

Transient detection in infrared multiphoton decomposition of (chloromethyl)silane and 1,3-disilacyclobutane: evidence for cleavage of SiCH₄ intermediates

M. Santos^{a,*}, L. Díaz^a, J. Pola^b

^a Instituto de Estructura de la Materia, CFMAC, CSIC, Serrano 121, 28006 Madrid, Spain

^b Laser Chemistry Group, Institute of Chemical Process Fundamentals, Academy of Sciences of Czech Republic, 165 02 Prague 6, Czech Republic

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Abstract

The transients produced in the infrared multiphoton decomposition (IRMPD) of (chloromethyl)silane—HClSi:, H₂Si: and H₂C:—and of 1,3-disilacyclobutane—H₂Si: and H₂C:—have been identified by laser-induced fluorescence (LIF). The nascent HClSi: and H₂Si: populations are generated with a high degree of excitation and the species produced from (chloromethyl)silane possess more rotational and vibrational energy than those produced from 1,3-disilacyclobutane. The obtained quenching rate and radiative lifetime for HClSi: are $(4.6 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ per molecule s}^{-1}$ and $369 \pm 10 \text{ ns}$, respectively. The formation of H₂Si: and H₂C: in IRMPD of both (chloromethyl)silane and 1,3-disilacyclobutane adds to previous knowledge on decomposition of (chloromethyl)silane and 1,3-disilacyclobutane and suggests that these transients are produced from the same SiCH₄ (H₃Si(H)C: and (CH₃)HSi:) intermediates.

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1. Introduction

During the last decade, the technique of laser-induced chemical vapour deposition (LCVD) was used for the growth of SiC materials [1,2] and taken advantage of IR multiphoton decomposition (IRMPD) of organosilanes [3–6]. The knowledge of the course of the decomposition process is essential for understanding the properties of the deposited materials.

In this field, the study of intermediary short-lived species by means of real time techniques gives valuable information on the occurrence of different channels of the photo-fragmentation. In particular, the detection of chlorosilylene, HClSi: reported for the first time by Herzberg and Verma [7], is a useful diagnostic tool in the LCVD processes [8] and has been reported [9,10] in a number of spectroscopic and kinetics studies.

We have previously identified transient species formed in the photolysis of several organosilanes. Specifically, the examination of the spontaneous and laser-induced fluorescence (LIF) after IR laser photolysis in 2-chloroethenylsilane (CES) and silacyclopent-3-ene (SCP) has allowed the identification of H₂Si:, H₂C:, C₂ and H₂ as dissociation products

in the IRMPD of these molecules [11,12]. Other studies on UV photolysis of CES at 193 and 212 nm revealed formation of HClSi:, SiH, C₂ and Si but not of H₂Si: species [9,11].

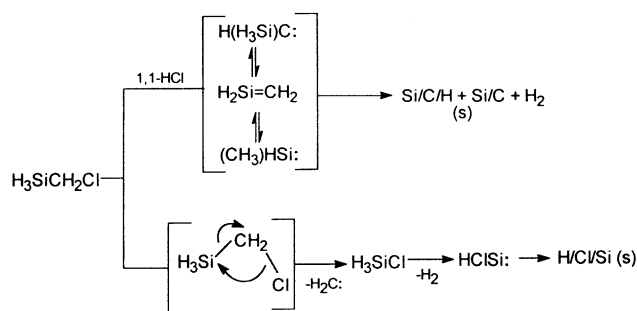
Following our general objective to explore the relationship between the decomposition mechanism of organosilane and the properties of the deposited solid materials, we have recently shown that the IRMPD of (chloromethyl)silane, ClH₂CSiH₃ (CMS), is initiated by 1,1-HCl and H₂C: elimination (Scheme 1) [13].

This conclusion was based on the characterisation of the final volatile products of the laser-induced thermalolysis of isotopomeric H₃SiCH₂Cl and D₃SiCH₂Cl (chloromethyl)silanes. The brief analysis by LIF detected the presence of chlorosilylene (HClSi:), silylene (H₂Si:) and methylene (H₂C:) in the IRMPD of CMS. These findings suggested [13] that HClSi: and H₂C: arise from CMS dissociation with elimination of carbene and dehydrogenation of chlorosilane, and H₂Si: and H₂C: from the photolysis of CMS through a decomposition of intermediary silylcarbene, H₃SiCH:, the species calculated [14] to be in equilibrium with silene H₂Si=CH₂ and methylsilylene CH₃(H)Si: (Scheme 2).

