Electron scattering from disilane (Si₂H₆) molecules. Absolute total cross section measurements from 1 to 370 eV

Czesław Szmytkowski, Paweł Możejko and Grzegorz Kasperski

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

Abstract
Absolute grand total cross sections (TCSs) for electron–disilane (Si_2H_6)
scattering have been measured over the energy range from 1 to 370 eV in
a linear transmission experiment. The low-energy TCS is dominated by a
broad resonant-like enhancement. In the region of the maximum the present
grand TCS values appeared to be distinctly lower than previously reported
integral elastic cross section data. A comparison of total electron scattering
cross sections for the two simplest silicon hydrides and relevant hydrocarbons
is given.

1. Introduction

The interest in collisions involving electrons and disilane molecules is mainly stimulated by
the possible importance of this compound in semiconductor technology (Kushner 1988, Hanna
et al 1996). For modelling and diagnostics of disilane containing low-temperature plasmas,
which may be applicable in the processing and fabrication of microelectronic materials and
devices, an extensive range of accurate and reliable data on particular electron-impact Si_2H_6
processes is required.

　　Despite this, investigations into electron–disilane scattering have received only a moderate
amount of interest. The earliest measurements of electron–disilane scattering were presented
by Potzinger and Lampe (1969) and concerned energetics of the positive- and negative-
fragment-ion formation at low impact energies. Cross sections for the production of numerous
negative-ion fragments by electron attachment and ion pair formation have been measured
more recently by Krishnakumar *et al* (1991) in a crossed-beam experiment. Perrin *et al*
(1982) reported measurements of the total dissociation cross section of disilane molecules
in a multipole discharge reactor, whilst Perrin and Aarts (1983) determined, with the same
technique, emission cross sections of electronically excited neutral and ionized fragments
produced by electron-induced dissociation. Experimental total and partial cross sections for
electron collisional ionization at energies ranging from threshold to 300 eV have been presented
by Chatham *et al* (1984) while Krishnakumar and Srivastava (1995) extended measurements

to cover energies up to 1000 eV. Dillon *et al* (1994) obtained angular distributions of elastically scattered electrons over a range of 10–130° at incident energies between 2 and 100 eV and determined integral elastic and momentum transfer cross sections in this energy regime. In addition, they made observations of low-energy shape resonance in vibrational excitation functions. It is worth emphasizing that all those cross sections have been placed on an absolute scale by use of normalization procedures. Hayashi (1985) compiled the early electron–disilane scattering data and also gave references to less accessible works on swarm experiments. Theoretical interest in electron–disilane scattering has been confined to elastic low-energy (Winstead *et al* 1991, Bettega *et al* 1993, 1998, Dillon *et al* 1994) and intermediate-energy elastic (Możejko *et al* 2000) scattering and electron induced ionization (Ali *et al* 1997, Deutsch *et al* 1998).

To our best knowledge, no $e^- - Si_2H_6$ grand total cross section (TCS), either experimental or theoretical, is available in the literature.

The present measurements of the grand TCS across energies from very low ($\sim$1 eV) up to intermediate (370 eV) are intended to yield a reliable set of absolute data. As the grand TCS forms the upper limit of any particular cross section it can serve as a test for the correctness of procedures used for normalization of relative data. Absolute results for the disilane molecule may also be used to assess the reliability of theoretical electron-scattering models and the potential of computational procedures applied for polyatomic targets. The present results, together with data reported so far, could provide an impulse for a preliminary examination of systematics in the electron scattering cross sections of polyatomic X_nY_m homologues (X = C, Si, Ge, . . . and Y = H, F, Cl, . . .).

2. Experiment

The experiment was performed with an electrostatic electron spectrometer described in detail in previous papers (Szmytkowski *et al* 1998, Szmytkowski and Możejko 2001) and only a brief outline of the apparatus and procedure will be given here. A monochromatic electron beam ($\Delta E = 80$ meV, FWHM) of variable energy is produced by a system consisting of a thermionic electron source, a 127° electrostatic energy dispersing element and electrostatic optics. The energy scale of the electrons was calibrated to within ± 0.1 eV by reference to the resonance structure of N_2 in the 2 eV region. The electrons of desired energy are then directed into a collision cell containing the target gas of interest. Those electrons which emerge from the cell through the exit orifice are energy discriminated with a retarding field analyser and collected with a Faraday cup detector. The TCS $Q(E)$ at each electron impact energy E is measured through attenuation of the incident electron beam and derived using the Bouguer–de Beer–Lambert relationship

$$I(E, n) = I(E, 0) \exp[-Q(E)nl],$$

where $I(E, n)$ and $I(E, 0)$ are the electron current intensities with and without the gas target respectively, n is the target number density and l is the effective path length of impact electrons through the target. The density number, n, was evaluated from the ideal gas law based on absolute measurements of the target pressure in the reaction volume and the target temperature. Pressure readings were corrected for the thermal transpiration effect according to the Knudsen (1910) formula.

