Water ice nanoparticles: size and temperature effects on the mid-infrared spectrum

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Mid-infrared spectra have been measured for cubic ice ($I_h$) nanoparticles (3–150 nm diameter) formed by rapid collisional cooling over a wide range of temperatures (5–209 K). Spectral diagnostics, such as the ratio of surface related dangling OH to interior H-bonded OH stretch bands, reveal the manner in which particle size depends on bath gas temperature and density, and on water molecule concentration. For particles smaller than 5 nm strained intermolecular bonds on the surface and subsurface cause the predominant OH stretch peak position to be dramatically blue shifted by up to 40 cm$^{-1}$. In the size regime of 8–200 nm the position of the OH stretch absorption band maximum is relatively unaffected by particle size and it is possible to measure the temperature dependence of the peak position without influences from the surface or scattering. The band maximum shifts in a linear fashion from 3218 cm$^{-1}$ at 30 K to 3253 cm$^{-1}$ at 209 K, which may assist with temperature profiling of ice particles in atmospheric clouds and extraterrestrial systems. Over the same temperature range the librational mode band shifts very little, from 870 to 860 cm$^{-1}$. In the water stretching and bending regions discrete spectral features associated with the surface or sub-surface layers have been detected in particles as large as 80 nm.

1. Introduction

Molecular ices play an important role in interstellar and atmospheric chemical processing where they can act as a reaction medium.1,2 Their physical and chemical properties vary greatly with composition, with temperature and with particle size – the large molecular aggregates found in aerosols can behave very differently from the corresponding bulk material.3 The interactions of such aerosols with infrared radiation are significant in two major contexts. Firstly, radiative processes associated with emission and extinction are fundamental to energy transfer and considering blackbody radiation curves the IR region in particular is central in non-stellar environments such as planetary and interstellar clouds where temperatures are moderate. Secondly, infrared spectroscopy is uniquely suited to remotely probing the properties of these ices, including their temperature, and particle characteristics. Accurate laboratory data is essential to interpret such measurements.

The effect of temperature on the infrared spectrum of these ices is often inferred from laboratory studies on films of ice deposited on a substrate where the thickness of the film can be easily controlled and measured,4–7 but the spectra of such films often differ from those of aerosol particles. Films that are thin enough to allow sufficient optical transmission are affected by the reflections that occur at substrate/film/vacuum interfaces, which depend on both the real $(n)$ and imaginary $(k)$ refractive indices of the materials.8 Other reasons cited for these differences include the difficulty of producing thin films of uniform structure and composition, and without crystal defects.9 Measurements in the aerosol phase eliminate these influences and allow for investigations on how the spectrum changes with particle characteristics such as size and shape.

Experimental methods for the formation of these aerosols include collisional cooling,10 supersonic jet expansion,11,12 rapid expansion of supercritical solutions (RESS),13 acoustic levitation14 and electrospray.14b,c In this study water ice aerosols were generated using an enclosive flow cooling cell, which is thoroughly described elsewhere.15–17 This type of cell has been used previously to investigate the influence of temperature on aerosols of CO and CO$_2$,17 N$_2$O,18,19

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dihydroxyacetone\textsuperscript{20} and small hydrocarbons,\textsuperscript{21–23} revealing that the effective “phase diagram” for aerosol formation can be very different from that of bulk material in thermal equilibrium. The size and shape of particles of NH\textsubscript{3} (and deuterated isotopomers), NH\textsubscript{3}/CO\textsubscript{2},\textsuperscript{24} CO\textsubscript{2},\textsuperscript{25} N\textsubscript{2}O,\textsuperscript{26} fluoromethane\textsuperscript{27} and acetylene\textsuperscript{28} has also been studied. Similar effects have been investigated in binary particles of 13CO\textsubscript{2}/12CO\textsubscript{2},\textsuperscript{29,30} D\textsubscript{2}O/H\textsubscript{2}O\textsuperscript{31} and CO\textsubscript{2}/SO\textsubscript{2},\textsuperscript{32} O\textsubscript{3}/HCl\textsuperscript{33} HCl/NH\textsubscript{3}\textsuperscript{34} and CO\textsubscript{2}/H\textsubscript{2}O.\textsuperscript{35–36} Finally the nucleation and temporal evolution of particles have also been examined for particles of H\textsubscript{2}O\textsuperscript{37} CO\textsubscript{2}/H\textsubscript{2}O\textsuperscript{38} and O\textsubscript{3}/HCl\textsuperscript{33}