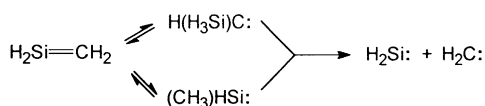
In this paper, we present a detailed examination of LIF after IRMPD of CMS and also a brief examination of LIF after IRMPD of 1,3-disilacyclobutane (DSCB). The latter

* Corresponding author.

E-mail address: imts406@iem.cfmac.csic.es (M. Santos).



Scheme 1.



Scheme 2.

reaction having been previously studied [15,16] and revealed as controlled by expulsion of silene provides a standard reaction to which the IRMPD of CMS can be compared. We reveal that the IRMPD of CMS is controlled by formation of $\text{H}_2\text{Si:}$, HClSi: and $\text{H}_2\text{C:}$ transients and that of DSCB yields $\text{H}_2\text{Si:}$ and $\text{H}_2\text{C:}$ species. We diagnose relative energy of these species and suggest that $\text{H}_2\text{Si:}$ and $\text{H}_2\text{C:}$ transients produced in the IRMPD of CMS and DSCB originate from cleavage of a common precursor.

2. Experimental

A Lumonics K-103 TEA CO_2 laser was employed for the IRMPD of the CMS and DSCB samples. It is equipped with frontal Ge multimode optics (35% reflectivity) and a rear diffraction grating with 135 lines/mm blazed at $10.6\ \mu\text{m}$. The laser was provided with a low jitter trigger device (Lumonics 524) supplying jitters between the IR and UV pulses shorter than 100 ns in the pump and probe experiments.

The CO_2 laser irradiation of CMS and DSCB was carried out by using the respective 10P(32) line at $933\ \text{cm}^{-1}$ and 10R(18) line at $975\ \text{cm}^{-1}$ that are coincident with the SiH_x stretching mode of these compounds. These wavelengths were checked with a 16-A spectrum analyser (Optical Eng. Co.). The laser operated with a mixture of CO_2 , N_2 and He in the proportion 8:8:84, the pulse temporal profile being monitored with a photon drag detector (Rofin Sinar 7415). The pulse consisted in a spike (60 ns, FWHM) and a tail lasting approximately $3\ \mu\text{s}$.

In general, the photolysis experiments are performed under gas-flow conditions of neat CMS or DSCB samples in Pyrex cells of 4.5 cm diameter and 15.5 or 43 cm length, fitted with a pair of NaCl windows orthogonal to a pair of quartz windows. Focused geometry was used by placing lens (10 and 24 cm focal length) in front of the cell for

the CO_2 laser beam. The output of a N_2 -pumped dye laser (PRA LN 107, 0.04 nm bandwidth, 500 ps temporal width), counter-propagating to the infrared laser beam, was focused by a 50 cm quartz lens at the focus of the infrared beam.

The LIF experiments were carried out in three spectral regions by using three different dyes: coumarin 440 and 485 for the 420–475 nm and 480–510 nm regions, respectively and rhodamine 590 for the 575–600 nm region. The induced fluorescence was collected through a quartz window at the right angle to the laser axis, filtered through a 10 cm monochromator, 2 mm slit (bandpass of 6.4 nm) at the first two regions and through a cut-off filter at the third region. The filtered signal was detected by means of a photo-multiplier (Hamamatsu R-928) fed with 800 or 1000 V.

The CO_2 laser pulse, picked up with the photon drag detector, triggers a Tektronix TDS 540 digital oscilloscope that is used to collect the LIF signals and send them to a personal computer where they are averaged and analysed. The delay between the CO_2 and probe laser pulses ($1\ \mu\text{s}$, if not stated otherwise) was controlled by a Berkeley Nucleonics digital delay generator (BNC 7036A) within ~ 50 ns. The CO_2 laser fluence was calculated as the ratio of the pulse energy (measured in front of the lens with Lumonics 20D pyroelectric detectors) and the $1/e$ cross-sectional beam area (measured at the cell position with a pyroelectric array Delta Development Mark IV). In our experimental conditions, a fluence of $50 \pm 5\ \text{J}/\text{cm}^2$ was used for the irradiation of CMS and of $12 \pm 3\ \text{J}/\text{cm}^2$ for the irradiation of DSCB. Each experimental point was obtained by averaging over 20 measurements. Sample pressures in the cell were measured with (0–1 and 0–10 hPa) MKS Baratron gauges. Typical pressure values of 0.3 and 0.05 hPa were used for CMS and DSCB, respectively.

CMS and DSCB were prepared by procedures reported elsewhere [17–19] and their purity (better than 97%) was confirmed by gas-chromatography.

