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Relationship between electron-scattering grand total and ionization total cross sections

Stanisław Kwitniewski*, Elżbieta Ptasńska-Denga, Czesław Szmytkowski

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

Abstract

Regression formula which relates *grand* total cross section and ionization total cross section for electron scattering from simple hydrocarbons and from perfluorinated molecules has been proposed. This formula was then used to evaluate the ionization total cross sections for WF_6 and for structured isomers of C_3H_4 and C_4H_6 , at intermediate electron-impact energies. For WF_6 the estimated ionization cross section is compared with available experimental and theoretical data. In addition, for C_3H_4 and C_4H_6 ionization total cross sections were calculated with the binary-encounter Bethe (BEB) model to compare with the values predicted from the regression formula. Grand total cross section for electron scattering from UF_6 molecules was also estimated over energy range from 20 to 400 eV.

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1. Introduction

The reliable electron-atom/molecule interaction cross sections, electron transport and rate coefficients are urgently needed to elucidate the details of the observed phenomena in the low-temperature plasma and as input data for accurate modelling processes in gas phase systems in which electrons are involved. To date, recommended values of quantities related to electron scattering are available for many atomic and simple molecular species (for more references see [Trajmar and McConkey, 1994](#); [Crompton, 1994](#); [Christophorou and Olthoff, 2000](#); [Shirai et al., 2002](#)), though the reliability some of those results is somewhat uncertain and a number of available data leave much to be desired. Moreover, electron scattering results for more complex and/or unstable compounds are rather scanty and this fact is primarily attributable to insuperable experimental

or computational problems arising at determining of the scattering properties for such targets. That is why the numerous efforts are being undertaken to find easy-to-apply simple formula, which would reproduce with reasonable precision the magnitude and energy dependence of the scattering quantities for different targets and, in addition, would provide capability to predict these quantities for targets for which at the time such data are not available.

The regression formulae found so far, reproduce the experimental findings quite satisfactory, though only for selected groups of targets and usually within a limited range of electron impact energy. They connect selected electron-collision cross sections (mainly total cross section and/or ionization cross section) with various target physical properties, e.g. the number of target electrons ([Floeder et al., 1985](#); [García and Manero, 1997](#)), the target electric polarizability ([Szmytkowski, 1989](#); [Nishimura and Tawara, 1991](#); [Christophorou and Illenberger, 1993](#); [García and Manero, 1997](#)), the number of C atoms in hydrocarbons ([Schram et al.,](#)

*Corresponding author.

E-mail address: stanley@mif.pg.gda.pl (S. Kwitniewski).

1966) or with the geometric cross section (Christophorou et al., 1976), etc. Lacking are the relationships which interconnect basic collision cross sections for different particular processes.

The aim of this work is to find a correlation between two fundamental electron scattering cross sections: *grand* total cross section, Q_{tot} , and ionization total cross section, Q_{ion} , for simple hydrocarbons and for several perfluorinated molecules, over intermediate energy range. Such regression formula would be useful for easy estimation of one of the necessary cross sections if values of the other one are known from the experiment or theory. In addition, analytical expression can be useful in approximate computational procedures used for modelling the plasma processes relevant to some applications.

2. Procedure and results

To obtain the correlation between electron-collision *grand* total cross sections, Q_{tot} and ionization total cross sections, Q_{ion} , we examined the ratio $Q_{\text{ion}}/Q_{\text{tot}}$ for selected groups of target molecules: simple hydrocarbons (CH_4 , C_2H_6 , C_3H_6 , C_3H_8 , C_6H_6) and some of their perfluorinated counterparts (CF_4 , C_2F_6 , C_3F_6 , C_4F_6). The $Q_{\text{ion}}/Q_{\text{tot}}$ values at different electron impact energy, E , were calculated with the use of experimental data from the same laboratories, if available: the absolute total cross section data, obtained in linear transmission experiments carried out in our laboratory (Zecca et al., 1991; Szymkowski et al., 1992; Szymkowski and Krzysztofowicz, 1995; Możejko et al., 1996; Kasperski et al., 1997; Szymkowski et al., 2000, 2002a,b;

Szymkowski and Kwitniewski, 2002a–c), while ionization total cross sections come from two laboratories (Nishimura and Tawara, 1994; Bart et al., 2001). At those energies where cross section values, necessary for calculation of the $Q_{\text{ion}}/Q_{\text{tot}}$, were not available directly they were estimated through interpolation.

