Infrared Spectra of Large H_2O Clusters: New Understanding of the Elusive Bending Mode of Ice

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Infrared spectroscopic data for large water clusters, ranging from ∼100 to 64 000 molecules, have been extended to the O−H stretch and bending mode regions of H_2O. The stretch-mode spectra and analysis parallel results reported recently for D_2O large clusters. Ambiguities in the current understanding of the bending region of the spectra of amorphous and crystalline ice are addressed using insights derived from the cluster infrared spectra and ab initio reduced-dimensionality models of ice and of the ice surface. The 1400−1700 cm^{-1} spectral range, for *annealed* amorphous ice and crystalline cubic ice at 10 K, is characterized by a broad absorption lacking distinct features assignable to water bending vibrations. The spectra suggest that the bend-mode intensity of the bulk ices is either inherently very weak, diffused through interaction with the librational overtone, or both. However, this is not the case for large water clusters, which display distinct and relatively narrow bands attributed to the bending modes of subsets of *surface* water molecules. The new computational results suggest a strong but irregular dependence of the bend-mode frequency and band intensity on the strength and tetrahedrality of the hydrogen bonding. The computed intensity does decrease substantially for 4-coordinated vs lower-coordinated waters, but the highest frequency corresponds to double-donor 3-coordinated surface water molecules. A significant decrease of the *librational-mode* frequency, for those cases for which hydrogen bonding is reduced relative to ice I, is known to reduce the overlap of the bending mode with the librational overtone. Thus, for liquid water, *microporous* amorphous ice and the ice surface, which deviate strongly from tetrahedral bonding and for which the hydrogen bonding is diminished, the bend-mode absorption assumes a more normal intensity and bandwidth. From this basis a qualitative interpretation is presented of the infrared spectra for the region from ∼500 to ∼2400 cm^{-1}.

Introduction

Vibrational spectra of condensed forms of H_2O have been studied extensively over the years, and still, there are various poorly understood aspects. One of them, the intramolecular bending and its interplay with libration, is addressed qualitatively in the present article. The bending band is clearly visible in spectra of liquid water and microporous amorphous ice at 1645 and ∼1670 cm^{-1}, respectively.[1,2] A similar band is not found in spectra of low-temperature crystalline ice;[3] rather, the pertinent spectral region contains a single very broad band, assigned to the libration overtone, but no clearly differentiated feature that can be assigned to bending. Just a trace of such a feature, superimposed on the libration overtone, is visible for well-annealed amorphous ice.[2]

Here, an attempt is made to clarify the issue by investigating bending spectra of water clusters as a function of size, in the size range of hundreds to thousands of water molecules. In this size range the clusters were shown to undergo a transition from amorphous structure to a structure characterized by a crystalline core and disordered surface. A rather striking evolution of the bending spectra as a function of cluster size and intermolecular coupling is presented and discussed.

Spectra of Large Water Clusters. The infrared spectra of large water clusters as a function of size is of basic interest since such clusters represent a transition from small water clusters to the condensed phases of water. The spectra and structures of the small clusters $(H_2O)_n$ have been studied very extensively in recent years[4] and, not unexpectedly, have been shown to vary markedly with small changes of n. For example, for $n = 5$ or less the stable structures are cyclic, while three-dimensional cage structures are favored for larger clusters. It can be presumed that sensitivity to n will largely decay through the range in cluster size from ∼20 to 1000 molecules. Although spectra have been reported for clusters in this size range,[5,6] interpretation has been largely frustrated by a lack of information on the cluster sizes as well as interference from bands of smaller clusters.

The 1000 molecule water cluster has a particular significance, since it has been known for some time that the electron diffraction patterns, for cold clusters of that size and larger,

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indicate the presence of "crystalline" cubic ice.[7] Smaller clusters, in the 300 molecule range, were shown to be noncrystalline. Even the 1000 molecule clusters gave a significant noncrystalline diffraction signal, the origin of which seems clear from the recent spectroscopic and computational results for clusters in this size range.[8] The new results indicate that clusters larger than ~500 molecules can be viewed as composed of a central crystalline core, a disordered surface, and a strained subsurface region that joins the core and surface. At least half the molecules in a 1000 molecule cluster are included in the badly disordered surface which, having a unique structure, gives a diffraction pattern that is not matched using standard amorphous ice models.[7] On the other hand, the strained subsurface structure is virtually crystalline down to a particle size near 400 molecules;[8] but nevertheless it has a unique infrared spectrum modified by the strain and, presumably, somewhat broadened diffraction peaks. Smaller clusters (<200 molecules) contain only an amorphous interior along with the disordered surface.

