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THE SiH VIBRATIONAL STRETCH AS AN INDICATOR OF THE CHEMICAL STATE OF INTERSTELLAR GRAINS

MARLA H. MOORE,[1,2] TOSHIHIKO TANABÉ,[2,3] AND JOSEPH A. NUTH[2]

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ABSTRACT

We have measured the infrared spectra of amorphous silicate grains and films formed in a variety of laboratory experiments. We have found that the frequency of the SiH fundamental stretch is extremely sensitive to the chemical environment of the grain in which the silicon is bound and varies from 2270 cm^{-1} in oxidized grains to 2110 cm^{-1} in a reducing environment. We propose that features previously observed in W33A could be due to —SiH groups in amorphous silica (2190 cm^{-1}), partially reduced silica (2165 cm^{-1}), silicon nitride (2140 cm^{-1}) or slightly oxidized silicon carbide (~2120 cm^{-1}). We predict that observations at 2270 cm^{-1} will reveal a feature due to —SiH groups in highly oxidized interstellar and circumstellar grains. Such a feature might also appear in the spectra of comets.

Subject headings: infrared: spectra — interstellar: grains — laboratory spectra — line identifications — molecular processes — stars: circumstellar shells

1. INTRODUCTION

An absorption feature at 4.6 μm was first observed by Soifer et al. (1979) in W33A. Lacy et al. (1984) later demonstrated the presence of three components within this band using higher resolution observations. Two of these features were attributed to CO. The third component at 2165 cm^{-1} was attributed by them to one or more molecules containing CN bonds. Larson et al. (1985) suggested that the 2165 cm^{-1} feature was the signature of CH_3NC, whereas Grim & Greenberg (1987) assigned the feature at 2165 cm^{-1} to OCN^- ions trapped in icy mantles on the surfaces of grains. Nuth & Moore (1988) proposed that the 4.6 μm feature observed in W33A might be due to SiH groups bound either into or on the surfaces of amorphous silicate grains.

The idea that metal hydrides might exist on or in grains in some interstellar environments is relatively new. Seab & Shull (1985) calculated the efficiency with which interstellar grains may be destroyed in shocks and indicated that on an average, a grain may be destroyed 10 times between formation in a circumstellar environment and incorporation into a protostellar nebula. If correct, these calculations would indicate that a considerable mass of the interstellar dust grew in situ from the vapor. Based on the relative cosmic abundances of H, O, C, N and Si (2800:17:10:2:1, respectively; e.g., see Lewis 1972), one might expect silicon hydrides along with icy mixtures (hydrides of carbon, nitrogen, and oxygen) to coexist on the surfaces of the grains. These refractory and icy coatings would be subject to both UV and cosmic-ray bombardment as well as thermal processing.

Two additional mechanisms are available for the incorporation of SiH groups into interstellar silicates. First, SiH_4, SiC_2, and SiO have all been observed in the outflows around well-studied carbon-rich red giants (Tielens 1990), and it is also predicted that some quantity of SiH is stable even in the atmospheres of oxygen-rich stars (Tsuji 1973). Reactive condensation of these silicon hydride compounds to form amorphous silicates would not be expected to eliminate quantitatively all hydrogen atoms from the final grains based on laboratory studies of the reaction of silane and oxygen in a hydrogen flow condensation system (Tanabé & Nuth 1991). Therefore it is possible that some circumstellar silicate or silicon carbide grains may exhibit absorption near 4.6 μm. Another mechanism by which silicate grains might pick up hydrogen would be ion implantation of hydrogen atoms into amorphous silicates following nova or supernova shocks in the general interstellar medium. It is possible that such shock processes could first partially reduce even fully oxidized silicates via ion-sputtering processes (e.g., Yin, Ghose, & Adler 1972) and this gradual chemical reduction could increase the efficiency with which hydrogen is implanted. Stein (1975) studied the implantation of H^+ and D^+ into silicon at energies between 70 and 400 keV. He observed the formation of absorption bands between 4.5 and 5.5 μm following H^+ irradiation and between 6.2 and 7.5 μm following D^+ irradiation and attributed these features to —SiH and —SiD groups, respectively.

