Electron–hexafluoropropene (C_3F_6) scattering at intermediate energies

Czesław Szmytkowski, Paweł Możejko and Stanisław Kwitnewski

Atomic Physics Division, Department of Atomic Physics and Luminescence, Faculty of Applied Physics and Mathematics, Technical University of Gdańsk, ul. Gabriela Narutowicza 11/12, 80-952 Gdańsk, Poland

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

Online at stacks.iop.org/JPhysB/35/1267

Abstract

The absolute total cross section for electron–hexafluoropropene (C_3F_6) scattering has been measured over the energy range from 30 to 370 eV in a linear electron-beam transmission experiment under single-collision conditions. Between 30 and 70 eV the total cross section appears to be relatively high and nearly constant, and above 70 eV it decreases monotonically with increasing energy. Such behaviour of the total cross section energy function seems to be generally true for perfluorinated targets. Some other features in electron scattering cross sections for perfluorinated targets are noted and discussed.

The integral elastic e^-–C_3F_6 scattering cross section has been calculated using an independent atom method with a static + polarization model potential. Results for impact energies above 70 eV are in good agreement with values evaluated from experimental (total and ionization) cross-section data.

1. Introduction

There is much interest in collisions of electrons with perfluorinated molecules due to the widespread use of fluorine-containing compounds as reactive agents in plasma-assisted fabrication (e.g. CF_4, C_2F_6, C_4F_8) or as gaseous insulating components in the electrical industry (e.g. SF_6). A consequence of the many industrial uses of perfluorides is their increased accumulation in the earth's atmosphere. These man-made compounds, however, are greenhouse gases with a relatively high global warming potential (Nakamura *et al* 2001). Therefore, studies of basic electron-assisted processes, which are significant for modelling low-temperature plasmas (Christophorou and Olthoff 2001), with perfluorocarbon molecules of low environmental impact (like C_3F_6) are essential.

In the majority of experimental studies of electron–C_3F_6 collision phenomena, measurements have been primarily focused on the efficiency of formation of negative and positive ions. Investigations of dissociative electron attachment to the C_3F_6 molecule leading to production of negative fluorine ions were carried out at low impact energies by Bibby and Carter (1966). Harland and Thynne (1972) obtained negative ion mass spectra up to 70 eV. Peak maxima related to anion formation via dissociative electron capture have also been observed by Lifshitz and Grajower (1972–3). Hunter *et al* (1983) determined the electron attachment rate constant in a swarm experiment. They also observed numerous fragments and cluster negative ions produced in a corona discharge. The kinetics of low-energy electron attachment processes has recently been investigated by Jarvis *et al* (1996). All these measurements gave intensities (except for the electron attachment rate) in arbitrary units only. Production of positive ions in direct ionization and via dissociative channels has been studied by Chelobov *et al* (1963). Beran and Kevan (1969) have measured the total positive-ion electron ionization cross section at 70 eV. Ionization cross sections up to 200 eV were obtained very recently by Bart *et al* (2001). No experimental data on the elastic and total cross sections (TCS) for e^-–C_3F_6 scattering have been found in the literature. Theoretical works concerning electron–C_3F_6 collisions are much more sparse. Only very recently Jiang *et al* (2000) calculated the TCS at intermediate and high impact energies (30–3000 eV) by applying sum rules to atomic calculations with a complex interaction potential. Apart from a simple additivity model (AR), in which the electron–molecule cross section was obtained as a sum of the cross sections of all atomic constituents of the target molecule, they used also a modified model (EGAR) in which an energy-dependent geometric shielding effect in the molecule was semiempirically included.

The present experiment on electron–hexafluropropene scattering is part of our programme concerned with the systematic electron-scattering TCS measurements which are intended to yield a reliable set of absolute data for polyatomic compounds. On the basis of the comprehensive sets of quantitative data one would attempt to find possible regularities in the electron scattering (for TCS see Floeder *et al* (1985), Szmytkowski (1989), Nishimura and Tawara (1991), Zecca *et al* (1992) and García and Manero (1997)). Systematic relations, if found, may indicate the role of some microscopic properties of the target in the electron interactions, while the semiempirical formulae describing the correlations may be useful in the estimation of cross sections (García and Blanco 2000, Szmytkowski and Ptasińska-Denga 2001) for targets for which measurements are not yet possible and/or calculations not available and may also provide some stimulus for theoretical investigations. Although the TCS data as they stand do not give information on particular scattering processes, they could, together with other available scattering results, be used for estimation of the upper limit of another required cross section.

