Scattering of electrons from hydride molecules: PH$_3$

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Abstract
An absolute total cross section (TCS) for electron scattering from phosphine (PH$_3$) molecules was obtained in a linear transmission experiment at energies ranging from low (0.5 eV) to intermediate (370 eV). The dominant behaviour of the TCS energy function is a very pronounced low-energy enhancement with two distinct resonant-like humps peaked at around 2.4 and 6 eV. Above 10 eV the TCS is a rather featureless, monotonically decreasing function of energy. Our experimental results are compared with the theoretical predictions and intermediate-energy measurements. The similarities and differences of experimental TCS data for isoelectronic hydrides containing third-period atoms (SiH$_4$, PH$_3$, H$_2$S and HCl) are also pointed out and discussed.

1. Introduction

Reliable, quantitative data on the elementary processes involving electrons are necessary for understanding fundamental physics and, on the application side, are required as input information for predictive modelling of the basic physico-chemical processes which are of interest in many areas of science and technology: from atmospheric and interstellar phenomena to industrial plasma, gaseous electronics, energy conversion, biophysics and nanometer-scale electronics. During the last few decades a wealth of new information has been gained on the response of matter to electron irradiation. In spite of this progress, however, very little is yet known about electron collision even with such a small molecular compound such as the phosphine (PH$_3$) molecule.

Phosphine is a gas widely used in the processing of materials for micro- and opto-electronics. PH$_3$ is also considered as a suitable source of phosphorous dopants for the realization of atomic-scale devices for quantum computing (Simmons *et al* 2003). Besides its use in the semiconductor industry, PH$_3$ has other applications ranging from surface hardening to its utilization as a grain fumigant. PH$_3$ has recently been found (Eismann *et al* 1997,

Glindemann *et al* 2003) to be a ubiquitous trace gas in the lower and the upper terrestial troposphere ejected from numerous anthropogenic and environmental emission sources. Furthermore, molecules of PH_3 were identified in the tropospheres of the giant planets (see e.g. Encrenaz *et al* (1995)).

Much of the early experimental studies on e^-–PH_3 scattering focused on the discrete features related to particular processes and to their location on the energy scale; the measured electron-scattering intensities were reported in arbitrary units only. Mohr and Nicoll (1932) investigated an angular distribution of electrons scattered elastically from the PH_3 molecule. Later, appearance potentials for negative ion formation via dissociative electron attachment to PH_3 have been determined by Rosenbaum and Neuert (1954), Ebinghaus *et al* (1964) and Halmann and Platzner (1969). More recently, vibrational electron-impact excitation of PH_3 has been studied by Tronc and Edard (1989) while electronic excitation spectra have been investigated by Ben Arfa and Tronc (1991). So far much less is known about the absolute intensity of particular processes accompanying electron scattering from phosphine molecules. Electron-impact total ionization cross sections have been obtained (at 75 eV) by Otvos and Stevenson (1956) and (from the positive ion formation threshold to 180 eV) by Märk and Egger (1977). In swarm experiments, Cottrell *et al* (1968) and Millican and Walker (1987) measured the coefficients for electron transport in PH_3. Very recently an absolute *grand* total cross section from intermediate to high incident energies (90–3500 eV) has been measured by Ariyasinghe *et al* (2003). To our knowledge no low-energy electron-scattering TCS measurements have ever been reported for this molecular target.

On the theoretical side, calculations on electron scattering phenomena in PH_3 have started not earlier than in the past decade and concerned the elastic e^-–PH_3 collision (Winstead *et al* 1992, Bettega *et al* 1996), vibrationally elastic electron scattering (Yuan and Zhang 1993, Varella *et al* 1999) and the total (elastic plus absorption) cross section (Jain and Baluja 1992), at different levels of approximation.

This paper presents the results from measurements of absolute total cross sections for scattering of 0.5–370 eV electrons by the PH_3 molecule. TCS results for PH_3 are then compared with respective data for other 18-electron third-period hydrides (SiH_4, H_2S and HCl) as well as with Si_2H_6. Some similarities and differences are also pointed out.

