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# Experimental absolute total cross sections for low-energy electron collisions with tetrahedral compounds of germanium: GeF<sub>4</sub>

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Received 5 May 1998

**Abstract.** Absolute total cross section (TCS) of the electron collision with GeF<sub>4</sub> molecules has been measured in a linear transmission experiment for impact energies from 0.5 to 250 eV. The TCS function is dominated by a steep rise towards low energies below 3 eV. At energies above the minimum at 3 eV the TCS shows another enhancement spanned up to about 70 eV on which some resonant-like features are visible: the maximum centred near 6.5 eV and two weak peaks at 16 and 25 eV, respectively.

A comparison with the recent measurements taken in the same laboratory for GeH<sub>4</sub> and GeCl<sub>4</sub> and for other targets of the same symmetry is made to search for similarities and/or differences between electron scattering TCSs for tetrahedral molecules. The data demonstrate that the general shape of the low-energy TCS for tetrahedral molecules depends on external rather than on central atoms.

## 1. Introduction

Reliable, accurate experimental data concerning electron scattering from atoms, molecules or their clusters are of great importance in many fields of pure and applied science, ranging from space sciences, radiation physics and chemistry to gaseous electronics, energy conversion and submicron-scale electronics (see Smith and Adams 1989, Summers 1994, Capitelli *et al* 1994, Christophorou *et al* 1995). Among a variety of measurable quantities describing the scattering processes, the grand total cross section (TCS) is the most reliable because it can be determined without any normalization procedures. Therefore, it can serve as a standard value for normalization of data for particular scattering processes and as one of a range of experimental quantitative tests of the reliability of theoretical models and computational procedures. In those cases where direct measurements of inelastic processes are inaccessible, reasonable estimates of individual cross sections may be based on experimental TCS and elastic measurements or calculations.

So far, the attention has been primarily focused on the manner in which the TCSs of individual targets vary with the energy of electrons. On the whole, comparatively little effort has concerned the variation of TCS from target to target. Systematic studies of TCSs for families of targets (see Brüche 1929, Floeder *et al* 1985, Szmytkowski 1989, Nishimura and Tawara 1991, Jain and Baluja 1992, Szmytkowski and Krzysztofowicz 1995, Garcia and Manero 1997) can, apart from yielding data necessary in various fields, provide some stimulating insight into the role played by physical properties of the target

in the scattering process and, consequently, serve as a guide for theoretical investigations. Finally, establishing TCS correlations with target parameters (e.g. polarizability, number of target electrons, dipole moment, target geometry) and derivation of relevant semi-empirical formulae can help in estimating cross sections for those targets for which data are still lacking.

Recently a series of measurements of absolute total electron scattering cross sections for selected sequences of target species (e.g. isoelectronic and/or of similar molecular structure) have been carried out in our laboratory. The experiments were intended to discover how a change in the target structure influences the magnitude and the energy dependence of the measured cross section. Special attention was paid to resonant-like features observed at low scattering energies.

The main objective of the measurements reported in this work was to provide the absolute grand TCS data for electron–germanium tetrafluoride molecule collisions at electron impact energies ranging from low to intermediate (0.5–250 eV). The germanium tetrafluoride molecule, among other perfluorinated compounds, becomes of interest in the manufacture of microcircuits (Flamm 1987) and photovoltaic cells (Kalb and Moskowitz 1989). Due to its near-spherical geometry, GeF<sub>4</sub> might be a useful system on which the quality of the computational models employed to describe the scattering process can be tested. Reports available in the literature on the works which concern the electron–GeF<sub>4</sub> scattering processes are very scarce and are limited to experiments only. Caunt *et al* (1951) determined the Ge–F bond length from measurements of electron diffraction on germanium tetrafluoride gas. Mason and Tuckett (1987) studied the emission spectrum of the molecular ion, GeF<sub>4</sub><sup>+</sup>, resulting from electron impact ionization of GeF<sub>4</sub> molecule. Recently, energy loss spectra of electrons scattered from GeF<sub>4</sub> at intermediate impact energy, 200 eV, have been reported by Kuroki *et al* (1994). We are not aware of any previous experimental e<sup>−</sup>–GeF<sub>4</sub> TCS data and any theoretical calculations related to this target.

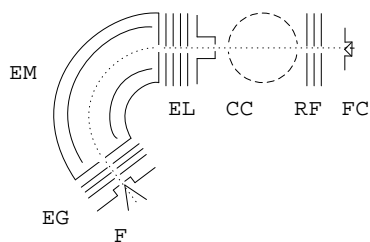
This experiment completes our programme of TCS measurements for electron scattering on tetrahedral compounds of germanium GeY<sub>4</sub> (Y = H, F, Cl). Present results, together with our previous data for homologous series of targets, allow us to undertake an attempt to single out regularities in the TCSs which are common to a class of tetrahedral molecules.

## 2. Experimental

The absolute TCSs for electron scattering from GeF<sub>4</sub> molecules were determined by the linear transmission method. The method is based on measurements of the attenuation of the intensity of the projectile-particle beam transmitted through the volume filled with the target particles.