Absolute e^-–C_3F_6 scattering TCS measured in this work, together with the recent ionization cross section of Bart *et al* (2001), have been used here for estimation of the ‘experimental’ cross section for elastic scattering. These ‘elastic’ data prompted us to calculate the integral elastic cross section. Calculations for intermediate and high impact energies were performed in the independent atom approximation with a static + polarization model potential.

2. Methods and procedures

2.1. Experimental

The absolute TCSs presented in this paper were determined by the linear beam-transmission method under single-collision conditions. The method relates the scattering cross section to the transparency of the target at a given pressure for a beam of projectiles (Bederson and Kieffer 1971). The apparatus used in the reported experiment was based on an electrostatic electron spectrometer extensively used in series of experiments and described in detail elsewhere (e.g. Szmytkowski *et al* 1998, Szmytkowski and Możejko 2001) and only a brief outline of the apparatus and experimental procedure will be given here. The spectrometer consists of a thermionic electron source, a 127° cylindrical deflector working as an energy dispersing element, electron-optical lens systems controlling the trajectory and energy of the electron beam, a reaction chamber followed by a retarding field element and a Faraday cup collector. The electrons of desired energy E ($\Delta E \sim 0.1$ eV, fwhm) are directed into the reaction cell filled with the target gas under study. Those electrons which cross the scattering region and emerge from the cell through the exit orifice are energetically discriminated by the retarding field analyser and finally collected with a Faraday cup detector.

The TCS, $Q(E)$, at each electron impact energy E studied was derived by measuring intensities of the incident electron beam, with ($I(E,n)$) and without ($I(E,0)$) the target in the scattering cell, and applying the Bouguer–de Beer–Lambert formula

$$I(E,n) = I(E,0)\exp[-Q(E)nl].$$

The absolute number density, n, was evaluated from the ideal gas law based on absolute measurements of the gas-target pressure in the reaction volume and its temperature, taking into account a thermal transpiration effect according to the Knudsen (1910) formula.

In the pilot runs, it was noticed that the current of electrons leaving the electron gun was sensitive to the presence of C_3F_6 effusing from the scattering cell into the volume of the electron optics. To lessen the influence of this effect on the measured TCS, the experiment was carried out at the constant background pressure of the target gas (0.5 mPa) in the region of electron optics.

Measurements at given energy E were carried out in a series of runs using a range of target pressures and different sets of parameters controlling the electron beam. It was found that the TCSs obtained in the same series at the same energy were, within the random experimental uncertainties, independent of the intensity of the electron beam and the applied target pressure. The statistical uncertainty (one standard deviation of the weighted mean value) of the measured TCS is less than 1% over the entire energy range investigated. The overall systematic uncertainty in the measured cross section is estimated as a combination of potential systematic errors of measured individual quantities used for the derivation of the TCS; it amounts to about 5% below 100 eV increasing to 7% at the highest applied energies. More details on the analysis of uncertainties in our experiments have been given elsewhere (cf Szmytkowski *et al* 1997). The final TCS value at each particular energy is a weighted mean of data obtained in independent series (7–24) of individual runs (5–10 in a series).

The sample gas of 99+% grade (Sigma–Aldrich) was used directly from a cylinder without any further purification.

2.2. Theoretical

Elastic cross sections for e^-–C_3F_6 collisions at intermediate and high impact energies have been obtained with the independent atom method (IAM) (Massey *et al* 1969, Raj 1991) with a static + polarization model potential. In the IAM approximation, the integral cross section for elastic scattering of electrons by a molecule is given by

$$\sigma(E) = \frac{4\pi}{k}\sum_{i=1}^{N} \mathrm{Im}\, f_i(\theta = 0, k) = \sum_{i=1}^{N} \sigma_i(E)$$

where $\sigma_i(E)$ is the integral elastic cross section of the ith atom of the target molecule, E is the energy of the incident electron, $f_i(\theta, k)$ is the scattering amplitude due to the ith atom of the molecule, θ is the scattering angle and $k = \sqrt{2E}$ is the wave number of the incident

Table 1. Absolute TCS measured for electron impact on C_3F_6 molecules in units of 10^{-20} m^2.