The spectra reported by us for large clusters, for distributions with average size ranging from 2 to 40 nm, were limited to the O−D stretch-mode region for pure D_2O clusters and clusters containing 18% HDO in H_2O clusters. Here, these data are extended to include H_2O cluster O−H stretch- and bend-mode spectra, with particular emphasis placed on the nature of the absorption bands in the bend-mode region. As for the D_2O clusters, the H_2O average cluster sizes have been determined by measurement of integrated intensities of monolayers of adsorbed CF_4.[9,10]

Frequency and Intensity of the Molecular Bending Mode in Condensed Phases of Water. The position (1594.6 cm^{-1}) of the bending mode of water in the gas phase is well-known. The intensity is less certain. Values in the range 49.2−103.3 km/mol have been reported,[11] while recent high-level ab initio calculations suggest a value near 73 km/mol.[12] The corresponding mode of liquid H_2O is also prominent in the infrared spectrum, so the reported values of 1645 cm^{-1} and 63 km/mol [1] have been accepted without controversy. However, the situation is complex for the solid phases of water, in particular crystalline and annealed amorphous ice, for which the bending mode band positions have been notoriously hard to establish and for which no *quantitative* data are available for the bending mode intensity. Further, the associated uncertainties have impacted the understanding of other aspects of ice vibrational spectra, most particularly the Fermi resonance of the overtone of the bending mode with the symmetric stretch-mode fundamental. The reasons for uncertainties about the bending mode of the icy phases of water are 2-fold. First, and most importantly, the *overtone* of the water librational mode, for which the fundamental frequency is in the 800 cm^{-1} region, produces a significant absorption with a bandwidth of ~300 cm^{-1} that can envelop the absorption of the bending mode.[3] Second, there are indications that the infrared intensity of the water bend vibration decreases as the number and/or strength of H-bonds to water increases.[13−15] The decrease appears to culminate in a particularly low oscillator strength for crystalline ice at low temperatures,[16,17] a factor in making the direct observation of the bend band within the broad absorption of the librational overtone impossible.

The variations in the position and apparent intensity of the bending mode of water with the nature of the H-bonding environment can be judged from the comparison in Figure 1 of the spectrum of both microporous (d) and annealed amorphous solid water (ASW) (b) with that of cubic crystalline ice (a). The overall band shape for microporous ASW prepared at 12 K[2] is not radically different than that for liquid water, which is also shown in Figure 1e.[1,18] That is, a prominent "narrow" absorption, reasonably assigned to the bending mode, protrudes at the high-frequency edge of a broad band attributed to the librational overtone. (The peak of the narrower band of microporous ASW is near 1670 cm^{-1}, ~25 cm^{-1} above the corresponding feature of the liquid spectrum.) The "narrow" feature loses much of its intensity upon annealing and cooling of ASW, a process known to produce a structure with increased average H-bond numbers and strength along with a closer approach to the tetrahedral bonding geometry.[19] Finally, upon crystallization and cooling of the ice, the "narrow" feature disappears, as if dissolved within the band of the librational overtone.[2,14] In this sequence, from microporous ASW to crystalline ice, the position of the combined bend−librational overtone intensity appears to move to lower frequency.[2] This is part of a spectroscopic puzzle, since both the librational mode and the bending mode are expected to move to higher frequency as the H-bond strength increases.

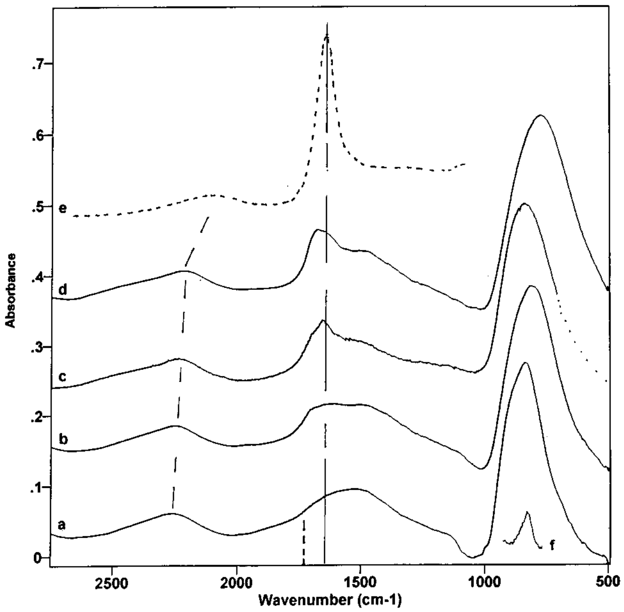

Figure 1. Infrared spectra for various phases of condensed H_2O: (a) crystalline ice at 12 K; (b) ASW at 12 K after 12 K preparation and annealing at 130 K for 1 h; (c) 100 K aerosol of 3 nm water clusters, (d) microporous ASW at 12 K after 12 K deposit; (e) $H_2O(l)$ reproduced from ref 8. The (f) segment is for a few percent HDO in D_2O cubic ice. The absorbance scale applies only to a, b, and c. The dashed vertical line marks the position of the bend mode of H_2O isolated in D_2O cubic ice.[16,17] The slanted dashed line emphasizes the variation of the ~2200 cm^{-1} band with water phase. The ~800 cm^{-1} librational band position for the clusters (c) is blue-shifted by a shape effect.[29]

