

## Far-infrared spectra of cosmic-type pure and mixed ices

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**Abstract.** — We have measured the far-infrared spectra of pure H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>CO, CH<sub>4</sub>, and CO ices and H<sub>2</sub>O-dominated binary mixtures of CH<sub>3</sub>OH, NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>CO, CH<sub>4</sub>, and CO from 500 cm<sup>-1</sup> (20 μm) to 100 cm<sup>-1</sup> (100 μm) at low temperatures. We also examined spectra of several more complex ices. These results represent a consistent set of data on astrophysically relevant molecules and mixtures over a wide range of temperatures. This set provides information in a spectral region that will be increasingly accessible with the advent of future orbiting observatories. Spectra of both the amorphous and crystalline phases of each of the pure molecular ices are unique. Spectra of icy mixtures, however, are in general dominated by H<sub>2</sub>O ice features over the entire range of temperatures studied. One exception to this is the H<sub>2</sub>O + CH<sub>3</sub>OH ice which evolves from an amorphous deposit to form a multi-line crystalline-like spectrum we have identified with the recently reported CH<sub>3</sub>OH clathrate hydrate. Implications of these results on the identification of extraterrestrial ices based on observations in the far-infrared are included.

**Key words:** infrared: interstellar: lines — interstellar medium: clouds — molecular data — dust

### 1. Introduction

H<sub>2</sub>O ice and H<sub>2</sub>O-dominated icy mixtures are believed to be important constituents of interstellar grains, of comets, and of many of the outer planetary satellites. Extraterrestrial H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>, CO<sub>2</sub>, CO, and CH<sub>4</sub> in the condensed phase have all been identified by comparing observations made in the near-infrared or mid-infrared (extending typically from 10,000 cm<sup>-1</sup> (1 μm) to 400 cm<sup>-1</sup> (25 μm)) with laboratory reference spectra. These spectral regions include specific information on the stretching and bending modes of molecules. Examples of detections of condensed phase molecules are: H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub>, and CO<sub>2</sub> in dense interstellar clouds (Tielens 1989 and references therein; Allamandola et al. 1993; Graham & Chen 1991; and d'Hendecourt & de Muizon 1989, respectively), CO<sub>2</sub> and CO tentatively identified on Triton (Cruikshank et al. 1991), and CO and CH<sub>4</sub> on Pluto (Owen 1992).

Of all the extraterrestrial environments for ices, cold interstellar regions represent a promising place to search for far infrared (far-IR) signatures with relatively minimal conflicting background emissions. However, observations are limited because telescopes must operate from aircraft above the Earth's lower atmosphere which is opaque be-

tween 250 cm<sup>-1</sup> (40 μm) and 33 cm<sup>-1</sup> (300 μm). An example of an early far-IR observation of a dense interstellar cloud region, is the detection of the 222 cm<sup>-1</sup> (45 μm) feature in Orion's Kleinman-Low nebula (Papoular et al. 1978; Erickson et al. 1981, and Drapatz et al. 1983) which was interpreted as due to H<sub>2</sub>O ice. Later, Forveille et al. (1987) observed a striking increase in the 167 cm<sup>-1</sup> (60 μm) band of IRAS 09371 and proposed that H<sub>2</sub>O ice emission was responsible; a large quantity of ice was confirmed by the mid-IR detection of H<sub>2</sub>O ice (Rouan et al. 1988; Hodapp et al. 1988 and Geballe et al. 1988). The recent more detailed observations of IRAS 09371 by Omont et al. (1990) showed an emission band in the 250 cm<sup>-1</sup> (40 μm) to 143 cm<sup>-1</sup> (70 μm) region which they fitted with the spectrum of crystalline H<sub>2</sub>O ice on crystalline silicate grains at 46 K. Omont et al. (1990) also published data for OH 127.8 and OH 231.8 in the far-IR.

H<sub>2</sub>O and other simple polyatomic molecules condense to form molecular crystals which have, compared to near-IR and mid-IR spectra, broad far-IR features due to lattice modes (intermolecular vibrations). These modes involve the relative motion of the molecules as a whole and can be either translational modes (displacements) or librational modes (torsional in origin). The far-IR intramolecular modes often give information on lattice structure or transitions between phases. Amorphous H<sub>2</sub>O ice, for

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example, formed by condensation at  $T < 100$  K, is not stable against thermal cycling. It converts irreversibly to a polycrystalline phase during warming to  $T > 120$  K. The far-IR spectra of  $\text{H}_2\text{O}$  show distinct differences between the amorphous and crystalline phases.

Our previous far-IR laboratory investigations focused on the phase changes in  $\text{H}_2\text{O}$  ice induced by proton irradiation and were motivated by the identification of crystalline  $\text{H}_2\text{O}$  at 46 K by Omont et al. (1990) in IRAS 09371. Our studies resulted in estimates of the rate of radiation amorphization of crystalline ice in simulated cosmic environments (see Moore & Hudson 1992 and references therein). In those experiments we also examined the thermally induced phase change of  $\text{H}_2\text{O}$  and the reversible changes in the peak position of the principal maximum at  $222\text{ cm}^{-1}$  ( $45\text{ }\mu\text{m}$ ) with temperature.

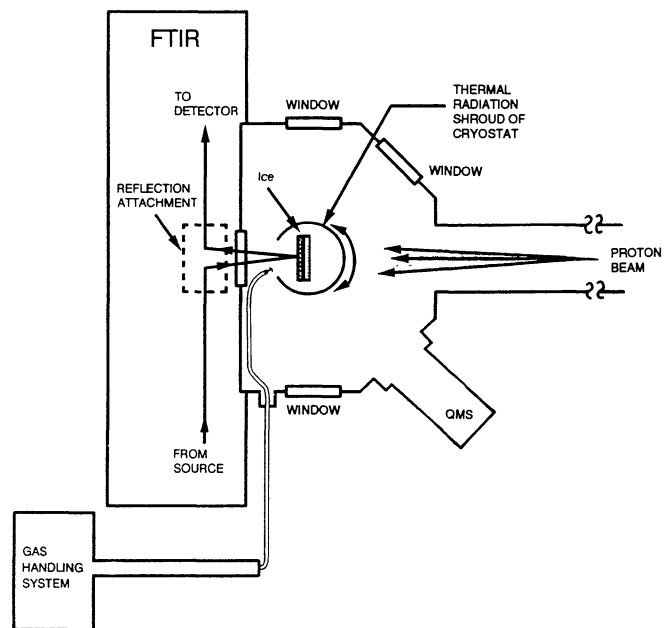
In the present work we have measured the far-IR spectra of pure amorphous and annealed crystalline  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{CO}$  ices. These pure ices have absorption peaks which, like  $\text{H}_2\text{O}$ , show reversible and irreversible changes with temperature. This data set also includes the far-IR spectra of  $\text{H}_2\text{O}$ -dominated binary mixtures of these same molecules, along with  $\text{CH}_4$  and  $\text{CO}$ , in the amorphous and annealed crystalline phases. The most unique far-IR spectrum resulted when an  $\text{H}_2\text{O} + \text{CH}_3\text{OH}$  (100:50) mixture was slowly warmed resulting in a characteristic set of absorption bands which we have identified (Hudson & Moore 1993) with the recently reported  $\text{CH}_3\text{OH}$  clathrate hydrate (Blake et al. 1991).

It is our intention that this set of data be a source of peak positions of some relevant molecular ices in different phases in the far-IR. This set is unique because it represents the use of a single experimental procedure to study a large number of pure and mixed ices of interest to astronomers over a variety of temperatures which are astrophysically relevant.

