Absolute total cross-section measurements for electron collisions with tetrahydrofuran

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The absolute total cross section (TCS) for electron collisions with tetrahydrofuran C_4H_8O in the gas phase has been measured using the linear transmission technique within $1-370$ eV energy range. The total cross section function for e^--C_4H_8O collisions is characterized by the relatively high magnitude and the broad enhancement spanned between 4 and 12 eV, with some resonantlike structures. This enhancement can be explained as a result of overlapping core-excited resonances. At higher collision energies the magnitude of the measured total cross section monotonically decreases with the energy increase. At low impact energies some additional weak resonant features are visible near 1.9 and 3.5 eV. The reported TCS results are higher by 30% than recently published by Zecca *et al.* [J. Phys. B **38**, 2079 (1995)]. They are also distinctly different from the recent *R*-matrix calculations. At intermediate energy range the present data agree well with the sum of calculated elastic and ionization cross sections.

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I. INTRODUCTION

The recent interest in interactions of slow electrons with biomolecules or their molecular analogs is strongly related to the importance of secondary electrons in the ionizing radiation damage to the living cells [1]. It has been shown that low-energy electrons (LEEs) can induce significant number of single or double strand breaks in the DNA [2]. Such low energy (0–20 eV) electrons are produced in a large quantity ($\sim 4 \times 10^4$ electrons per MeV [3,4]) by primary high energetic ionizing radiation (e.g., β, x, γ rays). Further studies on LEE interaction with DNA and its constituents both in gas and condensed phase have shown that damage of DNA can occur via resonant electron scattering (Refs. [5–13], and references therein). However, LEE interactions with a fragment of DNA molecule or its large subunit result in so many different products created in direct and indirect processes [1], that detailed analysis and explanation of LEEs damage to DNA are rather difficult. Therefore, for complete understanding and better physical description of all events leading to DNA damage induced by ionizing radiation comprehensive studies of LEE interactions with deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and their subunits, as well as with molecular constituents of these biomolecules are necessary. Especially, LEE interactions with components of DNA backbone, which consists of repeated sugar-phosphate units, have to be studied extensively.

In the present experiment, we have investigated, with a linear transmission technique, electron collisions with the tetrahydrofuran (THF) molecule, which can be treated as the simplest molecular analog of the deoxyribose unit. In the first approximation, such a backbone structure can be represented as a series of THF molecules bonded to phosphate units and DNA bases. In Fig. 1 a short chain fragment of the single stranded deoxyribose backbone of DNA is shown. The objective of our studies is to provide the absolute total cross section (TCS) for electron scattering from THF molecule measured over a wide collision energy range (1–370 eV) with a high accuracy. Precisely measured absolute TCSs may be useful not only for the analysis of scattering phenomena but also for normalization of data obtained in arbitrary units only.

Previous experimental and theoretical studies concerning the scattering of low-energy electrons with THF can be summarized as follows. Experiments on LEE interactions with gas-phase and solid tetrahydrofuran molecules are, up to date, rather sparse. Near threshold electron energy-loss (EEL) spectra have been recorded for THF molecules by Bremner *et al.* [14]. The intermolecular vibrational excitation of tetrahydrofuran in the gas and solid phase induced by 1–30 eV electrons has been studied with high-resolution electron-energy-loss spectroscopy (HREELS) technique [15]. LEE damage to condensed THF molecules has been investigated within 5–40 eV energy range using the electron stimulated desorption (ESD) technique [16,17] and electron energy-loss spectroscopy (EELS) [16]. The low-energy electron-induced production of aldehydes within a thin film of solid THF condensed on a solid Kr substrate has been studied using the HREELS [18], while reactive scattering of O^- within films of THF and production of OH^- anions have been investigated by means of the ESD technique [19]. Differential cross sections for elastic electron collisions with THF molecule have been measured with the crossed-beam method for scattering angles ranging from 10° to 110°, within 20–300 eV incident electron energy range [20]. Recently, TCS measurements for electron scattering from THF have been reported for energies between 2 and 21 eV [21].

