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The three micron "ice" band in grain mantles

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Summary.

Laboratory optical constants for a 3 μm "ice" band in mixtures representing interstellar grain mantles are applied to the absorption observed towards two different types of object: the protostellar source BN and the late type star OH 231.8 + 4.2 (OH 0739-14). In BN, simultaneous reproduction of the extinction and polarization band shapes including the long wavelength wing is achieved by normal size particles ($\approx 0.15 \mu\text{m}$) with molecular mantles containing mixtures of H_2O with certain molecules among which are those such as NH_3 that form hydrogen bonded complexes. With mantle mixtures the match is better than with the abnormally large pure amorphous H_2O particles ($a \approx 0.4 \mu\text{m}$) which produce the required long wavelength wing by scattering rather than absorption. On the other hand, the 3 μm absorption in OH 231.8 + 4.2 which contains no such wing can best be fitted with pure amorphous H_2O grains which have been heated to (or created at) about 80 K. The difference in the grain mantle composition between young stellar objects (like BN) and late type stars losing mass (like OH 231.8 + 4.2) is attributed to a fundamental difference in the formation and evolution mechanism of the grains in which the former are condensed in interstellar space and the latter are condensed in the outgoing matter from the star.

Keywords: interstellar dust mantle - infrared - extinction and polarization - three micron band.

1. INTRODUCTION

One of the most direct ways to study the properties of dust in dense interstellar media is by infrared spectroscopy. Broad spectral features in extinction or emission appear superimposed on the infrared continua of a number of interstellar sources obscured by dense regions of dust. Because of their spectral width most of these features are attributed to vibrational transitions in solids.

Absorption, emission and linear polarization at the frequency of 1030 cm^{-1} ($9.7 \mu\text{m}$) observed in most infrared objects is commonly interpreted as due to silicate particles (see recent reviews by Aitken, 1981; Dyck and Lonsdale, 1981). The most intense feature next to the "silicate" band is the 3250 cm^{-1} ($3.08 \mu\text{m}$) "ice" band generally attributed to solid H_2O . This band is seen in spectra of sources asso-

ciated with dense molecular clouds in absorption (Aitkin, 1981) and linear polarization (Dyck and Lonsdale, 1981). A number of other minor absorption features are also present in some interstellar spectra. They are seen in conjunction with the "ice" band (Willner et al., 1980). Infrared spectra of some interstellar objects show emission features not attributed to silicates. These features do not occur at the same frequency as those seen in absorption (Aitkin, 1981).

The 3250 cm^{-1} "ice" band and the other absorption and emission features are the subject of a number of theoretical and experimental investigations in the Leiden Astrophysics laboratory. Studies of vibrational transitions of simple molecules in solid mixtures have shown that molecules in accretion mantles of interstellar dust particles can account for the infrared bands both in emission (Allamandola and Norman, 1978 ab; Allamandola, Greenberg and Norman, 1979) and absorption (Allamandola, Greenberg and Norman, 1979; Hagen, Allamandola and Greenberg, 1980b). In the present paper we extend this work and describe a study of the influence of different mantle constituents on extinction and polarization due to H_2O absorption in grain mantles, in particular on the 3250 cm^{-1} band. A comparison of the experimental results with the presently available interstellar spectra allows us to draw conclusions on the grain mantle composition in certain objects. However it is also our intention to provide incentives for extended spectrophotometric observations of different interstellar sources at moderate resolution and high signal to noise ratio. Interpretation of such observations in the light of the results presented here may yield a better knowledge of the grain mantle composition in different interstellar regions.

H_2O ice and mixtures of solid H_2O , NH_3 and CH_4 were believed to be important constituents of interstellar grains ever since the earliest grain models were put forward (Hulst, van de, 1943, 1949; Greenberg, 1968). This encouraged Danielson et al., (1965) and Knacke et al. (1969) to search for the strongest ice absorption in the infrared, the 3250 cm^{-1} band, in a number of highly reddened stars. These first searches turned out negative. A few years later a strong infrared absorption at 3250 cm^{-1} , identified with H_2O ice, was detected in the spectrum of the protostellar BN project (Gillett and Forrest, 1973; Gillett et al., 1975). This was followed by detection of the band in the $4750\text{-}2440 \text{ cm}^{-1}$ region of the spectra of an ir source in the Rosette nebula (Cohen, 1976), molecular clouds (Merrill et al., 1976), HII regions (Soifer et al., 1976; Willner et al., 1979b), the young stellar object W33A (Capps et al., 1978), OH maser source OH 231.8 + 4.2 \equiv OH 0739-14 (Gillett and Soifer, 1976), OH 26.5 + 0.6 (Forrest et al., 1978)

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and a highly obscured infrared source in the Corona Australis dark cloud (Whittet and Blades, 1980). With the exception of OH 231.8 + 4.2 the shapes of the spectral features of the different sources are similar if one takes into account the available resolution and signal to noise ratio, but the relative intensities are variable (Willner et al., 1980). In some spectra, in particular when the minor absorptions are relatively strong, the 3250 cm^{-1} "ice" band exhibits substructure peaking at about 3380, 2940 and 2860 cm^{-1} . The "ice" band and the minor absorption bands are definitely not a general characteristic of interstellar spectra. These absorptions are only observed towards sources in high density molecular clouds. It has been suggested that the "ice" band could be severely reduced by photolysis of the ice mixture resulting in the oxygen being not in the form of polymeric water but rather in the form of free radicals or complex molecules (Donn and Jackson, 1970; Greenberg et al., 1971). Linear polarization in the 3250 cm^{-1} "ice" band has been measured towards BN (Capps et al., 1978; Kobayashi et al., 1980). In planetary spectroscopy infrared features due to solid H_2O were detected on Mars, the moons of Jupiter, and the moons and rings of Saturn (Fink and Larson, 1979).

