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Gas-phase infrared laser photolysis of phenylsilane

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Abstract

The IRMPA and IRMPD processes of phenylsilane were investigated from absorption measurements, reaction probabilities and quantitative product analysis. The laser absorption cross-section was determined as $\sigma_L = (1.34 \pm 0.08) \times 10^{-18}\,\mathrm{cm^2}$ which coincides with the conventional IR absorption cross-section. It was found that neat $PhSiH_3$ or in the presence of Ar behaves like the so-called 'large molecules' showing no restrictions to the multiphoton absorption process. Decomposition occurs through collisional assisted processes of energy pooling. End product analysis from IRMPD of $PhSiH_3$ shows that the main dissociation channel is the three-center molecular elimination of H_2 and PhSiH. Thus, IRMPD of $PhSiH_3$ proves to be a convenient technique for the generation of PhSiH radicals. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Gas phase; IR multiphoton laser photolysis; Phenylsilane

1. Introduction

In the last years, an extensive number of works on selective laser photolysis were performed to generate free radicals as a suitable method to study the reactions of these free radicals with different surfaces [1–3]. The deposition of amorphous or crystalline silicon by chemically photoassisted vapour deposition (CVD) has proved to be an excellent example of the relation between reaction dynamics in the gas phase, gas-surface chemistry, the laser-assisted chemistry and the laser spectroscopic analysis of systems of technological interest to elucidate dissociation and deposition mechanisms [1,4,5]. These are some of the reasons for an increasing interest in the study of the kinetics and mechanisms of silicon containing compounds and of the organosilanes since it is necessary to obtain thermochemical data and reliable kinetic parameters as well as to determine the reactivities of these molecules and their radicals [3,6]. The basic topic lies in the production of SiH_n radicals since these radicals play an important role in the silicon chemical vapour deposition processes [3,4,7].

Among the different silicon containing compounds, $C_6H_5SiH_3$ ($PhSiH_3$) has been used as precursor to generate SiH_n radicals [8]. $PhSiH_3$ has been spectroscopically characterised in the UV [9,10] and IR [11,12] regions and there

are three types of decomposition studies carried out on this molecule, these are, photochemical decomposition using UV laser irradiation [9,13–18], thermal decomposition [19] and infrared multiple photon decomposition (IRMPD) [5,20,21].

Photochemical decomposition induced by UV laser irradiation of $PhSiH_3$ is a well-known method for the production of SiH_2 (silylene) radicals [22–25] to study the reaction kinetics of these radicals with different compounds [14,26–40]. Baggott et al. [13] characterised the photodissociation process of $PhSiH_3$ at 193 nm and analysed the final products, H_2 and C_6H_6 (PhH), by gas chromatography. Their results showed that the production of C_6H_5SiH (PhSiH) by a three-center molecular elimination of H_2 is favoured by a 6-fold factor over the formation of SiH_2 and PhH.

Formation of different fragments and intermediates such as SiH_2, SiH, Si [5,8,9,16,17,21,23–25,28], C_2 [5,17] and SiC_2 [16] has been reported from the photolysis of $PhSiH_3$ in some cases by secondary multiphoton dissociation processes. However, in none of these studies has the presence of the $C_6H_5SiH_2$ radical been observed. The SiH_2 and SiH radicals and the Si atoms can be detected by LIF [8,21,23–25,41–44], whereas only an absorption band between 450 and 550 nm centered at 514 nm can be assigned to the PhSiH radical [45] due to the lack of detailed spectroscopic studies of this radical.

Studies on the thermal decomposition of $PhSiH_3$ have suggested two primary dissociation pathways in agree-

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ment with those proposed from the UV photolysis studies. RRKM calculations fit the experimental data rendering the Arrhenius parameters for the two dissociation channels. In this case also, the reaction that produces H_2 and PhSiH is favoured ($\sim$5-fold factor) over the formation of PhH and SiH_2. The benzene yields are almost the same, within experimental error, as those observed in the decomposition by UV photolysis.

In the IRMPD of $PhSiH_3$, the results obtained by Steinfeld [5] showed the three-center elimination of H_2 and PhSiH as the most probable primary dissociation channel. However, the principal aim of this study was the spectroscopic characterisation of the SiH_2 radical so a further analysis is required for the complete description of the IR multiple photon processes of $PhSiH_3$ following pulsed CO_2 laser irradiation. The IRMPD of $PhSiH_3$ [5] gives low yields of SiH_2 compared with the alkylsilanes under similar conditions [5,46,47] despite the fact that $PhSiH_3$ decomposes more readily even under collision-free conditions. In the case of alkylsilanes, SiH_2 is a main dissociation product which arises from the secondary IR dissociation of primary photolysis products.

Results obtained from the UV and IR photochemical decomposition of $PhSiH_3$, except those on the thermal decomposition, are scarce with respect to the determination of kinetic parameters and thermochemical data but coincide in the proposed primary decomposition mechanism.

In this work, we report the results obtained from a detailed study of the infrared multiphoton absorption (IRMPA) processes [48–51] of $PhSiH_3$ through determination of the absorption cross-sections, σ_L, and their dependencies on laser fluence and pressure. The mean number of infrared photons absorbed per molecule was determined as a function of the fluence and of the pressure of $PhSiH_3$ to characterise the molecular properties of the laser absorption process. The effect of added Ar on the collisional relaxation processes [52] of the vibrationally excited $PhSiH_3$ molecules was also investigated. The IRMPD of $PhSiH_3$ was characterised from dissociation fraction measurements and fractional product yields and their variation as a function of the fluence as well as of the reactant gas pressure [48–55]. These data are compared with previous works dealing with IRMPD and with the studies on the UV and thermal decomposition processes related to the proposed dissociation mechanism and the branching ratios into the different dissociation channels.

2. Experimental details

A pulsed T.E.A. CO_2 laser (Tachisto Model 217-G, Laser Systems) was used as the infrared radiation source delivering 1.5 J/cm^2 at the P(28) line of the 00^01–10^00 transition (936.8 cm^{-1}) which is resonant with the ν_{19} mode of $PhSiH_3$ at 10.6 μm. The pulse consisted of an initial part of $\approx$40 ns FWHM followed by a tail which extends up to

500 ns. The laser irradiation frequency was determined with a CO_2 Laser Spectrum Analyzer model 16A (Optical Engineering) and the pulse energy was measured with a power meter (Scientech 362).

$PhSiH_3$ 99% was commercially obtained from Aldrich and purified by vacuum distillation. Infrared spectroscopy and gas chromatography showed pure $PhSiH_3$. Argon 99.999% AGA was used as inert gas.

