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Role of methylation in electron scattering on $X(CH_3)_4$ (X= C, Si, Ge) molecules

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Abstract. To investigate how replacement of H atom with methyl group (CH_3) – in tetrahedral compounds of carbon, silicon and germanium – affects electron scattering process, total cross sections (TCS) for electron scattering from $C(CH_3)_4$, $Si(CH_3)_4$ and $Ge(CH_3)_4$ molecules have been compared with data for CH_4, SiH_4 and GeH_4 molecules. All examined data have been obtained with the same experimental setup. The shape of all discussed TCS energy dependences is very similar and is characterized by a dominant maximum peaked below 10 eV. For methylated compounds a gentle structure is also visible on high energy slope of main enhancement, between $10 - 20$ eV. A simple formula for TCS evaluation for partially methylated carbon, silicon and germanium compounds is also proposed.

1. Introduction

In recent years, modern techniques of nanostructure production, like focus electron beam induced deposition (FEBID) method [1], have been of great interest. The precursors used in FEBID method often contain methyl groups, which must be removed from precursor prior to deposition of metallic compound onto substrate. Therefore it is important to understand how the CH_3 groups affect processes occurring during electron collisions with chemical compounds.

Among quantities which characterize electron collisions with molecules, total cross section is the one which contains overall information on scattering phenomena and can be measured in an absolute way and/or evaluated in theoretical calculations. In this work, we present our investigations on the role of methylation based on comparison of electron-scattering total cross section results for $C(CH_3)_4$, $Si(CH_3)_4$, $Ge(CH_3)_4$, CH_4, SiH_4 and GeH_4 molecules. The comparison for these molecular compounds can also help to find some regularities in the TCS energy dependence. These correlations may allow to estimate the TCS for methylated compounds of carbon, silicon and germanium for which there is no experimental or theoretical collisional data. Up to date, some efforts have been made to find correlations between total cross section value and physico-chemical parameters of numerous molecular targets (e.g. [2, 3, 4, 5]). The specific trends in electron-scattering total cross section energy dependence have been previously observed for hydrocarbon and perfluorocarbon target molecules: *isomer effect* [6] and *perfluorination effect* [7]. Moreover, *group additivity rule* has been formulated for nitrides and cyclic ethers [8]. Methylation effect has been also noticed in our previous experimental studies in which we have examined TCS
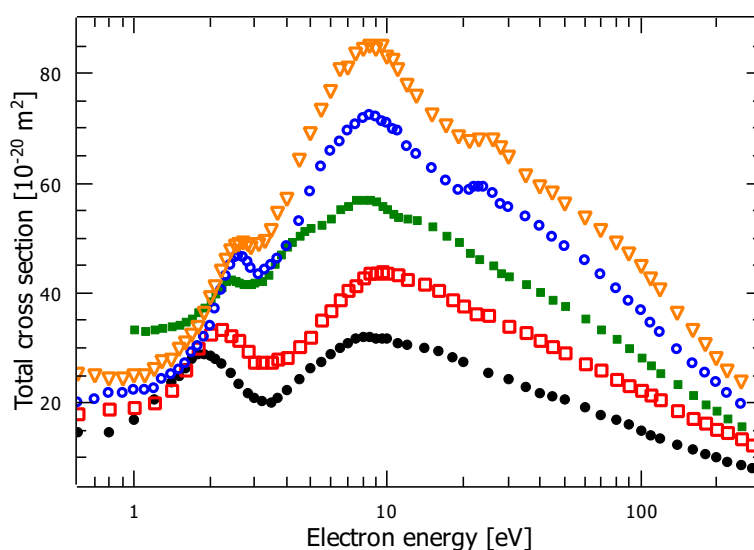
Figure 1. TCS for electron scattering from: 2,3-dimethyl-2-butene ($\triangledown$) , 2-methyl-2-butene ($\circ$), 2-methylpropene ($\blacksquare$), propene ($\square$), ethylene ($\bullet$) [9].

