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Fluorination effects in electron-scattering processes—comparative study

Czesław Szmytkowski*, Elżbieta Ptasńska-Denga

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

Abstract

Systematic studies of electron interaction with perfluorinated targets carried out recently in our laboratory revealed a distinct increase of the total cross section, Q_{tot} , over the impact energy range from a dozen or so to several tens of electronvolts. A likely reason for this striking feature is a significant contribution of elastic processes in this energy range. The ratio of the total ionization electron-scattering cross section to the total cross section can be expressed with a simple regression formula. That formula was used to estimate the GeH_4 ionization cross section. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Electron-scattering; Cross section; Fluorination effect

1. Introduction

Compounds containing fluorine atoms are widely used in gas dielectric mixtures or as etching and doping agents in plasma enhanced manufacturing of submicron-scale electronic devices. For the optimal design of gaseous insulators, plasma reactors, and (last but not least) recognition of the environmental impact of perfluorides there must be full identification and understanding of fundamental processes in these media; this requires access to comprehensive and reliable sets of quantitative electron-impact cross section data. Although several experimental investigations of electron

interactions with perfluorides have appeared in the literature, the available results are still fragmentary.

To give reliable absolute electron-scattering data we have recently undertaken systematic measurements of electron-scattering total cross section, Q_{tot} , for polyatomic molecules, among them for a group of perfluorinated targets, over a wide energy range. Series of experiments have been carried out with an electrostatic electron spectrometer [1] working in a linear transmission mode, for the impact energies from about 0.5 to 250 eV.

2. Results and discussion

The measurements for perfluorinated molecules [2–6] are summarized in Fig. 1 while the results for some perhydrogenated targets [7–11] are shown in Fig. 2 for comparison. The feature which evidently

* Corresponding author.

E-mail address: czsz@mif.pg.gda.pl (Cz. Szmytkowski).

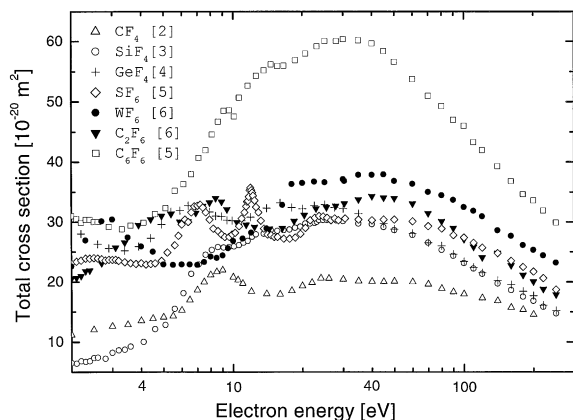


Fig. 1. Absolute experimental electron-scattering total cross sections for perfluorinated molecules.

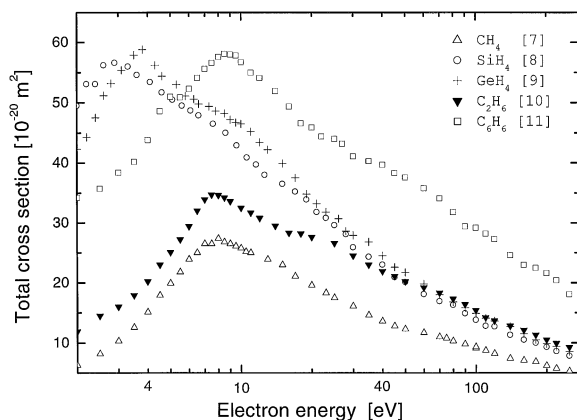


Fig. 2. Absolute experimental electron-scattering total cross sections for perhydrogenated molecules.

distinguishes total cross sections measured for perfluorides from those for other targets is the very broad maximum observed in the perfluorides total cross sections, spanned between the first ionization threshold and above several times the ionization potential. Instead, a common and well-known feature of the electron-scattering total cross section above the ionization threshold for non-perfluorinated targets is the monotonic decrease of the cross section with increasing energy (e.g. Fig. 2). In order to recognize the origin of the above mentioned difference, we have examined the total cross section share between elastic and ionization cross

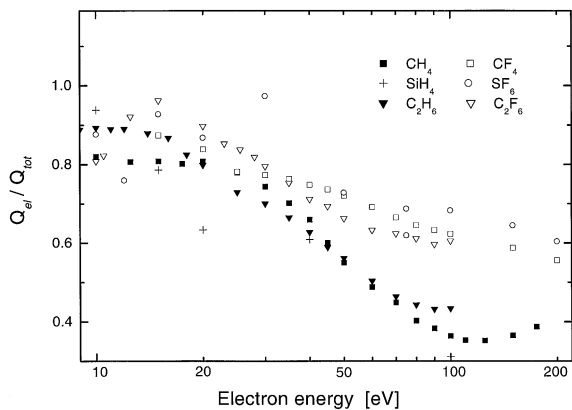


Fig. 3. Ratio, Q_{el}/Q_{tot} , of the experimental elastic to the total electron-scattering cross section for perfluorinated and perhydrogenated molecules. For the source of Q_{el} and Q_{tot} data, the reader is referred to the text.

section channels, the ones which play the major role in the electron-scattering above the first ionization threshold. To examine how the partitioning scheme changes when fluorine atoms in a molecule are substituted with hydrogen atoms, a comparison is made between groups of perfluorides and perhydrides of similar geometries. To compare the contribution of the elastic cross section, Q_{el} , and the ionization cross section, Q_{ion} , to the *grand* total cross section, Q_{tot} , we derived the ratios Q_{el}/Q_{tot} and Q_{ion}/Q_{tot} as a function of impact energy. For the sake of comparison, the data from the same experiment have been chosen, if available: total cross sections as measured in our laboratory, in Gdańsk [2–11], elastic cross sections [e.g. 12–17] mainly from the Sophia University group, while total ionization cross sections come from different sources [e.g. 18–21]. At the energies in question where the cross section data necessary for comparison were not available they were estimated from interpolation.