The experiments were performed at room temperature irradiating samples of neat $PhSiH_3$ and in some cases of $PhSiH_3$ and Ar as bath gas. Capacitance manometers models 220CA-10A2B and 220CA-1000A2B (MKS Instruments) were used for pressure ranges between 0.001 and 10.000 Torr and between 1.0 and 1000.0 Torr, respectively. The pressure of $PhSiH_3$ was varied between 0.070 and 3.000 Torr and between 0.500 and 15.0 Torr for the absorption and decomposition experiments, respectively. Different pressures of Argon as inert gas ranging from 5.000 to 40.0 Torr were used in some experiments.

The IRMPA studies were performed to determine the absorption cross-sections, σ_L, under collisionless conditions from direct measurements of the energy absorbed by the sample at different pressures. The experimental setup has been described previously [48]. Briefly, the experiments were performed with Pyrex cylindrical cells sealed with NaCl windows of different optical path lengths (20, 50 and 90 cm) to obtain an absorption range between 15 and 85%. The laser beam was collimated to give a uniform energy flow through the cell, using a diaphragm to reduce its diameter. The initial fluence (Φ_0) was calculated as the ratio of the energy of the pulse divided by the cross-section of the laser beam. The fluence range used was 0.09–0.30 J/cm^2. The intensity of the laser beam was attenuated by placing polyethylene films in the beam pathway. The absorption measurements to determine σ_L were carried out under constant incident fluence. For absorptions lower than 10% we considered that the incident fluence, Φ_0, was almost the same as the transmitted fluence and therefore, $\Phi = \Phi_0$, whereas when there was a fluence gradient (absorptions higher than 80%), the fluence was calculated as a mean value between the incident and exit fluences. For the calorimetric measurements, the laser beam was split using a ZnSe lens. A fraction of the beam intensity (E) goes through the absorption cell whereas the remaining fraction is used as reference (E_0). The intensity ratio of both beams was monitored with an energy Ratiometer equipped with two pyroelectric detectors (Laser Precision RJ 7620 with RJP-735 probes). The transmittance of the sample, T, was calculated as the ratio between the fraction of energy transmitted with the reactant in the cell and the fraction of energy transmitted with the empty cell, as given by Eq. (1):

$$T = \frac{(E_0/E)_{\text{reactant}}}{(E_0/E)_{\text{empty}}} = \frac{I}{I_0} \qquad (1)$$

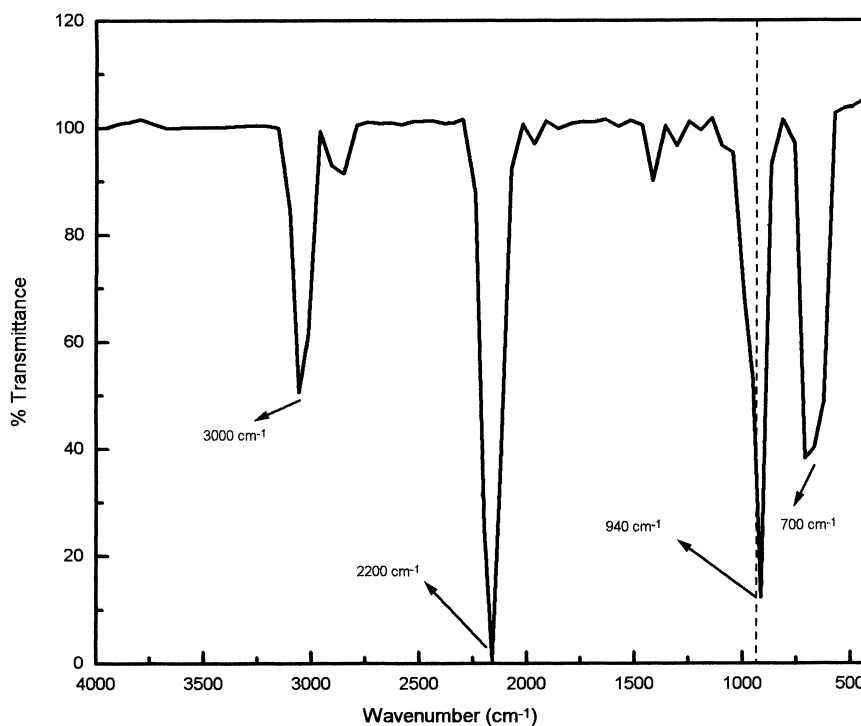so that the transmittance of the sample can be related with

Fig. 1. Infrared spectrum of 5 Torr of PhSiH$_3$ in a 20-cm path length cell. The dashed line shows the irradiation line used, P(28), at 936.8 cm^{-1}.

the length of the cell and the pressure of PhSiH$_3$ using Beer's law.

The dissociation experiments demand fluences higher than the absorption measurements, it was necessary therefore, to use a system of telescopic lenses. These IR multiphoton dissociation experiments were carried out in a cylindrical Pyrex cell (2.4 cm diameter), 12.0-cm optical path length equipped with KBr windows at both ends which was placed axially to the laser beam. A collimated beam was used with and without focusing. When necessary, a parallel geometry of irradiation was employed with a set of BaF$_2$ and NaCl lenses of 15 and 5 cm focal distances, respectively. The fluences were varied between 0.08 and 0.60 J/cm^2. The samples were generally irradiated with up to 1000 laser pulses. The reaction progress was followed by IR absorption measurements before and after irradiation of each sample. A Buck Scientific Model 500 IR spectrometer was used for this purpose whereas the high resolution FTIR spectra of each sample were obtained with a Nicolet FTIR 5SXC spectrometer with a 2 cm^{-1} resolution. End products analysis was performed by gas chromatography on silica-gel columns of different lengths (1, 2, 4 and 6 m) and on a 4 m Dow Corning oil column, at different column temperatures using H$_2$ as carrier gas. Infrared spectroscopy, UV–Vis spectroscopy (Shimadzu UV-1601) and mass spectrometry (Finnigan 3300F) were also used for identification, not only of the gaseous products but also for the solid film deposited on the KBr windows of the cell.

