

Electron collisions with tetrafluoroethylene (C₂F₄) and ethylene (C₂H₄) molecules

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Absolute total cross sections (TCSs) for 0.6–370 eV electrons scattered by tetrafluoroethylene (C₂F₄) molecules have been measured using a linear transmission method. The TCS energy function for C₂F₄ shows one very broad enhancement with the maximum value of 30×10^{-20} m² 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 (C₂H₄) has also been measured and compared with the TCS for C₂F₄. Effect of substitution of fluorine atoms for hydrogen (perfluorination effect) was indicated and discussed. The reported TCS for C₂H₄ is distinctly higher than experimental data existing so far.

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I. INTRODUCTION

Earlier experimental works on electron scattering from C₂F₄ (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^- -C₂F₄ 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^- -C₂F₄ 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 C₂F₄ 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 C₂F₄ over a wide energy range, from 0.6 to 370 eV. The C₂F₄ 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^- -C₂H₄ 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_g) and when it is evacuated (I_0), the gas pressure p in the center of the scattering volume, and the temperature of the cell (T_c). Based

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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

$$Q(E) = \frac{k\sqrt{T_m T_c}}{pL} \ln \frac{I_0}{I_g}, \quad (1)$$

in which the ideal gas law ($p = nkT$) is applied and the thermal 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 oscillatory 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 increasing contamination of the electron optics with the target molecules, the declared inaccuracy of the energy scale (~ 0.08 eV) is higher than that resulting from the calibration (0.05 eV).

Handling the gas target, energy setting and processing incoming 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, decreasing 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 systematical effects which may influence measurements of the 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 scattering cell leading to inhomogeneous target distribution inside the cell, close to the apertures. In consequence, there is a notable presence of the target molecules also outside apertures, leading to possible incorrect determination of the effective path length of electrons across the sample volume. Based on calculations [22], adopted to the present experimental 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 pressure (1–1.5%) and the sample impurity, we estimated uncertainty of pL to be about 3.5%. Gas escaping from the scattering 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 scattered elastically through small angles in the forward direction 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 direction 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 calculated 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 purification.

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 transmission 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 perfluorination 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 Winstead 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 30×10^{-20} m², confronting with the value nearly 11×10^{-20} m² 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 inspection of the TCS curve reveals additional weak structures located, in the main, on the low-energy slope of the enhancement. At first, we observe the small bump located near 2.8

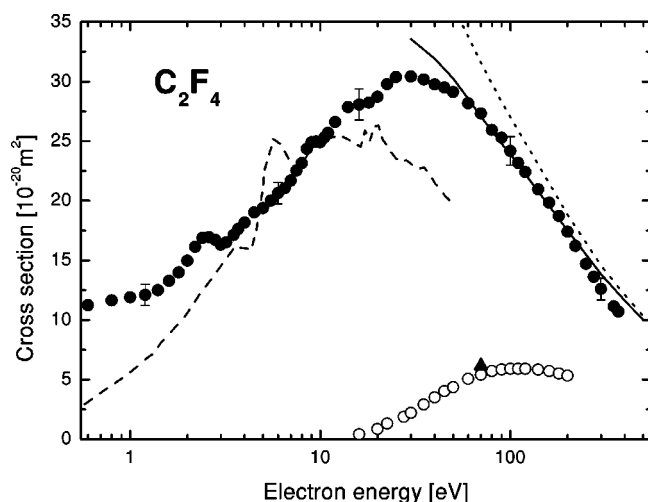


FIG. 1. Total cross sections for e^- - C_2F_4 scattering: solid circles, present experiment; error bars represent overall (systematical and statistical) uncertainties; solid line, additivity rule (AR) calculations [10]; and dotted line, energy-dependent geometric AR calculations [10]. Experimental ionization cross sections: solid triangle, Ref. [1]; open circles, Ref. [2]. Calculated integral elastic cross section: dashed line [11].

eV. 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 resonantlike 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

TABLE I. Absolute total cross section (TCS) measured for electron impact on C_2F_4 molecule in units of 10^{-20} m^2 .

Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS
0.6	11.2	3.7	17.6	11	25.7	80	25.9
0.8	11.6	4.0	18.2	12	26.6	90	25.3
1.0	11.9	4.5	19.0	14	27.8	100	24.2
1.2	12.1	5.0	19.4	16	28.1	110	23.2
1.4	12.5	5.5	20.0	18	28.2	120	22.4
1.6	13.3	6.0	20.6	20	28.7	140	21.0
1.8	14.0	6.5	21.0	22.5	29.8	160	19.8
2.0	15.0	7.0	21.7	25	30.4	180	18.7
2.2	16.1	7.5	22.5	30	30.4	200	17.4
2.4	16.6	8.0	23.2	35	30.2	220	16.2
2.6	16.8	8.5	24.4	40	29.8	250	14.7
2.8	16.8	9.0	24.9	45	29.5	275	13.6
3.0	16.3	9.5	25.0	50	29.1	300	12.6
3.2	16.5	10	24.9	60	28.2	350	11.1
3.5	17.1	10.5	25.3	70	27.3	370	10.7

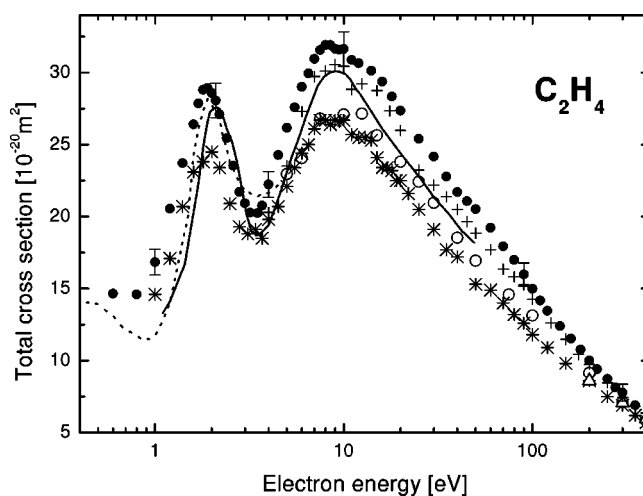


FIG. 2. Experimental total cross sections for e^- - C_2H_4 scattering: solid circles, present work; solid line, Ref. [13]; open circles, Ref. [14]; asterisks, Ref. [15]; crosses, Ref. [16]; dotted line, Ref. [17]; and open triangles, Ref. [18].

negative-ion yield [3–5] indicating that the observed TCS structures may reflect the resonance effects. Presence of resonant states between 7 and 20 eV is also predicted in calculations [11]. Looking above threshold, it becomes clear that the ionization processes contribute relatively little to the TCS. This ionization share in TCS does not exceed 30% [2] even in the vicinity of the total ionization cross-section maximum located near 150 eV. Such a relation of ionization and total cross sections seems to be a common feature of perfluorides [23].

Although not shown here, we have also compared the e^- - C_2F_4 TCS with TCSs for other perfluorocarbons. We have noticed a considerable correspondence in the shape of TCS for C_2F_4 with that for C_6F_6 [24] (both molecules are planar in their ground states); the accord is especially close for energies above 6 eV. This similarity becomes particularly striking when TCS for C_2F_4 is multiplied by factor 2; then the curves for C_2F_4 and C_6F_6 overlap and even very small structures in both curves look similar. Another distinctive common feature of both TCSs is the absence of the pronounced minimum around 16 eV, visible in TCS curve for other perfluorocarbons studied so far [23], instead, only a shoulder near 16 eV is marked.

A reasonable agreement, in the intermediate energy range, between the TCS calculated by Jiang *et al.* [10] using an additivity rule (AR) approximation and the present experimental data indicates that the AR approximation, and especially its energy-dependent geometric AR approach, may provide reasonable predictions of TCS for small molecules at higher impact energies.