## 2. Experimental procedure

Figure 1 is a schematic representation of the experimental setup. Thin icy films were formed by slowly condensing either pure or premixed gases onto an aluminium substrate ( $5\text{ cm}^2$  area) cooled by a closed-cycle cryostat ( $T_{\text{min}} \sim 13$  K). Surrounding the substrate is a six-sided vacuum chamber designed to allow a variety of in-situ measurements. The ice film is shown facing the IR spectrometer, but it could also be rotated to face any direction. Far-infrared absorption spectra were recorded with a Mattson (Polaris) Fourier-transform infrared (FTIR) single-beam spectrometer equipped with a  $6\text{ }\mu\text{m}$  mylar beam splitter. Using a focus projection attachment, the IR beam was directed at right angles to the spectrometer bench, through a 1.6 mm thick high-density polyethylene window, where it passed through the ice film, reflected at the ice-aluminum interface, and again passed through

the ice film before traveling to the detector. We used this technique to measure the transmission-reflection-transmission spectra (TRT-spectra) from  $500\text{ cm}^{-1}$  to  $100\text{ cm}^{-1}$  ( $20\text{ }\mu\text{m}$  to  $100\text{ }\mu\text{m}$ ) as 60-scan accumulations ( $\sim 3$  min total accumulation time) with a resolution of  $4\text{ cm}^{-1}$ . It has been recognized that band intensities and widths may differ slightly between transmission spectra and TRT-spectra, although the line positions should be the same (e.g. Kitta & Kträttschmer 1983). In general our far-IR TRT data for  $\text{H}_2\text{O}$  and  $\text{NH}_3$  (the ices with the highest reflectivities) had a slightly larger area when normalized to a spectrum recorded in transmission. We attribute this to the fact that we detect the attenuated beam component along with some fraction of the reflected beam (see Hudson & Moore 1993). Spectra presented in this paper have not been corrected for reflection losses.



**Fig. 1.** Experimental set-up showing the FTIR, QMS (quadrupole mass spectrometer), incoming proton beam, and central location of the cryostat containing the ice films

Each single-beam spectrum was ratioed with the background spectrum of a blank substrate at 13 K. Absorptions due to any residual water vapor within the optical path had minimal effect on the ratioed spectra if the background and single beam spectra were recorded with the same dry nitrogen purge conditions. Apparent noise in some spectra is due to incomplete cancellation from varying purge conditions.

The water used to make the ice samples was triply distilled with a resistance greater than  $10^7$  ohm-cm and with dissolved gases removed by freeze-pump-thaw cycling. Methanol (American Burdick and Jackson, HPLC grade) was also degassed by freeze-pump-thaw cycling.

Ammonia (Matheson, anhydrous), carbon dioxide (Air Products, 99.5% pure), methane (Matheson, UHP grade) and carbon monoxide (Airco, 99.99% pure) gases were used without further purification. Solid paraformaldehyde (Fisher Scientific Co., purified) was warmed in a vacuum bottle to produce monomeric formaldehyde.

Thin films of amorphous ices were in general less than 10  $\mu\text{m}$  thick (determined by using appropriate optical constants) and were condensed at a rate of  $\sim 10 \mu\text{m hr}^{-1}$ . Amorphous  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{CO}$  were warmed from 13 K to 155 K, 130 K,  $\sim 110$  K, 65 K and 85 K respectively, and held there about 5 minutes to convert them to a crystalline phase. The ice samples could be rotated  $180^\circ$  from the direction of the FTIR to face the proton source which was permanently interfaced with our experimental set-up. Details of the proton source and techniques for monitoring the resulting dose (protons  $\text{cm}^{-2}$ ) have been discussed elsewhere (Moore & Hudson 1992).

### 3. Experimental results

Far-IR spectra of pure, binary, and several more complex ices have been measured from  $500 \text{ cm}^{-1}$  to  $100 \text{ cm}^{-1}$  ( $20 \mu\text{m}$  to  $100 \mu\text{m}$ ) at temperatures from 13 K to 165 K. Spectra of pure  $\text{H}_2\text{O}$  taken from earlier publications (Moore & Hudson 1992), are included for completeness. The absorbance scale in our figures has been expanded arbitrarily unless otherwise specified.

#### 3.1. Far-IR spectra of amorphous and crystalline pure ices

The far-IR spectra of  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_4$ , and  $\text{CO}$  have been measured from  $500 \text{ cm}^{-1}$  to  $100 \text{ cm}^{-1}$  over a temperature range from 13 K to as high as 155 K. Figures 2 and 3 compare the spectra of these ices in the amorphous and crystalline phases, respectively. Spectra have been offset for clarity. All curves have the absorbance scale shown for Fig. 2g. Some spectra are displayed at different magnifications (as indicated). Table 1 lists the corresponding peak positions.

##### 3.1.1. $\text{H}_2\text{O}$

The far-IR bands of amorphous and crystalline  $\text{H}_2\text{O}$  ice at 13 K are shown in Fig. 2a and Fig. 3a respectively. When the amorphous ice (peak position,  $220 \text{ cm}^{-1}$ ,  $45.5 \mu\text{m}$ ) was warmed, its spectrum changed irreversibly into the sharper crystalline form with absorptions at  $223 \text{ cm}^{-1}$  ( $44.8 \mu\text{m}$ ) and  $158 \text{ cm}^{-1}$  ( $63.3 \mu\text{m}$ ). Noticeable sublimation of  $\text{H}_2\text{O}$  ice occurs within 5 to 10 minutes at a temperature of 170 K. The ice's physical thickness is estimated to be  $\sim 2.5 \mu\text{m}$  based on absorption coefficients at 10 K for amorphous  $\text{H}_2\text{O}$  (Hudgins et al. 1993). Documentation of changes in the amorphous and crystalline

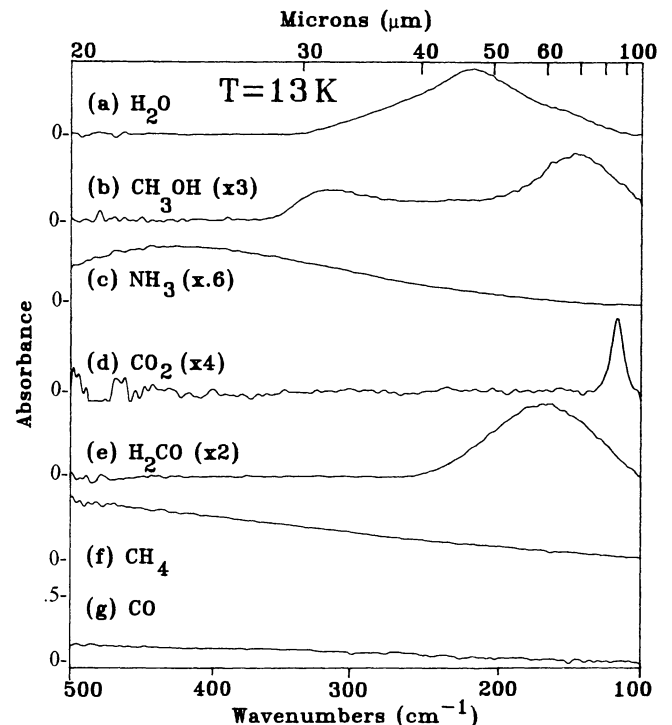


Fig. 2a-g. Far-IR spectra of pure amorphous ices deposited at  $T \sim 13$  K; peak positions are listed in Table 1

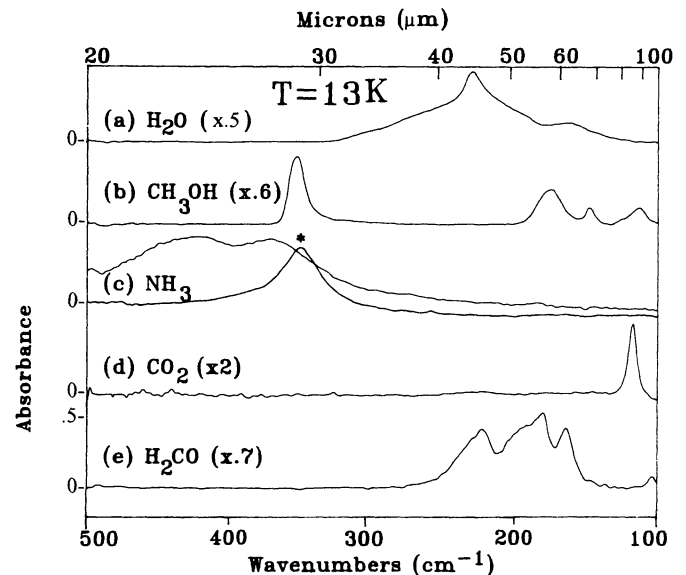


Fig. 3. Far-IR spectra of pure crystalline phase ices of (a)  $\text{H}_2\text{O}$ , (b)  $\text{CH}_3\text{OH}$ , (c)  $\text{NH}_3$  (double peaked), (d)  $\text{CO}_2$  and (e)  $\text{H}_2\text{CO}$  were formed by annealing at 155 K, 130 K,  $\sim 110$  K, 65 K and 85 K respectively; peak positions are listed in Table 1 (the single \*  $\text{NH}_3$  peak results after direct deposit at 77 K before recoiling to 13K)

far-IR spectra as a function of temperature has been discussed in an earlier publication (Moore & Hudson 1992)

and has also been examined by Breukers (1991). Some of these results are included in this paper for comparison with other molecular ices.