3. Results and discussion

3.1. Fluence and pressure dependence of the absorption cross-section

The IR spectrum, obtained with 5 Torr of PhSiH$_3$ in a 20-cm optical path length cell is shown in Fig. 1. Also, shown in the spectrum is the laser irradiation line used, P(28), for the determination of the laser absorption cross-section, σ_L, which was measured at 936.8 cm^{-1}, for pressures between 0.070 and 3.000 Torr and fluences ranging between 0.09 and 0.3 J/cm^2. The experimental results obtained as a function of the reactant pressure, at three different fluences, are shown in Fig. 2. The σ_L remains constant with increasing pressure of PhSiH$_3$ in all the pressure range studied. Thus, σ_L is a pressure independent molecular property and its value can be calculated from Beer's law according to the following equation:

$$\sigma_L = \frac{N \ln T}{bP} \qquad (2)$$

where T is the transmittance, b the optical path length of the cell in cm, N a constant equal to 3.23×10^{-16} cm^3 Torr^{-1} and P the pressure of PhSiH$_3$ in Torr [29]. Therefore, plotting $\ln T$ as a function of the pressure of PhSiH$_3$ a value of σ_L $(1.34 \pm 0.08) \times 10^{-18}$ cm^2 was obtained from the slope. From the FTIR spectrum of PhSiH$_3$ obtained by conventional IR spectroscopy, the infrared absorption cross-section
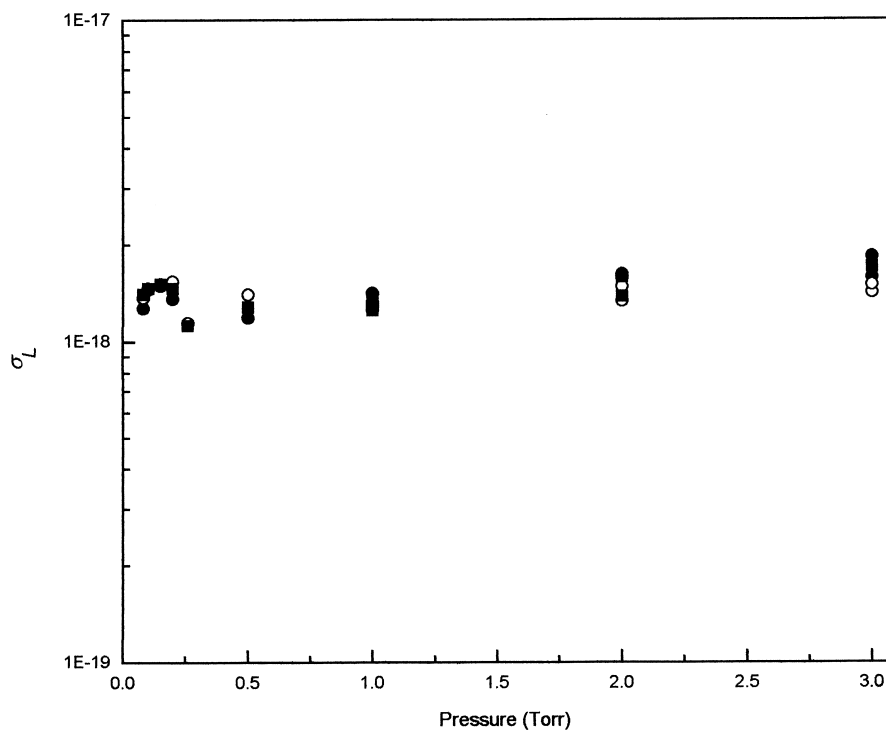
Fig. 2. Laser absorption cross-section of $PhSiH_3$ as a function of pressure, at different fluences. ($\bullet$) 0.09 J/cm^2; ($\bigcirc$) 0.18 J/cm^2; ($\blacksquare$) 0.27 J/cm^2.

(σ_0) of this compound was calculated using Beer's law and a value of $\sigma_0 = (1.1 \pm 0.1) \times 10^{-18}$ cm^2 was obtained which is in good agreement with the value of σ_L obtained from the laser experiments. The dependence of σ_L on the fluence in the pressure range mentioned above is shown in Fig. 3. There is no significant variation of σ_L with the fluence and it is approximately equal to σ_0 within experimental error.

The mean number of IR photons absorbed per pulse per molecule in the irradiated volume, $\langle n \rangle$, was determined
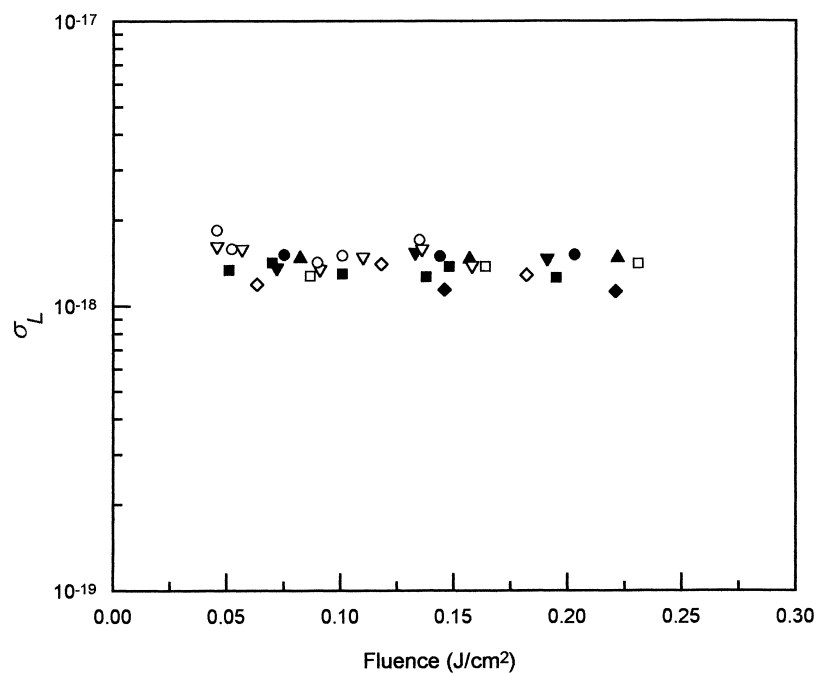