Before presenting and discussing the results of the reported measurements, it is appropriate to mention some difficulties we met in the course of the experiment related to the compound under study; their accumulation and arduousness were exceptional in the whole of our practice of TCS measurements. Above all, the presence of disilane molecules in the region of the

filament, due to effusion of the gas from the collision cell through its orifices, essentially reduced the electron current emission from the filament and this effect even increased with time of exposure to the gas. To carry out the experiment it was necessary to increase the cathode current to 1.5 A (in a typical experiment ∼1.1 A). Moreover, we have noticed that changes of the disilane partial pressure, of the order of several per cent, in the region of the filament clearly influenced the filament emission and intensity of the primary electron current, $I(0)$, and in consequence might affect the measured cross section values. In order to lessen variations of partial target pressure in the electron optics region the target sample was supplied alternately into the collision cell or on its periphery in such a way that conditions along the path of the electron beam outside the reaction volume were stable throughout the experiment, irrespective of whether the target gas was present in or absent from the collision chamber. The working pressure of disilane in the scattering cell was maintained below 150 mPa, ensuring negligibility of multiple-scattering events at the sufficient attenuation ($I(E, 0)/I(E, n) \leqslant 1.5$) of the electron beam while keeping the partial pressure of disilane in the region of the electron gun as low as possible (∼0.3 mPa). The background pressure in the electron optics container was about 5 μPa. Moreover, the presence of the gas in the region of the electron optics strongly influenced the surface of the electrodes and in consequence lowered the electron beam transmission through the lens system; these effects also accumulated with time of exposure to the gas. Restoration of adequate conditions for measurements was possible only after frequent cleaning of the electron optics elements. Finally, it should be added that numerous vacuum system elements suffered from the strong influence of the target gas. As a result, the present experiment was exceptionally laborious and its duration very prolonged.

Measurements at given energy E were carried out in series at different target pressures. It was found that the TCSs obtained in the same series at the same energy were, within the random experimental uncertainties (3–4% between 1 and 5 eV and less than 2% above 10 eV), independent of the electron-beam intensity and the applied target pressure. Somewhat higher divergence (∼5%) appeared between TCSs derived in series taken just before and after cleaning of the electron optics. The overall systematic uncertainty in the measured cross section, estimated from a combination of potential systematic errors of measured individual quantities used for TCS derivation, amounts to about 10% below 5 eV, decreasing to 5% between 10 and 100 eV and increasing to 6% at the highest applied energies. More details on the analysis of uncertainties in our experiments have been given elsewhere (cf Szmytkowski *et al* 1997). The final TCS value at each particular energy is a weighted mean of a large number of data obtained in independent series (four to 24) of individual runs (five to ten in a series). Below 1 eV instabilities of the primary electron beam were so high that in consequence the scatter of results in a series exceeded the estimated systematic uncertainties considerably.

The sample gas, of semiconductor grade (Aldrich, 99.998%), was used directly from the cylinder without any further purification.

3. Results and discussion

The absolute TCSs for electron impact energy from 1 to 370 eV, determined as described in section 2, are presented in numerical form in table 1 and are shown in figure 1. Figure 2 compares the present measured TCSs with the available integral elastic and total ionization cross sections, both experimental and theoretical.

The most visible feature of the e$^-$–Si$_2$H$_6$ TCS energy dependence is the broad enhancement located at low energies. The variation of the TCS function between 1.5 and 20 eV suggests that it may consist of two structures: the first quite prominent peak with the

Table 1. Absolute TCS measured for electron impact on Si_2H_6 molecule in units of 10^{-20} m^2.

