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New Electronic State of SiH and SiD Radicals Observed by Resonance-Enhanced Multiphoton Ionization Spectroscopy

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A previously unreported electronic state of the silylidyne radicals, SiH and SiD, was observed by resonance-enhanced multiphoton ionization spectroscopy. The spectra of the SiH and SiD radicals appeared over the laser wavelength interval between 426 and 430 nm. The spectra arose from simultaneous two-photon absorption which prepared the F (4p) Rydberg state that lies at 46 700 cm^{-1}. Absorption of a third laser photon ionized the radicals.

Introduction

This paper presents a previously unreported electronic state of the silylidyne radicals, SiH and SiD, which was observed using resonance-enhanced multiphoton ionization (REMPI) spectroscopy. The REMPI spectra of these radicals appeared as unresolved rotational bands between 426 and 430 nm. The resonance-enhanced ionization originated from simultaneous two-photon absorption which prepared a Rydberg state that lies at 46 700 cm^{-1}. The REMPI bands presented here permit the sensitive detection of SiH radicals in reactive environments.

The SiH radical plays a role at the gas–surface interface during the chemical vapor deposition (CVD) of silicon films from silane, SiH$_4$.[1,2] SiH$_3$, SiH$_2$, and Si radicals also play roles during CVD processes. Currently, electron impact (EI) ionization is often used to measure relative concentrations of the SiH$_n$ radicals. Upon EI ionization the SiH$_n$ radicals fragment into SiH$_{n-x}^+$ daughters which complicates good relative concentration measurements. Today, using REMPI detection methods, experimentalists may rapidly determine the concentration profile of SiH$_3$,[3–5] SiH, and atomic Si[6] in the same experimental configuration and under the same conditions. In contrast to EI ionization we have found that laser ionization of SiH$_3$ and SiH prepares only the SiH$_3$ and SiH molecular ions. Thus, relative concentrations of SiH$_3$ and SiH radicals derived from REMPI detection should prove easier to interpret than EI results.

Previous workers have observed spectra of the ground and a few excited states of the SiH radical using a variety of methods: flash photolysis,[7,8] vacuum-ultraviolet (vacuum-UV) absorption,[9,10] laser magnetic resonance,[11,12] diode laser absorption,[13] and laser induced fluorescence.[14] The ground state of the SiH radical has the electron configuration

$$...(3s\sigma)^2(3p\sigma)^2(3p\pi) \qquad X\ ^2\Pi_r$$

This X $^2\Pi_r$ state is split by a spin–orbit constant of $A_0 = 142.83$ cm^{-1}.[15]

Apparatus and Methods

A detailed description of our apparatus and experimental methods for collecting REMPI spectra are presented elsewhere.[16] Briefly, SiH radicals were produced in a flow reactor operated at ~2 Torr by sequential hydrogen abstraction from SiH$_4$ by atomic fluorine. A portion of the flow reactor effluent that contained SiH radicals effused into a high-vacuum chamber (~5 × 10^{-5} Torr) and was ionized by a focused laser beam (energy = 10–20 mJ/pulse; bandwidth = 0.2 cm^{-1} fwhm; focal length = 250 mm). The ions were extracted into a time-of-flight mass spectrometer, detected with a gated integrator, and averaged and archived by a computer data acquisition system. The spectrum presented here consists of the mass selected ion current as a function of laser wavelength. The dye laser was calibrated by the optogalvanic method[17] using a table of neon lines.[18] The

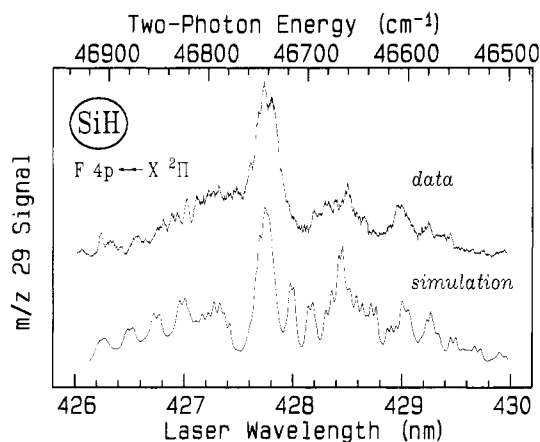REMPI spectrum between 426 and 430 nm was obtained by using Stilbene 420 dye.

