

Total cross section measurements for electron scattering on silicon tetrafluoride

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Abstract

Total cross sections for electron scattering on SiF₄ have been measured between 0.6 and 3500 eV. An absolute transmission method has been used on two different apparatuses. Evidence for a Ramsauer minimum is found at about 1 eV collision energy. A discussion is given of possible resonant states at low energies. © 1998 Published by Elsevier Science B.V.

1. Introduction

Gaseous silicon halides are widely used in technologies of plasma growth and etching for semiconductor industries. In spite of this, their interactions with charged particles are known in a fragmentary way. In particular, for electron scattering in silicon tetrafluoride (SiF₄) only a few partial cross-section determinations exist: for ionization (up to 125 eV) [1], dissociation into neutrals [2] and dissociative attachment [3]. The electronic excitation differential cross-sections were studied in the limit of forward scattering [4]. Ultraviolet emission cross-sections were given for ionic fragments [5].

Total electron scattering cross-sections were measured between 0.2 eV and 12 eV in a trochoidal spectrometer [6]. In this type of measurement the effective scattering length can differ substantially from the physical length of the scattering chamber. Preliminary results for absolute total cross-sections

between 2 eV and 50 eV were announced by Ma et al. [7], but we are not aware of numerical data.

2. Experimental

The present experiment has been performed by using two different apparatuses, both implementing a transmission method, as described in our previous reports [8,9]. An electrostatic 127° electron spectrometer was used in Gdańsk, covering the 0.6 to 250 eV energy range [10]. A modified Ramsauer-like apparatus was used in Trento performing measurements from 80 to 3500 eV [11]. The length of the interaction region was 30.5 mm in the Gdańsk apparatus and 140.2 mm in the Trento apparatus. It has been demonstrated [10,12] that in both apparatuses the effective scattering length is coincident with the geometrical length, within the measurement errors. The angular acceptance of the collector (the solid angle formed by the collector aperture as seen from

the center of the scattering chamber) was 0.7 and 0.3 msr in the Gdańsk and Trento apparatus, respectively. A retarding field analyzer was used at the exit of the scattering chamber in the Gdańsk apparatus; the bending magnetic field in the Trento apparatus discriminates inelastically scattered electrons if they loose more than 1/16 of their initial energy.

The total cross section $\sigma(E)$ at a given energy E was obtained by measuring the electron currents collected without (I_0) and with (I_p) the target gas, at a pressure p in the scattering chamber. The relationship

$$\sigma(E) = \frac{kT}{pL} \ln \frac{I_0(E)}{I_p(E)}, \quad (1)$$

where k stands for Boltzmann's constant, L is the length of the interaction region and T the gas temperature connects the cross section with the directly measured quantities. Total cross section values given in the following are weighted averages over at least 20 determinations, each of them performed for 8–10 pressure values.

In the high energy experiment two currents, the one reaching the scattering chamber walls (I_s) and the one to the collector (I_c) were simultaneously measured at different pressures of the target gas:

$$\frac{I_{ci}}{I_{ci} + I_{si}} = \frac{I_{cj}}{I_{cj} + I_{sj}} \exp[-\sigma L(n_i - n_j)], \quad (2)$$

where the i and j indexes refer to pressures p_i and p_j , respectively. In a single run, values I_s and I_c for several (5–7) pressures were determined. Four to ten runs were performed at each energy. The measurements of both currents are essential at high energies, where ion bombardment of the cathode can lead to large beam instabilities and large errors in the measured cross section.

The energy scale in the low energy experiment was calibrated to within 60 meV against the vibrational structure in the total cross section of molecular nitrogen at around 2.3 eV [13]. In the high energy apparatus the energy determination spread of ± 0.5 eV results mainly from an adjustment procedure performed by the data acquisition computer.

In the low energy experiment the systematic error due to the uncertainty in the pressure, temperature and the length of the interaction region determinations, was within $\pm 3\%$. The total systematic error

increases to 5% below 1 eV, due to an additional error in measuring low electron currents in the 10^{-12} A range. In the region of a rapid change of the cross section from 4 to 10 eV, the energy scale uncertainty introduces an additional error of about 2%.

No differential cross section data exist to allow the estimate of the angular resolution error in SiF₄. To give an order of magnitude, we mention that the angular resolution error of the Gdańsk apparatus at 250 eV due to elastically scattered electrons has been evaluated to be close to 1% for CH₄ [9]. No data were available for inelastically scattered electrons.