The electron beam was formed by an electron-optical system (figure 1) composed of a number of electrostatic elements: an electron gun (EG) with a thermionic electron source (F), a 127° cylindrical monochromator (EM) and a system of electron lenses (EL). Electrons of desired energy  $E$  ( $\Delta E = 70$  meV, FWHM) were directed into an attenuation cell (CC) filled with the gas-target of interest. Those electrons which emerged from the scattering volume through the exit orifice were discriminated energetically with a retarding field (RF) element. The transmitted electrons were finally collected in a Faraday cup detector (FC). The magnetic field in the region of the electron optics was reduced below 0.1  $\mu$ T with the system of Helmholtz coils.

In the ideal transmission experiment the TCS  $Q(E)$  can be derived at each electron impact energy by measuring the transmitted electron intensity both with,  $I_g(E)$ , and without,  $I_0(E)$ , a target sample in the scattering chamber and by applying the Bouguer–Lambert–de



**Figure 1.** Schematic diagram of the apparatus set-up used in this experiment: F, filament; EG, electron gun; EM, cylindrical 127° monochromator; EL, system of electrostatic electron lenses; CC, collision cell; RF, retarding field analyser; FC, Faraday cup.

### Beer attenuation formula

$$I_g(E) = I_0(E) \exp \left[ - Q(E) \int_a^b dl n(l) \right], \quad (1)$$

where  $n(l)$  is a distribution of target number density along the whole electron trajectory over which the scattering events take place. Because of inevitable effusion of the target particles through the entrance and exit orifices of the scattering cell, the limits of the volume where scattering events are possible ( $n \neq 0$ ) are not precisely defined and determination of the integral in equation (1) is one of critical points in every transmission experiment. We have found, following the Nelson and Colgate (1973) calculations, that for the geometry of the reaction volume applied in the present experiment the integral can be (within 0.5% accuracy) approximated with the product  $nL$ , where the effective absorption length  $L$  is equal to the geometrical distance ( $= 30.5$  mm) between the entrance and exit apertures of the scattering cell, while an effective number density of the target in the scattering cell,  $n$ , can be derived from the gas-target pressure  $p$  in the cell and its temperature  $T$ . The absolute value of pressure was measured with a capacitance gauge calibrated by the manufacturer (MKS) before the present experiment. To prevent multiple-scattering events the pressure of the target was maintained below 0.1 Pa at low impact energies and did not exceed 0.2 Pa at the highest energies applied. Since the operating temperature of the manometer head  $T_m$  ( $= 322$  K) differed by a few degrees from the temperature  $T_{sc}$  of the scattering chamber, the gas density,  $n$ , was determined from the ideal gas formula corrected for the thermal transpiration effect (Knudsen 1910)

$$n = \frac{p_m}{k\sqrt{T_m T_{sc}}},$$

where  $k$  is the Boltzmann constant and  $p_m$  is the pressure reading. No significant difference was noted when more complicated semiempirical formulae (e.g. Poulter *et al* 1983) were used. To maintain stability of the electron beam entering the reaction volume during measurements both with and without target flow into the scattering cell, the pressure in the region of the filament and electron optics was kept constant when changing between the two modes of operation.

The experimental energy scale was defined by the voltage applied to a lens element and the energy calibration was carried out by reference to the resonant oscillatory structure observed around 2.3 eV when, together with the investigated compound, some amount of N<sub>2</sub> was admitted to the reaction chamber. This procedure gives us the ability to establish the absolute scattering energy with an accuracy of about  $\pm 50$  meV. We have noticed, however, that the energy scale may shift in the course of the experiment, most probably

due to an influence of the gas-target on the electron optics elements. As a result, the overall uncertainty of the impact energy in the present experiment was estimated to be  $\pm 80$  meV.

Another inherent effect arising in the transmission technique, which tends to lower the measured cross section, is the incomplete discrimination by the detector system of the electrons which are scattered through small angles in the forward direction. The uncertainty in the TCS, related to this effect, increases with impact energy. The application of a retarding electrostatic field behind the sample chamber discriminates only against electrons which are scattered inelastically in the forward direction. Evaluation of the extent to which the forward elastically scattered electrons could affect measurements needs (i) knowledge of the angular distribution of electrons scattered at angles accepted by the detector system or (ii) extrapolation of results taken at higher angles. Unfortunately, for GeF<sub>4</sub> such data are not available yet. Our rough estimation based on the results for CF<sub>4</sub> (Boesten *et al* 1992) shows that lowering of the TCS due to forward scattering should not exceed 2% at 100 eV.

Handling the gas target, energy setting and processing ingoing data were controlled with a PC.