Water ice is of particular interest because of its ubiquity. In the context of earth’s atmosphere and climate, the formation of water ice aerosols produces high altitude cirrus clouds. In this work we examine the effects of size and temperature on the mid-IR spectrum of water nanoparticles. A study on much larger aerosol particles (\(\approx 1\ \mu\text{m}\) diameter) at temperatures of 130–210 K extracted refractive indices from aerosol particle spectra.\textsuperscript{3} This was done by scaling the absorptive (imaginary) component directly to the spectra of clusters with diameter \(\approx 600\ \text{nm}\), a size considered small enough for scattering to have a limited effect. The real component was obtained through Kramers–Kronig analysis of larger particle spectra affected by scattering. Similar enhanced studies have been performed in the very large close-to-reality AIDA aerosol and cloud chamber for a higher size range up to 15 \(\mu\text{m}\),\textsuperscript{38,39} with among other things the goal to examine the influence of particle aspect ratio on the mid-IR extinction spectra.\textsuperscript{63} Further analyses were used to extend the temperature range to 230 K for ice and 273 K for liquid and supercooled liquid water.\textsuperscript{40,41} It is worth mentioning that water ice aerosols differ considerably from liquid and supercooled liquid water aerosols in their mid-IR spectra.\textsuperscript{41} The temperature dependence of these refractive indices has been used to remotely determine the temperature of ice in Earth’s mesosphere where particle sizes are \(< 200\ \text{nm}\).\textsuperscript{42–44}

On a size scale that is smaller still (\(< 20\ \text{nm}\)), a number of studies\textsuperscript{35–50} have shown that reduced particle size can have a dramatic influence on the shape and position of absorption bands, particularly for the OH stretching modes. In the spectra of collisionally cooled particles, the most dramatic changes are seen for diameters less than 4 \(\text{nm}\), as the sharp band at around 3220 \text{cm}^{-1} associated with crystalline ice begins to diminish.\textsuperscript{50} In a study on mass selected sodium doped water clusters Pradzynski and co-workers\textsuperscript{51} observed a change in the spectrum at \(n \approx 275\) (2.5 nm diameter) attributed to the onset of a crystalline core. This core is believed to be surrounded by disordered 4 coordinate molecules in a subsurface and 3 coordinate on the surface.\textsuperscript{50} Spectral features from the subsurface and surface are still evident in the IR spectrum for clusters as large as 100 000 molecules.\textsuperscript{52} The onset of crystallinity was estimated in an electron diffraction study by Torchet to be between \(n = 200–1000\).\textsuperscript{53}

In this work we have measured the mid-IR spectrum (750–8000 cm\textsuperscript{1}) of water ice aerosols over a wider range of temperatures (5–209 K) in a size regime (3–100 nm) where scattering effects are negligible, and where the onset of vanishing crystalline behaviour may be observed for particles smaller than around 5 nm. This work complements a related study in which the far IR spectra of ice aerosols formed under similar conditions showed shifts in the position of the intermolecular translational mode near 230 cm\textsuperscript{1} compared to thin film spectra.\textsuperscript{8}

In thin film experiments slow surface deposition of water in a high vacuum environment results in the formation of amorphous ice at temperatures below 110 K.\textsuperscript{54} In contrast, the present mid IR spectra and comparable far IR spectra\textsuperscript{5} provide evidence that collisional cooling produces crystalline ice even down to 5 K. Particle formation has been found to occur rapidly (\(< 0.1\ \text{s}\)) and to produce spherical particles of cubic ice (I\textsubscript{c}).\textsuperscript{37,50} At higher temperatures (>170 K) a transition to the hexagonal phase is possible, however the mid-IR spectra of cubic (I\textsubscript{c}) and hexagonal (I\textsubscript{h}) are identical.\textsuperscript{55} Electron diffraction\textsuperscript{36–58} and electron microscopy\textsuperscript{59} studies on ice formed in supersonic expansions show the cubic ice is kinetically favoured over hexagonal. There is also a thermodynamic preference for cubic ice when particles are smaller than 15 nm.\textsuperscript{60} More recent molecular dynamics\textsuperscript{61} and X-ray diffraction studies\textsuperscript{62} have shown that ice formed from supercooled liquid water is actually a hybrid form of ice I with stacked cubic and hexagonal layers. Further molecular dynamics work suggests that this is also true for water nanoparticles at atmospherically relevant temperatures 150–200 K,\textsuperscript{63} and suggest that purely cubic ice may be formed only rarely under special conditions. It is quite possible that some of the “cubic” ice particles formed in this and previous studies are hybrid instead.