2. Experimental details

The absolute total electron-scattering cross section for the PH_3 molecule presented in this paper has been obtained using a linear electron-beam transmission technique under single-collision conditions (see Bederson and Kieffer (1971)). The total cross section, $Q(E)$, at a given energy E was derived by measuring intensities of the transmitted electron current in the presence (I_g) and absence (I_0) of the target molecules in the scattering chamber and by applying the Bouguer–de Beer–Lambert (BBL) formula

$$Q(E) = \frac{1}{nL} \ln \left(\frac{I_0}{I_g} \right),$$

where the other quantities used are: length of the scattering cell (L), and the absolute number density of target molecules (n) derived from the ideal gas law based on absolute measurements of the gas-target pressure in the reaction volume and its temperature, taking into account a thermal transpiration effect (Knudsen 1910). The experimental set-up and the procedure used in the present study are the same as those employed in the earlier extensive TCS measurements and are described in detail elsewhere (e.g. Szmytkowski and Możejko (2001)). The electron spectrometer used in the present experiment consists of an electron source followed by an
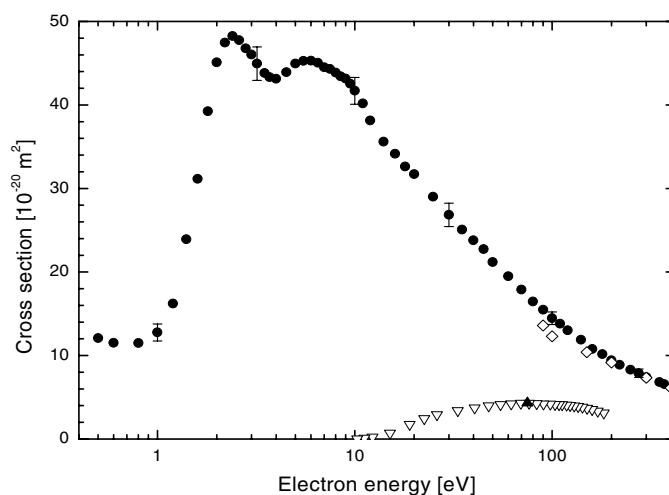
Figure 1. Energy dependence of experimental cross sections for the electron–PH$_3$ scattering. Grand total cross section: ●, present (error bars represent overall uncertainties, statistical plus systematical); ◇, Ariyasinghe *et al* (2003). Ionization total cross section: ▲, Otvos and Stevenson (1956); ▽, Märk and Egger (1977).

electrostatic 127° cylindrical monochromator, a reaction cell, a retarding-potential energy analyser and an electron detector. The magnetic field in the region of electron optics is reduced below 0.1 μT. Absolute calibration of the electron energy scale was carried out by recording the well-known resonant oscillatory structure appearing in the transmission current, around 2.3 eV when molecular nitrogen is admixtured.

The final TCS value at each impact energy is a weighted mean of results from several (3–7) series of individual measurements (7–10 in a series). The TCS uncertainty of a random nature (one standard deviation of the weighted mean value) is estimated to be about 2% below 1 eV and to be less than 1% over the whole remaining energy range studied. The overall systematical uncertainty in our absolute TCS, estimated as a combination of potential systematic errors of all quantities taken directly in the experiment, is about 8% below 2 eV, decreasing gradually to 5% in the range 5–150 eV, and amounts to about 7% at the highest applied energies. The main component of systematic error (3–4%) arises from uncertainty in the determination of factor nL in the BBL formula. The details of the analysis of systematic uncertainties have already been discussed elsewhere (Szmytkowski *et al* 1997). A commercially supplied sample of PH$_3$ (of electronic grade purity 99.9995 + % from Aldrich Chem Comp) was used directly from the container without further purification.

3. Results and discussion

3.1. Phosphine, PH$_3$

Figure 1 shows the variation of absolute electron-scattering TCS for phosphine measured in this work over the energy range 0.5–370 eV. The TCS values are listed in table 1. Due to the lack of literature on other low-energy e$^-$–PH$_3$ TCS results, a comparison can be made only with the very recent experimental TCS data obtained by Ariyasinghe *et al* (2003) above 90 eV. Agreement of both TCSs in the overlapping intermediate energy range is

Table 1. Absolute total cross section (TCS) for electron scattering from phosphine (PH_3) molecules in units of 10^{-20} m^2.

Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS
0.5	12.1	3.5	43.8	11	40.2	90	15.5
0.6	11.5	3.7	43.3	12	38.1	100	14.5
0.8	11.5	4.0	43.1	14	35.6	110	13.8
1.0	12.8	4.5	43.9	16	34.2	120	13.0
1.2	16.2	5.0	45.0	18	32.6	140	11.9
1.4	23.9	5.5	45.3	20	31.7	160	10.8
1.6	31.2	6.0	45.3	25	29.0	180	10.2
1.8	39.2	6.5	45.0	30	26.8	200	9.42
2.0	45.1	7.0	44.5	35	25.1	220	8.88
2.2	47.5	7.5	44.3	40	23.8	250	8.30
2.4	48.3	8.0	43.8	45	22.7	275	7.88
2.6	47.7	8.5	43.4	50	21.2	300	7.42
2.8	46.8	9.0	43.2	60	19.5	350	6.83
3.0	46.0	9.5	42.5	70	17.9	370	6.57
3.2	45.0	10.0	41.7	80	16.4		

quite good. For completeness, experimental electron-impact total ionization cross sections (Otvos and Stevenson 1956, Märk and Egger 1977) are also presented.