### 3.1.2. CH<sub>3</sub>OH

The far-IR bands of amorphous and crystalline CH<sub>3</sub>OH are shown in Fig. 2b and Fig. 3b respectively. The ice sample's physical thickness is estimated to be  $\sim 3.5 \mu\text{m}$  based on the absorption coefficient at 10 K for amorphous CH<sub>3</sub>OH (Hudgins et al. 1993). The change from amorphous (peak positions 321 and 148 cm<sup>-1</sup>) to crystalline (peak positions, 353, 175, 147, 113 cm<sup>-1</sup>) begins between 100 K and 120 K and is completed in 5 minutes by raising the temperature to 130 K. Noticeable sublimation of the sample occurs within 5 to 10 minutes at a temperature of 155 K.

### 3.1.3. NH<sub>3</sub>

The far-IR bands of NH<sub>3</sub> in the amorphous, and crystalline phases are shown in Fig. 2c and Fig. 3c respectively. The ice's physical thickness is estimated to be  $\sim 0.5 \mu\text{m}$  based on the absorption coefficient for cubic crystalline NH<sub>3</sub> at 88 K (Sill et al. 1980). When amorphous deposits (peak at 423 cm<sup>-1</sup>) were warmed slowly, a double-peaked (422 cm<sup>-1</sup> and 372 cm<sup>-1</sup>) spectrum was observed to form between 60 K and 70 K. We call this a transition phase. The double-peaked spectrum evolved with increased warming (several hours at 105 K, or by pulsing the ice temperature to 120 K) into an asymmetrically shaped single peaked spectrum (resulting peak position is 352 cm<sup>-1</sup> after recooling to 13 K). Some sublimation of the sample occurred at these higher annealing temperatures. A symmetrically shaped, single-peaked spectrum of NH<sub>3</sub> ice, attributed to cubic phase NH<sub>3</sub>, was formed by directly condensing NH<sub>3</sub> at 77 K in agreement with Sill et al. (1980).

### 3.1.4. CO<sub>2</sub>

The far-IR bands of amorphous and crystalline CO<sub>2</sub> are shown in Fig. 2d and Fig. 3d respectively. The ice's physical thickness is estimated to be  $\sim 2.5 \mu\text{m}$  based on the absorption coefficient at 100 K (Warren, 1986). When the amorphous ice (single peak at 117 cm<sup>-1</sup>) is slowly warmed it converts to a sharper crystalline peak between 60 K to 65 K. Changes in the line width and intensity are not obvious when comparing Fig. 2d and Fig. 3d because of the scaling factor used in Fig. 2d. Sublimation is observed when the ice is maintained at  $T > 100 \text{ K}$ .

### 3.1.5. H<sub>2</sub>CO

The far-IR bands of amorphous and crystalline H<sub>2</sub>CO are shown in Fig. 2e and Fig. 3e respectively. The ice thickness is estimated to be on the order of a few micrometers based on the amount of gas deposited. The thickness was not

calculated more precisely because absorption coefficients are not known. When the amorphous ice (single peak at 164 cm<sup>-1</sup>) was slowly warmed it converted to the crystalline phase above  $T = 70 \text{ K}$  (peak positions at  $T = 13 \text{ K}$  are: 223, 191 shoulder, 180, 164, and 103 cm<sup>-1</sup>). Rapid sublimation was observed beginning at 110 K.

### 3.1.6. CH<sub>4</sub> and CO

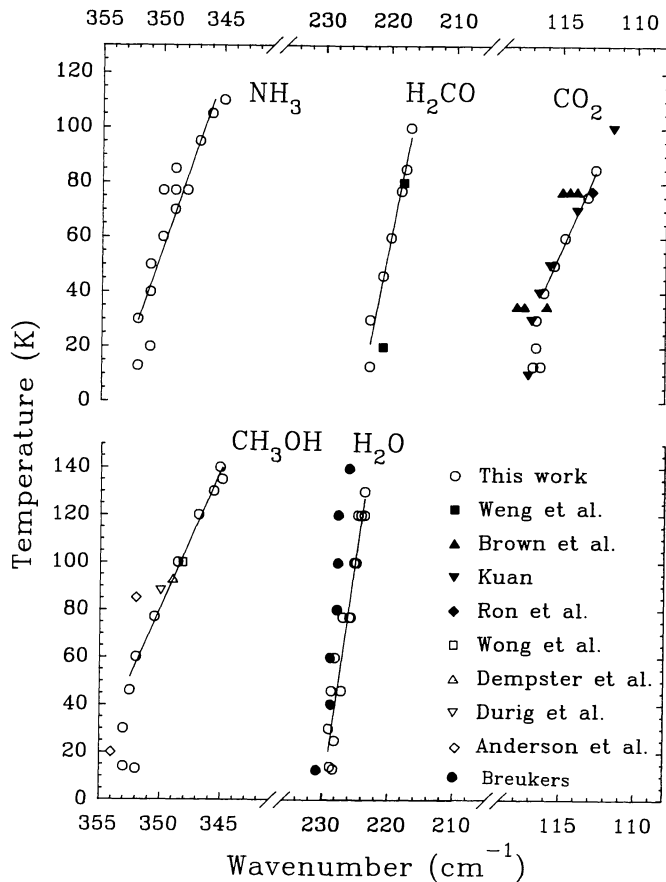
CH<sub>4</sub> and CO have absorptions at frequencies lower than our 100 cm<sup>-1</sup> cut-off (Savoie & Fournier 1970; Ron & Schnepf 1967, respectively). Deposits of each ice resulted in a relatively straight line showing greater absorbance at higher frequencies (Figs. 2f and 2g). Rapid sublimation of both CH<sub>4</sub> and CO was detected between 45 K and 55 K using a mass spectrometer.

## 3.2. Temperature dependence of peak frequencies of several crystalline ices

The peak frequency of the principal maximum of crystalline H<sub>2</sub>O changed reversibly with temperature (Breukers 1991; Moore & Hudson 1992). Figure 4 shows data for H<sub>2</sub>O compared with the following: the most intense absorption of solid CH<sub>3</sub>OH near 353 cm<sup>-1</sup>, NH<sub>3</sub> near 352 cm<sup>-1</sup>, H<sub>2</sub>CO near 223 cm<sup>-1</sup> (chosen because this band remains unobscured over the temperature range), and CO<sub>2</sub> near 117 cm<sup>-1</sup>. Included for completeness are data from other experimenters for similarly prepared ices. The solid lines are least squares fits of our measured data points; usually the lower temperature data points were not included in the fits because the peaks typically do not change much below 30 K to 40 K. The peak frequency of each ice shifts to lower frequencies as the temperature increases and can be directly related to the ice's temperature.