Results and Analysis

Berkowitz et al.[19] have demonstrated that the sequential reaction of fluorine atoms with SiH$_4$ produces SiH$_3$, SiH$_2$(X̃ ^{1}A$_1$), SiH$_2$(ã ^{3}B$_1$), and SiH radicals. In our experiments we conducted this reaction in a flow reactor to produce SiH radicals. Our search for REMPI spectra of SiH radicals extended between 360 and 450 nm. However, the only ion signal that we attribute to SiH radicals appeared between 426 and 430 nm. The upper trace of Figure 1 shows the m/z 29 REMPI spectrum of the SiH radical. The chemical evidence and mass spectra support an assignment of this REMPI spectrum to the SiH radical. The molecular ion signal (m/z 29) depended upon the relative concentrations of silane and atomic fluorine. Consistent with the report by Berkowitz et al.,[19] we found that the SiH radical signals were strongest when the flow reactor was operated at large [F]/[SiH$_4$] mole ratios. Whenever the microwave discharge that generated the fluorine atoms was extinguished, the REMPI signals ceased. When SiD$_4$ replaced SiH$_4$ in the flow reactor, the ion signal shifted from m/z 29 (SiH$^+$) to m/z 30 (SiD$^+$). No similar spectra were observed at masses that corresponded to Si$^+$, SiH$_2^+$, or SiH$_3^+$.

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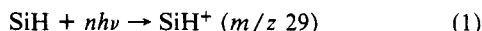(19) Berkowitz, J.; Greene, J. P.; Cho, H.; Ruscic, B. *J. Chem. Phys.* **1986**, *86*, 1235.

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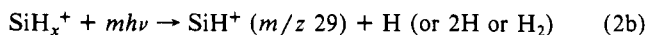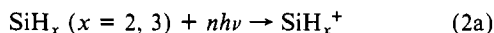† Formerly called the National Bureau of Standards.

Figure 1. The m/z 29 REMPI spectrum of the SiH radical observed between 426 and 430 nm (upper trace) and a computer simulation of the REMPI spectrum based upon $^2\Pi \leftarrow\!\leftarrow X\ ^2\Pi_r$ transitions (lower trace). The main peak at 427.8 nm is composed of the Q_{11} and Q_{21} branches; the feature centered at 428.4 nm is composed of the Q_{21}, Q_{22}, P_{11}, P_{21} branches and the $O_{11}(3)$ line. The broad shoulder between 426 and 427.5 nm is composed of the R_{11} and R_{21} branches and a few lines of the S_{11} and S_{21} branches.

The assignment of the spectrum to the SiH radical requires that we show that the m/z 29 spectrum arose through the process

$$SiH + nh\nu \rightarrow SiH^+\ (m/z\ 29) \qquad (1)$$

rather than through the process

$$SiH_x\ (x = 2, 3) + nh\nu \rightarrow SiH_x^+ \qquad (2a)$$

$$SiH_x^+ + mh\nu \rightarrow SiH^+\ (m/z\ 29) + H\ (or\ 2H\ or\ H_2) \qquad (2b)$$

Although process 2 would also generate a m/z 29 REMPI spectrum, this spectrum would reflect the spectroscopic constants of the SiH_x radical. Computer simulations of the rotational band contour confirmed that the signal arose from the SiH radical through process 1. Reasonable simulations of the band contour were produced only when we postulated (1) that the resonant state resides at the sum of two photons, (2) that the spectrum arises from a linear radical which has rotational constants between 7.4 and 7.6 cm^{-1}, (3) that the rotational temperature is 300 ± 100 K, (4) that the lower state possesses the same spin–orbit constant as the SiH radical, (5) that the upper state is of $^2\Sigma^+$ symmetry or of $^2\Pi$, $^2\Delta$, or $^2\Phi$ symmetry with a small spin–orbit constant, and (6) that the laser beam optically saturated each transition. The fidelity of the fit is not sensitive to the line width of each rotational transition but favors large line widths ($\Delta\nu_r = 4$–10 cm^{-1}).

