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Time-resolved study of the transients produced in the CO_2 and ArF laser flash photolysis of gaseous silacyclobutane and 1,3-disilacyclobutane

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A time-resolved study of the transients produced in the TEA CO_2 or ArF laser-induced decomposition of gaseous silacyclobutane (SCB) and 1,3-disilacyclobutane (DSCB) is reported. Both compounds produce transient $H_2C{=}SiH_2$ as the major primary product, which has been identified by its optical absorption spectrum, with $\lambda_{max} \approx 260$ nm. Under conditions of low laser fluence, this species has two decay channels: a unimolecular process ($k = 2.3 \pm 0.7 \times 10^4$ s^{-1}) and a reaction with the parent compound ($k_{SCB} = 2.0 \pm 0.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $k_{DSCB} = 3.0 \pm 0.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}). At high fluence (7.2 J cm^{-2} for the CO_2 laser and 6 J cm^{-2} for the ArF laser), the transient absorption signals become very complex owing to the onset of a number of other reactions and the formation of several additional transient species which appear to have strong absorption in the 250–650 nm region, with peaks/shoulders at *ca.* 260, 320 and 435 nm but these could not be identified unambiguously.

Silacyclobutane (SCB) and 1,3-disilacyclobutane (DSCB) have been proposed as potentially ideal precursors for the chemical vapour deposition (CVD) of thin films of Si–C–H and SiC materials, which find use in advanced ceramic, lithographic and electronic applications.[1–6] These compounds experience a significant strain in the four-membered ring, thereby offering the prospect of decomposition at lower temperatures, to yield silene $H_2Si{=}CH_2$, with a built-in 1 : 1 Si : C ratio, relatively weak Si—H bonds and, above all, a strong double bond between the silicon and the carbon. In view of this, several studies on the thermal decomposition of gaseous SCB and DSCB on hot surfaces have been reported.[7–12] Attempts have also been made to understand the kinetics and mechanism of the deposition of SiC on these hot surfaces, with limited success; the decomposition of SCB[7–11] or DSCB[12] has been found to be quite complex.

To investigate whether the thermal decomposition of SCB or DSCB is complicated by the heterogeneity of the experimental conditions, studies on the homogeneous decomposition induced by CO_2 laser[13] and UV light[14] have been performed. In these studies, information on the mechanism of decomposition has been obtained indirectly from the distribution of the end products under different experimental conditions.

The aim of the present work was to understand the mechanism of the decomposition of SCB and DSCB under homogeneous conditions by directly observing the growth and decay of the transient intermediates in real time. The decomposition was induced either by a pulsed CO_2 laser or by an ArF laser, and detection of the transients was achieved by observing their optical absorption using kinetic spectrophotometry.

Experimental

Infrared multiphoton dissociation (IRMPD) experiments were performed using a grating tuned pulsed TEA CO_2 laser (Lambda Physik model EMG 201E) operated on the 10 P(20) line (944.19 cm^{-1}). This wavelength was confirmed with the help of a CO_2 spectrum analyser (Optical Engineering Inc., CA). The output laser beam was rectangular (25 mm × 15 mm) with a temporal profile consisting of a 100 ns (FWHM) peak followed by a tail of *ca.* 1 μs. The focusing of the laser beam was achieved either by a BaF_2 lens (focal length, 25 cm) or by a Ge lens (focal length, 10 cm), to obtain the fluence of 1.35 and 7.2 J cm^{-2}, respectively. The energy of the laser was measured by using a pyroelectric detector (Gentec model ED-200).

193 nm (ArF) laser flash photolysis was carried out using an excimer laser (Oxford Lasers, model KX2). A fused quartz lens (focal length, 50 cm), kept at different positions between the sample cell and the laser, was used to vary the fluence in the range 0.04–6 J cm^{-2}.

