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The UV absorption spectrum of SiH_3

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Flash photolysis of $CCl_4/SiH_4/N_2$ mixtures in the far-UV gives rise to strong transient absorptions in the region 205–250 nm which are attributed to the first experimental observation of the $(\tilde{A}\,^2A_1 \leftarrow \tilde{X}\,^2A_1)$ transition of the SiH_3 radical.

1. Introduction

The spectroscopy of the SiH_3 radical is of considerable practical and theoretical interest. The radical plays an important role in chemical vapour deposition processes [1], and new techniques for its detection would be of great use in expanding the limited kinetic database on its reactions. In addition, SiH_3, isovalent with CH_3, provides a benchmark for the performance of electronic structure calculations of species containing second-row elements. Despite considerable experimental efforts over the years [2–4], the single-photon absorption spectrum of SiH_3 has escaped observation. This is largely due to the difficulty of producing monovalent silicon-based radicals – photolytic methods based on those classically used to produce carbon-based radicals invariably produce the thermodynamically favoured divalent silicon species, plus a stable molecule. Recently, however, Potzinger and co-workers have produced trialkyl(methyl, ethyl and *n*-propyl)silyl radicals via the mercury-sensitized photolysis of the corresponding silanes [5]. All three alkylsilyl radicals display strong, broad absorption bands peaking at around 260 nm, confirming earlier observations of the trimethylsilyl radical spectrum [6,7]. It was not possible to produce SiH_3 in the same manner, however, owing to polymer formation [5]. In recent years, SiH_3 has been successfully produced by the fast reaction of Cl atoms with SiH_4 [8,9], and has been detected by time-resolved LMR [9], resonance-enhanced multiphoton ionization (REMPI) [10,11], photoionization mass spectrometry [12] and time-resolved IR diode-laser spectroscopy [13]. Detectable quantities of SiH_3 have also been produced by the ArF laser photolysis of SiH_3Br and SiH_3I, although the quantum yields are low (around 0.1 for SiH_3Br) [13]. Extensive MRD-CI calculations by Olbrich [14] suggest that the first excited (Rydberg) state lies at 41860 cm^{-1} and that this state is dissociative with respect to SiH_2 and H. The short lifetime of the excited state suggests in turn that the absorption band will be structureless and that the REMPI and LIF techniques will not be suitable in this wavelength region.

2. Experimental

The flash photolysis/UV absorption apparatus used in this study has been described in detail previously [15]. In short, it consists of a 1.5 ℓ cylindrical quartz cell, 70 cm long and 4.5 cm wide. Radicals are generated by the flash photolysis of slowly flowing gas mixtures and are detected by time-resolved UV absorption. The analysis beam is provided by a deuterium lamp. Experimental optical density–time profiles are collected on a digital storage oscilloscope, averaged, typically over 10–30 shots, and subsequently analysed by non-linear least-squares methods. The only difference between the experimental setup used in the present study and that previously described [15] is that the pyrex outer sleeve was removed from the spectrosil quartz flash lamp,

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so that far-UV rather than near-UV photolysis could be used.

Chlorine atoms were produced by the broad-band far-UV ($\lambda > 190$ nm) photolysis of CCl_4

$$CCl_4 + h\nu(\lambda > 190\,\text{nm}) \rightarrow CCl_3 + Cl\,, \quad (P1)$$

$$\rightarrow CCl_2 + Cl + Cl\,. \quad (P2)$$

In the present experiments, the CCl_4 molecule absorbs radiation in the far-UV, the absorption cross-section increasing from 17×10^{-20} cm^2 molecule^{-1} at 220 nm to 144×10^{-20} cm^2 molecule^{-1} at 190 nm [16], around where the ordinary quartz of the photolysis cell cuts off. The relative importance of photolysis channels (P1) and (P2) depends on the wavelength. At 253.7 and 213.9 nm, only (P1) is important [17,18], whereas the ratio of (P1) to (P2) is 2.8 at 184.9 nm and 0.33 at 163.3 nm [17,18]. It is, thus, expected that (P1) will largely dominate in the present experiments, although small amounts of CCl_2 will be produced via (P2).

All experiments were performed at room temperature and atmospheric pressure. Reagent concentrations were, in units of molecule cm^{-3}: SiH_4 $(0.3–12) \times 10^{16}$; CCl_4 $(0.9–6.7) \times 10^{16}$; balance N_2. Nitrogen (AGA, >99.5%), silane (l'Air Liquide, electronic grade) and carbon tetrachloride (Prolabo, normapur grade) were used without further purification.

