

FAR-INFRARED INVESTIGATIONS OF A METHANOL CLATHRATE HYDRATE: IMPLICATIONS FOR ASTRONOMICAL OBSERVATIONS

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ABSTRACT

Observations of nonterrestrial clathrate hydrates are still lacking despite the fact that clathrates first were suggested to exist in cometary and interstellar ices over 40 years ago. Spectroscopy, the most direct method of astronomical detection, has been hampered by the similarity of clathrate hydrate spectra to those of unenclathrated guest molecules and solid H₂O. We have prepared a methanol (CH₃OH) clathrate hydrate, using a recently published procedure, and have investigated its far-infrared spectrum. The spectrum is quite different from that of either unenclathrated CH₃OH or solid H₂O and so should be of value in astronomical searches for this clathrate.

Subject headings: comets: general — cosmic rays — molecular processes

1. INTRODUCTION

Clathrate hydrates are crystalline solids consisting of cages of hydrogen-bonded H₂O molecules enclosing a “guest” species, usually a stable molecule. The cages’ structure is distinctive and is different from the arrangement of H₂O (Davidson 1973; Jeffrey 1984). Although it was suggested more than 4 decades ago that these hydrates exist in cometary and interstellar ices (Delsemme & Swings 1952), there is as yet no direct evidence for clathrate hydrates in any nonterrestrial object. Astronomical observations of infrared (IR) sources might be expected to detect clathrate hydrates, but near-IR (Smythe 1975), mid-IR (Bertie & Othen 1973a; Bertie & Solinas 1975), and far-IR (Bertie & Jacobs 1977, 1978) spectra of clathrates often are dominated by broad features of the H₂O cages, which usually resemble H₂O ice spectra, and by guest molecule features, which typically differ little from spectra of the pure unenclathrated guest. In this *Letter* we present the far-infrared spectrum of a methanol (CH₃OH) clathrate hydrate. The spectrum is very different from that of either pure H₂O or pure CH₃OH, and should be valuable in searches for the CH₃OH clathrate hydrate in astronomical objects. The fact that the guest molecule is CH₃OH is of special importance since this molecule has been observed in several recent comets (Bocklee-Morvan et al. 1991; Hoban et al. 1991) and is thought to be important in some interstellar clouds (Tielens & Allamandola 1987; Grim et al. 1991).

Clathrates are most commonly identified in the laboratory by X-ray or electron diffraction. Infrared spectroscopy can also be used for clathrate hydrate identification, most reliably in systems where clathrate formation is known to occur from diffraction data (Bertie & Othen 1972, 1973b; Bertie & Devlin 1983). Blake et al. (1991) recently have published an elegant set of experiments along these lines in which electron diffraction and mid-IR spectroscopy were combined to investigate the CH₃OH clathrate hydrate. When an amorphous H₂O:CH₃OH = 2:1 mixture was deposited at 85 K and warmed to 130 K, electron microscopy and electron diffraction showed that a single polycrystalline phase formed, with some remaining amorphous material. The diffraction pattern of the

crystalline phase was indexed as the type II (Davidson 1973; Jeffrey 1984) CH₃OH clathrate hydrate. However, the authors reported that only “a small change was noticed in the profiles of some of the CH₃OH bands” in the mid-IR spectrum. Spectroscopic evidence for enclathration was obtained by using a small amount of CO₂ as a tracer gas in a H₂O:CH₃OH mixture. (Earlier work had established the IR spectra of CO₂ clathrates; Fleyfel & Devlin 1991.)

We have independently verified the results of Blake et al. (1991) for the mid-IR spectrum (4000–400 cm⁻¹ or 2.5–25 μm) of the CH₃OH clathrate hydrate: spectra from 13 to 140 K indeed are dominated by absorptions of CH₃OH and H₂O. However, by working in the far-infrared region from 400 to 100 cm⁻¹ (25–100 μm) we have found some rather pronounced spectral features, different from those of either CH₃OH or H₂O alone. We also have irradiated the CH₃OH clathrate with a proton beam to simulate cosmic-ray bombardment. To our knowledge these are the only in situ radiation chemical experiments that have been done on a cometary or interstellar clathrate hydrate analog.

