

Infrared Spectrum of the Silicon Hydride Cation SiH_7^+

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ABSTRACT

Silanium ions are an important class of hypervalent molecules, and the determination of their structure will yield insights into the nature of nonclassical bonding and provide a contrast to the bonding in carbonium ions. We report the infrared spectrum of the mass-selected silicon hydride cluster ion $^{28}\text{SiH}_7^+$, detected by vibrational predissociation spectroscopy. Silanium ions were formed in a pulsed high pressure glow discharge and cooled by the subsequent supersonic expansion. Photodissociation spectra were obtained using a tandem time-of-flight mass spectrometer: SiH_7^+ ions were mass-selected and excited by a tunable infrared laser. The resulting photofragments were detected using a reflectron as a mass analyzer. We observed a vibrational band at 3865 cm^{-1} , which was the only one observed from 3500 cm^{-1} to 4200 cm^{-1} . This result suggests that the molecule might form a symmetric complex with the structure $\text{H}_2\cdot\text{SiH}_3^+\cdot\text{H}_2$, in contrast to the species CH_7^+ , which has the structure $\text{CH}_5^+\cdot\text{H}_2$.

1. INTRODUCTION

Recent investigations of the chemistry of silicon hydride cations have been motivated by the possible role of ion-molecule reactions in the gas phase silane chemistry occurring during chemical vapor deposition (CVD) of silicon films, especially plasma-enhanced CVD. Both experimental¹⁻⁹ and theoretical¹⁰⁻¹³ studies have focused on reactions of Si^+ and SiH_3^+ with silane that produce hydrogenated silicon cluster ions Si_nH_m^+ . The theoretical calculations¹⁰⁻¹³ suggest that these cluster ions exhibit rather novel nonclassical bonding, analogous to but distinct from the nonclassical bonding observed in carbonium ions.¹⁴ Such bonding might even exist in monosilane cluster ions. For example, in the case of SiH_5^+ , theoretical calculations suggest that an H_2 is bound to SiH_3^+ through a three-center two-electron bond,¹⁵ with a bond strength much weaker than that in CH_5^+ .

Although the gas phase chemistry of silicon hydride ions has been studied extensively, there have been few spectroscopic studies to date. Dyke *et al.*¹⁶ have reported the frequency of the out-of-plane bending mode of SiH_3^+ from a photoelectron spectrum of the SiH_3 radical. Smith, Martineau and Davies¹⁷ have recently reported a high resolution infrared absorption spectrum of SiH_3^+ cation detected in a glow discharge. SiH_3^+ is the dominant ion in low pressure silane discharges, and no other species have thus far been detected by this method.

Using an ion trapping tandem mass spectrometer apparatus, Lee and co-workers have obtained infrared vibrational predissociation and multiphoton photodissociation spectra for a number of ionic clusters.¹⁸⁻²⁰ This technique has proved to be a powerful method for obtaining spectra of mass-selected clusters. We have recently developed a simpler apparatus using pulsed techniques, based on the ion photodissociation spectrometer developed by Johnson and Lineberger.²¹ We have begun to apply the vibrational predissociation method to silicon hydride cations and in this paper we report our initial results on the infrared spectrum of the SiH_7^+ cation.

2. EXPERIMENTAL

Silanium ions were generated in a pulsed high pressure discharge source which we developed recently. A mixture of 1% silane in UHP helium was mixed with UHP hydrogen using a MKS flow system to form a mixture of approximately 30 ppm SiH_4 in H_2 at 1000 torr. The gas expanded through a piezo-driven pulsed valve²² with a pulse width of 200 μs into a 0.5 mm diameter channel. The gas then entered a small chamber with two tungsten electrodes (0.5 mm diameter) where a high voltage pulse (typically - 1kV, 100 μs wide) was applied to the anode; the timing suggested that the best conditions for ion formation occurred when the high voltage was applied during the leading edge of the gas pulse. Ions were swept out by the gas pulse through a 1 mm diameter, 1.5 cm long channel and into the first differential vacuum chamber (pumped by a 10" diffusion pump and maintained at a pressure of $2\text{-}10 \times 10^{-5}$ Torr). The plasma was cooled as the gas flowed through the channel and underwent supersonic expansion. The effectiveness of the cooling was demonstrated by the formation of cluster ions with binding energies of 3 kcal/mol or less, such as $\text{H}_3\text{O}^+(\text{H}_2)$. A typical TOF mass spectrum is shown in Fig. 1. The source was operated at a repetition rate of 30 Hz, and produced intense and stable silanium ion beams for hours during which no adjustments were needed.