Fig. 3. Laser absorption cross-section of $PhSiH_3$ as a function of fluence, at different pressures: ($\square$) 0.08 Torr; ($\blacktriangle$) 0.11 Torr; ($\bullet$) 0.15 Torr; ($\blacktriangledown$) 0.20 Torr; ($\blacklozenge$) 0.258 Torr; ($\lozenge$) 0.51 Torr; ($\blacksquare$) 1.01 Torr; ($\triangledown$) 2.04 Torr; ($\bigcirc$) 3.05 Torr.
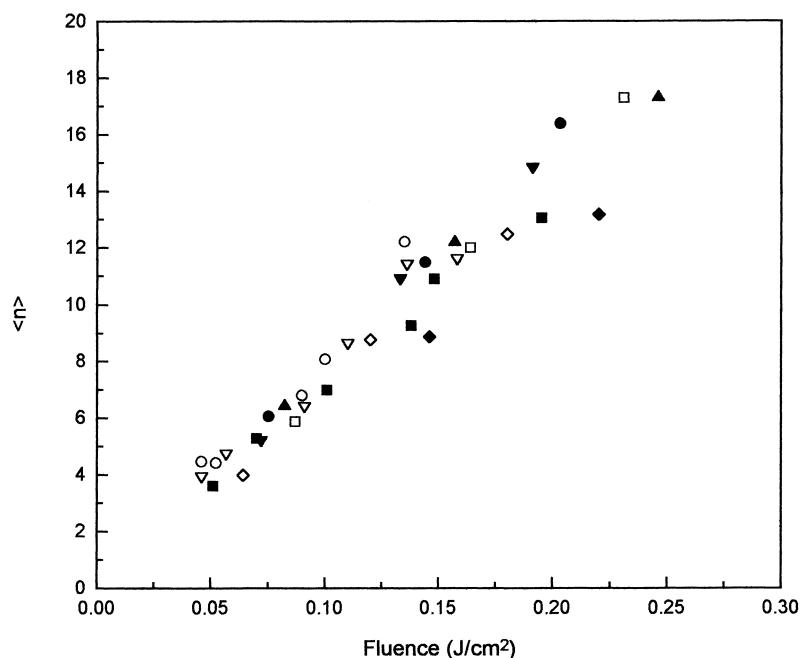
Fig. 4. Average number of IR photons absorbed by PhSiH$_3$ vs. fluence at different pressures: ($\square$) 0.08 Torr; ($\blacktriangle$) 0.11 Torr; ($\bullet$) 0.15 Torr; ($\blacktriangledown$) 0.20 Torr; ($\blacklozenge$) 0.258 Torr; ($\lozenge$) 0.51 Torr; ($\blacksquare$) 1.01 Torr; ($\triangledown$) 2.04 Torr; ($\bigcirc$) 3.05 Torr.

according to Eq. (3):

$$\langle n \rangle = \frac{\sigma_L \Phi}{hc\tilde{\nu}} \tag{3}$$

where Φ is the fluence in J/cm^2, h the Planck's constant in J s, c the velocity of light in cm s^{-1} and $\tilde{\nu}$ is the laser wave number in cm^{-1}.

A plot of $\langle n \rangle$ as a function of the fluence is given in Fig. 4 at different pressures of PhSiH$_3$. A linear dependence is observed as the fluence increases with no significant variation of the slope with pressure variation of the PhSiH$_3$. The absorption measurements are affected when the dissociated fraction of PhSiH$_3$ per pulse becomes progressively more important and this occurs, in the pressure range studied, at fluences higher than 0.3 J/cm^2. Therefore, the highest values of fluence and pressure used in this study to measure σ_L and $\langle n \rangle$ were 0.3 J/cm^2 and 3 Torr, respectively. Under these experimental conditions, a maximum value of $\langle n \rangle = 18$ photons/pulse was obtained. As can be observed in Fig. 4, $\langle n \rangle = 18$ is the highest measured experimental value; it is not however the limit that is reached near the reaction threshold when $\langle n \rangle$ remains constant with increasing fluence.

In experiments with different amounts of added Ar, up to 40.0 Torr, as inert gas at a constant pressure of 0.500 Torr of PhSiH$_3$ and at two different fluences, the value of the mean number of IR photons absorbed does not show significant changes, indicating that σ_L is independent of the total pressure (Fig. 5).

These results show that the absolute value of σ_L is not only independent of the pressure of PhSiH$_3$ and follows Beer's law but also that it remains constant with the addition of Ar as inert gas. Collisions of PhSiH$_3$ with Ar will

mean that the energy absorbed by the molecules will be lost by efficient V–T energy transfer processes without affecting the value of σ_L which indicates that there are no restrictions to absorption due to a rotational bottleneck. The fact that no increase of the absorption cross-section by collisional assistance is observed is typical of the so-called 'large molecules' for which the high density of vibrational states assures the resonant condition and thus all the molecules absorb the laser radiation and can be excited to energies above the reaction threshold in competition with collisional deactivation during the pulse [48–51,56].

The appearance of an apparent threshold for the dissociation of PhSiH$_3$ was evidenced by the presence of Si powders in the reaction cell and also by an intense luminescence observed only under certain experimental conditions of laser fluence and pressure of PhSiH$_3$. This threshold for dissociation at dissociated fraction $X_d = (0.09 \pm 0.04)$ at fluences lower than 0.1 J/cm^2 is observed in Fig. 6. In the same figure at the top, a plot of the dissociated fraction as a function of fluence for a sample of 5 Torr of PhSiH$_3$ irradiated at $\lambda = 936.8$ cm^{-1} with 100 laser pulses is shown and compared with results obtained by Steinfeld et al. [20], at $\lambda = 933.0$ cm^{-1}. Both sets of data coincide even though different irradiation lines were used.