Energy (eV)	TCS Si_2H_6	Energy (eV)	TCS Si_2H_6	Energy (eV)	TCS Si_2H_6
1.0	49.6	5.3	70.6	35	44.3
1.1	51.8	5.8	69.0	40	41.5
1.2	56.4	6.3	69.7	45	38.4
1.3	60.2	6.8	68.1	50	36.6
1.4	61.8	7.3	68.4	60	34.0
1.5	66.8	7.8	69.0	70	32.3
1.6	70.4	8.3	67.8	80	30.4
1.7	71.8	8.8	67.0	90	27.5
1.8	74.4	9.3	66.6	100	26.2
1.9	75.0	9.8	64.7	110	25.8
2.0	76.1	10.3	64.5	120	24.7
2.1	77.1	11.3	63.7	140	22.8
2.2	75.3	12.3	62.5	160	21.4
2.3	76.6	14.3	60.5	180	19.4
2.6	76.4	16.3	58.5	200	18.0
2.8	77.3	18.3	56.6	220	15.8
3.0	75.3	20.3	55.6	250	14.9
3.3	73.3	22.8	53.4	275	14.2
3.8	71.0	25.3	50.4	300	13.1
4.3	69.3	27.8	48.0	350	11.5
4.8	69.0	30.0	46.2	370	11.4
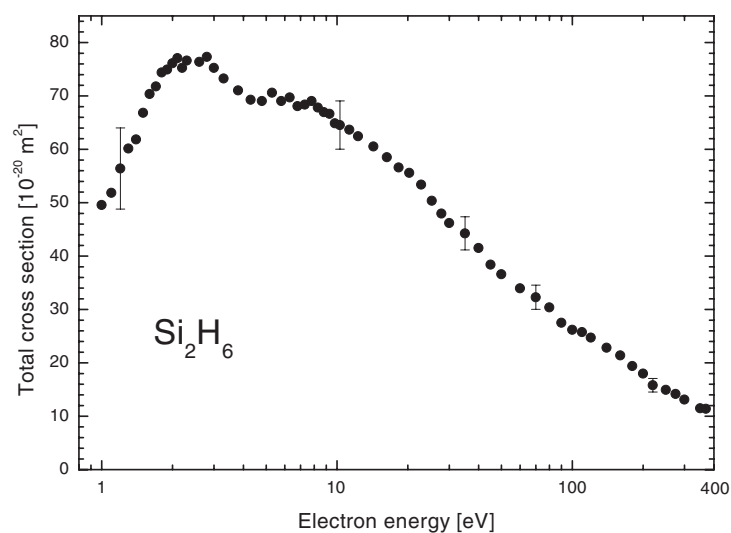
Figure 1. Absolute total electron–Si_2H_6 scattering cross section: ●, present results. The error bars on selected points represent the total (systematic plus statistical) experimental uncertainties.

maximum value of 78×10^{-20} m^2 is located around 2.5 eV while the second much weaker structure appears near 7 eV. The two-peaked maximum, with nearly the same peak positions, is also visible (figure 2) in the integral elastic cross section calculated by Bettega *et al* (1993). This agreement is, however, somewhat surprising as calculations have been performed in the static-exchange approximation, which usually locates maxima at too high energies. In contrast
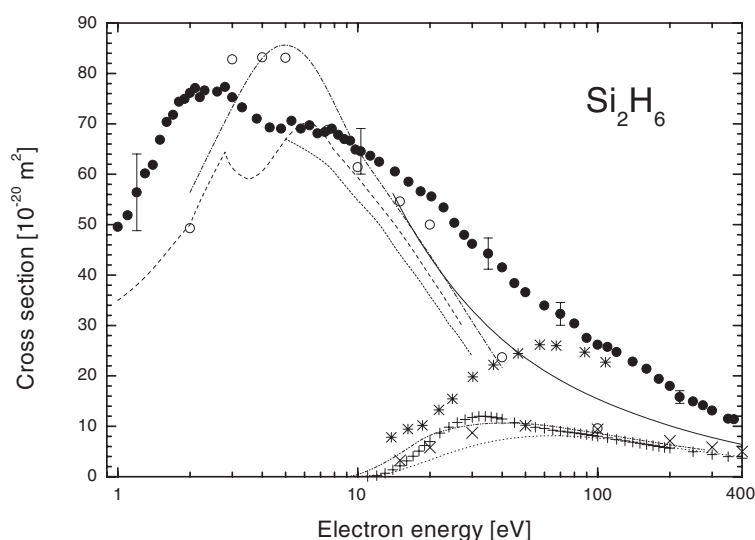
Figure 2. Electron scattering cross sections for disilane. Experimental: ●, TCS, present; ○, integral elastic, Dillon *et al* (1994); *, total dissociation, Perrin *et al* (1982); ×, total ionization, Chatham *et al* (1984); +, total ionization, Krishnakumar and Srivastava (1995). Theoretical: - - - -, integral elastic, Schwinger multichannel variational (SMC) method, static-exchange approximation, Winstead *et al* (1991); — — —, integral elastic, static-exchange approximation, SMC with pseudopotentials, Bettega *et al* (1993); — · —, integral elastic, continuum multiple scattering (CMS), static-exchange-polarization, Dillon *et al* (1994); ——, integral elastic, independent atom model (IAM), Możejko *et al* (2001); · · · · ·, total ionization, binary-encounter-Bethe model (BEB), Ali *et al* (1994); — · · —, total ionization, modified additivity rule (MAR), Deutsch *et al* (1998).

to this type of behaviour elastic measurements and continuum multiple-scattering calculations of Dillon *et al* (1994) exhibit only a single broad maximum centred close to 5 eV.