Since the bending-mode band for pure H_2O cubic ice is not observable in the infrared spectrum, a direct comparison of position and intensity, with that of ASW, is not possible. However, observations have been aided by the use of a few percent *isolated intact* H_2O molecules in D_2O cubic ice and ASW.[14,16,17,20] Such isolation narrows the H_2O librational band of ice so that its overtone no longer overlaps the bending-mode band.[14,20] As a result, the "decoupled" H_2O bend becomes visible as a separate band despite some interference from the weak D_2O ice band near 1600 cm^{-1}. The band positions reported for *isolated* H_2O molecules in ASW and cubic D_2O ice at 90 K were 1711 [14] and 1735 cm^{-1},[17] respectively. From observations on an ice sample before and after crystallization (Figure 3b,c of ref 14), the bend mode of isolated HDO (1480 cm^{-1}) for the amorphous phase was estimated to have an intensity at least twice that of HDO in cubic ice at 90 K, and the cubic ice intensity decreases further upon cooling to 12 K.[16]

There has been limited evidence for many years that the bend-mode oscillator strength decreases with increased H-bonding,[13] based on band intensities of water clusters isolated in an argon matrix. Nevertheless, the situation has been less than clear, and the most recent report of band intensities for liquid water led to the conclusion that the bend-mode band intensity is independent of the strength of the hydrogen bonding.[1] For the decrease in intensity with increasing H-bonding noted for amorphous and crystalline ice to be credible, the assignment of the bend-mode absorption bands of the two ice phases must be firmly established. The frequency values of 1711 and 1735 cm^{-1} are significantly higher than many literature citations, which are often based on the value of the center of the broad librational overtone band (Figure 1 a,b). However, there have been strong independent arguments that higher frequency values (1700–1750) are to be expected,[21,22] and an ab initio computation found a trend to higher frequencies with an increasing size of small water clusters.[23] The most thorough argument, presented by Falk,[22] is embodied in an empirical linear plot that relates the bend-mode frequency to the H-bonding through the average value of the stretch-mode frequencies. From decoupled bend-mode frequencies of the gas phase and several dilute solutions, a plot was obtained that extrapolates to a cubic ice frequency of 1708 cm^{-1} at 90 K.[15]

Recently, bend-mode absorption has been reported for the three types of water molecules that are common to the surface of ice nanocrystals.[15] A structured band extending from about 1640 to 1740 cm^{-1} was resolved into three components assigned to the 3-coordinated dangling OH molecules (1652 cm^{-1}), the 3-coordinated dangling oxygen molecules (1684 cm^{-1}), and the 4-coordinated surface molecules (1702 cm^{-1}). Although the band resolution was somewhat arbitrary, the band positions were largely consistent with expectations from Falk's linear plot. The suggested assignment and band intensities also implied a decrease in oscillator strength with increasing frequency of the bending mode (increased H-bonding).

It can be concluded that the available data and interpretations are indicative of condensed phase H_2O bend-mode frequencies that increase with H-bonding strength from the value of 1645 cm^{-1} of liquid water to 1735 cm^{-1} for H_2O in crystalline D_2O ice at 90 K. Further, the band intensity appears to decrease with increased H-bonding; however, this appearance may reflect strong coupling with the librational overtone[1,24] rather than a decrease in oscillator strength. It is reasonable that the bending vibration, which involves mostly H-atom motion perpendicular to the OH bonds, is coupled strongly to the libration overtones, which involve similar motion. Thus, the excitations in the common spectral range might correspond to compound modes that include both types of motion. Further, the excitation energy in this spectral range is close to the energy of a hydrogen bond, so strong anharmonic coupling effects are likely. As a result, the bending band may be invisible, because it is "dissolved" in the libration overtone band.

This possibility is supported by the fact that the frequency of the *librational* mode is known to increase as the H-bonding of a system is strengthened. For example, the librational mode frequency increases from below 600 cm^{-1} for liquid water[18] to near 770 cm^{-1} for microporous amorphous ice to ~810 cm^{-1} for annealed amorphous ice to ~840 cm^{-1} for cold crystalline ice.[2] Consequently, overlap of the librational overtone band with that of the bending mode of water increases through the series H_2O(l), ice surface water molecules ~ microporous ASW, ASW, and crystalline ice. In this respect, it seems significant that the infrared absorption of the bending mode of H_2O(l),[1] the ice surface,[15] and microporous amorphous ice[2,14] is readily observed directly, but is observable for fully annealed amorphous ice and low-temperature crystalline ice only by using isotopic substitution which diminishes the overlap by narrowing the broad band of the overtone of the librational mode.

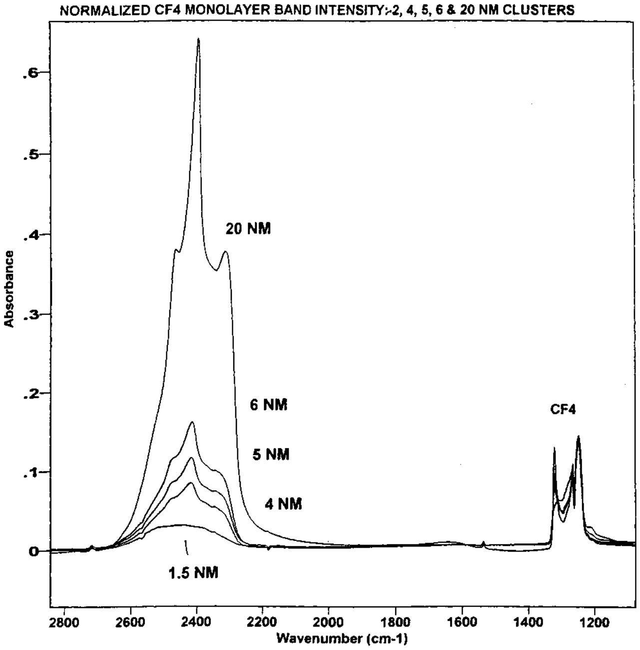

Figure 2. Infrared spectra of aerosols of D_2O large clusters, of the indicated average diameter, coated with a near monolayer of CF_4. The spectra all correspond to the same cluster surface area through normalization of the area of the adsorbed CF_4 antisymmetric stretch-mode bands. Consequently, the area of the O–D stretch-mode absorption is proportional to the average particle size.

