Size and temperature dependence in the far-IR spectra of water ice particles

Chris Medcraft¹, Don McNaughton¹, Chris D. Thompson¹, Dominique Appadoo², Sigurd Bauerecker³, Evan G. Robertson⁴*

¹School of Chemistry, Monash University, Wellington Rd., Clayton, Victoria 3800, Australia
²Australian Synchrotron, Blackburn Rd, Clayton, Victoria 3168, Australia
³Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Hans-Sommer-Strasse 10, D-38106 Braunschweig, Germany
⁴Department of Chemistry & La Trobe Institute of Molecular Sciences, La Trobe University, Bundoora, Victoria 3086, Australia

*Corresponding author email: E.Robertson@latrobe.edu.au

Abstract

Spectra of water-ice aerosol particles have been measured in the far-IR region using synchrotron radiation. The particles in the nanoscale size regime of 1-100 nm were formed by rapid collisional cooling at temperatures ranging from 4-190 K. The spectra show the characteristic bands centred near 44 μm (230 cm⁻¹) and 62 μm (160 cm⁻¹) associated with the intermolecular lattice modes of crystalline ice at all temperatures, in contrast to previous studies of thin films formed by vapour deposition where amorphous ice is generated below 140 K. The bands shift to higher wavenumber values as the temperature is reduced consistent with the trend seen in earlier studies, but in our experiments the actual peak positions in the aerosol particle spectra are consistently higher by ca. 4 cm⁻¹. This finding has implications for the potential use of these spectral features as a temperature probe. The particle sizes are small enough for their spectra to be free of scattering effects, and therefore provide a means to assess imaginary refractive index values obtained through Kramers-Kronig analyses of thin film spectra.

List Keywords

Infrared: general, ISM: molecules, radiative transfer, techniques: spectroscopic
Introduction

Water ice is ubiquitous throughout the universe; it has been detected in nearly every location where physical conditions permit it. The infrared (IR) spectrum of water ice varies with purity, phase, particle size and shape, and perhaps most importantly, temperature (Moore & Hudson 1994; Buch et al. 2004; Bauerecker et al. 2007). Amorphous ice is formed when deposition occurs at temperatures at or below 100 K; crystalline ice can be formed either directly by depositing above 100 K or by forming amorphous ice at temperatures lower than 100 K and then tempering to 155 K (Moore & Hudson 1992). This phase transition to crystalline ice is thermally irreversible, therefore the phase of water ice detected in astronomical bodies may provide a thermal history of sorts (Zheng et al. 2009). The near-IR bands of water have been used to gauge the temperature of Saturn’s rings and satellites (Fink & Larson 1975; Larson and Fink 1977); the mid-IR OH-stretching mode has been used to determine the temperature of a number of different protostellar nebulae (Smith 1989).

The far-IR spectrum of crystalline ice has two characteristic peaks; one sharp peak near 44 μm (230 cm\(^{-1}\), the transverse optic mode) and a broader one near 62 μm (160 cm\(^{-1}\), the longitudinal acoustic) whereas amorphous ice has one broad peak near 45 μm (220 cm\(^{-1}\)). Additionally, both crystalline bands undergo a gradual red shift of approximately 6 cm\(^{-1}\) (1.5 μm) when cooled from 150 K to 10 K (Moore et al. 2001). These features were used to fit the emission from IRAS 09371 + 1212 to temperatures of 46 K indicating that significant cooling has occurred since crystallisation (Omont et al. 1990).

Existing laboratory data on the far-IR spectroscopy of water ice comes from studies on thin films, deposited either on a window for transmission spectra (Smith et al. 1994) or on a mirror for transmission-reflection-transmission (TRT) spectra (Moore et al. 2001). In this study, we report the far-IR spectra of nanometre sized aerosol particles comprised of cubic (I\(_{\text{c}}\)) phase ice at temperatures from 5 K to 195 K.