3. Results and discussion

3.1. IRMPD of (chloromethyl)silane

The excitation spectra of the photo-fragments resulting from the IRMPD of CMS (0.3 hPa) and recorded by scanning the probe laser between 415 and 470 nm (region I) and between 485 and 560 nm (region II) are given in Fig. 1. The possible assignments of the bands of these spectra are given in Table 1 (the definitive assignments are bold faced) [7,8,11,20–23]. All the bands detected in the regions I and II could be due to the ($\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$) transition of the ν_2 mode of the HClSi: transient, or to the ($\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$) transition of the ν_2 mode of the $\text{H}_2\text{Si:}$ transient. As can be seen, both transients would be formed with large vibrational excitation in the ground state, although the correspondence of the transitions of the $\text{H}_2\text{Si:}$ transient to rather high

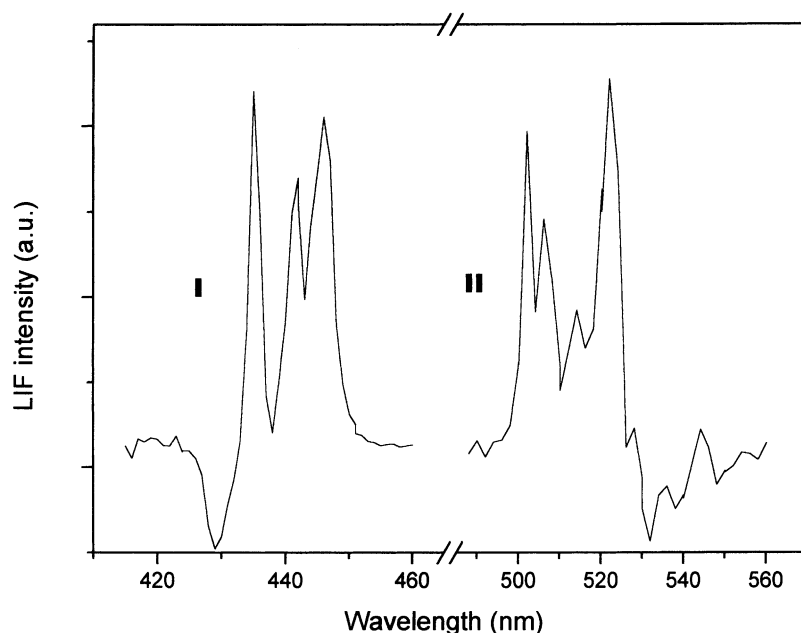


Fig. 1. LIF excitation spectra upon IRMPD of 0.3 hPa of CMS.

vibrational levels of the first excited electronic state is not in keeping with low band intensities expected from the values of the Frank–Condon factors for these transitions [21].

In order to discern between the HCISi: and H₂Si: transients, we have obtained the LIF dispersion spectra by exciting some of the bands in the regions I and II (Fig. 2) and assigned them in Table 2. The dispersion spectra obtained from the probed excitation bands can be described as related only to the HCISi: transitions. The assignment of the bands at 434.9 and 441.6 nm to deexcitations from high vibrational levels of the H₂Si: transient is not very probable. The dispersion spectrum obtained for the band centred at 543.9 nm is very similar to that obtained for the band at 501.8 nm, suggesting that a population of states excited to the $\nu' = 3$ level of the first electronic state undergoes a non-radiative decay to the $\nu' = 0$ level and from there it gives rise to the observed ($0 \rightarrow n$) transitions. Then, according to the above

Table 2
Possible assignments of the dispersion spectra

Excitation band (nm)	Possible assignments of the dispersed bands	
	HCISi	SiH ₂
434.9	($4 \rightarrow n$), $n = 0-4$	($9 \rightarrow 1, 2$); ($6 \rightarrow 0, 1$)
441.6 ^a	($3 \rightarrow 0, 2$); ($5 \rightarrow 2$)	($10 \rightarrow 2, 3$)
446.0	($1 \rightarrow 1$); ($2 \rightarrow 2, 3$); ($3 \rightarrow 4, 5$)	
501.8 ^a	($0 \rightarrow n$), $n = 0-4$	
543.9	($0 \rightarrow n$), $n = 0-4$	

The definitive assignments of the bands to HCISi: radical are explained in the text.

^a Shown in Fig. 2.