Attempts to fit the interstellar 3250 cm^{-1} absorption with laboratory spectra of H_2O ice (polycrystalline cubic, I_c , or hexagonal, I_h) at 100 K (from Bertie et al., 1969) or 267 K (from Irvine and Pollack, 1968) were unsuccessful. The main discrepancies between the laboratory ice band and the interstellar feature were in the large width, the extension to higher frequencies and the low frequency wing of the interstellar band which were absent in the laboratory spectra. Two approaches were chosen to resolve the discrepancies. Firstly the effect of grain size on the extinction was examined employing Mie theory, but a satisfactory fit of the spectra of H_2O I_c or I_h and the interstellar spectra could not be obtained (Cohen, 1976; Merrill et al., 1976; Mukai et al., 1978). Secondly solid mixtures of H_2O and other species such as NH_3 were suggested (Merrill et al., 1976). Several alternative compounds, not H_2O , were also proposed as carriers of the 3250 cm^{-1} band. Notable among these are polysaccharides (Hoyle and Wickramasinghe, 1977; Hoyle et al., 1978; see Henbest, 1980 and Whittet and Butchart, 1981, for a critical discussion), HCN and C_2H_2 (Mukai et al., 1978), complex organic material, "tholins", produced by electrical discharge or ultraviolet light (Sagan and Khare, 1979; see Whittet, 1979, for a critical discussion) and carbyne (Webster, 1980). In line with calculations of the composition of grain mantles as they accrete in the dense interstellar medium (Tielens and Hagen, 1982) we presently limit our discussions to the simplest candidate for the interstellar absorptions: H_2O .

The first laboratory studies aiming at the simulation of the interstellar "ice" band were performed before its actual detection. Infrared spectra of amorphous solid H_2O , produced by condensation of H_2O vapor on a 77 K infrared transparent window, were measured at 77 K and 20 K (Knacke et al., 1969). The same authors briefly discussed the effect of dilution of H_2O in CH_4 and NH_3 . Hunter and Donn (1971) concluded on the basis of spectra of mixtures of H_2O , NH_3 and N_2 at 77 K that complex formation by hydrogen bonding between H_2O and NH_3 does not affect the infrared spectrum. A mixture of N_2 with 5% H_2O was shown to produce a number of sharp, but weak infrared absorption lines due to small aggregates of H_2O molecules at 3700-3355 cm^{-1} (Hunter and Donn, 1971).

After numerous interstellar spectra had become available, laboratory studies attempting to reproduce the interstellar "ice" band were taken up once again.

The spectrum of amorphous solid H_2O at 77 K was measured by Léger et al. (1979) who noticed an excellent agreement with the BN spectrum for the high frequency side of the 3250 cm^{-1} band. In our laboratory the solid H_2O spectrum was measured over the temperature range from 10 to 140K (Hagen, Tielens and Greenberg, 1981, Hagen and Tielens, 1982a). We found a strong temperature dependence of the spectrum. It was concluded that of all the H_2O spectra measured, that of unannealed amorphous solid H_2O , as it forms by very slow condensation at 10 K, fits the observed interstellar "ice" band best. The low frequency wing of the interstellar 3250 cm^{-1} band however was not present in the laboratory spectra of solid H_2O . In contrast to earlier work (Hunter and Donn, 1971) we found that mixing of H_2O with other species in the solid leads to a significant change of the spectrum and could produce the low frequency wing (Hagen, 1979; Hagen et al., 1980ab). This is in line with the well known capacity of H_2O to form strong hydrogen bands with other molecules (Pimentel and McClellan, 1960). Again, in contrast to the earlier work by Hunter and Donn (1971) in very diluted mixtures of H_2O and NH_3 with inert species, sharp infrared absorption lines were observed due to H_2O , NH_3 as well as mixed aggregates (complexes of hydrogen bonded species; Hagen, 1982). Elsewhere (Hagen, Tielens and Greenberg, 1982, hereafter referred to as HTG82) we have examined the effects of different concentrations of other components in a mixture and the thermal history on the spectrum. A brief summary of the results from that paper are given below.

Temperature and thermal history determine the width and peak frequencies of the infrared absorptions of solid H_2O and solid mixtures containing H_2O . Moderate resolution interstellar spectra of high signal to noise ratio of the 3250 cm^{-1} band can provide information on the thermal history of dust grains. The non-detection of the H_2O ν_L absorption (librational band, ~ 800 cm^{-1}) in the presently available observed spectra with a low frequency cut-off at 750 cm^{-1} can be explained by the shallowness and very low peak frequency (763 cm^{-1}) of solid H_2O , as it is formed by condensation at 10 K. The previously considered higher temperature forms of H_2O ice have smaller widths and higher peak frequencies.

Dilution of solid H_2O with non hydrogen binding molecules gives rise to considerable changes in the H_2O spectral features. The changes include (1) the appearance of a new feature at 3700 cm^{-1} and a shoulder to the 3250 cm^{-1} absorption at 3220 cm^{-1} , (2) a shift to the blue and an increase of the width of the 3250 cm^{-1} absorption and (3) an increasing relative intensity of the 1650 cm^{-1} peak. Observations of these features in interstellar spectra allow an estimate of the degree of dilution. Finally it is important to note that (4) dilution to less than 66% H_2O shifts the peak of the H_2O ν_L (800 cm^{-1}) absorption outside the frequency region covered by the presently available interstellar spectra. This adds a possible reason for its non-detection to the temperature effect mentioned above. The general shape of the H_2O features is maintained for H_2O concentrations as low as 33%. At concentrations below 10% the broad absorptions of solid H_2O are replaced by a number of sharp but weak lines.