2. Experimental

A gaseous mixture of water and carrier gas was prepared by filling a vacuum chamber containing distilled water kept at 50 °C with \(\approx 3\) atmospheres of carrier gas (He or N\textsubscript{2}). A one second pulse of this wet gas at 2.7 atm was injected into the cell containing bath gas (He or N\textsubscript{2}) at a set temperature. The final concentration of sample in the carrier gas is difficult to quantify however it was found to be reproducibly constant throughout the experiments. Based on vapour pressure data we estimate the concentration to be of the order of 0.1–1%. The plume of sample gas is cooled rapidly \textit{via} inelastic collisions with the bath gas until the water becomes supersaturated and particles begin to nucleate.

The temperature and pressure of the bath gas was varied using a combination of different coolants and heaters inside the cell. Temperatures in the range of 4–40 K were obtained with liquid helium as the coolant; at these temperatures evacuating the cell between samples was impossible due to cryopumping. Once the liquid helium had evaporated the spectra at intermediate temperatures (40–77 K) were recorded as the cell warmed up. Between 77 K and 160 K liquid nitrogen was used and above 160 K a flow of cold N\textsubscript{2} gas was used to provide greater temperature stability.

We have recently coupled this cell to the Bruker IFS125/HR spectrometer at the Far Infrared and High Resolution Infrared beamline of the Australian Synchrotron. By selecting various optical components nearly the entire infrared region is accessible (10–8000 cm\textsuperscript{1}). In this work we used the instrument’s internal
source (tungsten lamp) with KBr windows and beamsplitter and an MCT detector to obtain spectra from 750–8000 cm\(^{-1}\). This allowed for the simultaneous measurement of the fundamental vibrational modes of water as well as the intermolecular librational mode \(\approx 800\) cm\(^{-1}\) whilst still having sufficient sensitivity to observe any scattering at high wavenumber.

The spectra that are presented in Section 3.6 and some data points in Fig. 7 were recorded using an identical cold cell located at the Technische Universität Braunschweig on a Nicolet Magna 550 FTIR spectrometer equipped with a Globar light source, a KBr beamsplitter, KBr windows and an external InSb detector.

3. Results and discussion

3.1 Temporal evolution

Sample spectra at 4 cm\(^{-1}\) resolution were recorded continuously every \(\approx 0.8\) seconds (0.4 s to record and a 0.4 s wait between spectra) as the water was injected and for about 3 minutes afterwards. These were ratioed against a reference background spectrum recorded with only the cold bath gas in the cell. The absorbance in the OH-stretching region was seen to grow to a maximum over a period of approximately 2 s and then slowly decay as the particles diffuse out of the optical path. After the maximum is reached the peak location shifts to slightly lower wavenumber, at most by \(\approx 5\) cm\(^{-1}\). This shift may be due to the particles growing in size\(^{48}\) (see Section 3.4) or due to the continued cooling of the particles (see Section 3.3). No further shift occurs after approximately 4 seconds indicating that the particles have ceased changing size or temperature. The spectra presented here are averages of scans recorded after the initial shift whilst the absorbance slowly decreased. With changing temperature and pressure of the bath gas the most significant change of the temporal evolution profile was in the lifetime of the particles.

3.2 Temperature series

Fig. 1 shows the OH stretching region for particles formed in various bath gas temperatures. The appearance in the warmer spectra of a central peak with two shoulders is characteristic of the OH stretching modes in bulk crystalline ice, and these features have been interpreted through a collective oscillating dipole model.\(^{48}\) The central peak becomes sharper and shifts to lower wavenumber value as the temperature is reduced due to the reduced population of low frequency vibrational modes. Below 30 K however the central peak becomes less dominant while the signal from the dangling-OH band shows a marked increase; this is due to a decrease in particle size as well as nitrogen adsorption (see Section 3.4). Above 174 K rovibrational lines associated with the water monomer are increasingly evident. The dangling OH band that is visible below this temperature may be present at higher temperatures but if so it is obscured by the monomer lines.