Table 1
Possible assignments of the bands of the excitation spectra of Fig. 1

Excitation wavelength (nm)	Wavenumber (cm ⁻¹)	Intensity	Possible assignments ^a
434.9	22992	+++	HCISi (4 ← 0); SiH ₂ (9 ← 0)
441.6	22644	++	HCISi (5 ← 1); SiH ₂ (10 ← 1); SiC (0 ← 0)
446.0	22421	+++	HCISi (3 ← 0)
501.8	19929	+++	HCISi (0 ← 1); SiH ₂ (10 ← 4)
505.9	19766	++	HCISi (1 ← 2)
514.0	19456	+	HCISi (2 ← 3); SiH ₂ (6 ← 1)
521.7	19166	+++	HCISi (3 ← 4); SiH ₂ (9 ← 4)
535.1	18689	+	HCISi (2 ← 4); SiH ₂ (5 ← 1)
543.9	18384	++	HCISi (3 ← 5); SiH ₂ (8 ← 4)
553.9	18053	+	HCISi (1 ← 4); SiH ₂ (3 ← 0)

The definitive assignments of the bands to HCISi: radical are explained in the text.

^a Transitions ($0, \nu'_2, 0$) ← ($0, \nu'_2, 0$) in HCISi and SiH₂ are shorten to ($\nu' \leftarrow \nu''$).

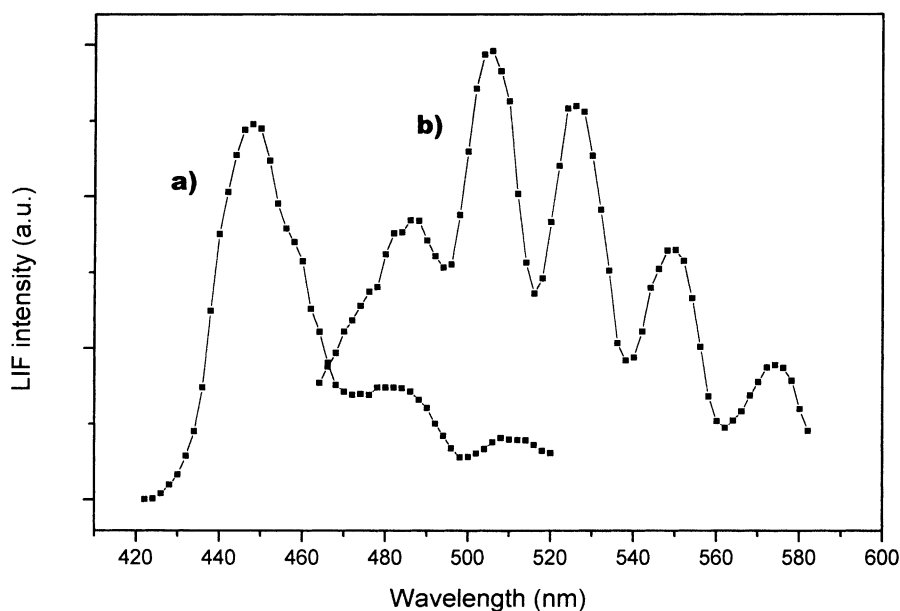


Fig. 2. LIF dispersion spectra obtained by exciting bands at 441.6 nm (a) and 501.8 nm (b).

discussion, we assign the bands of the excitation spectra in Fig. 1, regions I and II, to the presence of the HCISi: transient.

Although the resolution of our apparatus is not enough to obtain a rotationally resolved spectrum, we have resolved (0.2 nm step) a small interval of the region I (Fig. 3). The reliability of its profile has been confirmed by repeated recording of the spectrum. Some rotational transitions that could correspond to the Q branches of the (0, 3, 0–0, 0, 0), (0, 2, 1–0, 0, 0) and (1, 3, 0–0, 0, 0) vibrations of the ν_2 mode of

HCISi: [7] are detected. The band at 446.0 nm being wider and double indicates that this spectral region is contributed [8] by both, (0, 3, 0–0, 0, 0) transition of the ν_2 mode and the (1, 0, 0–0, 0, 0) transition of the ν_1 mode of the HCISi: transient. An intense band detected at 441.6 nm is supportive of the presence of some amount of SiC whose 0–0 transition appears at this wavelength [22,23]. This finding is in line with the provisional assignment in Table 1 and we have checked that its presence in the corresponding dispersion spectrum cannot be ruled out.