Infrared spectra of condensed mixtures of H_2O, NH_3, and CH_4 before and after irradiation have been reported by Moore et al. (1983), and some spectral information exists on mixed condensates formed using $SiH_4 + H_2O$ and $SiH_4 + Fe(CO)_5 + H_2O$ (Nuth & Moore 1988). However, there has been no study of the evolution of the SiH spectral line in mixed condensates (binary mixtures of SiH_4 with H_2O, NH_3, or CH_4) as a function of irradiation, thermal processing, and oxidation. The infrared spectra of mixtures are, to a good approximation, usually the sum of the spectrum of each component. However, various intramolecular factors cause shifts in group frequencies (Lord & Miller 1956). The SiH group is similar to a single-bonded diatomic molecule (without coupled vibrations or hydrogen bonding). Therefore the electronegativity (EN) of adjacent atoms or groups is the one intramolecular factor which could affect the position of the SiH group. Smith & Angelotti (1959) have documented that the frequency of the SiH fundamental increases with increased EN of the group bound to the silicon. They suggest that increasing EN, which causes a withdrawing of electrons from the silicon also causes a

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[1] Department of Chemistry and Biochemistry, University of Maryland.

[2] Astrochemistry Branch, Laboratory for Extraterrestrial Physics, GSFC, Greenbelt, MD 20771.

[3] NAS/NRC Resident Research Associate on leave from the Institute of Astronomy, The University of Tokyo, Mitaka, 181, Tokyo.

shortening of the SiH bond resulting in the increased vibrational frequency.

In this *Letter* we report observations of the variation in the frequency of the SiH fundamental stretch in both residues of irradiated condensates initially containing silane, and in silicate smokes condensed from silane-oxygen mixtures in a hydrogen flow. We show that the position of this feature is sensitive to the general oxidation state and chemical make-up of the grain, and we suggest that observations of this feature in dark clouds, the diffuse ISM, circumstellar outflows and even in comets may be used to constrain the structure of grains in these environments.

2. EXPERIMENTAL PROCEDURE

Grains exhibiting the SiH fundamental stretch were prepared in two separate and very different experimental systems. In the first system silicon-containing residues were prepared from low-temperature condensates of silane and water, ammonia, or methane, in an apparatus previously described by Moore (1984). In all cases the appropriate gas mixture is made in a 5 liter bulb with typical ratios of $SiH_4 + H_2O$ (1:1), and $SiH_4 + NH_3$ (1:4) and $SiH_4 + CH_4$ (1:4). Silane gas was electronic grade (Air Products). H_2O was triply distilled (resistance $> 10^7$ ohm cm) water. Anhydrous NH_3 was research grade (Matheson) and CH_4 was ultra–high purity (Matheson). The gas mixture was slowly deposited onto a polished aluminum substrate mounted on the cold finger of a cryostat at 15 K until a condensate a few microns thick was formed: the infrared spectrum (resolution of 4 cm^{-1}) of this film was recorded using a Mattson Polaris FTIR. The sample was then irradiated with 700 keV protons, after which the spectrum of the film was again recorded. Additional cycles of irradiation/spectra were carried out until a cumulative incident dose of protons was either 1×10^{15} protons cm^{-2} or 1.5×10^{15} protons cm^{-2}. After irradiation at 15 K, the sample was warmed slowly to room temperature in increments of 50 K or less. The average warming rate was less than 3 K $minute^{-1}$. After each incremental warm-up, the infrared specrum was obtained. In all cases the infrared spectrum of the residue remaining on the aluminum substrate was obtained in a vacuum, then in air, and after remaining in air for up to several months. Spectra in air were measured using a Spectra Tech microscope coupled to a Nicolet 710 FTIR.

The second reaction system was used to prepare silicon oxide smokes from a mixture of $SiH_4 + O_2$ in a hydrogen flow at temperatures ranging from ~500 up to 1400 K in an experimental apparatus described by Nelson et al. (1987) and by Nuth et al. (1988). In this system electronic grade silane (Air Products) was introduced into a flow of hydrogen (technical grade) and then mixed with a stream of oxygen (technical grade) inside an alumina-lined, resistively heated, graphite furnace. Combustion of the silane and hydrogen occurred both inside the 1 inch (2.5 cm) diameter, 3 inch (7.5 cm) long alumina furnace tube as well as after the gas exited the furnace into a region nominally at room temperature. Smoke particles were collected on polished aluminum substrates and the infrared absorbance spectra of these smokes were obtained using a Mattson Polaris FTIR. Some samples were then exposed to either water vapor or vacuum at elevated temperatures, and the changes in the infrared spectra were monitored at periodic intervals over many weeks (Tanabé & Nuth 1991) as the particles oxidized and lost hydrogen from the evolving silicate structure.