Fig. 3 shows the Q_{el}/Q_{tot} ratio for some hydrogenated and perfluorinated molecules between 20 and 100 eV. It is evident from this figure that over this energy range the contribution of elastic processes for perfluorinated molecules is markedly higher than for perhydrides. At about 25 eV the contribution of elastic cross section is somewhat

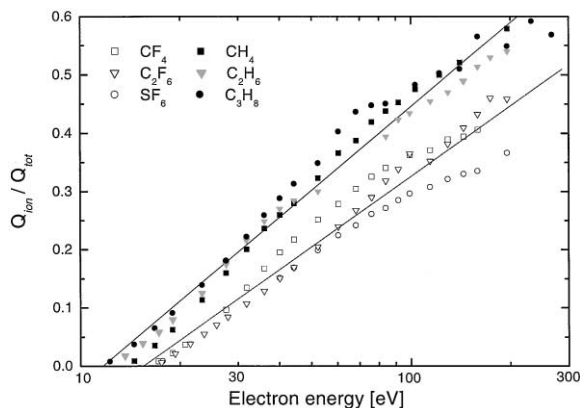


Fig. 4. Ratio, Q_{ion}/Q_{tot} , of the experimental total ionization to the total electron-scattering cross section for perfluorinated and perhydrogenated molecules. For the source of Q_{ion} and Q_{tot} data the reader is referred to the text. Lines represent a linear fit to the respective data set.

higher than 80% for perfluorides while for perhydrides it is nearly 10% lower. With the impact energy increase the role of elastic processes on electron-scattering decreases, down to 65% for perfluorides and to 40% for perhydrides, at 90 eV. At higher impact energies, beyond 100 eV, the inference about the role of elastic processes in the electron-scattering is problematic due to scarcity of experimental results. From some data it results, however, that the contribution of elastic scattering at intermediate energies changes only slightly.

Fig. 4 shows the ratio, Q_{ion}/Q_{tot} , of the total ionization cross section and the total cross section for the selected hydrogenated and perfluorinated molecules. Over the energy range between 20 and 300 eV the contribution of the ionization clearly depends on the outermost (H or F) atoms; it is lower for perfluorinated targets. The ratio Q_{ion}/Q_{tot} almost triples between 25 and 100 eV for both groups of molecules: it rises from 15% up to about 40% for perhydrides while increases from 10% to 30% for perfluorides. This rise is accompanied by a fall of the elastic contribution, as mentioned above. Below 60 eV the total ionization cross section for perfluorides is lower than that for the respective perhydrides. This tendency undergoes a pronounced inversion at higher energies, especially close to the ionization cross section max-

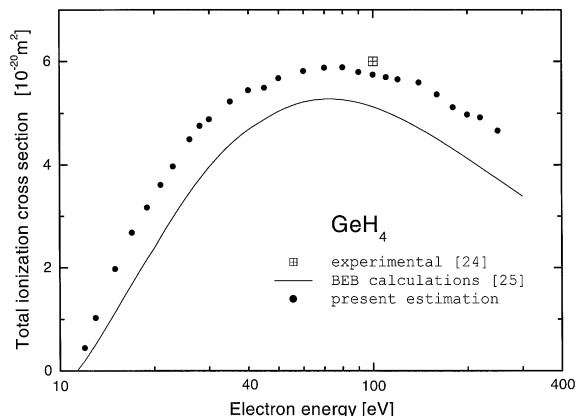


Fig. 5. Total electron impact ionization cross section for GeH_4 molecule.

imum, which for perfluorides is located at distinctly higher energy (near 140 eV) than for other targets (around 75 eV). It is worth noting that some other fluorination effects have already been mentioned in the literature [22,23].

The observed change of the Q_{ion}/Q_{tot} ratio with the electron impact energy E between 30 and 300 eV can be described with a regression formula with only two parameters for the fit:

$$\frac{Q_{ion}}{Q_{tot}} = A \ln \frac{A}{B}$$

The best fit values of A , for perfluorides and for perhydrides do not differ excessively and are 0.17 and 0.18, respectively. The parameter B can be related to the electron binding energy. The scatter of the experimental points around the regression lines is partly related to considerably large experimental uncertainties; due to these errors, in some cases, the sum of experimental elastic and ionization cross sections exceeds the respective measured total cross section. The above relationship may be appropriate for estimation of the total ionization cross section due to the electron impact if the total cross section is available, with the confidence interval within the combined experimental error, or if the ionization cross section is accessible, the total cross section can be calculated. Applying this empirical formula to the GeH_4 molecule the

total ionization cross section was calculated (Fig. 5). The ionization cross section evaluated in this way is, at 100 eV, in very good agreement with the only experimental value [24]. Both the energy dependence and the magnitude of the estimated $Q_{ion}(E)$ are reasonably close, over the entire energy range of interest, to the recent BEB model calculations [25]. Results similar to ours have been recently obtained with DM formalism by Märk and coworkers [26].

3. Conclusions

The analysis of electron-scattering data for per-fluorinated and perhydrogenated targets indicates the predominant role of elastic processes for per-fluorides at intermediate energies. Ionization cross section and total cross section can be related through a simple formula. That formula enabled us to determine ionization cross section for the GeH_4 molecule.

Acknowledgements

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