

Research Note

The 3.1 μm Absorption in Molecular Clouds Is Probably Due to Amorphous H_2O Ice

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Summary. The attribution to H_2O ice of the 3.1 μm absorption line in the spectra of molecular clouds has been controversial because of a poor fit between the observations and the laboratory spectrum of crystalline ice. We present here reasons for expecting that solid H_2O in space consists in fact of amorphous rather than crystalline ice. A preliminary laboratory determination of the infrared spectrum of amorphous ice is presented. Comparison with three molecular cloud spectra indicates that the 3.1 μm line can be explained by the absorption of amorphous H_2O ice. If this identification is correct, the abundance of water ice estimated from the maximum of the absorption line should be increased by a factor 1.5. The 12.5 μm line observed in amorphous ice cannot explain the observed 9.7 μm absorption feature in molecular clouds but it may affect its observed shape.

Key words: interstellar dust – amorphous ice – molecular cloud – grains

I. Introduction

The composition of interstellar dust and the size of particles are, more than ever, controversial subjects. Gillet and Forrest (1973) and Merrill et al. (1976), observed several infrared sources with molecular clouds in the intervening line of sight. In most cases the spectra show a narrow absorption feature centered at 3250 cm^{-1} (3.08 μm), which is tentatively attributed to ice by comparison with spectra obtained in the laboratory. However, the authors were disturbed by the lack of a precise fit between the spectra (Fig. 2). They suggest that there may be a mixture of H_2O and NH_3 ices.

Greenberg (1972) examined the influence of the particle shape on the line shape of the ice band: the short wavelength side of the line was not affected, therefore a satisfactory fit with the observations was not possible.

In 1978, Mukai et al. re-examined the situation. They calculated the expected spectrum for ice particles with several improvements:

- (i) taking into account different sizes and shapes for grains;
- (ii) considering a distribution of them;
- (iii) including variable graphite core-ice mantle grains.

They were unable to fit their predictions with the astronomical observations, using the range of variables available. They wondered whether ice is really responsible for the 3.1 μm absorption in

molecular clouds. A similarity to lines in carbon stars spectra suggests to them that the actual carriers might be organic molecules such as HCN or C_2H_2 , but this introduces new difficulties.

All these comparisons are made with the infrared spectrum of *crystalline* water ice. The purpose of this paper is to re-examine this point.

Water ice has numerous phases. However, at low pressures, the situation is simple (see Hobbs). When water vapor is condensed on substrates below 135 K, amorphous ice (I_a) is formed, between 135 and 190 K cubic ice results, and between 190 and 273 K, the product is the familiar hexagonal ice. The infrared spectrum of these last two species is the same, reflecting their very similar structure (same first neighbours, same number of second neighbours). Hereafter, we shall refer to them as crystalline ice (I_c).

II. Interstellar Ice Is Probably Amorphous

If it is assumed that the 3 μm absorption takes place in cold molecular clouds ($T < 30\text{ K}$), the above description suggests that *the interstellar ice is expected to be amorphous*. What is more, the H_2O molecules are probably deposited (or formed) on the grains with other molecules containing C, N, and O. This is an additional reason for the ice to be amorphous. The amorphous state however is metastable with respect to crystalline ice (McMillan et al., 1965; Sugisaki et al., 1968). The possibility of recrystallization must be considered even if the temperature is low, since the time scale is very different for laboratory and for cosmic grains.

The time τ for crystallization is:

$$1/\tau = \nu_0 \exp(-\Delta G/kT), \quad (1)$$

where G is an activation energy and ν_0 a frequency that depends on the microscopic process (Chik, 1978). If crystallization is local, displacing molecules one after the other, ν_0 would be the thermally excited vibration frequency of the solid:

$$h\nu_0 \simeq kT \quad (\text{for temperatures lower than the Debye temperature}). \quad (2)$$

But crystallization is in fact more a collective process where a germ has to be formed. The relevant vibrations are those whose wavelength is of the order of the germ size:

$$h\nu_0 \simeq h\nu_a \frac{a_0}{d}, \quad (3)$$

where ν_a is the Debye frequency, a_0 the distance between molecules and d the germ size. The germ cannot be larger than the