## 3.3. Far-IR spectra of amorphous and crystalline binary icy mixtures

The spectra of amorphous and crystalline H<sub>2</sub>O-dominated icy mixtures containing  $\sim 12\%$  of an added molecule are shown in Fig. 5. Spectral pairs are offset for clarity. Peak positions are tabulated in Table 2. Pure H<sub>2</sub>O is included in Fig. 5a for reference. The amorphous binary ice deposits reflect the broad symmetrical band shape of pure amorphous H<sub>2</sub>O, although, there is a trend for the maximum to occur at a slightly lower frequency in the mixtures. Mixtures were annealed to 155 K for 5 minutes to induce crystallization, and then re-cooled to 13 K. Spectra of the crystalline mixtures are dominated by a sharp peak near 223 cm<sup>-1</sup> (44.8  $\mu\text{m}$ ) like that of pure H<sub>2</sub>O. Many had a secondary peak similar in position to the one seen in pure H<sub>2</sub>O ice. Spectra compared after normalizing at the principal maximum, show that the ratio between the peak absorbances of the principal and secondary maximum was always smaller in the mixtures.



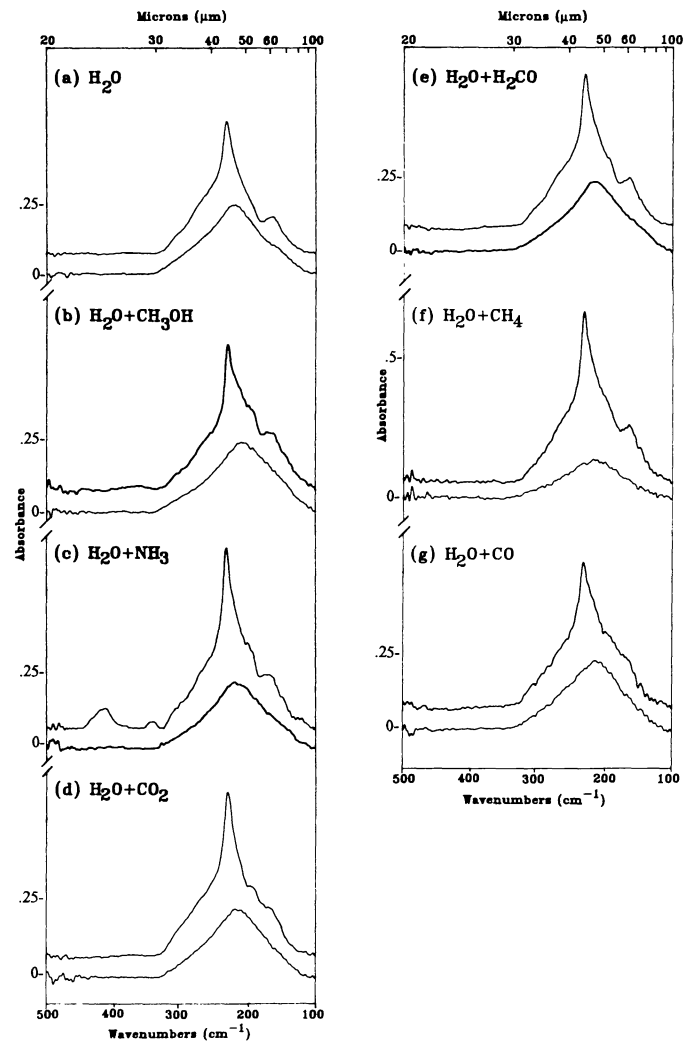
**Fig. 4.** Reversible changes in peak frequencies for crystalline ices as a function of temperatures:  $\text{NH}_3$  data for  $352\text{ cm}^{-1}$  peak,  $\text{H}_2\text{CO}$  data for  $223\text{ cm}^{-1}$  peak,  $\text{CO}_2$  data for  $117\text{ cm}^{-1}$  peak,  $\text{CH}_3\text{OH}$  data for  $353\text{ cm}^{-1}$  peak, and  $\text{H}_2\text{O}$  data for  $230\text{ cm}^{-1}$  peak

The FWHM (full width at half maximum) of the mixtures varied within 20% of that of pure  $\text{H}_2\text{O}$ .

### 3.4. Mixtures selected for concentration and temperature study

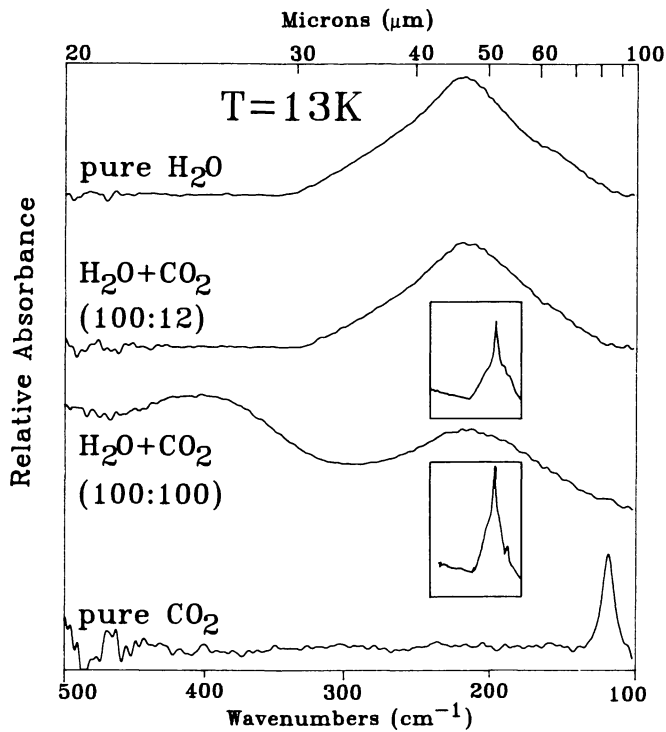
The far-IR spectra of an  $\text{H}_2\text{O} + \text{CO}_2$  mixture was examined at two different concentrations. When the concentration of  $\text{CO}_2$  is  $\sim 12\%$  (compared to  $\text{H}_2\text{O}$ ) the amorphous spectrum is indistinguishable from that of amorphous water. With an equal amount of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , the amorphous spectrum has a high frequency broad absorption near  $400\text{ cm}^{-1}$  along with the lower frequency feature. Figure 6 shows these spectra compared to the spectra of amorphous pure  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . The  $400\text{ cm}^{-1}$  absorption decreased with increasing temperatures and was gone at  $120\text{ K}$ . Both of these mixtures resulted in an annealed spectrum whose primary maximum is located near  $230\text{ cm}^{-1}$  (the boxed-in inserts in Fig. 6 show the annealed spectra).

Mixtures of  $\text{H}_2\text{O} + \text{CH}_3\text{OH}$  were also selected for a concentration and temperature study. The results are



**Fig. 5.** (a) Far-IR spectra of pure amorphous and crystalline phase  $\text{H}_2\text{O}$  ice is compared with the far-IR spectra (b-g) of amorphous and crystalline phase ices of  $\text{H}_2\text{O}$  combined with  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_4$  and  $\text{CO}$  ( $\sim 100:12$ )

summarized in Figs. 7 and 8. When the concentration of  $\text{CH}_3\text{OH}$  is  $\sim 12\%$  (compared to  $\text{H}_2\text{O}$ ) the amorphous spectrum shows one broad absorption feature resembling amorphous water with a high frequency tail. With an  $\sim 50\%$   $\text{CH}_3\text{OH}$  concentration, the broad absorption feature has a distinguishable  $\text{CH}_3\text{OH}$  shoulder in the  $300\text{ cm}^{-1}$  region. The evolution of this mixture with increased temperature is followed in Fig. 8. Figure 8a is the amorphous deposit at  $13\text{ K}$ . Warming this ice to  $130\text{ K} < T < 140\text{ K}$  at a rate of  $3\text{--}6\text{ K min}^{-1}$  resulted in the spectrum in Fig. 8b. Either holding the sample at this temperature for several hours or warming to  $145\text{ K} < T < 148\text{ K}$  for less than 15 min, resulted in the simultaneous growth of the five absorption features shown in Figs. 8c, 8d, and 8e. These absorptions sharpened as the temperature was reduced, and one feature split into two components at  $13\text{ K}$  (Fig. 8f). The identification of