Here the objective is to extend information about the H_2O bending mode to include the position, shapes, and relative intensities of the bands of *surface* molecule bending modes of large water clusters having an average size ranging from ~200 to ~64 000 water molecules (or from ~2 to 16 nm). Since stretch-mode spectra have recently been reported for similarly sized D_2O clusters, the new data complete a look at the fundamental modes of large water clusters. As previously reported for ice nanocrystals, and as can be seen in Figure 1c, the bending-mode absorption is prominent in the infrared spectra of large water clusters. Further, ab initio calculations are presented of the H_2O bending frequency and intensity in reduced-dimensionality models representing portions of the ice surface and interior. The combined results will be compared with existing information, in an analysis of questions regarding bending-mode position and intensity for the bulk phases of ice and the general form of the infrared spectra ranging from 500 to 2400 cm^{-1}.

Experimental Section

The 2–16 nm ice particles have been prepared as aerosols by rapid expansion of a 1.0% mixture of water vapor in He(g) into a thick-walled cluster cell held at 100 K within a vacuum container. The clusters form as liquid droplets (with a presumed log-normal size distribution) that freeze while cooling rapidly toward temperatures near 100 K. The cluster size has been adjusted by varying the loading pressure from 20 to 300 Torr. FTIR spectra have been measured at 4 cm^{-1} resolution using

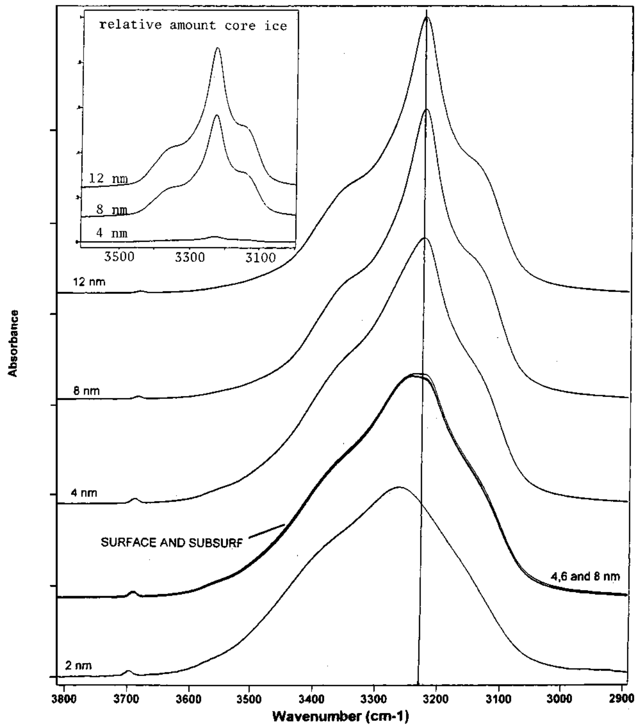

Figure 3. FTIR spectra in the O−H stretch-mode region of H_2O particles in the 12 to 2 nm range as aerosols in He(g) at 100 K. The three overlaid spectra are for 4, 6 and 8 nm particles with the core component removed. The inset shows the relative magnitude of the crystalline core components for 4, 8 and 12 nm particles.

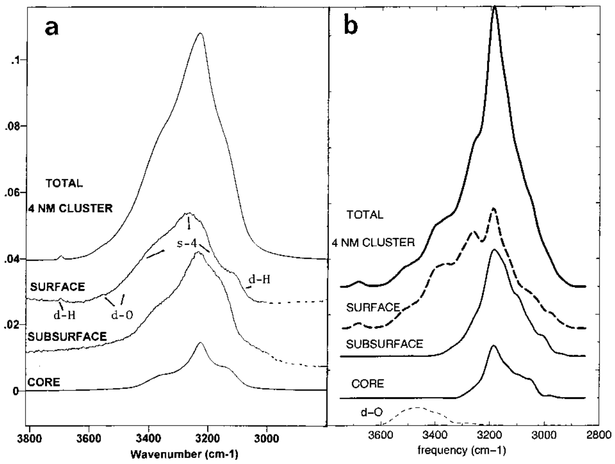

Figure 4. The experimental (a) and computed (b) spectra of 4 nm H_2O clusters at 100 K. The spectra of the three components, surface, subsurface and core, are given to scale. The separation of the spectra into components is described in the text. The dashed curve, labeled d-O, is the contribution of the 3-coordinated double-donor surface water molecules to the computed spectrum. The label d-H refers to the surface molecules with dangling O−H bonds, which also have a bonded OH frequency near 3100 cm^{-1}.