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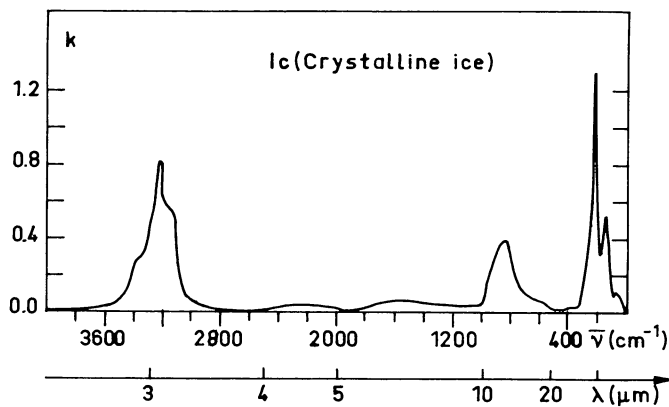


Fig. 1. Imaginary part of the refractive index of crystalline ice

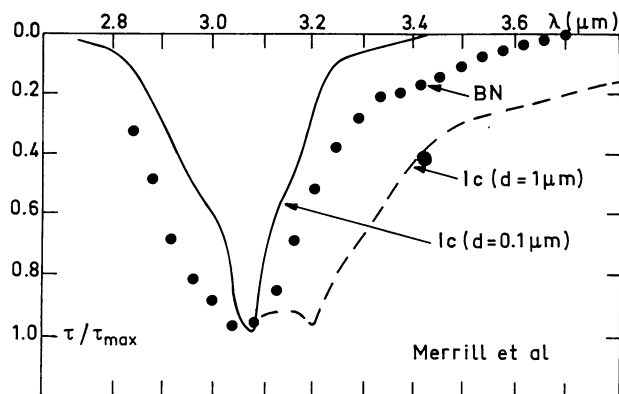


Fig. 2. Tentative attribution of the 3 μm absorption line of BN to the extinction spectra of crystalline ice spheres of variable diameter (d). Adjusting d cannot give a satisfying fit on the short wavelength side of the line

grain, hence $d \leq 2000 \text{ \AA}$. With typical values ($h\nu_a = 200 \text{ cm}^{-1}$, $T < 30 \text{ K}$, $a_0 = 3 \text{ \AA}$), (2) and (3) give limits for v_0 :

$$10^{10} \text{ s}^{-1} < v_0 < 5 \cdot 10^{11} \text{ s}^{-1}. \quad (4)$$

Recrystallization of ice occurs in the laboratory at $T_1 = 135 \text{ K}$ within a few seconds ($\tau_1 \sim 1 \text{ s}$) (McMillan). The time τ_2 at temperature $T_2 < 30 \text{ K}$ can be calculated using relations (1) and (4):

$$\tau_2 > 3 \cdot 10^{27} \text{ yr (if } T_2 < 30 \text{ K)}, \quad (5)$$

thermal fluctuations should not therefore cause appreciable crystallization of amorphous ice in cold space conditions.

The presence of other molecules in the condensate is an additional factor that hinders recrystallization. The effect of ultraviolet radiation should also be considered (see Greenberg, 1968).

Very recently, Papoular et al. (1979) have observed Orion in the infrared range of the translational phonon of ice: $50 \mu\text{m}$ (200 cm^{-1}). They found a feature which they attributed to amorphous ice.

For those reasons, we attempt to attribute the observed lines to amorphous rather than crystalline ice. The $3 \mu\text{m}$ (3300 cm^{-1}) absorption line in molecular clouds should be re-examined and compared with that of I_a . The $12 \mu\text{m}$ (800 cm^{-1}) region should

also be carefully looked at because a substantial increase of the absorption coefficient for I_a with respect to I_c might explain a strong absorption in observed spectra and would affect the usual interpretation of the $8\text{--}13 \mu\text{m}$ band in molecular clouds in term of silicates.

