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Research Note

Si-H bonds produced by ion implantation in silicon and frozen silanes

G. Strazzulla[1], G.A. Baratta[1], G. Compagnini[2], M.E. Palumbo[1], and M.A. Satorre[3]

[1] Osservatorio Astrofisico di Catania, Città Universitaria, I-95125 Catania, Italy
[2] Dipartimento di Chimica dell' Università di Catania, Italy
[3] Departament Fisica Aplicada EPSA (UPV), Escola Politecnica Superior Alcoi, Alicante, Spain

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Abstract. In a recent paper Pendleton et al. (1998) present new spectra of embedded protostars which exhibit a broad absorption feature near 4.62 μm (2165 cm^{-1}). In the literature this band is referred to as the "X(C≡N)" band. However Pendleton et al. (1998) cannot exclude the possibility of a different identification (such as an Si-H related compound) for which they claim the need of experimental data. To contribute to fulfill this request we present here new laboratory results on: (1) the formation of Si-H bonds induced by implantation of 30 keV H^+, $H_2{}^+$ and CH^+ ions into silicon and (2) the production of Si-H-containing refractory species by ion irradiation (60 keV Ar ions) of frozen dichlorosilane ($SiCl_2H_2$). The obtained results and others already available in the literature have been compared with astronomical observations. Even if we are aware that the sample we consider here is far from being complete, we suggest that it is possible to exclude that a refractory species containing Si-H groups can be responsible for the interstellar feature.

Key words: dust, extinction – ISM: molecules – infrared: ISM: lines and bands

1. Introduction

In a recent paper Pendleton et al. (1998) present new spectra of embedded protostars which exhibit a broad absorption feature near 4.62 μm (2165 cm^{-1}). In the literature this band is referred to as the "X(C≡N)" band. Pendleton et al. (1998) do also a comprehensive review of the possible responsible species, based on the currently available, but incomplete, laboratory data. Their conclusion is that the 4.62 μm (2165 cm^{-1}) band continues to be likely assigned to a X(C≡N) species and that the best candidate is a residue obtained by ion irradiation of frozen mixtures H_2O:NH_3(or N_2):CH_4 (Palumbo et al. 1998). In addition the possibility of a completely different identification (such as an Si-H related compound), for which they claim the need of experimental data, cannot be ruled out.

Here we present new laboratory results on: (1) the formation of Si-H bonds induced by implantation of $\simeq$ 30 keV H^+, $H_2{}^+$ and CH^+ ions into silicon and (2) the production of Si-H-containing refractory species by ion irradiation (60 keV Ar ions) of frozen dichlorosilane ($SiCl_2H_2$).

Our results are compared with others already published. In particular Nuth & Moore (1988) present experimental results relative to ion irradiation of SiH_4:H_2O and $Fe(CO)_5$:SiH_4:H_2O frozen mixtures and reveal the synthesis of refractory residues containing Si-H bonds. Nuth et al. (1992) examine solid samples and outline that spectral features due to Si-H bonds are extremely sensitive to the oxidation state of the "silicate" in which they are embedded in. Their peak positions range from 2278 cm^{-1} (4.39 μm) in highly oxidized environments to 2110 cm^{-1} (4.74 μm) in silicon carbide. Recently Blanco et al. (1998) show the presence of an Si-H IR feature in silicate dust grains produced in laboratory by means of laser evaporation of solid targets in atmospheres containing hydrogen. In particular they found features peaking at 2246 cm^{-1} (4.45 μm) for enstatite particles and at 2204 cm^{-1} (4.54 μm) for olivine grains.

2. Experimental results

2.1. Experimental set-up

A high-vacuum chamber (P$\sim 10^{-7}$ mbar) is placed in the sample compartment of an FTIR Perkin-Elmer spectrophotometer (mod. 1710) (4400-400 cm^{-1} = 2.27-25 μm), the IR beam enters and leaves the chamber through two KBr windows. In the case of ion implantation, the silicon crystal is irradiated at room temperature by 30 keV H^+, $H_2{}^+$ and CH^+ ions. After a given ion fluence the IR spectrum is recorded. Samples are then extracted from the chamber and some of them are annealed for 1 hr at high temperatures (500-1000 °C). Their IR spectra are then recorded.

In the case of irradiation of frozen dichlorosilane a CsI substrate is cooled (10-300 K) by a closed-cycle helium refrigerator. The gas is admitted in the scattering chamber and forms frozen films onto the cold substrate. In some cases, a He-Ne laser beam is used to monitor the thickness of the sample, by watching in real time to the interference pattern between the reflections on the interfaces vacuum-sample and sample-substrate.

Send offprint requests to: G. Strazzulla, (gianni@alpha4.ct.astro.it)

Table 1. Peak position (cm^{-1} and μm) and FWHM of the Si-H stretching IR band measured for solid samples and for residues formed by irradiation of frozen silanes.