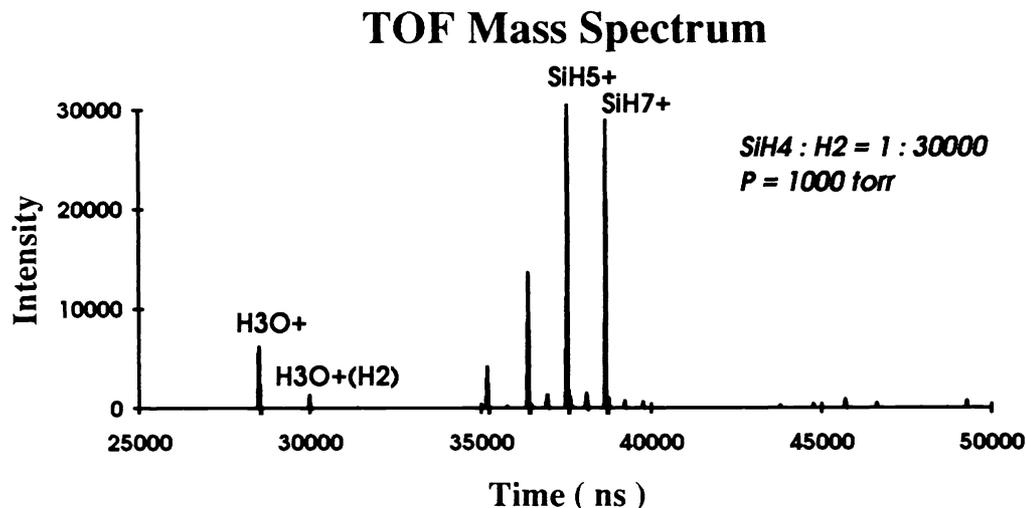


Fig. 1. Time-of-flight mass spectrum of the silanium ions. The pulsed valve stagnation pressure was 1000 Torr. The gas mixing ratio $\text{SiH}_4 : \text{H}_2$ was 1 : 30000.

The plasma expanded supersonically and was collimated by a 3 mm diameter skimmer to enter a second chamber (6" diffusion pump, 5×10^{-6} Torr) containing time-of-flight ion optics. A pulsed electric field applied between two plates 3 cm apart extracted the positive ions between them. The ions were further accelerated by additional electric fields and then entered a field-free region with a final kinetic energy of 1 keV. After passing through a third differential pumping region (4" diffusion pump, 1×10^{-6} Torr) and into a photolysis/detection chamber (500 L/s turbomolecular pump, 3×10^{-7} Torr), the ions encountered a 1 cm long mass gate where a pulsed transverse field was applied to deflect all incident ions except those of the mass of interest. The selected ions were focused into a packet 9 mm long and 5 mm in diameter at 1.5 m downstream from the acceleration optics, where they were intersected by the infrared laser beam. The ions were then mass-analyzed by a 15 cm long reflectron tilted at 2° , and detected by a microchannel plate detector. The signal was amplified and then

collected by a LeCroy 8818 transient digitizer (100 MSamples/s) and 6010 signal averager.

The tunable, pulsed infrared radiation was produced by a LiNbO₃ optical parametric oscillator (OPO). The OPO, based on the design of Brosnan and Byer,²³ was pumped by a Continuum 661s Nd:YAG laser which generated 250 mJ pulses at 1.06 μm . To avoid damaging the LiNbO₃ crystal, the pump beam was collimated and multipassed 14 meters to achieve near-Gaussian beam profile with a spot size of 3.5 mm ($1/e^2$ diameter) at the OPO entrance. The OPO was continuously tunable from 2700 cm^{-1} to 4300 cm^{-1} by simultaneously adjusting the crystal angle and the grating. Typical OPO pulse energies were 5-8 mJ with a linewidth of 1.5 cm^{-1} . The optical path from the laser to the vacuum chamber was purged with dry air to eliminate absorption due to ambient water vapor.

A single-field reflectron was used for mass analysis of the fragment ions. Because of the negligible kinetic energy released during the vibrational predissociation, the photofragment ion (mass m_f) had the same velocity as its parent ion (mass m_i). By reducing the reflectron electric field by a factor of m_f/m_i , the fragment ion would experience the same acceleration in the new field as the parent ion did in the original reflectron field, thus reaching the detector at exactly the parent ion arrival time in the original field. Using this procedure, the mass of the photofragment ion was determined.

Spectra were recorded by stepping the OPO wavelength and averaging the photofragment signal for 400 laser shots at each wavelength. To achieve better signal-to-noise ratio, we averaged 10 such scans. Background signal, primarily caused by collision-induced dissociation in the ion optics chamber, was subtracted by firing the laser beam alternately at the parent ion arrival time and 10 μs before the ion arrival, and taking the difference. The data were then normalized with respect to the OPO laser intensity, which was measured by a Molelectron joulemeter. The OPO laser wavelength was calibrated during the scan by simultaneously recording the vibrational spectrum of acetylene in a photoacoustic cell.