B. Ethylene, C_2H_4

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

TABLE II. Absolute TCS measured for electron impact on C_2H_4 molecule in units of $10^{-20} m^2$.

Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS
0.6	14.6	3.0	20.9	10	31.6	90	16.0
0.8	14.6	3.2	20.3	11	31.0	100	15.0
1.0	16.8	3.5	20.2	12	30.7	110	14.2
1.2	20.6	3.7	20.8	14	30.1	120	13.4
1.4	23.7	4.0	22.2	16	29.4	140	12.4
1.5	24.9	4.5	24.3	18	28.3	160	11.5
1.6	26.4	5.0	26.2	20	27.4	180	10.8
1.7	27.9	5.5	27.6	25	25.4	200	10.0
1.8	28.8	6.0	29.0	30	24.2	220	9.40
1.9	28.9	6.5	30.0	35	22.8	250	8.73
2.0	28.6	7.0	31.0	40	21.7	275	8.14
2.1	28.1	7.5	31.6	45	21.1	300	7.77
2.2	27.1	8.0	31.9	50	20.5	350	6.90
2.4	25.4	8.5	31.9	60	19.2	370	6.65
2.6	23.5	9.0	31.7	70	17.9		
2.8	21.7	9.5	31.6	80	17.0		

Mori [15] and Lunt *et al.* [17] are also included for completeness. Table II presents our measured e^- - C_2H_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_2H_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^- - C_2H_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_2F_4 and for C_2H_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

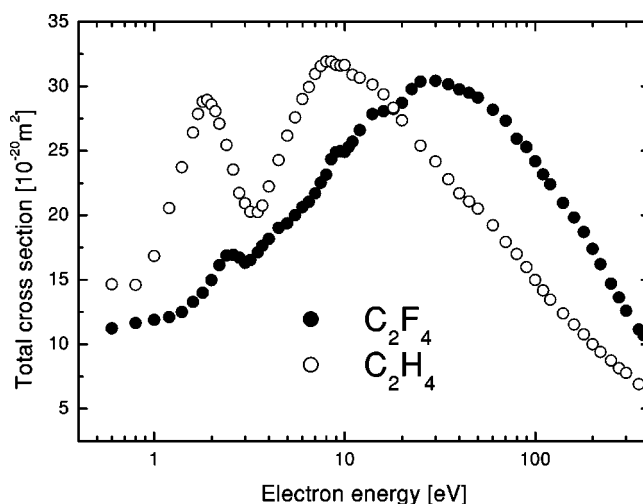


FIG. 3. Illustration of perfluorination effect. Present experimental total cross sections: solid circles, C_2F_4 ; open circles, C_2H_4 .

magnitude of TCS, the studied energy range can be divided into two regions: below about 18 eV the TCS for C_2F_4 is distinctly lower than TCS for C_2H_4 while above that energy, at intermediates, the ordering of compared TCS curves changes—the TCS for C_2F_4 is higher than that for C_2H_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_2F_4 precludes the quantitative analysis, but basing on relations for other perfluorocarbons we suppose that the increase of TCS for C_2F_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_2F_4 and C_6F_6 molecules, we have compared the relation of their TCSs to TCSs for corresponding hydrocarbons, C_2H_4 and C_6H_6 . Again, we have noted some similarities in TCS ratios within these pairs, C_2F_4 - C_2H_4 and C_6F_6 - C_6H_6 . For C_2F_4 and C_6F_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_2F_4 and for C_2H_4 molecules measured in a linear transmission experiment from 0.6 to 370 eV. To the best of our knowledge, the results for C_2F_4 are the first experimental TCS. The obtained data may be valuable for basic physics and for applications. The TCS

energy dependence for C_2F_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 C_2F_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 C_2H_4 and C_2F_4 indicates distinct perfluorination effect over the entire impact energy range studied.