In the Gdańsk experiment, the pressure meter read-out was corrected by Knudsen's thermal transpiration factor $\sqrt{T_s/T_B}$ by measuring both the scattering chamber temperature (T_s) and the Baratron capacitance head temperature (T_B) which was stabilized at 322 K. In the high energy experiment the temperature of the pressure meter was electronically tracking the temperature of the scattering cell to within 0.1°C. This avoids any possible higher-order correction to the thermal transpiration formula and reduces the overall systematic error to 2.5%.

Similar to the low energy apparatus, it is not possible to evaluate the angular resolution error of the Trento apparatus for SiF₄. Again, to set an order of magnitude, we recall that the angular resolution error due to forward elastic scattering has been evaluated as 2% at 3000 eV in CH₄ [9]. An additional error of a few percent results from the poor energetic discrimination of inelastically scattered electrons, which is typical of the Trento apparatus. Note that in the case of non-polar, spherical-like molecules the overall angular resolution error in the Trento apparatus is believed to be less than 10% even at 4000 eV.

In the Gdańsk experiment the statistical uncertainty was typically 1%. At certain energies (at around 8 or 15 eV) more runs were performed with different spectrometer settings in order to reduce the statistical uncertainty of the average cross section value to below 1%.

The typical statistical uncertainty was 2.5% at energies 200–3500 eV. Below 150 eV the statistical error of the Trento data rises up to 5%. This reflects a lower stability of the beam due to influence of stray magnetic fields, usually leading to a slow drift of the I_c current during a computer driven measurement run.

The gas purity (from Air Products, Belgium) was 99.6%, with main impurities being air (< 0.35%) and SO₂ (< 0.05%).

3. Results

The results of present measurements are given in Table 1 and compared with total cross sections of Wan et al. [6] and with available partial cross sections in Fig. 1. The two data sets from collaborating laboratories merge at 80–250 eV within the combined statistical uncertainty. This suggests an agreement of the absolute calibrations of the two instruments which is better than the above quoted systematic errors.

The measured total cross section exhibits a minimum at 1.5 eV and rises quickly (by a factor of 3) between 2 and 7 eV. Some weak structures are superimposed on a broad peak at higher energies. A maximum value of $30 \times 10^{-20} \text{ m}^2$ is reached at 24 eV. Above 100 eV the total cross section falls monotonically to the value of $2.2 \times 10^{-20} \text{ m}^2$ at 3500 eV.

The present data agree well with the shape of the

measurements of Wan et al. [6] in the 5–12 eV range the data are 6% higher on the average. This number remains well inside the combined experimental error bars, the uncertainty of the pressure determination in the experiment of Wan et al. [6] alone, amounting to 11%. The relative difference is higher at lower energies, amounting to 15% at 1 eV. We note, that a guiding magnetic field in the Wan et al. [6] experiment can lead to an underestimation of the total cross section, if a significant amount of electrons undergo inelastic scattering in the forward direction. This can be in the case of the direct (non-resonant) vibrational excitations at low energies.

The SiF₄ total cross section in the limit of thermal energies. Theoretical calculations [14] for the elastic cross section indicate the presence of a shallow Ramsauer minimum at about 1.5 eV and a low energy rise. However, the absolute theoretical values exceed the present data by a factor of 4 in the minimum, see Fig. 1.

Note that, without excluding the presence of the Ramsauer minimum in the elastic channel, the low energy rise of the total cross sections can also result from vibrational excitation. Born's approximation

