

Low-energy electron-hexafluoropropene (C₃F₆) scattering

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(Received 8 February 2002; published 30 July 2002)

Absolute total cross sections for electron scattering by C₃F₆ molecules in the energy range from 0.5 to 30 eV have been measured using a beam transmission method. Two resonant-like maxima in the total cross sections function are clearly visible: the first, small maximum is centered near 3.2 eV, the second one, much pronounced, is located at 9.5 eV. No previous experimental data have been found in the literature for comparison. The effect of fluorination is indicated.

DOI: 10.1103/PhysRevA.66.014701

PACS number(s): 34.80.-i

I. INTRODUCTION

Electron scattering properties of perfluorinated molecules at various impact energies are of great importance due to their wide application in the electrical industries [1] and in plasma-assisted fabrication of electronic microcircuits [2]. Comprehensive and reliable sets of quantitative electron-impact cross sections and rate coefficients at various impact conditions are necessary for optimal design of working gaseous media [3], (and references therein). Besides this applied research area, the electron scattering is a subject of considerable interest of experimental and theoretical atomic physics.

Current interest in electron-hexafluoropropene interactions is related to the possibility of using this compound, of relatively low global warming potential (GWP) [4], as a replacement for perfluorides applied to date which appear to have a higher GWP. Another motivation for investigating the scattering of electrons by hexafluoropropene is to provide data which may improve an understanding of how substitution of hydrogen atoms by fluoride atoms in hydrocarbons changes their interaction with electrons.

Experiments on thermal and low-energy electron interaction with C₃F₆ molecules are rather scarce. They are mainly concerned with the dissociative electron attachment process leading to the formation of negative ions [5–9], as well as with ionization phenomena [7,10–12]. Apart from very recent experiment [12], earlier measurements give resulting magnitudes in the relative scale only. The lack in the literature of experimental absolute data for low-energy total electron scattering cross section has prompted the present experimental study.

In the present Brief Report we report e^- -C₃F₆ scattering total cross sections (TCS) measured absolutely in the low energy range, 0.5–30 eV, by a linear transmission method.

II. EXPERIMENT

The apparatus and experimental procedure for the present study are the same as used in previous absolute total cross section measurements reported from our laboratory [13,14]

and only a brief description is given here. The method is based on the measurements of the attenuation of a linear electron beam through the target volume. Total cross section, $Q(E)$, at given energy, E , is extracted from the well-known Bouguer–de Beer–Lambert attenuation law

$$I_l(E) = I_0(E) \exp \left[-Q(E) \int_0^l n(x) dx \right], \quad (1)$$

where I_l is the electron beam intensity remaining after traversing a length l of the target whose number density along the pathway is $n(x)$, and I_0 is the intensity in the absence of the target in the reaction volume.

A monochromatic beam of electrons ($\Delta E \sim 80$ meV, full width at half maximum) of variable energy is produced by an electron-optical system consisting of a thermionic electron source, electrostatic zoom lens, a 127° cylindrical electrostatic energy dispersive element, followed with a lens system which determines impact energy of the electron beam and directs it into a reaction chamber. Those electrons which emerge from the reaction region through the cell exit orifice are energy discriminated with a planar retarding field filter to eliminate the electrons which lost energy in the scattering of more than a few tenths of an eV or were scattered at high angles. Finally, electrons are collected with a Faraday cup detector. The earth magnetic field in the electron optics volume is compensated by a system of Helmholtz coils to a value below 0.1 μ T.

Measurements are performed for incident electron beam current $I_0 \sim 1$ pA. In this range, no dependence of measured total cross section on electron beam intensity is observed. The electron energy scale is calibrated against the well known resonant vibrational structure visible around 2.3 eV in electron transmission current when nitrogen is admixed to the gas sample under study.

Effusion of target particles across orifices, through which electrons enter and leave the reaction chamber, creates a serious problem in the determination of the effective scattering path length. Following the calculations [15], we have found that in the present experimental conditions the integral in formula (1) may be replaced, within an accuracy of 0.5%, with the product, nL , of the geometrical distance, L , between orifices of the scattering chamber, and the target density number, n , in the center of the scattering cell. The density

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number, n , is evaluated from the ideal-gas law ($p = nk\sqrt{T_c T_m}$, k is the Boltzmann constant), and based on the measurements of the target pressure, p , in the scattering cell and the target temperature. The measured pressure readings are corrected for the effect of thermal transpiration [16] related to some difference between temperature of the scattering cell, T_c (315–320 K), and temperature of the capacitance manometer head, $T_m = 322$ K. The uncertainty of the pressure measurements is mainly related to the calibration of the MKS Baratron and the zero drift. We have estimated the uncertainty of the target pressure determination to be lower than 1%.

