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Absolute total cross-section measurements for electron scattering from silicon tetrachloride, $SiCl_4$, molecules

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Abstract. The absolute total cross-sections for electron scattering on $SiCl_4$ molecules have been measured in two distinct electron-transmission experiments, in Gdańsk and in Trento laboratory, for impact energy ranging from 0.3 to 250 eV and from 75 to 4000 eV, respectively. The e^-–$SiCl_4$ total cross-section function shows two very distinct resonant-like features: the strong peak at 1.9 eV and much broader main maximum centered near 10 eV with some additional substructure close to 5 eV. The present results are compared with low-energy total experimental data and elastic theoretical calculations for electron collisions with silicon tetrachloride molecules.

PACS. 34.80−i Electron scattering

1 Introduction

Much investigation of the interaction of electrons with silicon-containing compounds in collisional processes has concentrated on monosilane because of its importance in semiconductor industries. Interactions of $SiCl_4$ with electrons are known only in a fragmentary way.

Experimental studies on electron scattering from $SiCl_4$ molecules were mainly related to formation of negative ions in dissociative attachment processes at low incident energies [1–7]. Optical spectra induced by electron impact ionization of $SiCl_4$ were observed by Lambert *et al.* [8]. All those measurements gave intensities in arbitrary units only. The first absolute e^-–$SiCl_4$ scattering data were reported by Wan *et al.* [9]. They determined total cross-section in a transmission experiment for energies between 0.2 and 12 eV. We are not aware of any other experimental total cross-sections for e^--$SiCl_4$ collision.

The theoretical investigations of electron scattering from $SiCl_4$ molecules concentrated on elastic processes. Tossell and Davenport [10] calculated low-energy (0.2–6 eV) cross-section for elastic e^--$SiCl_4$ collisions using the multiple scattering Xα (MS-Xα) method. Integral elastic cross-sections from 1 to 16 eV were computed by Natalense *et al.* [11] at the static-exchange approximation with the Schwinger multichannel (SMC) method with pseudopotentials. Very recently, derivatives of integral elastic cross-sections, calculated with MS-Xα method, have been presented by Modelli *et al.* [7]. No total cross-section calculations are available for comparison.

As part of an extended study of electron interactions with polyatomic molecules we report, in this article, the results of accurate absolute total cross-section measurements for electron collisions with tetrachlorosilane at incident electron energies from 0.3 up to 4000 eV.

2 Experimental

Total cross-section (TCS) measurements reported in the present work were performed in two distinct laboratories with two different apparatus setups. The TCS for electron impact energy ranging from 0.3 to 250 eV was measured in Gdańsk using the electrostatic electron spectrometer. TCS's at higher impact energies (from 75 to 4000 eV) were determined with the modified Ramsauer-type apparatus in Trento laboratory. In both experiments electron transmission method was applied. The method relates the total cross-section to the transparency of the target at a given pressure for a beam of electrons [12].

2.1 Low-energy apparatus (Gdańsk) and procedure

In the low-energy experiment an electron beam of intensity between 1 and 100 pA, with an energy spread of 70 meV, was produced with an electron gun, followed with 127° electrostatic cylindrical monochromator and a system of electrostatic lenses. The electron beam was then directed into a collision cell and those electrons which passed the interaction volume without being scattered were energetically discriminated by a retarding field analyzer and

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finally detected by the Faraday cup collector. The energy scale of the incident electrons was calibrated with reference to the resonant oscillatory structure around 2.3 eV observed in the presence of molecular nitrogen. The total cross-section $Q(E)$ at given energy, E, was evaluated from the Bouguer-de Beer-Lambert relationship:

$$Q(E) = \frac{1}{(nL)_{\text{eff}}} \ln \frac{I_0(E)}{I_p(E)}, \tag{1}$$

where

$$(nL)_{\text{eff}} = \int_a^b n(z)\mathrm{d}z; \tag{2}$$

$I_0(E)$ and $I_p(E)$ are intensities of unattenuated and attenuated electron beam of energy E, respectively, $n(z)$ is the vapour-target number density at point z of the electron pathway, while integration is carried out over the path of the electron beam where $n(z) \neq 0$, and L is the distance along which the scattering events take place.

