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LASER-EXCITED FLUORESCENCE DETECTION OF SiH_2 PRODUCED IN IR MPD OF ORGANOSILANES

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SiH_2 has been identified as a photolysis product in the infrared multiple-photon dissociation of $RSiH_3$ (R = *n*-butyl, phenyl), arising from secondary IR MPD of the silane produced in the initial four-center elimination step. The radiative lifetimes of $\tilde{A}^1B_1$ levels show a strong rotational-state dependence.

1. Introduction

The infrared multiple-photon dissociation (IR MPD) of organosilanes has been observed [1] to yield olefins, silane, and a deposit on adjacent surfaces identified as amorphous silicon (a:Si–H). The low silane:olefin product ratios found in those experiments, and the accompanying deposition of a:Si–H, were attributed to secondary IR MPD of the vibrationally hot silane produced in the initial photolysis steps to yield silylene (SiH_2). In order to verify this proposed mechanism, we have used laser-excited fluorescence (LIF) to detect the SiH_2 produced in this reaction. This technique has recently been used to observe SiH_2 produced in the UV photolysis of phenylsilane with an ArF excimer laser at 193 nm [2]. Profiling of reactive species by LIF or other spectroscopic probes is an important method for studying the mechanisms of gas–surface interactions such as chemical vapor deposition [3].

2. Experimental

In these experiments, organosilanes were dissociated by IR MPD and the resulting SiH_2 detected by LIF.

Phenylsilane and *n*-butylsilane were obtained from Silar Industries and were degassed using several liquid-nitrogen freeze–pump–thaw cycles. A slow flow of neat gas at 5 to 20 mTorr pressure (1 Torr = 133.3 Pa) was established by pumping on the liquid silanes at room temperature with a liquid-nitrogen-trapped turbomolecular pump. Pressures were controlled with a leak valve.

The photolysis laser used was a line tunable CO_2 TEA laser (Laser Science PRF-150s) which provides a 120 ns fwhm pulse with a 1 μs tail. Infrared fluences in the range 0.5 to 5 J/cm^2 were obtained by focusing 5–50 mJ pulses with a 500 mm focal length BaF_2 lens. The visible-wavelength probe beam, collinear and counterpropagating to the CO_2 laser, probed only the central portion of the photolysis region. An attenuated XeCl-excimer-pumped dye laser (Lambda Physik EMG 101E, FL2002) with rhodamine 6G dye produced pulses with 50 μJ in 10 ns fwhm and 0.5 cm^{-1} spectral width which excited transitions in the SiH_2 $\tilde{A}\,^1B_1(020) \leftarrow \tilde{X}\,^1A_1(000)$ vibronic band. The total laser-induced fluorescence from a single rotational level was imaged through a colored glass filter (Corning 2-62) onto a red sensitive photomultiplier tube (Hamamatsu R669). A wideband pulse amplifier (LeCroy VV100B), and a gated integrator/boxcar averager (EG&G PAR 165/162) were used to collect the signal. To reduce problems with jitter and drift of the synchronous-out trigger pulse from the excimer laser, a fast UV photodiode (EG&G FND1000), which detected scattered light from the excimer laser, was used to trigger the boxcar averager. Because the trigger pulse was produced only a few nanoseconds before the

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LIF signal, it was necessary to delay the signal by using a 100 foot long coaxial cable.

The experiments were driven by a 20 Hz clock and a digital delay generator (Berkeley Nucleonics 7050) which allowed the photolysis and probe lasers to be synchronized within ±100 ns. The uncertainty in time is a result of jitter between the trigger pulse in and the emitted photons for each laser. The spectra were collected with a laboratory computer system (MINC-11/03) and stored on floppy disks. Spectra presented in this communication were neither corrected for wavelength dependence of the optical detection system nor were they normalized to photolysis or probe laser power intensities.