Energy (eV)	TCS	Energy (eV)	TCS
30	36.9	120	29.8
35	36.9	140	28.3
40	37.3	160	26.9
45	37.7	180	25.0
50	37.7	200	24.1
60	37.1	220	23.1
70	36.1	250	21.4
80	35.0	275	20.1
90	33.4	300	19.2
100	32.4	350	17.3
110	31.3	370	16.5

electron. To obtain the atomic scattering amplitudes and the elastic electron–atom scattering cross section, we numerically solved the radial Schrödinger equation

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} - 2(V_{\mathrm{stat}}(r) + V_{\mathrm{polar}}(r)) + k^2\right) u_l(r) = 0$$

under the boundary conditions

$$u_l(0) = 0, \qquad u_l(r) \overset{r\to\infty}{\longrightarrow} A_l \hat{j}_l(kr) + B_l \hat{n}_l(kr)$$

where $\hat{j}_l(kr)$ and $\hat{n}_l(kr)$ are the Riccati–Bessel and Riccati–Neumann functions respectively. $V_{\mathrm{stat}}(r)$ is the static potential of the atom determined following the procedure of Salvat *et al* (1987)

$$V_{\mathrm{stat}}(r) = -\frac{Z}{r}\sum_{m=1}^{3} a_m \exp(-\beta_m r)$$

where Z is the nuclear charge of the atom and a_m and β_m are parameters obtained by numerical fitting to the Dirac–Hartree–Fock–Slater screening function (Salvat *et al* 1987). The polarization potential $V_{\mathrm{polar}}(r)$ was expressed in the form proposed by Padial and Norcross (1984)

$$V_{\mathrm{polar}}(r) = \begin{cases} \nu(r) & r \leqslant r_c \\ -\alpha/2r^4 & r > r_c \end{cases}$$

where $\nu(r)$ is the free-electron-gas correlation energy (Pedrew and Zunger 1981), α is the static electric dipole polarizability of the atom and r_c is the first crossing point of the curves of $\nu(r)$ and $-\alpha/2r^4$ (Zhang *et al* 1992).

3. Results and discussion

3.1. Experimental TCS

The experimental absolute TCSs for electron scattering on C_3F_6 molecules from the low to higher-intermediate impact energies (30–370 eV), determined as described in section 2, are listed in table 1. They are also plotted in figure 1 together with the only available TCS results from the calculations of Jiang *et al* (2000).

From the lowest applied energy, 30 eV, up to 60–70 eV the experimental e^-–C_3F_6 TCS appears to be slowly varying with energy, with a value close to 38 × 10^{-20} m^2, and then it

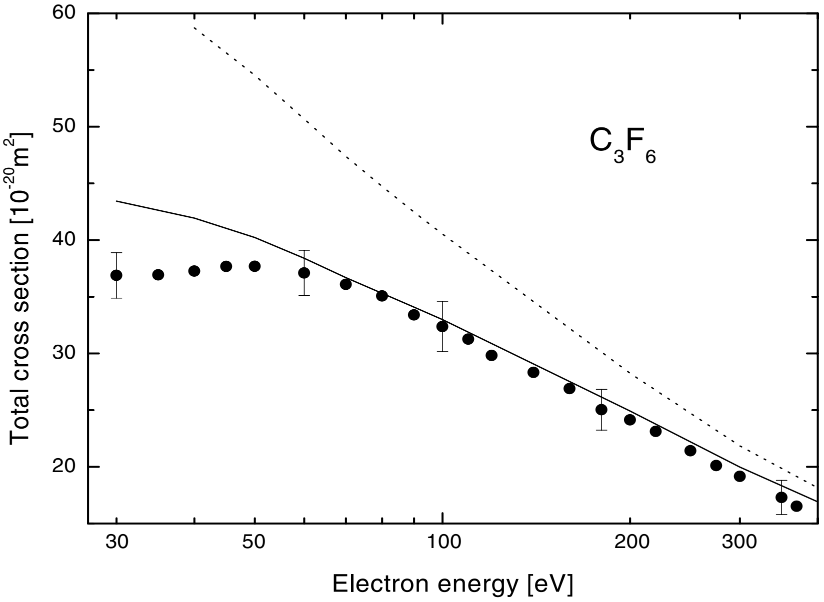

Figure 1. Total electron–C_3F_6 scattering cross section. Experimental: (•) present; the error bars at selected points represent the overall (systematic plus statistical) experimental uncertainties. Theoretical: (- - - -) additivity rule (AR), Jiang *et al* (2000); (——) energy-dependent geometric additivity rule (EGAR), Jiang *et al* (2000).

