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Intermediate-energy total cross sections for electron scattering on GeH_4

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Abstract. Absolute total cross sections for electron scattering on GeH_4 molecules have been measured between 75 and 4000 eV. The dependence of the total cross section on energy is revealed to be different than for the lighter hydrides, CH_4 and SiH_4. It has been noticed that in the high energy limit the total cross sections for hydrides tend to the values of the corresponding isoelectronic noble gases. Self-consistency between different experimental partial cross sections and the absolute total cross section is checked for CH_4, SiH_4 and GeH_4. Upper limits for dissociation into neutral fragments are set for these gases. By comparison of the partial cross sections selected in this way, a conclusion on different partitioning schemes for noble gases and noble-like molecules (CH_4, SiH_4, GeH_4) is drawn. At intermediate energies the inelastic processes dominate the electron scattering on molecules. At 100 eV the elastic cross sections are almost equal for the pairs CH_4–Ne, SiH_4–Ar, GeH_4–Kr.

1. Introduction

Electron scattering on germane (GeH_4), in spite of its great importance for understanding discharge mechanisms in processes of plasma deposition and doping in the semiconductor industries (see, e.g., Stutzman *et al* 1989), has received little experimental attention. Recently, Dillon *et al* (1993) have measured elastic and vibrational excitation cross sections between 1 and 100 eV. Electron-impact dissociation and ionization have been evaluated in a discharge experiment by Perrin and Aarts (1983). To our knowledge, no electron-beam measurements of ionization, electronic excitation, electron attachment or total cross sections have been performed until now.

Germane belongs to the group of quasi-spherical molecules (T_d point group) and is particularly similar to silane (SiH_4) as far as concerns the bond length and the polarizability. The values of selected molecular parameters for methane, silane and germane are given in table 1. Silane and methane exhibit striking similarities in the energy dependency of their total cross sections: the Ramsauer minimum occurs at about 0.3 eV followed by a broad maximum in the few eV range (Ferch *et al* 1985, Wan *et al* 1989). Above 75 eV the total cross sections for both molecules behave in a Born-like way, decreasing inversely with energy at the high energy limit (Zecca *et al* 1992a). Recent measurements of elastic scattering (Dillon *et al* 1993) indicate that similar

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Table 1. Some molecular parameters of CH_4, SiH_4 and GeH_4. If not stated separately, the data are from Lide (1991).

Molecule	Bond length (Å)	Bond strength (kcal mol^{-1})	Ionization potential (eV)	Polarizability (Å^3)
CH_4	1.09	104.8	12.6	2.59
SiH_4	1.48	90.1[a]	11.3[b]	4.5[c]
GeH_4	1.53	78.0[d]	10.47[f]	4.0[i]
		84.8[e]	10.51[g]	5.2[j]
			11.31[h]	6.57[c]

[a] Ho *et al* (1985).
[b] Chatham *et al* (1984) (electron beam).
[c] Gianturco *et al* (1992).
[d] Agrawalla and Setser (1987).
[e] Binning and Curtiss (1990b).
[f] Binning and Curtiss (1990a).
[g] Ruščić *et al* (1990) (photoionization mass spectrometry).
[h] Potts and Price (1972) (photoelectron spectroscopy).
[i] Estimated from values for $GeCl_4$ and GeH_3Cl.
[j] Used by Dillon *et al* (1993).

features as for methane and silane can also be observed in the total cross section for germane.

Recently, a number of theoretical calculations have been performed for low-energy elastic electron scattering in GeH_4. All these calculations agree on the existence of a resonant-like broad peak around 5 eV, but differ in predicting absolute values of their cross section. While Bettega *et al* (1993) pointed out that their calculated SiH_4 and GeH_4 integral elastic cross sections practically coincide in the 1–20 eV energy range, the calculations of Winstead *et al* (1991) indicated lower cross section values for GeH_4 than for SiH_4, between 5 and 20 eV. This latter result would also be in contradiction with the analysis of March *et al* (1994) where on the basis of a phenomenological comparison of simple hydrides (CH_4, NH_3, H_2O, SiH_4) a relation between the maximum of the total cross section σ_{max} and the bond length R_b of the molecule was proposed:

$$\sigma_{max} = \pi(eR_b)^2 \tag{1}$$

with $e = 2.72$. As predicted by March *et al*, the maximum cross sections for SiH_4 and GeH_4 should amount to about 52 and 53 Å^2, respectively. The recent measurements of Sueoka *et al* (1994) for SiH_4 yielded the value of 53.8 Å^2 at 2.8 eV, in good agreement with this semiempirical analysis.