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- [1] J.A. Beran and L. Kevan, *J. Phys. Chem.* **73**, 3866 (1969).
 [2] M. Bart, P.W. Harland, J.E. Hudson, and C. Vallance, *Phys. Chem. Chem. Phys.* **3**, 800 (2001).
 [3] J.C.J. Thynne and K.A.G. MacNeil, *Int. J. Mass Spectrom. Ion Phys.* **5**, 329 (1970).
 [4] M. Heni, E. Illenberger, H. Baumgärtel, and S. Süzer, *Chem. Phys. Lett.* **87**, 244 (1982).
 [5] F. Weik and E. Illenberger, *J. Chem. Phys.* **103**, 1406 (1995).
 [6] M.J. Coggiola, W.M. Flicker, O.A. Mosher, and A. Kuppermann, *J. Chem. Phys.* **65**, 2655 (1976).
 [7] N.S. Chiu, P.D. Burrow, and K.D. Jordan, *Chem. Phys. Lett.* **23**, 121 (1979).
 [8] A.N. Goyette, J. de Urquijo, Y. Wang, L.G. Christophorou, and J.K. Olthoff, *J. Chem. Phys.* **114**, 8932 (2001).
 [9] K. Yoshida, S. Goto, H. Tagashira, C. Winstead, B.V. McKoy, and W.L. Morgan, *J. Appl. Phys.* **91**, 2637 (2002).
 [10] Y. Jiang, J. Sun, and L. Wan, *Phys. Rev. A* **62**, 062712 (2000).
 [11] C. Winstead and V. McKoy, *J. Chem. Phys.* **116**, 1380 (2002).
 [12] S. Samukawa and T. Mukai, *J. Vac. Sci. Technol. A* **17**, 2463 (1999); *Thin Solid Films* **374**, 235 (2000); S. Samukawa, T. Mukai, and K. Tsuda, *J. Vac. Sci. Technol. A* **17**, 2551 (1999).
 [13] E. Brüche, *Ann. Phys. (Leipzig)* **2**, 909 (1929).
 [14] K. Floeder, D. Fromme, W. Raith, A. Schwab, and G. Sinapius, *J. Phys. B* **18**, 3347 (1985).
 [15] O. Sueoka and S. Mori, *J. Phys. B* **19**, 4035 (1986).
 [16] H. Nishimura and H. Tawara, *J. Phys. B* **24**, L363 (1991).
 [17] S.L. Lunt, J. Randell, J.-P. Ziesel, G. Mrotzek, and D. Field, *J. Phys. B* **27**, 1407 (1994).
 [18] W.M. Ariyasinghe and D. Powers, *Phys. Rev. A* **66**, 052716 (2002).
 [19] B. Bederson and L.J. Kieffer, *Rev. Mod. Phys.* **43**, 601 (1971).
 [20] Cz. Szmytkowski and P. Mozejko, *Vacuum* **63**, 549 (2001).
 [21] M. Knudsen, *Ann. Phys. (Leipzig)* **31**, 205 (1910).
 [22] R.N. Nelson and S.O. Colgate, *Phys. Rev. A* **8**, 3045 (1973).
 [23] Cz. Szmytkowski and E. Ptasińska-Denga, *Vacuum* **63**, 545 (2001).
 [24] G. Kasperski, P. Mozejko, and Cz. Szmytkowski, *Z. Phys. D: At., Mol. Clusters* **42**, 187 (1997).
 [25] L. Sanche and G.J. Schulz, *J. Chem. Phys.* **58**, 479 (1973).
 [26] I.C. Walker, A. Stamatovic, and S.F. Wong, *J. Chem. Phys.* **69**, 5532 (1978).
 [27] R. Panajotovic, M. Kitajima, H. Tanaka, M. Jelisavcic, J. Lower, L. Campbell, M.J. Brunger, and S.J. Buckman, *J. Phys. B* **36**, 1615 (2003).
 [28] D. Rapp and P. Englander-Golden, *J. Chem. Phys.* **43**, 1464 (1965).
 [29] D.E. Golden, *Adv. At. Mol. Phys.* **14**, 1 (1978).