At each energy, individual cross section measurements were carried out over a wide range of electron optics and gas pressure conditions. The results proved to be independent (within the limits of statistical uncertainties) of the pressure of the target and the intensity of the electron beam. The final value of the TCS at each particular impact energy is an average of a large number of data obtained in independent series (5–20) of individual runs ( $\sim 10$  in a series). Statistical uncertainties (one standard deviation of weighted mean values) do not exceed 1% over the entire energy range studied, 0.5–250 eV. In the very low energy region, below 0.4 eV, these uncertainties gradually increase. The direct sum of potential individual systematic errors has been estimated to be up to 9% on the steep slope of the cross section function below 1.5 eV, decreasing below 3% between 10 and 100 eV, and increasing up to 4% at the highest energies applied.

Additional details concerning the method used and the apparatus may be found elsewhere (Krzysztofowicz and Szmytkowski 1995).

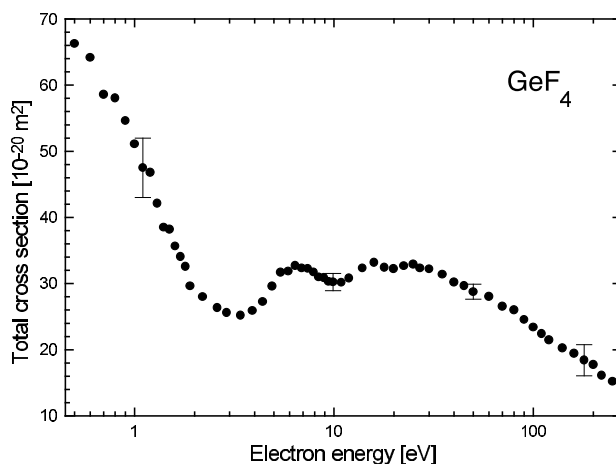
The germanium tetrafluoride sample was purchased from Aldrich and was used without further purification.

### 3. Results and discussion

In this section we present our absolute grand TCSs for electron scattering from germanium tetrafluoride at a number of incident energies ranging from 0.5 to 250 eV (figure 2 and table 1). No other experimental TCSs for e<sup>-</sup>-GeF<sub>4</sub> scattering or theoretical calculations have been found in the literature for comparison. In addition, the results obtained in this work are compared with our recent measurements for the remaining germanium compounds of tetrahedral symmetry (figure 3(a) and table 1) and for other tetrahedral, XY<sub>4</sub> (X = C, Si and Y = H, F, Cl), molecules (figures 3(b), (c) and 4(a)–(c)). Based upon these results, an effort will be made to illuminate features that are common across a class of related species, and then existing variations are also discussed.

#### 3.1. GeF<sub>4</sub>

The most striking feature of the e<sup>-</sup>-GeF<sub>4</sub> TCS function is observed at impact energies  $E < 2$  eV where the cross section dramatically increases as the collision energy becomes smaller (figure 2): at 0.5 eV the cross section reaches a value close to  $66 \times 10^{-20}$  m<sup>2</sup>. Many studies have shown that an increase of the TCS at very low energies seems rather typical for



**Figure 2.** Absolute electron-GeF<sub>4</sub> scattering TCS. Experimental: ●, grand total, present absolute. The error bars in selected points represent the total (systematic plus statistical) experimental uncertainties.

electron scattering off polar molecules. For targets which possess a permanent electric dipole moment such behaviour is mainly explained through long-range direct scattering processes (Itikawa 1978). Recently, increasingly more numerous examples of very effective low-energy electron scattering from some nonpolar polyatomic systems (e.g. CO<sub>2</sub> and SF<sub>6</sub>) have become evident with large near-zero energy TCSs. That ‘anomaly’, in the case of nonpolar targets, is interpreted in terms of indirect (resonant) processes: virtual-state mechanism—CO<sub>2</sub>, creation of metastable parent negative-ion—SF<sub>6</sub>. Low-energy e<sup>-</sup>-GeF<sub>4</sub> scattering elastic calculations (Szmytkowski and Szmytkowski 1998) revealed that the steep rise of the cross section towards lower energies, below 3 eV, can be mainly related to *a*<sub>1</sub>-symmetry component in the elastic channel.

Around 3 eV the e<sup>-</sup>-GeF<sub>4</sub> TCS exhibits a local minimum with a value of  $25 \times 10^{-20} \text{ m}^2$ . This feature results from the gradual decrease of the *a*<sub>1</sub> channel contribution and concurrent increase of the *t*<sub>2</sub> component as the impact energy increases. As the energy further increases a distinct narrow peak centred around 6.5 eV is visible with a maximum value of  $33 \times 10^{-20} \text{ m}^2$ . Calculations (Szmytkowski and Szmytkowski 1998) suggest that at energies in the vicinity of this maximum electron scattering on germanium tetrafluoride might be dominated by the formation of a shape resonant state of *t*<sub>2</sub> symmetry. Such a resonance is associated with temporary capture of the extra electron by the target molecule and creation of a short-lived negative-ion state. For energies close to 10 eV another shallow minimum is visible followed by a very broad hump spanning up to 60 eV on which two weak features, peaked near 16 and 25 eV, are distinguished. The presence of such structures indicates that some high-energy resonant processes may be possible. Above 30 eV the TCS falls steadily with increasing energy and reaches a value of  $15 \times 10^{-20} \text{ m}^2$  at the highest applied energy of 250 eV. A slight change of the slope of the grand TCS function, near 80 eV, coincides with the typical position of the maximum in TCSs for ionization by electron collisions.