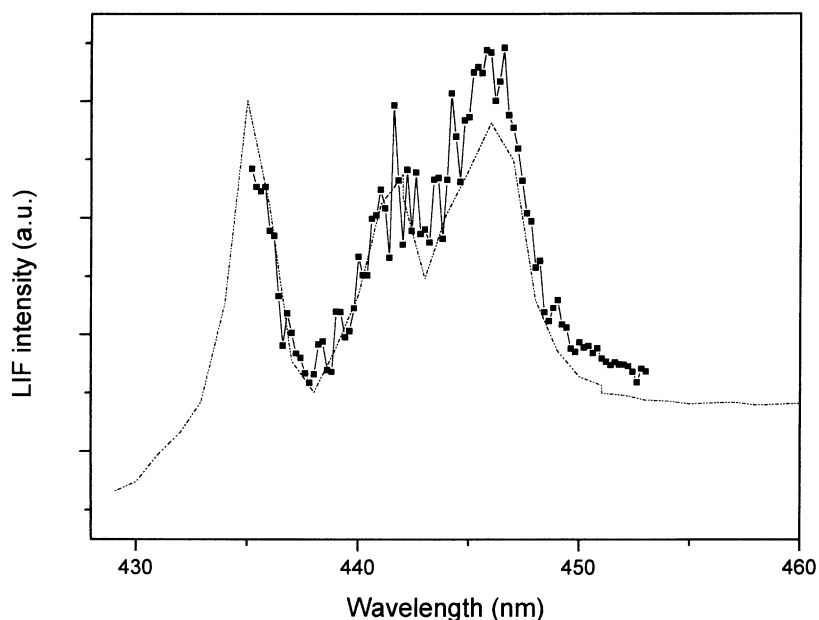


Fig. 3. Detailed excitation spectrum for a part of region I. Dotted line is the region I spectrum of Fig. 1.

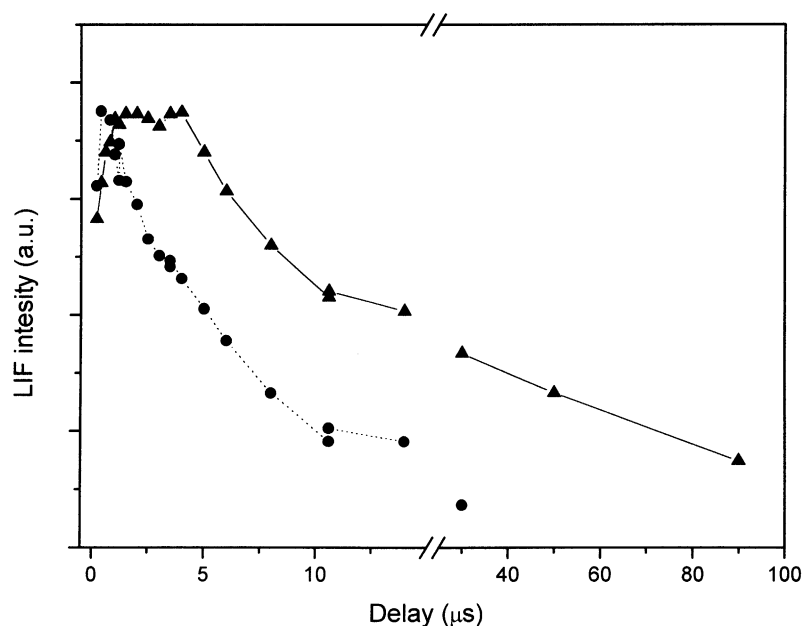


Fig. 4. LIF intensity of HClSi: vs. time delay between decomposing and probing laser pulses. Solid curve relates to excitation of ($3 \leftarrow 0$) transition and dotted one to excitation of ($0 \leftarrow 1$) transition.

To study the time evolution of the HClSi: transient we have obtained the delay curves (Fig. 4) by varying the delay between the CO₂ and dye laser pulses for 0.2 hPa. The solid curve is related to the excitation at 446 nm ($3 \leftarrow 0$) transition and the dashed one to the excitation at 502 nm ($0 \leftarrow 1$) transition). These curves show the time evolution of the HClSi: populations at both levels. It is seen that the $\nu'' = 0$ population increases much slower and lasts much longer than that of the $\nu'' = 1$, reaching its broad maximum (3 μ s width) more than 1 μ s later. This behaviour can be explained by assuming that the ground state is populated through the deexcitation of higher vibrational levels, which implies a high degree of vibrational excitation of the nascent HClSi: transients. The time elapsed between the two maxima of Fig. 4 (>2 μ s) is related to the vibrational relaxation time of the vibrationally excited species.

The spectrum of the region I (Fig. 1) was obtained by using 1 μ s delay between the decomposition-inducing and probing pulses and we have checked that the same spectrum can be obtained by using the 9 μ s delay. However, the spectrum in the region II was obtained at 1 μ s delay and at the delay of 9 μ s, no spectrum can be observed due to low intensity of the signals. Interestingly, the spectrum in the region II obtained by collecting the induced signal through tuning the monochromator below the excitation wavelength was more intense than that obtained through tuning the monochromator above the exciting wavelength. These findings are indicative of the upper electronic levels being populated through resonant hot absorption bands from vibrationally excited levels of the ground electronic state (Table 1). All these results indicate that a high proportion of the newly formed HClSi: transients are produced at high rovibrational temperatures

[8]. This fact, together with the failure to detect H₃SiCl among the final products [13], suggest that chlorosilane is formed with an energy content enough for dehydrogenation to take place, giving rise to hot HClSi: (Scheme 1) [24].