The lower trace of Figure 1 displays one of the acceptable computer simulations. This computer simulation is based upon $^2\Pi \leftarrow\!\leftarrow X\ ^2\Pi_r$ transitions. The rotational term values were computed by using the equations

$$F(J) = B\{(J + \tfrac{1}{2})^2 - \Lambda^2 - \tfrac{1}{2}[4(J + \tfrac{1}{2})^2 + Y(Y - 4)\Lambda^2]^{1/2}\} - DJ^4 \qquad for\ J = N + \tfrac{1}{2}$$

$$F(J) = B\{(J + \tfrac{1}{2})^2 - \Lambda^2 + \tfrac{1}{2}[4(J + \tfrac{1}{2})^2 + Y(Y - 4)\Lambda^2]^{1/2}\} - D(J + 1)^4 \qquad for\ J = N - \tfrac{1}{2}$$

where $Y = A/B$. The spectroscopic constants used were $T' = 46\,698$ cm^{-1}, $A' = 10$ cm^{-1}, $B' = 7.5566$ cm^{-1}, $D' = 3.81 \times 10^{-4}$ cm^{-1}, $\Lambda' = 1$, $T'' = 0$ cm^{-1}, $A'' = 142$ cm^{-1}, $B'' = 7.3901$ cm^{-1}, $D'' = 3.97 \times 10^{-4}$ cm^{-1}, and $\Lambda'' = 1$. A rotational line width of $\Delta\nu_r = 4$ cm^{-1} was adopted. The simulations showed that the spectrum did not arise from the symmetric top, SiH_3. The rotational constants, $B \sim 7.4$–7.6 cm^{-1}, conform to values expected of the SiH radical and are too large to originate from the SiH_2 radical. Thus, this analysis establishes that the REMPI spectrum originates from SiH radicals. Since this two-photon-absorption spectrum does not correspond to any features identified previously in the vacuum-UV absorption spectrum of SiH, the REMPI spectrum has revealed a new excited electronic state. We have labeled this state with the letter F.

Although the spectrum in Figure 1 shows a rotational band contour, individual rotational lines are not resolved. Since spectra recorded at successively lower laser pulse energies do not show better resolved features, intensity broadening of spectral lines by the laser beam does not account for the modest resolution. Previously, using the same apparatus and laser beam conditions, we have observed REMPI spectra of CF ($B_v \sim 1.4$–1.7 cm^{-1})[20] and NH ($B_v \sim 14$–16 cm^{-1})[21] with measurable ($\Delta\nu_r \leq 0.5$ cm^{-1}), but negligible, intensity broadening. Thus, we conclude that the rotational linewidth is large because the natural lifetime of the F state is very short, i.e., $\tau_0 \sim 1.3$ ps. For a two-photon transition between two $^2\Pi$ states 20 rotational branches contribute to the spectrum. Because these branches overlap extensively, the broad line width of each adjacent rotational transition causes the branches to coalesce into unresolved bands. The modest resolution intrinsic to the spectrum precludes any definitive upper state symmetry assignment.

The Q_{11} branch shifts only 8 ± 10 cm^{-1} between the REMPI spectra of SiH and SiD radicals. This small frequency shift shows that the present band system is an electronic origin. We have calculated the isotope shift of the Q_{11} branch using the reported values[15] of ω_e, $\omega_e x_e$, and B_0 for ground-state SiH, SiD, and SiH$^+$ and using estimated values for SiD$^+$. We have assumed that the excited state will reflect the vibrational constants of the ion. For the origin we calculate that the Q_{11} branch should exhibit an isotope shift of 16 cm^{-1}. In contrast, for other transitions (e.g., 1–0, 0–1, 2–0, ...) the Q_{11} branch should exhibit isotope shifts of greater than 45 cm^{-1}. Thus, we assign the REMPI spectrum in Figure 1 as the origin band of the F state. The F state of the SiH radical lies at $T_0 = 46\,700 \pm 10$ cm^{-1}.