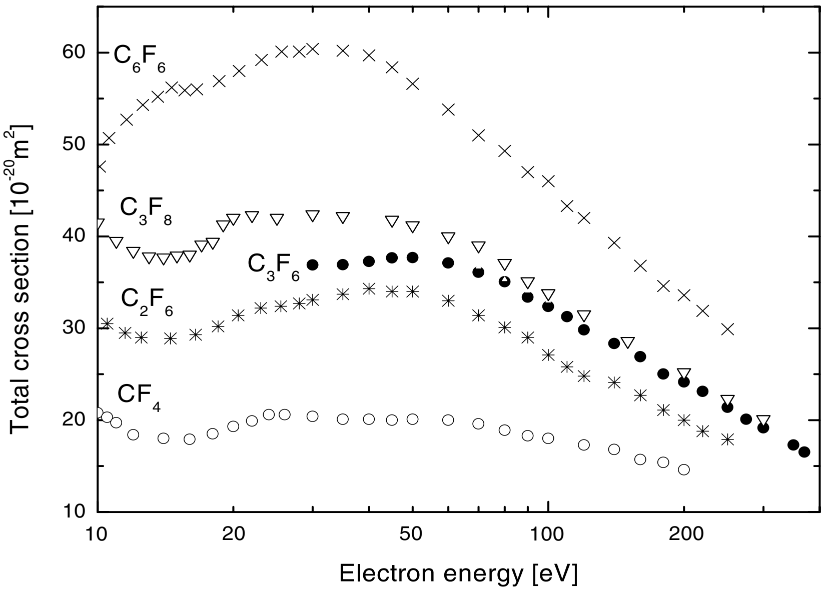

Figure 2. Electron-scattering total cross sections for perfluorocarbon molecules. (○) CF_4, Szmytkowski *et al* (1992); (∗) C_2F_6, Szmytkowski *et al* (2000); (•) C_3F_6, present; (∇) C_3F_8, Tanaka *et al* (1999); (×) C_6F_6, Kasperski *et al* (1997).

decreases monotonically down to 16.5×10^{-20} m^2 when the electron impact energy increases to 370 eV. The behaviour of the TCS function between 30 and 70 eV is worth noting as it differs strikingly from that observed for most molecules for which experimental TCS data are already known: typically, the TCS starts to descend close behind the first ionization threshold. For perfluorinated targets, however, as has already been noted (Szmytkowski *et al* 1998, 2000, Tanaka *et al* 1999), the TCS has a very broad, flat hump spanning from a dozen or so to some tens of electronvolts. Results illustrating this effect for the series of perfluorocarbons are summarized in figure 2. Inspection of this figure leads one to expect that, as for other perfluorinated targets, the C_3F_6 TCS curve ranging from 30 to 70 eV is the upper part of a very broad maximum.

In order to identify which process in electron scattering by perfluorides may be responsible for the observed increase of the TCS between 30 and 70 eV, we have recently examined the contribution of two main constituents of TCS—those resulting from elastic and from ionization channels. On the basis of available (elastic, ionization and TCSs) experimental data for a number of molecules we found (Szmytkowski and Ptasińska-Denga 2001) that the 'anomalous' TCS increase for perfluorides may be related to the markedly increasing role of direct elastic processes in this energy region. The ratio of the elastic cross section to the TCS, $Q_{\mathrm{el}}/Q_{\mathrm{tot}}$, for perfluorides slowly decreases from about 0.75 at 30 eV to slightly above 0.6 at 70 eV, on average, while for their perhydrogenated counterparts the respective values are from about 0.7 down to nearly 0.45. Some contribution from numerous weak resonant processes in this energy regime is, however, also possible (Dehmer *et al* 1978, Gianturco *et al* 1995).

Another feature which distinguishes the TCS for perfluorides from that for other targets is the variation of TCS from target to target (i.e. with related target parameters). At intermediate energies, 50–400 eV, the TCS varies with the static electric polarizability, α, like $\sim\alpha^b$, where $b \geqslant 1$ for perfluorides and $b \simeq 0.5$–0.8 for some other targets (Szmytkowski 1989, Nishimura and Tawara 1991, Joshipura and Vinodkumar 1999). Using this relationship together with the present TCS data we estimated the electric polarizability of the C_3F_6 molecule: the α value of $(7.1 \pm 0.5) \times 10^{-30}$ m^3 is in reasonable agreement with that (6.03×10^{-30} m^3) calculated from empirical bond polarizabilities and used by Beran and Kevan (1969).