Theoretical works concerning e^--THF scattering are even less numerous. The cross section for elastic electron scattering from THF molecule has been computed [22] with the

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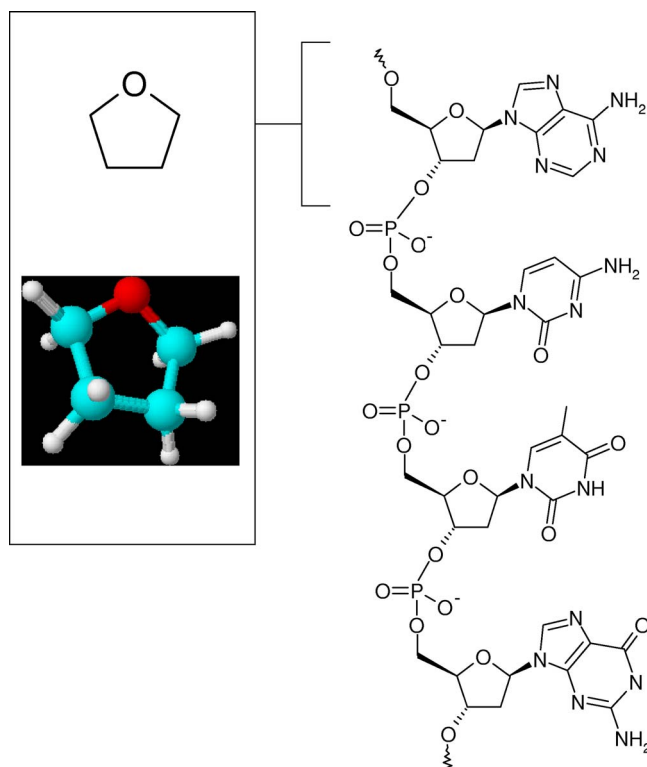
FIG. 1. (Color online) A short chain fragment of the single stranded deoxyribose backbone of DNA and the chemical structure of the THF molecule.

independent atom method (IAM) for intermediate collision energies (50–2000 eV). The same authors reported the cross section for electron impact ionization of THF derived using the binary-encounter-Bethe (BEB) model in the energy range from the ionization threshold up to 4000 eV [22]. Recently, the total (elastic+electronically inelastic) integral cross section for LEE collisions with THF has been calculated using the R-matrix method for incident energies below 10 eV [23].

In Sec. II, the experimental technique and procedures, which have been employed in the reported experiment, are described. The results of our measurements are presented, discussed, and compared with available experimental and theoretical data in Sec. III.

II. EXPERIMENT

Procedures and instruments employed in the present experiment are essentially the same as in our earlier TCS studies [24–26]. They have been described in details previously [27,28], thus only a brief outlook is provided here. For the absolute total cross section measurements, an electron spectrometer working in the linear transmission configuration has been used. The monoenergetic (ΔE=80 meV) electron beam has been produced and formed with an electron gun coupled to a 127° cylindrical electrostatic condenser and a system of electrostatic electron lenses. Electrons of a given energy E have been directed into a scattering cell filled with the vapor target. Those electrons which emerged from the cell through the exit orifice have been discriminated energetically with a

retarding field analyzer. In that way, the electrons inelastically scattered in the forward direction have not been registered. Finally, the transmitted electrons have been collected with the Faraday cup detector. The electron spectrometer optics has been housed within a stainless steel vacuum chamber maintained at a base pressure of 10^{-7} Torr. The magnetic field in the region of the electron spectrometer optics and in the interaction region has been reduced below 0.1 μT with the system of Helmholtz coils. The absolute experimental energy scale has been calibrated with reference to the well known resonant oscillatory structure around 2.3 eV in molecular nitrogen (see, e.g., Ref. [29]).

