Electron collisions with tetrafluoroethylene (C\textsubscript{2}F\textsubscript{4}) and ethylene (C\textsubscript{2}H\textsubscript{4}) molecules

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Absolute total cross sections (TCSs) for 0.6–370 eV electrons scattered by tetrafluoroethylene (C\textsubscript{2}F\textsubscript{4}) molecules have been measured using a linear transmission method. The TCS energy function for C\textsubscript{2}F\textsubscript{4} shows one very broad enhancement with the maximum value of 30×10\textsuperscript{-20} m\textsuperscript{2} located around 30 eV. On the low-energy slope of the TCS curve some weak features near 2.8, 9.5, and 16 eV are discernible. Above 50 eV the present TCS agrees well with theoretical predictions. Absolute TCS for ethylene (C\textsubscript{2}H\textsubscript{4}) has also been measured and compared with the TCS for C\textsubscript{2}F\textsubscript{4}. Effect of substitution of fluorine atoms for hydrogen (perfluorination effect) was indicated and discussed. The reported TCS for C\textsubscript{2}H\textsubscript{4} is distinctly higher than experimental data existing so far.

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I. INTRODUCTION

Earlier experimental works on electron scattering from C\textsubscript{2}F\textsubscript{4} (the simplest perfluorocarbon with double carbon-carbon bond) are hardly enough and include ionization cross section measurements [1,2], mass spectrometric studies of negative-ion formation [3–5], investigations of electronic excitation spectra [6], and electron-transmission study of low-energy resonance formation [7]. Electron-transport and rate coefficients were determined with a swarm technique [8,9]. These studies provided a number of detailed information on the e\textsuperscript{−}–C\textsubscript{2}F\textsubscript{4} scattering. However, obtained intensities of studied processes are in part given only in arbitrary units, and thus their application to modeling or comparison with theoretical calculations is rather problematic. Theoretical studies which concern e\textsuperscript{−}–C\textsubscript{2}F\textsubscript{4} scattering are even more limited and have been reported quite recently. They have focused on the calculations of total cross section (TCS) from intermediate to high energies [10] as well as on low-energy elastic and excitation [9,11] processes involved in the scattering. To our knowledge, there are no measurements of total electron-scattering cross sections for C\textsubscript{2}F\textsubscript{4} in the literature so far.

The grand total cross section is the sum of the integral cross sections for all scattering channels and consequently gives less detailed information about collision. Usually, the features visible in the energy dependence of cross sections for particular channels are in the TCS energy function apparently smoothed out or even bleary. Nevertheless, TCS can be easily obtained in absolute scale, within an accuracy of 3–10 %, from quantities directly measured in experiment without any normalization procedure. That is why the accurate experimental TCS may serve as one of the ranges of experimental quantitative tests of the reliability of theoretical models and computational procedures. TCS may also be used as a standard value for the estimation of the upper limit for the electron-scattering cross sections obtained in arbitrary units or for which direct measurements and/or calculations are yet not accessible. Moreover, due to its accuracy, the TCS can be helpful in comparative studies.

The main objective of the present work was to provide accurate absolute electron-scattering cross-section data for C\textsubscript{2}F\textsubscript{4} over a wide energy range, from 0.6 to 370 eV. The C\textsubscript{2}F\textsubscript{4} is an industrial compound, which is widely used in the fabrication of fluoropolymers (e.g., polytetrafluoroethylene). It is also considered as a reactive agent for environmentally friendly plasma-assisted manufacturing of nanoelectronic devices [12]. For the understanding and control of processes in the plasmas as well as plasma-surface interactions, the knowledge of reliable quantitative electron-impact cross sections is required. It is also interesting to study how substitution of fluorine atoms for hydrogen in a molecule (perfluorination effect) reflects in the shape and magnitude of TCS. For this purpose, however, one needs access to a comprehensive set of data for hydrocarbons and their perfluorinated counterparts. There are already quite a few of e\textsuperscript{−}–C\textsubscript{2}H\textsubscript{4} TCS data in the literature [13–18] but they differ substantially as to the magnitude in the overlapping energy range. Therefore, for proper comparison, it is much more appropriate to take the data from the same laboratory, and that is why the TCS for ethylene was also measured in this work.