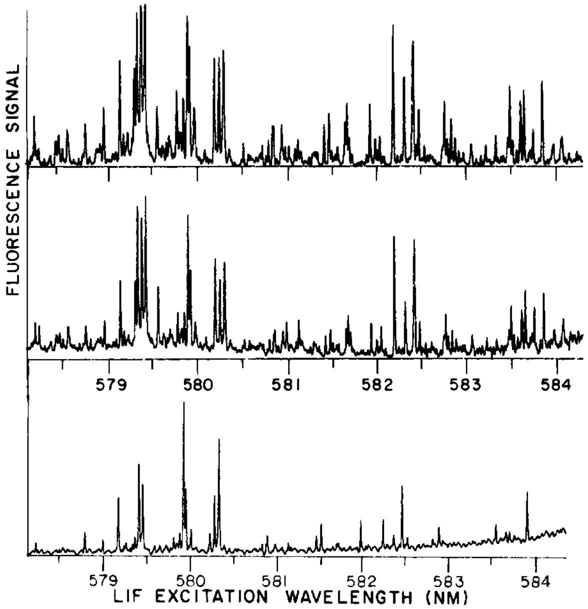

Fig. 1. LIF excitation spectra of SiH_2 in (020)–(000) band of $\tilde{A}\,^1B_1-\tilde{X}\,^1A_1$ transition. Upper trace: 15 mTorr *n*-butylsilane, CO_2 10P(20) line. Middle trace: 25 mTorr phenylsilane, CO_2 10P(32) line. Both spectra are recorded at "zero" delay between infrared and visible laser pulse, and with fluorescence detection gate set to 0–50 ns following excitation. Bottom trace: 20 mTorr *n*-butylsilane in 400 mTorr He, probed 36 μs *after* the photolysis laser, and with sensitivity increased by a factor of 25.

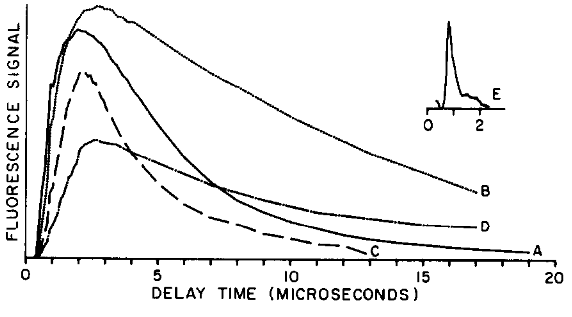

Fig. 2. SiH_2 LIF signal versus delay time between IR photolysis pulse and visible excitation pulse. (A) 20 mTorr *n*-butylsilane, no buffer gas. (B) 20 mTorr *n*-butylsilane with 800 mTorr He. (C) 20 mTorr phenylsilane, no buffer gas. (D) 20 mTorr phenylsilane with 800 mTorr He. The phenylsilane traces (C) and (D) are displayed at 25 times higher sensitivity than the butylsilane traces (A) and (B). Also shown as inset (E) is the CO_2 laser pulse profile measured with a photon drag detector and transient digitizer.

3. Results and discussion

3.1. *Production of SiH_2*

SiH_2 was observed as a product in the IR MPD of both *n*-butylsilane and phenylsilane, either under collision-free conditions (10–25 mTorr) or with added buffer gas (0.4–0.8 Torr He). The LIF signals from phenylsilane are a factor of 30–50 weaker than with butylsilane, indicating that significantly less SiH_2 is produced in the former system. Since the IR MPD of phenylsilane is considerably more facile than for butylsilane or other *n*-alkylsilanes [1], the production of SiH_2 (via $SiH_4^{\ddagger}$) must be a relatively minor channel in the decomposition of the phenyl system. Fig. 1 shows LIF excitation spectra in the (020–000) band of the $\tilde{A}\,^1B_1-\tilde{X}\,^1A_1$ transition of SiH_2 [4,5]. The spectra of SiH_2 derived from butyl- and phenyl-silane are quite similar, indicating equivalent product rotational-state distributions in the two cases.

By delaying the visible LIF excitation laser pulse with respect to the IR photolysis pulse, we can monitor the formation and decay kinetics of SiH_2. The result of this experiment is shown in fig. 2. From the rapid (≈1 μs) rise in the LIF signal, it is clear that SiH_2 production occurs during the IR pulse under collision-free conditions, in accordance with the mechanism suggested in ref. [1]. The rapid decay of the SiH_2 density, as measured by the LIF signal under collision-free conditions, is due to kinetic transport out of the volume probed by the excitation pulse [6]. The observed 1/e time (≈3 to 4 μs) is consistent with a thermal velocity distribution, i.e. the SiH_2 species are not translationally hot. In the presence of buffer gas, this transport process is slowed by collisions to the diffusion limit. There is no indication of a homogeneous gas phase reaction removing SiH_2; this species thus appears to be sufficiently long lived to provide efficient transport of silicon to a nearby surface in the deposition process.