The formation of the excited H₃SiCl in the IRMPD of CMS should occur [13] via the expulsion of methylene that should manifest itself in the region II of Fig. 1. We have obtained a better resolved excitation spectrum (0.2 nm step) when using for the detection an interference filter centred at 560 nm, coincident with the ($15 \rightarrow 0$) transition of H₂C: at 563 nm [25,26]. Several bands corresponding to the $\bar{b}(0, 16, 0) \leftarrow \bar{a}(0, 0, 0)$ transition of the H₂C: transient have been detected. Later on the presence of H₂C: will be confirmed.

The IRMPD of CMS was described [13] to take place via unimolecular processes. To study the influence of collisions in the production of the HClSi: transient, we have measured the LIF intensity at different initial pressure of CMS by exciting at 446 nm and collecting the induced fluorescence at 464 nm, i.e. according to our assignment exciting the ($3 \leftarrow 0$) and collecting the ($1 \rightarrow 1$) transitions of the HClSi: transient. The measurements have been made at 1 μ s time delay between the dissociating and probing pulses. At these conditions, Fig. 4 suggests that, for 0.2 hPa, the diffusion out of the probed volume or the recombination process are still rather small. The obtained curve is given in Fig. 5 where a non-collisional linear dependence [27] extrapolated from the lower pressure values is also included (dotted line). Fig. 5 suggests that collisions with CMS and with the other products formed in the dissociation process are strongly quenching the HClSi:-induced LIF signal. On the other hand, the fact that the HClSi: transient is formed at pressures as low

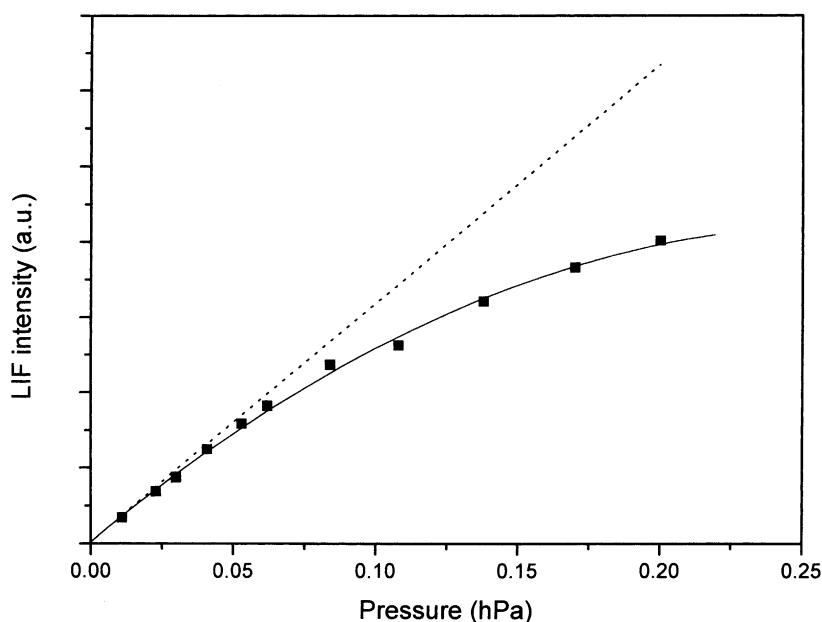


Fig. 5. Dependence of LIF intensity from HCISi: on CMS pressure. The dotted line is a non-collisional linear dependence extrapolated from the lower pressure values.

as 0.01 hPa and that its maximum production is observed at the time of the pulse (Fig. 4) points to disregard any collisional processes in the HCISi: formation.

Temporal profiles of the LIF signals for different bands can be fitted to single exponential functions giving decay times in the range of 220–290 ns. Specifically for the band at 446 nm, the quenching of HCISi: by CMS and other produced fragments can be estimated using the Stern–Volmer equation and measuring the decrease of the fluorescence lifetime upon increasing the CMS pressure. A quenching constant $k_{\text{CMS}} = (4.6 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ per molecule s}^{-1}$ and a radiative lifetime for the $\nu' = 1$ state of the $(\bar{A}^1A'' \leftarrow \bar{X}^1A')$ band system of HCISi: of $369 \pm 10 \text{ ns}$ were obtained. The k_{CMS} value obtained is in keeping with the obtained pressure dependence of HCISi: LIF signal (Fig. 5). For the radiative lifetime, we obtain a lower value than the one given by Harper and Clouthier [8] for the same band system ($432 \pm 20 \text{ ns}$). This difference may be associated to the presence of other products produced in the IRMPD of CMS in our experimental conditions.