Optical absorption due to the transient chemical species was recorded using a pulsed 250 W xenon arc lamp (the source of the analysing light beam was located at right angles to the laser beam), an *f*/3.4 grating monochromator (Applied Photophysics Ltd, UK), a Hamamatsu R-928 photomultiplier and a Tektronix digital storage oscilloscope (model TDS 540A, 500 MHz). The absorption signal S_λ at any wavelength was obtained as an average of N single-shot events [$N = 4$ to 20, depending on the signal-to-noise (S/N) ratio of the single-shot event]. N single-shot events of the baseline were also averaged to obtain a baseline B_λ, which was subtracted from S_λ to give a net absorption signal ($S_\lambda - B_\lambda$) with a superior S/N ratio. This was made possible by the built-in mathematical functions of the oscilloscope. Data from the oscilloscope were transferred to a Wipro model 386SX personal computer for further processing. In addition, the same computer was also used to control the operation of the CO_2 and excimer lasers, the lamp pulsing unit, the Uniblitz shutters and the oscilloscope using software jointly developed by the Chemistry and the Computer Divisions of the Bhabha Atomic Research Centre.

Irradiation of gaseous SCB or DSCB was conducted in a cylindrical stainless-steel cell (volume 260 cm^3), which was fitted with a PTFE stopcock for filling or evacuating the sample gas and with two pairs of optical windows for the passage of the laser and analysing light beams at right angles to each other. The pair facing the analysing light beam always consisted of two fused quartz windows. The material used for the other pair was either KCl (for the CO_2 laser) or MgF_2 (for the 193 nm laser). Further experimental details are described elsewhere.[15]

Transient spectra were corrected for the progressive loss of laser intensity in the probe region due to (1) the ageing of the laser gas mixture, and (2) the grey–black reaction product

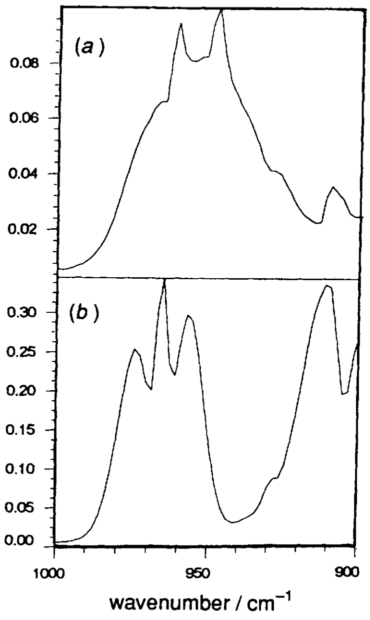


Fig. 1 IR spectra of (*a*) SCB; (*b*) DSCB (pathlength 10 cm, $P = 0.33$ kPa)

deposited on the KCl or the MgF_2 window facing the laser. The deposit was more pronounced at higher fluence. The correction was accomplished by monitoring the transient absorption signal at 260 nm both before and after recording the absorption signal at any other wavelength and computing the loss in the intensity per pulse from these data. The loss in intensity was significant at higher fluence of the laser, although it was negligible at low fluence.

Rate-constant values were obtained by a least-squares fit to the experimental data using standard statistical methods, and the reported errors correspond to 2σ.

UV spectra of SCB and DSCB were recorded by means of a spectrophotometer.[14] Stable products were characterised by a Mattson FTIR spectrometer (Model Cygnus 100). Samples of SCB and DSCB were prepared by earlier reported procedures[14] and their purities (>99%) were checked by gas chromatography (Shimadzu 14A gas chromatograph coupled with a Chromatopac C-R5A computing integrator).

Results and Discussion

Both SCB and DSCB show good IR absorption spectra in the emission range of the CO_2 laser (Fig. 1) and can be decomposed by tuning the TEA CO_2 laser into their $\delta(SiH_2)$ absorption band. They also absorb below 220 nm in the UV region (Fig. 2) with a broad maximum around 195 nm, which can be excited at a 193 nm (ArF laser) in order to study their photochemistry and to obtain complementary information, if any, on the transients produced in their IRMPD.