Dilution of H_2O with hydrogen bonding molecules alters its spectrum considerably. Simple empirical relations are established between the basic (or acidic) properties of the dilutant and its influence on the spectra. Strong bases induce a low frequency wing to the 3250 cm^{-1} absorption in solid mixtures through hydrogen bond formation with H_2O . The simplest base producing the wing is NH_3 . Molecules that may also contribute to the low frequency wing of the 3250

cm^{-1} band include other bases, H_2CO , H_2O_2 or mixtures of hydrocarbons. The presence of NH_3 in grain mantles can be verified with interstellar absorption spectra. NH_3 in mixtures with H_2O is characterized by (1)

absorption at 3380 cm^{-1} superimposed on the 3250 cm^{-1} band, (2) a relatively strong 1650 cm^{-1} absorption and (3) low frequency wings of the 3250 cm^{-1} and 1650 cm^{-1} absorptions. The wing of the 1650 cm^{-1} absorption disappears when inert molecules are also present in the solid.

In the present paper optical constants derived from laboratory spectra are used to calculate extinction and polarization in the 3250 cm^{-1} band. Excluding particle shape effects (Greenberg, 1972) the chief causes for differences between absorption shapes are differences in mixtures, temperature and size. Emphasis is placed here on the discrimination between two possible causes of the low frequency wing of the 3250 cm^{-1} band: grain size effects versus molecule mixture effects.

2. EXTINCTION AND POLARIZATION CROSS SECTIONS

In order to compare the laboratory results with infrared observations of interstellar sources extinction and polarization profiles of small particles have to be calculated. This is done in the following way. The particles are represented by infinite core-mantle cylinders. It is assumed that the magnetic field is perpendicular to the line of sight and that the particles are spinning with their symmetry axis in a plane perpendicular to the direction of the magnetic field i.e. perfect Davis-Greenstein alignment (Davis and Greenstein, 1951). Defining Q_{\parallel} and Q_{\perp} as the extinction efficiencies per unit length for the electric vector parallel and perpendicular to the symmetry axis of the infinite cylinder we can write for the extinction and polarization:

$$Q_{\text{ext}} = \frac{3}{4} (Q_{\parallel} + 3Q_{\perp}) \quad (1)$$

$$Q_{\text{pol}} = \frac{3}{4} (Q_{\parallel} - Q_{\perp}) \quad (2)$$

Strictly speaking this expression is only valid in the rayleigh limit for spheroids (Greenberg and Shah, 1966; Greenberg, 1969).

The extinction (K) and linear polarization ($\Delta\sigma$) cross sections are given by

$$K = \int_a^{\infty} N(a) 2a L(a) Q_{\text{ext}}(a) da \quad (3)$$

$$\Delta\sigma = \int_a^{\infty} N(a) 2a L(a) Q_{\text{pol}}(a) da \quad (4)$$

where $N(a)$ and $L(a)$ are the size and length distribution functions and where we have used a single core size, a_c . In the calculations it is assumed that the size and length distribution functions are given by

$$N(a) = \exp \left\{ -5 \left(\frac{a-a_c}{a_1} \right)^3 \right\} \quad (5)$$

and

$$L(a) = 2ea \quad (6)$$

where a_1 is an effective cut off size parameter and e is a constant elongation factor. For the core we have chosen a size of 500 \AA and the optical constants appropriate for interstellar silicate grains around 3250 cm^{-1} ($m_c = 1.55 - 0.05i$; Jones and Merrill, 1976; Bedijn, 1977). The free parameters in these calculations are therefore the optical constants of the grain mantle, m_m , and the cut-off size parameter, a_1 , or equally well the mean size of the mantle, $a \approx a_c + 0.3 a_1$ (Greenberg, 1968).

The optical constants of the grain mantle depend on the temperature and the composition of the grain

mantle (HTG82). We shall first consider amorphous solid water $\text{H}_2\text{O}(\text{as})$.

In fig. 1 the extinction and linear polarization efficiencies of amorphous solid water, $\text{H}_2\text{O}(\text{as})$, grain mantles at 10 K are presented for different sizes. The optical constants are taken from Hagen et al. (1981). All curves are normalized to the peak value. For small sizes the extinction profile peaks at shorter wavelength than the peak in the imaginary part of the complex index of refraction. For larger sizes the peak in the extinction shifts to longer wavelengths. The polarization is more asymmetric than the extinction and generally reaches a maximum at longer wavelengths. This is due to the fact that Q_{\parallel} and Q_{\perp} reach maxima at different wavelengths. Upon increasing the particle size, the extinction and polarization features broaden and a low frequency wing develops, due to scattering by large grains. The wing is more pronounced in polarization than in the extinction (Greenberg and Hong, 1976). Using a size distribution given by eq. 5, broadens the feature and produces a shift of the peaks to lower frequencies. In effect the curves resemble those of a single particle with a size somewhat larger than the mean size.

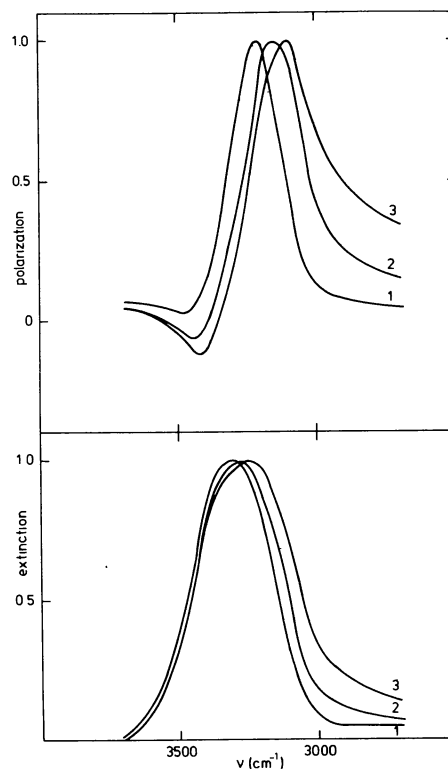


Fig. 1. Extinction and polarization cross sections (3250 cm^{-1} feature) of grain mantles consisting of unannealed $\text{H}_2\text{O}(\text{as})$ ($T = 10 \text{ K}$).