3. RESULTS AND DISCUSSION

An absorption band of SiH₇⁺ was observed in the 3800 - 3925 cm^{-1} region, as shown in Fig. 2. This band has clear P, Q, and R branches, with the Q branch centered at 3865 cm^{-1} . The only photofragment ion observed was SiH₅⁺, indicating that the photodissociation process involved was SiH₇⁺ \rightarrow SiH₅⁺ + H₂. Due to the broad linewidth of the OPO laser (1.5 cm^{-1}), rotational structure of this band was not resolved. There were no other absorptions found from 3500 cm^{-1} to 4200 cm^{-1} .

Based on the relatively high frequency and the strength of this absorption band, we assign it to an H-H stretching motion. This stretch is strongly perturbed, as evidenced by its 300 cm^{-1} frequency shift from the free H₂ fundamental of 4161 cm^{-1} . This assignment supports the notion that SiH₇⁺ is an ionic cluster with at least one H₂ molecule bound to the charge center. The H-H stretch obtains its transition dipole moment through coupling with degrees of freedom that possess oscillator strength, e.g. motion of the charge center relative to the center of mass.

Since the SiH₇⁺ ion was never observed before experimentally, theoretical calculations on its structure have not yet been carried out. Hu *et al.* have done calculations on SiH₅⁺ with various *ab initio* methods.¹⁵ Their optimized structure for SiH₅⁺ is a weakly bound complex of SiH₃⁺ and H₂ subunits (Fig. 3a). The best theoretical estimate of the dissociation energy D_0 for SiH₅⁺ is 10.3 kcal/mol, less than the experimental value of 17.8 kcal/mol. They also report a harmonic frequency of 3991 cm^{-1} for the perturbed H-H stretch, although *ab initio* frequencies are generally 5% to 10% higher than experimental values.

Vibrational Spectrum

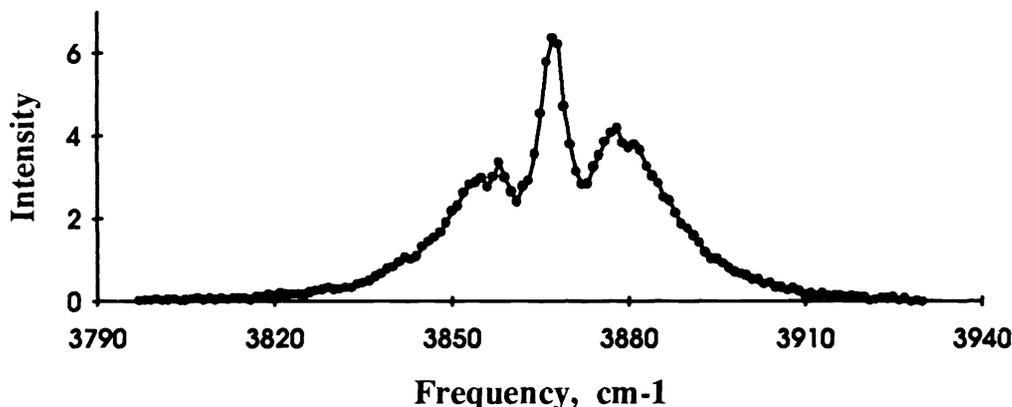


Fig. 2. Vibrational predissociation spectrum of the SiH_7^+ ion in the 3800 cm^{-1} - 3925 cm^{-1} region. No other absorptions were found from 3500 cm^{-1} to 4200 cm^{-1} .

The observed frequency of 3865 cm^{-1} for SiH_7^+ is close to the harmonic frequency of 3991 cm^{-1} for SiH_5^+ predicted by Hu *et al.* This agreement at first suggests that SiH_7^+ could be a complex with an H_2 molecule very weakly bound to the SiH_5^+ ion core, analogous to the structure proposed by Boo, Price, and Lee for the CH_7^+ ion (Fig. 3b).²⁰ However, the H_2 moiety would be perturbed by the SiH_5^+ core and therefore exhibit an absorption band slightly below 4161 cm^{-1} , the vibrational frequency of a free H_2 . In all previous cases involving an ion-molecule cluster with H_2 ligands, such an absorption band has been observed. We scanned the region from 3500 cm^{-1} to 4200 cm^{-1} , but found no evidence of a second absorption band belonging to SiH_7^+ . In addition, we observed that the SiH_7^+ ions could exist even under "hot" source conditions that makes mostly SiH^+ ions, which suggests that the SiH_7^+ binding energy is much larger than that of CH_7^+ .