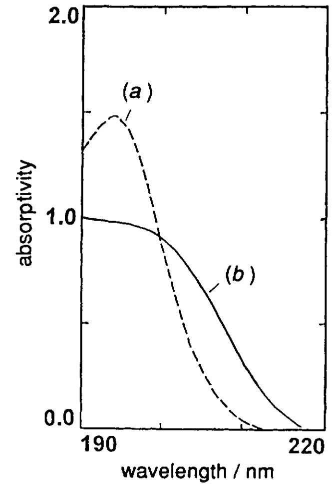


Fig. 2 UV spectra of (*a*) SCB; (*b*) DSCB (pathlength 6 cm, $P = 1.0$ kPa)

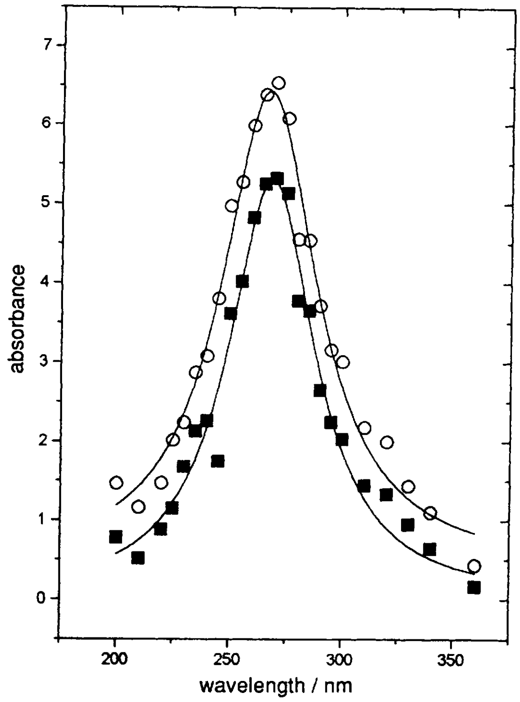
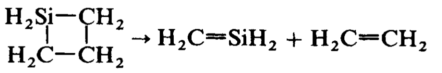


Fig. 3 Transient absorption spectra following IRMPD of SCB. $P = 0.67$ kPa, laser fluence = 1.35 J cm^{-2}; ○, 4 μs; ■, 12 μs after the laser pulse

IRMPD of SCB

IRMPD of SCB (0.67 kPa) using the CO_2 laser fluence of 1.35 J cm^{-2} yields a transient absorption spectrum, as shown in Fig. 3. The spectrum has a λ_{max} at about 260 nm and remains practically the same during the course of the decay of the transient species. Furthermore, it resembles the spectrum of silene, $H_2C{=}SiH_2$, reported in the literature.[16] These observations indicate the occurrence of the following reaction:



$$\begin{array}{l} H_2Si{-}CH_2 \\ \;\;|\qquad\; | \\ H_2C{-}CH_2 \end{array} \rightarrow H_2C{=}SiH_2 + H_2C{=}CH_2 \qquad (1a)$$

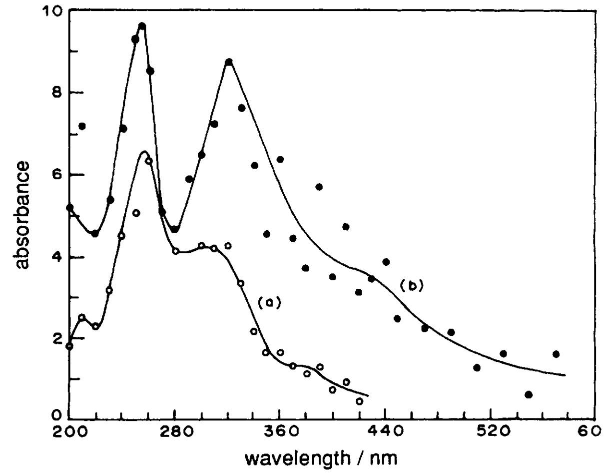


Fig. 4 Transient absorption spectra following IRMPD of SCB. $P = 1.0$ kPa, laser fluence = 7.2 J cm^{-2}: ○, 4 μs; ●, 90 μs after the laser pulse.

