ionization processes to the electron scattering at low–intermediate energies. The share of the elastic cross section in the TCS for perfluorides amounts to 80% at 30 eV and nearly 65% at 90 eV. For their perhydrogenated counterparts it is lower and decreases more rapidly with the energy increase: from 70% at 30 eV down to 40% at 90 eV.

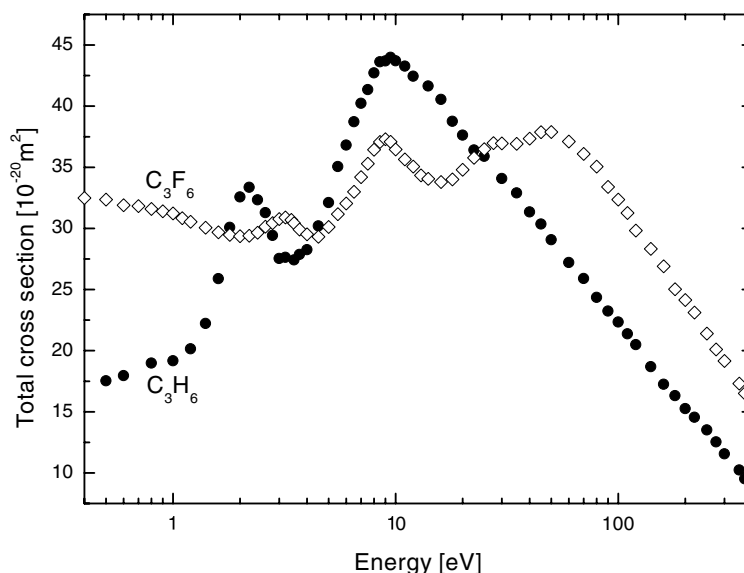


Figure 4. Comparison of electron-scattering TCSs for the propene and hexafluoropropene molecules: (●), C_3H_6 , present; (◇), C_3F_6 , Szmytkowski *et al* (2002a, 2002b).

The contribution of ionization processes at 90 eV is nearly 30% for perfluorides and about 40% for perhydrides. It is worth noting that, in general, the observed relationship between propene and hexafluoropropene TCSs (figure 4) corresponds with the tendency observed earlier for other perhydrogenated and perfluorinated compounds (Szmytkowski and Ptańska-Denga 2001) and it enables us to suggest that the observed tendency is common for pairs of such molecules.

4. Conclusions

In this paper we have reported the results of our absolute TCS measurements for electron scattering from the isomers of the C_3H_6 molecule for incident electron energies ranging from 0.5 up to 370 eV. The shape and the magnitude of the cross sections for the pair of isomers is distinctly different. The TCS for propene is generally higher than that for cyclopropane; only below 1 eV and above 100 eV do they converge. The TCS for propene has two maxima: at 2.2 eV and around 9.5 eV. In the TCS for cyclopropane the small hump is centred near 2.6 eV, the shoulder is located near 6 eV, the main maximum is centred at 9.5 eV and the change of the slope is visible near 40 eV. The resonant character of these features is indicated. Comparison of the present propene and earlier hexafluoropropene TCSs demonstrates the distinct fluorination effect.

Acknowledgments

The work has been sponsored, in part, by the Polish State Committee for Scientific Research (KBN) and by the Ministry of National Education.

References

- Allan M 1993 *J. Am. Chem. Soc.* **115** 6418–19
 Allan M and Andric L 1996 *J. Chem. Phys.* **105** 3559–68

- Beran J A and Kevan L 1969 *J. Phys. Chem.* **73** 3866–76
- Beyer T, Nestmann B M, Sarpal B K and Peyerimhoff S D 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 3431–44
- Bobeldijk M, van der Zande W J and Kistemaker P G 1994 *Chem. Phys.* **179** 125–30
- Boesten L, Takagi T, Tanaka H, Kimura M, Sato H and Dillon M A 1993 *Proc. XVIII ICPEAC (Aarhus)* p 273
- Bowman C R and Gordon D E 1967 *J. Chem. Phys.* **46** 1878–83
- Bowman C R and Miller W D 1965 *J. Chem. Phys.* **42** 681–6
- Čurík R and Gianturco F A 2002a *J. Phys. B: At. Mol. Opt. Phys.* **35** 717–32
- Čurík R and Gianturco F A 2002b *J. Phys. B: At. Mol. Opt. Phys.* **35** 1235–50
- Dance D F and Walker I C 1973 *Proc. R. Soc. A* **334** 259–77
- Deutsch H, Becker K, Janev R K, Probst M and Märk T D 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** L865–72
- Duncan C W and Walker I C 1974 *J. Chem. Soc. Faraday Trans. II* **70** 577–85
- Flicker W M, Mosher O A and Kuppermann A 1975 *Chem. Phys. Lett.* **36** 56–60
- Floeder K, Fromme D, Raith W, Schwab A and Sinapius G 1985 *J. Phys. B: At. Mol. Phys.* **18** 3347–59
- Göötz B, Winterling H and Swiderek P 1999 *J. Electron Spectrosc.* **105** 1–4
- Harrison A G, Jones E G, Gupta S K and Nagy G P 1966 *Can. J. Chem.* **44** 1967–73
- Hitchcock A P, Newbury D C, Ishii I, Stöhr J, Horsley J A, Redwing R D, Johnson A L and Sette F 1986 *J. Chem. Phys.* **85** 4849–62
- Jiang Y, Sun J and Wan L 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 5025–32
- Jordan K D and Burrow P D 1980 *J. Am. Chem. Soc.* **102** 6882–3
- Kasperski G, Możejko P and Szmytkowski Cz 1997 *Z. Phys. D* **42** 187–91
- Knudsen M 1910 *Ann. Phys., Lpz.* **31** 205–29
- Lampe F W, Franklin J L and Field F H 1957 *J. Am. Chem. Soc.* **79** 6129–32
- Lunt S L, Randell J, Ziesel J-P, Mrotzek G and Field D 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 4225–41
- Możejko P, Kasperski G, Szmytkowski Cz, Karwasz G P, Brusa R S and Zecca A 1996 *Chem. Phys. Lett.* **257** 309–13
- Możejko P and Szmytkowski Cz 2002 submitted
- Nestmann B M 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 3929–48
- Nishimura H and Tawara H 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** L363–6
- Nishimura H and Tawara H 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 2063–74
- Otvos J V and Stevenson D P 1956 *J. Am. Chem. Soc.* **78** 546–51
- Rutkowsky J, Drost H and Spangenberg H-J 1980 *Ann. Phys., Lpz.* **37** 259–70
- Schram B L, van der Wiel M J, de Heer F J and Moustafa H R 1966 *J. Chem. Phys.* **44** 49–54
- Szmytkowski Cz and Krzysztowicz A M 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 4291–300
- Szmytkowski Cz, Możejko P and Kasperski G 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 3917–28
- Szmytkowski Cz and Ptańska-Denga E 2001 *Vacuum* **63** 545–8
- Szmytkowski Cz, Możejko P and Kwitniewski S 2002a *J. Phys. B: At. Mol. Opt. Phys.* **35** 1267–74
- Szmytkowski Cz, Kwitniewski S, Możejko P and Ptańska-Denga E 2002b submitted
- Winstead C, Sun Q and McKoy V 1992 *J. Chem. Phys.* **96** 4246–51