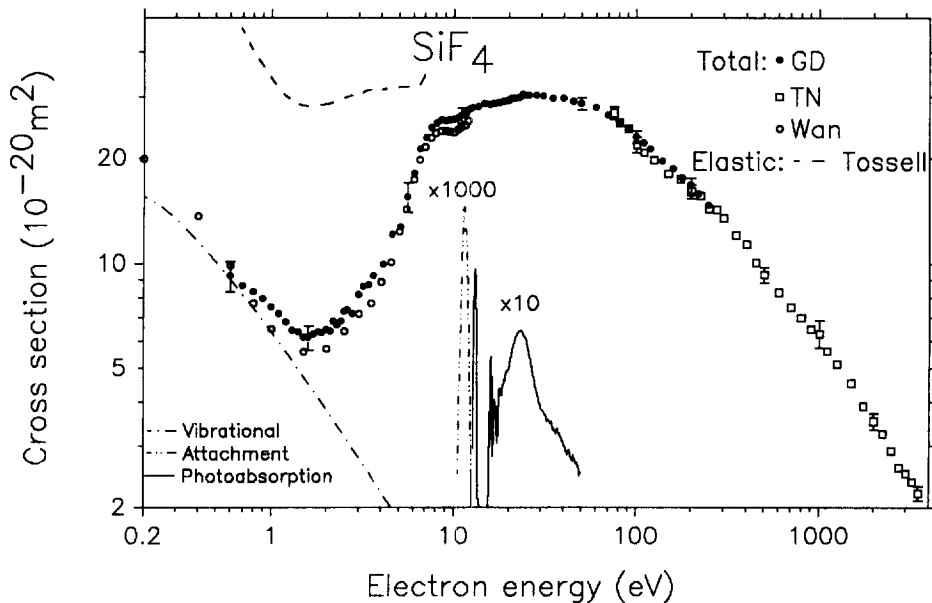


Fig. 1. Integral cross sections for electron scattering on SiF₄. Total: full circles, present Gdańsk data; open squares, present Trento data, open circles, experimental of Ref. [6]; broken line, theoretical elastic of Ref. [14]. Vibrational, dash-dot line, Born model, see text. Attachment, dash-dot-dot line, Ref. [5]. Photoabsorption, continuous line, electron-scattering experiment of Ref. [4].

can be used to evaluate the absolute values of the vibrational excitation integral cross section. In this approximation the integral cross section for the direct (non-resonant) vibrational excitation can be calculated as [15]

$$\sigma_{\text{vib}}(v \rightarrow v') = \frac{8\pi}{3k^2} g' |\langle v' | D | v \rangle|^2 \ln \frac{k+k'}{|k-k'|}, \quad (3)$$

where $|\langle v' | D | v \rangle|$ is the dipole matrix element for the transition between the v and v' vibrational states and k and k' are the wavenumbers before and after the transition, respectively. The applicability of the Born approximation has been proved, within experimental uncertainty, for such tetrahedral molecules as CH_4 [16] and CF_4 [17].

In the evaluation of the vibrational cross section for SiF_4 from Eq. (3), the transition dipole moments of Ref. [18] have been used. The result for the sum of the fundamental vibrational modes is presented in Fig. 1. The vibrational cross section matches well with the low energy rise of the present data; this indicates also its high share in the total cross section minimum.

The difference between the experimental total values and the present vibrational cross section estimate gives a rough evaluation for the elastic cross section. This difference reaches a minimum of less than $1 \times 10^{-20} \text{ m}^2$ at about 0.6–0.8 eV, depending somewhat on the total cross section data set chosen (Ref. [6] or present). Furthermore, such an estimate of the elastic cross section gives a value of $4 \times 10^{-20} \text{ m}^2$ at 0.2 eV.

In the region 7–22 eV several shoulder structures and weak maxima are visible in the total cross section. These structures remain within the summed statistical and systematical uncertainty of the present experiment. However, the maxima at 8.5 and 14.0 eV persisted in all measurement series, independently from the electron optics settings. As follows from our previous measurements for the total cross section in air and SO_2 [10], they cannot be caused by gas contaminants. Therefore, we consider the structures not to be an experimental artifact, but to correspond to resonances in the elastic channel and/or to local maxima for inelastic processes in SiF_4 . The shoulder structure at 8.5 eV is also visible in the total cross section measurements of Wan et al. [6]. Dis-

Table 1

Absolute total cross section (TCS) for electron scattering on SiF_4 molecules in units of 10^{-20} m^2 . The first and the second TCS columns are results from Gdańsk, the third column are results from Trento

Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS
0.6	9.3	10.6	26.1	75	26.9
0.7	8.6	11.1	26.5	80	25.3
0.8	8.3	11.6	26.8	90	24.3
0.9	7.9	12.1	27.5	100	21.9
1.0	7.5	12.6	27.9	110	20.8
1.1	7.2	13.6	28.0	125	19.8
1.2	6.8	14.6	28.6	150	18.1
1.3	6.5	15.6	28.5	175	17.4
1.4	6.4	16.6	28.6	200	16.1
1.5	6.2	17.6	28.7	225	15.7
1.6	6.1	18.6	29.0	250	14.4
1.7	6.3	19.6	29.2	275	14.2
1.8	6.4	20.1	29.3	300	13.5
1.9	6.3	20.6	29.7	350	12.1
2.0	6.5	21.6	29.7	400	11.4
2.1	6.4	22.6	29.8	450	10.1
2.2	6.8	23.1	30.0	500	9.30
2.3	6.7	23.6	30.3	600	8.28
2.4	6.8	24.6	30.3	700	7.52
2.5	7.3	25.6	30.3	800	6.99
2.6	7.4	28.1	30.2	900	6.50
2.8	7.2	30	30.1	1000	6.30
3.0	8.2	35	29.7	1100	5.61
3.2	8.6	40	29.6	1250	5.15
3.4	8.7	45	29.1	1500	4.53
3.6	9.2	50	28.6	1750	3.89
4.1	10.0	60	27.8	2000	3.52
4.6	12.1	70	26.5	2250	3.24
5.1	12.8	80	25.3	2500	2.90
5.6	15.5	90	24.3	2750	2.60
6.1	18.1	100	23.1	3000	2.50
6.6	21.3	110	22.2	3250	2.37
7.1	22.9	120	21.3	3500	2.19
7.6	24.5	140	19.7		
8.1	25.3	160	18.6		
8.6	25.8	180	17.5		
9.1	25.7	200	16.8		
9.6	25.8	220	15.8		
10.1	25.9	250	14.7		