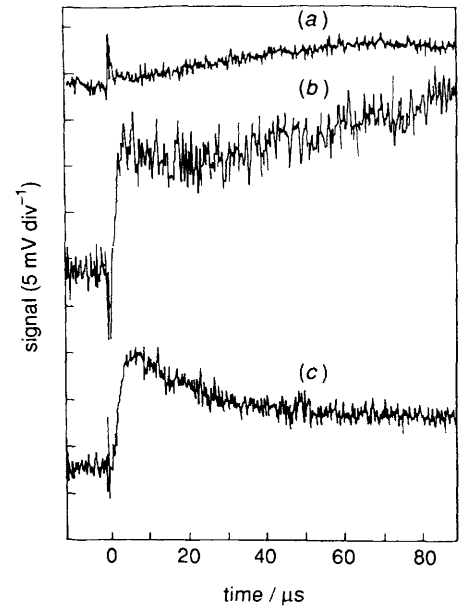


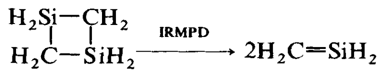
Fig. 5 Transient absorption profiles following IRMPD of SCB. $P = 1.05$ kPa, (*a*) $\lambda = 460$ nm, laser fluence = 7.2 J cm^{-2}, $I_0 = 920$ mV; (*b*) $\lambda = 260$ nm, laser fluence = 7.2 J cm^{-2}, $I_0 = 918$ mV; (*c*) $\lambda = 260$ nm, laser fluence = 1.35 J cm^{-2}, $I_0 = 953$ mV.

At lower laser fluence, the transient absorption signal was too weak to be discerned from the noise. At higher fluence (7.2 J cm^{-2}) the transient absorption extends to higher wavelengths, it has two shoulders at 302 and 380 nm, and shows the growth with time of an additional peak at *ca.* 320 nm and a shoulder at *ca.* 430 nm (Fig. 4). This suggests the transformation of the initial transient species into new ones. Typical transient signals obtained under different experimental conditions are shown in Fig. 5.

Another striking observation at high fluence was the formation of a grey–black deposit on the KCl windows facing the laser. This deposit was characterised by FTIR spectra and was found to contain frequencies reported for SiC.[13,14]

IRMPD of DSCB

The transient absorption spectra and profiles of the transient absorption obtained in the IRMPD of DSCB are shown in Fig. 6 and 7, respectively. In Fig. 6, the spectrum at 4 µs has an absorption band at 260 nm, indicating the formation of $H_2C{=}SiH_2$ according to reaction (1*b*).



$$\begin{matrix} H_2Si-CH_2 \\ | \quad\quad | \\ H_2C-SiH_2 \end{matrix} \xrightarrow{\text{IRMPD}} 2H_2C{=}SiH_2 \qquad (1b)$$

In addition, the presence of a shoulder at *ca.* 330 nm and a slow growth of an absorption peak at *ca.* 430 nm are also observed. The transient signals in Fig. 7 are stronger, but qualitatively similar to those in Fig. 5. At higher laser fluence, they all exhibit a complex kinetic behaviour and the exact shape of the transient signal depends on the monitoring wavelength. However, all the signals appear to be composed of both formation and decay curves. Observations at longer timescales, both at 260 and 460 nm, showed at least three formation and decay cycles before the transient absorption reached the baseline (*ca.* 30 ms).

Kinetic analysis of the transient signal in [Fig. 7(*c*)] shows the absorbance at 460 nm growing with a rate constant of $(4.3 \pm 0.5) \times 10^4$ s^{-1}. On the other hand, that in Fig. 7(*b*), during the initial 5 µs, gives a decay constant of $(1.4 \pm 0.3) \times 10^5$ s^{-1}, thereby indicating some more routes for the decay of the absorbance at 260 nm.

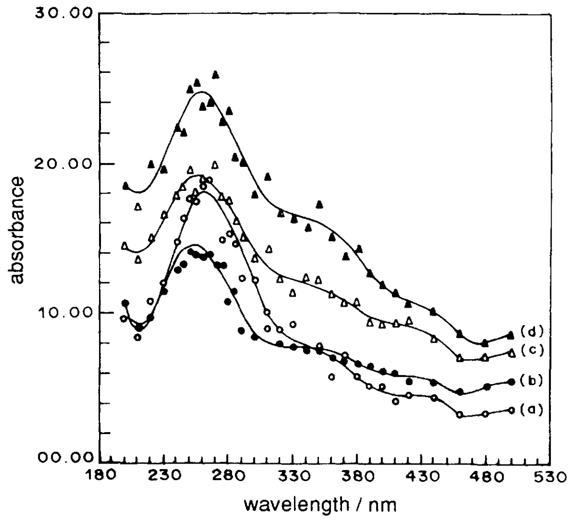


Fig. 6 Transient absorption spectra following IRMPD of DSCB. $P = 0.53$ kPa, laser fluence = 7.2 J cm^{-2}. ○, 4 µs; ●, 20 µs; △, 50 µs; and ▲, 90 µs after the pulse.