Investigations of Dillon *et al* (1994) indicate that in the region of the TCS enhancement elastic scattering dominates and that the cross section increase may be attributed to a shape resonance formation through temporary trapping of the impinging electron into the lowest unoccupied orbitals of the molecule (LUMO). The resulting short-lived negative ion, $(Si_2H_6^-)^*$, can decay either via autodetachment of the extra electron or via a dissociative channel leading to production of the neutral and fragment anion. Resonances occurring in electron scattering often enhance inelastic cross sections and generate distinct structures in some energy regimes. Therefore, compared with elastic scattering, inelastic channels offer advantages for the study of resonances. The creation of the e^-–Si_2H_6 compound state at around 2 eV, close to the first maximum of the present TCS, was very clearly manifested by a prominent peak observed by Dillon *et al* (1994) in an inelastic decay channel involving vibrational excitation of the disilane electronic ground state. Unfortunately, the vibrational excitation function was presented in relative units only and estimation of the role of this inelastic scattering channel is therefore as yet not possible. Further evidence for the formation of low-energy resonances comes from studies of the competitive dissociation decay channel. The fragmentation of disilane resonant states into a variety of negative ions was first observed by Potzinger and Lampe (1969) around 7 and 15 eV, in the energy regime of the second feature observed in the TCS. Those early findings were verified subsequently by Krishnakumar *et al* (1991), who, in addition, detected fragment molecular anions also at lower electron impact energies, between 1 and 2 eV. From

their measurements it follows, however, that the contribution of the dissociative attachment channel to the TCS is rather small, and near 7 eV, where the yield of negative ions reaches the maximum, it amounts to no more than 0.02%. In contrast to the major structure, around 2 eV, which was attributed to shape resonance creation, the second feature, near 7–8 eV, may be due to the combined influence of the overlapping Feshbach resonances created when the extra electron is bond to electronically excited states of the disilane molecule.

In default of other TCS data we may compare our results only with the 'total' cross section which is the direct sum of available cross sections for processes contributing greatly to the scattering. With regard to the very general trend the present TCS function is roughly similar to integral elastic measurements of Dillon *et al* (1994) and calculations of Bettega *et al* (1993) and Dillon *et al* (1994) (figure 2). The sharp increase is visible on the low-energy side of each cross section function, both elastic and total, while above 10 eV the cross section smoothly decreases with the energy increase. Some peculiarity, however, is evident with respect to the absolute magnitude of experimental findings: around the maximum the elastic data are about 20% higher than the TCSs. Although the apparent differences do not exceed the limits of combined declared uncertainties of compared experiments they are, however, too distinct, so are worthy of some comment on their possible origin. If the low-energy elastic data were correct that would imply that the TCS around the maximum should amount to nearly 100×10^{-20} m^2, a value which in this energy regime was hitherto obtained only for strongly polar molecules. It also would mean that the maximum TCS value for disilane would be twice that for silane while the inspection of data for hydrocarbons (e.g. Brüche 1930) and perfluorocarbons (cf Szmytkowski *et al* 1992, 2000, Sanabia *et al* 1998) reveals that the electron total scattering cross section does not increase drastically with the increase of the number of carbon atoms in the molecule and one would expect a similar trend for silicon-substituted hydrides. It is worth noting that the TCSs for more than 40 targets obtained so far in our group are among the highest or even exceeded data from other laboratories, especially in the low-energy region. The above, of course highly conjectural, arguments suggest that the surprising proportion of elastic and total experimental values may arise through the normalization procedure in the elastic experiment.

From the ionization threshold upwards, where electron ejection processes become more important with the increase of impact energy, the TCS monotonically decreases and the agreement between the TCS and the sum of its main constituents (elastic + ionization) is quite satisfactory. On the other hand, the sum of the experimental elastic (Dillon *et al* 1994) and dissociative (Perrin and Aarts 1983) cross sections yields, at 100 eV, a value in excess of the grand TCS. The same effect has already been observed for silane (Szmytkowski *et al* 1997) and was accounted for by an overestimation of the dissociative cross section.