III. Experiments

To obtain the IR absorption of amorphous ice we have used a grating spectrophotometer with transmitting and reflecting filters. The source is a high pressure mercury vapor lamp and the detector is a Golay cell. The spectrophotometer operates under vacuum and its wavelength range runs from 50 cm^{-1} ($200 \mu\text{m}$) to $20,000 \text{ cm}^{-1}$ ($0.5 \mu\text{m}$). Bidistilled water vapor is condensed on a high purity silicon substrate ($300 \Omega \text{ cm}^{-1}$) cooled to 77 K .

Olander and Rice (1972) determined that the rate of deposition of ice should be very low (a few $10 \mu\text{m h}^{-1}$) to obtain pure amorphous ice, otherwise the sample is likely to be contaminated with crystalline ice. In our experiment, the ice films are $0.5\text{--}5 \mu\text{m}$ thick and grown at a maximum speed of $20 \mu\text{m h}^{-1}$. We checked that doubling this speed has no effect on the IR spectra obtained.

Narten et al. (1976) performed X-ray diffraction on amorphous ice deposited at different temperatures (10 and 77 K). They concluded that there are at least two forms of amorphous solid water: a low density form condensed at 77 K (0.94 g cm^{-3}) and a high density one condensed at 10 K (1.1 g cm^{-3}). Sivakumar et al. (1977) however have performed Raman spectra on samples (slowly) deposited at both temperatures. They found only one type of spectrum, attributed to the low density form. Further investigation on the experimental conditions that determine the species formed would be useful in identifying the composition of interstellar grains. In this study (77 K), we presumably work on the usual low density form of I_a (0.94 g cm^{-3} and $0\text{--}0$ distance of 2.76 \AA).

IV. Results and Comparison with Observations

1. The $3.1 \mu\text{m}$ Line

Figure 2 shows the extinction spectra of BN observed by Merrill et al. (1976) and the spectra they expect for I_c spheres with diameter respectively 0.1 and $1 \mu\text{m}$. There is a negligible scattering with $0.1 \mu\text{m}$ particles ($a \ll \lambda$) and the corresponding curve is just the I_c absorption. For $1 \mu\text{m}$ particles, there is an important contribution of scattering only for the long wavelength side of the line (because the refractive index goes from ~ 1 below the transition to ~ 1.6 above the transition). Adjusting the grain size would probably give a fit to that side of the observed feature. However, disagreement seems unavoidable for the *short wavelength side of the lines*, a certainly disturbing point to interpret the observed line as due to crystalline ice.

a) Laboratory Spectra

Figure 3 reports our experimental absorption $\alpha(\nu)$ for crystalline (I_c) and amorphous (I_a) ice in the range of the OH stretching vibration ($3800\text{--}3000 \text{ cm}^{-1}$; $2.6\text{--}3.3 \mu\text{m}$). The two curves correspond to the same amount of H_2O since the same samples are transformed from the amorphous state (as deposited at 77 K) to the crystalline state by slowly warming to 150 K and cooling again (there is not yet appreciable sublimation at that temperature). Buontempo (1972) and Bergren et al. (1978) reported similar, although not identical, spectra.