3.2. Fluence and pressure dependence of the reaction probability

The reaction probability for the decomposition of PhSiH$_3$, $P(\Phi)$, taken as the number of molecules reacting per pulse divided by the total number of molecules in the irradiated volume [48], was independent of the number of pulses used
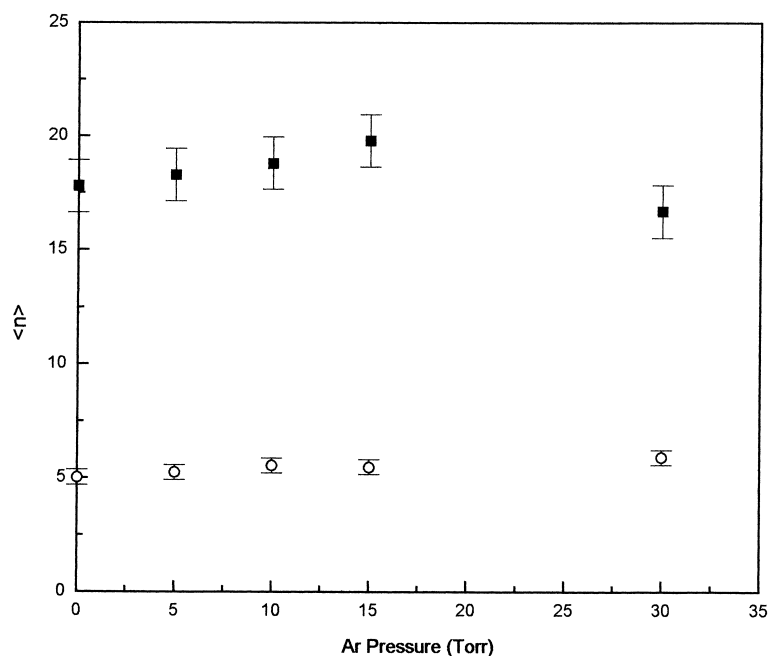
Fig. 5. Average number of IR photons absorbed as a function of the pressure of inert gas (Ar), for 0.500 Torr of $PhSiH_3$, at two different fluences: ($\bigcirc$) 0.11 J/cm^2 and ($\blacksquare$) 0.55 J/cm^2.
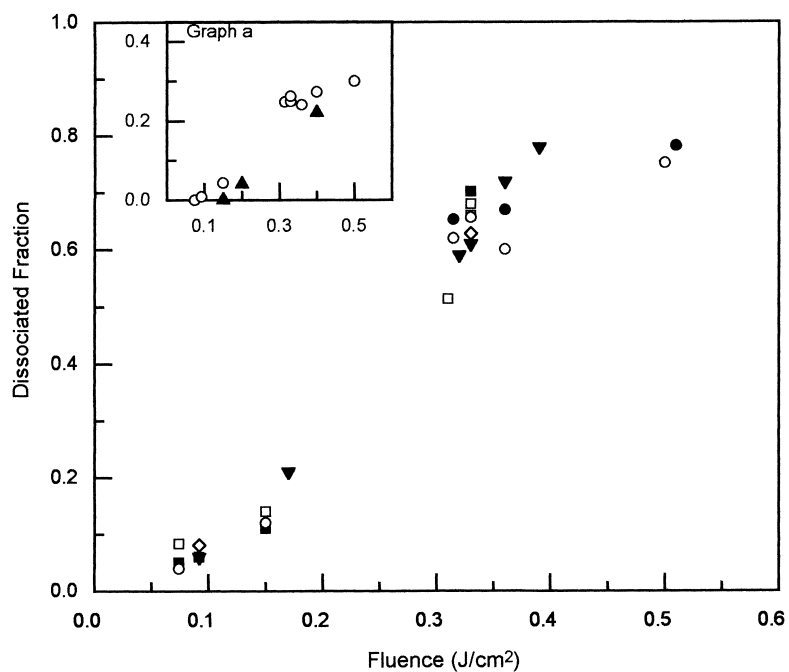

Fig. 6. Dissociated fraction of $PhSiH_3$ as a function of fluence at different pressures: ($\diamondsuit$) 0.50 Torr; ($\square$) 1.00 Torr; ($\blacksquare$) 4.00 Torr; ($\bigcirc$) 5.00 Torr; ($\blacktriangledown$) 10.00 Torr; ($\bullet$) 15.00 Torr. Graph a: Dependence of the dissociated fraction on fluence for 5 Torr of $PhSiH_3$ irradiated with 100 CO_2 laser pulses, at two different wavelengths: Our work ($\bigcirc$) at $\lambda = 936.8$ cm^{-1}, line P(28); Steinfeld ($\blacktriangle$) at $\lambda = 933.0$ cm^{-1}, line P(32).

to irradiate the sample. $P(\Phi)$ was measured as a function of fluence in the range 0.08–0.6 J/cm^2 for different pressures of $PhSiH_3$ between 0.5 and 15 Torr. As is usual for this type of experiment [55], the reaction yields increase with fluence and are independent of the reactant pressure as shown in

Fig. 7. The experimental results for the reaction probability were fitted to a polynomial function reaching a limit at a value of $P(\Phi) = (0.017 \pm 0.013)$ (Fig. 7). The results obtained by plotting $P(\Phi)$ versus pressure at different fluences are shown in Fig. 8. The reaction probability remains inde-
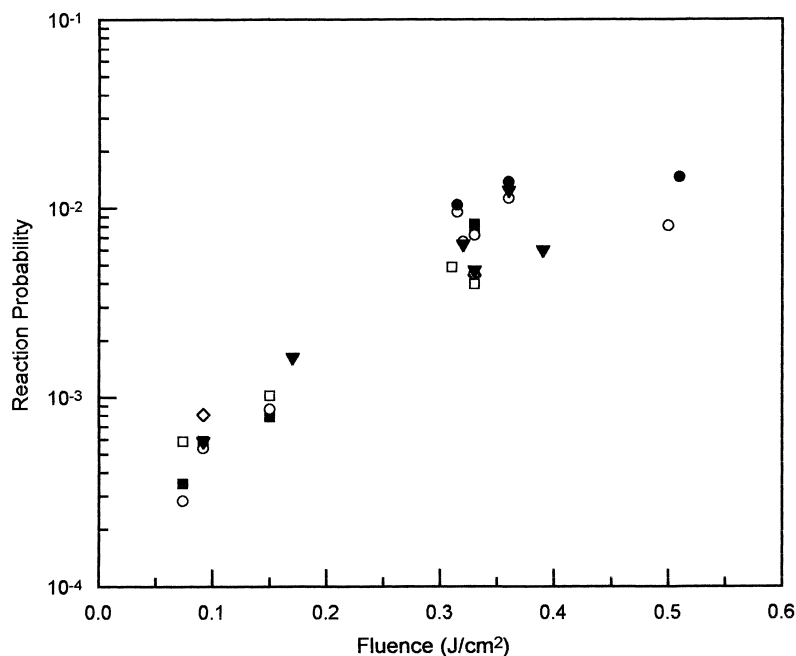
Fig. 7. Reaction probability as a function of fluence at different pressures of PhSiH$_3$: ($\diamond$) 0.50 Torr; ($\square$) 1.00 Torr; ($\blacksquare$) 4.00 Torr; ($\bigcirc$) 5.00 Torr; ($\blacktriangledown$) 10.00 Torr; ($\bullet$) 15.00 Torr.

pendent of pressure at constant fluence, although the absolute value of $P(\Phi)$ increases with fluence reaching a maximum of $P(\Phi) = (0.017 \pm 0.013)$ as observed also in Fig. 8.

Contrary to what we observe on irradiation of 15 Torr of neat PhSiH$_3$, namely decomposition and powder formation, the addition of 15 Torr of Ar to 0.500 Torr of PhSiH$_3$ does not produce significant dissociation, as shown in Fig. 5, where

$\langle n \rangle$ remains constant at each fluence for different pressures of added Ar.