2. EXPERIMENTAL PROCEDURE

The experimental procedure followed was largely the same as that used for the study of other ices (Hudson & Donn 1991; Hudson & Moore 1992; Moore & Hudson 1992). Most of our experiments used slightly greater warming rates and annealing times at the higher temperatures than those of Blake et al. (1991), but otherwise our procedures were identical to theirs. Briefly, a gas-phase mixture was prepared in a high-vacuum line and slowly deposited at 13 K on a precooled, polished aluminum substrate in a vacuum chamber. An IR beam was passed through the resulting ice mixture (thickness ~4 μm) where it reflected off the underlying substrate, back through the ice mixture, and on to a detector. A spectrum of the blank substrate at 13 K served as the reference for spectral ratioing. Spectra were recorded as 60 scan accumulations with 4 cm⁻¹ resolution. No corrections have been applied to the IR data for reflection and so the relative intensities of some of the features

we report may be slightly different in transmission spectra, although the line positions should be the same. Most experiments were done with $\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1$ mixtures or 2:1 mixtures with a few percent of other molecules added. Supporting experiments involved H_2O or CH_3OH alone, to examine the spectra of crystalline and amorphous phases of each compound. Radiation experiments were performed with 0.7 MeV protons from a Van de Graaff accelerator. Samples deposited at 77 K gave essentially the same results as those deposited at 13 K.

Our temperatures in the 100–140 K region appear to be ~ 10 K higher than those of Blake et al. (1991) for the same phenomena, such as sublimation of H_2O ice. This is probably because our ices were formed, and the temperatures were measured, on a metal substrate whereas their experiments used nonmetallic substrates (carbon, CsI, polyethylene).

3. RESULTS

Experiments usually began with deposition of a $\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1$ mixture at 13 K over 30 minutes, the spectrum of a typical amorphous sample being shown in Figure 1a. Warming the sample to 130 K at 3–6 K minute^{-1} gave the spectrum of Figure 1b. Either holding the sample at 130 K for several hours or warming to 140 K for about 15 minutes, gave the spectrum shown in Figure 1c. When the sample then was cooled to 14 K, the lines marked by asterisks (*) in Figure 1c sharpened and shifted slightly, and one line split into two components. The resulting spectrum is seen in Figure 2a. Spectra of amorphous (*dashed line*) and crystalline (*solid line*) CH_3OH and H_2O are given in the lower part of Figure 2 for 14 K. Careful comparison shows that the small,

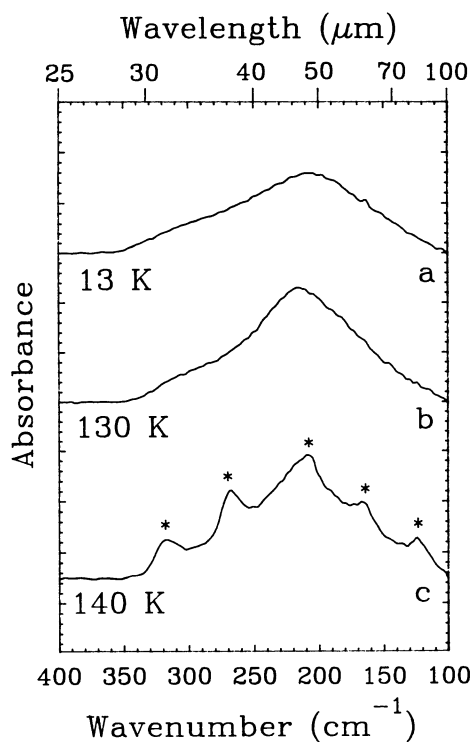


FIG. 1.—Evolution of the far-IR spectrum of the $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ mixture. (a) 13 K, (b) 130 K, (c) 140 K. Spectra have been displaced vertically for clarity. The initial ice had a thickness of $\sim 4 \mu\text{m}$. Features marked with asterisks (*) in Fig. 1c sharpen and shift slightly upon recooling as shown in Fig. 2a.

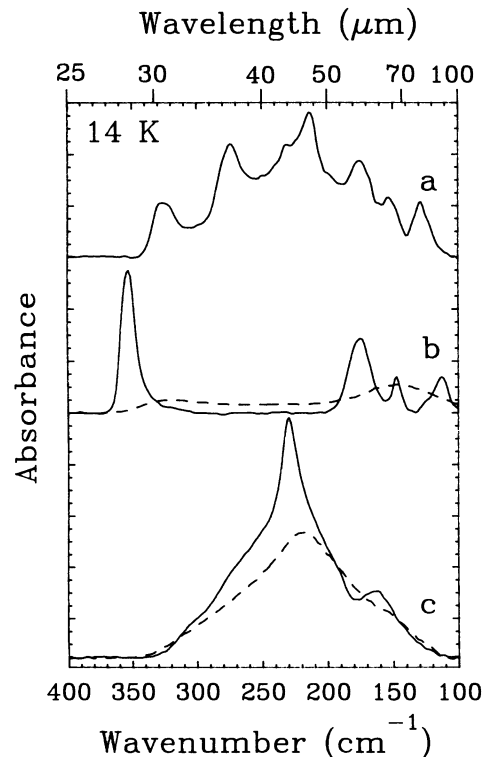


FIG. 2.—Far-IR spectra at 14 K. (a) $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ mixture after warming from 13 to 140 K and then recooling; (b) pure amorphous (*dashed line*) and pure crystalline (*solid line*) CH_3OH ; (c) pure amorphous (*dashed line*) and pure crystalline (*solid line*) H_2O . The crystalline samples in (b) and (c) were made by briefly warming the amorphous solid to either 130 K (CH_3OH) or 155 K (H_2O) and then recooling. Spectra have been displaced vertically for clarity and scaled for a common sample thickness of $\sim 4 \mu\text{m}$.

sharp feature near 230 cm^{-1} ($43 \mu\text{m}$) in Figure 2a is probably due to crystalline H_2O (Fig. 2c).