At the bottom of Fig. 1 is a schematic representation of the molecular origin of the evolving band profile which is valid for small particles (\(< 4\) nm\(^{47,50,51}\)). The central peak originates from the concerted vibrations of 4-coordinate molecules in the core of the particles; the high wavenumber shoulder is from surface molecules with ‘dangling’ oxygen atoms that are double H-bond donors but not double acceptors. The low wavenumber shoulder originates from the hydrogen bonded side of single donor surface molecules whilst the small peak near \(3700\) cm\(^{-1}\) is due to the corresponding non H-bonded, ‘dangling hydrogen’ vibration.\(^{50}\) Particularly in the realms of small water cluster studies these vibrations of single H-bond donor water molecules are also known as ‘free OH’, not to be confused with the symmetric and antisymmetric OH stretch fundamentals of free (unbound) water monomers. These trends in the OH stretch modes of incompletely coordinated surface water molecules are evident even in clusters as small as 8 water molecules.\(^{64}\)

3.3 Temperature dependence

The relationship between central peak position and temperature is summarised in Fig. 2. A general trend is seen in our data and the literature values where the peak position shifts to lower wavenumber at lower temperatures. Contraction of the intermolecular hydrogen bonds as the crystals cool weakens and lengthens the intramolecular bonds thus shifting the vibrational frequency lower.\(^{65,66}\) The thermal influence of lattice expansion or contraction also affects the extent of mode coupling and hence contributes to the shifts in band position.
An approximate trend line illustrates the temperature dependence in our data. The gradient of 0.20 cm$^{-1}$ K$^{-1}$ is somewhat greater than the ca. 0.12 cm$^{-1}$ K$^{-1}$ seen for the Raman OH stretch band of dilute HOD in D$_2$O where the thermal effect on mode coupling is removed.\(^6\)\(^7\)

Notably, our data is blue shifted by $\approx$ 10 cm$^{-1}$ compared to the literature values. Most of the literature values in Fig. 2 (unfilled symbols) are from thin film studies where ice is deposited onto a substrate; thicknesses ranged from 0.1–0.9 $\mu$m. One reason for the discrepancy in peak positions is that films thin enough to allow sufficient optical transmission are affected by the reflections that occur at substrate/film/vacuum interfaces. As film thickness, $h$, is reduced to around $\lambda/4\pi$ 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.\(^8\)

The higher peak wavenumber position in our aerosol spectra might suggest the particulate ice has some amorphous character, given that the peak of amorphous ice is also found at considerably higher wavenumber value, ca. 3304 cm$^{-1}$ at 10 K.\(^7\)\(^1\) However, this possibility is ruled out by consideration of the translational mode in the far IR spectrum, where the 4 cm$^{-1}$ blue-shift for aerosol spectra is in the opposite direction to that expected for amorphous ice.\(^8\) The same argument holds for the librational mode region discussed later in Section 3.7.

The series of points from Clapp et al.\(^7\)\(^2\) were obtained from a flow through aerosol chamber instead. The particles are said to nucleate at 130 K and then flow into a secondary region where they are warmed to each of the temperatures shown. The particles are stated to be “around 0.3 $\mu$m in radius” and were assumed to be small enough for the scattering contribution to be minimal. However, scattering of light with wavelength $\lambda$ is significant for particles with dimensions approaching $\lambda/2\pi$,\(^7\)\(^3\) which at 3230 cm$^{-1}$ (3.1 $\mu$m) implies sizes of $\approx$ 0.5 $\mu$m. This is also the approximate threshold for a size effect on the absorptive component, as the dipoles spanning the width of the particle can no longer oscillate in phase and the absorbance becomes non ideal. Discrete dipole simulations that account for both scattering and absorption indicate that spherical water ice particles of diameter 0.6 $\mu$m have their OH stretch peak red-shifted ca. 8 cm$^{-1}$ compared to those of diameter 0.2 $\mu$m.\(^7\)\(^4\) As our particles are more than 10 times smaller we can be much more confident that they are free of such effects.