Fig. 1 presents the energy dependence of the $Q_{\text{ion}}/Q_{\text{tot}}$ ratio for simple hydrocarbons, while Fig. 2 shows this ratio for some perfluorinated hydrocarbons. From these figures it is visible that for all molecules and over the energies examined the $Q_{\text{ion}}/Q_{\text{tot}}$ curves are very similar with respect to the shape. It is also evident that the contribution of the ionization to the total scattering increases rapidly for both groups of molecules when collision energy increases to about 100 eV. Above that energy the increase of the $Q_{\text{ion}}/Q_{\text{tot}}$ is much more slower.

The energy dependence of the $Q_{\text{ion}}/Q_{\text{tot}}$ for hydrocarbons and perfluorocarbons (Figs. 1 and 2) was nicely fitted by empirical formula with three parameters:

$$\frac{Q_{\text{ion}}}{Q_{\text{tot}}} = A \left(1 - \exp\left(\frac{B-E}{C}\right) \right). \quad (1)$$

Parameters A and B have very simple physical meanings: the parameter A shows the contribution of all ionization processes to overall scattering at very high impact energies, while B can be related to the electron binding energy. The values of these parameters obtained by fitting are listed in Table 1 for all investigated molecules. It is worth to note, that the parameter A for all examined hydrocarbons is (within 10%) close to $\frac{1}{2}$, while for perfluorocarbons (Table 1) is nearly $\frac{1}{3}$. Lower value of A for perfluorocarbons reflects previous remarks (cf. Szymkowski and Ptasńska-Denga, 2001) that the

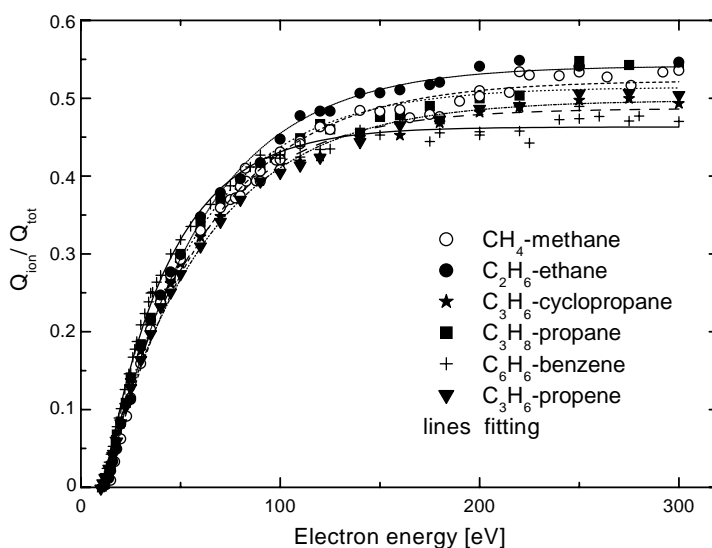


Fig. 1. Energy dependence of the $Q_{\text{ion}}/Q_{\text{tot}}$ ratio for hydrocarbons. Points represent values evaluated from the experimental data (referenced in the text). Lines show fitting to experimental points by the empirical formula, Eq. (1).