It is important to study such particles directly, primarily because their spectroscopic properties may be distinctly different from those of bulk materials or films. As noted by (Hudgins et al. 1993) this may result in a mismatch between astrophysical or atmospheric spectra and those from films. At the small particle limit surface effects increasingly contribute to the spectral profile, particularly in the region of strong transitions. At the other
end of the size scale, scattering of radiation with wavelength $\lambda$ becomes significant as the
dimensions of the particle approach $\lambda/2\pi$. Furthermore, analysis of IR spectra from particles
smaller than this allows determination of the frequency-dependent imaginary component of
the refractive index of a material, and consequently the real component also (Clapp et al.

Such constants are required for modelling of complex systems such as those found in
planetary atmospheres. The atmospheres of Saturn and Jupiter both contain significant
amounts of water (Roos-Serote et al. 2004) and, depending on the altitude, clouds of solid
water, NH$_3$, NH$_4$SH can form (West et al. 2004; Baines et al. 2002). Various compounds such
as hydrocarbons and phosphine (PH$_3$) are found in smaller quantities and form a complex,
dynamic chemical environment (Dougherty & Esposito 2009). One of the principal aims of
the CIRS mission on board the Cassini orbiter is the investigation of aerosols in the
atmospheres of Saturn and Titan (Fouchet et al. 2009).

Saturn’s rings are primarily composed of nearly pure crystalline water ice particles with a
large distribution of particle sizes from sub-micrometre sized dust to small moonlets (Poulet
& Cuzzi 2002; Esposito 2010). Small amounts of impurities give the rings a visibly red
colour. The nature of these impurities is an active area of research with tholins, polyaromatic
hydrocarbons and oxidised iron (hematite) being suggested as possible absorbers (Fouchet et
al. 2009).

Water ice clouds are known to play an important role in the water cycle of Mars and
influence the planet’s radiative forcing balance (Montmessin et al. 2004; Michaels et al.
2006), but detailed mechanisms of formation are still being established. Laboratory studies
have found significant temperature dependant barriers to ice formation by heterogeneous
nucleation on mineral dust particles (Iraci et al. 2010), and recent observations suggest the
frequent presence of water vapour in excess of saturation, by an amount far surpassing that
encountered in Earth’s atmosphere (Maltagliati et al. 2011).

Observations in the near-IR of the exoplanet GJ1214b suggest that it contains a water rich
atmosphere where cloud formation may be possible (Berta et al. 2012). Although the
expected temperature in the upper atmosphere is too high for ice formation ($\approx$500 K) (Miller-
Ricci Kempton et al. 2012), if the atmospheres of exoplanets with lower temperatures are to be fully understood laboratory data is needed over a wide range of wavelengths, temperatures and particle size. Here we present the first laboratory far-infrared spectra of water ice in the aerosol phase.

**Experimental**

The aerosols were generated using an enclosive flow cooling (EFC) cell (Bauerecker et al. 2001), shown schematically in Figure 1. A number of studies using this type of cell have demonstrated the distinct spectral properties of aerosol particles in the mid-IR region (Bauerecker 2005; Kunzmann et al. 2001; Medcraft et al. 2009; Robertson et al. 2009; Taraschewski et al. 2005; Signorell et al. 2003). Our cell has now been coupled to the Bruker IFS125HR spectrometer at the Far Infrared and High Resolution Infrared beamline of the Australian Synchrotron. The synchrotron provides a continuous source of light that is brighter than thermal sources and results in spectra with improved signal to noise ratio in the far-IR region. By selecting suitable optical components nearly the entire infrared region is presently accessible (10 – 8000 cm⁻¹). The present far IR experiments used a 6 μm mylar beamsplitter, high density polyethylene (HDPE) or polymethylpentene (TPX) windows, with a silicon bolometer detector to measure spectra in the range 50 – 380 cm⁻¹. For the mid IR region (700-4000 cm⁻¹) a mercury cadmium telluride detector, KBr beamsplitter, and KBr cell windows were used. Wavenumber calibration is accurate to within 10⁻³ cm⁻¹. The multi-pass cell has a White design (Bauerecker et al. 2001), with optical pathlength set to 5-7.5 m (up to 20 m maximum pathlength). It contained gas (N₂ or He, see table 1) in thermal equilibrium with the inner cooling cell wall to serve as a buffer and cool the sample via inelastic collisions. Heating was controlled via three heaters on the inner cylinder and two on the mirrors (see Figure 1) and temperature measured via five separate thermocouples (K-type) mounted on the inner cylinder and mirrors as well as one rhodium-iron thermistor (for liquid helium temperatures). The coolant around the outer cylinder was either liquid He, liquid N₂, or preheated N₂ vapour continually flowing from a liquid bath, see Table 1.