193 nm laser flash photolysis of SCB and DSCB

193 nm laser flash photolysis of SCB and DSCB (0.53 kPa) using a laser fluence of 0.04 J cm^{-2} yields the transient absorption spectra (○) and (■) that are shown in Fig. 8. These spectra with $\lambda_{max} \approx 260$ nm are practically identical to each other, as well as to the spectrum of $H_2C{=}SiH_2$ reported in the literature,[16,17] but are narrower compared with those obtained by IRMPD (Fig. 3). This is contrary to the general behaviour, *i.e.* the higher the excitation energy, the wider is the energy distribution among the products, leading to a broader absorption spectrum. Therefore, the observed broadening of the spectrum in the case of IRMPD suggests further absorption of CO_2 photons by the nascent product $H_2C{=}SiH_2$, leading to the formation of 'hot' silene molecules. This conclusion is supported by the good IR absorption by the transient silene in the CO_2 laser region.[16,17]

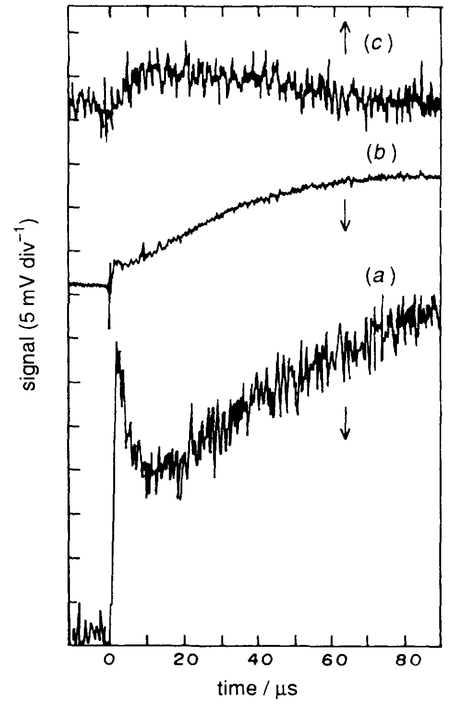


Fig. 7 Transient absorption profiles following IRMPD of DSCB. $P = 0.53$ kPa, (*a*) $\lambda = 260$ nm, laser fluence = 0.9 J cm^{-2}, $I_0 = 927$ mV; (*b*) $\lambda = 260$ nm, laser fluence = 7.2 J cm^{-2}, $I_0 = 978$ mV; (*c*) $\lambda = 460$ nm, laser fluence = 7.2 J cm^{-2}, $I_0 = 1021$ mV.

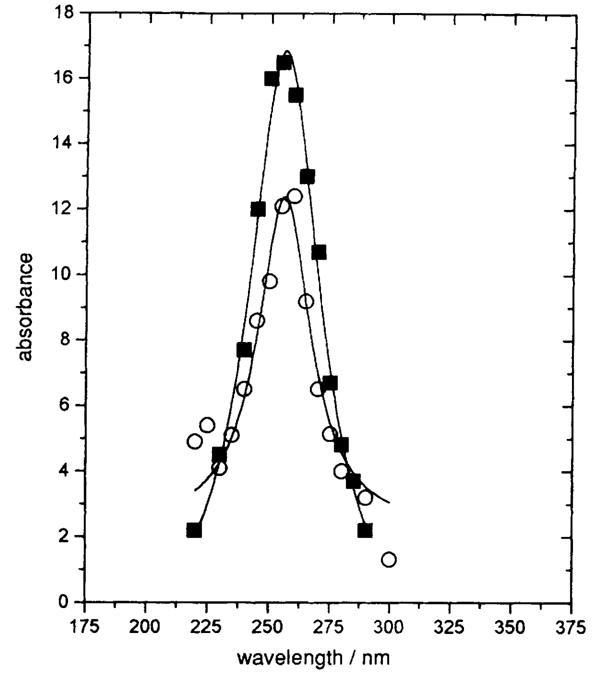


Fig. 8 Optical absorption spectra of the transients. $P = 0.53$ kPa; excitation $\lambda = 193$ nm. ○, SCB and ■, DSCB, 4 µs after the pulse.