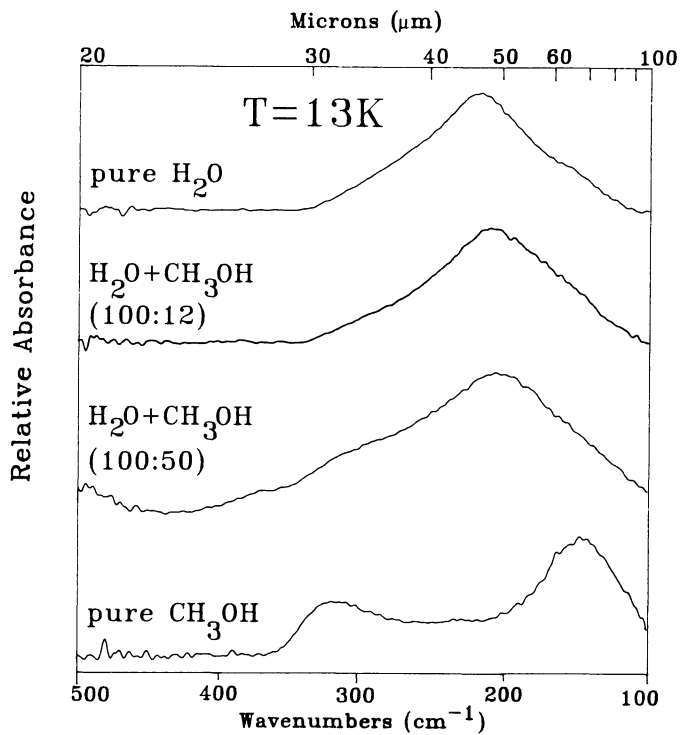


**Fig. 6.** Far-IR spectra of amorphous ices formed from two different concentrations of an  $\text{H}_2\text{O} + \text{CO}_2$  mixture are compared with spectra of pure amorphous  $\text{H}_2\text{O}$  and  $\text{CO}_2$  ices; spectra of both annealed mixtures are shown in the inserts

this far-infrared multi-line spectrum with the clathrate hydrate and a discussion of the x-ray diffraction studies which led to the original identification of the methanol clathrate hydrate using a similar formation method is given elsewhere (Hudson & Moore 1993 and Blake et al. 1991, respectively). The clathrate spectrum is quite different from that of either pure  $\text{CH}_3\text{OH}$  or pure  $\text{H}_2\text{O}$  as shown in the insert spectrum in Fig. 8. Table 3 includes the peak positions for the  $\text{CH}_3\text{OH}$  clathrate hydrate at 13 K and at 148 K.

### 3.5. Far-IR spectra of multi-component ices

We studied two ices made of a multi-component mixture (a more realistic simulation of proposed interstellar ices) with two different concentrations:  $\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{CO} + \text{NH}_3$  (100:50:2:2 and 100:50:9:2). We wanted to examine what effect the addition of other molecular species had on the far-IR spectrum. Figure 9 compares the spectra of these two multi-component ices (formed by slow warming) with the spectrum of  $\text{H}_2\text{O} + \text{CH}_3\text{OH}$  (100:50) warmed to  $T > 145$  K. Spectra have been offset for clarity. Figure 9a is the methanol clathrate at 148 K (distinctive methanol clathrate peaks are marked with an asterisk). These peaks are somewhat weaker in the spectra at 155 K when 2%  $\text{NH}_3$  and 2%  $\text{CO}$  relative to water were present in the mixture (Fig. 9b).

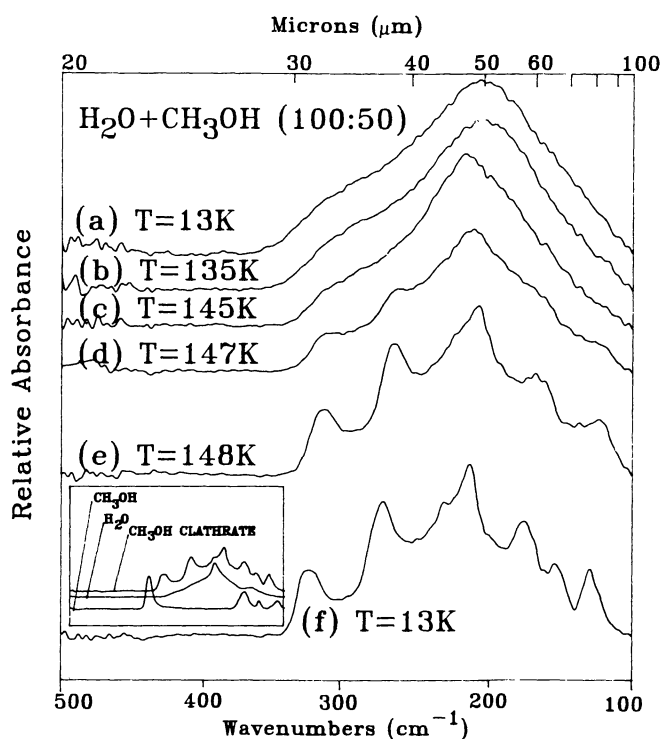


**Fig. 7.** Far-IR spectra of amorphous ices formed from two different concentrations of an  $\text{H}_2\text{O} + \text{CH}_3\text{OH}$  mixture are compared with spectra of pure amorphous  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  ices

The spectrum at 150 K shows that the characteristic multi-line features of the methanol clathrate are substantially weaker when 9%  $\text{CO}$  and 2%  $\text{NH}_3$  relative to water were included. Peak frequencies for spectra shown in Fig. 9 are included in Table 3. Spectra of other multi-component mixtures formed by including  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ , or  $\text{H}_2\text{CO}$  in an  $\text{H}_2\text{O} + \text{CH}_3\text{OH}$  (100:50) mixture (spectra not shown) supported our observation that the characteristic multi-line features of the methanol clathrate are weakened when impurities are added.

### 3.6. Far-IR spectra of proton irradiated methanol clathrate

Figure 10 shows a sequence of far-IR spectra of the  $\text{CH}_3\text{OH}$  clathrate hydrate before (Fig. 10a), and after proton irradiation. Spectra are offset for clarity. The multi-line spectrum of the  $\text{CH}_3\text{OH}$  clathrate hydrate shown in Fig. 10a becomes less intense with increasing doses of radiation (Figs. 10b and 10c). After a dose of  $10^{15}$  protons  $\text{cm}^{-2}$  (Fig. 10d), the spectrum is indistinguishable from the broad underlying absorption. The irradiated ice was warmed-up to see if the clathrate pattern would reappear, but only a single peaked spectrum similar to pure amorphous  $\text{H}_2\text{O}$  (Moore & Hudson, 1992, see Fig. 5) was formed. Continued warming of this ice converted it to a