Sample	Peak position cm^{-1} (μm)	FWHM cm^{-1}	Ref.
Solid Samples (Room T)			
oxidized	2278 (4.39)	...	Nuth et al. 1992
enstatite	2246 (4.45)	...	Blanco et al. 1998
olivine	2204 (4.54)	...	Blanco et al. 1998
SiC	2110 (4.39)	...	Nuth et al. 1992
Si-H from ion impl.	2099 (4.76)	106	this work
Residues from frozen silanes (200 K)			
$Fe(CO)_5$:SiH_4:H_2O	2170 (4.61)	...	
	2150 (4.65)	...	
	2110 (4.74)	...	Nuth & Moore 1988
SiH_4:H_2O	2140 (4.67)	...	
	2120 (4.67)	...	Nuth & Moore 1988
$SiCl_2H_2$	2198 (4.55)	66	this work

All of the spectra shown in the next sections have been obtained with a resolution of 2 cm^{-1} and are ratioed to the background spectrum. The substrate plane forms an angle of 45 degrees with the IR beam and the ion beam so that, before, during and after irradiation, spectra can be obtained without tilting the sample. After irradiation the samples can be warmed up at a rate of a few degree/minute and spectra taken at chosen temperatures in the range 10-250 K.

Ion beams are obtained from an ion implanter (30 kV). The beam sweeps on the target and produces a 2×2 cm^2 spot (greater than the spot of the IR beam). From the ion implanter doubly-ionized ion beams can also be obtained reaching energy up to 60 keV.

We have irradiated our icy samples with 60 keV Ar^{++}. Ion current densities in the range of 10^{-1} to a few μA cm^{-2} have been used in order to avoid a macroscopic heating of the target.

2.2. Ion implantation in silicon

Ion implantation of reactive species into amorphous or crystalline matrices has been used to investigate the formation of stable surfaces (e.g. silicon oxide, nitride, carbide), thin films or buried layers (Celler et al. 1986; Stein 1985; Compagnini & Calcagno 1994). We have implanted crystalline silicon wafers with 30 keV H^+, $H_2{}^+$ and CH^+. Silicon has been used as a reference material. IR spectra of these samples show a broad absorption band at about 2100 cm^{-1} (Si-H stretch, see Figs. 1a and b). The implantation of CH ions produces also the formation of Si-C bonds as testified by the appearance of a band at about 750 cm^{-1} (Si-C stretching mode).

The Si-H band is stable up to high temperatures. The integrated intensity of the band decreases with annealing temperature, testifying for a loss of H, and disappears at temperatures above 600 °C. Peak positions and FWHM are: 2099 cm^{-1} (4.76 μm) and 106 cm^{-1} for the sample as implanted at room temperature; 2096 cm^{-1} (4.77 μm) with 91 cm^{-1} at 500 °C; 2084 cm^{-1} (4.8 μm) with 65 cm^{-1} at 600 °C.

2.3. Ion irradiation of frozen silanes

$SiCl_2H_2$ was deposited, at a grown rate of about 2.1 Å/sec on the cold (10 K) substrate. The thickness was measured during deposition from the interference fringes of a He-Ne laser. The Si-H stretches give rise to two peaks at 2252 cm^{-1} (4.44 μm) and 2228 cm^{-1} (4.49 μm) (see Fig. 1c).

After ion implantation the integrated intensity of the band decreases, mainly because of a loss of hydrogen, and thus a decrease of the number of Si-H bonds. Peak position and shape of the band do not vary appreciably. After implantation and warm up of the sample a residue is left over containing Si-H groups (see Fig. 1d). The band is now much broader and peaks at lower wavenumbers: 2211 cm^{-1} (4.52 μm) at 150 K and 2193 cm^{-1} (4.56 μm) at 250 K.

3. Discussion

In Table 1 we compare our results with some others available in the literature. The table reports results relative to solid samples and to residues obtained after ion irradiation of frozen silanes. A common characteristic of all of the listed samples is that the bands are very broad. Although we have not found the FWHM value in the literature samples a visual inspection of the published spectra show that all of the FWHM are of the order of 100 cm^{-1}.

In Fig. 1 we compare some of our spectra (normalized to the maximum of the optical depth; full lines) with that of the embedded source W33A (points; Pendleton et al. 1998). The latter spectrum exhibits three bands at 2140 cm^{-1} (4.67 μm), easily attributed to frozen CO (Tielens et al. 1991), at 2040 cm^{-1} (4.9 μm) attributed to OCS (Palumbo et al. 1995) and at