The most striking behaviour of the TCS energy function for e^-–PH_3 scattering is its drastic increase from nearly 12×10^{-20} m^2 up to 48×10^{-20} m^2 in the range between 1 and 2.5 eV. The narrow TCS maximum is located close to 2.4 eV and is followed by a shallow minimum near 4 eV and a much broader flat hump centred near 6 eV, superimposed with another very weak structure discernible around 9 eV. The character of TCS variations at energies between 1 and 10 eV suggests the e^-–PH_3 collision in the low-energy range is substantially affected by resonant processes in which the incoming electron of proper energy is temporarily captured into the unoccupied molecular orbital, generally of anti-bonding character. The resulting transitory negative ion (resonance) decomposes either via rejecting the excess electron by leaving the parent molecule in one of the accessible vibrational levels, or through a competitive channel with the fragmentation of the molecule into stable fragment negative-ion and neutral. Clear demonstration of the existence of several transient PH_3^- states in the region of 2–10 eV comes from experiments in which various fragment negative ions (PH_2^-, PH^-, P^- and H^-) were observed: in the vicinity of 3 eV, between 6 and 10 eV and around 15 eV (Rosenbaum and Neuert 1954, Ebinghaus *et al* 1964, Halmann and Platzner 1969). Also an experiment on the vibrational excitation indicates the presence of a shape resonant state near 2.1 eV (Tronc and Edard 1989). Tossell *et al* (1985), besides the resonant-like feature centred at 1.9 eV (observed in derivative with respect to the energy of the electron-current transmitted through PH_3), also reported a second resonance at the energy of 5.5 eV. That feature, discernible also in the present experiment around 6 eV, may be related to the formation of core-excited resonances. To better understand the events occurring in the region of the 2–10 eV enhancement, further experiments, especially quantitative, and calculations are required.

Above 10 eV the TCS becomes a monotonically decreasing function of energy. Towards higher energies, beyond 20 eV, the experimental TCS data can be satisfactorily fitted with the regression formula $Q \sim E^{-0.5}$, which means that at intermediate energies the TCS is proportional to the time the projectile electron needs to traverse a target-molecule dimension. The contribution of electron impact ionization to the scattering processes in PH_3 appears
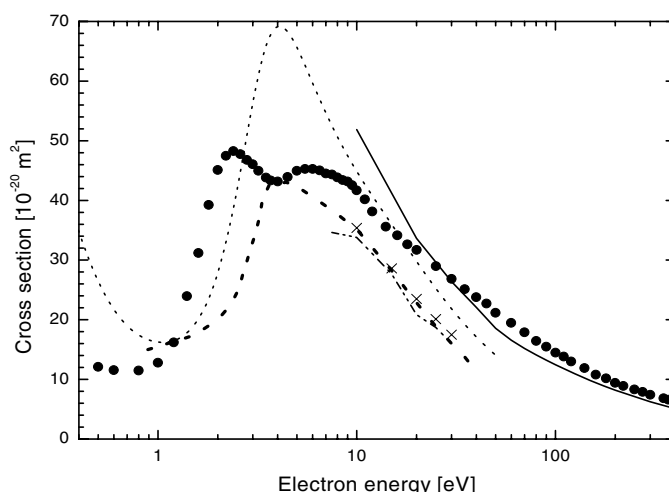
Figure 2. Comparison of present (●) experimental e⁻–PH₃ TCS and theoretical cross sections: - - - -, elastic, Winstead *et al* (1992); ×, elastic, Bettega *et al* (1996); ······, vibrationally elastic, Yuan and Zhang (1993); — · · —, vibrationally elastic, Varella *et al* (1999); ——, total (elastic plus absorption), Jain and Baluja (1992).

to be relatively low and near 100 eV the ratio of the total ionization cross section and the *grand* TCS does not exceed 0.3, while usually for other hydrogen-containing molecules (e.g. hydrocarbons) it is much closer to 0.4 (cf Szmytkowski and Ptasińska-Denga (2001)). At the high energy limit of the present experiment, at 370 eV, the TCS decreases to about 6×10^{-20} m².