1. Infinite cylinders with a size of 1000 \AA
2. Infinite cylinders with a size of 3000 \AA
3. Infinite cylinders with a size distribution given by eq. 5, mean size is 3000 \AA

In fig. 2 we show the effect of increasing the temperature of $\text{H}_2\text{O}(\text{as})$ grain mantles. As expected, upon raising the temperature, the extinction and polarization peak at lower frequency and are less broad (Hagen et al., 1981).

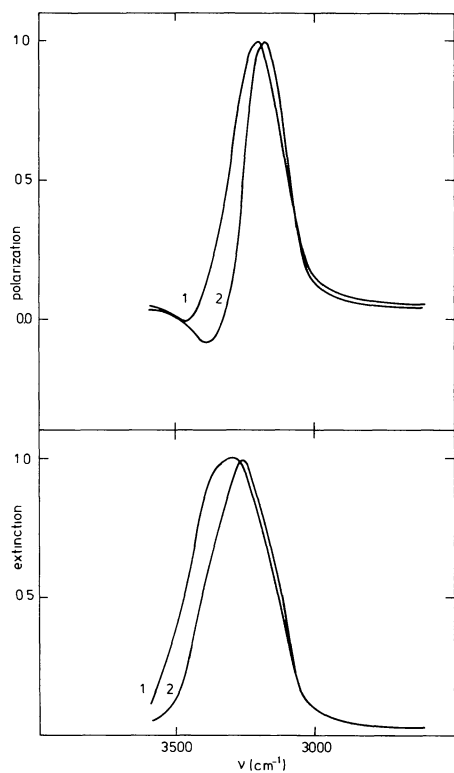


Fig. 2
Extinction and polarization cross sections (3250 cm^{-1} feature) of grain mantles consisting of $\text{H}_2\text{O}(\text{as})$. The infinite cylinders have a size distribution given by eq. 5, and a mean size of 1000 \AA .
1. unannealed $\text{H}_2\text{O}(\text{as})$ ($T = 10 \text{ K}$)
2. partially annealed $\text{H}_2\text{O}(\text{as})$ (deposited at 10 K , warmed-up to 80 K and recooled to 10 K).

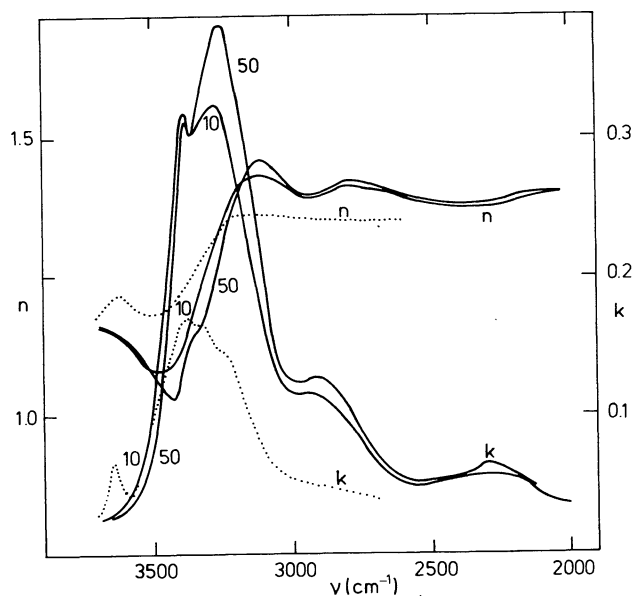


Fig. 3. Real and imaginary parts of the index of refraction for two ice mixtures. Dotted curve for $\text{H}_2\text{O}/\text{NH}_3/\text{CO}=5:1:6$ deposited and measured at 10K . Solid curve marked 10 for $\text{H}_2\text{O}/\text{NH}_3=3:1$ deposited and measured at 10K . Solid curve marked 50 for the same mixture after warm-up to 50K and recooling to 10K .

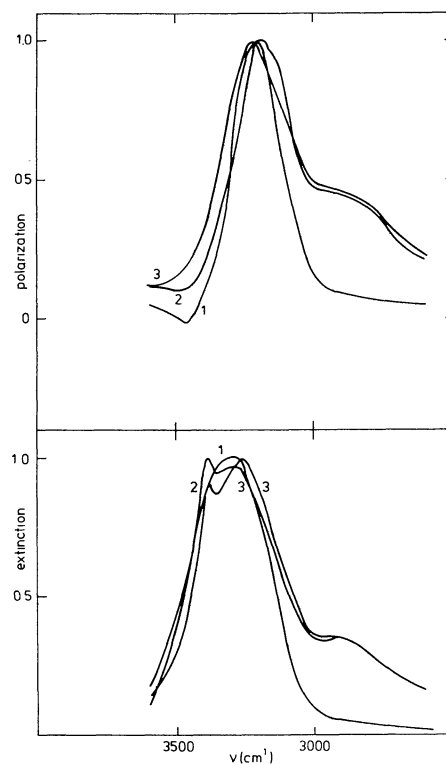


Fig. 4.
Extinction and polarization cross sections (3250 cm^{-1} feature) of infinite cylinders with a size distribution given by eq. 5 and a mean size of 1000 \AA .
1. Unannealed $\text{H}_2\text{O}(\text{as})$ ($T = 10 \text{ K}$)
2. Unannealed mixture of $\text{H}_2\text{O}/\text{NH}_3$ (3:1) ($T = 10 \text{ K}$).
3. Partially annealed mixture of $\text{H}_2\text{O}/\text{NH}_3$ (3:1) (deposited at 10 K , warmed-up to 50 K and recooled to 10 K)