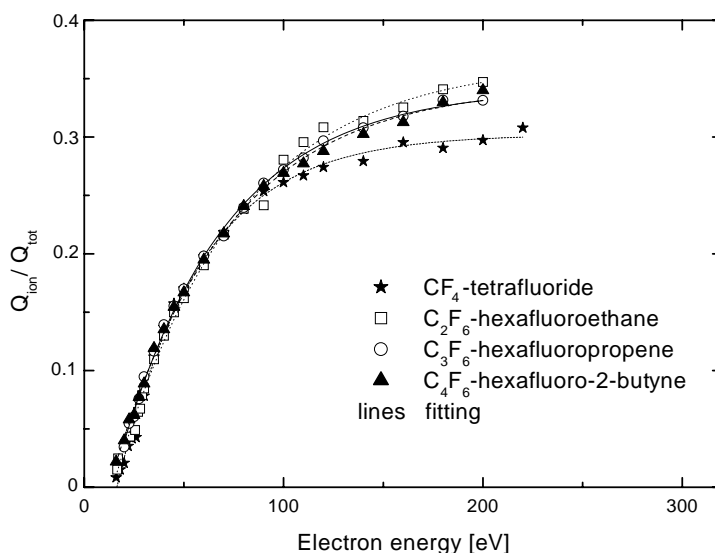


Fig. 2. Energy dependence of the $Q_{\text{ion}}/Q_{\text{tot}}$ ratio for perfluorocarbons. Points represent values evaluated from the experimental data (referenced in the text). Lines show fitting by the empirical formula, Eq. (1).

Table 1
Coefficients of the regression formula, Eq. (1), for examined molecules

	A	B (eV)	C (eV)
Methane (CH ₄)	0.52	12.5	50.8
Ethane (C ₂ H ₆)	0.54	12.5	47.7
Propene (C ₃ H ₆)	0.50	10.5	51.3
Cyclopropane (C ₃ H ₆)	0.49	10.8	46.0
Propane (C ₃ H ₈)	0.51	11.4	46.7
Benzene (C ₆ H ₆)	0.46	11.4	33.2
Tetrafluoromethane (CF ₄)	0.30	16.6	41.3
Hexafluoroethane (C ₂ F ₆)	0.36	14.2	61.4
Perfluoropropene (C ₃ F ₆)	0.34	13.5	53.8
Hexafluoro-2-butyne (C ₄ F ₆)	0.34	12.4	57.1

contribution of ionization to the scattering for perfluorides is distinctly lower than that for other molecules. Values of parameter B obtained from the fit agree fairly well (within 10%) with ionization potentials of respective molecule (Lias, 1995).

Having in hand the regression formula, Eq. (1), and the appropriate cross sections, e.g. absolute grand total cross section, we are able to evaluate values of total cross sections for electron-induced ionization of molecules. The inverse procedure is obviously admissible. For calculations with the use of Eq. (1), the averages of A and C values listed in Table 1 for hydrocarbons or perfluorocarbons are used, while ionization potential of respective molecule is used for B (Lias, 1995). Where available, we compare our estimated cross sections with

experimental data and with the results of cross-section calculations.

Before using the regression formula, Eq. (1), for evaluation of cross sections for targets for which such data are not accessible, we applied it to calculation of the electron-impact ionization total cross sections for WF₆ molecule for which some results were already reported. Grand total cross sections necessary for the estimation were taken from our recent experiment (Szmytkowski et al., 2000). Estimated in accordance with Eq. (1) cross section for WF₆, is presented in Fig. 3 together with available experimental determination (Basner et al., 1993)¹ and theoretical (Deutsch et al., 1994;² Probst et al., 2001; Kim and Irikura, 2000) results. As can be seen in Fig. 3, our estimations are in the best agreement with the calculations reported by Kim and Irikura (2000) obtained with the binary-encounter-Bethe (BEB) approach, while differ substantially from experimental data of Basner et al. (1993) and calculations obtained with the modified additive model (cf. Deutsch et al., 1994). The maximum of the cross section curve obtained by Probst et al. (2001) with Deutsch-Märk (DM) approximation, tends to be shifted to lower energies. A closer examination reveals that the deviation of parameter B within ± 1 eV from the ionization potential shifts the cross section curve in energy scale and this influences the cross section more distinctly near threshold only. The variation of parameter C from minimal to maximal value (Table 1) has

¹ Their experimental ionization total cross section for WF₆ has been read from Fig. 6 in the paper of Probst et al. (2001).

² For WF₆ results see Fig. 6 in Probst et al. (2001).