In all experiments, the lines (marked in Fig. 1c) in the $\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1$ mixtures grew in the spectrum simultaneously as the sample was warmed to 140 K, indicating a common origin. When the sample was warmed further to 150 K they disappeared simultaneously and the spectrum was replaced by that of polycrystalline H_2O (Fig. 2c), indicating loss of CH_3OH .

Separate experiments investigated the influence of a third compound on the spectral changes in the figures. Three sets of gas-phase $\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1$ mixtures were made, with CO added in the first set, NH_3 in the second, and H_2CO in the third. Little changes in the spectra, from those in Figures 1 and 2, were seen when the added molecule's concentration was under $\sim 5\%$ (mole or molecule percent). However, above this value the lines indicated by asterisks (*) in Figure 1 were substantially weaker if not completely absent. There appeared to be an inverse relation between the concentration of the third component (CO, NH_3 , or H_2CO) and the strength of the lines marked in Figure 1c.

Another set of experiments involved proton irradiation of ice samples. When the original amorphous $\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1$ mixture was irradiated (incident fluence = $10^{14} p^+ \text{ cm}^{-2}$ absorbed dose $\approx 1 \text{ eV molecule}^{-1}$) at 13 K, none of the lines indicated in Figure 1c appeared on subsequent warming. Other samples were warmed from 13 K to produce the lines in Figure 1c and then re-cooled to either 13 or 77 K. Subsequent

irradiation removed each of the indicated lines and a second stage of warming failed to bring them back.

4. DISCUSSION

Our spectrum in Figure 2a shows six lines superposed on a much broader underlying feature resembling amorphous CH₃OH and H₂O bands. The abrupt, irreversible production of the sharper lines on warming the originally amorphous H₂O:CH₃OH = 2:1 mixture is reminiscent of the changes seen on forming a crystalline phase in other amorphous materials, such as CH₃OH (Fig. 2b), H₂O (Fig. 2c), and CO₂ (Falk & Seto 1986). This suggests that the lines in Figure 2a, and those marked in Figure 1c for a higher temperature, also belong to a crystalline phase.

A comparison of Figure 2a for the H₂O:CH₃OH mixture with the spectrum of crystalline CH₃OH in Figure 2b shows distinct differences. Attributing just some of the sharper lines from the mixture to crystalline CH₃OH would contradict the conclusion that all of the features are evidently due to one chemical species since they increase together on warming the original condensate from 13 to 130 K and decrease together on additional warming to 150 K. Furthermore, while it is conceivable that the 175 and 148 cm⁻¹ bands may arise from crystalline CH₃OH formed when the clathrate hydrate structure develops, this explanation would contradict the electron diffraction result that only one crystalline phase was present under the same conditions, namely a clathrate hydrate (Blake et al. 1991). Since we have used the same experimental procedure as Blake et al., we assign all the sharp lines marked in Figure 1c and shown in Figure 2a to the type II CH₃OH clathrate hydrate. The positions of the clathrate hydrate's absorbances, and of others shown in the figures, are summarized in Table 1.

Several lines of evidence support our assignment. First, adding a third molecule (CO, NH₃, or H₂CO) to the H₂O:CH₃OH mixture substantially weakened all the lines assigned to the clathrate hydrate. This can be attributed to the disruption of clathrate hydrate cages by the added (impurity) species. Second, when the original amorphous H₂O:CH₃OH = 2:1 mixture was irradiated before warming, none of the CH₃OH clathrate hydrate absorbances appeared at 130–140 K, presumably because of the presence of radiation products such as H₂CO and CO. Third, when the original amorphous mixture was warmed to 140 K to form the clathrate, then recooled to either 13 or 77 K and irradiated, all clathrate lines were lost, leaving a far-IR spectrum dominated by features of

amorphous CH₃OH and amorphous H₂O, similar to Figure 1a. This is consistent with the known radiation-induced amorphization of crystalline materials, such as crystalline H₂O ice (Hudson & Moore 1992; Moore & Hudson 1992). Rewarming the irradiated sample failed to give the CH₃OH clathrate hydrate spectrum, again probably because of the radiation products.