Above 70 eV, the energy dependence of the experimental electron scattering TCS for hexafluoropropene can be nicely approximated with the regression formula $Q \sim E^{-0.5}$. Such an energy dependence means that for these energies the TCS is proportional to the time spent by the incident electron in the vicinity of the target molecule.

Comparison of the theoretical (Jiang *et al* 2000) and the present experimental results (figure 1) shows that at all overlapped energies both theoretical calculations (in the AR and EGAR approximations) give TCSs which are systematically higher than experimental data. Of these two approximations the modified additivity rule approach (EGAR)—taking into account the geometrical screening of the inner atoms in molecules by the outermost ones—gives results which are in much better agreement with experiment. However, while in the energy range investigated the experiment shows two quite distinct regions of cross-section energy dependence, both calculated TCSs decrease monotonically when the impact energy increases. In consequence, at 30 eV a deviation of EGAR results from the experimental TCS amounts to about 18% while above 60 eV the EGAR calculations and the experiment lie well within experimental error limits. A similar relation of the Jiang *et al* calculations to experimental data is also seen for other molecular systems, namely hydrocarbons (Jiang *et al* 1997, 2000) and perfluorocarbons (Jiang *et al* 2000).

3.2. Elastic cross section

Using the model static + polarization potential we have calculated the integral elastic-scattering cross section at intermediate and high electron impact energies, 30–3000 eV. The calculated results at intermediate energies are shown in figure 3 along with the 'elastic' experimental

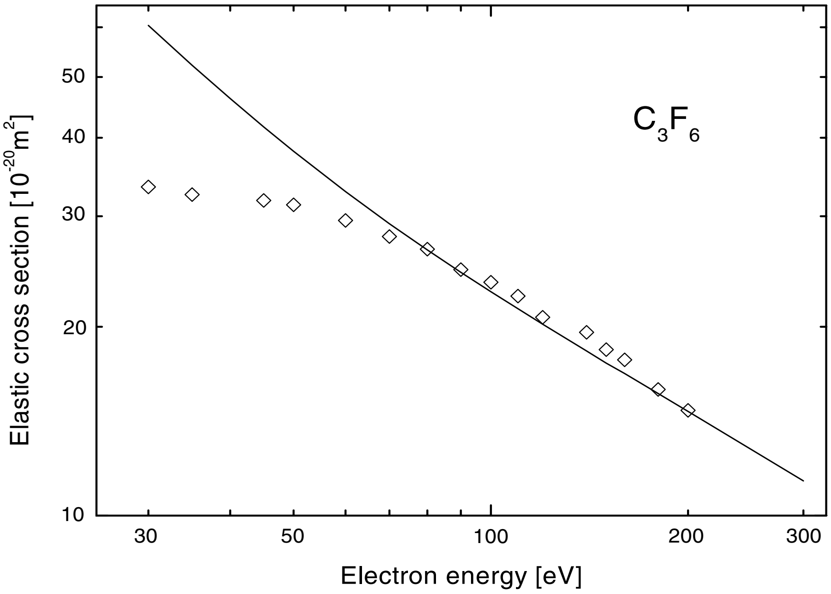

Figure 3. Electron elastic-scattering cross sections for the C_3F_6 molecule. (——) integral elastic, present calculations, IAM; (◇) experimental 'elastic', as a difference of total cross section (present) and ionization cross section (Bart *et al* 2001).

cross section estimated as the difference of the 'total' TCS (measured in the present work) and the total ionization cross section of Bart *et al* (2001) taken below 200 eV. General good agreement of the calculations with the estimated elastic results is observed for higher impact energies, above 70 eV. At lower energies, the applied approximation clearly overestimates the expectations based on experimental findings. Our calculated integral elastic cross sections showed a similar relationship to the experimental data for other polyatomic targets as well.