The absolute total cross section $\sigma(E)$ at each investigated collision energy E has been derived using the de Beer–Lambert relationship

$$\sigma(E) = \frac{1}{nL} \ln \frac{I_0(E)}{I_g(E)}, \qquad (1)$$

where $I_g(E)$ and $I_0(E)$ are intensities of electron beam with and without the gas target in the scattering chamber of the length L (=30.5 mm), respectively. The number density n of the target has been determined from absolute measurements of the gas target pressure and its temperature, taking into account the thermal transpiration effect [30,31]. It is worth noting that the temperature of the scattering cell T_c (310–320 K), differs only slightly from the temperature of the mks capacitance manometer head T_m=322 K, and the correction due to the thermal transpiration effects does not exceed 2%. To establish thermal conditions comparable to those in the scattering region, the vapor sample supplying line and the leak valve have been heated to about 315 K. The THF vapor has been obtained from a liquid THF sample (Aldrich) of a quoted purity of 99.9%, which has been degassed with a number of freeze-pump-thaw cycles.

To provide constant conditions in the course of the experiment for the electron beam in the region of the electron gun and electron optics elements, the target sample has been supplied alternately into the scattering cell and its surrounding in such a way that the background pressure in the region of the electron optics has been constant irrespective of whether the target is present in the scattering cell or not. To minimize the influence of potential apparatus effects, the measurements for a given collision energy have been carried out in a series of runs performed in slightly different conditions, i.e., for different vapor-target pressures and electron beam intensities. This way, it has been proved that the results are independent on the applied target pressures and electron beam intensities.

The final value of TCS for each energy studied is an average of data measured in independent series (3–9) of individual runs (~10 in a series). Statistical uncertainties (one standard deviation of weighted mean values) are usually well below 1% over the entire energy range studied. The direct sum of all potential individual systematic errors, related to determination of quantities necessary to TCS derivation has been estimated to be up to 10% at the lowest applied energies, decreasing below 5% between 10 and 100 eV, and increasing to 6% at the highest collision energies applied.

TABLE I. Absolute total cross section (TCS) for electron scattering from tetrahydrofuran (C_4H_8O) molecules in units of 10^{-20} m^2.

Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS
1.0	43.4	4.7	50.0	30	44.4
1.1	43.3	5.0	50.7	35	43.9
1.2	43.3	5.5	51.2	40	43.2
1.3	43.1	6.0	52.0	45	42.1
1.4	42.5	6.5	51.9	50	41.0
1.5	42.6	7.0	51.3	60	38.4
1.6	42.5	7.5	51.1	70	35.6
1.7	42.3	8.0	51.1	80	33.4
1.8	42.7	8.5	51.1	90	31.6
1.9	42.8	9.0	50.8	100	30.0
2.0	42.7	9.5	50.5	110	29.1
2.1	41.0	10.0	49.8	120	27.6
2.2	40.5	10.5	49.3	140	26.1
2.4	39.5	11.0	48.6	160	24.2
2.6	40.1	12.0	48.2	180	22.4
2.8	41.6	13.0	47.3	200	20.5
3.0	42.2	15.0	46.5	220	19.3
3.3	42.6	17.0	46.9	250	17.7
3.5	43.0	19.0	46.4	270	16.7
3.7	42.9	21.0	45.9	300	15.1
4.0	42.8	23.5	45.7	350	13.7
4.2	45.3	26.0	45.2	370	12.8
4.5	48.6	28.5	44.7		

FIG. 2. Absolute total cross sections for e^--C_4H_8O collisions: ●, present results; ×, Ref. [21]. The error bars in selected points represent the total (systematic plus statistical) experimental uncertainties.

III. RESULTS AND DISCUSSION

Absolute electron-scattering total cross sections for THF (C_4H_8O) molecule measured in the present experiment are listed in the numerical form in Table I. They are also shown in Fig. 2 together with the measurements of Zecca *et al.* [21]. In Fig. 3, the present experimental results are compared with other available data including theoretical cross sections for particular collisional processes.