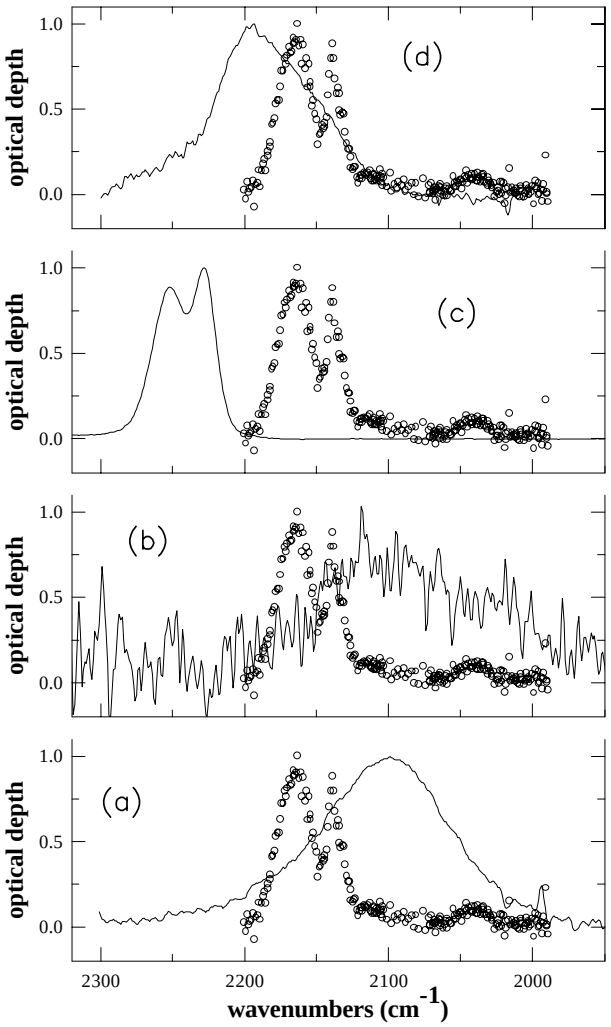

Fig. 1a–d. Normalized IR spectra, in the region of the Si-H stretching, of some laboratory samples are compared with the spectrum obtained for the astronomical source W33A (Pendleton et al. 1998). The laboratory samples are: **a** Si-H band obtained after implantation of 30 keV CH^+ ions (4×10^{17}/cm^2) in silicon; **b** Si-H band obtained after implantation of 30 keV H^+ ions (8×10^{16}/cm^2) in silicon; **c** as deposited (at 10 K) $SiCl_2H_2$; and **d** residue (at 250 K) obtained after ion irradiation of frozen $SiCl_2H_2$.

2165 cm^{-1} (4.62 μm) (the "X(C≡N)" band) for which we are searching a laboratory analog.

We can see that the bands due to H implanted in silicon and to the residue from frozen dichlorosilane not only peak in wrong positions but also are much broader than the one of the astronomical source. Furthermore the Si-H bond in the residue obtained by ion irradiation of SiH_4:H_2O mixtures (Nuth & Moore 1988) gives rise to a double peak which does not fit the observed spectra. Finally, for all of the samples listed in Table 1 the Si-H band is larger than the astronomical one. As discussed above this seems to be a general characteristic of this feature whatever is the process by which it is formed. Thus refractory Si-H containing species are not good candidate to reproduce the observed feature, even if it would be possible to find a particular sample whose SiH band peaks in the right position.

On the other hand, the band due to silanes deposited at 10 K, suffers the further problem to exhibit two peaks instead of the single peak of the astronomical sources. In fact frozen SiH_4 exhibits two peaks at 2216 cm^{-1} (4.51 μm) and 2176 cm^{-1} (4.6 μm) (Lloret & Abouaf-Marguin 1986) that shift to 2200 cm^{-1} (4.55 μm) 2165 cm^{-1} (4.62 μm) in water ice matrices (Nuth & Moore 1988). Thus also frozen silanes are not good candidates to reproduce the astronomical feature.

A (remote) possibility exists to find a particular silane that peaks at the right position, has the right width and exhibits a single peak. However the constancy of the astronomical feature, observed along different lines of sight with different physical parameters, would require an explanation of why that one particular species is formed over all other choices. Recently Furton & Witt (1998, private communication) have studied the IR spectra of a large number of various Si-H containing materials deposited as thin films produced by plasma enhanced chemical vapor deposition of various silanes. None of them matches the observed feature very well.

In principle we cannot exclude that a broad Si-H component contributes, at the level of a few percent to the observed feature (see Fig. 1, panels a and b). However because the residues as well as the solid materials we have here discussed are refractories, we would expect that the band should be observable in the diffuse interstellar medium as well. This contrast with the recent ISO results: the spectrum taken along the line of sight to Cyg OB2 no.12, that is likely view through the diffuse interstellar medium does not show any sign of the 4.62 μm band (Whittet et al. 1997).

In conclusion, we have examined the profile of the Si-H stretching mode in several samples produced by different processes. Even if we are aware that the considered sample is far from being complete, we suggest that it is possible to exclude that a refractory species containing Si-H groups can be responsible for the observed interstellar feature.

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