II. EXPERIMENTAL PROCEDURE AND ERROR ANALYSIS

The experiment has been performed with a linear electron-transmission technique [19] which is based on the measurements of the attenuation of an electron beam passing through the target under study. The apparatus and experimental procedure used in the present study were described elsewhere in detail (e.g., Ref. [20]). Briefly, electrons from 127° cylindrical electrostatic monochromator and system of electron lenses enter a scattering chamber followed with a retarding field (RF) assembly and a Faraday cup as a detector. Directly measured quantities in our experiment are intensity of the electron current transmitted through the scattering cell when the cell is filled with sample gas (I\textsubscript{s}) and when it is evacuated (I\textsubscript{0}), the gas pressure p in the center of the scattering volume, and the temperature of the cell (T\textsubscript{c}). Based
on these quantities, the absolute total cross section $Q(E)$ at a
given energy $E$ is derived from the Bouguer–de Beer–Lambert (BBL) attenuation formula

$$Q(E) = \frac{k\sqrt{T_m T_e}}{pL} \ln I_0,$$  

(1)

in which the ideal gas law ($p = n k T$) is applied and the ther-
mal transpiration effect [21] is accounted for ($T_m = 322$ K is
the temperature of mks manometer head); $k$ is the Boltzmann
constant and $L = 30.5$ mm is the distance between entrance
and exit apertures of the scattering cell. The magnetic field in
the electron optics volume of the spectrometer is reduced to a
value below $10^{-7}$ T.

The energy scale has been calibrated against the oscilla-
tory structure visible around 2.3 eV in the transmitted current
when molecular nitrogen was admixed to the gas under study. As consecutive calibrations revealed some shift in the
energy in the course of the experiment, probably due to in-
creasing contamination of the electron optics with the target
molecules, the declared inaccuracy of the energy scale ($\sim 0.08$ eV) is higher than that resulting from the calibration
(0.05 eV).

Handling the gas target, energy setting and processing in-
going data were controlled with a PC. The TCS data have
been taken at target pressures ranging from 60 to 200 mPa,
which ensured single-collision conditions, without noticeable
influence on the measured TCS. The final TCS value at each
energy is a weighted mean of results from several (3–10)
series of individual measurements (6–10 in a series). The
statistical variations of TCS (one standard deviation of the
weighted mean value) are almost 2% below 1.2 eV, decreas-
ing with increasing impact energy to a level of 0.3–0.7 % for
higher energies studied.

The final accuracy of TCS is mainly determined by the
possible systematical uncertainties of the experiment. In the
following we present in more detail the main sources of sys-
tematical effects which may influence measurements of the
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following we present in more detail the main sources of sys-
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parameters in Eq. (1). While obtaining accurate electron-
scattering TCS in a transmission-type experiment, a serious
problem arises due to relatively high uncertainty of the factor
$pL$ in the denominator of the BBL relationship [Eq. (1)].
This uncertainty is mainly connected with the unavoidable
effusion of the target molecules through orifices of the scatter-
ing cell leading to inhomogeneous target distribution in-
side the cell, close to the apertures. In consequence, there
is a notable presence of the target molecules also outside ap-
ertures, leading to possible incorrect determination of the
effective path length of electrons across the sample volume.
Based on calculations [22], adopted to the present experi-
mental conditions, which show that the end effects in the
used collision cell are nearly compensated (to within 0.6%),
and taking into account the uncertainty of the measured pres-
sure (1–1.5 %) and the sample impurity, we estimated uncer-
tainty of $pL$ to be about 3.5%. Gas escaping from the scatter-
ing cell may also affect the electron-beam intensity
outside the cell. To lessen the influence of sample molecules
on $I_0$, and therefore on the measured TCS, the gas sample
was supplied alternately into the reaction chamber and the
outer vacuum volume in such a way that the background
pressure in the region of filament and electron optics was
kept constant irrespective of whether the gas was present in
or absent from the collision cell. The estimated uncertainties
in reading of the electron current intensities are up to 2.5%
below 2 eV, decreasing to 1% at the highest applied energies.
The temperature of the scattering cell was measured to
within the 0.5% level. Another source of uncertainty relates
to inability to discriminate against electrons which are scat-
tered elastically through small angles in the forward direc-
tion and which contribute to the transmitted current, resulting
in the lowering of the measured TCS; the RF filter prevents
only the electrons scattered inelastically in the forward direc-
tion to be detected together with those unscattered. Estimated
amounts by which the present $e^{-}$-$C_2F_4$ TCS may be too low
are about 1–2% at low impact energies (based on the calcu-
lated electron angular distributions [9]) and are 3–4 % at
higher energies (the value assumed to be equal to estimations
available for other molecules due to the lack of appropriate
data for $C_2F_4$). The overall uncertainty of the measured TCS
(as indicated in the figures) is obtained as a combination in
quadrature of total systematical and statistical uncertainties.