300 scans of a Bio-Rad FTS 575C spectrometer. Over 75% of the clusters remain in the aerosol phase for the ∼5 min used to measure the infrared spectra. In some cases difference spectra between large and smaller clusters have been used to better display the absorption bands produced by the surface water molecules of the particles.

As in previous studies, the average size of the clusters has been determined from integrated infrared band intensities for monolayer amounts of adsorbed CF_4.[9,10] This is demonstrated for D_2O clusters in Figure 2, in which the band area of the antisymmetric stretch of a monolayer of adsorbed CF_4, which is a measure of the ice surface area, is held constant as the cluster size is varied. The amount of ice for a fixed amount of surface (i.e., volume/area) is proportional to the radius of the "spherical" clusters; therefore, in Figure 2, the ratio of cluster diameters can be approximated from the ratios of the integrated O−D stretch band areas. Initially, an absolute size measurement of ∼20 nm particles was obtained by comparing the integrated band intensity of an adsorbed monolayer of CF_4 with that of CF_4(g) for a known pressure and cell length. The average diameters of the large cluster samples have been related to that absolute measurement through relative CF_4-monolayer integrated intensities together with the integrated intensities of the ice O−H stretch band of the corresponding samples. These average diameters are consistent with values deduced recently using transmission electron microscopy,[26a] as well as earlier estimates made using the ratio of intensities of the d-H band to intensities of the main ice stretch-mode band.[26b]

Results

Large-Cluster O−H Stretch Spectra. The variation of large cluster spectra, in the O−H stretch region, with decreasing size is shown from top to bottom in Figure 3. The variation in spectra with cluster sizes, ranging from 12 to 4 nm, is a result of the different magnitudes of the *crystalline* core component. As observed previously for D_2O large clusters,[8] the core component varies from over 50% for 12 nm to a few percent for 4 nm clusters. That this variation is the only significant change with size is shown by the overlaid spectra near the bottom of the figure. With the core ice spectrum removed (by the amounts indicated in the inset of Figure 3), the remaining spectra are essentially identical. This "invariant" residual spectrum is assigned to the surface and subsurface, the dominant components of a 4 nm cluster.[8] As has been discussed for large D_2O clusters and as is indicated by the shift of the of the peak frequency of the bottom spectrum of Figure 3, spectra of clusters smaller than ∼2 nm (125 molecules) reflect an amorphous interior.

Since both the core and subsurface spectra are known, the latter from relaxation studies of ice nanocrystals coated with an intermediately strong adsorbate (SO_2),[27] a cluster spectrum can be separated into the three component spectra. The spectra of the three components of a 4 nm H_2O cluster are shown to scale in Figure 4a. Calculated H_2O spectra of a 4 nm cluster are shown in Figure 4b for comparison. The calculation employed a model that is described in more detail in ref 8 (where it was used for the interpretation of HDO large-cluster spectra). The approximately spherical relaxed 4 nm ice particle included 979 water molecules in a structure characterized by a crystalline (cubic ice) interior and a disordered surface. Diameters of 1.8 and 2.4 nm were used to define subsurface and surface component boundaries. In the calculation of the spectra, OH bonds were represented as local Morse oscillators, coupled by intramolecular and intermolecular (dipole−dipole) interaction.[28,29] The spectrum of the relaxed structure was calculated using a scheme developed to study $n = 8-10$ cage clusters.[30] The bond frequency is calibrated as a function of the electric field component ($E_{||}$) along the OH bond, at the H atom; the field is calculated at a cluster minimum, using the permanent charges and the induced dipoles of the polarizable potential (EMP).

There is a reasonable qualitative agreement between the calculated and the experimental spectra, further supporting the interpretation in terms of surface, subsurface, and crystallike spectral components. The dominant contribution to the *surface* spectrum is from 4-coordinated molecules in the disordered

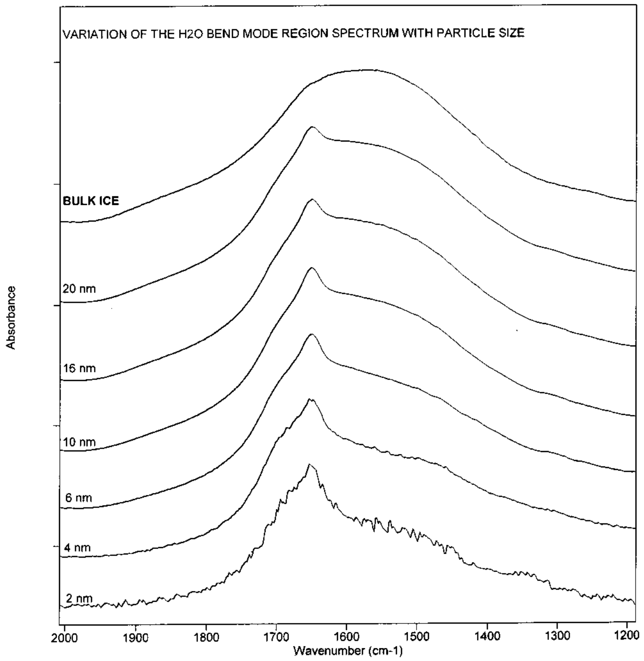

Figure 5. The 6-micron bend-mode region FTIR spectra of ice particles, with average diameters ranging from 2 to 20 nm, compared to that of bulk ice.

upper layer; a minor contribution on the low-frequency side originates from the bonded OH of the molecules with dangling OH. The 3-coordinated molecules with a dangling O contribute predominantly in the high-frequency wing of the broad bonded-OH band as indicated by the dashed curve at the bottom of Figure 4b.