The excitation in the 575–600 nm range gave much weaker signals than in the other two regions, which disabled the use of the monochromator and caused the whole deexcitation signal to be collected by means of the cut-off filter at 610 nm (Fig. 6). The rise from 590 nm is due to unfiltered scattered probe laser. This excitation spectrum presents two broad and unstructured bands centred at 578.5 and 585 nm that can be assigned to the $(\bar{A}_1B_1 \leftarrow \bar{X}^1A_1)$ $(0, 2, 0) \leftarrow (0, 0, 0)$ and $(0, 3, 0) \leftarrow (0, 1, 0)$ transitions of the $\text{H}_2\text{Si:}$ transient. These bands were also detected in the IRMPD of CES [11]. The width and lack of structure of these bands suggest a high content of internal (vibrational

and rotational) excitation of the formed $\text{H}_2\text{Si:}$ transient [28], hiding the bands of other possible species. There are also some narrow and weak bands centred at 579.8, 591.4, 593.4 and 594.4 nm. The first of them is due to the $(0, 16, 0) \leftarrow (0, 1, 0)$ of $\text{H}_2\text{C:}$ and the others are assignable [25,29] to $(0, 14, 0) \leftarrow (0, 0, 0)$ transitions of $\text{H}_2\text{C:}$ transient. The sharp bands centred at 580.5 and 588.6 nm correspond to molecular H_2 (transitions ending on $2p^3\Pi$ levels) [30,31]. The production of H_2 in electronically states have been detected in IRMPD produced at high fluence conditions as those obtained in focused irradiation [32,33]. At these terms, some laser-induced resonant breakdown could take place in the focal zone and excited or super-excited molecular states may be produced.

3.2. Inferences on the decomposition mechanism and IRMPD of 1,3-disilacyclobutane

The diagnosis of the transients in the IRMPD of CMS confirms our earlier proposed mechanism [13] of CMS decomposition involving initial 1,1-HCl elimination [13] and yielding short-lived $\text{H}_3\text{SiCH:}$ silylmethylene that undergoes isomerisation, dehydrogenation (Scheme 1) and decomposition into $\text{H}_2\text{C:}$ and $\text{H}_2\text{Si:}$ transients (Scheme 2).

Silylmethylene was earlier computed as the highest energy isomer of three elusive gaseous SiCH_4 species [14,34] of which experimental identification has been recently provided only for silene [16,35,36]. It can rearrange into silene $\text{H}_2\text{Si=CH}_2$ and further [14,37] to methylsilylene $(\text{CH}_3)\text{HSi:}$. All these species are very reactive and should eagerly participate, as documented [15] for silene, in polymerisation [38] reactions. Their dehydrogenation resulting in the

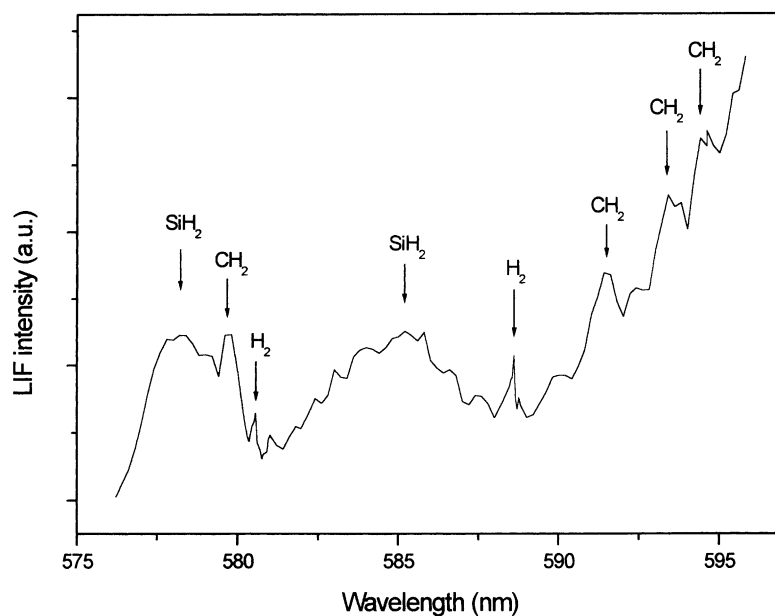


Fig. 6. Excitation spectrum of transients formed in the IRMPD of CMS in the 575–600 nm region.

formation of Si/C/H solids has been also considered [15]. The suggested cleavage at the Si–C bond of silylmethylene and methylsilylene is getting support from examination of LIF after IRMPD of 1,3-disilacyclobutane.