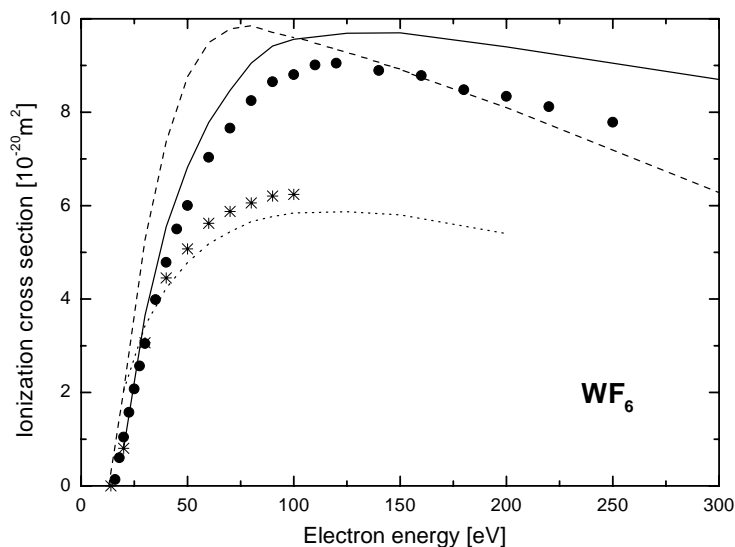


Fig. 3. Ionization total cross section for electron scattering from WF_6 : crosses, Basner et al. (1993), experimental; full line, Kim and Irikura (2000), BEB calculations; broken line, Probst et al. (2001), DM model; dotted line, Deutsch et al. (1994), modified additive rule; filled circles, present estimation.

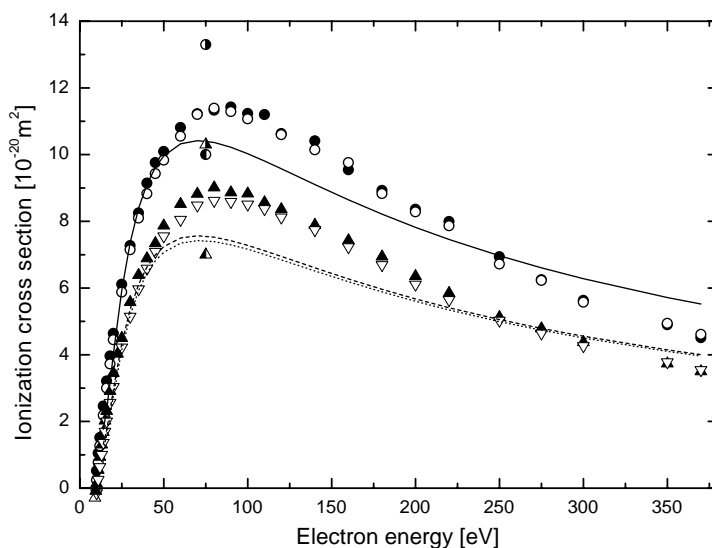


Fig. 4. Ionization total cross section for electron scattering from isomers of C_3H_4 and C_4H_6 molecules. Estimated in accordance with Eq. (1), present: filled triangles, 1,2-propadiene; open down-triangles, propyne; filled circles, 1,3-butadiene; open circles, 2-butyne. Maximum values estimated according to Bart et al. (2001): 1,2-propadiene: right-filled triangle, linear relationship; left-filled triangle, additivity bond contributions; 1,3-butadiene: right-filled circle, linear relationship; left-filled circle, additivity bond contributions. Calculated with BEB model, present: dashed line, 1,2-propadiene; dotted line, propyne; full line, 1,3-butadiene.

more significant influence (up to about 10%) below 100–150 eV.

Fig. 4 shows our predicted electron-impact ionization total cross sections, Q_{ion} , for two isomers of C_3H_4 (1,2-propadiene and propyne) and of C_4H_6 (1,3-butadiene

and 2-butyne), respectively. The overall accuracy in Q_{ion} determination is estimated to be $\pm 20\%$, the uncertainty comparable with typical error in Q_{ion} measurements. The shape of the ionization efficiency curves obtained with the use of Eq. (1) and the location of the maximum