We therefore propose that SiH_7^+ has the structure shown in Fig. 3c: a planar or nearly planar SiH_3^+ with two H_2 ligands bound to opposite faces of the ion. The two H_2 ligands are approximately the same distance from the Si atom. This structure should result in two H-H stretching bands: the symmetric and antisymmetric combinations of the two H_2 stretches. The symmetric combination, which has the two H_2 ligands expanding and contracting simultaneously, would induce little movement of the charge center and thus should have much weaker absorption intensity. Our current interpretation of the spectrum is that it is in fact weaker and obscured by the stronger antisymmetric mode.

Our proposed structure for SiH_7^+ is quite distinct from the structure proposed by Boo *et al.* for CH_7^+ .²⁰ The differences can be rationalized by comparing the CH_5^+ and SiH_5^+ ions. The dissociation energy for $\text{CH}_5^+ \rightarrow \text{CH}_3^+ + \text{H}_2$ is 40 kcal/mol , and the strong three-center two-electron bond in CH_5^+ results in charge delocalization among the three centers. In contrast, the dissociation energy for $\text{SiH}_5^+ \rightarrow \text{SiH}_3^+ + \text{H}_2$ is only 17.8 kcal/mol . The SiH_5^+ ion is thus closer to an $\text{SiH}_3^+(\text{H}_2)$ complex, as Hu *et al.* predict.¹⁵ A second H_2 will bind to the Si atom, since some of the charge remains localized there.

Molecular Structures

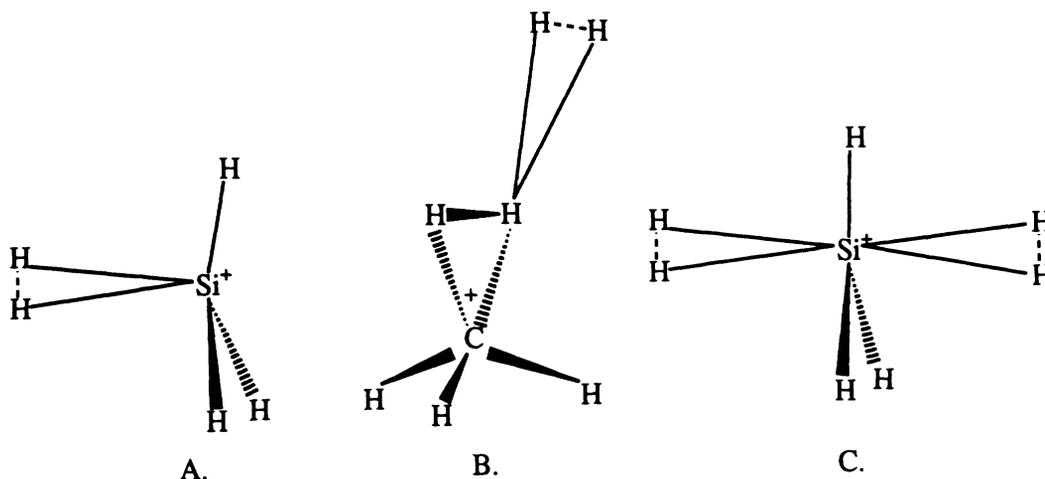


Fig. 3. (a): SiH_5^+ structure predicted by Hu *et al.* (b): CH_7^+ structure based on the experimental results of Boo *et al.* (c): Our proposed structure for SiH_7^+ .

These results shed some light on the structure of SiH_5^+ and SiH_7^+ . A more definitive structure determination requires recording the rotationally resolved spectrum. If the H_2 ligands are about 2 Å from the planar SiH_3^+ , then SiH_7^+ is a prolate top with a rotational constant B of 0.85 cm^{-1} . Our newly upgraded OPO has a linewidth of 0.15 cm^{-1} and will easily resolve the spectra. The next step in silanium ion spectroscopy would be SiH_5^+ . Since the dissociation energy for $\text{SiH}_5^+ \rightarrow \text{SiH}_3^+ + \text{H}_2$ is 17.8 kcal/mol, SiH_5^+ spectra can be obtained through two-photon photodissociation. Larger silicon hydride ions are also believed to possess unusual geometries. In Si_2H_7^+ , for example, the two Si atoms are thought to bond through an H atom, with a structure of $\text{H}_3\text{Si}-\text{H}^+-\text{SiH}_3$. By using multiphoton dissociation techniques, we hope to probe the structure and novel bonding of these fascinating species as well.

4. ACKNOWLEDGMENT

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