As discussed in HTG82, the optical constants of the grain mantle depend strongly on the relative concentration of impurities. We illustrate this in fig. 3 for two different mixtures. In fig. 4 the normalized extinction and polarization efficiencies of an $\text{H}_2\text{O}/\text{NH}_3$ mixture are compared with those of $\text{H}_2\text{O}(\text{as})$. The introduction of NH_3 in the mantle broadens the features and gives rise to a low frequency wing which is due to the intrinsic absorption and therefore present even for small sizes. In the extinction profiles a separate peak at 3380 cm^{-1} is present due to NH_3 . Upon increasing the grain size, the low frequency wing becomes more prominent and the peak at 3380 cm^{-1} diminishes. The strength of the wing and the 3380 cm^{-1} feature are of course a function of the NH_3 concentration. Again increasing the temperature shifts the peaks to lower frequencies and narrows the features. The strength of the wing and the prominence of the 3380 cm^{-1} peak also diminishes.

3. COMPARISON WITH OBSERVATIONS

a The 3250 cm^{-1} feature in dense molecular clouds.

The near infrared spectrophotometry of sources with molecular cloud material along the line of sight reveal an extinction feature at $3250 \mu\text{m}$ which is generally attributed to H_2O ice (Merrill et al., 1976).

This feature is quite broad and shows a low frequency wing. The shape of this feature does not vary much from one source to the other (Willner et al., 1982). In the following discussion we shall concentrate on the observations of the BN source in Orion.

The near infrared emission from BN is strongly polarized. The linear polarization rises from about 5% at 4 μm to about 35% at 1.6 μm . A large degree of circular polarization has also been measured from BN at near infrared frequencies (Breger and Hardop, 1973; Loer et al., 1973; Dyck et al., 1973, 1974; Capps et al., 1978; Kobayashi et al., 1980; Serkowski and Rieke, 1973; Lonsdale et al., 1980). The linear polarization of the 3250 cm^{-1} feature peaks at lower frequencies than the extinction feature (Kobayashi, et al., 1980).

Two models have been proposed to explain the observed polarization towards BN. In one model the polarization is caused by extinction by elongated particles aligned by the magnetic field (Dyck and Beichman, 1974; Dennison, 1977). In the other model the polarization is due to scattering of light by grains in a disk geometry (Elsasser and Staude, 1978). In the latter model however it is difficult to explain the large linear polarization at 20 μm (Knacke and Capps, 1979) and the difference in the peak wavelength of the extinction and polarization feature (Kobayashi et al., 1980).

In order to compare our laboratory based theoretical calculations of the extinction and polarization efficiencies across the 3250 cm^{-1} band with the observations of BN the following procedure is adopted. The observed extinction profile is determined by drawing a smooth continuum from 400 cm^{-1} to 2600 cm^{-1} where zero absorption is assumed. The profile is then normalized at the peak value. The results of the theoretical calculations are treated in the same way. For the linear polarization the situation is slightly more complicated. For reasonable grain sizes the ratio of the continuum polarization around 5000 cm^{-1} to the peak 3250 cm^{-1} polarization produced by "ice" grain mantles is small. This implies that most of the observed continuum 5000 cm^{-1} polarization is produced by other particles than those that produce the 3250 cm^{-1} feature in polarization. A similar conclusion has been drawn for the particles that produce the 1030 cm^{-1} polarization (Lonsdale et al., 1980). That the 5000 cm^{-1} continuum polarization seems to be due to an interstellar grain component other than silicates or H_2O "ice" is supported by the observations that the large value of the wavelength of maximum continuum polarization, λ_{max} , and of the color excess ratio, R , inside dense clouds are not due to coating of grains with H_2O ice (Harris et al., 1978; Whittet and Blades, 1980). A grain model has been proposed which may explain this (Greenberg, 1982a,b). In this model the grain mantle consists of two layers, the inner one being an organic refractory residue from photoprocessed ices; and the outer one having a high fraction ($\sim 60\%$) of H_2O ice. Grains which have organic refractory mantles alone are adequate to explain the average extinction and polarization in the diffuse cloud medium, the thickness of these mantles being probably a bit less than would be required of simple ice mantles. It may be shown that a very large total extinction is required to be able to observe the ice band even for grains with larger than average values of λ_{max} and R . This has been demonstrated for the case presented by Whittet et al. (1981) by methods like those applied to the BN ice band (Greenberg, 1982a). It has been suggested in the latter that approximately one half of the extinction in the BN object is produced by grains which have only refractory organic mantles and therefore exhibit no H_2O ice structure.

It may also be that the increase in λ_{max} and R inside dense clouds is due to the growth of grain mantles containing only a small fraction of H_2O ($< 10\%$). The infrared spectrum of such a grain mantle will not show the 3250 cm^{-1} band (HTG82). Furthermore, calculations of gas phase and surface chemistry inside dense molecular clouds show that under certain conditions grain mantles may contain mainly molecules other than H_2O , eg CO_2 or CO and O_2 (Tielens and Hagen, 1982).