One should note that the assignment of band components of the ice surface spectra is most meaningful for isolated HDO for which an O−D band position is a direct measure of the strength of hydrogen bonds of a particular subset of O−D bonds. These observed features, for 18% HDO in H_2O ice, have previously been assigned from simulated spectra for a 1000 molecule relaxed cluster composed of HDO molecules (with no inter- or intramolecular O−D coupling).[8] By contrast, surface vibrational modes of H_2O and D_2O particles are collective, so the spectra are significantly modified and broadened by inter- and intramolecular coupling. The more complex form of the modes for H_2O and D_2O cluster surfaces should be kept in mind when considering their assignments.

Large-Cluster H_2O Bend-Mode Spectra. The infrared absorbance of large clusters through the bend-mode region of the spectrum can be analyzed much as the stretch-mode spectra. The raw large-cluster spectra in this region are presented in Figure 5 for particles ranging in size from 2 to 20 nm. The comparison with the spectrum of bulk crystalline ice indicates that the sharper feature on the high-frequency side of each of the cluster spectra is unique to the clusters and decreases as a fraction of the total intensity as the particle size increases. It is also clear that the limiting spectrum of this size sequence is the broad bulk ice spectrum, as the bulk ice component, centered at ~1560 cm^{-1}, intensifies with particle size and is dominant already for the 20 nm clusters. It is, therefore, expected that removal of the crystalline core component, as done for the O−H stretch bands of Figure 3, would reveal a nearly invariant combined surface and subsurface spectrum.

The overlaid spectra of Figure 6 show the result of the removal of the crystalline core ice component from the cluster spectra of Figure 5. In each case, the same fraction of core ice has been removed as was subtracted to obtain the surface and subsurface spectra in the stretch-mode region (Figure 3). Again, the result demonstrates that the combined surface and subsurface spectra are largely independent of cluster size over the range from 4 to 16 nm (1000−64 000 molecules). The combined spectra have been resolved into the component surface and subsurface bend-mode spectra (Figure 7), by using the assumption that the subsurface spectrum of this region matches the core ice spectrum (top spectrum of Figure 5). This is based on the conclusion reached in our previous study that the subsurface ice is strained crystalline ice, which resembles cubic ice more than does ASW;[8] ASW, like crystalline ice, has a very broad and nearly featureless absorbance in this spectral region (Figure

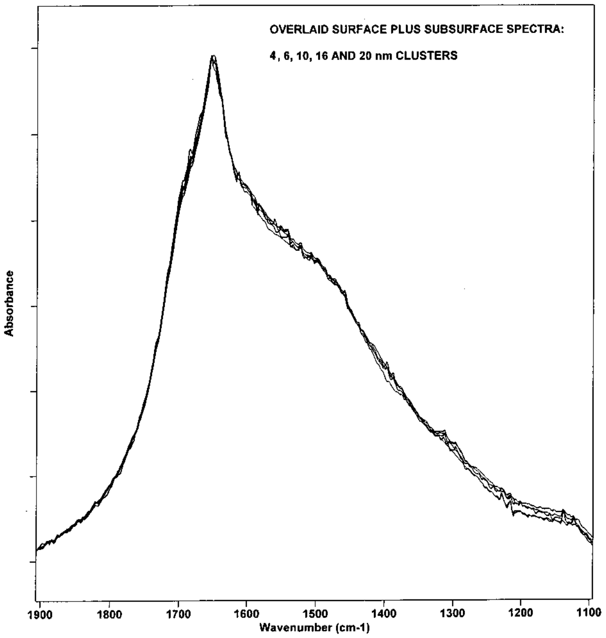

Figure 6. Superimposed infrared spectra, in the 6 micron region, of ice particles of various average size (3, 6, 10, 16, and 20 nm), after removal of the crystalline core component.

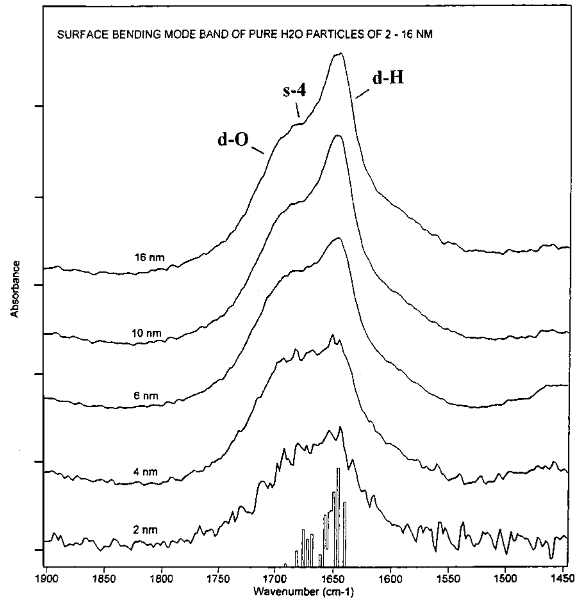

Figure 7. Infrared spectra of the surface bending mode region of various sized ice particles, from removal of the subsurface component spectra of the bands of Figure 7. The histogram at the bottom of the figure represents the distribution of computed band intensities vs frequency for the four cases of Table 1.