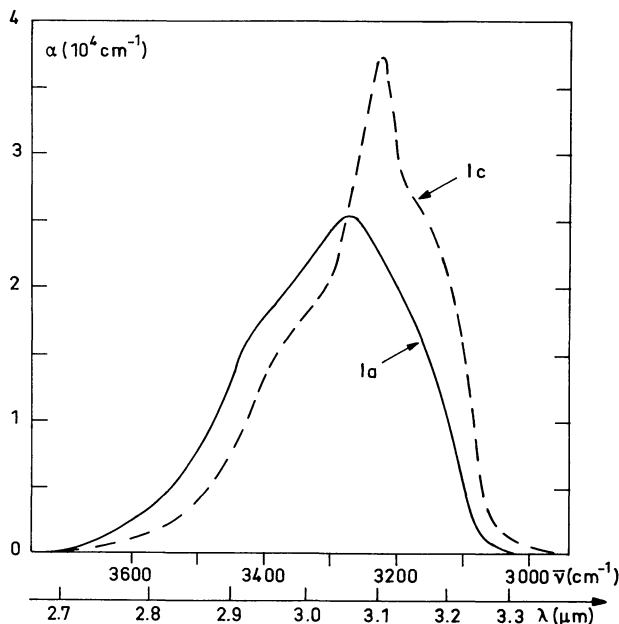


Fig. 3. Laboratory absorption of crystalline (I_c) and amorphous (I_a) ice at 77 K. The two curves correspond to the same amount of material (and same volume as both densities are assumed to be 0.94 g cm^{-3})

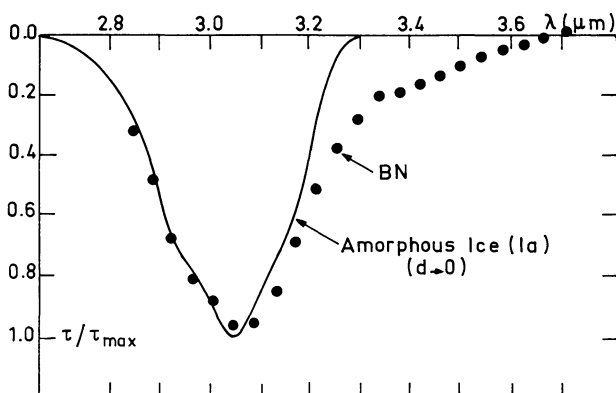


Fig. 4. Comparison of the $3 \mu\text{m}$ extinction line in BN molecular cloud and the absorption of amorphous H_2O ice. The astronomical data are from Merrill et al. Contrary to the comparison with crystalline ice the fit is good for short wave-length side of the line. For the long wavelength wing see the text

It should be noticed that:

1. The I_a line is shifted roughly 50 cm^{-1} ($0.05 \mu\text{m}$) towards high energy in comparison with the corresponding line for I_c . Its maximum is at 3270 cm^{-1} ($3.06 \mu\text{m}$).

This indicates that the reduction of the OH stretching energy (3700 cm^{-1} , $2.7 \mu\text{m}$ for water vapor) due to the H bonding between H_2O molecules is less important in the amorphous solid than in the crystalline one. The fine structure of the two lines is seen to be the same although broader for I_a because H_2O molecules have many different environments in the amorphous solid.

2. The absorption at the maximum of the line is weaker for I_a than for I_c : $\alpha_c/\alpha_a \approx 1.5$.

b) Comparison of Line Shape with Observations

The laboratory spectra are obtained at 77 K whereas the space grains are probably at lower temperatures. From Raman scattering on I_a by Sivakumar et al. (1977) it can be deduced that lowering the temperature to 10 K would only shift the peak by 6 cm^{-1} ($0.006 \mu\text{m}$), which is of little importance.

To make a precise comparison between the astronomical observations at $3 \mu\text{m}$ and the IR absorption of I_a , one needs $n(\nu)$ and $k(\nu)$, the real and imaginary parts of the index. They will be determined in the near future for the entire $100 - 2.5 \mu\text{m}$ range. We can however already compare the observed line shape with the absorption of grains with vanishing diameter (absorption, no scattering). Figure 4 shows such a comparison for BN (CRL 2591, NGC 2264 IR are similar). Contrary to the comparison with crystalline ice, the agreement is excellent for the short wavelength side of the line. As in the calculations made by Merrill et al. and Mukai et al., the introduction of scattering due to finite grain size will give a long wavelength wing to the line and a fit can probably be found by adjusting the grain size.