A diluted sample of water vapour was prepared by filling a reservoir containing distilled liquid water and heated to 50 °C with ~3 atmospheres of carrier gas (He or N₂). A one-second pulse of this warm, wet sample gas at 270 kPa (~400 mL) was injected into the central zone of the multi-pass cell containing the cold bath gas (He or N₂). Under these conditions, the sample is cooled rapidly via inelastic collisions with the bath gas until the water becomes
supersaturated and particles begin to nucleate. Particle formation has been found to occur rapidly (< 1 s), e.g., by use of rapid-scan IR spectroscopy (Bauerecker et al. 2007) and to produce spherical nanoparticles (Bauerecker et al. 2007) of crystalline ice (Buch et al. 2004). Spectra were measured at 1 or 2 cm\(^{-1}\) resolution, over a period up to 5 minutes, depending on the lifetime of the aerosol. Table 1 contains a summary of the experimental conditions used to measure the spectra at different temperatures.

Figure 1: Schematic diagram of experimental setup.
Table 1: Summary of Experimental Conditions and Results

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<th>Error in TO Peak position (cm⁻¹)</th>
<th>Max Abs</th>
<th>LA Peak Position (cm⁻¹)</th>
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<th>Bath Pressure (mbar)</th>
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Results

The spectra measured at different temperatures are shown in Figure 2. Sharp rotational lines from water monomers are visible only at temperatures at and above 173 K. The broader absorption features near 44 µm (≈ 230 cm⁻¹) and 62 µm (≈ 160 cm⁻¹), evident in all the spectra, result from intermolecular vibrations (crystal lattice modes) where the water molecule as a whole translates with respect to neighbouring molecules (Bertie 1968; Bertie & Whalley 1967). These features are due to the transverse optical mode and the longitudinal acoustic mode, respectively. Their appearance and position provide clear evidence that crystalline rather than amorphous ice is formed at all temperatures down to 5 K. The spectrum of amorphous ice has only one distinct maximum that for a given temperature is found around 10 cm⁻¹ lower than the 230 cm⁻¹ band of crystalline ice (Moore & Hudson 1992). The production of crystalline ice under conditions of rapid collisional cooling contrasts with earlier thin film experiments in which slow deposition of water on a surface in
a high vacuum environment results in the formation of amorphous ice at temperatures below 110 K (Moore & Hudson 1992).

Figure 2: Far-IR spectra of water ice aerosol at various bath gas temperatures. At temperatures above 78 K the carrier and bath gas is N$_2$, below 78 K it is He. For a full set of experimental conditions for each spectrum see Table 2. Artefacts around 300 cm\(^{-1}\) seen in the spectra below 78 K are due to absorption by TPX windows. These spectra have been scaled by a factor of 7 relative to the higher temperature spectra.