In the “target in” operational mode, the pressure in the region of electron optics is nearly three orders of magnitude lower than that in the scattering cell. We have observed, however, that even such slight presence of the target particles in the region of cathode and electron optics influences the flux of the primary electron beam I_0 which may essentially change the measured cross section. To solve this problem, a by pass is used which directs the target flow into the scattering chamber or into the outer vacuum volume, alternately in such a way that the cathode and other parts of electron optics are exposed to the same partial pressure of the target-gas without and with the target in the scattering chamber. Handling the target, energy setting, and processing ingoing data are operated under computer control.

Individual cross section measurements are made at target pressure in the scattering cell ranging from nearly 0.06 to about 0.3 Pa which ensures the single-scattering conditions. The results proved to be independent (within the limits of statistical uncertainties) of the applied pressure.

The final value of the total cross section at each particular electron impact energy is an average of a large number of data obtained in independent series (6–24) of individual runs (7–10 in a series). Reproducibility from run to run, even measured some months apart, is good. Statistical uncertainty (one standard deviation of weighted mean values) of the measured total cross section does not exceed 1% over the whole energy range investigated.

The quadratic sum of all relevant individual potential systematic errors has been estimated to be nearly 5% below 2 eV and gradually decreasing below 3% in the range 5–30 eV. The increase of the uncertainty below 4 eV is mainly related to the steep changes of the cross section function in this energy range, where a small drift in energy may bring about a relatively great change in the measured cross section. The above figures account roughly for the uncertainty related to incomplete discrimination against small-angle elastic scattering. An exact estimation of this effect is not, however, possible as the pertinent angular distribution data are not available yet.

The hexafluoropropene sample (Sigma-Aldrich, Grade 99+) was studied without further purification.

III. RESULTS AND DISCUSSION

The present experimental absolute total cross sections (TCSs) for electron-hexafluoropropene scattering over the energy range from 0.5 to 30 eV are shown in Fig. 1. No other

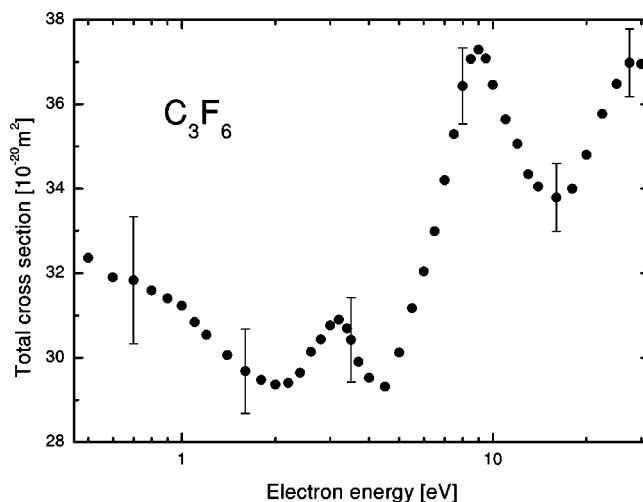


FIG. 1. Experimental absolute electron-scattering total cross section for hexafluoropropene (C_3F_6). Error bars include statistical and systematic uncertainties.

experimental TCS for e^- - C_3F_6 scattering has been found in the literature for comparison.

Four distinct regions can be discerned in the energy dependence of the obtained TCS for e^- - C_3F_6 scattering. From the lowest applied energies the TCS decreases smoothly with the energy increase to a minimum ($29.4 \times 10^{-20} \text{ m}^2$) located at around 2 eV. As the contribution from the dissociative electron attachment is negligible below 2 eV [6], the long-range permanent electric dipole field of the hexafluoropropene molecule is likely to be responsible for the enhancement of TCS towards very low energies. Between 2 and 4.5 eV a small but clearly marked peak centered around 3.2 eV is visible with a maximum value of $30.9 \times 10^{-20} \text{ m}^2$. This resonant-like narrow feature may be associated with the temporary capture of the extra electron by the target molecule with creation of an intermediate parent anion (C_3F_6^-)*. The transient negative-ion can subsequently decompose either via a dissociative channel with production of negative and neutral fragments and/or through electron autodetachment leading to vibrationally excited states of the parent molecule. Some indication that processes responsible for the observed 2–4.5 eV TCS enhancement may be of resonant character comes from experiments [6,7] in which the peaks close to 3 eV in negative ion spectra related to products (F^- , C_3F_5^-) of the C_3F_6^- dissociation have been observed. As the dissociation of the resonant state into neutral and negative-ion fragments is not very effective at these energies, one would expect that the feature observed between 2 and 4.5 eV is mainly related to the competitive electron autodetachment channel with vibrational excitation of the target molecule. In the absence of e^- - C_3F_6 experiments for a vibrational channel the results of very recent measurements [17] for difluoroethane isomers are worth noting. They revealed distinct enhancement just between 2 and 4 eV in cross section functions for the excitation of the C=C and C–F stretch vibrations. Above 4.5 eV the e^- - C_3F_6 TCS rises steeply and near 9 eV it reaches its maximum value of $37.3 \times 10^{-20} \text{ m}^2$. Numerous dissociative products (F^- , CF_3^- , C_3F_3^- , and C_3F_5^-)