for selected alkenes (ethylene, propene, 2-methylpropene, 2-methyl-2-butene and 2,3-dimethyl-2-butene [9]) and dienes (allene, 1,2-butadiene and 2-methyl-1,3-butadiene molecules [10]). In figure 1 we have compared experimental TCS for selected alkenes [9], which have respectively 0, 1, 2, 3, and 4 methyl groups. The curves have very similar energy dependence over the whole investigated energy range. One of the most important observation is that, at energies above 4 eV, the TCS value increases by nearly the same value with the number of methyl groups attached around C=C bond. It is also clear that the magnitude and position of low-energy resonant peak is affected by presence of methyl groups, mainly due to redistribution of the electric charge in the methylated compounds via interaction of methyl group orbitals with the C=C orbitals [9]. The substitutional and additivity effects have been also observed and indicated for selected alkyne molecules: 1-butyne, propene and acetylene [11]. It was shown [11] that semi-empirical TCS for propyne, TCS(C_3H_4), and 1-butyne, TCS(C_4H_6), molecules can be easily obtained from the following simple rules:

$$\text{TCS}_{(C_3H_4)}(E) = \sigma_{C_2H_2}(E) + \frac{1}{2}\sigma_{C_2H_4}(E) \tag{1}$$

and

$$\text{TCS}_{(C_4H_6)}(E) = \sigma_{C_2H_2}(E) + \sigma_{C_2H_4}(E), \tag{2}$$

where $\sigma_{C_2H_2}(E)$ and $\sigma_{C_2H_4}(E)$ are the experimental TCS data [12, 13] and E denotes the incident electron energy. The obtained TCSs are in reasonable agreement with experimental data in the intermediate energy range (50-250 eV) [11]. It is worth also noting here that two theoretical methods: additivity rule [14] and independent atom method representation (IAM) [15] in combination with the screened additivity rule (SCAR) including interferences (+I)[16] are based on the general assumption that at intermediate- and high-impact electron energies the question of electron-molecule scattering can be reduced to the electron-atom collision problem.

2. Experimental details
All discussed experimental TCS data were obtained in our laboratory using electrostatic 127° electron spectrometer working in a linear transmission mode, described elsewhere [17]. Briefly,

the electron beam with given energy E is directed into scattering chamber filled with studied molecules at a constant pressure p. The energy resolution of electron beam, $\Delta E = 100$ meV (FWHM). The energy scale was calibrated with respect to the well known resonant oscillatory structure visible around 2.3 eV when the target was mixed with N_2 molecules. The electrons that have not been scattered are detected by the Faraday cup collector. TCS can be determined from measured quantities using the Beer-Lambert-Bouguer (BLB) law:

$$TCS(E) = \frac{k\sqrt{T_m T_t}}{pL} \ln \frac{I_0(E)}{I_t(E)}, \tag{3}$$

where k denotes the Boltzmann constant, $I_t(E)$ and $I_0(E)$ are the intensities of the electron beam, passing the length L through the scattering chamber, taken in the presence and absence of the target molecules, respectively. T_m and T_t mean the temperature of manometer head and scattering cell. The target vapour pressure, p, was measured using a capacitance manometer and was kept within 80-180 mPa range, which ensured single-scattering conditions. The temperature of the scattering cell, T_t, is usually lower than $T_m = 322$ K by 10-20 K. Thus, recorded values of the target pressure, p, have been corrected taking into account the thermal transpiration effect [18]. The final absolute TCS value at each electron energy is a weighted mean of results from several measurement series.

3. Results

To investigate how substitution of CH_3 groups affects TCS energy dependence, we compared results for tetrahedral molecules XH_4 (X=C, Si, Ge) [19, 20, 21] with their fully methylated derivatives $X(CH_3)_4$ [22]. TCS curves for methylated compounds are shown in figure 2.

It is clearly visible that the shapes of the TCS curves for all targets are very similar to each other. Therefore we can conclude that substitution of H atoms with the CH_3 units does not influence the shape of the TCS energy dependence too much. TCSs for both molecular families are characterized by one dominant resonant-like maximum peaking at energies between 3 and 8 eV. For $Si(CH_3)_4$ and $Ge(CH_3)_4$ molecules the main maxima are shifted toward higher energies by 2.6 and 1.8 eV in comparison with SiH_4 and GeH_4 molecules, respectively. However, the TCS maximum for $C(CH_3)_4$ is shifted toward lower energy by 1.5 eV with respect to the CH_4 maximum. That results in higher TCS values around 2 eV of smaller SiH_4 and GeH_4 molecules compared to their methylated counterparts, while the TCS for CH_4 is lower than that for $C(CH_3)_4$ in the entire examined energy range. Table 1 summarizes the energies at which the TCSs have maxima.

Table 1. Electron energies [eV] at which TCSs have maxima.