3. Results

Photolysis of CCl_4/N_2 mixtures produced weak absorptions in the region 210–240 nm; the wavelength dependence of the initial absorption was characteristic of the spectrum of the CCl_3 radical in this region [19]. In the absence of other gases, the radicals produced in the photolysis will be removed by reaction among themselves:

$$CCl_3 + CCl_3 + M \rightarrow C_2Cl_6 + M\,, \quad (1)$$

$$CCl_3 + Cl + M \rightarrow CCl_4 + M\,, \quad (2)$$

$$Cl + Cl + M \rightarrow Cl_2 + M\,. \quad (3)$$

The CCl_3 absorptions followed approximately second-order kinetics, but with a rate of disappearance which was significantly faster than that expected on the basis of the CCl_3 self-reaction alone. The association reaction of CCl_3 with Cl atoms is around 20 times faster than the self-reaction at room temperature and atmospheric pressure [19], so this observation is consistent with the presence of Cl atoms in the system. The initial absorption due to CCl_3 varied linearly with CCl_4 concentration over the range $(0.9–6.7) \times 10^{16}$ molecule cm^{-3}; typical initial CCl_3 concentrations were $(1–4) \times 10^{13}$ molecule cm^{-3}.

Silane does not absorb above 170 nm [20] and so is unaffected by the photolysis radiation from our flash lamp. In the presence of SiH_4, the following additional reactions may occur:

$$Cl + SiH_4 \rightarrow HCl + SiH_3\,, \quad (4)$$

$$CCl_3 + SiH_3 \rightarrow \text{products}\,, \quad (5)$$

$$SiH_3 + SiH_3 \rightarrow Si_2H_6\ [21]\,. \quad (6)$$

Reaction (4) is known to be very fast (k_4/cm^3 molecule^{-1} s^{-1} $= 3 \times 10^{-10}$ [8,9]) and will be the only loss process for Cl atoms in the presence of excess SiH_4. The abstraction reaction of CCl_3 with SiH_4 to form SiH_3 is expected to be negligibly slow in these experiments – the analogous reaction of CH_3 has a rate constant of 1.0×10^{-17} at 298 K [22] and CCl_3 would be expected to be even less reactive.

On adding small concentrations of SiH_4 to the photolysis mixture, we observed strong transient absorptions in the region 205–250 nm, with an apparent maximum at around 215 nm. At this wavelength, which is near to the maximum of the CCl_3 spectrum at 211 nm [19], the peak absorptions were around a factor three larger than those observed in the absence of SiH_4; at longer wavelengths, this ratio was larger. The largest contribution of CCl_3 to the initial absorption was at the shortest wavelengths, where it approached 40%. An optical density profile showing the main features of the transient behaviour is shown in fig. 1a. At all wavelengths, a rapid reaction, giving rise to a residual absorption after around 20 ms, was observed. The residual absorption, seemingly corresponding to a stable product, was around 25% of the peak absorption at wavelengths of 215 nm and longer, but somewhat stronger at shorter wavelengths. Initial absorptions were extracted from second-order fits to decay traces collected on a 2 ms timescale, as shown in fig. 1b. Over such short times, less than half of the initial absorption had decayed.