Under the same experimental conditions, the observed absorbance of the transient product is 1.4 times higher for DSCB compared with that for SCB. This is twice the ratio of absorption coefficient of DSCB to that of SCB at 193 nm, thereby suggesting almost the same quantum efficiency of photodissociation for both the compounds. In addition, this also suggests the occurrence of reactions similar to reactions (1*a*) and (1*b*) in the 193 nm photolysis.

The transient absorption signal decays by first-order kinetics and the typical decay profiles are given in Fig. 9. Since the signal does not reach the baseline, a proportional correction for the final absorption is made and the corrected decay curve [Fig. 9(c)] is given, together with the least-squares fit. The rate constant is found to vary linearly with the pressure of SCB or DSCB; a typical plot with a least-squares fit to the experimental data is shown in Fig. 10. The presence of an intercept suggests that there are two first-order processes for the decay of the transient; one depending on the pressure of the reactant and the other independent of it, *i.e.* reactions (2) and (3).

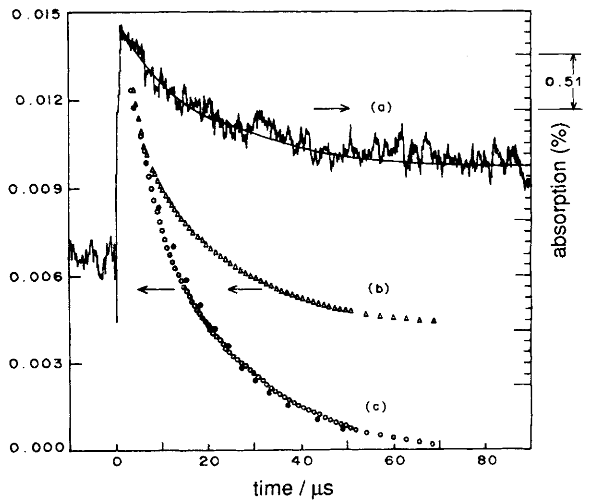


Fig. 9 Kinetic analysis of the transient decay. Molecule, DSCB; excitation λ, 193 nm; monitoring λ, 260 nm. (a) and (b) Raw data. (c) Corrected data (○) and least-squares fit (●).

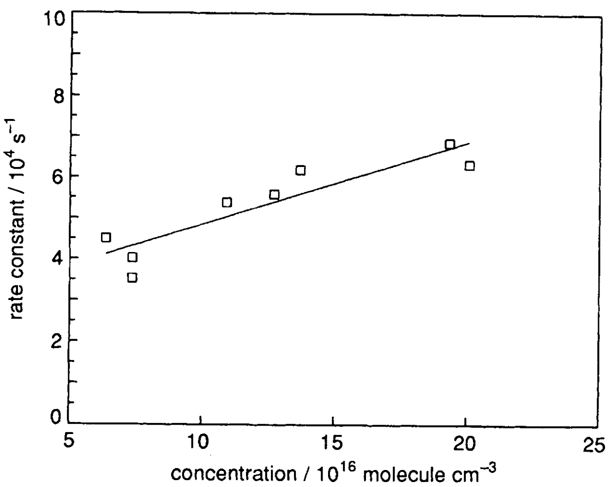


Fig. 10 Dependence of first-order rate constants on the pressure of SCB. Excitation λ, 193 nm; monitoring λ, 260 nm; (□), experimental data, (——), least-squares fit.

$$H_2C{=}SiH_2 + SCB \rightarrow \text{products} \qquad (2a)$$

$$H_2C{=}SiH_2 + DSCB \rightarrow \text{products} \qquad (2b)$$

$$H_2C{=}SiH_2 \rightarrow \text{products} \qquad (3)$$

From the slope in Fig. 10, the rate constant for reaction (2*a*) is calculated to be $(2.0 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. From a similar plot for DSCB the rate constant for reaction (2*b*) is obtained as $(3 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. From the intercepts of these two plots, an average value of the rate constant for reaction (3) turns out to be $(2.3 \pm 0.7) \times 10^4$ s^{-1}.