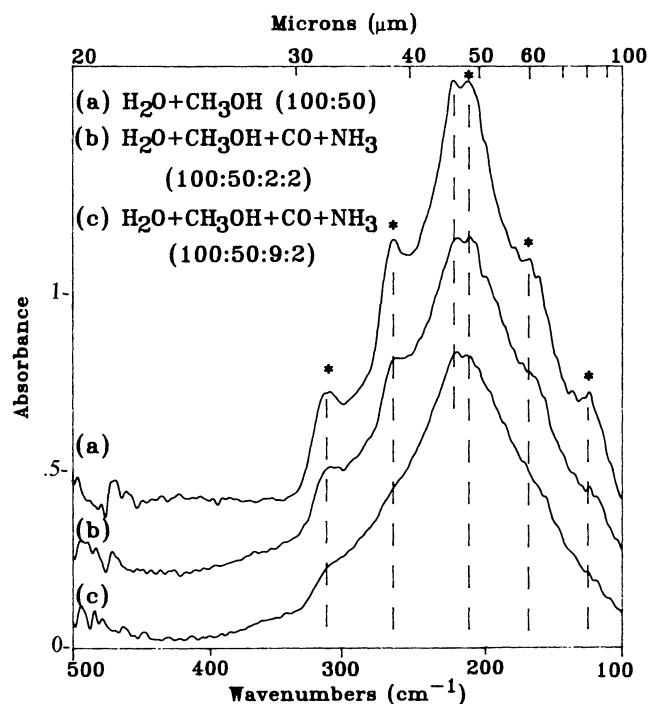
**Fig. 8a-f.** Evolution of the far-IR spectrum of an  $\text{H}_2\text{O} + \text{CH}_3\text{OH}$  mixture during warming shows the development of multi-line features associated with the  $\text{CH}_3\text{OH}$  clathrate hydrate; the insert spectra demonstrate there are many differences between the spectrum of the  $\text{CH}_3\text{OH}$  clathrate hydrate at 13 K and the spectrum of either pure crystalline  $\text{CH}_3\text{OH}$  or  $\text{H}_2\text{O}$  (peak positions listed in Table 3)

crystalline,  $\text{H}_2\text{O}$ -like spectrum which is shown in Fig. 10f (ice was recooled to 13 K).

## 4. Discussion

### 4.1. Pure ices

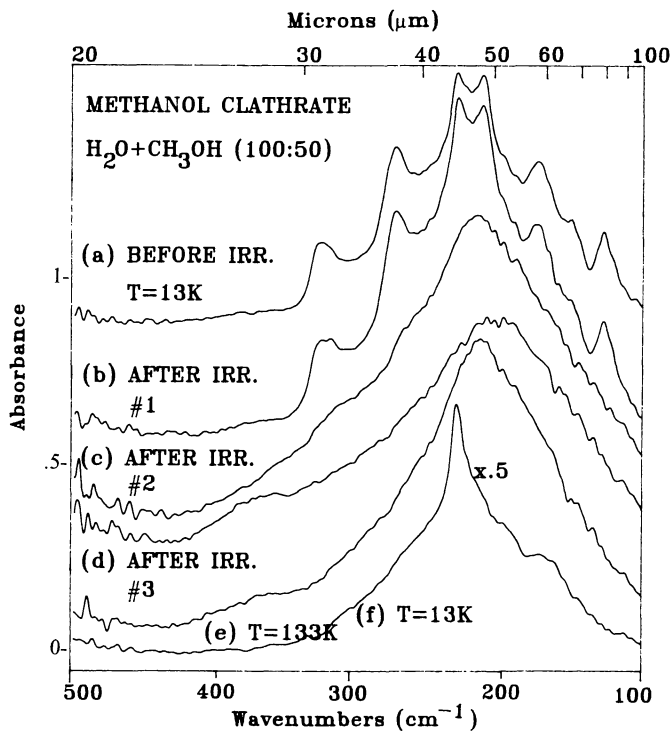
The far-IR spectra of pure  $\text{H}_2\text{O}$  and its conversion from the amorphous to the crystalline phase is discussed in detail in an earlier paper (Moore & Hudson 1992). A brief summary is included here since other spectra we discuss are compared with  $\text{H}_2\text{O}$  and the dominant species in our icy mixtures is  $\text{H}_2\text{O}$ . The low temperature ( $T = 13$  K) amorphous form of  $\text{H}_2\text{O}$  has a single broad symmetrical band centered at  $220\text{ cm}^{-1}$  ( $45.5\text{ }\mu\text{m}$ ) (Moore et al. 1992; Hudgins et al 1993). This peak sharpens and shifts to lower frequencies as the temperature is raised. The irreversible conversion of amorphous  $\text{H}_2\text{O}$  to the crystalline form is complete at 155 K in about 10 minutes. The absorptions at  $223\text{ cm}^{-1}$  ( $44.8\text{ }\mu\text{m}$ ) and at  $162\text{ cm}^{-1}$  ( $61.7\text{ }\mu\text{m}$ ) in the crystalline phase correspond to the transverse optical and longitudinal acoustic vibrational modes. The libration mode of  $\text{H}_2\text{O}$  lies beyond our  $500\text{ cm}^{-1}$  ( $20\text{ }\mu\text{m}$ ) high frequency cut-off. Optical constants in the far-IR for  $\text{H}_2\text{O}$



**Fig. 9.** (a) The multi-line far-IR features associated with the methanol clathrate at  $T > 145$  K (marked with an \*) are compared with the weaker “clathrate-like” features formed in more complex ices shown in b and c warmed to  $T = 155$  K and  $T = 150$  K respectively (peak positions listed in Table 3); peak near  $222\text{ cm}^{-1}$  ( $45\text{ }\mu\text{m}$ ) is attributed to crystalline  $\text{H}_2\text{O}$

ice are discussed by Bertie et al. (1969) and Hudgins et al. (1993).

Our spectra show that the amorphous form of  $\text{CH}_3\text{OH}$  has two broad bands centered at  $319\text{ cm}^{-1}$  ( $31.3\text{ }\mu\text{m}$ ) and  $148\text{ cm}^{-1}$  ( $67.6\text{ }\mu\text{m}$ ) at 13 K. These bands are in good agreement with the spectra and optical constants recently published by Hudgins et al. (1993). After warming amorphous  $\text{CH}_3\text{OH}$  to 130 K a stable spectrum with sharper and more numerous peaks was formed which we identify with the crystalline  $\alpha$ -phase of  $\text{CH}_3\text{OH}$  in agreement with Wong & Whalley (1971). At  $T = 13$  K, lattice vibrations were measured at  $353$ ,  $175$ ,  $147$  and  $113\text{ cm}^{-1}$  ( $28.3$ ,  $57.1$ ,  $68.0$ , and  $88.5\text{ }\mu\text{m}$  respectively). A higher temperature  $\beta$ -phase, stable between 160 K and 170 K was not examined. The  $353\text{ cm}^{-1}$  and  $147\text{ cm}^{-1}$  peaks are in close agreement with the positions published by Anderson et al. (1988) at 20 K; they associated these with the translational and librational modes respectively. We do not see the weaker features reported by Anderson et al. (1988) at  $328$ ,  $278$ ,  $231$ , and  $216\text{ cm}^{-1}$ , and our lowest frequency band is at  $113\text{ cm}^{-1}$  not at  $121\text{ cm}^{-1}$ . The position of our strongest bands at 100 K (spectra not shown in this paper) agree with published spectra recorded in the 80 K to 100 K range by Dempster & Zerbi (1971), Durig et al. (1971), Wong & Whalley, (1971) and Anderson et al. (1988).



**Fig. 10.** (a) The far-IR spectrum at 13 K of a methanol clathrate before irradiation, (b-d) increasing amounts of radiation (#1, #2, #3 doses represent  $10^{13}$ ,  $10^{14}$ ,  $10^{15}$  protons  $\text{cm}^{-2}$ , respectively) weaken the multi-line clathrate pattern, (e) rewarming the irradiated ice does not reform the clathrate structure, (f) far-IR spectrum at 13 K after annealing the irradiated ice to 155 K results in crystalline  $\text{H}_2\text{O}$ -like features (peak positions listed in Table 3)