2. Experimental

The transmission apparatus previously described by Zecca *et al* (1987) was used. The 140.2 mm long gas chamber allowed measurements with an angular resolution of 3.4×10^{-4} sr. The Ramsauer method of measuring both currents to the scattering chamber and to the collector, together with differential pumping and the use of a deviation valve allowed the influence of the gas presence on the electron beam to be minimized. In order to avoid decomposition of GeH_4 inside the rotary pumps, venting

with nitrogen was performed. The gas purity was 99.99% (from Air Products, France). The cross section σ was evaluated from the formula:

$$I_{ci}/(I_{ci}+I_{si}) = I_{cj}/(I_{cj}+I_{sj}) \exp[-\sigma L(N_i - N_j) \tag{2}$$

where I_{ci} and I_{si} are the collector and the scattering chamber currents, respectively, measured at a pressure corresponding to the target gas density N_i, and L is the scattering chamber length.

Typically seven or eight pressures were measured in one run and the average cross section for the pairs was compared with the value obtained from the linear regression. Final values given in this work are average of at least four runs for each energy. More measurements (up to 20 runs) were performed at lower energies. The overall systematic error of the measurements amounts to 3% and the typical statistical error is lower than 2.5%.

Table 2. Absolute total cross sections for electron scattering on GeH_4 (in 10^{-20} m^2). Statistical errors (one standard deviation of the mean value) are given in per cent.

Energy (eV)	Cross section	Error	Energy (eV)	Cross section	Error
75	19.4	2.7	700	4.73	0.7
80	19.3	1.6	800	4.34	0.8
90	18.2	1.9	900	3.97	0.6
100	17.3	1.7	1000	3.65	0.5
110	16.6	1.5	1250	3.05	0.4
125	14.6	3.1	1500	2.64	1.7
150	13.1	1.8	1750	2.29	1.6
175	12.1	0.8	2000	2.09	1.9
200	11.1	1.0	2250	1.88	0.7
225	10.3	1.6	2500	1.72	0.8
250	9.36	2.2	2750	1.57	1.3
300	8.59	1.2	3000	1.49	1.0
350	7.63	1.2	3250	1.38	1.0
400	7.02	0.7	3500	1.34	0.9
500	6.43	0.9	4000	1.16	0.8
600	6.07	0.6			

Results of the present measurements are given in table 2 and are compared with the theoretical results and the experimental partial cross sections in figure 1. In the 75–4000 eV energy range the total cross sections descend monotically from 19.5 to 1.5×10^{-20} cm^2. The present data agree well (within 5%) with the optical model calculations of Baluja *et al* (1992) for energies above 1000 eV. At 100 eV the calculations underestimate the experimental total cross section by almost 30%. The same kind of discrepancy with the optical model can be noticed for SiH_4 (compare Jain and Baluja 1992 and Zecca *et al* 1992a). However, the GeH_4 calculations of Baluja *et al* (1992) predict well the experimental (Dillon *et al* 1993) elastic cross section at 100 eV (see figure 1). On the other hand, the theoretical absorption cross section (which should account for all open inelastic channels, i.e. ionization, excitation but no dissociation) agrees well with the experimental ionization cross section alone. Detailed analysis of the inelastic contributions to the total cross section will be performed, on the basis of available experimental data, in section 4.