Due to effusion of sample molecules through entrance and exit orifices of the scattering chamber, the presence of target particles is not limited to the sample cell and number of scattering events leading to noticeable attenuation of transmitted electron beam may also occur outside the scattering cell. For the same reason the distribution of the target density over the electron pathway in the cell, which is nearly constant in its central part, drops off abruptly close to orifices. Such behaviour was also confirmed by our calculations based on Nelson and Colgate work [13]. Moreover, we found that for our experimental conditions $(nL)_{\text{eff}}$ can be reasonably approximated (within 0.5%) by product of geometrical length of the scattering cell L (= 30.5 mm) and the number density n of the target determined in the centre of the cell. The density number n was derived from its relation to the sample pressure as measured in the centre of the electron pathway in the cell, p, and target temperature, T, using the ideal gas law. Thermal transpiration effect, due to small difference in temperatures of the gas chamber and baratron manometer head (MKS), was accounted for by applying Knudsen formula [14]. In the case of our experiment number density values obtained with this simple formula are in very good accordance with the values obtained from more sophisticated empirical expressions [15].

All quantities in equation (1) needed for the derivation of the TCS were determined absolutely with devices of high accuracy. The experimental procedure was controlled by computer.

To provide the reasonable experimental conditions the electron optics of the spectrometer was placed in the vacuum chamber with the background pressure below 2 μPa. In the course of the experiment the pressure of the target in the scattering chamber was kept between 100 and 200 mPa. These limits of pressure were sufficient to exclude multiple-scattering events at the lowest and the highest incident electron energies, respectively. The external (mainly Earth's) magnetic field in the region of electron optics was reduced with the system of Helmholtz coils to the values lower than 0.1 μT.

Statistical experimental uncertainties (one standard deviation of weighted mean values) are about 1.5% below 1 eV and do not exceed 1% at higher applied energies. In order to lessen the influence of apparatus effects the measurements were carried out for each given energy, E, in 6–15 independent series of single (~ 10) runs using different sets of electron-beam and target-pressure conditions.

The direct sum of potential individual systematic errors is lower than 10% below 2.5 eV, does not exceed 5% around 5 eV, decreases below 4% between 10 and 100 eV, increasing to 5% at the highest applied energies (250 eV). The main contributions to the resulting systematical error arise from: i) the inability to eliminate the electrons elastically scattered in forward direction, ii) the imperfect discrimination of electrons inelastically scattered with small energy losses into small forward angles (angular acceptance of the detector equal to 0.7 msr), iii) the possible small shift of the electron impact energy in the course of the run, especially importunate in the range of sharp resonant structures, and iv) the inability to determine correctly the length of the interaction region in a target of inhomogenous density.

The $SiCl_4$ sample (Aldrich, 99.999% pure) was degased before use by numerous freeze-pump-thaw cycles at the liquid-N_2 temperature to remove air and other impurities not frozen at this temperature. The sample vapour was admitted alternately to the scattering cell and the vacuum chamber in such a way that the target pressure in the electron optics region was constant in the course of experiment.

Further details concerning the low-energy setup used and the experimental procedures applied may be found elsewhere [16,17].

2.2 High-energy apparatus (Trento)

In the high-energy experiment the modified Ramsauer technique was applied. The electron beam was formed in the 180°-sector of the transverse magnetic field with five apertures. The electron orbit radius was equal to 0.2 m. The scattering chamber was divided by an additional aperture into two parts. The first part constitutes the gas cell and the second one is of a gridded structure, open for gas pumping and electrically opaque for scattered electrons. The purpose of this geometry is to improve the angular resolution of the high-energy measurements.