Silene was assumed [15] as the most important intermediate of the IRMPD of 1,3-disilacyclobutane, which was supported by transient UV spectroscopy studies (Scheme 3) [16]. The IRMPD of DSCB can thus be considered as a reaction suitable to compare with the IRMPD of CMS.

In our LIF examination of IRMPD of DSCB, we obtained the excitation spectrum in the 575–600 nm spectral region



Scheme 3.

(Fig. 7). Correction for the scattered probe laser has been made. This spectrum being contributed by bands of H_2Si -, H_2C - and H_2 species gives support for both dehydrogenation and decomposition of the SiCH_4 transients into methene and silylene. We remark that much more structured profile and sharper bands suggest a lower content of rovibrational

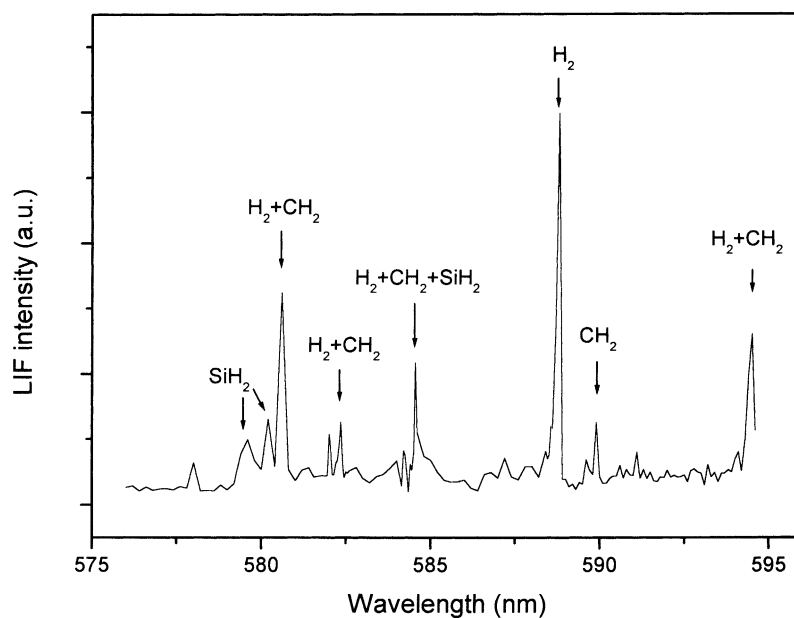


Fig. 7. Excitation spectrum of transients produced in the IRMPD of DSCB.

energy for H₂C: and H₂Si: transients [28] when formed from DSCB than when formed from CMS (see Fig. 6). These facts suggest a more energetic formation of silene in CMS than in DSCB probably due to the parent molecule dissociation behaviours. This different behaviour is indicated by the different fluence values needed to obtain measurable LIF signal in each molecule.

We consider that the energy of the IR laser pulse being efficiently absorbed [39] in H₂Si=CH₂, and in H(H₃Si)C: species, should enhance their internal energy and facilitate their dehydrogenation and/or cleavage at the Si–C bond yielding H₂C:, H₂Si: and H₂. This IR laser enhancement of the reactivity of the SiCH₄ transients can, in principle, occur in IRMPD of both DSCB and CMS. The higher energy content of the H₂Si: and H₂C: observed in the latter decomposition can reflect the effect of different reaction–coordinate–energy diagrams and/or different extent of absorption of laser radiation of the SiCH₄ species in both IRMPD processes.

4. Conclusions

We have analysed the transients formed in the IRMPD of CMS and DSCB by using the laser-induced fluorescence technique.

The HClSi:, H₂Si: and H₂C: transients along with molecular hydrogen were identified in the decomposition of CMS and possible presence of SiC has been detected. It has been established that all the transients are rovibrationally excited and that the IRMPD of CMS proceeds as a non-collisional process whose yield is inhibited by homogeneous and heterogeneous collisions. The rate of HClSi: quenching with CMS and dissociation products measured for the band at 446.0 nm was determined as $(4.6 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ per molecule s}^{-1}$ which corresponds to a radiative lifetime of $369 \pm 10 \text{ ns}$.

The IRMPD of DSCB produces H₂Si: and H₂C: transients and molecular hydrogen. The transients are formed with a lower rovibrational excitation than when produced by the IRMPD of CMS.

The present observation of methylene and silylene in the IRMPD of CMS and DSCB and the previous observation of silene in the IRMPD [16] and thermal decomposition [31,32] of DSCB gives strong support to decomposition of the silene and its isomers into methylene and silylene.

Acknowledgements

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