(near 75 eV) closely resemble typical energy dependence of ionization total cross section for molecules not containing fluorine atoms. As there are no literature Q_{ion} data for C_3H_4 and C_4H_6 molecules, to verify the reliability of our estimated values we calculated the maximum ionization total cross sections, Q_{max} , based both on the linear relationship (Bart et al., 2001) between Q_{max} and the quantity $(\alpha/IP)^{0.5}$, in which α is the molecular polarizability and IP is the ionization potential of the target studied, as well as on the additivity of the bond contributions (Bart et al., 2001). For 1,3-butadiene the maximum values of ionization total cross section calculated with the aforementioned approaches are 13.3 and $10.0 \times 10^{-20} \text{ m}^2$, respectively, compared with our maximum value of $11.4 \times 10^{-20} \text{ m}^2$ (see Fig. 4), while for 1,2-propadiene respective values are 10.2 , 7.0 , and $9.0 \times 10^{-20} \text{ m}^2$. A close agreement of our estimations with the values calculated independently seems to support the conviction on usefulness of our empirical relationship. Additionally we calculated ionization total cross sections for C_3H_4 and C_4H_6 molecules using BEB model (molecular orbital constants were taken from Kim and Irikura, 2000). The magnitude of theoretical BEB cross sections is in the vicinity of the maximum lower than results obtained with the use of our regression formula and the maximum is located at lower energy. It is noteworthy that isomeric effect in ionization cross section is rather weak.

As another example of the applicability of Eq. (1) we present (Fig. 5) the grand total cross section, Q_{tot} , for electron collisions with UF_6 molecules for impact energies ranging from 16 to 400 eV. The accuracy of the Q_{tot} , determined this way, is estimated to be about

50%, mainly due to uncertainty of the experimental ionization total cross section data of Compton (1977), used for calculations. To our best knowledge, no experimental electron-impact Q_{tot} or theoretical calculations for UF_6 have been available for comparison so far. Fig. 5 shows that the general shape of estimated Q_{tot} for UF_6 is in the considered energy range quite similar to the experimental Q_{tot} for WF_6 . Both curves indicate very broad intermediate-energy enhancement, the feature characteristic for perfluorinated targets (Szmytkowski and Ptasinska-Denga, 2001), although, the location of the maximum center is for UF_6 curve shifted to higher energies. The magnitude of UF_6 total cross section is nearly twice higher than that of WF_6 (Szmytkowski et al., 2000), as one would expect, due to considerably larger central atom of UF_6 molecule.

3. Summary

We have examined experimental data for *grand* total cross section, Q_{tot} , and ionization total cross section, Q_{ion} , for electron scattering from small hydrocarbons and perfluorocarbons. Simple regression formula for the energy dependence of $Q_{\text{ion}}/Q_{\text{tot}}$ ratio has been proposed. The formula has been used to estimate electron-impact ionization total cross section for WF_6 , and structured isomers of C_3H_4 , and C_4H_6 , as well as for estimation of grand total cross section for UF_6 molecule. Our results for C_3H_4 , C_4H_6 , and UF_6 are, to our best knowledge, the first predictions for these targets. In addition, BEB model was applied for calculations of electron-impact ionization total cross sections of C_3H_4 and C_4H_6 .

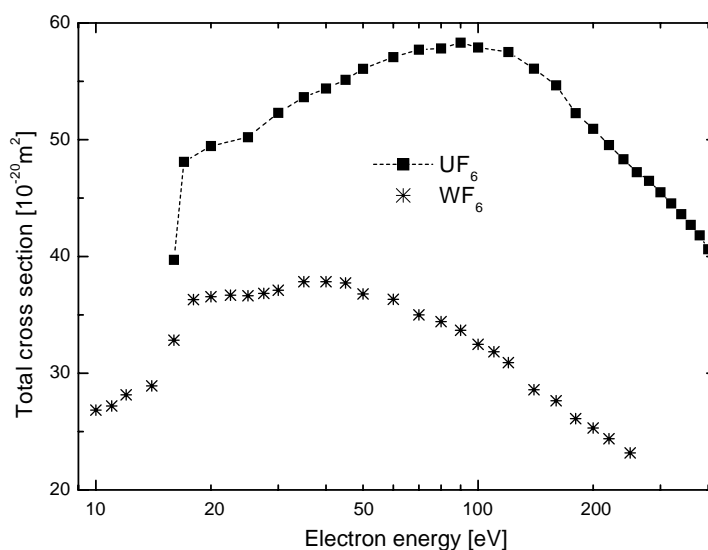


Fig. 5. Grand total cross section for electron scattering from UF_6 molecule estimated in accordance with Eq. (1). Experimental total cross section for WF_6 molecule (Szmytkowski et al., 2000) is shown for the comparison.

Acknowledgements

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