Observations show that the continuum linear polarization in the infrared can be reasonably well represented by a slightly modified Serkowski law (Wilking et al., 1980).

$$\frac{P}{P_{\text{max}}} = \text{EXP} \left[-1.7 \lambda_{\text{max}} \left(\ln \frac{\lambda_{\text{max}}}{\lambda} \right)^2 \right] \quad (7)$$

After normalization at 4750 cm^{-1} this law fits the observations from 6000 cm^{-1} to 4750 cm^{-1} reasonably well for $\lambda_{\text{max}} = 0.55 \mu\text{m}$, the mean value of λ_{max} in the diffuse interstellar medium. The choice of λ_{max} is not critical. λ_{max} equal to 0.7 gives a slightly different continuum.

We have added the theoretical polarization profiles of "ice" mantles to this continuum in such a way that the peak polarization in the feature is equal to the mean of the observed peak values (Capps et al., 1978; Kobayashi et al., 1980).

In fig. 5 and 6 the extinction and polarization by unannealed ($T = 10 \text{ K}$) amorphous solid water $\text{H}_2\text{O}(\text{as})$ with a mean size of 4000 \AA and of an unannealed ($T = 10 \text{ K}$) and annealed (warmed up to 50 K and recooled) mixture of H_2O and NH_3 ($\text{H}_2\text{O}/\text{NH}_3 = 3:1$) with a mean size of 1500 \AA are compared with the observations towards BN.

We first concentrate on $\text{H}_2\text{O}(\text{as})$. A reasonable fit to the extinction profile can be obtained for a mean size of 4000 \AA . The low frequency wing of this feature is then due to scattering by large grains. However, the calculated polarization profile is not in agreement with the observations. Due to the large mean size of the grains the peak in the polarization has shifted to about 3100 cm^{-1} and the high frequency side

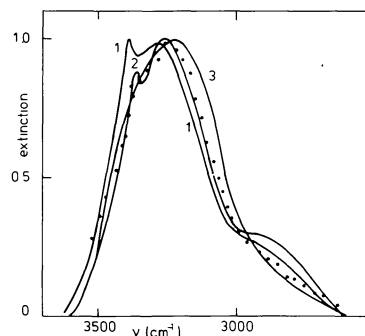


Fig. 5
Comparison of the extinction cross sections (3250 cm^{-1} feature) of infinite cylinders with the observations towards BN (dots) (Gillett et al., 1975)

1. Unannealed mixture of $\text{H}_2\text{O}/\text{NH}_3$ (3:1) ($T = 10 \text{ K}$) with a mean size of 1500 \AA
2. Partially annealed mixture of $\text{H}_2\text{O}/\text{NH}_3$ (3:1) (deposited at 10 K, warmed-up to 50 K and recooled to 10 K). Mean size 1500 \AA
3. Unannealed $\text{H}_2\text{O}(\text{as})$ ($T = 10 \text{ K}$) with a mean size of 4000 \AA

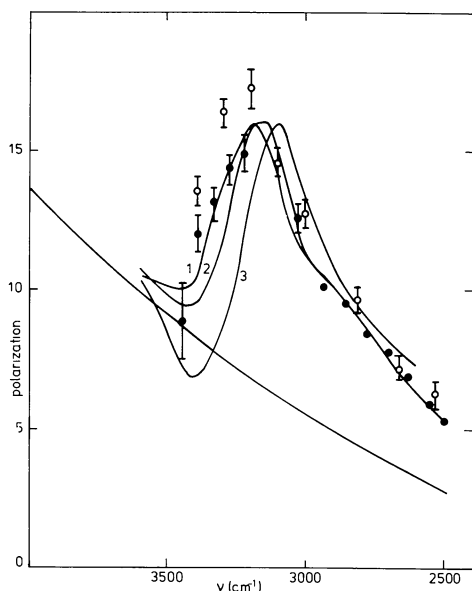


Fig. 6
Polarization cross sections (3250 cm^{-1} feature) of infinite cylinders with a size distribution given by eq. 5, compared with the observation towards BN. 1, 2 and 3 as in fig. 5.
Open circles: observations of Kobayashi et al. (1980)
Filled circles: observations of Capps et al. (1978)

of the profile rises sharply. Raising the temperature of the H_2O grain mantles to 80 K does not improve the fits (cf. fig. 2). The extinction profile becomes too narrow, the high frequency cut off falls short and the rise in the polarization on the high frequency side becomes even sharper than at 10 K. We conclude therefore that infinite cylinders of pure amorphous solid water $\text{H}_2\text{O}(\text{as})$ can not simultaneously reproduce the extinction and polarization profiles observed towards BN. We expect that this conclusion also holds for grain shapes other than infinite cylinders. Generally the large mean size of the particles needed to explain the low frequency wing of the observed extinction and polarization feature by scattering will produce a highly asymmetric feature in polarization which does not resemble the observations.

Adding a small amount of NH_3 to the mixture produces a low frequency wing due to absorption. As a result a smaller mean size can be chosen and the polarization feature is more symmetric (fig. 6). For a mean size of 1500 \AA the extinction and polarization cross-sections of the unannealed ($T = 10\text{ K}$) $\text{H}_2\text{O}/\text{NH}_3$ (3/1) mixture have a low frequency wing in accordance with the observations. The extinction profile has however two peaks at 3280 and 3380 cm^{-1} . It has been pointed out that sometimes the profile of the interstellar 3250 cm^{-1} feature shows evidence for a double humped peak with maxima at about 3360 and 3250 cm^{-1} (Hagen, et al., 1980b). The 3380 cm^{-1} peak in the calculated extinction profile is due to the NH -stretching vibration in NH_3 . There are three ways in which the prominence of this peak can be diminished. First, obviously, the concentration of NH_3 can be reduced. Second, upon raising the temperature the 3250 cm^{-1} peak shifts to lower frequency and the strength of the 3380 cm^{-1} peak decreases. This is illustrated in fig. 5 for the $\text{H}_2\text{O}/\text{NH}_3$ mixture annealed to 50 K and