To complement the presented data, it is worth noting that one or two very uncertain measurements performed between 0.5 and 1 eV (not presented in figure 1) suggest a further decrease of the TCS function towards very low impact energies. Si_2H_6 is a symmetric non-polar molecule and it has a high electrical dipole polarizability (11 Å^3), therefore one would expect that at epithermal electron energies the disilane molecule is, like SiH_4, CH_4 and C_2H_6, very transparent to electrons and that the electron–disilane TCS possesses a Ramsauer–Townsend minimum.

Having in hand the results for carbon compounds (CH_4, C_2H_6) and their silicon containing homologues (SiH_4, Si_2H_6) we can search for some trends in these molecules. It is clearly visible that substitution of a silicon atom in place of the carbon effects the shift of the resonant peak position from 7 to 8 eV for carbon compounds down to 2–4 eV for silicon hydrides (figure 3). Such behaviour suggests that the lowest energy resonance is mainly associated with temporary trapping of the extra electron in a X–H (X = C, Si) molecular orbital. More attentive inspection of the TCS energy dependences for C_2H_6 and Si_2H_6 reveals that for both molecules a weak
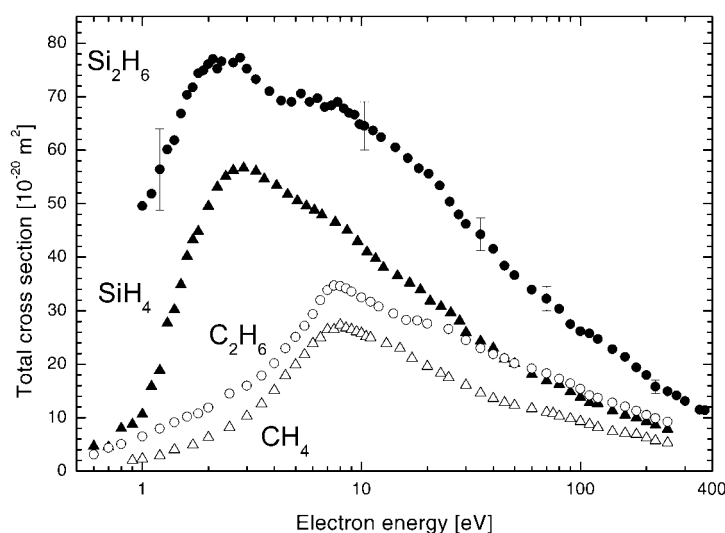
Figure 3. TCS for electron scattering from perhydrogenated molecules: ●, Si$_2$H$_6$, present; ▲, SiH$_4$, Szmytkowski *et al* (1997); ○, C$_2$H$_6$, Szmytkowski and Krzysztofowicz (1995); △, CH$_4$, Zecca *et al* (1991).

structure is superimposed on the high-energy side of the enhancement, while cross sections for methane and silane have a sharp maximum without any additive features. This means that the detailed structure of the TCS function may be sensitive to the length of the molecular backbone chain. At intermediate energies where direct scattering processes dominate there is evident a straightforward relation between the size of the target molecule and the magnitude of the respective intermediate TCS: the larger the molecule, the higher the cross section (figure 3). From 30 eV upwards, all compared TCS functions monotonically decrease with increase of electron incident energy and their energy dependence can be reasonably described with a simple formula: $Q(E) = A \times E^{-a}$, where parameter a is slightly below 0.5 for hydrocarbons while somewhat above 0.5 for their silicon analogues. Such energy dependence demonstrates that the intermediate TCS is roughly proportional to the time the electron needs to pass by target molecule dimension.

4. Conclusions

In this paper we have presented the results of our absolute TCS measurements for electron scattering from the Si$_2$H$_6$ molecule over a wide range of incident electron energies, from the low- (1 eV) up to the intermediate- (370 eV) energy regime. The TCS function at low energies is dominated by strong resonant enhancement. There is rather poor accordance with regard to the positions of the features visible in the present TCS function and in elastic results while there is serious disagreement in absolute magnitude between experimental elastic and TCS data. We suggest that the elastic integral data in the region of the cross section enhancement might be overestimated.

As the experiments published so far cannot satisfactorily explain the role of particular processes in the low-energy resonant-like enhancement, further and more detailed studies on electron–disilane scattering are necessary. Extension of measurements towards lower energies would solve a question of the Ramsauer–Townsend minimum presence.

Acknowledgment

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