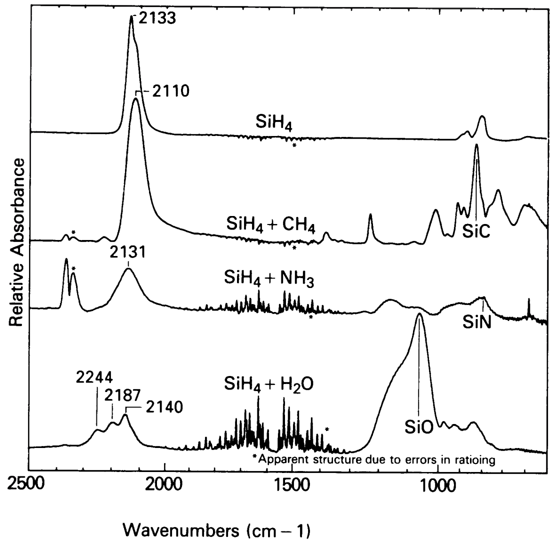

FIG. 1.—Infrared spectra from 2500 to 500 cm^{-1} of the room-temperature residues remaining after warm-up in a vacuum of various proton-bombarded condensates. Ratioing errors are due to incomplete purging of atmospheric CO_2 and water between background and sample measurements.

3. RESULTS

The infrared spectra of room temperature residues from the proton bombardment and warm-up of SiH_4, $SiH_4 + CH_4$, $SiH_4 + NH_3$, and $SiH_4 + H_2O$ mixtures is shown in Figure 1. The position of the SiH fundamental in these residues varies from 2110 cm^{-1} (4.74 μm) in the $SiH_4 + CH_4$ residue to 2244 cm^{-1} (4.46 μm) for one component of the $SiH_4 + H_2O$ residue. Spectral changes which occur after the $SiH_4 + CH_4$ residue is exposed to air at room temperature for various times are shown in Figure 2. This feature clearly undergoes relatively

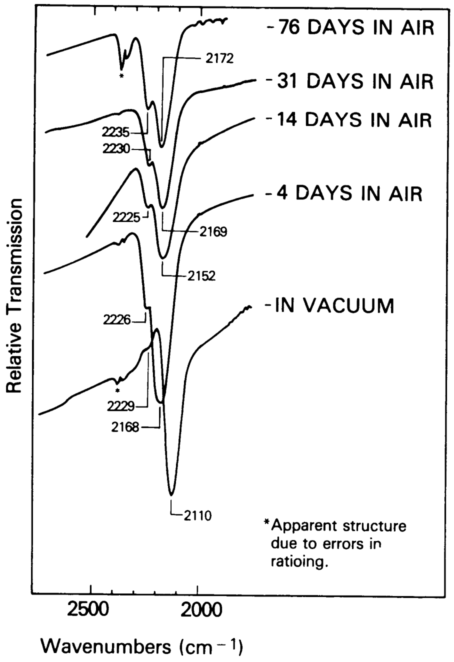

FIG. 2.—Infrared spectra of the evolving feature in the room-temperature residue of the irradiated SiH_4—CH_4 condensate as a function of time in air.

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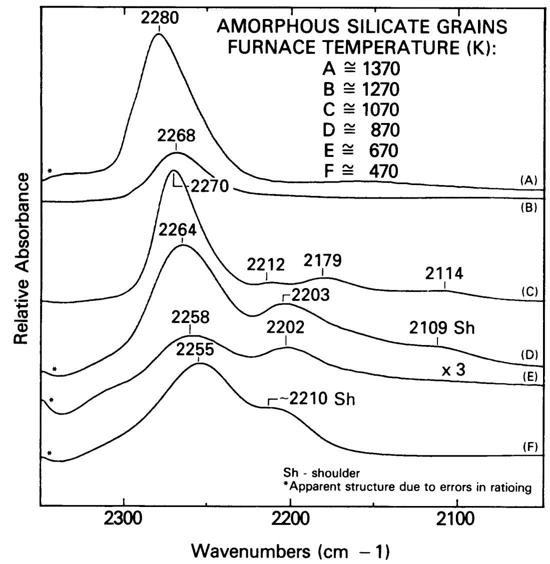

FIG. 3.—Infrared spectra of the Si_2O_3 smoke formed by combustion of $SiH_4—O_2$ in hydrogen.

rapid changes both in position and shape as a result of interaction with the atmosphere.