Since the spectrum of the CH₃OH clathrate hydrate in Figure 2a has not been subjected to a complete theoretical analysis, and since deuterium substitution experiments have not been done, little can be said about each line's origin. However, it is likely that the spectrum is due to both inter- and intramolecular vibrations. The features at 274 and 214 cm⁻¹ are probably due to intramolecular vibrations since similar lines are seen in the spectra of CH₃OH isolated in argon matrices (Barnes & Hallam 1970), but not in pure CH₃OH (Fig. 2b). Their presence in our spectra is additional evidence for enclathrated molecules. The feature at 326 cm⁻¹ is probably the counterpart of the 353 cm⁻¹ band in crystalline CH₃OH, which is due either to intermolecular O···O vibrations or O—H···O hydrogen-bond stretching (Wong & Whalley 1971; During et al. 1971). Assignments for the remaining features are less certain but probably they too are intermolecular in origin.

The overall appearance of our CH₃OH clathrate hydrate far-IR spectrum is quite different from clathrate hydrate spectra in which the guest molecule undergoes little or no hydrogen bonding with the H₂O cages, such spectra being strongly dominated by a broad absorption from the H₂O cages (Bertie & Solinas 1975). The presence of relatively sharp features from our annealed H₂O:CH₃OH = 2:1 mixture suggests that interaction of the trapped CH₃OH with the surrounding H₂O molecules occurs. This is supported by the electron diffraction data (Blake et al. 1991) and even earlier X-ray diffraction studies of ethanol (C₂H₅OH) clathrate hydrates (Boutron & Kaufman 1978). Although the diffraction data reveal formation of type II clathrate hydrates for CH₃OH and C₂H₅OH, it has been noted that some variations from the usual type II crystal structure probably exist (Blake et al. 1991; Boutron & Kaufman 1978; Potts & Davidson 1965). The nature and extent of these variations remain to be determined. Hydrogen bonding as well as hindered rotation of the methyl group or the entire molecule may be important.

Since there are almost certainly H₂O-dominated amorphous ice mixtures in space (Smoluchowski 1978, 1981, 1983; Leger et al. 1979; Hagen, Tielens, & Greenberg 1981), which conceiv-

TABLE 1
PEAK POSITIONS IN FAR-INFRARED SPECTRA

Material	Temperature (K)	Peak Positions (cm ⁻¹)
CH ₃ OH clathrate hydrate	14	326, 274, 214, 175, 154, 129
CH ₃ OH clathrate hydrate	140	317, 268, 209, 167, 125
Amorphous H ₂ O:CH ₃ OH 2:1	13	306 (broad shoulder), 206
Amorphous H ₂ O:CH ₃ OH 2:1	130	306 (broad shoulder), 216
Amorphous CH ₃ OH	14	318, 146
Crystalline CH ₃ OH	14	353, 175, 148, 113
Crystalline CH ₃ OH ^a	140	345, 163, 107
Amorphous H ₂ O	14	220
Amorphous H ₂ O ^a	130	217
Crystalline H ₂ O	14	230, 163
Crystalline H ₂ O ^a	140	223, 162

^a Included for comparison purposes. Amorphous CH₃OH and amorphous H₂O are unstable at 140 K and convert to crystalline phases.

ably could form clathrate hydrates on warming, it is worth summarizing CH₃OH clathrate formation, stability, and detection based on laboratory experience. Our results show that CH₃OH clathrate formation can be inhibited by the presence of "impurities," both those present initially and those formed by irradiation. In addition, ionizing radiation destroys the clathrate. Finally, there appears to be only a narrow range of temperature which produces the clathrate without forming polycrystalline H₂O ice.

These conditions aside, even if CH₃OH clathrate hydrate does form and exist in astronomical objects, it could be difficult to detect and identify. For example, on the surface of a cometary nucleus with a temperature below 150 K, certainly beyond the orbit of Mars, most of the observed energy in the 25–100 μ m (far-infrared) region should be from thermal emission. Locating such a nucleus, and acquiring good quality spectra, would be challenging. Dense interstellar molecular clouds also could be searched in the far-IR for the CH₃OH clathrate hydrate. However interpretation of interstellar emissions or absorptions can involve tedious modeling. Neverthe-

less, the laboratory spectrum observed for the type II CH₃OH clathrate hydrate is sufficiently unique that its presence in the spectrum of an astronomical object may help determine the object's thermal and radiation history.

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Note added in proof.—A comprehensive examination of water:methanol ices in interstellar clouds has recently been published in Allamandola et al. (1992) (Allamandola, L. J., Sandford, S. A., Tielens, A. G. G. M., & Herbst, T. M., *ApJ*, 399, 134 [1992]).