The effect of added Ar on the collisional deactivation of vibrationally excited PhSiH$_3$ is evidenced by the reaction probability, a pressure increase produces vibrational deactivation of the excited molecule. This shows that the dissociation process is not given by an effect of total pressure
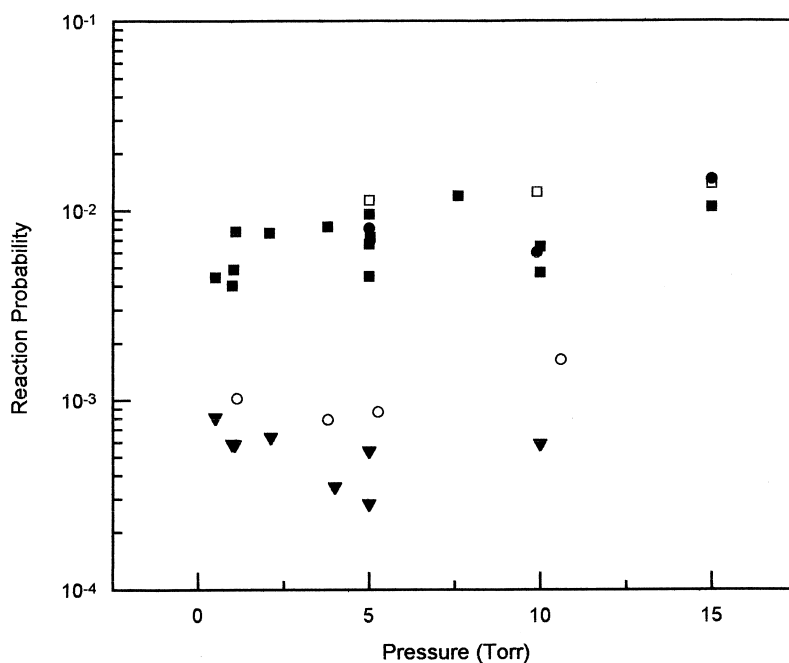

Fig. 8. Reaction probability as a function of the pressure of PhSiH$_3$ at different fluences: ($\blacktriangledown$) 0.08 J/cm^2; ($\bigcirc$) 0.15 J/cm^2; ($\blacksquare$) 0.33 J/cm^2; ($\square$) 0.36 J/cm^2; ($\bullet$) 0.45 J/cm^2.

but implies collisional assistance whereby an intermolecular energy transfer process produces excitation followed by decomposition, a well-known process of energy pooling [57,58]. This is due to the fact that the laser pulse produces an internal energy distribution which, by collisions, turns into a new distribution putting molecules above the threshold energy level leading to dissociation [57–59].

3.3. Characterisation of the products formed by IRMPD

The IRMPD of $PhSiH_3$ not only yields gaseous products but also formation of a film on the windows and the inner surface of the irradiation cell is observed. The presence of these surface films on the KBr windows could produce a reduction of the laser transmitted radiation by absorption of IR laser photons, becoming an additional source of photolysis products such as PhH, as well as affecting the IR absorption measurements of $PhSiH_3$. However, control measurements did not show any detectable reduction of the laser radiation. In agreement with this observation, preliminary analysis for the characterisation of the film by IR spectroscopy showed the absence of any IR absorption bands at the laser wavelength used, $936.8\,cm^{-1}$ (Fig. 11). Besides, the formation of photoproducts by direct absorption of the film is negligible with respect to the reaction products obtained by laser photolysis of $PhSiH_3$.

The PhH measured was found to increase with laser fluence for a given $PhSiH_3$ pressure, as expected if PhH is a primary molecular product of the photodissociation. After collecting the volatile gas products at 77 K, a residual pressure was observed that can be attributed only to the formation of H_2.

In all the experiments, the presence of H_2, PhH and $PhSiH_3$ was determined. From FTIR and conventional IR analysis, the reaction yields were determined from the decrease in the intensity of the characteristic IR absorbance peaks of $PhSiH_3$ [20]. The irradiation conditions varied progressively from 25 up to 1000 laser pulses and comparison of the IR spectra of 7 Torr of $PhSiH_3$ taken before and after irradiation with 500 pulses at a fluence of $0.44\,J/cm^2$ is shown in Fig. 9. A decrease in the intensity of the absorption bands of $PhSiH_3$ can be observed. The experimental results obtained are shown in Fig. 6, where the dissociation fraction shows a marked increase with fluence up to $\approx 0.35\,J/cm^2$ and reaches a maximum limit at high fluences of $X_d = 0.81 \pm 0.03$. This effect has already been observed in other chemical systems [60]. In Fig. 10, the dissociated fraction as a function of the pressure of $PhSiH_3$ is shown to remain constant for various pressures although as the fluence increases, so does the absolute value of X_d up to a maximum. The mass spectra of the samples of $PhSiH_3$ between 3 and 10 Torr irradiated at fluences between 0.4 and $0.9\,J/cm^2$ reveal the presence of unreacted $PhSiH_3$ at m/z 108 and PhH at m/z 78. These analyses did not show the presence of compounds of high molecular weight,
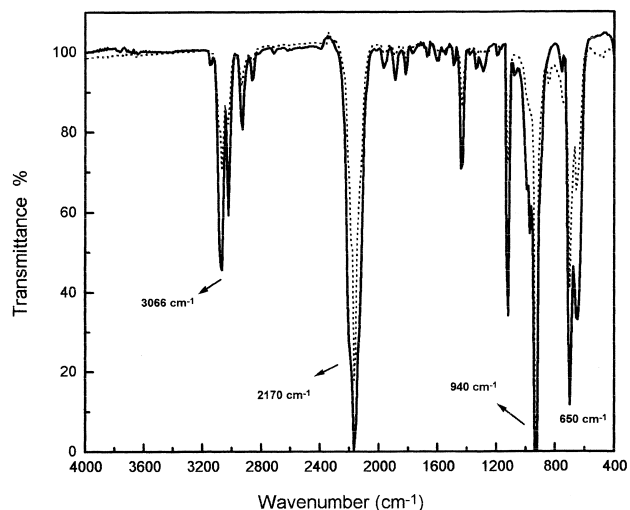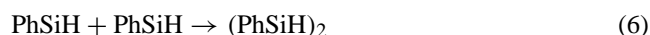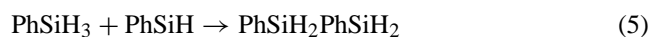

Fig. 9. IR spectra of 7 Torr of $PhSiH_3$ before and after irradiation at fluence $0.44\,J/cm^2$. The full line is the spectrum of the sample before irradiation. The dotted line is the spectrum of the sample after irradiation.