Both, the collector (I_{c}) current and the intensity of electrons scattered onto chamber walls (I_{s}) were measured and used in the evaluation of the total cross-section. The measurements of both currents in this method are essential at high energies, where ion bombardment of the cathode can lead to beam instabilities and in consequence to considerable error in the measured cross-section. The angular acceptance of the collector was equal to 0.34 msr. No retarding field element was applied. A coarse energy discrimination ($\Delta E/E \simeq 1/20$) was operated by the magnetic field.

The total cross-section, $Q(E)$, was derived from the formula

$$\frac{I_{ci}(E)}{I_{ci}(E)+I_{si}(E)} = \frac{I_{cj}(E)}{I_{cj}(E)+I_{sj}(E)}\ \exp\left(-Q(E)L(n_i-n_j)\right), \qquad (3)$$

where pairs i and j of the currents correspond to two target densities n_i and n_j, respectively, and L is the effective scattering length equal to the geometrical length of the interaction region (0.14 m). The vapour target densities were evaluated from absolute measurements of the pressure and the temperature of the target in the scattering chamber. The temperature of the pressure meter gauge was tracking the temperature of the scattering cell to within 0.1°C. This avoids the need of any thermal transpiration correction and reduces the overall systematic error.

Several series of individual measurements have been performed at each energy, an average cross-section being calculated for each series. The final values are mean and weighted values of these averages. The experiment was controlled by computer.

Statistical uncertainties do not exceed 3% and the overall systematic error (apart from the angular resolution error) is lower than 4% in the whole energy range. The angular resolution error due to elastic scattering in the limit of Born's approximation rises linearly with energy. We are not aware of any small-angle differential cross-section measurements or calculations at high energies for $SiCl_4$. The angular resolution error estimated on the basis of data for the CH_2F_2 molecule [19] (with the geometry similar to that of $SiCl_4$), due to elastic scattering, was evaluated as 1% at 1000 eV. An error in the inelastic channel should be negligible in the low-energy limit of Trento measurements, due to the above-mentioned energy selection. Instead, it can be higher than the elastic angular resolution error at energies above 1000 eV. The lack of the differential cross-section data for $SiCl_4$ does not allow for more precise determination.

The $SiCl_4$ of 99.999% purity from Air Products in a steel pressurized cylinder was used. The main contaminants were $SiHCl_3$. Standard freeze-pump-thaw cycles at liquid-nitrogen temperature were performed.

More detailed description of the experimental equipment and techniques can be found in [18].

3 Results and discussion

The absolute e^-–$SiCl_4$ grand total cross-section obtained in the two reported experiments are listed jointly in Table 1, while in Figure 1 the TCS's measured in the present experiments are plotted as a function of the electron impact energy together with earlier absolute low-energy results of Wan *et al.* [9].

Table 1. Absolute total cross-section (TCS) for electron scattering on $SiCl_4$ molecules in units of 10^{-20} m^2. The first and the second TCS columns are results from Gdańsk laboratory while the third TCS column are results from Trento.

E (eV)	TCS	E (eV)	TCS	E (eV)	TCS
0.3	39.8	7.7	72.4	100	43.1
0.4	39.1	8.2	74.0	110	42.6
0.5	38.9	8.7	75.6	125	40.9
0.6	39.1	9.2	76.9	150	38.3
0.7	39.5	9.7	76.8	175	36.6
0.8	40.2	10.2	76.1	200	32.7
0.9	41.0	11.2	74.3	225	30.5
1.0	41.6	12.2	73.2	250	29.2
1.1	44.7	14.0	69.7	275	28.4
1.2	47.3	16.0	67.7	300	26.8
1.3	50.1	18.0	66.0	350	23.9
1.4	51.9	20.0	64.8	400	22.6
1.5	54.6	22.5	61.9	450	21.6
1.6	57.9	25.0	60.7	500	20.4
1.7	60.0	27.5	59.4	600	17.5
1.8	60.7	30.0	57.6	700	15.8
1.9	61.2	35	55.6	800	14.5
2.0	60.0	40	53.4	900	13.0
2.1	58.8	45	51.9	1000	11.8
2.2	57.3	50	50.6	1100	11.2
2.3	54.7	60	48.9	1200	10.0
2.5	50.3	70	46.2	1300	9.50
2.7	46.5	75	44.7	1500	8.60
2.9	44.4	80	43.5	1750	7.40
3.1	44.3	90	41.4	2000	6.60
3.2	44.0	100	39.5	2250	5.80
3.7	46.5	110	37.7	2500	5.30
4.2	51.3	120	36.2	2750	4.91
4.7	58.4	125	35.1	3000	4.69
4.9	62.8	140	33.8	3250	4.23
5.2	66.6	160	31.3	3470	3.98
5.5	68.7	175	30.0	4000	3.67
5.7	66.8	180	29.1		
5.9	66.2	200	27.8		
6.2	64.9	220	26.9		
6.7	66.9	225	26.4		
7.2	69.9	250	24.9		