### 3.2. XY<sub>4</sub> molecules (*X* = C, Si, Ge and *Y* = H, F, Cl)

The present experiment on electron-GeF<sub>4</sub> scattering completes a series of our measurements of grand TCSs for germanium tetrahedral compounds (GeH<sub>4</sub>: Mozejko *et al* 1996, GeCl<sub>4</sub>:

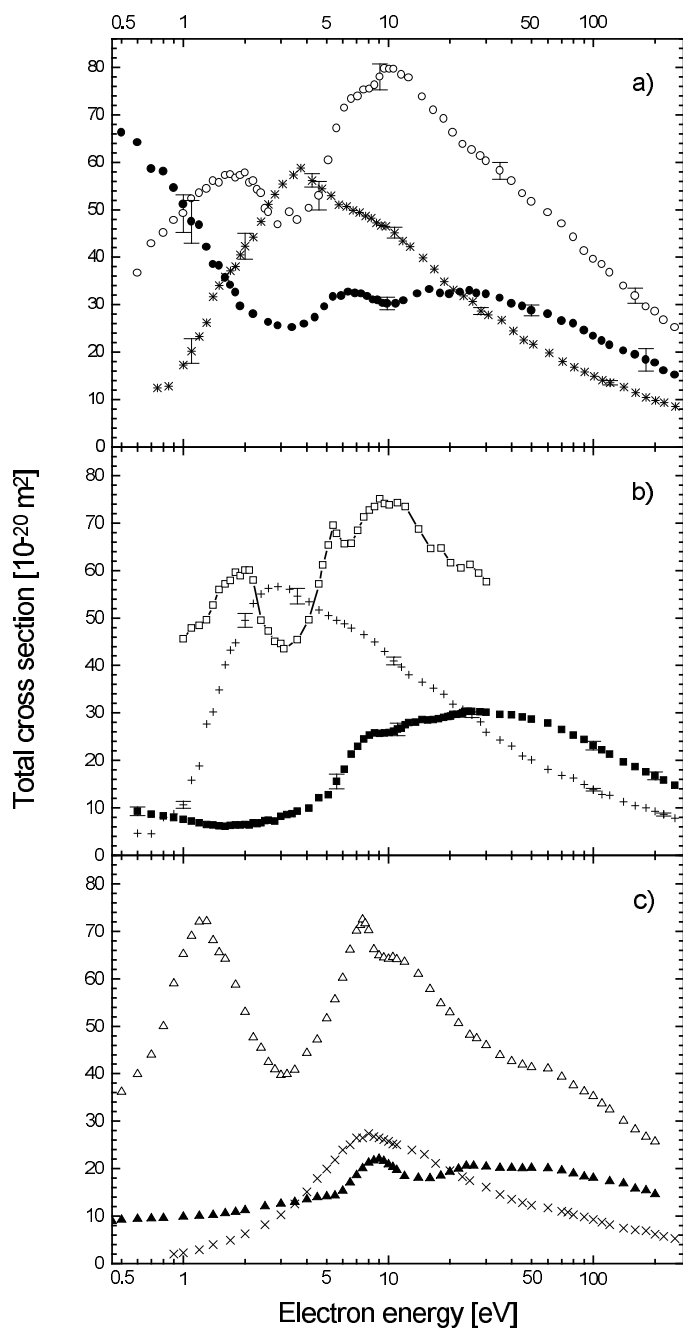
**Table 1.** Absolute TCSs measured for electron impact on GeF<sub>4</sub>, GeCl<sub>4</sub> and GeH<sub>4</sub> molecules, respectively, in units of 10<sup>-20</sup> m<sup>2</sup>.