### 3.4 Determining particle size

Bath gas temperature affects not only the characteristic IR absorption of the material, but also the size of the particles that are formed. As a consequence, the two coldest spectra from our data set in Fig. 2 have peaks blue shifted by $\approx$ 30 cm$^{-1}$ from the general trend. To help interpret this shift and explore size dependence in the IR spectra, spectral features shown in Fig. 3 were used to estimate the particle dimensions.

First, the wavelength dependence of long wavelength scattering allows for an estimation of the particle sizes. Discrete dipole simulations\(^7\)\(^5\) show that particles larger than 600 nm exhibit significant scattering at 4000 cm$^{-1}$. At higher temperatures we observed a very slight increase in the baseline around 8000 cm$^{-1}$ and at this wavelength (1.25 $\mu$m) scattering becomes significant ($\lambda/2\pi$) for particle diameters of $\approx$ 200 nm (see Fig. 3a), setting an upper bound on the average particle size. Second, at temperatures below 174 K the spectra show evidence of the OH dangling bond at $\approx$ 3700 cm$^{-1}$ (Fig. 3b). The integrated area of this band is roughly proportional to surface area whilst the area of bonded OH band is proportional to volume. The ratio of these two bands can therefore be used to estimate the average particle size via an empirical relationship.\(^7\) Third, some of these estimates were confirmed by comparing spectra to those of 2–20 nm ice particles in the H–O–H bending region (Fig. 3c).\(^7\)\(^6\) We assume that our particles have a log-normal size distribution\(^7\)\(^7\) and the estimates in Fig. 4 are the mean particle size of this distribution.

Nitrogen that is adsorbed on the particle surface enhances the intensity of the dangling-OH bands, which must be accounted for when estimating particle size. This enhancement factor is 2–3 for particle diameters <3 nm and 1.5–2 for 4–10 nm particles (see Fig. 16 in ref. 50). When N$_2$ is adsorbed it also
causes a ≈ 20 cm$^{-1}$ red shift in the d-OH band$^{73,74}$ which was observed in a number of our spectra below ≈ 45 K. It is assumed that N$_2$ was introduced along with the sample as trace amounts of air; only very small amounts of CO$_2$ were observed < 0.01 absorbance in the ν$_3$ region. The low temperature size estimates in Fig. 4 incorporate the appropriate “self-consistent” d-OH enhancement factor, and the comparatively large uncertainty that is shown for those points reflects the uncertainty in the enhancement factor. These estimates are in accordance with a recent study where ab initio calculated spectra have been compared to experimental spectra resulting in an enhancement factor of 3–4 for small water particles.$^{74}$ Despite this it is clear that the strongly blue-shifted spectra observed at the coldest temperatures result from particles of around 2–5 nm where surface effects become very important (see Fig. 12 in ref. 50).

### 3.5 Bath gas concentration

The solid data points in Fig. 4 show the particle size at various temperatures where the bath gas density was equivalent. The unfilled squares are from particles formed with varying bath gas concentration. The size of particles produced in this cell is dependent on the degree of supersaturation of water vapour as it nucleates, which in turn depends on the bath gas temperature. Increasing temperature leads to decreased nucleation rate and larger particles. With sample amount and bath gas concentration kept constant, the correlation between size and temperature shown by the solid black data points in Fig. 4 is very strong.

It is also clear from the hollow data points of Fig. 4 that bath gas concentration has a controlling variable along with temperature. Fig. 5 shows spectra taken over a range of different bath gas concentrations at three different temperatures. The spectra taken around 5 K and 78 K both show an increase in particle size with increasing bath gas density. However the spectra taken at 154 K appear to show a maximum particle size at a density around 4 mol m$^{-3}$.