Distinguishing the hexagonal (I\(_h\)) or cubic (I\(_c\)) forms of ice is not so straightforward. Their mid-IR spectra are identical (Devlin & Buch 2003; Bauerecker et al. 2007) and the far-IR spectra are very similar (Bertie & Whalley 1967), except for the subtle difference reported by Bertie & Jacobs (1977) that in hexagonal ice the 160 cm\(^{-1}\) band appears as a barely resolved doublet at 4 K. The apparent absence of such a doublet in the spectra of Figure 2 suggests the cubic form but is hardly conclusive. However electron microscopy (Delzeit & Blake 2001) and electron diffraction studies on ice formed in supersonic expansions (Bartell 1996; Bartell...
Huang 1994; Huang & Bartell 1995) have shown that cubic ice is kinetically favoured over hexagonal ice. Cubic ice has a much lower interfacial free energy which reduces the barrier for formation of cubic ice cores, resulting in a much higher nucleation rate than that of hexagonal ice (Buch et al. 2004). For small ice crystals (<15 nm) there is also a thermodynamic preference for cubic ice (Johari 2005). For larger cubic ice crystals an irreversible conversion to hexagonal ice can occur when above 170 K, however it is extremely slow (Hallbrucker & Mayer 1987; Starr et al. 2003). We can therefore safely assume that all our particles are cubic ice, at least for the particles below 180 K.

In Figure 3, the variation of peak position with temperature in this work is compared with earlier studies. The trend of peak wavenumber value decreasing with temperature is observed in all the studies, but our data is in disagreement with the majority of the published literature values in having peak positions consistently higher by ~4 cm$^{-1}$ for all but the coldest temperatures. The temperature dependant intensity ratio of 44 µm to 62 µm bands (see Table 1) is also inconsistent with the data in Figure 3b of Moore et al. (2001).

Temperature

The general temperature dependence can be explained by the contraction of the hydrogen bonds between molecules as the volume of the crystalline unit cell decreases with temperature (Dougherty 1998). The reduction of absorptions occurring from thermally excited lattice energy levels also influences this shift in peak position with temperature (Whalley & Bertie 1967). The hydrogen bond length is at a minimum at approximately 73 K. Below this temperature the intermolecular bond distance increases (Rottger et al. 1994), so the lattice vibrational modes might be expected to reflect this. Intriguingly, we do observe a levelling in the peak positions below 80 K. Both Moore’s and Schmitt’s data also show this, although it went unremarked and a linear trend line was fitted to their data. In contrast, Smith’s data appears to show no signs of this marked change in gradient. We note in caution that any traces of nitrogen gas introduced along with the helium in the experiments below 30 K could condense onto the particle surfaces and could have some effect on the spectrum. In the mid IR (2600 – 3800 cm$^{-1}$) a red shift of the dangling O-H band of about 20 cm$^{-1}$ can be observed for the OH-stretch band complex of water particles due to N$_2$ adsorption; the band centre region is apparently not affected (Hujo et al. 2011; Sadlej et al. 1995; Devlin et
al. 1994; Rowland et al. 1991). In the present experiment we have no evidence for the
presence of N₂ impurity.

At temperatures lower than 20 K our data show a further slight increase in peak wavenumber
value with decreasing temperature. These low temperature spectra (<20 K) provide the only
points that agree with the earlier literature values from Smith et al. (1994) and Bertie &
Jacobs (1977) who used samples of powdered ices to obtain a peak maximum of 233 cm⁻¹ at
4 K. However, in our experiments at these coldest temperatures the small particle size (see
Figure 4) becomes a critical consideration which has more bearing on the observed spectral
changes than the direct effect of temperature on crystalline ice.

![Figure 3: Peak maximum position vs temperature for the transverse optical (TO) and
longitudinal acoustic (LA) lattice modes of crystalline ice and the single peak
maximum from amorphous ice. Error bars on our data are estimates of the
temperature deviation during the experiment and the uncertainty of the peak centre
due to noise. The other peak positions were obtained from tables presented in Smith et
al. (1994, series III), Moore et al. (2001, series b), Schmitt et al. (1998), Bertie &
Whalley (1967) and Bertie & Jacobs (1977).]