To date, nearly all REMPI spectra of radicals have originated from Rydberg states.[22] The energy of the F state also conforms to a Rydberg state assignment. We dismiss valence state assignments for the F state because previous workers have assigned all reasonable candidates to bands observed in the vacuum-UV absorption spectra.[7-10] Using the Rydberg formula ($h\nu = IP - R/(n - \delta)^2$) and the ionization potential of the SiH radical (IP = 7.91 eV[19]), we obtain $n = 4$ and $\delta = 1.47$. This solution corresponds to a 4p Rydberg state, either of $^2\Sigma^+$ or $^2\Pi$ symmetry.[23,24] For comparison, the $\tilde{E}\ ^2A_2''$ (4p) Rydberg state of the SiH$_3$ radical also manifests a quantum defect of $\delta = 1.47$.[4,5] A SiH radical in a 4p Rydberg state will ionize after absorbing one laser photon. Thus, ion signals are generated through a 2+1 REMPI mechanism.

The Rydberg formula predicts that the 5p Rydberg states of silylidyne should appear near 55 000 cm^{-1} (364 nm in two photons). No m/z 29 or m/z 30 spectra attributable to silylidyne radicals were observed. The absence of the 5p Rydberg states is not distressing. Theory predicts that the 5p states will appear with less intensity than the 4p Rydberg states.[22] An increase in the rate of nonradiative relaxation could also quench the signal.

Although the present spectrum exhibits only modest resolution, REMPI spectroscopy can detect silylidyne with good sensitivity. When we assume that 100% of the SiH$_4$ molecules introduced into the flow reactor are converted into SiH radicals, the estimated concentration of silylidyne radicals at the laser focus is $\sim 10^9$/cm^3. Because the reaction which produces SiH radicals is the third member of the reaction chain involving F + SiH$_4$, SiH$_3$, and SiH$_2$, 100% conversion of SiH$_4$ into SiH radicals cannot be achieved. Thus, this estimate of detection sensitivity represents an upper limit.

Discussion

Previous vacuum-UV absorption studies have shown that the states of silylidyne between 30 000 and 50 000 cm^{-1} have sharp

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dissociation thresholds—only the $v = 0$ level of each state is observed and the rotational structure is truncated by predissociation.[7-10] Similarly, the REMPI spectrum of the F (4p) Rydberg state shows no vibrational progression. The modest resolution indicates that the lifetime of the F state is short.

One of the striking results of this study is the absence of the D $^2\Delta$ ($\nu_{00} = 48\,510$ cm^{-1}) and E $^2\Sigma^+$ ($\nu_{00} = 52\,399$ cm^{-1}) states from the REMPI spectrum. These states lie adjacent in energy to the F (4p) Rydberg state ($\nu_{00} = 46\,700$ cm^{-1}). Verma[7] observed the D state with vacuum-UV spectroscopy and assigned it as a valence state with the electron configuration:

$$...(3s\sigma)(3p\sigma)^2(3p\pi)^2 \quad D\ ^2\Delta$$
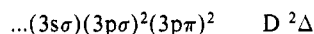
Herzberg et al.[8] observed the D and E states with vacuum-UV spectroscopy and assigned them either to

$$...(3s\sigma)(3p\sigma)^2(3p\pi)^2 \quad D\ ^2\Delta,\ E\ ^2\Sigma^+$$
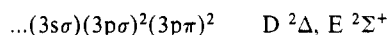
which agrees with Verma's assignment, or to

$$...(3s\sigma)^2(3p\sigma)^2(3d\delta) \quad D\ ^2\Delta$$

$$...(3s\sigma)^2(3p\sigma)^2(4s\sigma) \quad E\ ^2\Sigma^+$$
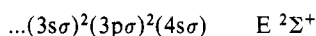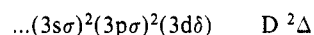
The first assignment is to valence states and the second is to Rydberg states. In the REMPI spectrum these states would have appeared through two-photon allowed transitions at laser wavelengths of 412 and 382 nm, respectively.