Clearly bath gas concentration has a dramatic influence on particle size. However the mechanism for particle formation is complicated by a number of confounding processes. The collision rate of sample gas to bath gas affects the cooling efficiency and diffusion rates which affect the degree of supersaturation and effective sample concentration upon nucleation. Once the particles are formed Brownian motion, agglomeration, deposition and evaporation rates (Ostwald ripening) are also likely to change with bath gas concentration. These processes are also influenced by temperature and particle size so a complete explanation on how bath gas density affects particle size is challenging. However we suggest that the most significant factor is how the plume of sample gas expands into the optical volume. When the bath gas concentration is high the plume of gas cannot expand as much as at lower densities although one has to consider the fast injection of sample gas as a merely turbulent process. The higher bath gas concentration could result in a higher local availability of water so particles are able to grow larger. The increase in intensity with bath gas concentration also suggests that more sample gas is retained in the optical volume at higher bath gas concentrations. Evaporation becomes more significant at higher temperatures and may be responsible for the more subtle trend seen at 154 K. Brownian motion driven agglomeration of bigger particles needs a quasi-liquid layer on the surface of the particles which occurs at temperatures > 245 K.$^{75,76}$ This is well above the highest temperatures used in this study. So we regard this process as unlikely to play a significant role here.

The band shapes in the 5 K spectra also change significantly with changing particle size. At 3.1 nm the band has no prominent central peak while at 3.9 nm this feature is easily apparent. The reason for this change is clear when one
considers the origin of the central peak coming from molecules in the core of the particles (see Fig. 1) and only ≈11% of molecules in 4 nm particles (110 of 1000 molecules) are located in the core. For smaller particles this core region becomes increasingly strained and less ordered becoming entirely amorphous for particles of £2.6 nm.

Fig. 5 also shows that the position of the peak absorption shifts with particle size at 78 K: there is a pronounced difference in the peak location of the 4.4 nm spectrum (3249 cm⁻¹) and the 7.0 nm spectrum (3228 cm⁻¹). In Fig. 2 the data points of the two coldest spectra show a similar large shift and are far above the general peak position vs. temperature trend. The average particle size for both of these is less than 5 nm (Fig. 4). The peak positions of the spectra taken at 154 K are all ≈3240 cm⁻¹ despite the large range of estimated particle sizes. This behaviour, which has been reported previously, is due to the lower sensitivity of peak position at intermediate particle sizes since the crystalline core dominates the spectrum.

### 3.6 Sample concentration

The concentration of water vapour in the input gas is also shown to directly affect particle size and consequently the spectra. Because the water concentration in the input gas is small for the whole sequence, the way in which the sample gas plume expands can be regarded as identical for all the spectra here, in contrast to the conditions of Section 3.5. Fig. 6 shows four spectra that were all recorded at 78 K and 32 mol m⁻³ of helium bath gas. The concentration of water in the input helium gas (100 ml at 2 bar prepressure, 50 ms pulse) was varied by diluting a given amount of pure water (about 0.01 ml adsorbed in a porous cellulose probe which was placed in a bypass parallel to the sample gas flow) via a constantly pulsed helium flow. The concentration of water vapour in the helium carrier gas for each spectrum is shown on the left of Fig. 6.

Decreasing the concentration of water vapour in the input gas produces a similar trend to that seen in the central panel of Fig. 5. At lower sample concentrations there is less water available for particle growth so therefore particles are smaller. This result supports our supposition that bath gas concentration influences particle size primarily by changing the local concentration of the sample gas.

### 3.7 Bending and libration modes

The bending mode near 1650 cm⁻¹ and librational mode near 850 cm⁻¹ are shown in Fig. 7. In the higher wavenumber region a sharp feature present near 1650 cm⁻¹ is superimposed on the broad band centred around 1600 cm⁻¹ which is attributed to mixing of the bend and librational overtone in crystalline ice. The sharp peak has been shown to originate from the (largely unmixed) bending mode of molecules on the surface and subsurface of particles; we observe this feature for sizes up to ≈25 nm. Despite the wide range of temperatures the band shape and position of the bending mode was found to be nearly identical to spectra of similar sized particles measured at 100 K.