**Particle size**

Particle size is limited by the amount of available water and the nucleation rate, which in turn
depend on temperature and bath gas pressure. In order to help interpret the far-IR data we
performed a similar set of experiments in the mid-IR region. This region provides a number
of markers that allow estimation of particle size; these include short wavelength scattering, the ratio of absorption intensity of surface to bulk molecules, and the shape of the H-O-H bending mode absorption (Buch et al. 2004). Estimates of particle size shown in Figure 4 and Table 1 were based on the integrated intensity ratios of the dangling-OH and bonded-OH bands: the relation to particle size is expressed in figure 11 of Buch et al. (2004). The formation of smaller particles at colder temperature is attributed to a greater nucleation rate as the water vapour becomes more supersaturated.

Figure 4: Plot of the estimated particle size vs temperature, with size calculated from mid-IR spectra measured using equivalent experimental conditions of temperature and buffer gas pressure to those used for far-IR measurements. The error bars are 20% of the particle size, estimated from the propagation of errors in the measured integrated intensities of the mid-IR bands. Number of molecules is calculated assuming particles are spherical and have the density of bulk ice at each temperature.

Different spectral effects become significant for particles at large and small size scales. With smaller particles the contribution of the more disordered surface (and subsurface) layer of water molecules is increasingly evident. In the mid-IR region, the onset of spectroscopic change occurs at a particle diameter of around 3 – 4 nm (Buch et al. 2004). As the size is reduced even further, the OH stretch modes are blue-shifted towards the peak absorption of amorphous ice (ca. 3304 cm\(^{-1}\) at 10 K (Hudgins et al. 1993). The effect on the collective translational motions of the far-IR lattice modes is less predictable. The more strained and disordered intermolecular H-bonding network in smaller particles might be expected to reduce the vibrational wavenumber values, again towards the peak absorptions for amorphous ice, but it appears from Figure 3 that this is not the case. In our experiments the 3 nm size threshold is reached at ca. 30 K. Below this temperature, the particles decrease to \(\approx\)1 nm position while the band centre rises by 2 cm\(^{-1}\).
We deduce that above 30 K, the ice aerosol particles are large enough so that surface effects only marginally influence the spectra, compare Figure 4 and Buch et al. (2004), but also small enough to be entirely free of scattering which becomes significant as the particle dimensions approach $\lambda/2\pi$ (i.e. 7 $\mu$m for the 230 cm$^{-1}$ band). Thus, the measured aerosol spectra depend only on the purely absorptive component which is governed by the imaginary component of the refractive index, $k$, and not on scattering which is related to the real component, $n$.

**Comparison with thin film spectra**

Clapp et al. (1995) point out some of the reasons why thin film spectra deposited on infrared transparent substrates may differ from aerosol spectra. One consideration is the reflections that occur at substrate/film/vacuum interfaces. These depend on the real ($n$) and imaginary ($k$) refractive indices of the materials and on the film thickness. Figure 5 illustrates one aspect of this - the effect of film thickness. Simulated absorption spectra are shown for crystalline water ice films of different thicknesses in vacuum, based on equations (2)-(4) of Hudgins et al. (1993). The film thickness may be characterised by the parameter $\beta = 4\pi h/\lambda$ where $\lambda$ is the wavelength at which $k$ is a maximum. In the thick film limit where $\beta >> 1$ the absorbance spectrum, and the peak width and peak maximum are most similar to the plot of $k$, but as $\beta$ approaches a value of 1 the peak maximum is shifted to lower wavenumber (higher wavelength) due to the sharp change in real refractive index, $n$, that occurs in the vicinity of a strong absorption band. This trend accords with the slightly higher wavenumber values at temperatures over 80 K obtained by Moore et al. (2001) for a film estimated to be 7.2 $\mu$m thick when compared to “series III” of Smith et al. (1994) with film thickness estimated at 2.9 $\mu$m. However, it appears unlikely that this effect can account for the further blue-shift in peak maxima for the aerosol data compared to the thin film data that is evident in figure 3.