Molecule	E_{max}
CH_4	8.0
SiH_4	3.0
GeH_4	3.8
$C(CH_3)_4$	6.5
$Si(CH_3)_4$	5.6
$Ge(CH_3)_4$	5.6

In general, the methylation causes a significant increase in the TCS value in the entire energy range. That is mainly related to increase in the geometrical size of the molecules [3, 23, 24].
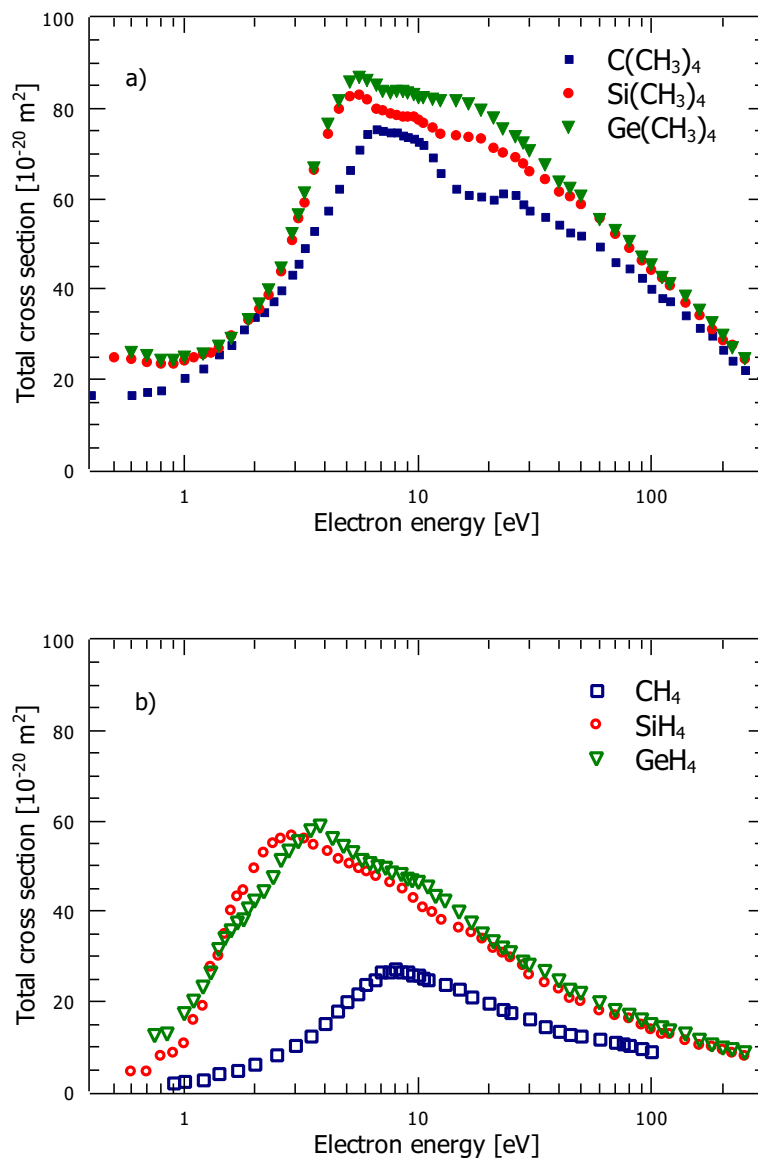
Figure 2. (a): TCS for electron scattering from: $C(CH_3)_4$ (■) [22], $Si(CH_3)_4$ (●) [22] and $Ge(CH_3)_4$ (▼) [22]. (b): TCS for electron scattering from: CH_4 (□) [19], SiH_4 (○) [21] and GeH_4 (▽) [20].

Influence of methylation is visible also above 10 eV, where for fully methylated compounds some gentle structure appears. These additional enhancements extend between 12 and 25 eV.

Figure 3 shows the experimental TCS curves for CH_4 and $C(CH_3)_4$ and the estimated TCS curves for selected methylated carbon compounds, which were obtained using a simple empirical additivity rule:

$$\text{TCS}_{CH_n(CH_3)_m}(E) = \sigma_{CH_4}(E) - m\sigma_H(E) + m\sigma_{CH_3}(E), \tag{4}$$