The characteristic feature of the measured TCS for THF molecule is its relatively high magnitude what in part reflects the large geometrical size of the molecule. Below 4 eV the TCS changes rather slightly with energy except for the region around 2.4 eV where the TCS function exhibits a local minimum of 39×10^{-20} m^2. Between 1.4 and 2 eV the TCS is almost constant and for energies below 1.4 eV it increases nearly to 43×10^{-20} at 1 eV, the lowest energy used. Since THF is the polar molecule ($\mu = 1.75$ D), one might expect a steep increase of TCS at such low energies. A strong increase of the e^--THF cross section towards zero energy has been predicted by recent R-matrix calculations [23] (see Fig. 3). On the other hand, it is possible that the distinct increase of TCS will occur only for energies lower than 1 eV. This expectation is based on the assumption that the shape of TCS below 4 eV may be described as a catenarylike curve (with
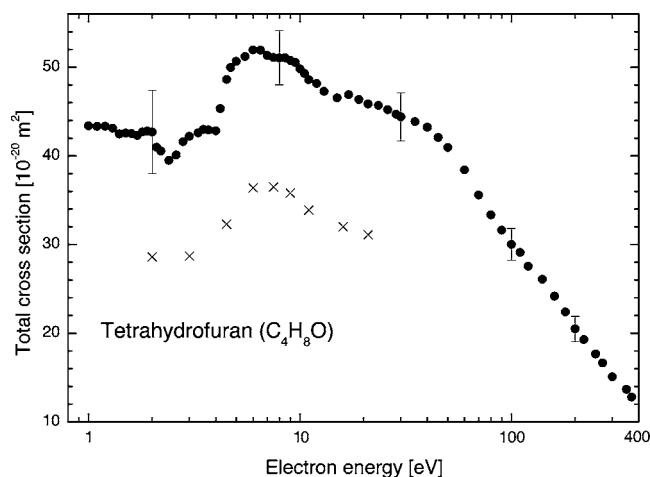
its minimum near 2.4 eV), on which two humps peaked near 1.9 and 3.5 eV are superimposed. Above the minimum at 2.4 eV the TCS increases and a weak local maximum is visible at 3.5 eV with a value of 43×10^{-20} m^2. There are indirect but convincing indications that the maximum between 3 and 4 eV may be explained in terms of resonant processes leading to vibrational excitations of C-H stretching and/or CH_2 scissoring modes in THF, and that is not attributed to the presence of oxygen atom. Indeed, Allan and Andric [32] have observed resonant structures located between 2.6 and 3.2 eV in vibrationally inelastic cross sections for electron scattering on other cyclic molecules comprising CH_2 groups such as cyclopropane (c-C_3H_6), ethylene oxide (C_2H_4O), and cyclopentane (c-C_5H_{10}).