The low temperature amorphous form of  $\text{NH}_3$  has one broad band centered at  $423 \text{ cm}^{-1}$  ( $23.6 \mu\text{m}$ ). During warming from 60 K to 70 K the spectrum changed to two overlapping peaks of similar intensity near  $422 \text{ cm}^{-1}$  and  $372 \text{ cm}^{-1}$  ( $23.7 \mu\text{m}$  and  $26.9 \mu\text{m}$ ). This double-peaked transition phase, probably associated with the metastable phase of  $\text{NH}_3$ , evolved with warming as the higher frequency component decreased. Annealing these metastable ices to 115 K to convert them to the cubic crystalline phase was, however, not entirely successful because of the rapid sublimation of  $\text{NH}_3$ . At 115 K the loss rate for the thin films was greater than the conversion rate to the cubic phase. Nevertheless, the dominant peak in our  $\text{NH}_3$  ices (annealed to 115 K and recooled to 70 K) is  $355 \text{ cm}^{-1}$  ( $28.2 \mu\text{m}$ ); these ices retained a short wavelength shoulder and are most likely part cubic and part metastable. Ices deposited at 77 K show a symmetrical peak. This absorption band is attributed to a librational mode (see e.g. Ferraro et al. 1980). The position of the most intense peak at  $355 \text{ cm}^{-1}$  is different from the published value of  $360 \text{ cm}^{-1}$  ( $27.8 \mu\text{m}$ ) for cubic  $\text{NH}_3$  deposited at  $83 \text{ K} < T < 100 \text{ K}$  and recorded on a variety of substrates (see Ferraro et

al. 1980; Sill et al. 1980; Binbrek & Anderson 1972; Redding & Hornig 1951; Anderson & Gebbie 1965; Anderson & Walmsley 1965). The difference in the position of the maxima between our experiments and others may be due to one or more of the following: (1) internal reflections which have not been corrected in our experiments which may cause a peak frequency dependence on thickness, (2) reflected radiation reaching the detector (a consequence of the configuration when measuring TRT-spectra) which could be significant since  $\text{NH}_3$  has a reflectivity near 65% at  $355 \text{ cm}^{-1}$  (Martonchik et al. 1984) (this reflectivity is larger than the reflectivity calculated for any other ice we studied in the far-IR). Our transition phase and cubic phase  $\text{NH}_3$  spectra also showed weaker absorptions which agree with published values at  $258 \text{ cm}^{-1}$  ( $38.8 \mu\text{m}$ ), attributed to another libration mode, and at  $183 \text{ cm}^{-1}$  and  $138 \text{ cm}^{-1}$  ( $54.6 \mu\text{m}$  and  $72.5 \mu\text{m}$ ) associated with translational modes. We also detected another weak absorption near  $273 \text{ cm}^{-1}$  ( $36.6 \mu\text{m}$ ). Absorption coefficients for solid crystalline  $\text{NH}_3$  in the far-IR have been published (Sill et al. 1980) and optical constants have been summarized by Martonchik et al. (1984).

$\text{CO}_2$  films condensed at 13 K produced an amorphous ice with a single absorption band at  $117 \text{ cm}^{-1}$  ( $85.5 \mu\text{m}$ ). The ice transformed irreversibly to a crystalline phase between 60 K and 65 K. Our data are in good agreement with the results of Kuan (1969) who discussed changes in the far-IR spectrum of solid  $\text{CO}_2$  at temperatures below 77 K. The  $117 \text{ cm}^{-1}$  band is associated with a translational lattice mode (e.g. see Brown & King 1970). Other data on  $\text{CO}_2$  in the 77 K region have been reported by Anderson & Gebbie (1965) and Ron & Schnepf (1967). The optical constants of  $\text{CO}_2$  ice in the far-IR, with an emphasis on values for temperatures above 77 K, are summarized by Warren (1986).

Amorphous  $\text{H}_2\text{CO}$  ice condensed at 13 K has a single broad absorption at  $164 \text{ cm}^{-1}$  ( $61 \mu\text{m}$ ). Amorphous deposits evolved into a multi-peaked spectrum of crystalline  $\text{H}_2\text{CO}$  when the temperature was increased to the 75 K region with peaks at 219, 179, and  $163 \text{ cm}^{-1}$  ( $45.7$ ,  $55.9$ , and  $61.3 \mu\text{m}$ ). When recooled to  $T = 13 \text{ K}$ , the peaks were generally sharper and blue shifts of up to  $5 \text{ cm}^{-1}$  were observed resulting in the 13 K detection of the  $103 \text{ cm}^{-1}$  band attributed to a translational lattice mode (Weng et al. 1989). Our results for crystalline  $\text{H}_2\text{CO}$  at both 77 K and at 13 K are in good agreement with recently reported peak positions in the far-IR by Weng et al. (1989).

#### 4.2. Ice mixtures

Our results show that the far-IR spectra of pure  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{CO}$  in the amorphous and crystalline phases are unique, but the distinctive spectral characteristics of these molecules are suppressed in mixed ices in 12:100 ratios with  $\text{H}_2\text{O}$ . Although spectra of mixtures might be expected to reflect the sum of their weighted



components, in fact we have shown there is little variation from the amorphous spectrum of pure H<sub>2</sub>O even when a second component made up 50% of the mixture.

When the ice mixtures are annealed to form a crystalline phase, the resulting spectra are nearly identical to the spectrum of pure crystalline H<sub>2</sub>O which has a dominant band at 223 cm<sup>-1</sup> (44.8 μm). Annealing these mixtures to 155 K would be expected to result in the loss of some fraction of the more volatile species, however, we know from laboratory experiments performed by one of us (Hudson & Donn 1991) that varying amounts of trapped gases can still be retained by H<sub>2</sub>O ice. The FWHM of the mixtures are within 20% of the FWHM of pure H<sub>2</sub>O ice. Another parameter we measured was the absorbance ratio of the principal maximum to the well resolved secondary maximum (162 cm<sup>-1</sup>, 61.7 μm) in crystalline pure H<sub>2</sub>O ice. The same ratio in the mixtures is always smaller. The H<sub>2</sub>O + CO<sub>2</sub> and H<sub>2</sub>O + CO ices did not develop the secondary maximum, only a weak shoulder in the 162 cm<sup>-1</sup> area. Since spectra have not been corrected for reflection losses, absolute values for the FWHM and the ratio values for each ice mixture are not meaningful.

The most unique far-IR result came from the study of H<sub>2</sub>O + CH<sub>3</sub>OH (100:50) mixtures. Amorphous deposits of this ice evolved during slow warming into a multi-peaked spectrum we have associated with the methanol clathrate hydrate (Hudson & Moore 1993), based on an earlier identification by Blake et al. (1991). Our spectra of multi-component ices show that the clathrate hydrate peaks are weakened in the presence of additional molecular species which probably interfere with the formation of the clathrate structure during warming.

Results from our proton irradiation experiments demonstrates that the far-IR multi-line spectrum associated with the CH<sub>3</sub>OH clathrate hydrate structure becomes less intense as the radiation dose is increased. These results are reminiscent of the amorphization of crystalline water ice due to ion irradiation (Moore & Hudson 1992; Baratta et al. 1991 and Strazzulla et al. 1992). Our results also show that the clathrate structure does not reform when the irradiated ice is warmed possibly due to the fact that the ice is "contaminated" with radiation products which interfere with the reformation of the clathrate structure. This interpretation was supported by additional experiments in which a freshly-condensed amorphous ice (composed of H<sub>2</sub>O + CH<sub>3</sub>OH, 100:50) was irradiated after which it failed to form the clathrate structure during warming.

## 5. Conclusion

We present a large number of far-IR spectra of ices made and studied with a single experimental procedure which used a self-consistent set of deposition, warming rates, and annealing temperatures. Our results include spectra

of astrophysically relevant pure and mixed ices in both the amorphous and crystalline phases. It is believed that this set of data will help connect the current fragmentary state of the literature of far-IR laboratory measurements.

Our results show that in the far-IR region we studied, the spectral features of each pure ice is unique in both the amorphous and crystalline phases. The far-IR data includes peak positions of pure ices which can be matched with far-IR observations to search for likely candidates. The plot of the reversible changes in the peak frequency with temperature for several crystalline ice absorptions shows that these peak positions are directly related to the temperature of the ice.