The distinguishable feature of the measured e^--$SiCl_4$ total cross-section, in the whole energy range of interest, is its relatively great magnitude in comparison with the geometrical dimension of the $SiCl_4$ molecule. For the lowest energies applied in our experiment, namely for 0.3 eV, TCS is equal to 40×10^{-20} m^2. Increase of the incident energy dramatically increases the total cross-section up to 61×10^{-20} m^2 at the strong peak centered at 1.9 eV. At 3 eV TCS has a local minimum of 44×10^{-20} m^2. The second, very broad maximum is situated around 9 eV with some additional, well-visible, substructure located on the left-hand side of the maximum slope near 5 eV. Above 10 eV the value of the TCS constantly decreases with the increasing energy and at the highest applied energy, 4 keV, TCS falls down to 3.67×10^{-20} m^2.

With respect to the shape, the present total cross-section function is in good accordance with the experimental data of Wan *et al.* [9] but our results yield distinctly higher values. The discrepancies, amounting up to

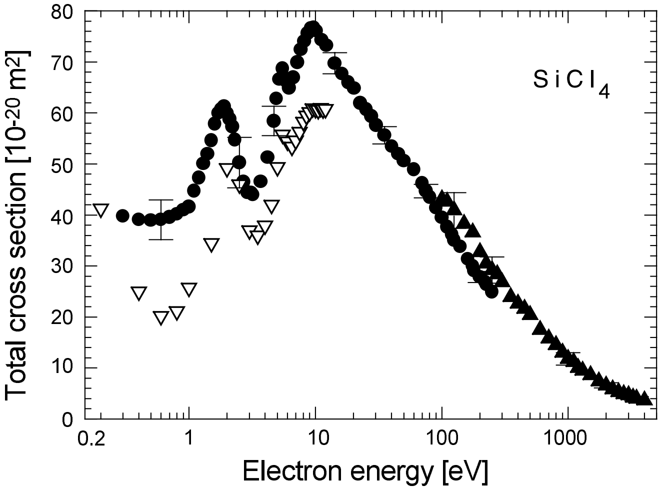

Fig. 1. Absolute experimental total electron-$SiCl_4$ scattering cross-sections: ● present experiment, Gdańsk; ▲ present experiment, Trento; ▽ Wan *et al.* [9]. The error bars correspond to overall experimental uncertainties estimated at selected points.