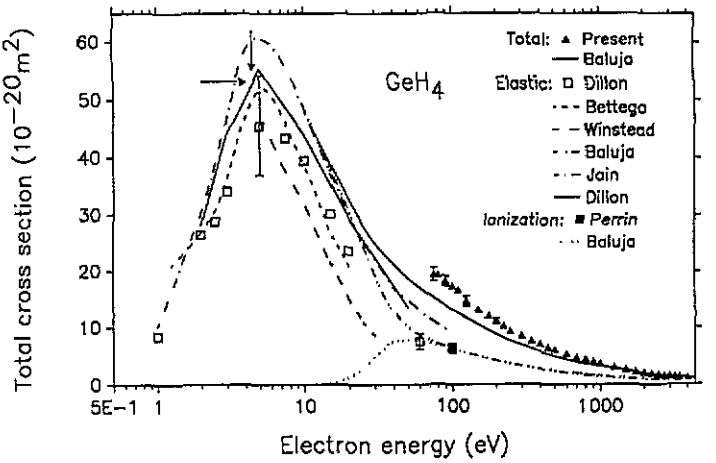

Figure 1. Total and partial cross sections for electron scattering on GeH_4. Total: present absolute (▲), error bars shown in selected points correspond to the overall experimental uncertainty, theoretical of Baluja *et al* (1992) (——); elastic: experimental of Dillon *et al* (1993) (□), theoretical of Dillon *et al* (1993) (——), Bettega *et al* (1993) (- - -), Winstead *et al* (1991) (– –), Jain *et al* (1991) (— · —), Baluja *et al* (1992) (— · · —); ionization: plasma experiment of Perrin and Aarts (1983) (■), theory of Baluja *et al* (1992) (· · · ·). Two arrows indicate the position and value of the total cross section maximum, as predicted by the semiempirical model of March *et al* (1994).

3. Comparison with other spherical molecules and noble gases

In figure 2 the present data are compared with previous measurements from our laboratory for CH_4 and SiH_4. As seen from figure 2 the cross section at 100 eV for GeH_4 is 15% higher than that for SiH_4. The two cross sections are almost equal at 200 eV while

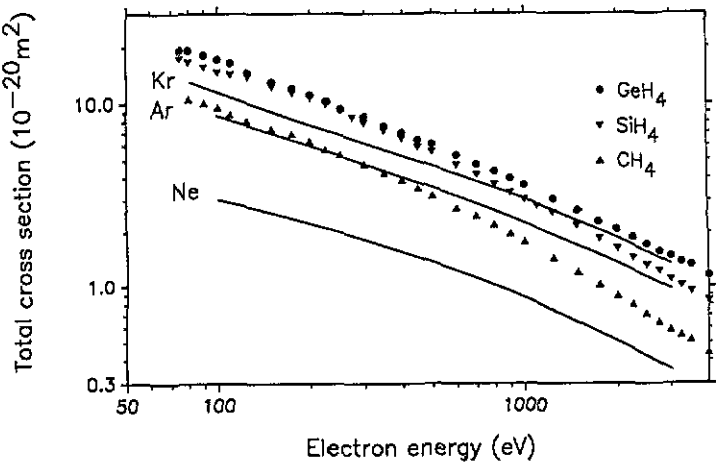

Figure 2. Comparison of the total cross sections for electron scattering on spherical hydrides and noble gases. The data are from the Trento laboratory (Zecca *et al* 1987, 1991a, b, 1992a and present).

at 4000 eV the value for GeH_4 is 30% higher than that for SiH_4. Clearly, these two gases follow a different energy dependence in the considered energy range.

It has been noticed by Zecca *et al* (1992a) for CH_4 and SiH_4 that above 100 eV the total cross section dependence on energy E can be approximated by a two-parameter Born-like formula

$$\sigma(E) = \frac{\sigma_0 E_0}{E + E_0}. \tag{3}$$

According to this equation, $\sigma(E)$ tends to a constant value σ_0 for $E \ll E_0$; for $E \gg E_0$, $\sigma(E)$ varies like E^{-1}. As can be seen from figure 2 the GeH_4 cross section behaves like E^{-1} only in the limit of the highest measured energies. The parametrization of the cross sections by the formula (3) yields the characteristic energy E_0 equal to 100, 128 and 333 eV for CH_4, SiH_4 and GeH_4, respectively. In order to reproduce the observed GeH_4 total cross section at energies below 200 eV, the inclusion of another Born-like term into equation (3) would be necessary. This procedure has been successfully applied by Zecca *et al* (1992b) to the cross sections of heavier chlorofluoromethanes. However, the lack of low-energy data for GeH_4 does not allow the two terms to be deconvoluted and in consequence σ_0 cannot be determined with reliable accuracy.

In figure 2 the total cross sections for the 'quasi-spherical' hybrides, CH_4, SiH_4 and GeH_4, are compared with the results from Trento laboratory (Zecca *et al* 1987, 1991a) for noble gases (Ne, Ar, Kr). A number of authors have compared the CH_4 total cross sections with that for Ar, although methane is isoelectronic with neon. The motivation for these comparisons rely on the fact that both gases exhibit similarities in the low-energy total cross sections. For both gases the Ramsauer minimum occurs at about 0.3 eV, followed by a broad peak at about 10 eV with values of 26×10^{-20} m^2 for CH_4 (Zecca *et al* 1991b) and 23×10^{-20} m^2 (Buckman and Lohmann 1986) for Ar. As seen from figure 2, the CH_4 and Ar total cross sections almost coincide also at 100 eV. However, these similarities can be partially accidental. For instance, the elastic cross section at the Ramsauer minimum is much higher for CH_4 (1.08 Å^2) (Schmidt 1991) than for Ar (0.21 Å^2) (Buckman and Lohmann 1986). At intermediate energies, we also notice different slopes of the cross section dependencies for atoms and for the molecules.