For energies higher than 4 eV, the TCS rapidly increases and reaches the maximum of 52×10^{-20} m^2 at 6 eV. That enhancement is spanned between 4.2 and 12 eV. In addition to the structure centered around 6 eV, the other weaker resonantlike feature at about 8.5 eV can be distinguished. There is a solid ground to believe that this effect can be explained as a superposition of several short-lived resonances formed in this energy range. That supposition comes from the fact that the EEL spectrum [14] shows a broad resonant structure near 6.4 eV, which has been identified as a core excited resonance of Rydberg character. Moreover, presence of three very narrow core-excited resonant structures, located between 6 and 10 eV, has been reported in the elastic cross section calculated by Bouchiha *et al.* [23]. Also the inelastic cross section calculated by the same authors exhibits resonant features in the vicinity of 8–9 eV, resulting from core-excited resonances [23]. Resonance-enhanced vibrational excitation of the gas-phase THF in the HREELS experiment has been reported by Lepage *et al.* [15]. Their excitation function of the CH_2 asymmetric stretch mode (ν_2) reveals a maximum near 8.4 eV. Even more distinct resonant features have been observed in the vibrational electron-induced excitation of THF within multilayer solid films; however, the respective maxima have been shifted down by about 1 eV in
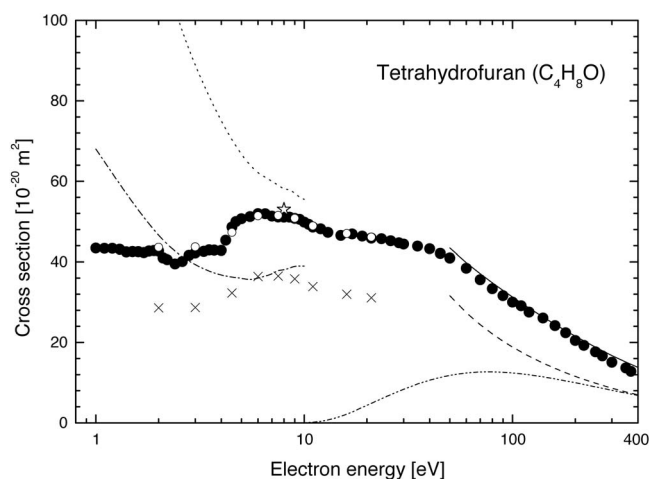
FIG. 3. Cross sections for e^--C_4H_8O collisions. Experimental absolute total: ●, present; ×, Ref. [21]. Theoretical: —, sum of elastic and ionization from Ref. [22]; –·–, ionization, Ref. [22]; – – –, elastic, Ref. [22]; ···, total with the Born correction [23]; –··–, total without the Born correction [23]. For comparison the following data are also included: ★, TCS for cyclopentane, Ref. [35]; ○, renormalized (by adding 15×10^{-20} m^2) data of Zecca *et al.* [21].
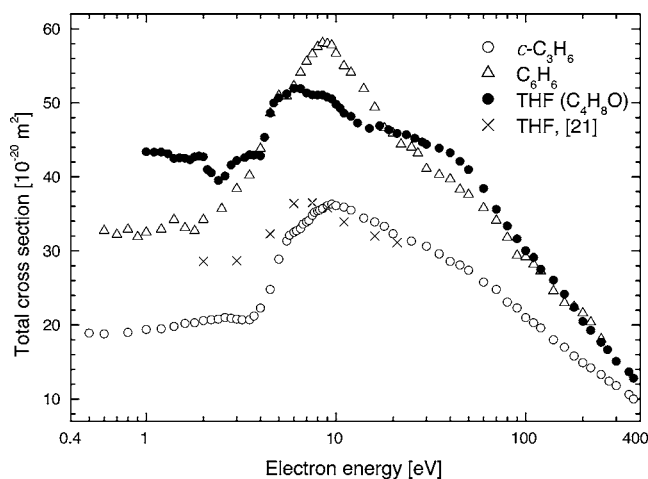

FIG. 4. Comparison of total cross sections for electron collisions with: ●, tetrahydrofuran, (C_4H_8O), present results; ×, tetrahydrofuran, Ref. [21]; △, benzene, (C_6H_6), Ref. [34]; ○, cyclopropane, (c-C_3H_6), Ref. [33].

comparison with those for the gaseous THF. That shift in energy can be explained in terms of the polarization interaction due to the presence of the solid substrate. The decomposition processes in condensed films of THF [18] have been also explained as a result of resonant processes. To support the resonant character of e^--THF collisions within 4–12 eV region, once again one can refer to experiments of Allan and Andric on electron-induced vibrational excitation of ring molecules [32]. Their vibrational inelastic cross sections for cyclopropane, ethylene oxide, cyclopentane, and cyclohexane show distinct resonantlike bands occurring between 5 and 8–12 eV with some of them being two peaked.

Between 10 and 50 eV the TCS for e^--THF scattering decreases rather slowly with the energy increase (Fig. 2). Such behavior of TCS in this energy range may be also partly related to resonant effects. In fact, between 10 and 20 eV Breton *et al.* [18] have observed some resonant structures in their HREELS experiment for solid state THF. Above 50 eV the experimental TCS function decreases monotonically with energy down to 12×10^{-20} m^2 at 370 eV.

In Fig. 4 the results for THF are compared with TCS functions measured in our laboratory for other ring molecules: cyclopropane (c-C_3H_6) [33] and benzene (C_6H_6) [34]. With respect to the shape, the TCS for THF closely resembles that for cyclopropane and weakly that for benzene. The magnitude of TCS for THF is comparable to that for benzene, especially at intermediate collision energies.