In figure 2, a comparison is made between our experimental TCS and the theoretical total (elastic plus absorption) cross section predictions of Jain and Baluja (1992). Between 10 and 20 eV, the calculated TCS distinctly overestimates the present experiment (at 10 eV by 25%) while above 20 eV the calculations are systematically lower than the experimental values; above 100 eV the discrepancy exceeds 15%. Unfortunately, there are no theoretical TCS results available in the resonant region, below 10 eV. Therefore, for comparison in the low-energy range we included (see figure 2) integral vibrationally elastic (Yuan and Zhang 1993, Varella *et al* 1999) and integral elastic (Winstead *et al* 1992, Bettega *et al* 1996) cross sections. Computations (Winstead *et al* 1992, Yuan and Zhang 1993) available in the energy range overlapping with the present low-energy experimental TCS data also show the strong cross section enhancement centred near 4 eV. Quantitatively, however, only the integral elastic cross section of Winstead *et al* (1992) is in reasonable agreement with the experiment, while the vibrationally elastic calculations of Yuan and Zhang (1993) drastically overestimate the experimental TCS around the centre of the enhancement. Neither of these computations predicts additive features superimposed on the low-energy enhancement such as those visible in the experiment with maxima at 2.4 and 6 eV.

It is also worth noting that according to general appearance, the TCS curve for PH₃ resembles that measured for disilane (Si₂H₆) molecule (Szmytkowski *et al* 2001). In particular, the locations of the low-energy maxima for both targets are very similar. The Si₂H₆ (H₃Si–SiH₃) molecule is composed of two SiH₃ radical groups of pyramidal (C₃ᵥ) structure, similar to that of the PH₃ molecule. From simple geometrical considerations it is seen that the molecular cross section of Si₂H₆, averaged over all orientations, is close to 5/3 of that for each of its components and, consequently, it is reasonable to assume a similar ratio of Si₂H₆ and PH₃ cross
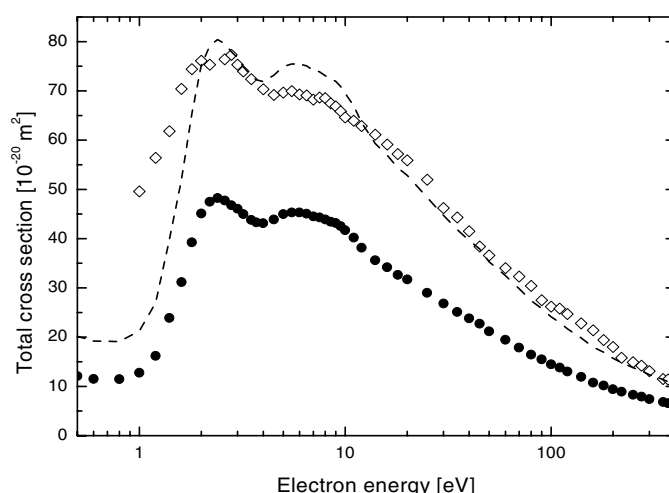
Figure 3. Comparison of experimental electron scattering TCS for: PH_3 (●, present) and Si_2H_6 (◇, Szmytkowski *et al* 2001); to better illustrate the similarity in the shape of compared TCSs; the data for PH_3 are also multiplied by 5/3 (- - - -).

sections. In fact, figure 3 indicates that this is the case and confirms previous observations (Szmytkowski and Kwitnewski 2003) that the TCS function for a more complex molecule may be roughly estimated from the TCSs of its submolecular components (*group additivity*). The same ratio of TCSs is also noted for another pair of molecules: C_2H_6 ($H_3C–CH_3$) and NH_3.

3.2. Third-period hydrides: SiH_4, PH_3, H_2S and HCl

Phosphine, along with SiH_4, H_2S and HCl, belongs to a family of hydrides containing third-period atoms. These compounds differ substantially in their constitution and geometry, therefore one might expect TCS differences across that series. On the other hand, the compared hydrides are isoelectronic ($n_e = 18$) and some similarities in the behaviour of their TCS energy functions may also be expected, especially in the resonant region.

In figure 4, the TCS curves for electron scattering from the third-period hydrides are compared. The experimental data used for comparison, and those for HCl, were taken in our laboratory (Szmytkowski and Maciąg 1986, Szmytkowski *et al* 1997, 2003). TCS (normalized) data for HCl of Hamada and Sueoka (1994) have been renormalized (by a factor of 1.2) with reference to results of Brüche (1927) near 25 eV. We believe that the magnitude of the pioneering results of Brüche (1927) is more adequate because in this energy region his TCS data for other targets are usually in reasonable agreement with very recent experiments. Substantial lowering of the Hamada and Sueoka results has also been concluded by Karwasz *et al* (2001) after the critical analysis of available experimental and theoretical HCl data. The lowering of normalized TCS in the experiment of Hamada and Sueoka may result from their normalization procedure.