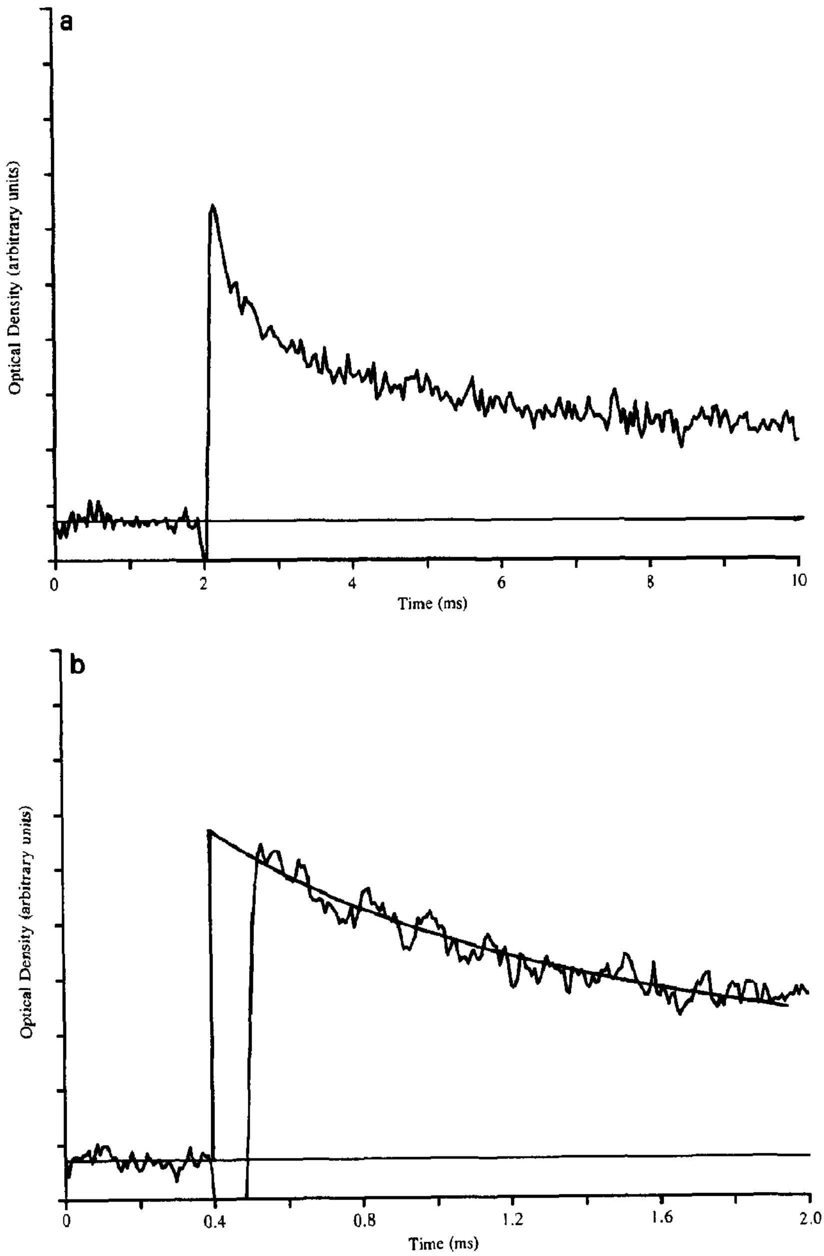

Fig. 1. (a) Representative optical density–time profile following the flash photolysis of a $CCl_4/SiH_4/N_2$ mixture. Reagent concentrations are (in units of 10^{16} molecule cm^{-3}): $[CCl_4]=6.72$; $[SiH_4]=0.80$; $[N_2]$ to 1 atm. Monitoring wavelength 230 nm. (b) Typical decay trace used to extrapolate to $t=0$. The solid line represents a simple second-order fit to the data. Monitoring wavelength 230 nm. Reagent concentrations are (in units of 10^{16} molecule cm^{-3}): $[CCl_4]=6.72$; $[SiH_4]=0.40$; $[N_2]$ to 1 atm.

In addition, the back extrapolation of the transient absorption over the 150 μs post-flash dead-time of our detection system amounts to only around 5% of the total initial absorption, and errors due to kinetic uncertainties are very small. Due to the strong UV cross-sections of CCl_4 at the shorter wavelengths [16] and the weak transient absorption at the longer wavelengths, it was not possible to cover the whole of the observed absorption band with the same CCl_4 concentration. Partial spectra (i.e. initial absorption versus wavelength) were recorded at four different CCl_4 concentrations over the range $(0.9\text{–}6.72)\times10^{16}$ molecule cm^{-3}. The average of these relative spectra, normalized to the initial absorption at 215 nm and corrected for the contribution of CCl_3, are shown in fig. 2; no systematic dependence of the shape of the spectra on CCl_4 concentration was observed. The initial absorption at 230 nm varied approximately linearly with $[CCl_4]$. The wavelength dependence of the residual absorption is shown in fig. 3. No variation in the strength of the initial absorption or the subsequent kinetics was observed on varying the SiH_4 concentration over the range $(0.31\text{–}12)\times10^{16}$ molecule cm^{-3}.

Additional experiments were attempted in which it was planned to photolyze molecular chlorine in the presence of silane. However, adding SiH_4 to a flowing gas mixture of Cl_2 and N_2 consumed the Cl_2 via a thermal reaction within the residence time of the gases in the cell (around 30 s), as observed by its absorption at 330 nm [16], even at concentrations of SiH_4 and Cl_2 below 10^{16} molecule cm^{-3}.

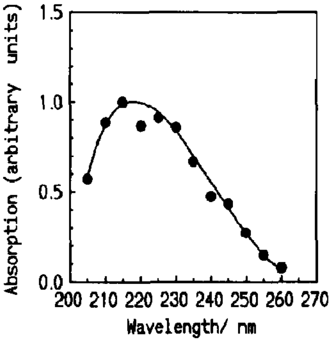

Fig. 2. Relative spectrum, normalized to 215 nm, of the initial absorbance produced on photolyzing $CCl_4/SiH_4/N_2$ mixtures at four different CCl_4 concentrations over the range (0.90–6.72) $\times10^{16}$ molecule cm^{-3}.