In H<sub>2</sub>O-dominated icy mixtures with 12% of an added molecule, the amorphous and crystalline spectra are nearly identical with the spectrum of pure H<sub>2</sub>O ice. We conclude that the observation of a single broad absorption centered near 222 cm<sup>-1</sup> in an extra-terrestrial source cannot be uniquely fitted with the spectrum of either pure H<sub>2</sub>O or of an H<sub>2</sub>O-dominated mixture, since the difference between the peak positions of these ices is only a few cm<sup>-1</sup>. Also amorphous-like H<sub>2</sub>O ice spectra could result from low temperature deposits or from radiation amorphization of crystalline ices, therefore conclusions on the thermal history of ices are not possible. The dramatic sharpening observed in the principal maximum during crystallization in both pure H<sub>2</sub>O and H<sub>2</sub>O-dominated ices can be used to identify the crystalline phase. Again, however, discriminating between pure H<sub>2</sub>O and H<sub>2</sub>O-dominated mixtures is quite difficult. The idea that two peaks are required for crystalline H<sub>2</sub>O-dominated ice mixtures was the rule for most of our simple binary ices, but both H<sub>2</sub>O + CO<sub>2</sub> and H<sub>2</sub>O + CO ice mixtures were the exception to the rule. The weakness or total absence of the secondary maximum may be one of the few discernible clues to icy mixture identifications in the far-IR especially those containing CO<sub>2</sub> and /or CO. Further laboratory studies are required to determine what role the concentration of impurities plays in the strength of the secondary maximum after crystallization.

Unique to this study are spectra which show the results on the effects of impurities and proton irradiation on the intensity of the unusual multi-line spectrum of an H<sub>2</sub>O + CH<sub>3</sub>OH (100:50) ice we associated with the methanol clathrate hydrate. We observed decreases in the intensity of this multi-line spectrum due to the presence of impurities within the condensed ice mixture and decreases in the intensity of the multi-line spectrum with increased irradiation (with laboratory doses of 10<sup>13</sup> to 10<sup>15</sup> protons cm<sup>-2</sup>)\*. These results suggest that the detection of this multi-line spectrum in an interstellar region

\* These laboratory doses are equivalent to ~ 10<sup>4</sup> to 10<sup>6</sup> years of cosmic-ray exposure for interstellar materials. This is calculated from an estimate (e.g. Strazzulla et al. 1983) that near 1 MeV cosmic-ray protons have a flux of 10 cm<sup>-2</sup> s<sup>-1</sup>

would mean the icy mixtures have experienced little radiation amorphization and that there is a relatively low concentration of impurities (<10%) compared to H<sub>2</sub>O and CH<sub>3</sub>OH. A search for the multi-line features in the far-IR is encouraged. Protostars NGC 7538 IRS 9, and W33A (Allamandola et al. 1992) may be good candidates since they contain a significant amount of CH<sub>3</sub>OH. Allamandola et al. (1992) point out that after H<sub>2</sub>O, CH<sub>3</sub>OH is the most abundant condensate in these observed sources even though the actual ratio of H<sub>2</sub>O to CH<sub>3</sub>OH varies between protostars and depends on which mid-IR bands are ratioed.

The use of the ESA/ISO space based telescope is on the horizon; it should be launched in 1995. It will observe within the 500 cm<sup>-1</sup> (20 μm) to 100 cm<sup>-1</sup> (100 μm) region. The huge reduction in background flux expected for ISO in orbit and the anticipated improved sensitivity due to stable pointing and lack of atmospheric blur should result in extremely high quality far-IR observations. It remains our best opportunity for an examination of far-IR sources in search of interstellar ices.

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**Table 1.** The positions of absorption peaks observed in the  $500\text{ cm}^{-1}$  ( $20\ \mu\text{m}$ ) to  $100\text{ cm}^{-1}$  ( $100\ \mu\text{m}$ ) region for several molecular ices in both the amorphous (Fig. 2) and crystalline (Fig. 3) phases

MOLECULAR ICE	TEMPERATURE (K)	PHASE	PEAK WAVENUMBER ( $\text{cm}^{-1}$ )
H <sub>2</sub> O	13	AMORPHOUS	220
	13/155/13	CRYSTALLINE	230, 162
CH <sub>3</sub> OH	13	AMORPHOUS	321, 148
	14/130/14	CRYSTALLINE	353, 175, 147, 113
NH <sub>3</sub>	14	AMORPHOUS	423
	14/70/14	TRANSITION	422, 372
	77/13	CRYSTALLINE	352
CO <sub>2</sub>	13	AMORPHOUS	117
	13/65/13/	CRYSTALLINE	117
H <sub>2</sub> CO	13	AMORPHOUS	164
	13/85/13	CRYSTALLINE	223, 191 sh, 180, 164, 103

**Table 2.** The positions of absorption peaks observed in the  $500\text{ cm}^{-1}$  ( $20\ \mu\text{m}$ ) to  $100\text{ cm}^{-1}$  ( $100\ \mu\text{m}$ ) region for H<sub>2</sub>O-dominated molecular ice mixtures in both the amorphous and crystalline (Fig. 5) phases; peak frequencies for pure H<sub>2</sub>O are included for comparison

MOLECULAR ICE	PHASE	PEAK WAVENUMBER ( $\text{cm}^{-1}$ ), T=13 K
H <sub>2</sub> O (PURE)	AMORPHOUS	220
	CRYSTALLINE	230, 162
H <sub>2</sub> O + CH <sub>3</sub> OH (100:12)	AMORPHOUS	211
	CRYSTALLINE	230, 170
H <sub>2</sub> O + NH <sub>3</sub> (100:12)	AMORPHOUS	218
	CRYSTALLINE	412, 343, 230, 170
H <sub>2</sub> O + CO <sub>2</sub> (100:12)	AMORPHOUS	219
	CRYSTALLINE	231, 194 sh, 168 sh
H <sub>2</sub> O + H <sub>2</sub> CO (100:12)	AMORPHOUS	216
	CRYSTALLINE	230, 195 sh, 164
H <sub>2</sub> O + CH <sub>4</sub> (100:12)	AMORPHOUS	218
	CRYSTALLINE	231, 164
H <sub>2</sub> O + CO (100:12)	AMORPHOUS	215
	CRYSTALLINE	232

**Table 3.** The positions of absorption peaks observed in the  $500\text{ cm}^{-1}$  ( $20\ \mu\text{m}$ ) to  $100\text{ cm}^{-1}$  ( $100\ \mu\text{m}$ ) region for the  $\text{CH}_3\text{OH}$  clathrate hydrate ice at different temperatures, in the presence of additional molecules, and after irradiation; these peak frequencies correspond to spectra in Figs. 8, 9 and 10

MOLECULAR ICE	TEMP. (K)	FIG. #	PEAK WAVENUMBER ( $\text{cm}^{-1}$ )
$\text{CH}_3\text{OH}$ clathrate hydrate	13	8f, 10a	327, 275, 232*, 214 176, 153, 129
$\text{CH}_3\text{OH}$ clathrate hydrate	148	9a	312, 267, 223*, 213, 168, 124
$\text{H}_2\text{O}+\text{CH}_3\text{OH}+\text{CO}+\text{NH}_3$ (100:50:2:2)	155	9b	313, 264, 220*, 211, 172, 124
$\text{H}_2\text{O}+\text{CH}_3\text{OH}+\text{CO}+\text{NH}_3$ (100:50:~9:2)	150	9c	313, 267sh, 220*, 213
$\text{CH}_3\text{OH}$ clathrate hydrate after $1\times 10^{13}\text{ p}^+\text{ cm}^{-2}$	13	10b	324, 275, 231*, 214, 177, 153, 130
$\text{CH}_3\text{OH}$ clathrate hydrate after $1\times 10^{14}\text{ p}^+\text{ cm}^{-2}$	13	10c	317sh, 265sh, 219
$\text{CH}_3\text{OH}$ clathrate hydrate after $1\times 10^{15}\text{ p}^+\text{ cm}^{-2}$	13	10d	206
IRRADIATED $\text{CH}_3\text{OH}$ clathrate hydrate, REWARMED	133	10e	216
IRRADIATED $\text{CH}_3\text{OH}$ clathrate hydrate, ANNEALED	13	10f	232, 176

\* peak position corresponds to crystalline  $\text{H}_2\text{O}$  ice