The LIF excitation spectra of SiH_2 in He buffer gas taken at delay times of 30–40 μs following the IR photolysis pulse show a considerable reduction in the number of intense lines, which implies extensive rotational cooling relative to the initial distribution and efficient collisional relaxation by He. This is illustrated in the lower panel of fig. 1.

3.2. *Lifetimes of* $SiH_2(\tilde{A}\,^1B_1)$

In the spectra shown in fig. 1, the fluorescence detection gate is set at "zero delay", i.e. all the photomultiplier signal is accepted which occurs between 0 and 50 ns following the LIF excitation pulse. When the gate is set to a delay of 60–260 ns with respect to the pulse, we see that most of the features are absent, indicating that their radiative lifetimes are less than 25–30 ns. A few features remain in the spectrum, however, corresponding to anomalously long-lived excited rovibronic states. These can be clearly seen in fig. 3.

Most of these long-lived features can be assigned to specific rotational levels of the $\tilde{A}\,^1B_1$ state, but there is no clear pattern to the J' values of these levels. It should be noted that the spectroscopy of this species is not completely understood – many unassigned lines were noted in the earlier absorption studies [5], such as those denoted by "?" in fig. 3. These features cannot be assigned to species such as SiH or Si_2, for which

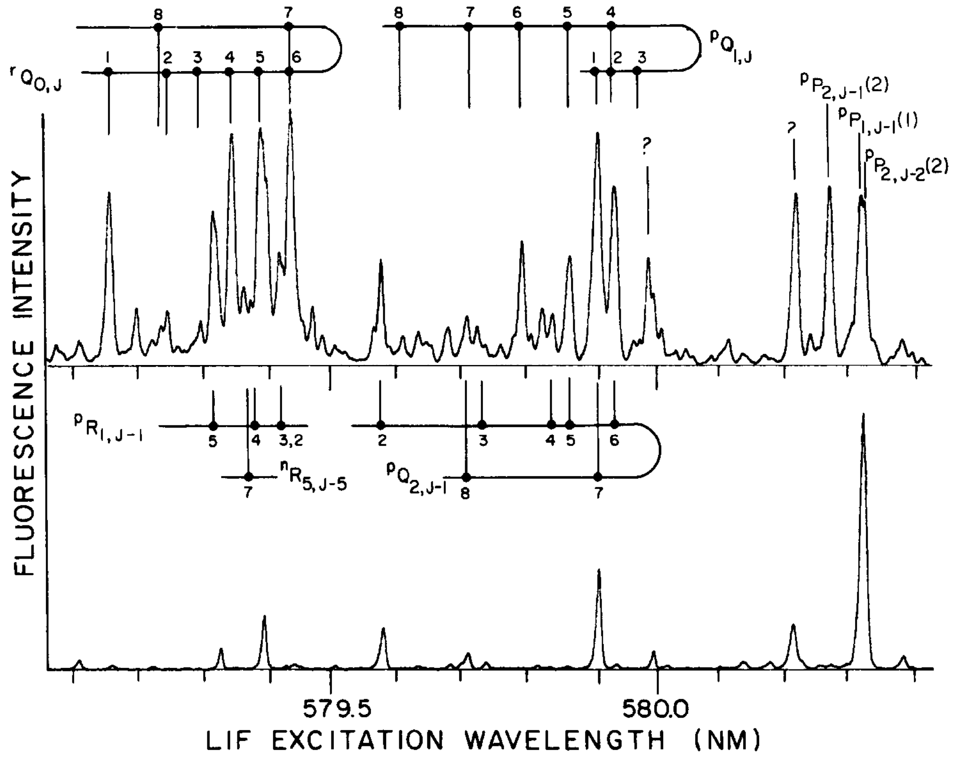

Fig. 3. Expanded section of LIF excitation spectrum of SiH_2 derived from 10 mTorr *n*-butylsilane, measured near peak of signal shown in fig. 2. Assignments are based on data in ref. [5]. Upper trace: detector gate set to 0–50 ns following excitation pulse. Lower trace: detector gate set to 60–260 ns following excitation pulse.

the lowest-lying transition is near 400 nm [7], or to atomic Si; the SiH_3 radical is expected to absorb near 250 nm. Measurements on expansion-cooled SiH_2 are currently under way, in an effort to resolve some of these uncertainties.