1b). Thus, the surface spectra of Figure 7 were obtained by subtracting a "corelike" contribution from each of the spectra of Figure 6 to remove the subsurface absorption.

The bending mode surface spectrum (Figure 7) changes noticeably in form but not position over the cluster range from 200 to 64 000 molecules, ultimately converging on the spectrum reported for ice nanocrystals.[15] The main variation occurs between 4 and 10 nm, as the feature on the low-frequency side (1650 cm^{-1}) strengthens and becomes the dominant aspect of the band system. This band system, which has a similar shape for D_2O clusters, changes more radically upon adsorption of a monolayer of ammonia. Adsorbed ammonia eliminates (for H_2O or D_2O) the dominant low-frequency component, as previously noted for the nanocrystals of ice.[15] This is even more obvious for HDO for which the low-frequency component is well separated from the rest of the band (Figure 8a,b). It is of interest to the computational results (see below) that adsorbed ammonia also reduces the intensity of the HDO band system on the high-frequency side, as is clear from the difference spectrum of Figure 8c. The band shape is also influenced by isotopic dilution in a manner also of interest in the context of the computational results. The inset of Figure 8 shows that much of the band structure (d) is lost for an isotopically scrambled cluster sample (e) (~25% H_2O, 25% D_2O, and 50% HDO) as the position of the strong component shifts to higher frequency.

Bend-Mode Computational Results for Ice and the Ice Surface. The compound bending−libration overtone feature is complex, and our knowledge of the dependence of the potential and the dipole on the bending coordinate is too limited for detailed modeling of the spectra on the same level as for the OH stretch. We therefore pursued a more limited goal of calculating the decoupled bend frequencies of H_2O in the ice interior and in the surface environment. The objective was to study the frequency and intensity dependence on the hydrogen-bond coordination for configurations found in the interior and on the ice surface.

Ab initio calculations were carried out on reduced-dimensionality models mimicking these environments. For the ice interior, the model included a central molecule and its four nearest neighbors in the icelike hydrogen-bonded configuration. More remote molecules were replaced by charges; a negative charge of −1.0728 e was placed on the O-atoms, and a positive charge of 0.5364 was placed on the H-atoms. This method to include the effect of long-range interactions on intramolecular vibrations was suggested in ab initio studies of water-containing systems by Hermansson et al.[31] This model is denoted below as int-ice.

A perfect crystalline surface is made up of 50% 3-coordinated molecules and 50% 4-coordinated molecules (in more sunken positions). The three coordinated molecules are of two varieties, with either a dangling-H atom (d-H) or a dangling-O atom (d-O). In disordered surfaces of particles, the percentage of low-coordinated molecules is reduced, while the percentage of 4-coordinated (s-4) molecules is enhanced; however, the bonding geometry of the latter is significantly distorted with respect to tetrahedral symmetry. In this initial study, no effort was made to investigate the entire range of surface configurations. The surface models included a molecule and its nearest neighbors, in a tetrahedral bonding configuration, while more remote neighbors were represented by charges. These models are denoted surf-4, surf-H, and surf-O, for an s-4 molecule, a d-H molecule, or a d-O molecule, respectively.

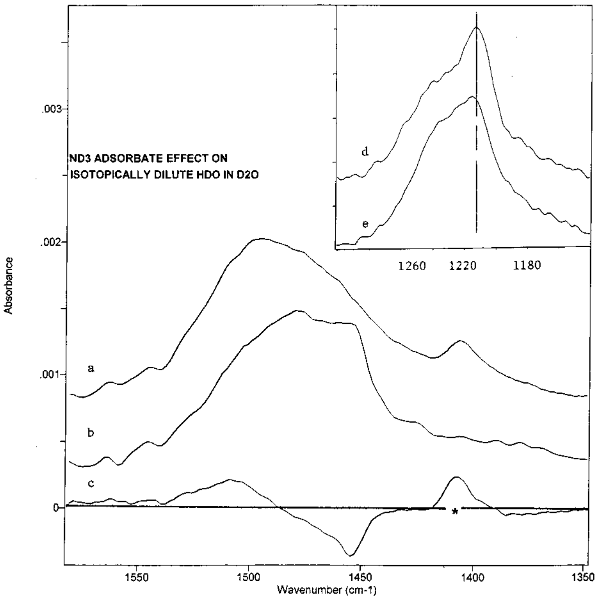

Figure 8. Infrared spectra of the surface bend-mode region of 18% HDO in H_2O large clusters bare (a) and with the surface saturated with ammonia (b). The difference spectrum from subtraction of the coated from the bare clusters is also shown. The asterisk marks the band identified as the HDO bend of the d-H molecules with D-donor bonding. The inset shows the effect of isotopic dilution on the shape of the surface bend-mode band of D_2O in an isotopically scrambled 50% H/50% D sample of ~8 nm clusters; (d) is for pure D_2O and (e) for the isotopic mixture.