In general, the present TCS energy function for THF very closely resembles the shape of TCS curve obtained by Zecca *et al.* [21], in the common energy range (Fig. 2). However, both TCSs differ distinctly with respect to the magnitude. The TCS values obtained by Zecca *et al.* are systematically lower by 15×10^{-20} m^2 (28–32 %) than our results. On the other hand, there are some indications that the present results are more realistic. Our TCS value at 8 eV for e^--THF scat-

tering (51×10^{-20} m^2) is very close to the TCS (53 $\times 10^{-20}$ m^2) reported by Kimura *et al.* [35] for cyclopentane, the isoelectronic analog of THF molecule (see Fig. 3). It is nearly common that above 6–8 eV isoelectronic molecules of a similar geometry have TCSs comparable in magnitude [36]. Moreover, above 40 eV the present measurements agree well with the sum of calculated elastic and ionization cross sections (Fig. 3). Total cross sections (elastic +ionization) computed this way usually reproduce experiments satisfactorily at intermediate energies (e.g., for NF$_3$ [24], SF$_4$ [25], and SO$_2$ClF [26]). It is also evident from Fig. 4 that the magnitude of our experimental TCS for THF is comparable to that for benzene, the molecule of similar size and geometry as THF, while the data of Zecca *et al.* are closer to TCS for a smaller ring molecule—cyclopropane.

Figure 3 shows that the shape and magnitude of the measured TCS are well described with the sum of elastic integral and ionization cross sections calculated [22] with the use of the independent atom model and the binary-encounter-Bethe approach, respectively. The same figure shows that both R-matrix calculations, with and without the Born correction (for details see Ref. [23]), have energy dependencies and magnitudes significantly different from the present experiment.

Summarizing, the total cross section for tetrahydrofuran (C_4H_8O) molecule, which can be treated as the simplest deoxyribose unit analog, has been measured in 1–370 eV energy range. The magnitude of TCS is relatively high, what reflects the large geometrical size of the molecule studied. The TCS function exhibits the broad enhancement spanned between 4 and 12 eV. Weak structures in the TCS, centered about 3.5, 6.5, and 8.5 eV, may be explained in terms of resonant electron scattering. It is worth noting that our TCS measurements for THF molecule are significantly higher (by ~30%) than earlier experimental data [21]. Good agreement has been found between the magnitude and shape of the present experimental TCS and combined elastic and ionization cross sections [22] computed for energies higher than

50 eV. For detailed explanation of all observed structures more experimental works concerning the electron collisions with THF, especially for particular scattering channels, are needed.

[1] L. Sanche, Eur. Phys. J. D **35**, 367 (2005).

[2] B. Boudaïffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, Science **287**, 1658 (2000).

[3] *International Commission on Radiation Units and Measurements*, IRCU Report No. 31 (IRCU, Washington, DC, 1979).

[4] V. Cobut, Y. Fongillo, J. P. Patau, T. Goulet, M. J. Frases, and J. P. Jay-Gerin, Radiat. Phys. Chem. **51**, 229 (1998).

[5] K. Aflatooni, G. A. Gallup, and P. D. Burrow, J. Phys. Chem. A **102**, 6205 (1998).

[6] M. A. Huels, B. Boudaiffa, P. Cloutier, D. Hunting, and L. Sanche, J. Am. Chem. Soc. **125**, 4467 (2003).

[7] X. Pan, P. Cloutier, D. Hunting, and L. Sanche, Phys. Rev. Lett. **90**, 208102 (2003).

[8] H. Abdoul-Carime, S. Gohlke, and E. Illenberger, Phys. Rev. Lett. **92**, 168103 (2004).

[9] S. Feil, K. Gluch, S. Matt-Lebner, P. Scheier, J. Limtrakul, M. Probst, H. Deutsch, K. Becker, A. Stamatovic, and T. D. Märk, J. Phys. B **37**, 3013 (2004).