Other possible causes of differences between film and aerosol spectra cited by Clapp et al. (1995) include the difficulty of producing films of uniform structure and composition, and without crystal defects. There is evidence that deposition of material on a substrate can favour amorphous rather than crystalline phases, e.g. in the case of CO (Dartois & Bauerecker 2008), or even inhibit formation of a crystalline phase entirely as in nitric acid trihydrate (Berland et al. 1994). The reason may be due to the cooling velocity during the
condensation and desublimation processes being normally much higher in the case of film deposits.

Figure 5: Absorbance curves (solid lines) calculated for crystalline water ice of three different film thicknesses, \( h \), in vacuum without substrate, from refractive index data at 136 K (Curtis et al. 2005). The parameter \( \beta = 4\pi h/\lambda \), where \( \lambda \) is the wavelength at which \( k \) is a maximum. The calculated absorbance maxima are 0.064 (for \( \beta = 0.1 \)), 0.49 (for \( \beta = 1.0 \)) and 4.6 (for \( \beta = 10 \)), but they have been rescaled and vertically offset for ready comparison with the trace of imaginary refractive index component, \( k \) (dotted line).

Other Factors

We note that the mid-IR spectra showed a trace of CO\(_2\) indicating some contamination by air. However, this cannot account for the observed blue-shift compared to thin film spectra. Above ~90 K CO\(_2\) (and also N\(_2\) and O\(_2\)) is still in the gas phase so is unlikely to be incorporated within or on the surface of the ice particles. Below this temperature CO\(_2\) might have co-condensed with the water (Taraschewski et al. 2005) but this would be expected to cause a \textit{red} shift in the band position (Moore & Hudson 1994). We have also performed separate experiments where pure CO\(_2\) was injected into the cell at varying time delays to the water sample injection and no shift in the far-IR water bands was observed.

Conclusions

The far-IR spectra of water ice aerosol particles measured as part of this study have revealed some interesting and very significant results that may have an impact on future modelling of complex astrophysical and atmospheric systems. First, it is clear that crystalline ice is formed at all temperatures under conditions of the rapid collisional cooling, with no evidence of
amorphous ice that is seen with slow vacuum deposition below 110 K. Second, at all but the
coldest temperatures (below 40 K) the lattice mode bands in the aerosol particle spectra are
blue-shifted by ca. 4 cm\(^{-1}\) compared to those of thin films. This has implications for the
potential use of the peak maximum as a temperature gauge: a 4 cm\(^{-1}\) shift is equivalent to a
temperature change of ca. 60 K. Third, the present results along with those of other groups
(Moore et al. 2001; Schmitt et al. 1998) hint at a change in the gradient at around 80 K,
possibly associated with a minimum in the hydrogen-bond distance at 73 K (Rottger et al.
1994). Fourth, the spectra of aerosol particles in the nm size regime, being free of scattering
effects associated with the real component of the refractive index, provide a means to
evaluate the wavelength and temperature dependant imaginary refractive indices. Usually the
real (\(n\)) and imaginary (\(k\)) components are correlated parameters that must be determined by
iterative calculation through Kramers-Kronig analysis that relies on the film thickness being
accurately known (Hudgins et al. 1993, Iwabuchi & Yang, 2011).

Given that water ice particles occur in the atmospheres of solar planets and their satellites, it
is essential to characterise the size dependence and the considerable temperature dependence
(Iwabuchi & Yang, 2011) of their mid and far IR spectra in relation to potential observation.
However, it is also important to be able to distinguish pure water particles from water coated
dust particles such as are found in regions of interstellar molecular clouds characterised by
high atomic H abundances, where the small molecules that form polar ices are dominated by
H\(_2\)O (Burke & Brown 2010). Spectral simulations for such heterogeneous particles
(Prokopjeva et al. 2007), or indeed for water ice in other forms such as Martian polar CO\(_2\)
and H\(_2\)O frosts (Johnson & Atreya 1996) must rely on accurate optical constants. Surveyed
across the electromagnetic spectrum, these optical constants are most uncertain in the far IR
region (Warren & Brandt 2008). Further studies will be directed towards rationalising the
observations made here, extracting optical constants and extending the study of temperature
and size effects to the mid-IR region.

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