<i>E</i> (eV)	TCS GeF <sub>4</sub>	TCS <sup>a</sup> GeCl <sub>4</sub>	TCS <sup>b</sup> GeH <sub>4</sub>	<i>E</i> (eV)	TCS GeF <sub>4</sub>	TCS <sup>a</sup> GeCl <sub>4</sub>	TCS <sup>b</sup> GeH <sub>4</sub>	<i>E</i> (eV)	TCS GeF <sub>4</sub>	TCS <sup>a</sup> GeCl <sub>4</sub>	TCS <sup>b</sup> GeH <sub>4</sub>
0.5	66.3			4.8			54.4	11.9	30.8		
0.6	64.2	36.7		4.9	29.6			12			43.4
0.7	58.6	42.9		5.1		60.4		12.6		77.8	
0.75			12.5	5.3			53.0	13			42.2
0.80	58.0	45.1		5.4	31.7			14	32.3		
0.85			12.8	5.6		67.2		15		73.8	39.9
0.9	54.6	47.8		5.8			51.1	16	33.2		
1.0	51.1	49.2	17.3	5.9	31.9			17		71.0	37.5
1.1	47.5	52.3	20.2	6.1		71.4		18	32.4		
1.2	46.8	53.5	23.3	6.3			50.6	19		69.1	34.8
1.3	42.1	54.4	26.2	6.4	32.7			20	32.2		
1.4	38.5	56.1	31.6	6.6		73.4		21		66.2	33.2
1.5	38.2	55.7	34.0	6.8			49.8	22.5	32.7		
1.6	35.7	57.2	35.8	6.9	32.4			23		63.8	31.8
1.7	34.1	57.4	37.2	7.1		73.9		25	32.9		
1.8	32.6	56.7	38.1	7.3			49.4	26		62.6	30.7
1.9	29.6	57.2	40.5	7.4	32.3			27.5	32.4		
2.0		57.8	42.3	7.6		75.3		28		61.3	28.6
2.1		55.7		7.8			48.6	30	32.2	60.3	27.9
2.2	28.0	56.0	44.3	7.9	31.7			35	31.4	58.2	26.8
2.3		54.2		8.1		75.4		40	30.2	56.0	24.5
2.4		53.5	47.5	8.4	31.0			45	29.7	53.4	22.6
2.5		50.2		8.5			48.2	50	28.8	51.7	21.7
2.6	26.3	49.5	51.2	8.6		76.3		60	28.1	49.4	19.8
2.8			53.2	8.9	30.9			70	26.5	47.0	18.0
2.9	25.6	46.9		9.0			47.2	80	26.0	44.3	16.8
3.1			55.4	9.1		78.0		90	24.6	41.3	15.8
3.3		49.5		9.4	30.3			100	23.4	39.6	14.9
3.4	25.2			9.5			46.7	110	22.4	38.5	14.1
3.5			57.9	9.6		79.7		120	21.5	36.8	13.6
3.6		47.9		9.9	30.2			140	20.2	33.9	12.7
3.8			58.8	10.0			46.5	160	19.5	31.9	11.5
3.9	25.9			10.1		79.6		180	18.4	29.6	10.5
4.1		50.3		10.6		79.6		200	17.7	28.6	9.83
4.3			56.2	10.9	30.2			220	16.1	26.8	9.41
4.4	27.3			11.0			45.2	250	15.2	25.2	8.55
4.6		53.0		11.6		78.4					

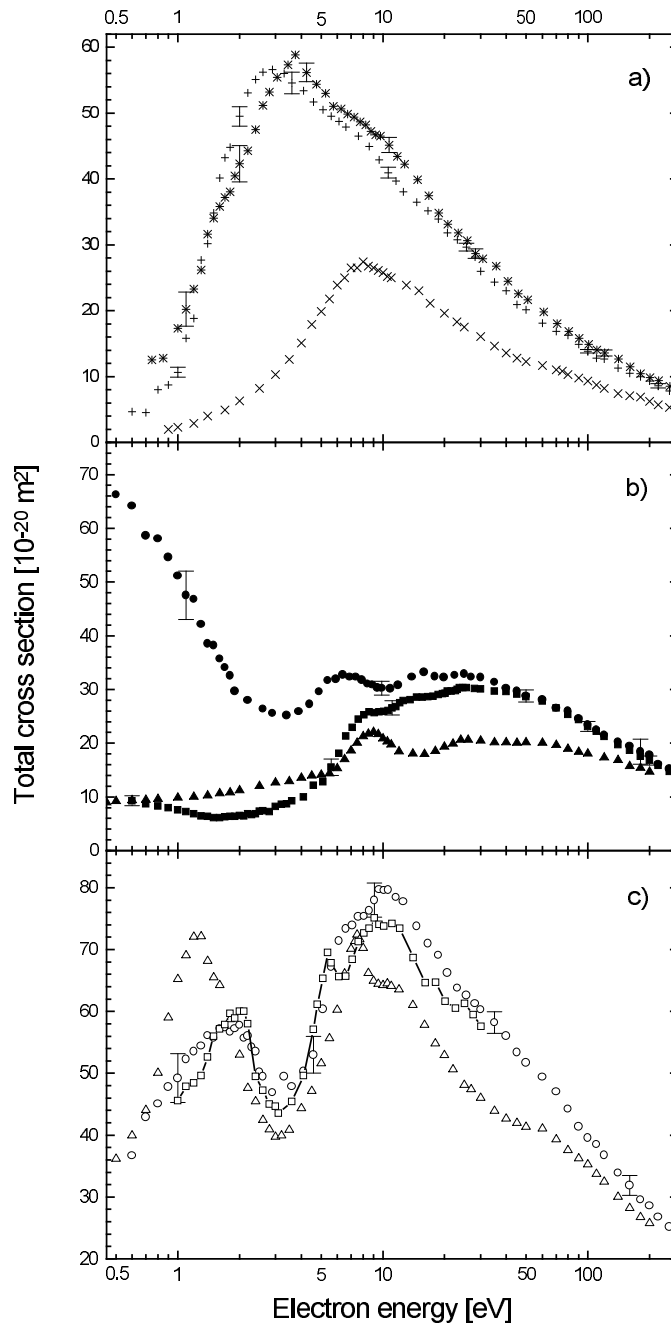
<sup>a</sup> Szmytkowski *et al* (1997).<sup>b</sup> Możejko *et al* (1996).