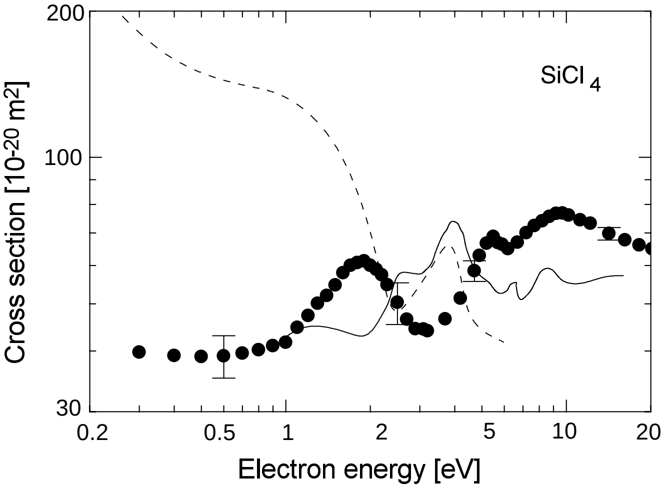

Fig. 2. Comparison between theoretical and experimental cross-sections for electron scattering on $SiCl_4$ molecules: — computed integral elastic cross-section [11]; –– calculated elastic cross-section [10]; ● present experimental absolute TCS from Gdańsk. The error bars correspond to overall experimental uncertainties estimated at selected points.

50% at the lowest energies are, however, well within the limits of combined declared uncertainties of both compared experiments. It is worth mentioning that the observed disagreement may partly result from the use of a guiding magnetic field in TCS experiment of Wan *et al.* [9] which may bring about additional systematic errors [20] usually lowering measured total cross-section. The results from Gdańsk laboratory are on average systematically 12% lower than data from Trento in the overlapping energy range. Nevertheless, this difference is still within limits of the combined overall uncertainties of presented data and may partly result from poorer angular resolution of the low-energy apparatus.

The first sharp structure in the total cross-section located around 1.9 eV may be attributed to a short-lived resonant state created when the incident electron is captured into an unoccupied t_2 orbital of the $SiCl_4$ molecule [10]. Weak resonant feature between 1 and 2 eV is also visible in elastic calculations [11]. A similar strong low-energy maximum has already been observed in TCS for other tetrachlorides: at 1.1 eV for CCl_4 [21] and near 2 eV for $GeCl_4$ [17] and it seems that formation of such resonance in the very low-energy range may be common feature of tetrachloride targets. Resulting temporary negative ion can decay either via autodetachment of the extra electron or via dissociative channel leading to production of the neutral and fragment anion. Around 2 eV, electron attachment experiments showed the presence of Cl^- [2, 4–6], $SiCl_3^-$ [2] and $SiCl_4^-$ [6] ions. Because at thermal energies the yield of parent negative ion, $SiCl_4^-$, production is very effective [2,4] one would expect that towards thermal electron energies total cross-section can rapidly increase, as in the case of CCl_4 molecule. The resonant contribution to the second broad TCS maximum, located around 10 eV, was evidenced by the presence of the number of fragment anions (Cl_2^-, $SiCl_2^-$, $SiCl_3^-$ and $SiCl_4^-$) observed between 4–9 eV [1–7], although at these energies numerous direct processes are also significant. Further, more detailed partitioning of the e^--$SiCl_4$ total cross-section is very umbiguous due to lack of quantitative experimental data on elastic and vibrationally inelastic electron scattering. Above the ionization threshold, processes leading to electron detachment become gradually more important with impact energy increase and near 100 eV the electron-scattering ionization total cross-section reaches its maximum value which usually amounts between one third and a half of the grand total cross-section. Basing on a semiempirical formula [22], we estimated total cross-section for electron induced ionization of $SiCl_4$ and we found that its values comprised in the limits of typical values.

In Figure 2 we compare the low-energy total cross-section obtained in Gdańsk laboratory with the elastic cross-sections calculated by Tossell and Davenport [10] and Natalense *et al.* [11]. It is clearly visible that the calculations give a rather wrong position of the low-energy cross-section maximum—just at the experimental minimum. Additionally, below 2 eV, elastic cross-sections calculated by Tossell and Davenport increase continuously towards lower energies while experimental data decrease in the same energy region.

4 Summary

In the present work we report results of a joint experiment on absolute electron scattering total cross-section measurements for the $SiCl_4$ molecule. Obtained data span from impact energy of 0.3 eV to 4 keV. Results show two distinct resonant structures: the first, very sharp peak near 1.9 eV and the second, very broad maximum centered at 10 eV. Further more detailed experiments are needed for the description of the $SiCl_4$ scattering processes.

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