where n denotes the number of hydrogen atoms bounded to the central atom and m indicates the number of methyl groups. TCS values for methyl group, $\sigma_{CH}(E)$, have been determined as
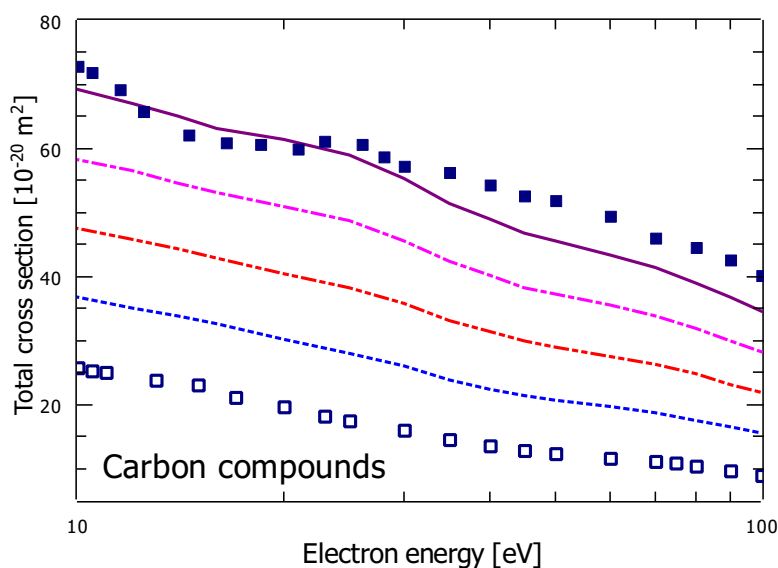
Figure 3. Experimental TCS for electron scattering from: CH_4 ($\square$) [19] and $C(CH_3)_4$ ($\blacksquare$) [22]. Estimated TCS (simple additivity rule) for electron scattering from: $C(CH_3)_4$ (——), $CH(CH_3)_3$ (— · —), $CH_2(CH_3)_2$ (— · · —), $CH_3(CH_3)$ (· · · · · ·).
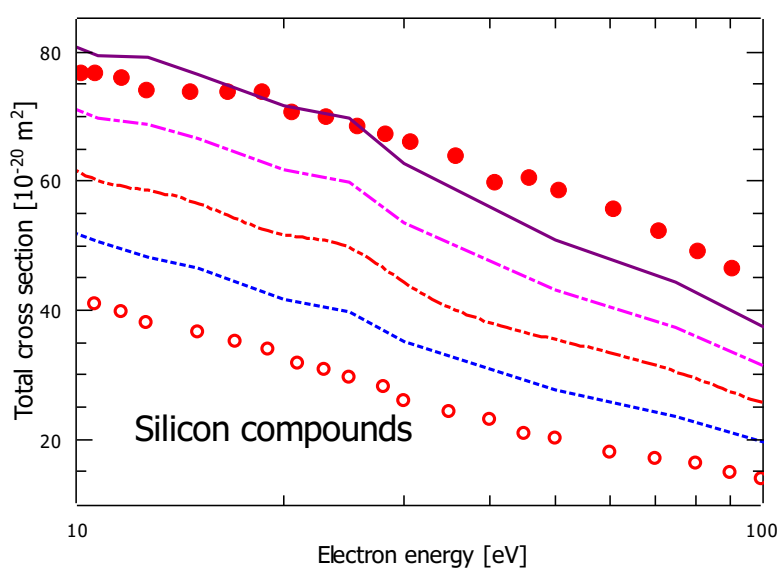

Figure 4. Experimental TCS for electron scattering from: SiH_4 ($\circ$) [21] and $Si(CH_3)_4$ ($\bullet$) [22]. Estimated TCS (simple additivity rule) for electron scattering from: $Si(CH_3)_4$ (——), $SiH(CH_3)_3$ (— · —), $SiH_2(CH_3)_2$ (— · · —), $SiH_3(CH_3)$ (· · · · · ·).