A low-energy dependence of TCS for electron collision with the compared hydrides is dominated by resonant-like features with the shape clearly depending upon details of the structure of different molecular targets. TCS curves for SiH_4, PH_3, H_2S and HCl have a distinct low-energy resonant maximum located near 2.9, 2.4, 2.3 and 3.7 eV, respectively. The similarity of the resonance energies suggests a similarity of molecular orbitals which contribute to the resonant state in each of these compounds (Tossell *et al* 1985). Besides the
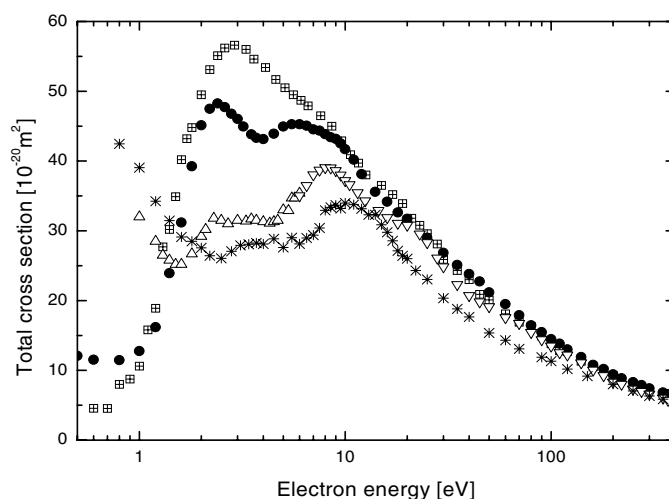
Figure 4. Comparison of experimental electron scattering TCS on third-period hydrides: SiH$_4$ (⊞, Szmytkowski *et al* 1997), PH$_3$ (●, present), H$_2$S (△, Szmytkowski and Maciąg 1986; ∇, Szmytkowski *et al* 2003) and HCl (∗, data of Hamada and Sueoka (1994) multiplied by a factor of 1.2 (see the text)).

Table 2. Parameters of isoelectronic ($n_e = 18$) hydrides containing third-period atoms: permanent electric dipole moment (μ), electrical polarizability (α) and the gas-kinetic collisional cross sections of molecules (σ) calculated using the van der Waals constant (**Lide** 1995–1996).

Molecule	μ (Debye)	α (10^{-30} m^3)	σ (10^{-20} m^2)
HCl	1.11	2.7	7.94
H$_2$S	0.98	3.9	8.35
H$_3$P	0.57	4.8	9.29
H$_4$Si	0	5.4	10.1

first low-energy maximum, the features located at higher energies are also seen. The location of the second feature shifts towards higher energy on going from SiH$_4$ to HCl: a slight change in the slope is visible near 7 eV in the SiH$_4$ curve, a distinct broad hump around 8 eV for PH$_3$, and a distinct maximum centred near 8.5 eV and 10 eV for H$_2$S and HCl, respectively. Note that the increase in the magnitude of the second feature across hydride series is accompanied by the decrease in their first maximum. According to the magnitude, the TCS in the resonant region clearly increases with increase in the size of the molecule and the target electrical polarizability (see table 2). The variation of TCS appearance below 1.5 eV (figure 4) can be explained in terms of different permanent electric dipole moments of compared molecules, that is, the long-range electron–molecule interaction.

At intermediate energies, unlike the low-energy scattering, the shape of the TCS energy function for members of the third-period hydride series is very similar. The difference in the magnitude of TCS across series at intermediate energies is rather small: the TCS increases slightly on going from HCl to SiH$_4$, following the growth in molecular size. This suggests that scattering at higher energies is dominated by the heavy component (Si, P, S or Cl atom) of the molecule, while the role of peripheral hydrogen atoms seems to be rather less important. It is interesting that around 200 eV, the experimental TCS for the considered hydride targets appears to be equal to the respective gas-kinetic molecular cross section (cf table 2).

4. Conclusion

We reported the total electron-scattering cross sections for PH$_3$ molecules measured in a linear transmission experiment from 0.5 to 370 eV. In the low-energy range, between 1 and 20 eV, the TCS curve shows very pronounced double peaked enhancement. The observed structure may be explained in terms of resonant scattering. The comparison of TCSs for 18-electron hydrides containing third-period atoms (SiH$_4$, PH$_3$, H$_2$S and HCl) shows interesting similarities in the low-energy range.

Acknowledgments

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