cussion of a possible origin of the 8.5 and 14 eV structures will be given in Section 4.

Above 20 eV an increasing contribution to the total cross section comes from ionization processes. Available data indicate that at 60 eV the most efficient is the dissociative ionization leading to the

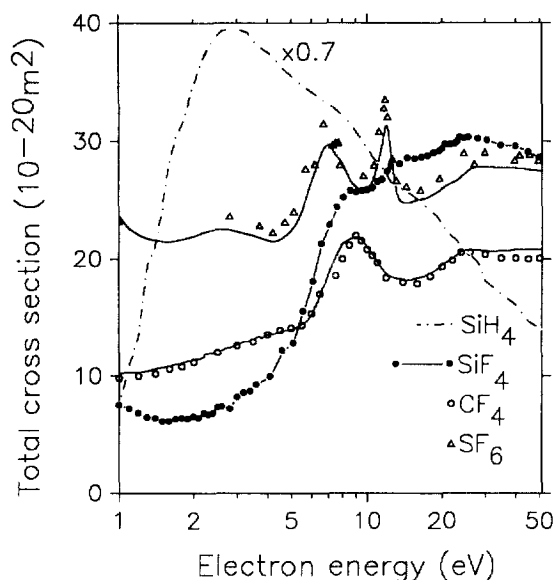


Fig. 2. Comparison of total cross sections for fluorine-containing molecules. SF_6 : rhombes, Ref. [28]; line, Ref. [26]. CF_4 : line, Ref. [27]; circles, Ref. [29]. SiF_4 : line with symbols, present. SiH_4 : dashed-dotted line, Ref. [21].

formation of SiF_3^+ ions; the cross section for this process [1] amounts to 25% of the present total cross section value. Formation of parent SiF_4^+ ions and dissociation into neutral SiF_3 radicals are one order of magnitude less probable [2] at this energy. This partitioning feature resembles the SiH_4 ionization/fragmentation pattern [2,19]. We also note a relatively low probability of forming ions and radicals in excited states for SiF_4 . The overall cross section for these processes, as estimated from UV emission is merely $0.13 \times 10^{-20} \text{ m}^2$ at 100 eV, 4 times less than for the CF_4 molecule [5].

The present measurements show that the energy dependence of the SiF_4 total cross section is essentially different from that for SiH_4 [20–22], see Fig. 2. The latter exceeds the SiF_4 total cross section in the whole 1–25 eV range [20,21], getting lower by a factor of 2 above 100 eV [22].

In comparison with other fluorides, above 100 eV the SiF_4 cross sections remain higher than that for CF_4 [23] but lower than that in SF_6 [24]. The relative difference remains constant in the 1000–3500 eV range, amounting to +20% and –33% for CF_4 and SF_6 , respectively.

4. Resonant states discussion

Low energy structures in the total cross section can be caused either by maxima in the inelastic (e.g. electronic excitation, dissociation and ionization) cross sections or by (resonant) features in the elastic cross section, possibly accompanied by enhanced vibrational excitations.

The results of Refs. [1,2] exclude the possibility that the presently observed structures at 8.5 and 14 eV could follow from peaks in the cross sections for fragmentation into neutrals or for ionization. Furthermore, the first peak lies below the threshold for the electronic excitation [4].

Electron scattering between 0.2 and 12 eV on SiH_4 , silicon halides (SiF_4 , SiCl_4 , SiBr_4 , SiI_4) and hydrochlorides (SiH_2Cl_2 , SiHCl_3) was studied experimentally and theoretically by Wan et al. [6]. All the tetrahedral molecules out of this list, apart from SiF_4 , showed in the experiment a resonant state at energies below 3 eV. This resonance results from a temporary capture of the incoming electron to an unoccupied molecular orbital. The energy of the resonance, visible both in the total scattering and in the dissociative attachment channels moves from 2.9 eV in SiH_4 to 2.2 eV in SiCl_4 and 1.2 eV in SiBr_4 [6].