$m/z > 120$, which might arise from insertion reactions of the radicals, such as SiH_2 and PhSiH in $PhSiH_3$ according to reactions (4) and (5), leading to the formation of $PhSi_2H_5$ (phenyldisilane) and $PhSiH_2PhSiH_2$ (1,1-diphenyldisilane), respectively [13,19]. Thus, although these species were not detected, they may have been formed and photolysed away. Under our analytical conditions, however, they were not observed. 1,1 diphenyldisilane has very low vapour pressure [61] and condensation would appear likely for this compound. The absence of these species in the gas phase could account for the formation of the surface film also through polymerization reactions such as Eq. (6):

$$PhSiH_3 + SiH_2 \rightarrow PhSiH_2SiH_3 \qquad (4)$$

$$PhSiH_3 + PhSiH \rightarrow PhSiH_2PhSiH_2 \qquad (5)$$

$$PhSiH + PhSiH \rightarrow (PhSiH)_2 \qquad (6)$$

Gas chromatographic analyses of the irradiated samples of $PhSiH_3$ revealed similar results to those obtained by IR spectroscopy. The presence of unreacted $PhSiH_3$ was detected as well as the formation of PhH from which the quantitative determinations were performed. In Fig. 10, the results obtained from GC and IR analyses are compared. It can be observed, in both cases, that the dissociated fraction is independent of the pressure of $PhSiH_3$ and there is good agreement between the dissociated fraction values obtained from both methods.

An IR spectroscopic study of the visible films of a yellow-brownish solid material deposited on the inner surface of the cell was performed. The IR spectrum obtained is shown in Fig. 11, which points to the presence of several bands centered at 3050, 2179 and $1100\,cm^{-1}$ corresponding to the C–H [62], Si–H and Si–O [20,63–65] stretching vibrations. From these results, we concluded that a solid
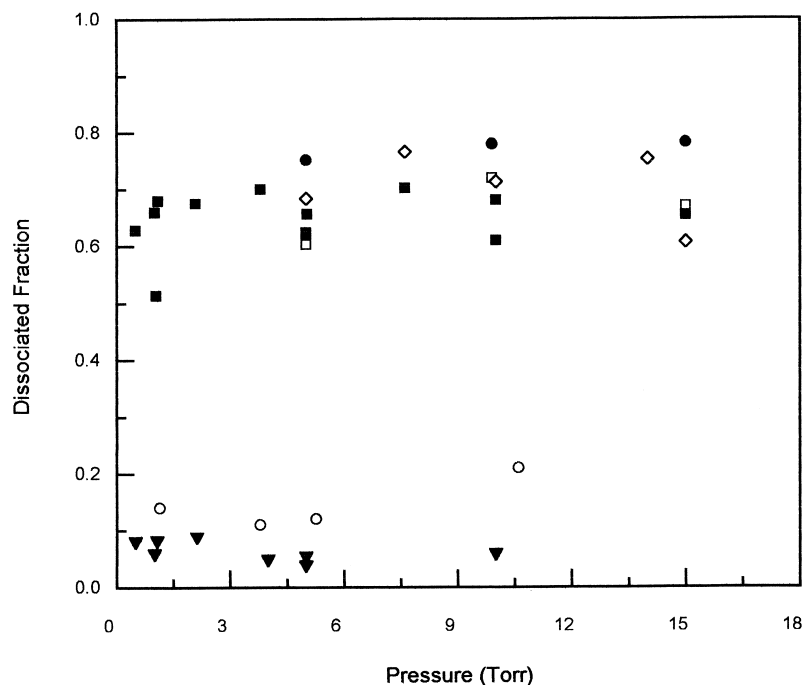
Fig. 10. Dissociated fraction vs. pressure of $PhSiH_3$ at different fluences: ($\blacktriangledown$) 0.08 J/cm^2; ($\bigcirc$) 0.15 J/cm^2; ($\blacksquare$) 0.33 J/cm^2; ($\square$) 0.36 J/cm^2; ($\bullet$) 0.45 J/cm^2; ($\diamond$) cromatographic data.
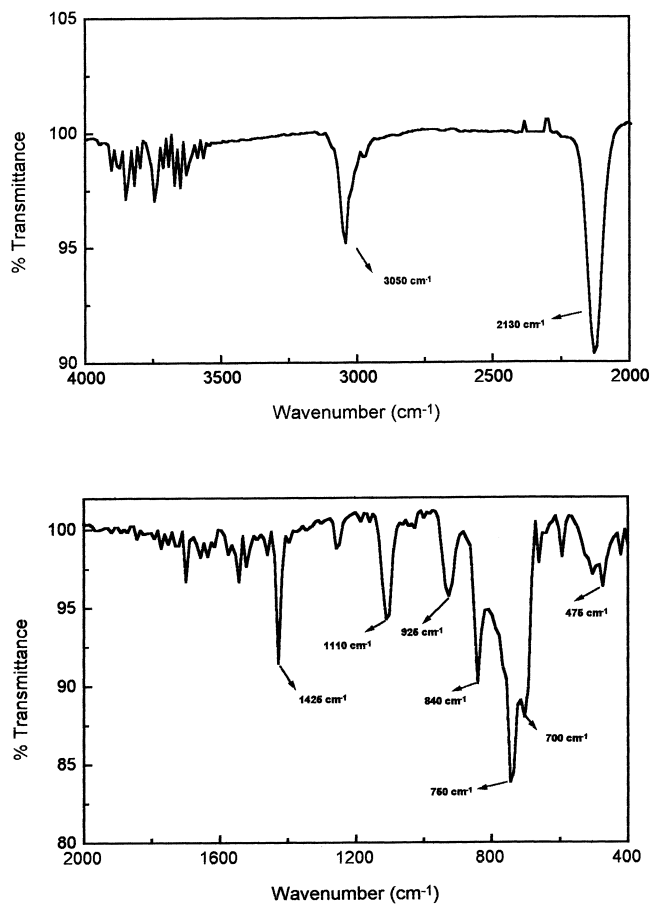

Fig. 11. IR spectrum of the solid material deposited by irradiation of $PhSiH_3$.

composed of Si, C, O and H is formed. The assigned bands are listed in Table 1. Our preliminary results are in good agreement with the more detailed characterisation performed on surface deposits of Si by IRMPD of $PhSiH_3$ in previous works [20], by determining their composition and morphology.

In Fig. 12, the measured yields of H_2 and PhH are given relative to the pressure of $PhSiH_3$ for all experiments with 1000 laser shots at a fluence of 0.33 J/cm^2. The yields were found to be constant over this range of pressure of $PhSiH_3$ studied with average values of 1.09 for H_2 and 0.064 for benzene ratio.