The librational band was also observed to be insensitive to temperature. Only an indirect temperature effect is observed: colder temperatures lead to smaller particles and the librational band begins to shift to lower wavenumber position and become broader once the size is reduced beyond 7 nm, consistent with earlier results from small aerosols at 100 K. This is again due to the decrease in the crystalline core component and increasing amorphous character. For particles greater than 7 nm the peak position remains very consistent, shifting only slightly from 870 cm⁻¹ at 36 K to 860 cm⁻¹ at 209 K. Earlier thin film studies found this band maximum in cubic water to be 835 cm⁻¹ at 10 K and reduced to 817 cm⁻¹ at 140 K, or 837 cm⁻¹ at 20 K down to 825 cm⁻¹ at 150 K. The trend with temperature has a similarly small, negative gradient.
The significant difference (ca. 40 cm\(^{-1}\)) in band maximum between thin film and aerosol spectrum was noted in the previous aerosol work and attributed to the shape dependence of strong infrared bands of solids affecting the film spectra.\(^{46}\) The difference cannot be attributed to non crystalline material in the aerosol as thin films of amorphous ice have peaks at still lower wavenumber (754 cm\(^{-1}\) at 15 K to 805 cm\(^{-1}\) at 120 K).\(^{7}\) A recent analysis of mesospheric ice temperature drew on data from different studies encompassing aerosol and thin film spectra to infer a much stronger temperature dependence for this librational band of crystalline ice and obtain a linear coefficient of \(-0.7\) cm\(^{-1}\) K\(^{-1}\) between 120 and 235 K.\(^{43}\) That relationship is not tenable in the light of the present data, and the resultant cloud temperature determinations need re-assessment. While neither of these bands appear to be useful as a temperature probe they may help characterise particle size or phase.

### 3.8 Particle size effects

Different spectral effects become significant for particles at large and small size scales, see Fig. 8. With smaller particles the contribution of the surface layer of water molecules is increasingly evident. In both the bending and stretching regions, distinct and relatively sharp spectral features associated with three-coordinate molecules in the top-most layer are seen. In the bending region where this band is superimposed over the broad band from the interior, the surface layer peak is evident up to a size of \(\approx 25\) nm. In the OH stretch region a unique band from the ‘dangling OH’ groups around 3700 cm\(^{-1}\) is fortuitously well separated from the interior band profile so that it is detectable in particles up to 78 nm where the intensity ratio is 1 : 11 800.

The top-most layer has amorphous character, but the disorder is also considered to extend further into a subsurface layer. Devlin and co-workers\(^{50,78}\) have conducted investigations on the subsurface based on difference spectra coming (a) from different stages of Ostwald ripening in combination with retarded relaxation of subsurface and (b) from structure evolution of the nanocrystals caused by invasive adsorbates such as SO\(_2\). These methods rely on an experimental setup\(^{45}\) in which a grid of water ice nanoparticles stays stable enough to be observed for hours. In contrast, the aerosol particles in our experiments are freely suspended in the bath gas, which provides an advantage in removing interactions between particles or with a substrate but does have the disadvantage that particles tend to diffuse out of the optical beam area on a timescale of minutes. Neverthe-less, we were able to reproduce the results of Devlin in at least one respect: the 77–79 K spectra of particles with sizes ranging from 4.4–56 nm in Fig. 5, could be generated satisfactorily using different ratios of two derived component spectra; one associated with the core and one associated with the surface (or surface and subsurface).

In experiments performed at 78 K (see the solid square data points in Fig. 8), the position of the dominant band is constant at around 3226 cm\(^{-1}\) until particles shrink to a diameter of 5 nm. At this point the band undergoes a blue shift of \(\approx 25\) cm\(^{-1}\). These observations have been interpreted in terms of a threshold size which allows for the presence of a crystalline core that is sufficient to dictate the structure of the surface layer.\(^{50}\) As particle size is reduced even further, the more disordered state that results is characterised by weaker hydrogen bonds with greater O⋯O distances and more strained O⋯O⋯O angles, and the OH stretch modes are correspondingly blue-shifted towards the peak absorption of amorphous ice, \(ca.\) 3304 cm\(^{-1}\) at 10 K.\(^{71}\)

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**Fig. 8** Peak OH stretching wavenumber as a function of particle size. The squares are for spectra taken at the Australian Synchrotron in Melbourne, with the solid filled squares all recorded around 78 K. The triangles are for spectra recorded with an identical cell located in Braunschweig. Literature values are from Buch\(^{50}\) Bauerecker (experimental spectra and discrete dipole approximation (DDA) simulations)\(^{37}\) and Clapp et al.\(^{9}\) The three horizontal lines show the band positions expected for crystalline ice at 0 K, 80 K and 209 K from the trend line in Fig. 2.
The spectra obtained via IR excitation-modulated photoionization show a similar trend, although the wavenumber of the peak maximum already reaches \( \approx 3200 \text{ cm}^{-1} \) for the largest clusters measured (\( \approx 475 \text{ molecules}, 3.0 \text{ nm} \)) and that spectrum has a distinct second maximum at \( \approx 3550 \text{ cm}^{-1} \). In our smallest particle spectra the librational mode band is also shifted down towards the range of positions found in disordered solids at 10 K (763 \text{ cm}^{-1} for microporous amorphous ice or 810 \text{ cm}^{-1} for annealed amorphous ice \(^7\)).