This gives us good indications that the $3.1 \mu\text{m}$ feature observed in infrared objects spectra can be explained by the absorption of amorphous water ice without invoking other materials such as NH_3 , HCN or C_2H_2 .

c) Ice Abundance in Clouds

Merrill et al. estimate the amount of ice in the line of sight for different clouds from the maximum absorption of the $3.1 \mu\text{m}$ line (optical depth at $3.08 \mu\text{m}$). But as the absorption coefficient is weaker for I_a than for I_c by a factor 1.5, the amount of material should be increased in the same proportion ($5.4 \cdot 10^{-5} \text{ g cm}^{-2}$ instead of $3.6 \cdot 10^{-5} \text{ g cm}^{-2}$ in the case of the BN cloud). This is substantial but it does not change the idea that ice is rarer in dust clouds than one would expect from crude consideration of the abundance of O and H in the galaxy.

2. The $12.5 \mu\text{m}$ Line

a) Laboratory Spectra

Another absorption occurs in I_c at 850 cm^{-1} ($11.8 \mu\text{m}$) (rotational vibrations of H_2O molecules) (see Fig. 1). Figure 5 gives this absorption for equal amounts of I_c and I_a . We notice that:

1. The I_a line is shifted to low energy by 40 cm^{-1} ($0.5 \mu\text{m}$) (the contrary happens with the $3 \mu\text{m}$ line). Its maximum occurs at about 800 cm^{-1} ($12.5 \mu\text{m}$).

2. The maximum absorption of I_a is reduced by 1.34 with respect to that of I_c .

b) Astronomical Implications

The intensity ratio of the $12.5 \mu\text{m}$ line to the $3.1 \mu\text{m}$ one is small for ice ($\approx 1/8$), about the same for I_c and I_a . If ice – amorphous or crystallized – were the principal carrier of both the 3.1 and $9.7 \mu\text{m}$ lines in molecular cloud spectra, the $9.7 \mu\text{m}$ feature would be expected to be much weaker than the $3.1 \mu\text{m}$ one. This is not observed (Merrill et al., 1976). In addition, the fit between the observed structure and the I_a absorption is very bad ($800/1030 \text{ cm}^{-1} - 12.5/9.7 \mu\text{m}$).

Other carriers such as silicates remain necessary to explain the $9.7 \mu\text{m}$ feature in cloud spectra. If the grains are core-mantle particles, the effect of the absorption in the $12.5 \mu\text{m}$ region by the mantle “ice” on the silicate core absorption at $9.7 \mu\text{m}$ should be

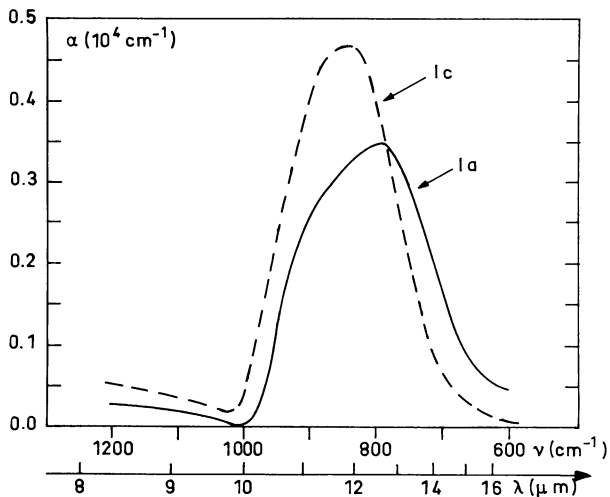


Fig. 5. Laboratory absorption of crystalline (I_c) and amorphous (I_a) ice at 77 K about 12 μm

taken into account to obtain the precise line profile (see Greenberg, 1978).

V. Conclusions

1. The 3.1 μm line in molecular clouds can in all probability be explained by the absorption of H₂O ice alone without invoking a contribution of NH₃, HCN or C₂H₂ molecules. However the rest of the spectrum indicates that dust contains other major constituents.

2. The water ice has to be *amorphous* rather than crystalline, as would be expected in cold and heterogeneous conditions.

3. The amount of ice estimated from the maximum absorption of the 3.1 μm line should be increased by a factor of 1.5.

4. The 9.7 μm line in molecular cloud spectra cannot be explained by water ice alone. The effect of the component at

12.5 μm due to H₂O absorption in the ice mantle should be taken into account in attempting to fit the observed line shape by other absorbants such as silicates.

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