The IRMPD of $PhSiH_3$ shows the formation of H_2 and PhH as primary reaction products whereas no evidence was found about the formation of other species by insertion reactions of RSiH to $PhSiH_3$ under the present experimental conditions. The results obtained in these experiments are consistent with the reaction mechanism that involves a primary dissociation channel of H_2 and PhSiH formation in a ~17-fold ratio higher than the minor but also primary

Table 1
Assignment of observed IR bands of the solid material

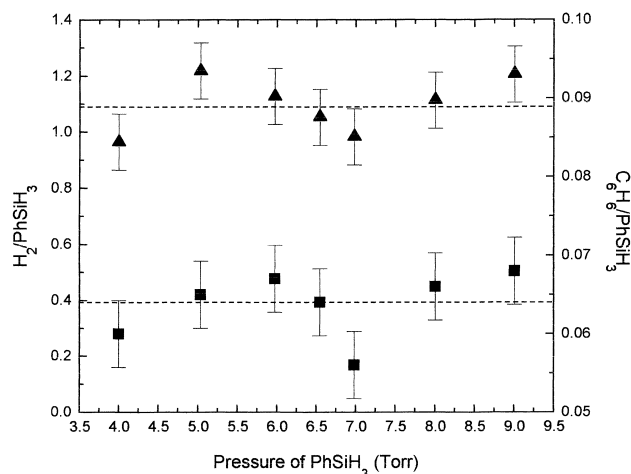| λ (cm^{-1})	Assignment
700–850	ν_{Si-C} (stretch bulk)
925	ν_{Si-C}
1050–1200	$\nu_{Si-O-Si}$ (stretch)
1425	ν_{Si-H} (stretch bulk)
2130	ν_{Si-H}
3050	ν_{C-H} (stretch aromatic)

Fig. 12. Variation of the measured yields of H_2 and PhH relative to PhSiH$_3$ at a fluence of 0.33 J/cm^2: H_2/PhSiH$_3$ (▲) experimental ratio; C_6H_6/PhSiH$_3$ (■), experimental ratio (- - -) mean value, 1.09; (. . .) mean value, 0.064.

Table 2
Observed values of the product ratios for the decomposition of PhSiH$_3$ by different experimental methods

Experimental method	H_2/ PhSiH$_3$	Benzene/ PhSiH$_3$	H_2/ Benzene	Reference
UV-photolysis	0.52	0.09	5.7	[13]
Thermal decomposition	0.84	0.16	5.2	[19]
IRMPD	1.09	0.064	17.0	this work

the number of photons calculated for each channel taking into account the corresponding activation energies [19] would be 22 and 23, respectively. These results are in good agreement with our experimental value of $\langle n \rangle$ which is a macroscopic average over all the molecules in the irradiation volume and, therefore a fraction of molecules will have the energy necessary to follow the decomposition pathway.

channel of PhH and SiH$_2$, as shown in Fig. 13. These results are in agreement with the mechanism reported by Steinfeld [5], and prove that the IRMPD process of PhSiH$_3$ is more selective for the generation of PhSiH radicals than the thermal or the UV photodecomposition methods as compared in Table 2.

From the IRMPA results, the mean number of IR photons absorbed by the molecule is 18. According to the proposed dissociation mechanism involving the elimination of H$_2$, Channel 1, and the formation of PhH, Channel 2:
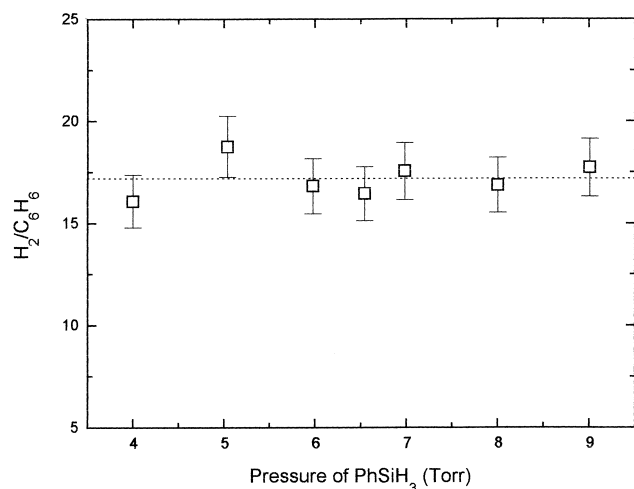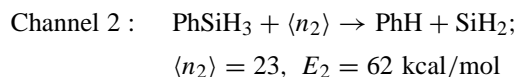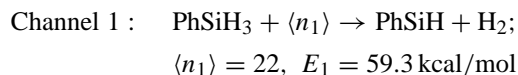
Channel 1 : $PhSiH_3 + \langle n_1 \rangle \rightarrow PhSiH + H_2$;

$\langle n_1 \rangle = 22, \ E_1 = 59.3 \, \text{kcal/mol}$

Channel 2 : $PhSiH_3 + \langle n_2 \rangle \rightarrow PhH + SiH_2$;

$\langle n_2 \rangle = 23, \ E_2 = 62 \, \text{kcal/mol}$

4. Conclusions

The IRMPA and IRMPD processes of PhSiH$_3$ were studied by absorption measurements, reaction probabilities, and quantitative analyses. The IR absorption cross-section of this molecule was determined as $\sigma_L = (1.34 \pm 0.08) \times 10^{-18} \, \text{cm}^2$ which coincides with the value obtained for the conventional IR absorption cross-section, σ_0. Pure PhSiH$_3$ or in the presence of Ar was found to follow the typical behaviour of the so-called 'large molecules', since no restrictions to the multiphoton absorption process were observed. Results, obtained from experiments with Ar added as an inert gas — which show that for a given pressure of PhSiH$_3$ $\langle n \rangle$ remains constant and the reaction probability decreases with increasing total pressure — allowed for the conclusion that decomposition occurs through collisional assisted intermolecular energy transfer processes of energy pooling.

The primary channel of H$_2$ and PhSiH formation, determined from end products analyses following IRMPD of PhSiH$_3$, is 17-fold higher than the production of PhH and SiH$_2$.

The mean value of IR photons absorbed, obtained from the IRMPA measurements coincides with the energetic values of the proposed decomposition channels making the IRMPD of PhSiH$_3$ a suitable technique for the generation of PhSiH radicals.

Analysis of the microscopic absorption cross-sections through modelling fitting of the experimental results still remains to be investigated.

Fig. 13. Pressure dependence of H_2/C_6H_6 product ratio in the IRMPD of PhSiH$_3$ at a fluence of 0.33 J/cm^2 with 1000 CO$_2$ laser pulses: H_2/C_6H_6 (□) experimental ratio; (. . .) mean value: 17.0.

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