In the high energy limit, as can be seen from figure 2, the total cross sections for quasi-spherical molecules tend toward the values for the corresponding isoelectronic atoms (CH_4–Ne, SiH_4–Ar, GeH_4–Kr). This is in general agreement with the Thomas–Fermi model of scattering, in which in the limit of high energies the total cross sections depends mainly on the total atomic number of the molecule (see March *et al* 1994 and references therein). However, in no case do the cross sections merge completely in the range of the present measurements: at 3000 eV the corresponding values differ by 9% for the GeH_4–Kr pair, 19% for SiH_4–Ar and as much as 65% for CH_4–Ne.

4. Partitioning

Due to the lack of experimental data, the analysis of the total cross section share between partial cross section channels can only be performed at 100 eV. According to the experimental data of Dillon *et al* (1993), 37% of the GeH_4 total cross section arises

Table 3. Partial cross sections (in 10^{-20} m^2) for electron scattering on CH_4, SiH_4 and GeH_4 at 100 eV. Total cross sections are from the Trento laboratory. The recommended upper limits for dissociation into neutrals are given in bold. These values were obtained by subtraction of the lower limits for the elastic scattering and ionization from the present and from Zecca *et al*'s (1992a) total cross sections.

Molecule	Total	Elastic	Ionization	Electronic excitation	Dissociation into neutrals
CH_4	9.61	3.2[a]	3.55[c]	0.11[e]	2.0[f]
		4.59[b]	3.66[d]		2.1[g]
					2.8[h]
SiH_4	14.7	4.3[i]	5.3[c]	0.16[g]	4.8[g]
			5.0[g]		**5.1**[h]
GeH_4	17.3	6.36[j]	6.0[g]	0.15[g]	13.0[g]
					4.9[h]

[a] Boesten and Tanaka (1991).
[b] Sakae *et al* (1989).
[c] Chatham *et al* (1984).
[d] Rapp and Englander-Golden (1965).
[e] Vušković and Trajmar (1983) (interpolated).
[f] Winters (1975).
[g] Perrin and Aarts (1983) and Perrin *et al* (1982) (plasma experiment).
[h] Upper limit from present partitioning analysis.
[i] Tanaka *et al* (1990).
[j] Dillon *et al* (1993).

from elastic scattering at this energy (see table 3). This result agrees well with the optical model of Baluja *et al* (1992) (see figure 1).

Some discrepancies are due to the inelastic scattering. Relying on the plasma experiment of Perrin and Aarts (1983), the ionization would contribute 35% of the total cross section at 100 eV. This, as started before, coincides with the absorption cross section calculated by Baluja *et al* (1992). But the total dissociation (charged plus neutral fragments) cross section has been evaluated in the same experiment by Perrin and Aarts to be as high as 19×10^{-20} m^2. This value exceeds the presently measured total scattering cross section. One has to remember that the experimental determination of dissociation into neutral fragments is extremely difficult, as it is essentially based on changes of pressure in the presence of electrons. Such factors as the pumping speed and desorption from surfaces for each species must be taken into account (see Winters 1975). On the other hand, the *ab initio* description of the molecular excitation (leading to different exit channels) is also a difficult task (compare Jain and Baluja 1992).

Some more light can be shed on the GeH_4 partitioning scheme by comparing data for CH_4 and SiH_4. More experimental data are available at intermediate energies for these molecules. Obviously, some discrepancies between partial cross sections from different groups exist, as seen in table 3. For the sake of comparison, data from the same experiment should be chosen. Taking the ionization data of Chatham *et al* (1984) and the elastic cross sections of Tanaka's group, one concludes that the partitioning scheme for all three molecules at 100 eV is essentially the same: on average 35% for elastic scattering and 35–40% for the ionization. In particular, the elastic cross section amounts to 33% of the total for CH_4 and 30% for SiH_4 (a bigger error has been declared for this gas by Tanaka *et al* (1990)). The remaining part of about 30% accounts for dissociation into neutral fragments and electronic excitation (these two categories can overlap if the neutral fragments are created in electronically excited states).