Preliminary measurements of the collision-free lifetimes for individual transitions give a range of values between ≈ 10 and >500 ns. Inoue and Suzuki [2] report a single lifetime of 60 ± 5 ns, but in their spectra it is clear that a number of rovibronic levels are excited simultaneously. With the 0.5 cm^{-1} excitation bandwidth used in our measurements, most of the SiH_2 fine structure is fully resolved.

The rotational-state dependence of radiative lifetimes has been studied in a small number of systems, such as SO_2 [8], I_2 [9], and ClO_2 [10], and S_2 [11]. The variations can be caused by hyperfine coupling [8] or rotational-state-dependent intersystem crossing [10,12]. Although theoretical models [12] suggest that the rotational-state effect on lifetimes of an individual electronic state should be small, measurements of collision-free single-rovibronic-level lifetimes in formaldehyde (H_2CO and D_2CO [13,14]) show a considerable variation with rotational state. These variations arise from a K'-dependent radiationless decay rate on which is superimposed a random variation arising from energy mismatches between the excited-state levels and nearby levels in the S_0 manifold. A related type of process may be occurring in SiH_2, similar to that occurring in S_2 [11], in which the lifetimes of the $B''\,^3\Pi_u$ state show a wide variation with spin and vibrational quantum numbers. This was attributed to homogeneous interaction with a nearby $B\,^3\Sigma_u^-$ state. In the case of SiH_2, the interaction may involve the $\tilde{a}\,^3B_1$ state [15], with the triplet mixing (and thus the radiative lifetime) showing irregular variations which reflect the detuning from the nearest triplet-state levels. A more complete study of the lifetimes is in progress, and will be reported in a subsequent publication.

4. Summary

Silylene (SiH_2) has been identified as a primary photolysis product in the infrared multiple-photon dissociation of alkyl- and aryl-silanes. In the former case, the SiH_2 most likely is produced by secondary IR MPD of the "hot" silane formed in the initial four-center elimination step; it is a minor product in the decomposition of phenylsilane. The radiative lifetimes of $\tilde{A}\,^1B_1$ levels show a strong rotational-state dependence, which is attributed to mixing with adjacent levels of the $\tilde{a}\,^1B_1$ state.

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References

[1] J.S. Francisco, S.A. Joyce, J.I. Steinfeld and F. Walsh, J. Phys. Chem. 88 (1984) 3098.
[2] G. Inoue and M. Suzuki, Chem. Phys. Letters 105 (1984) 641.
[3] P. Ho, M.E. Coltrin and W.G. Breiland, in: Laser Processing and Diagnostics, Proceedings of an International Conference, Ser. Chem. Phys. Vol. 39, ed. D. Bäuerle (Springer, Berlin, 1984) p. 515.
[4] I. Dubois, Can. J. Phys. 46 (1968) 2485.
[5] National Research Council of Canada, Depository of Unpublished Data, File No. 18-9D-764 (1968).
[6] S.E. Bialkowski, D.S. King and J.C. Stephenson, J. Chem. Phys. 72 (1980) 1156.
[7] K.P. Huber and G. Herzberg, Constants of diatomic molecules (Van Nostrand Reinhold, New York, 1979).
[8] H. Watanabe, S. Tsuchiya and S. Koda, J. Chem. Phys. 82 (1985) 5310.
[9] M. Broyer, J. Vigue and J.-C. Lehmann, J. Chem. Phys. 64 (1976) 4793.
[10] S. Michielsen, A.J. Merer, S.A. Rice, F.A. Novak, K.F. Freed and Y. Hamada, J. Chem. Phys. 74 (1981) 3089.
[11] Y. Matsumi, T. Suzuki, T. Munakata and T. Kasuya, J. Chem. Phys. 83 (1985) 3798.
[12] F.A. Novak and S.A. Rice, J. Chem. Phys. 73 (1980) 858.
[13] J.C. Weisshaar and C.B. Moore, J. Chem. Phys. 72 (1980) 5415.
[14] K. Shibuya, P.W. Fairchild and E.K.C. Lee, J. Chem. Phys. 75 (1981) 3397.
[15] M.E. Colvin, R.S. Grev, H.F. Schaefer III and J. Bicevano, Chem. Phys. Letters 99 (1983) 399.