Szmytkowski *et al* 1997) and for some other molecules of tetrahedral symmetry, XY<sub>4</sub> (CH<sub>4</sub>: Zecca *et al* 1991, CF<sub>4</sub> and CCl<sub>4</sub>: Szmytkowski *et al* 1992, SiH<sub>4</sub>: Szmytkowski *et al* 1997, SiF<sub>4</sub>: Karwasz *et al* 1998, SiCl<sub>4</sub>: Możejko *et al* 1998) thus we briefly summarize these results. The set of data obtained with the same experimental technique for a group of homologous targets enables us to search for possible similarities and to make some observations on the role of a central atom and/or external atoms in collisions of electrons with tetrahedral, near-spherical molecules.

The comprehensive discussion of particular features in the TCS energy dependence for examined targets has been given in aforementioned reports, therefore in the following



**Figure 3.** Comparison of TCS for electron scattering on (a) GeY<sub>4</sub>, (b) SiY<sub>4</sub>, and (c) CY<sub>4</sub> molecules. (a): ●, GeF<sub>4</sub>, present results; ○, GeCl<sub>4</sub>, Szmytkowski *et al* (1997); \*, GeH<sub>4</sub>, Możejko *et al* (1996). (b): ■, SiF<sub>4</sub>, Karwasz *et al* (1998); line with □, SiCl<sub>4</sub>, Możejko *et al* (1998), preliminary results; +, SiH<sub>4</sub>, Szmytkowski *et al* (1997). (c): ▲, CF<sub>4</sub>, Szmytkowski *et al* (1992); △, CCl<sub>4</sub>, Szmytkowski *et al* (1992); ×, CH<sub>4</sub>, Zecca *et al* (1991). The error bars in selected points represent the total (systematic plus statistical) experimental uncertainties.



**Figure 4.** Comparison of TCSs for electron scattering on (a)  $\text{XH}_4$ , (b)  $\text{XF}_4$  and (c)  $\text{XCl}_4$  molecules. (a):  $\times$ ,  $\text{CH}_4$ , Zecca *et al* (1991);  $+$ ,  $\text{SiH}_4$ , Szmytkowski *et al* (1997);  $*$ ,  $\text{GeH}_4$ , Mozejko *et al* (1996). (b):  $\blacktriangle$ ,  $\text{CF}_4$ , Szmytkowski *et al* (1992);  $\blacksquare$ ,  $\text{SiF}_4$ , Karwasz *et al* (1998);  $\bullet$ ,  $\text{GeF}_4$ , present results. (c):  $\triangle$ ,  $\text{CCl}_4$ , Szmytkowski *et al* (1992); line with  $\square$ ,  $\text{SiCl}_4$ , Mozejko *et al* (1998), preliminary results;  $\circ$ ,  $\text{GeCl}_4$ , Szmytkowski *et al* (1997). The error bars in selected points represent the total (systematic plus statistical) experimental uncertainties.

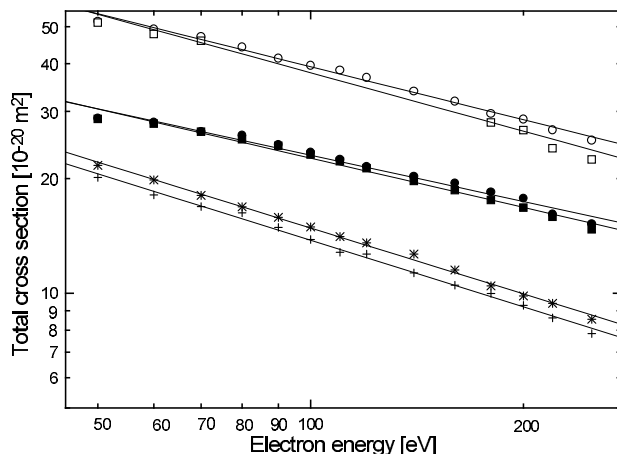
analysis we shall mainly focus on the common characteristics of the cross sections, both in shape and absolute magnitude. According to complexity of features observed in the measured TCS functions, all of the investigated energy range can be divided into two major regions (figures 3(a)–(c)). In the first region, ranging from 0.5 eV to slightly above the first ionization threshold of targets under study, the TCSs vary greatly with impact energy. Meanwhile, the complexity of the observed structures increases across the series of homologous targets XH<sub>4</sub>, XF<sub>4</sub> to XCl<sub>4</sub> (figures 4(a)–(c)). In the second energy regime, above 30 eV, TCSs become smooth functions of energy and for energies above several times the ionization potential cross sections monotonically decrease while energy increases. The most distinct feature, immediately visible in all presented TCS curves (figures 3(a)–(c)), over the whole investigated impact energy range, is the general qualitative similarity of the reported functions for tetrahedral targets possessing the same external atoms.