[10] X. Pan and L. Sanche, Phys. Rev. Lett. **94**, 198104 (2005).

[11] Y. Zheng, P. Cloutier, D. J. Hunting, J. R. Wagner, and L. Sanche, J. Chem. Phys. **124**, 064710 (2006).

[12] S. Tonzani and C. H. Greene, J. Chem. Phys. **124**, 054312 (2006).

[13] P. D. Burrow, G. A. Gallup, M. A. Scheer, S. Denfil, S. Ptasińska, T. Märk, and P. Scheier, J. Chem. Phys. **124**, 124310 (2006).

[14] L. J. Bremner, M. G. Curtis, and I. C. Walker, J. Chem. Soc., Faraday Trans. **87**, 1049 (1991).

[15] M. Lepage, S. Letarte, M. Michaud, F. Motte-Tollet, M.-J. Hubin-Franskin, D. Roy, and L. Sanche, J. Chem. Phys. **109**, 5980 (1998).

[16] D. Antic, L. Parenteau, M. Lepage, and L. Sanche, J. Phys. Chem. B **103**, 6611 (1999).

[17] D. Antic, L. Parentau, and L. Sanche, J. Phys. Chem. B **104**, 4711 (2000).

[18] S.-P. Breton, M. Michaud, C. Jäggle, P. Swiderek, and L. Sanche, J. Chem. Phys. **121**, 11240 (2004).

[19] M. A. Huels, L. Parenteau, and L. Sanche, J. Phys. Chem. B **108**, 16303 (2005).

[20] A. R. Milosavljević, A. Giuliani, D. Šević, M.-J. Hubin-Franskin, and B. P. Marinković, Eur. Phys. J. D **35**, 411 (2005).

[21] A. Zecca, Ch. Perazzolli, and M. J. Brunger, J. Phys. B **38**, 2079 (2005).

[22] P. Możejko and L. Sanche, Radiat. Phys. Chem. **73**, 77 (2005).

[23] D. Bouchiha, J. D. Gornfinkiel, L. G. Caron, and L. Sanche, J. Phys. B **39**, 975 (2006).

[24] Cz. Szmytkowski, A. Domaracka, P. Możejko, E. Ptasińska-Denga, L. Kłosowski, M. Piotrowicz, and G. Kasperski, Phys. Rev. A **70**, 032707 (2004).

[25] Cz. Szmytkowski, A. Domaracka, P. Możejko, E. Ptasińska-Denga, and S. Kwitnewski, J. Phys. B **38**, 745 (2005).

[26] Cz. Szmytkowski, P. Możejko, S. Kwitnewski, E. Ptasińska-Denga, and A. Domaracka, J. Phys. B **38**, 2945 (2005).

[27] Cz. Szmytkowski, P. Możejko, and G. Kasperski, J. Phys. B **31**, 3917 (1998).

[28] Cz. Szmytkowski and P. Możejko, Vacuum **63**, 549 (2001).

[29] Cz. Szmytkowski, K. Maciag, and G. Karwasz, Phys. Scr. **54**, 271 (1996).

[30] M. Knudsen, Ann. Phys. **31**, 205 (1910).

[31] K. F. Poulter, M. J. Rodgers, P. J. Nash, T. J. Thompson, and M. P. Perkin, Vacuum **33**, 311 (1983).

[32] M. Allan and L. Andric, J. Chem. Phys. **105**, 3559 (1996).

[33] Cz. Szmytkowski and S. Kwitnewski, J. Phys. B **35**, 2613 (2002).

[34] P. Możejko, G. Kasperski, Cz. Szmytkowski, G. P. Karwasz, R. S. Brusa, and A. Zecca, Chem. Phys. Lett. **257**, 309 (1996).

[35] M. Kimura, O. Sueoka, A. Hamada, and Y. Itikawa, Adv. Chem. Phys. **111**, 537 (2000).

[36] Cz. Szmytkowski and A. Krzysztofowicz, J. Phys. B **28**, 4291 (1995).