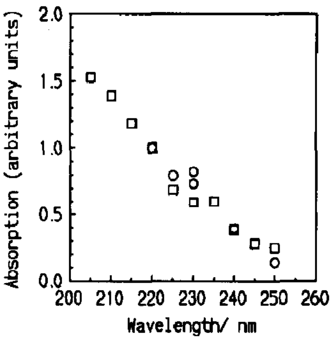

Fig. 3. Relative spectra of the residual absorption produced on photolyzing $CCl_4/SiH_4/N_2$ mixtures. CCl_4 concentrations (in units of 10^{16} molecule cm^{-3}) are: (○) 6.72 and (□) 1.79. In each case, the spectrum in normalized to the value at 220 nm.

4. Discussion

There is strong evidence supporting the attribution of the transient absorptions observed in the present experiments to the SiH_3 radical. Firstly, the chlorine atoms produced in the photolysis of CCl_4 will react with SiH_4 to produce SiH_3. The production of the absorbing species is complete within the post-flash dead-time of our detection system (150 μs), even at concentrations of SiH_4 as low as 0.31×10^{16} molecule cm^{-3}, which is compatible with a rate constant $k_4>3\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. In order for our perceived initial absorption to be in fact due to products of radical–radical reactions (e.g. reaction (5)), such reactions would have to be essentially completed within 150 μs, indicating a rate constant of around 3×10^{-10} cm^3 $molecule^{-1}$ s^{-1} for a typical initial radical concentration of 4×10^{13} molecule cm^{-3}. Such a rate constant appears unreasonably large for a reaction between two polyatomic free radicals.

The peak cross-section for $(CH_3)_3Si$ is around 3×10^{-17} cm^2 $molecule^{-1}$ [5], i.e. around twice as large as the peak absorption cross-section of the CCl_3 radical at 211 nm [19]. Our observations are consistent with a SiH_3 absorption band which is considerably stronger than that of CCl_3. Assuming that only photolysis channel (P1) operates, we conclude that $([SiH_3]/[CCl_3])_{t=0}=1.0$. In this way, we can estimate an *approximate* peak absorption cross-section for SiH_3 of 2.4×10^{-17} cm^2 $molecule^{-1}$ at 215 nm. Of course, if photolysis channel (P2) were important, then this method would underestimate the initial SiH_3 concentration. Assuming a worst case of $(P1)/(P2)=2.8$ (see above), we find that $([SiH_3]/[CCl_3])_{t=0}=1.7$ and $\sigma(SiH_3,\ 215\ nm)/cm^2\ molecule^{-1}=1.4\times10^{-17}$.

Finally, but importantly, high-level ab initio calculations by Olbrich [14] predict that the vertical transition of the ($\tilde{A}\,^2A_1 \leftarrow \tilde{X}\,^2A_1$) transition in SiH_3 lies at 239 nm. The electronic ground state of SiH_3 is pyramidal, whereas the excited state is planar and the absorption band should display significant intensity to either side of the vertical transition, as is observed. The band is also predicted to be diffuse, due to the short lifetime of the excited state with respect to dissociation, again in good agreement with our observations.

The strong residual absorptions observed in these experiments can be attributed to species formed in post-flash reactions. For example, the $Cl_3CSiH_3^*$ species formed in reaction (5) will contain around 90 kcal mol^{-1} excess energy [23], enough to produce silylenes if not collisionally stabilized

$$Cl_3CSiH_3^* + M \rightarrow Cl_3CSiH_3 + M\,, \qquad (5a)$$

$$Cl_3CSiH_3^* \rightarrow Cl_3CSiH + H_2\,, \qquad (5b)$$

$$\rightarrow CHCl_3 + SiH_2\,, \qquad (5c)$$

$$\rightarrow CCl_2 + SiH_3Cl\,. \qquad (5d)$$

Such elimination processes are well known in the pyrolysis of alkylsilanes [24]. Cl_3CSiH could go on to produce the silene $Cl_2C{=}SiHCl$ via a 1,2 Cl-atom shift, and silenes are known to absorb strongly in the far-UV [25]. Other possible contributors to the residual absorption are Cl_3CSiH_3 and unsaturated products of the reactions of the small quantities of CCl_2 produced by photolysis via reaction (5d). Such unknowns in the kinetics of the systems should not affect the initial absorption, however. The extrapolation of the optical density to $t=0$ is very short with respect to the subsequent timescale of its decay and any errors introduced by uncertainties in the kinetics can only be of the order of a few percent.

The presence of a contribution from CCl_3 to the initial absorption increases the uncertainty of our measurements, but only slightly, as this contribution was never more than 40%, and usually significantly less. Nevertheless, a convenient, clean, photolytic source of SiH_3 radicals has yet to be identified – photolysis of silyl halides produces SiH_3 in low yields [13], generation of Cl atoms by the photolysis of molecules other than Cl_2 leads to the unavoidable production of a second radical and SiH_4/Cl_2 mixtures are subject to thermal chain reactions.

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