Among the investigated tetrahedral molecules, TCS functions of tetrahedral hydrides, XH<sub>4</sub>, are the least complex (figure 4(a)). In the energy range 0.5–250 eV, each e<sup>−</sup>–XH<sub>4</sub> TCS curve has a single prominent structureless maximum located at 8, 1.9 and 3.5 eV for the sequence of central atoms C, Si, and Ge, respectively. The resonant character of these maxima has been well established both experimentally and theoretically (see the comprehensive discussion by Winstead and McKoy (1996)).

The energy dependences of the TCSs for the series of tetrafluorides (CF<sub>4</sub>, SiF<sub>4</sub>, GeF<sub>4</sub>) are more complex (figure 4(b)). The first, low-energy resonant peak is located at 9, 8.5, and 6.5 eV for the series of C, Si, and Ge central atoms, respectively. This structure is followed by a shallow minimum and a subsequent exceptionally broad maximum extending from a dozen or so to some tens of electron-volts on which some weak resonant-like structures are superimposed. Such a broad maximum (figure 4(b)) is characteristic of all perfluorinated compounds we have studied in our laboratory (CF<sub>4</sub>: Szmytkowski *et al* 1992, C<sub>6</sub>F<sub>6</sub> and SF<sub>6</sub>: Kasperski *et al* 1997, SiF<sub>4</sub>: Karwasz *et al* 1998; C<sub>2</sub>F<sub>6</sub>: Kasperski *et al* 1998). When the atomic number, *Z*, in the sequence of the central atoms (C, Si, and Ge) increases then (i) the width of the broad feature decreases and (ii) its centre shifts towards lower energies.

What distinguishes the series of XCl<sub>4</sub> targets (figure 4(c)) from other tetrahedral compounds investigated is the relatively high absolute magnitude of the TCSs of the XCl<sub>4</sub> systems and more structured energy dependence. Low-energy TCSs of tetrachlorides have a distinct low-energy resonant maximum located at 1.1 eV for CCl<sub>4</sub> and close to 2 eV for SiCl<sub>4</sub> and GeCl<sub>4</sub>. At 3 eV each e<sup>−</sup>–XCl<sub>4</sub> cross section exhibits a deep minimum with a depth decreasing as the number of electrons, *Z*, in the central atom increases. The impact energy region above 3 eV is characterized by the broad enhancement of the cross section for all tetrachlorides examined. On the broad hump, with a maximum value exceeding  $70 \times 10^{-20} \text{ m}^2$ , two features appear whose relative intensity varies substantially while changing the central atom of molecule. For the CCl<sub>4</sub> target, the first narrow peak located at 6.5 eV on the low-energy slope of the hump is very distinct while the second structure in the vicinity of 12 eV is barely visible. If we consider the SiCl<sub>4</sub> molecule, the first maximum placed at 5.5 eV is weaker than the second, much broader maximum situated around 10 eV. For GeCl<sub>4</sub>, the weak shoulder near 6 eV is merely noticeable whilst the second main structure is centred at 10 eV.

To complement the presented data, it is worth mentioning another behaviour common for all investigated tetrahedral molecules. The electron-scattering TCS of XY<sub>4</sub> molecules remarkably increases as the impact energy decreases towards near-thermal energies (e.g. CH<sub>4</sub>: Lohmann and Buckman 1986, CF<sub>4</sub>: Field *et al* 1984, CCl<sub>4</sub>: Wan *et al* 1989, SiY<sub>4</sub>: Wan *et al* 1991, Randell *et al* 1993, Lunt *et al* 1994). This increase is not evident from the results presented in figure 3 as it appears for every target, except GeF<sub>4</sub>, below the energy



**Figure 5.** Energy dependence of the TCS for  $\text{GeY}_4$  and  $\text{SiY}_4$  molecules: ●,  $\text{GeF}_4$ , present; ○,  $\text{GeCl}_4$ , Szmytkowski *et al* (1997); \*,  $\text{GeH}_4$ , Mozejko *et al* (1996); ■,  $\text{SiF}_4$ , Karwasz *et al* (1998); □,  $\text{SiCl}_4$ , Mozejko *et al* (1998), preliminary results; +,  $\text{SiH}_4$ , Szmytkowski *et al* (1997). Straight lines across the points illuminate the regression of TCS against impact electron energy.

range of our experiments. Multiple scattering  $X\alpha$  calculations of Tossel and Davenport (1984) revealed that for  $\text{CY}_4$  and  $\text{SiY}_4$  systems this very low-energy feature mainly arises in the elastic scattering channel. Going from thermal energies to some tenths of electronvolts the target molecules become more transparent to electrons over a narrow energy range and a distinct minimum in the TCS function arises. The exception is again the  $e^-$ - $\text{GeF}_4$  curve, which shows the minimum at higher energies, near 3 eV.