4. Conclusions

In this paper we have reported the results of our absolute TCS measurements for electron scattering from the C_3F_6 molecule for incident electron energies ranging from 30 up to 370 eV. Between 30 and 70 eV the TCS is nearly constant, and above 70 eV it decreases monotonically when energy increases. Considering the experimental TCSs for perfluorinated compounds obtained so far, we can conclude that at impact energies from a dozen or so to some tens of electronvolts the TCS for perfluorides has a very broad maximum; this increase in the TCS seems to be related to an increasing contribution of elastic scattering at intermediate energies. Such a behaviour of the TCS function for perfluorides is distinctly different from that observed for other targets.

We have also presented calculations of integral elastic scattering cross sections which at intermediate energies give data of reasonable reliability.

Acknowledgment

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

References

Bart M, Harland P W, Hudson J E and Vallance C 2001 *Phys. Chem. Chem. Phys.* **3** 800–6

Bederson B and Kieffer L J 1971 *Rev. Mod. Phys.* **43** 601–40

Beran J A and Kevan L 1969 *J. Phys. Chem.* **73** 3866–76

Bibby M M and Carter G 1966 *Trans. Faraday Soc.* **62** 2637–42

Chelobov F N, Dubov S S, Tikhomirov M V and Dobrovitskii M I 1963 *Dokl. Akad. Nauk* **151** 631–3

Christophorou L G and Olthoff J K 2001 *Adv. At. Mol. Opt. Phys.* **44** 59–98

Dehmer J L, Siegel J and Dill D 1978 *J. Chem. Phys.* **69** 5205–6

Floeder K, Fromme D, Raith W, Schwab A and Sinapius G 1985 *J. Phys. B: At. Mol. Phys.* **18** 3347–59

García G and Blanco F 2000 *Phys. Rev.* A **62** 044702-1–3

García G and Manero F 1997 *Chem. Phys. Lett.* **280** 419–22

Gianturco F A, Lucchese R R and Sanna N 1995 *J. Chem. Phys.* **100** 6464–71

Harland P W and Thynne J C J 1972 *Int. J. Mass Spectrom. Ion Phys.* **9** 253–66

Hunter S R, Christophorou L G, McCorkle D L, Sauers I, Ellis H W and James D R 1983 *J. Phys. D: Appl. Phys.* **16** 573–80

Jarvis G K, Peverall R and Mayhew C A 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** L713–8

Jiang Y, Sun J and Wan L 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 5025–32

Jiang Y, Sun J and Wan L 2000 *Phys. Rev.* A **62** 062712-1–6

Joshipura K N and Vinodkumar M 1999 *Eur. Phys. J.* D **5** 229–35

Kasperski G, Możejko P and Szmytkowski Cz 1997 *Z. Phys.* D **42** 187–91

Knudsen M 1910 *Ann. Phys., Lpz.* **31** 205–29

Lifshitz C and Grajower R 1972–3 *Int. J. Mass Spectrom. Ion Phys.* **10** 25–37

Massey H S W, Burhop E H S and Gilbody H B 1969 *Electronic and Ionic Impact Phenomena* vol 2 (Oxford: Clarendon) p 666

Nakamura M, Hori M, Gato T, Ito M and Ishii N 2001 *J. Vac. Sci. Technol.* A **19** 2134–41

Nishimura H and Tawara H 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** L363–6

Padial N T and Norcross D W 1984 *Phys. Rev.* A **29** 1742–8

Pedrew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048–79

Raj D 1991 *Phys. Lett.* A **160** 571–4

Salvat F, Martinez J D, Mayol R and Paradella J 1987 *Phys. Rev.* A **36** 467–74

Szmytkowski Cz 1989 *Z. Phys.* D **13** 69–73

Szmytkowski Cz, Krzysztofowicz A M, Janicki P and Rosenthal L 1992 *Chem. Phys. Lett.* **199** 191–7

Szmytkowski Cz and Możejko P 2001 *Vacuum* **63** 549–54

Szmytkowski Cz, Możejko P and Kasperski G 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 4363–72

Szmytkowski Cz, Możejko P and Kasperski G 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 3917–28

Szmytkowski Cz, Możejko P, Kasperski G and Ptasińska-Denga E 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** 15–22

Szmytkowski Cz and Ptasińska-Denga E 2001 *Vacuum* **63** 545–8

Tanaka H, Tachibana Y, Kitajima M, Sueoka O, Takaki H, Hamada A and Kimura M 1999 *Phys. Rev.* A **59** 2006–15

Zecca A, Karwasz G P and Brusa R S 1992 *Phys. Rev.* A **45** 2777–83

Zhang X, Sun J and Liu Y 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 1893–7