a half of the experimental TCS of ethane (H_3C–CH_3) molecules [25], while TCS for hydrogen atom, σ_H, has been approximated as half of TCS measured for H_2 molecules [26]. The TCS for CH_4 molecules, $\sigma_{CH_4}(E)$, has been taken from [19]. In the above semi-empirical method of total cross section evaluation molecular target is treated as an assembly of independent subunits. Figure 4 shows estimated TCS energy dependence for silicon compounds. Similarly, the estimated
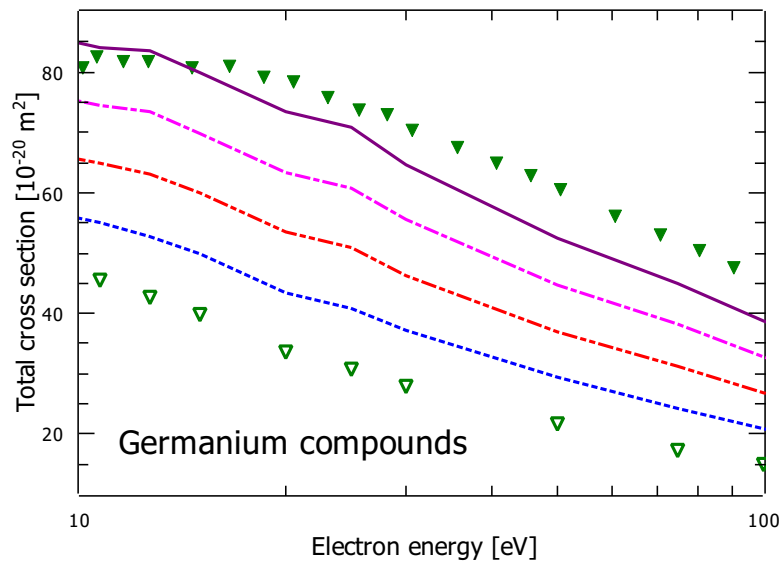
Figure 5. Experimental TCS for electron scattering from: GeH_4 ($\triangledown$) [20] and $Ge(CH_3)_4$ ($\blacktriangledown$) [22]. Estimated TCS (simple additivity rule) for electron scattering from: (——) $Ge(CH_3)_4$, (— · —) $GeH(CH_3)_3$, (— · · —) $GeH_2(CH_3)_2$, (······) $GeH_3(CH_3)$.

TCS curves for selected methylated silicon compounds, were obtained using a simple empirical additivity rule:

$$\text{TCS}_{SiH_n(CH_3)_m}(E) = \sigma_{SiH_4}(E) - m\sigma_H(E) + m\sigma_{CH_3}(E), \tag{5}$$

where the TCS for SiH_4 molecules, $\sigma_{SiH_4}(E)$, has been taken from [21]. Figure 5 presents estimated TCS energy dependence for germanium compounds. TCSs for methylated Ge compounds were calculated as the sum of experimental TCS for molecular fragments:

$$\text{TCS}_{GeH_n(CH_3)_m}(E) = \sigma_{GeH_4}(E) - m\sigma_H(E) + m\sigma_{CH_3}(E), \tag{6}$$

where the TCS for GeH_4 molecules, $\sigma_{GeH_4}(E)$, has been taken from [20].

Evaluated this way TCSs for $C(CH_3)_4$, $Si(CH_3)_4$ and $Ge(CH_3)_4$ molecules are in reasonable agreement with experimental data [22] in investigated energy range. Discrepancies between measured and evaluated data are less than 15% in the entire energy range. Taking into account declared potential experimental uncertainties it is possible to state that the data obtained from equations (4), (5) and (6) should provide TCS evaluation with about 20% accuracy. As can be seen from figures 3, 4 and 5, the presence of extra methyl groups in studied methylated compounds ($CH(CH_3)_3$, $CH_2(CH_3)_2$, $CH_3(CH_3)$, $SiH(CH_3)_3$, $SiH_2(CH_3)_2$, $SiH_3(CH_3)$, $GeH(CH_3)_3$, $GeH_2(CH_3)_2$ and $GeH_3(CH_3)$) results mainly in general increase of the TCS magnitude. Also, the structure in TCS function seen above 10 eV for methylated compounds of silicon and germanium becomes more visible with increasing number of methyl groups. This additional structure can be associated with increasing efficiency in the ionization channel at this energy range. Although TCS results obtained this way are rather rough, they can serve as the first approximation of total cross section for electron scattering from methylated tetrahedral compounds of carbon, silicon and germanium studied in this work.

4. Conclusions

Analysis of experimental TCSs for electron scattering from tetrahedral compounds of carbon, silicon and germanium and their fully methylated derivatives has shown that methylation affects

significantly the electron scattering processes. The methylation causes mainly increase in the TCS value in the entire energy range, which can be associated with growing geometrical size of the molecule. It was shown that applying the well-known additivity rule, the TCSs for $C(CH_3)_4$, $Si(CH_3)_4$, and $Ge(CH_3)_4$ molecules can be approximated quite well by a simple empirical formula obtained from the addition of cross sections of individual molecular sub-units. TCSs for partially methylated methane, silane and germane molecules are predicted for electron energies between 10 eV and 100 eV.

Acknowledgments

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