The differing number of laser photons required to ionize the SiH radical from each of its excited states may account for the presence and absence of REMPI bands. The SiH cations produced by excitation through Rydberg and valence states possess different electron configurations. SiH radicals which reside in the F (4p) Rydberg state may ionize through the optical transition

$$...(3s\sigma)^2(3p\sigma)^2...(4p)\ SiH\ (F\ (4p)) \xrightarrow{-e^-}$$

$$...(3s\sigma)^2(3p\sigma)^2\ SiH^+\ (X\ ^1\Sigma^+)\quad (3)$$
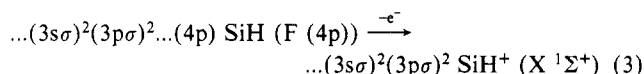
This ionization step (3) produces the X $^1\Sigma^+$ SiH cation and requires 17 100 cm^{-1}, i.e., no more than one laser photon. If the D and E states were Rydberg states, then they would also ionize to produce X $^1\Sigma^+$ cations through a process like (3). In this case we would expect the D and E states to produce measurable 2+1 REMPI signals. In contrast, the valence state assignments of the D and E states imply that they ionize through the optical transition

$$...(3s\sigma)(3p\sigma)^2(3p\pi)^2\ SiH\ (D\ or\ E) \xrightarrow{-e^-}$$

$$...(3s\sigma)(3p\sigma)^2(3p\pi)\ SiH^+\ (^1\Pi\ or\ ^3\Pi)\quad (4)$$
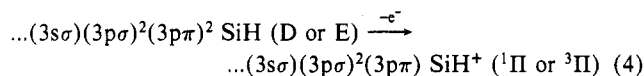
Ionization step 4 prepares an electronically excited cation. We estimate that (4) requires between 50 000 and 80 000 cm^{-1}. To acquire this energy, SiH (D or E) radicals must simultaneously absorb three or four photons; i.e., ion signals generated by resonances with the D or E valence states arise through 2+3 or 2+4 REMPI mechanisms. Compared to the one-photon-absorption rate, the rates for simultaneous absorption of three or four photons are very small. Thus, our laser can detect SiH radicals using a 2+1 REMPI mechanism through the F (4p) Rydberg state but cannot detect SiH radicals using 2+3 or 2+4 REMPI mechanisms which involve the valence states. We conclude that the absence of the D and E states from the REMPI spectrum supports the previously proposed, valence state assignments.

Inclusion of Polyaniline Filaments in Zeolite Molecular Sieves

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Polyaniline has been synthesized in the channels of mordenite (one-dimensional) and zeolite Y (three-dimensional). Aniline was diffused from hexane solution into dehydrated zeolite pores containing different concentrations of framework hydroxyl groups. Addition of $(NH_4)_2S_2O_8$ to an aqueous suspension of the loaded zeolites afforded intrazeolite polyaniline chains, as demonstrated by FTIR, electronic absorption data, and recovery of the included polymer. Stoichiometric, kinetic, XPS, and microscopic data and the absence of bulk conductivity of the polymer/zeolite powders lead to the conclusion that the polymer is formed *inside the host channel system*. While the polyaniline chains in mordenite channels appear to be more highly oxidized than in Y zeolite, both systems show spectroscopic features typical of emeraldine base and emeraldine salt polymers. The polyaniline/zeolite hybrids represent a new class of materials containing synthetic conductors encapsulated in crystalline inorganic hosts with channel systems of molecular dimensions.

Introduction

The design and understanding of well-defined conducting structures of nanometer dimensions is one of the most challenging goals of contemporary solid-state science. In particular, fundamental studies of the electronic structure and conduction mechanism of conducting polymers[1,2] would benefit greatly from such structures, and developments along this line could ultimately reduce the size of electronic circuitry to molecular dimensions.[3,4] The goal of our research program in this area is to design cor-

responding model systems via encapsulation of polymeric chain conductors in low-dimensional, ordered host lattices, particularly in zeolites.[5] Confined charge-carrier systems are also of interest due to potential quantum-size effects on the electronic structure which have been observed in colloidal semiconductor systems, both in suspension and stabilized in zeolite host systems.[6-8] Although there have been reports on the formation of conjugated polymers

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