In Fig. 8, the slight upward trend in OH stretch band position seen for intermediate sizes between 8 and 100 nm is solely due to the temperature variation as shown in Fig. 2. For sizes greater than \( \lambda/2\pi \) (\( \approx 500 \text{ nm} \)) scattering in the OH-stretching band region becomes increasingly important. This has the effect of red shifting the peak absorption by as much as 100 \text{ cm}^{-1}. For larger particle sizes the particle shape must also be taken into account as spherical particles may not be favoured for some formation conditions. For example the transition from a compact shape (spherical or cubic) to an elongated shape (5 : 1 hexagonal column) results in a blueshift of the band centre by more than 100 \text{ cm}^{-1} for water particles with a mean diameter of 1.6 \text{ \( \mu \)}m.\(^{37}\)

The trend in Fig. 8 is consistent except for some spectra around 5–8 nm. These spectra were all recorded at low bath gas concentration and show a strong but broadened central peak. This suggests the particles have a significant increase in core component which has some amorphous character, possibly due to the reduced cooling rate from the lower rate of bath gas collisions. The precise dynamics of this are currently uncertain and require further investigation; an increased time resolution may be required.

4. Discussion and conclusions

The mid infrared spectrum of water ice nanoparticles has been measured over a wide range of formation conditions using a long path collisional cooling cell. The results provide a coherent picture of two major direct influences on their spectroscopy: particle size and temperature. The former is in turn controlled by the sample gas and buffer gas concentrations and also by temperature. A size regime (8–200 nm) was found whereby the peak maximum positions of the OH stretching and librational modes were largely uninfluenced by particle size. This allowed for the measurement of the temperature dependence in the absence of scattering or surface effects. This happens to correspond to the size distribution found for mesospheric ice particles,\(^{42,43}\) which has been exploited to model ice spectra and thereby extract ice temperatures which are found to be in the 120–160 K range. However, those studies relied on imaginary refractive index constants, \( k \) derived directly from spectra of ice aerosols of around 600 \text{ nm} diameter.\(^9\) This present work (see Fig. 2) indicates that the previous data was shifted \( ca. 10 \text{ cm}^{-1} \) due to scattering from the moderately large sized particles. A shift of this magnitude, though apparently modest, corresponds to a temperature change of 50 K. The need to update the temperature dependant optical constants is clear.

This need is reinforced by the present results concerning the librational mode, which is found to be almost invariant with temperature over the range 36–209 K and therefore unsuitable for use as a temperature probe.

While it is clear that the spectra of “large” and “small” aerosol particles can be very different from bulk material (or in practice thin films), ironically enough suitable particle spectra can help to provide the most reliable optical constants for bulk material. But what is the “Goldilocks” zone of particle size most suitable for measuring spectra that reflects the purely absorptive component of crystalline ice? In the bending mode region the lower size limit would appear to be \( \approx 30 \text{ nm} \) in diameter where the sharper surface feature around 1650 \text{ cm}^{-1} finally peters out, but it may prove necessary to employ spectral subtraction to remove this persistent surface component. In the OH stretching mode region the peak maximum is consistent for sizes over 8 nm, but for a given temperature subtle changes in the overall band profile associated with the surface and subsurface layers continue until the size reaches 15 nm, see for example Fig. 5. The upper particle diameter limits are dictated by the wavelength dependant onset of scattering at sizes \( \approx \lambda/2\pi \), or more conservatively \( \lambda/4\pi \) corresponding to 250 nm for the OH stretch region, but 500 nm and 1 \text{ \( \mu \)}m for the bend and libration regions. In the context of obtaining the best optical constants, control of particle size may therefore prove to be very useful.

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