The infrared spectra of amorphous silicate grains condensed after combustion of SiH_4 and O_2 in hydrogen at nominal furnace temperatures near 1370, 1270, 1070, 870, 670, and 470 K are shown in Figure 3. Exposure of the sample to air at room temperature, to water vapor at 370 K, and to mild vacuum at 370 K over a period of several months results in a slight shift of the SiH peak position to lower energy and a dramatic reduction in the intensity of the absorption. Figure 4 shows the evolution of the 4.4 μm feature in silica smoke condensed at 1070 K and exposed to the atmosphere for various times.

4. DISCUSSION

It is obvious from Figure 1 that the frequency of the SiH fundamental is sensitive to the chemical environment in which the silicon atom resides; the higher the electronegativity of the surroundings, the higher the frequency of the fundamental [Note: $EN(O) > EN(N) > EN(C)$]. This observation is reinforced by Figure 2 which follows the changes in the SiH fundamental as the amorphous silicon-carbon residue is oxidized at room temperature in air. As the oxidation proceeds, and the environment surrounding the silicon becomes more electronegative by both addition of oxygen to the matrix and the possible loss of carbon as CO_2, the frequency and shape of the SiH fundamental increases from a single peak at 2110 cm^{-1} to a doublet whose stronger component is at 2172 cm^{-1} and whose weaker component is at 2235 cm^{-1}. Similar behavior occurs in each of the four residues when they are exposed to air: the centroid of each SiH feature moves to higher frequency.

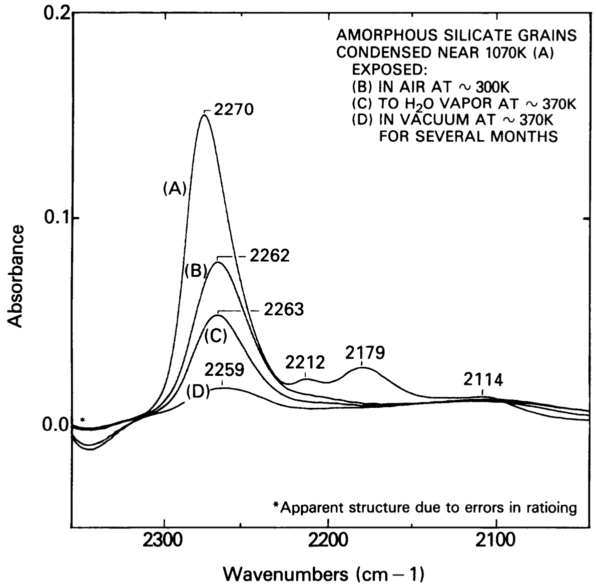

FIG. 4.—Infrared spectra of the evolving feature in the Si_2O_3 smoke formed at ~ 1070 K as a function of time in air at room temperature.

In the case of smokes condensed by the combustion of silane and oxygen in hydrogen, the smokes formed at the highest temperatures, and which therefore should be most completely oxidized, all have very strong absorption near 2270 cm^{-1} (Fig. 3). Smokes formed at lower temperatures, which are more likely to remain at least partially reduced, exhibit not only the strong absorption near 2270 cm^{-1}, but also weaker components near 2210 cm^{-1}, 2200 cm^{-1}, 2175 cm^{-1}, and possibly a very broad component near 2100 cm^{-1}. It is interesting that as these samples are oxidized in air at room temperature (Fig. 4), features at lower energy are destroyed more rapidly than those at higher energy.

The astrophysically important correlation which should be noted at this time is that of the average oxidation state in the immediate vicinity of the SiH group and the frequency of the SiH absorption band (or bands). The observation of features in the 4.6 μm region in cold clouds such as W33A could be indicative of SiH in a variety of oxidation states. Examination of Figure 3 in Larson et al. (1985) reveals a number of absorption features, three of the strongest of which occur at 2170–2160 (doublet), 2140, and 2040 cm^{-1}. Smaller peaks and shoulders can be seen at 2190, 2120, 2100, 2070, 2060, and 2020 cm^{-1}. Although it is highly unlikely that all of these features are due to SiH, features at 2190, 2160–2170, 2140, and 2110 cm^{-1} do correspond to absorptions measured in our laboratory samples in which SiH occurs in progressively more reducing environments.