Commercially supplied samples of $C_2H_4$ from Aldrich (a
stated minimum purity of 99.5%), and $C_2F_4$ manufactured by
ABCR (purity $>99\%$) were used without further purifica-

III. RESULTS AND DISCUSSION

In this section we present our electron-scattering TCSs for
the $C_2F_4$ and for $C_2H_4$ molecules obtained in the transmis-
sion experiment over energy range from 0.6 to 370 eV. The
obtained results are compared with previous experimental
and theoretical cross sections, if available. The perfluora-
tion effect is also indicated and discussed.

A. Tetrafluoroethylene, $C_2F_4$

The energy dependence of the measured $e^{-}$-$C_2F_4$ TCS is
presented in Fig. 1 along with TCS calculated by Jiang et al.
[10] in an independent atom approximation. Ionization cross
sections measured by Beran and Kevan [1] and Bart et al. [2]
as well as elastic cross section calculated recently by Win-
stead and McKoy [11] are also included for comparison. The
numerical TCS values from the present experiment are given
in Table I.

As the most pronounced feature of the measured TCS
energy function, we have found a very broad enhancement
centered around 30 eV where TCS reaches the value of about
$30 \times 10^{-20}$ m$^2$, confronting with the value nearly $11 \times 10^{-20}$ m$^2$ at the extremes of the energy range studied, i.e.,
at 0.6 and 370 eV. Variational calculations [9,11], though
giving distinctly too high elastic cross-section values—
between 4 and 10 eV they exceed even experimental TCS—
clearly suggest that the observed strong enhancement is
mainly caused by the elastic scattering. More thorough in-
spection of the TCS curve reveals additional weak structures
located, in the main, on the low-energy slope of the enhance-
ment. At first, we observe the small bump located near 2.8
Electron transmission [7] and dissociative electron attachment [3–5] spectroscopy indicate that this feature may be the manifestation of the short-lived negative-ion formation when the impinging electron is captured into the lowest empty molecular orbital. Calculations [9,11] confirm the presence of the low-energy resonant states although the fully resolved resonant-like feature in the integral elastic cross section is located only at 5 eV (cf. Fig. 1). Besides the 2.8-eV bump, some changes in inclination of the experimental TCS curve are discernible near 9.5 and 16 eV. The positions of these weak TCS features nearly coincide with the maxima in the integral elastic cross section [9].

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**FIG. 1.** Total cross sections for $e^{-}$-C$_2$F$_4$ scattering: solid circles, present experiment; error bars represent overall (systematical and statistical) uncertainties; solid line, additivity rule (AR) calculations [10]; and dotted line, energy-dependent geometric AR calculations [10]. Experimental ionization cross sections: solid triangle, Ref. [1]; and dotted line, energy-dependent geometric AR calculations [10].

**FIG. 2.** Experimental total cross sections for $e^{-}$-C$_2$H$_4$ scattering: solid circles, present work; solid line, Ref. [13]; open circles, Ref. [14]; asterisks, Ref. [15]; crosses, Ref. [16]; dotted line, Ref. [17]; and open triangles, Ref. [18].

TABLE I. Absolute total cross section (TCS) measured for electron impact on C$_2$F$_4$ molecule in units of 10$^{-20}$ m$^2$.

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**TABLE II.** Absolute total cross section (TCS) measured for electron impact on C$_2$H$_4$ molecule in units of 10$^{-20}$ m$^2$.

Present absolute TCS for ethylene in the incident electron energy of 0.6–370 eV is shown in Fig. 2. For comparison, existing absolute TCS data of Brüche [13], Floeder et al. [14], Nishimura and Tawara [16], and Ariyasinghe and Powers [18], are also shown. Normalized results of Sueoka and
Mori [15] and Lunt et al. [17] are also included for completeness. Table II presents our measured $e^-\text{-C}_2\text{H}_4$ TCS in numerical form.