For CH_4, Vušković and Trajmar (1983) have measured ratios of the electronic excitation to the elastic scattering cross section. The comparison of these data with the absolute elastic cross sections (Boesten and Tanaka 1991, Sakae *et al* 1989) allow attribution to the electronic excitation of as little as 9% of the total cross section at 30 eV and 4% at 200 eV. Measurements of Perrin and Aarts (1983) indicate that also for SiH_4 and GeH_4 the electronic excitation cross sections do not exceed several per cent of the total ones (see table 3). Therefore, the difference between the total cross section and the sum of ionization and elastic cross sections settles, within a few per cent uncertainty, the upper limit for the contribution from the neutral fragments dissociation. These limits amount at 100 eV to 2.8, 5.1 and 4.9×10^{-20} m^2 for CH_4, SiH_4 and GeH_4, respectively. This corresponds to about 30% of the total cross section for all three gases. The present upper limits for CH_4 and SiH_4 are in good agreement with the experimental evaluation of the neutral fragments dissociation by Winters (1975) and Perrin *et al* (1982). It is worth noting that the rise in the absolute values of the ionization and dissociation cross sections passing from CH_4 to SiH_4 and GeH_4 corresponds to lowering of the respective inelastic thresholds (see table 1). However, it would be difficult to establish any strict functional dependence at present.

It is interesting to compare the partitioning scheme for almost spherical molecules with the pattern for isoelectronic noble gases. This has been done in figure 3. For this analysis the semiempirical partial cross sections in noble gases of de Heer *et al* (1979), and the total values from the Pasadena laboratory (Kanik *et al* 1992, Nickel *et al* 1985) which also agree well with recent experiments, have been used. According to these data, the elastic scattering is the prevailing part of the cross section for Ne, Ar, and Kr at 100 eV. A striking feature is that the elastic cross sections for quasi-spherical molecules are, within experimental uncertainties, equal to those for the corresponding noble gases.

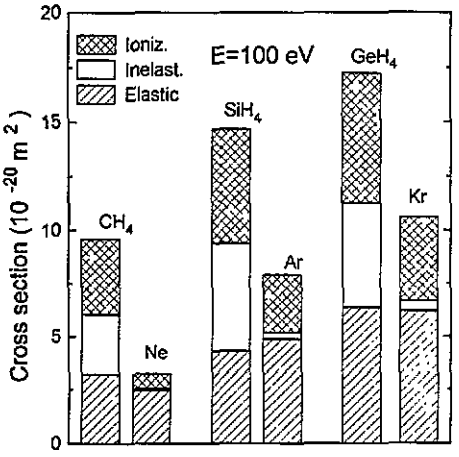

Figure 3. Comparison of partial cross sections for electron scattering on spherical hybrides and noble gases at 100 eV. The bar heights correspond to the experimental total cross sections (data of Nickel *et al* (1985) are taken for Ne and Ar, other are from the Trento laboratory). The hatched areas correspond to the elastic cross sections (the data of Tanaka's group for hydrides and of de Heer *et al* (1979) for noble gases); the cross-hatched to the ionization cross sections (Chatham *et al* (1984) for CH_4 and SiH_4, Perrin and Aarts (1983) for GeH_4, Krishnakumar and Srivastava (1988) for the noble gases); the remaining part accounts for the electronic excitation and the molecular dissociation.

It is the inelastic part (ionization and dissociation) which makes the total cross sections at 100 eV much higher for molecules than for the isoelectronic noble gases.

At the limit of high energies this different partitioning scheme still seems to hold, although the relative contributions of the partial cross sections vary in the case of molecules. For CH_4 the ionization part (Nishimura and Tawara 1994) rises continuously, to almost two-thirds of the total cross section at 3000 eV. On the other hand, the elastic cross section remains almost constant with energy, being about 40% of the total value at 700 eV (see also Zecca *et al* 1992a). The rise in the ionization channel must happen, therefore, at the expense of the dissociation into neutral fragments. For noble gases at 3000 eV, as follows from the partial cross sections of de Heer *et al* (1979), the elastic scattering is still the dominating channel (58% of the total cross section for Ne and Ar).

In order to generalize the above comparisons, the extension of partial cross section measurements in molecular gases towards energies higher than 100 eV is desirable.

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