At higher laser fluence (6 J cm^{-2}), the transient absorption signal becomes complicated and difficult to analyse. In addition, each laser shot leads to a grey deposit at the MgF_2 window facing the laser, which attenuates the fluence of the subsequent laser shots considerably. As a consequence, the complex appearance of the transient absorption signal becomes simpler after the initial laser shots, and looks similar to what is obtained at low laser fluence.

The grey deposit on the MgF_2 window shows a broad absorption peak at 2135 cm^{-1} in the FTIR spectrum, which matches with the frequency of Si—H vibration reported in the literature.[13,14] Lower wavenumber peaks could not be obtained because they lie outside the transmission region of MgF_2. A white polymeric deposit was also observed on the quartz window facing the analysing light beam, which was common to all the experiments using the TEA CO_2 or the 193 nm laser.

A striking similarity between the results of IRMPD and those of 193 nm photolysis suggests that the initial transient species in either case is the same, *i.e.* the ro-vibrationally excited silene.

$$SCB \xrightarrow[193\ \text{nm}]{nh\nu\ (\text{IR})} SCB^{*,\dagger} \xrightarrow[-C_2H_4]{} H_2Si{=}CH_2^{\dagger} \qquad (1a)$$

$$DSCB \xrightarrow[193\ \text{nm}]{nh\nu\ (\text{IR})} DSCB^{*,\dagger} \xrightarrow{} 2H_2Si{=}CH_2^{\dagger} \qquad (1b)$$

Because of its high reactivity, the $(H_2Si{=}CH_2)^{\dagger}$ molecule triggers a number of reactions, *e.g.* (i) dehydrogenation due to the excessive stretching of Si—H and C—H bonds to form HSi≡CH with λ_{max} expected to be around 260 nm (ii) reaction with SCB or DSCB and (iii) polymerisation, *i.e.*,

$$H_2C{=}SiH_2 + SCB/DSCB \rightarrow \text{polymer} \qquad (2)$$

$$H_2C{=}SiH_2 \rightarrow HC{\equiv}SiH + H_2 \qquad (3)$$

$$nCH_2{=}SiH_2 \rightarrow \text{polymer} \qquad (4)$$

The relative magnitudes of these reactions will be governed by the experimental conditions.

At high fluence, the laser pulse deposits a large amount of energy within a small reaction volume in a very short time (< 1 μs), *i.e.* almost adiabatically. This leads to a localised high temperature and high concentration of the reactive species. Under these conditions, a number of additional reaction pathways are possible, *viz.*

$$SCB^{\dagger} \longrightarrow {:}SiH_2 + CH_3{-}CH{=}CH_2 \qquad (5)$$

$$SCB^{\dagger} \xrightarrow[-H_2]{} {:}\underline{Si{-}CH_2{-}CH_2{-}CH_2} \longrightarrow H_2C{=}SiH_2 + C_2H_2 \qquad (6)$$

$$H_2C{=}SiH_2 \rightleftharpoons CH_3{-}(H)Si{:} \qquad (7)$$

and all the feasible bimolecular reactions among transient species.

Reaction (7) is based on the thermodynamically derived conclusion[18] that the conversion of silene to methylsilylene is favoured by an increase in the temperature, and on the difference in product distribution under low- and high-fluence conditions.[13,14] Also, polymerisation [reaction (4)] is reported to be very efficient under these conditions.

The $CH_3{-}(H)Si{:}$ has λ_{max} in the 460–480 nm region[19–21] and $:SiH_2$ has been reported to absorb in the 400–650 nm region.[22]

Thus, the formation and decay of several additional transient species with their optical absorption extending up to 650 nm qualitatively explain the results obtained under high laser fluence conditions.

Conclusion

Transient silene, $H_2C{=}SiH_2$, is the major primary product of the dissociation of SCB and DSCB induced by the CO_2 or ArF laser. Under conditions of low laser fluence, $H_2C{=}SiH_2$ decays mainly by reactions (2) and (3). At high fluence, the transient absorption signals become very complex owing to the onset of a number of additional reactions. Further investigations are required to pinpoint the transient species involved in these reactions.

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