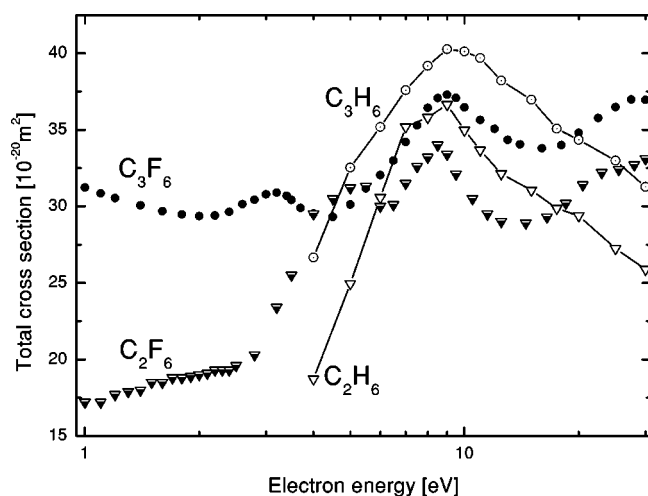


FIG. 2. Illustration of the perfluorination effect. Experimental total cross sections: filled circles, C_3F_6 , present data; open circles, C_3H_6 , [23]; half-filled triangles, C_2F_6 , [22]; open triangles, C_2H_6 , [23]; lines are drawn to guide the eye.

observed between 5 and 14 eV indicate the resonant character of some inelastic processes in this energy regime [6,7]. These results, however, do not allow us to estimate the absolute contribution of the resonant effects to the scattering. On the other hand, experiments for other perfluorinated molecules suggest that the dominating contribution to this enhancement should be attributed to elastic scattering [18,19]. For impact energies above the maximum, TCS for hexafluoropropene has a successive minimum ($33.8 \times 10^{-20} \text{ m}^2$) near 16 eV and then reaches $36.9 \times 10^{-20} \text{ m}^2$ while the energy increases to 30 eV. Recent studies for other perfluorocarbons [19–22] indicate that the observed enhancement may be a part of an exceedingly broad maximum spanned up to about 60–80 eV which seems to be characteristic for perfluorinated targets.

Having in hand experimental electron-scattering total cross section data for some perfluorides and for their perhydrogenated counterparts it would be interesting to find how the replacement of hydrogen atoms with fluorine atoms in the target molecule reflects in the respective TCSs. In order to illustrate the perfluorination effect we set the present low-energy TCS data for C_3F_6 against experimental results for propene, C_3H_6 [23] (see Fig. 2). The low-energy TCSs for C_2F_6 [22] and for C_2H_6 [23] are also plotted to emphasize

the effect. From Fig. 2 it is evident that perfluorination of hydrocarbon molecules essentially influences both the magnitude and shape of TCS. Around the maximum near 9 eV, the geometrically larger C_3F_6 molecule appears to be considerably less effective for the electron scattering than its hydrocarbon counterpart C_3H_6 . The relation of compared cross sections changes and the TCS for C_3F_6 becomes remarkably higher than that for a C_3H_6 molecule for impact energies below the hexafluoropropene TCS minimum, located at about 4 eV. Also above 20 eV, at intermediate energies, where direct processes dominate in the electron scattering and targets of larger geometrical size have usually higher TCS, such a relation between both compared TCSs is also valid (see Fig. 2), as one might intuitively expect. The same relation is also visible for the second pair of compared compounds, C_2F_6 and C_2H_6 . The above mentioned and other TCS data available so far allow us to expect that the observed TCS relation may be typical for all perfluorinated targets and their perhydrogenated analogs.

IV. SUMMARY

We have measured absolute total cross sections for hexafluoropropene (C_3F_6) at electron impact energies from 0.5 to 30 eV. Two distinct maxima have been observed in the TCS energy dependence. The first maximum, centered at 3.2 eV, is most probably associated with a resonance arising from the temporary trapping of an extra electron into the lowest antibonding orbitals of a C_3F_6 molecule. The second maximum, around 9 eV, may be related to a variety of direct processes accessible in this energy range, with a contribution of numerous overlapping weak resonances. To ascertain the role of particular processes responsible for the observed features one would require more quantitative partial cross section data. Above 16 eV a further increase of the cross section has been observed which resembles earlier findings for other perfluorides. The fluorination effect is indicated and discussed. The present data give reference for future more detailed experiments and theoretical calculations which might help in understanding the scattering dynamics.

ACKNOWLEDGMENT

This work was partly supported by the Polish State Committee for Scientific Research (KBN).

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