recooled to 10 K. It should be noted that the recoiling is not of major importance. In amorphous solids spectral characteristics like peak position and width do not change much upon recoiling (HTG82). The theoretical extinction and polarization curves are now in reasonable agreement with the observations. In order to shift the peak frequency to the observed value the mixture must be annealed somewhat. It is however conceivable that this shift in peak frequency can also be produced by choosing a different shape for the particle (Greenberg, 1972). Third, the mean size of the particles can be increased to about 2000 \AA . This shifts the 3280 cm^{-1} maximum to about 3250 cm^{-1} . The strength of the 3380 cm^{-1} feature also decreases somewhat. However it will still be clearly discernible. Furthermore the polarization peak would shift to 3100 cm^{-1} in disagreement with the observations. Finally the low frequency wing in the extinction and polarization would be more pronounced than observed. These objections rule out this possibility.

We wish to emphasize that the choice of the particular mixture is not of major importance. Any molecular mixture which produces a low frequency wing in absorption can be made to fit the extinction and polarization observations. Recent theoretical calculations of the composition of grain mantles in dense molecular clouds show that at a density of 10^4 cm^{-3} , they consist of H_2O ($\approx 60\%$) and H_2CO (25%). Traces of other molecules such as CO_2 (5%), NH_3 (1%), H_2O_2 (2%), HCONH_2 (0.5%) and NH_2OOH (0.2%) are also present (Tielens and Hagen, 1982). From the discussion in HTG, 1982 it is obvious that such a mixture would produce a 3250 cm^{-1} "ice" band, having a low frequency wing due partly to the CH -stretch in H_2CO and partly to hydrogen bond formation between H_2O and NH_3 , NH_2OOH , H_2O_2 or H_2CO . Further laboratory experiments on the 3250 cm^{-1} "ice" band in the spectra of these kind of mixtures should produce valuable information on the physical conditions in dense molecular clouds.

The librational band of $\text{H}_2\text{O}(\text{as})$ has not been detected superimposed on the 1030 cm^{-1} silicate feature in sources which show the 3250 cm^{-1} feature, despite large variations in the ice to silicate volume ratios. This has been used as an argument against the presence of solid H_2O (Capps et al., 1978; Aitken, 1981). The interstellar spectra on which this conclusion is based do not extend beyond 750 cm^{-1} . The librational bands in our spectra of unannealed $\text{H}_2\text{O}(\text{as})$ as well as the H_2O mixtures have absorption maxima close to this frequency and are very shallow. Only the crystalline forms of H_2O , I_c and I_h , have a librational frequency around 850 cm^{-1} . Furthermore complicated radiative transfer effects in the $10\text{ }\mu\text{m}$ silicate absorption feature may mask this additional absorption. We conclude that a comparison of the presently available interstellar spectra with our spectroscopic data on $\text{H}_2\text{O}(\text{as})$ and H_2O in molecular mixtures provides a plausible explanation for the absence of a librational band in the spectra of interstellar objects with 3250 cm^{-1} absorption bands. An observational test is of course provided by improving the signal to noise ratio at the low frequencies in interstellar spectra.

b Magnetic Alignment

It is interesting to try to derive a value for the strength of the magnetic field from the polarization observations. In equipartition, a rotating grain in a gas in the absence of external torques will have a rotational kinetic energy in equilibrium with the kinetic energy of the gas. The presence of a magnetic field introduces a torque. Energy is removed from one component of the grain rotation and the grains tend to be aligned by the magnetic field (Davis and Greenstein, 1951). There are thus two opposing

effects: the gas-grain collisions which tend to randomize the grain spinning motion and the magnetic field which tend to align the grains. A parameter

ξ can be defined which describes the effectiveness of the alignment (Jones and Spitzer, 1967)

$$\xi^2 = \frac{1 + \delta T_d/T}{1 + \delta} \quad (8)$$

where δ is the ratio of the mean magnetic torque to the mean torque of the gas-grain collisions, T_d is the grain temperature and T the gas temperature.

From our theoretical calculations of the extinction and polarization profiles we find that the ratio of peak polarization to peak extinction for perfect Davis-Greenstein alignment is about 0.2. The observed value is about 0.06. The reduction factor due to incomplete alignment is thus about 0.3, corresponding to a value of ξ in the range 0.4 to 0.6 (Greenberg, 1969). This is much smaller than the value obtained by Dyck and Beichman (1974) from their analysis of the extinction and polarization at 1030 cm^{-1} . However they did not take into account radiative transfer effects which are important in the 1000 cm^{-1} region and not in the 3000 cm^{-1} region. They have therefore underestimated the 1030 cm^{-1} extinction optical depth considerably. Using more realistic values Dennison (1977) found values in reasonable agreement with ours.