Wan et al. [6] noticed that the sum of this resonance energy and the ionization energy of a corresponding (i.e. occurring with respect to this particular molecular orbital) inner-shell excited state remains constant ($= 6.1 \text{ eV}$) for all the tetrahedral molecules considered. Based on this observation and the inner shell excitation data [25] they predicted a resonant energy of 2.9 eV for the t_2 state of SiF_4 . Neither their measurement [6] nor the present absolute measurements indicate the presence of such a resonance. According to continuum multiple-scattering parametric-exchange molecular-orbital calculations [14], only a broad shoulder in the t_2 resonant channel is visible at 3 eV. Note, however, a poor agreement of the calculations with the present absolute values, as seen in Fig. 1.

Ma et al. [7] reported two peaks in their total cross section measurements between 2 and 50 eV: the first one has been located between 7–9 eV and the second at 17 eV. Ma et al. noticed also that the first maximum resembles the low energy peaks ob-

served in the SF₆ [26] and CF₄ [27] data from their laboratory and by analogy attributed both resonances to the presence of fluorine atoms.

In Fig. 2 the present SiF₄ total cross sections have been compared with those of other fluorides, SF₆ and CF₄. In SF₆ two sharp peaks are visible below 20 eV [26,28], the first one occurring at 7.05 eV [26]. Only one pronounced peak is observable in CF₄ at 9 eV [27,29]. We note that the position of the first peak in SF₆, SiF₄ and CF₄ moves, in the order, to a higher energy and its absolute value lowers. Such a behavior of resonance maxima in the total cross section have been noticed also for the linear triatomic molecules CO₂, N₂O and OCS [30].

In SF₆ the 7.05 eV maximum is due to a temporary capture of the incoming electron to a triply degenerate f_{1u} molecular orbital belonging to the O-symmetry point group. The *l* = 1 and *l* = 3 partial waves are involved in this resonance [31]. In CF₄ the peak in the total (and vibrational) cross section has been attributed to the *l* = 1 electron capture into the similarly degenerate t₂, tetrahedral symmetry orbital [32,33]. By analogy, one could expect triply degenerate, i.e. t-symmetry for the 8.5 eV resonance in SiF₄. Detailed quantum chemistry calculations would be desirable.

The nature of the feature in the total cross section at about 14 eV is less clear. As indicated by electron scattering measurements in the photoabsorption limit [4], it could result from enhancement of the electronic excitation cross section. A sharp peak for the double 1t₁ – 3s, 5t₂ – 6a₁^{*} process [4] (the asterisk denoting a virtual valence orbital) is observed between 12 and 14.5 eV. The absolute value for the photoabsorption cross section maximum (1.0 × 10⁻²⁰ m²) is lower than the amplitude of the shoulder structure in the total cross section. Note, however, that the electronic excitation cross section can exceed the photoabsorption one and be clearly visible in the total cross section. However, the vicinity of the dissociative attachment peak makes a hypothesis on the resonant nature of this structure plausible.

The dissociative attachment cross-section in SiF₄ (for SiF₃⁻ and F⁻ production, predominantly) reaches a maximum of 1.5 × 10⁻²² m² at 11.4 eV [3,34], i.e. at a somewhat lower energy than the second peak observed in the present data. As noticed by Mann and Linder [17] for carbon halides CF₃Cl and CF₂Cl₂,

the peaks in the electron attachment cross section usually precede the maxima in the vibrational excitation. Such a coupling between the dissociative attachment and vibrational channels testify the existence of resonant processes.

In SiF₄ at 14 eV, the vicinity of the threshold for a double electronic excitation, could indicate the possibility of forming a Feshbach-resonance, with the two (one excited and one attached) electrons in the 3s6a₁^{*} molecular orbital configuration. A close spacing between atomic Rydberg and molecular valence levels [35] does not exclude, however, the possibility of other resonance configurations. Measurements of the vibrational excitation are needed to decide about the existence and the configuration of a possible resonant state at 13–14 eV.

5. Conclusions

The total cross section for electron scattering in SiF₄ exhibits a large maximum, changing by less than 20% between 10 and 100 eV.

The existence of a deep Ramsauer minimum in the elastic cross section, masked in the total cross section by the vibrational excitation can be deduced from present data below 4 eV. Resonant structures in the 7–20 eV range resemble features observed in total cross sections for other fluorides, CF₄ and SF₆.

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