It is interesting to note that a feature near 4.6 μm also appears in two spectra published by Tanabé et al. (1988) for smokes formed from a plasma containing silicon atoms at initial temperatures as high as 8000 K. In one case the plasma was carbon-rich and formed primarily amorphous silicon carbide grains: in the other case the plasma was oxygen-rich and the smokes contained both amorphous silicon oxides and carbides. A smoke formed from a hydrocarbon precursor and without silicon did not show a feature at 4.6 μm. These experiments demonstrate that SiH bonds can form concurrently with condensation of both amorphous silicon carbide and silicon oxide smokes even when all preexisting SiH bonds have previously been destroyed. They also strongly support the identification of the 4.6 μm feature as due to the SiH stretch. This identification is also supported by the experiments of Wada, Sakata, & Tokunaga (1990) who vaporized SiO at 1300 K into a low-pressure atmosphere of water vapor (10^{-5} torr). In these experiments Wada et al. observed features at both 4.45 and 4.64 μm after reaction of the SiO vapor with the ambient water vapor atmosphere.

If amorphous silicates are prevalent in the general interstellar medium then we predict that it should be possible to observe a feature near 2270 cm^{-1} which would be attributable to SiH in "highly oxidized" silicates (Fig. 3). Although it may also be possible to detect such a feature in the shells of oxygen-rich stars, the hydrogen in such silicates could be lost if the grain temperature remained too high (e.g., $T \geq 350$ K) for periods on the order of weeks to months (Fig. 4). Specific data on the loss rate of hydrogen from highly oxidized silicates (Tanabé & Nuth 1991) and from more reduced grain candidates (Moore, Tanabé, & Nuth 1991) should be available in the near future. If observations of W33A (Larson et al. 1985) can be used as a guide, then grains containing silicon atoms may exist in a variety of oxidation states in the cold clouds from which protostars collapse. This is not particularly surprising since such grains would tend, on average, to be quite old and might be expected to contain silicates formed both in circumstellar and interstellar environments by a variety of processes. "Silicate" grains containing carbon, hydrogen, and nitrogen as well as oxygen could be quite reactive if quickly heated during protostellar collapse and could potentially release interesting organic compounds as the grain anneals to a more stable form.

Recent airborne and ground-based spectrophotometry of comet Halley revealed the 10 μm emission band identified with the silicate material in cometary dust (Bregman et al. 1987). Spectra in the 2.5–5 μm region of Halley were obtained by the IKS-Vega instrument during its fly-by through the coma of the comet. Several small features were reported in the 4.4–4.6 μm region which would be consistent with the position of SiH groups. Unfortunately no firm conclusions can be reached from these observations due to the poor signal-to-noise ratio of these small features (Combes et al. 1987).

Observations of both interstellar clouds and comets between 4 and 5 μm could be extremely informative and should be carried out at the first available opportunity. There are few observations currently available over this wavelength range due to a significant problem with CO_2 absorption in the Earth's atmosphere. Future observations may reveal a peak due to the SiH stretch in highly oxidized silicates near 2270 cm^{-1} (4.4 μm) as well as a number of small peaks at longer wavelengths due to SiH in progressively more reducing environments.

5. SUMMARY

We have experimentally shown that the position of the SiH fundamental vibrational stretch is very sensitive to the chemical environment surrounding the silicon atom. In particular, silicon in an oxidizing environment will exhibit an SiH feature near 2270 cm^{-1} whereas silicon in a reducing grain could be responsible for a feature at 2110 cm^{-1}. As a reduced grain oxidizes the frequency of the SiH fundamental shifts to shorter wavelengths through a series of intermediate bands. Based on our laboratory experiments and the assumption that most silicon will reside in highly oxidized environments, we predict that when observations are possible over the entire region between 4 and 5 μm, a feature due to SiH should be observed near 2270 cm^{-1}. Furthermore, it is possible that a number of previously unidentified features in the spectra of W33A (Larson et al. 1985) could be due to SiH in a variety of chemical environments. More observations of both interstellar and circumstellar grains are needed over this important, but observationally difficult, wavelength range.

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