There is an excellent agreement with respect to the shape of the present TCS energy function with that obtained earlier in other laboratories. The TCS function for C$_2$H$_4$ shows two distinct maxima in the investigated energy range. The first maximum, resonant in character [25–27], is centered at about 1.9 eV where it reaches a value of $29 \times 10^{-20}$ m$^2$. Near 3.5 eV the TCS has a deep minimum with a value of $20 \times 10^{-20}$ m$^2$. The second TCS enhancement, located around 8–8.5 eV, is much broader with the maximum value of nearly $32 \times 10^{-20}$ m$^2$. Above 10 eV, the TCS continuously decreases with increasing energy down to $6.7 \times 10^{-20}$ m$^2$ at 370 eV. Between 50 and 100 eV some weak hump in the descending part of TCS is discernible, probably associated with ionization processes which for $e^-\text{-C}_2\text{H}_4$ collision have the cross section maximum in this energy range [28]. As to the magnitude, our results are in reasonable agreement with the data of Nishimura and Tawara [16] taken with a linear transmission technique and are distinctly higher (up to 15–20%) than the results obtained with techniques which employ magnetic field [13–15]; the presence of magnetic field in the scattering region makes, due to spiralling effect, an adequate estimation of the flight path $L$ of electrons in the target more difficult [29].

C. Perfluorination effect

In Fig. 3 we show a comparison of the energy dependences of present experimental TCS for C$_2$F$_4$ and for C$_2$H$_4$. From this figure it is evident that the substitution of fluorine atoms for hydrogen in ethylene changes drastically the magnitude and shape of TCS over the entire energy range studied. Concerning the influence of the perfluorination on the magnitude of TCS, the studied energy range can be divided into two regions: below about 18 eV the TCS for C$_2$F$_4$ is distinctly lower than TCS for C$_2$H$_4$ while above that energy, at intermediates, the ordering of compared TCS curves changes—the TCS for C$_2$F$_4$ is higher than that for C$_2$H$_4$.

The visible strong increase of intermediate energy TCS after perfluorination seems to be very characteristic for all perfluorides studied so far. Such a relation could be expected, taking into account the fact that the peripheric fluorine atoms are larger than the hydrogen ones, and that for higher energies the independent atom approximation is fairly fulfilled [10]. The lack of experimental elastic data for C$_2$F$_4$ precludes the quantitative analysis, but basing on relations for other perfluorocarbons we suppose that the increase of TCS for C$_2$F$_4$ may be connected with the essential increase of direct elastic scattering for perfluorocarbon, especially when the main contributor to the TCS—ionization—is relatively weak.

Motivated by aforementioned (Sec. III A) similarities in the shape of TCSs for C$_2$F$_4$ and C$_6$F$_6$ molecules, we have compared the relation of their TCSs to TCSs for corresponding hydrocarbons, C$_2$H$_4$ and C$_6$H$_6$. Again, we have noted some similarities in TCS ratios within these pairs, C$_2$F$_4$–C$_2$H$_4$ and C$_6$F$_6$–C$_6$H$_6$. For C$_2$F$_4$ and C$_6$F$_6$ molecules the low-energy TCSs do not exceed those for their hydrocarbon counterparts while for other perfluorocarbons and their hydrocarbon analogs the low-energy TCS relation is different, and below 4–6 eV for most of perfluorocarbons the electron scattering becomes again more effective than on corresponding hydrocarbons.

IV. SUMMARY

In this work, we reported the absolute total electron-scattering cross sections for C$_2$F$_4$ and for C$_2$H$_4$ molecules measured in a linear transmission experiment from 0.6 to 370 eV. To the best of our knowledge, the results for C$_2$F$_4$ are the first experimental TCS. The obtained data may be valuable for basic physics and for applications. The TCS

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energy dependence for $\text{C}_2\text{F}_4$ shows one very broad enhancement centered around 30 eV and some weak features on the ascending part of the curve. The largest contribution to the TCS of $\text{C}_2\text{F}_4$ comes from the elastic scattering. In addition, our measurements of the absolute TCS for ethylene are also reported. Present data for ethylene are in good agreement with previous results according to the shape of TCS energy function but are generally higher. A comparison of the TCSs for $\text{C}_2\text{H}_4$ and $\text{C}_2\text{F}_4$ indicates distinct perfluorination effect over the entire impact energy range studied.

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