The strength of the magnetic field, B , required to produce the alignment is given by

$$B^2 \approx 0.5 a n_H T_d T^{\frac{1}{2}} \frac{(1 - \xi^2)}{\xi^2 - T_d/T} \quad (9)$$

where n_H is the density of colliding species, a , is in μm and B in microgauss. For an order of magnitude estimate we insert $a = 0.15 \mu\text{m}$, $n_H \approx 10^4 \text{cm}^{-3}$, $T_d = 10 \text{K}$ and $T = 50 \text{K}$ resulting in $B \approx 1 \text{mG}$. This is a large value but perhaps not totally unreasonable. Recent determinations of magnetic field strength from Faraday rotation of background radio sources and from Zeeman splitting of the OH lines indicate a magnetic field strength of about 50 μG inside dense molecular clouds (Heiles, 1976; Heiles et al., 1981; Crutcher et al., 1975, 1981). An upper limit of 25 μG has been obtained for the magnetic field strength in the Orion molecular cloud from observations of the 50 emission lines (Clark et al., 1978). Theoretical work indicates that $B \propto n^{\kappa}$ with $\kappa = 1/2$ (Mouschovias, 1976). Assuming that the magnetic field and density in typical interstellar conditions are 3 μG and 1cm^{-3} respectively, cloud contraction to a density of 10^4cm^{-3} gives an expected field strength of 300 μG , which is a factor 3 less than that derived above. Possibly grains are more efficiently aligned due to either enhanced magnetic properties or superthermal rotation (Aannestad and Purcell, 1973; Purcell, 1975, 1979; Duley, 1978; Spitzer and McGlynn, 1979).

c The 3250 cm^{-1} feature in the spectrum of the source OH 231.8 + 4.2

The source OH 231.8 + 4.2 is probably a late type star which has undergone significant mass loss (Morris and Knapp, 1976). The 3250 cm^{-1} feature detected in the spectrum of this source differs considerably from the 3250 cm^{-1} feature commonly observed in molecular cloud regions. The feature is much narrower and lacks the low frequency wing. This indicates that the H_2O ice is relatively uncontaminated by impurities.

In fig. 7 we compare the observed 3250 cm^{-1} feature with theoretical calculations using unannealed and annealed amorphous solid water, $\text{H}_2\text{O}(\text{as})$, grain mantles. The unannealed $\text{H}_2\text{O}(\text{as})$ absorption is much too broad to explain the observations, but partially annealed $\text{H}_2\text{O}(\text{as})$ ($T \sim 80\text{K}$) provides a much better fit.

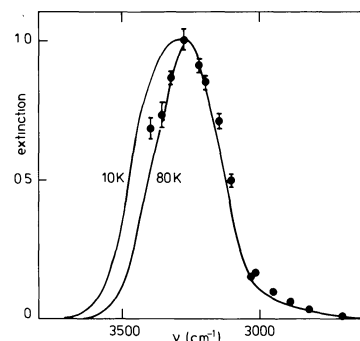


Fig. 7

Comparison of extinction cross sections (3250 cm^{-1} feature) of grain mantles consisting of $\text{H}_2\text{O}(\text{as})$ with the observations towards OH 231.8 + 4.2. The curve labeled 10 K is unannealed $\text{H}_2\text{O}(\text{as})$. 80 K is partially annealed $\text{H}_2\text{O}(\text{as})$ (deposited at 10 K, warmed-up to 80 K and recooled to 10 K).

We interpret the different composition of grain mantles around this star to a difference in formation mechanism. Grain mantles in interstellar molecular cloud regions are formed by accretion of gasphase atoms and molecules, mainly H, O, N, CO, O_2 and N_2 , on a grain at 10K. Extensive model calculations of gas-phase and surface chemistry show that H_2O ice mantles are likely to contain also H_2CO , NH_3 and H_2O_2 (Tielens and Hagen, 1982). Such a composition will broaden the 3250 cm^{-1} extinction feature and produce a low frequency wing.

Around late type stars the mantle formation mechanism is quite different. In the outflow of oxygen rich late type stars grains of silicate material are formed (condensation temperature $\sim 1000 \text{K}$). Upon expansion of the flow these grains cool down and other molecules present in the gasphase may condense out when the grains reach their condensation temperature. The condensation temperature for H_2O molecules is about 90K under these circumstances (Nakagawa, 1980). For molecules like NH_3 and H_2CO the condensation temperature is much lower ($\sim 50\text{K}$). By the time a grain reaches this temperature the local density has dropped by about a factor 20 as compared to the region where the grains are 90K and one expects no significant condensation of these molecules. In this way a relatively pure $\text{H}_2\text{O}(\text{as})$ grain mantle can be formed. This scenario is supported by the high temperature ($\sim 80\text{K}$) needed to explain the observations of the 3250 cm^{-1} extinction feature.

It is conceivable that around late type stars with a much larger mass loss rate other molecules such as NH_3 can be deposited later on the $\text{H}_2\text{O}(\text{as})$ layer. The spectrum of such an "onion layered" grain mantle will differ considerably from the spectra of the mixtures reported in this article, since the spectrum of a mixture is not the sum of the spectra of the pure components. In particular the low frequency wing of the 3250 cm^{-1} feature which can be produced by interaction between H_2O and a strong base like NH_3 , but it would be absent in the spectrum of a grain mantle composed of a layer of relatively pure $\text{H}_2\text{O}(\text{as})$ and a layer of NH_3 as an onion skin on top of it.

4 SUMMARY AND CONCLUSION

From a comparison of theoretically calculated extinction and polarization cross sections with the observations towards BN it is concluded that the

observed 3250 cm^{-1} feature can not be due to pure $\text{H}_2\text{O}(\text{as})$ mantles. Mixtures of $\text{H}_2\text{O}(\text{as})$ with other molecules, notably NH_3 , reproduce the extinction and polarization observations satisfactorily. The existence of such mixtures inside dense molecular clouds is in accordance with recent theoretical calculations of the grain mantle composition in those regions (Tielens and Hagen, 1982). Similar mixtures may result from photo-processing (Hagen, 1982).

Pure $\text{H}_2\text{O}(\text{as})$ grain mantles can explain the shape of the 3250 cm^{-1} feature observed towards the late type star OH 231.8 + 4.2. The temperature of these grains must at some time have been about 80K. It is suggested that these H_2O mantles form on silicate grains by condensation in the outflow of this star as soon as the silicate core reaches the condensation temperature of H_2O , about 90K.

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