Regression lines across respective experimental points (figure 5) reveal that for electron impact energies ranging from 50 eV to 250 eV the energy dependence of the compared TCSs can be expressed as  $Q(E) \sim E^{-0.5}$  indicating that the intermediate-energy electron-scattering TCSs for tetrahedral molecules are proportional to the time the electron spends in the vicinity of the target molecule. Such behaviour of the TCS is in accordance with our recent findings for methyl halides (Krzysztofowicz and Szmytkowski 1995) and for the family of  $\text{CH}_3\text{Y}$  ( $\text{Y} = \text{OH}, \text{NH}_2, \text{CH}_3$  and  $\text{SH}$ ) targets (Szmytkowski and Krzysztofowicz 1995, Szmytkowski *et al* 1995) as well as with the previous theoretical results of Vogt and Wannier (1954) obtained for the pure polarization potential. Similar correlation with energy was found for hydrocarbons by Floeder *et al* (1985) and Nishimura and Tawara (1991). Such energy dependence differs slightly from the  $E^{-0.78}$ -type observed recently by Garcia and Manero (1997) and more from  $E^{-1}$ -type derived by Zecca *et al* (1992, 1995), both for higher impact energies.

So far, our discussion has been limited to the general energy dependence of the TCS for different  $\text{XY}_4$  molecules. In view of the magnitude of TCSs it strongly depends on the impact energy range. At low energies, due to the presence of resonant structures, there seems to be no general trend of magnitude of TCS against the target structure. It is evident, however, that in the energy regime from about 1 eV up to 20 eV the cross sections of perfluorinated compounds are lower than those of tetrahedral hydrides. Above 20 eV the TCS function for targets with the same external atoms and the central atom of higher  $Z$  lies above that with lower  $Z$ . When the energy increases the difference in magnitudes steadily diminishes and above 100 eV the  $e^-$ - $\text{GeY}_4$  cross section functions merge into those for  $e^-$ - $\text{SiY}_4$  scattering (figures 3(a)–(c), and 5). More evident is the difference of TCS magnitudes

in the family of targets with the same central atom and different external atoms. The TCSs distinctly increase in the sequence of external atoms Y = H, F and Cl (figures 3).

Even a very superficial analysis of these results suggests clearly that for energies above 50 eV the e<sup>-</sup>-XY<sub>4</sub> TCSs are greater for molecules of greater electric dipole polarizability,  $\alpha$ . As the polarizability is a measure of the response of the target electron cloud to an external electric field, one may expect the electron scattering cross section to be correlated with the target polarizability. Indeed, the formula derived by Vogt and Wannier (1954) predicts that for the pure polarization potential the cross section for electron capture depends on the polarizability ( $\sim\alpha^{0.5}$ ). Since that time, correlations between experimental cross sections and the polarizability have been studied in some laboratories (Lampe *et al* 1957, Beran and Kevan 1968, Center and Mandl 1972, Christophorou *et al* 1976, Szmytkowski 1989, Nishimura and Tawara 1991, Szmytkowski and Krzysztofowicz 1995, Christophorou and Illenberger 1993, Garcia and Manero 1997). As a result, some regression formulae have been found for selected families of molecules in which the electron-scattering TCS varies from target to target, with their polarizability like  $\alpha^x$  with  $x$  lying between 0.5 and 1 for different groups of targets under consideration. At the same time, calculations carried out by Jain and Baluja (1992) for a large group of targets showed no correlation between the high-energy TCS and the polarizability. This evidently contradicts the very recent observations of Garcia and Manero (1997). On the other hand, intermediate-energy calculations of Joshipura (1997) confirm a strong correlation of the TCS with the polarizability reported by Szmytkowski (1989). More conclusive statements on correlation between the TCS and the polarizability for tetrahedral molecules seem to be not very productive at present as values of polarizabilities for these targets, derived with various techniques, differ too distinctly (up to 50%).

#### 4. Final remarks

In this work we presented the results of our absolute electron-scattering GeF<sub>4</sub> TCS measurements for impact energies from 0.5 to 250 eV. Generally, the shape of the e<sup>-</sup>-GeF<sub>4</sub> TCS is very similar to that for other perfluorinated tetrahedrals, apart from the low-energy minimum which for GeF<sub>4</sub> is located at higher energy, near 3 eV.

We also summarize our experiments on the determination of TCS for electron scattering on tetrahedral XY<sub>4</sub> targets (X = C, Si, Ge and Y = H, F, Cl). The results clearly indicate that external rather than central atoms have more appreciable influence on the energy dependence of the TCS. More definitive findings need more detailed experimental and theoretical studies of particular electron-scattering induced processes for these targets, especially at low and very low impact energies.

#### Acknowledgments

It is a pleasure to acknowledge Elżbieta Ptasińska-Denga for her assistance in the preliminary stages of the experiment. The authors would like to thank Dr Radosław Szmytkowski for stimulating discussion concerning some aspects of this work. This work was sponsored in part by the Polish State Committee for Scientific Research (KBN) under projects PB 317/P03/96/11 and 0540/P03/98/14.

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