The calculation employed a proton-disordered cubic ice particle containing 147 molecules, generated by a method of ref 32. In int-ice, the central molecule was used to calculate the ice bending frequency; its four near neighbors were included explicitly and the rest were replaced by charges. In calculations of the surface molecule bending frequencies, appropriate parts of this model were retained. The model was "cut" in such a way that the central molecule became either a d-H, a d-O, or an s-4 surface molecule (surf-H, surf-O, or surf-4 models). The use of a single H-atom configuration in the calculation is a limitation of this initial study; in the future, averaging over differently proton-disordered structures will be carried out.

The aug-cc-DZ basis was used in the calculation, which employed the Gaussian 98 program.[33] The calculated harmonic bending frequency and intensity of the monomer are 1622 cm^{-1} and 67 km/mol, respectively. The experimental frequency is 1595 cm^{-1}. As noted above, a broad range of experimental values have been reported for the intensity; recent high-level ab initio calculations suggest a value near 73 km/mol.[12] The aug-cc-DZ basis was used extensively in the past in a study of water clusters.[23] For the trimer, bending frequency shifts of +9, +12, and +37 cm^{-1} were reported, in good agreement with two measured bending features at +14 and +43 cm^{-1}.[5b]

The geometric parameters used in this study were near neighbor $R(\mathrm{O}\cdots\mathrm{O})$ distance of 2.705Å and intramolecular OH distance and HOH angle of 0.985 Å and 105°, respectively. These values are based on the above-mentioned ab initio study of water clusters in the same basis.[23] (The use of the longer experimental $R(\mathrm{O}\cdots\mathrm{O})$ of ice, 2.75 Å, did not significantly change the int-ice results.)

In the three surface models, the energy was first minimized with respect to all the coordinates of the central molecule and the length of the OH bonds directly connected to that molecule. In the int-ice model, minimization was carried out only with respect to bond lengths of the central molecule and of the bonds connected to that molecule; this was in order to preserve the tetrahedrality of the crystalline site. (Full minimization of the

TABLE 1: Computed Bend Mode Frequencies and Intensities for Differently Hydrogen-Bonded Water Molecules[a]

model	bending freq (shift; cm^{-1})	squared dipole deriv (rel to monomer)
$H_2O(g)$	1631 (0)	1.0
surf-H	1673 (42)	1.22
surf-O	1740 (109)	1.31
surf-4	1680 (49)	0.38
int-ice	1708 (77)	0.34

[a] See text for definitions of notations.

central molecule coordinates did not change the results significantly.) The minimization was carried out without the charges representing the remote molecules (minimization with charges did not work in the Gaussian program). The energy of the system was then mapped as a function of the HOH angle of the central molecule in the range ±20° around the minimum. The ab initio points were fitted into a Morse function, and finally the bending frequency was calculated using the diagonal G_{33} matrix element[34] as inverse mass. This calculation is, of course, approximate; it neglects both intra- and intermolecular coupling of the central molecule bending mode to other degrees of freedom. The isolated monomer bending frequency calculated in this way is within 9 cm^{-1} of the harmonic value. The bending vibration was found to be only weakly anharmonic, with w_ex_e of a few cm^{-1} in the different models. The squared dipole derivative was calculated numerically using dipole vectors at angles ±6° from the estimated minimum. The results are summarized in Table 1.

The calculated frequency shifts with respect to the gaseous monomer for d-H and d-O surface molecules are 42 and 109 cm^{-1}, respectively. For d-H molecules only one H-atom is bonded, while for d-O molecules, both H-atoms are bonded, so the difference in frequency shifts makes physical sense. This result suggests that the two types of 3-coordinated surface molecules contribute, respectively, to the low- and high-frequency ends of the measured surface bending band (which ranges from +50 to 100 cm^{-1} above the gaseous frequency; Figure 7). The positioning of the d-H and d-O components is consistent with the response observed for the surface bend band of HDO to coating of the clusters with ammonia (Figure 8). The difference between the two frequencies is also consistent with that noted by Scherer,[24] between symmetric and asymmetrically bonded water molecules, and the ab initio calculations for small cyclic water clusters by Van der Rest et al.,[35] who also found that the frequency shift increases as the number of bonded H-atoms of a molecule increases from one to two. The physical origin of the blue shift appears to be simple—the bending vibration distorts hydrogen bonds and therefore hydrogen bonding reinforces the intrinsic bending force constant. However the long-range interactions, represented by charges, also contribute nonnegligibly to the blue shifts (a few tens of cm^{-1}).

It is of interest to note that the calculated squared dipole derivative of 4-coordinated configurations in the interior and the surface (int-ice and surf-4) is reduced with respect to that of 3-coordinated surface molecules (surf-H and surf-O) by a factor of ~3.5. The low bending intensity of 4-coordinated ice molecules in a tetrahedral bonding environment seems consistent with experiment.[14,15]

The asymmetry of the bending feature (Figure 7) for larger ice particles is suggested to be an effect of intermolecular coupling between bending vibrations. To demonstrate the effect, bending normal modes and intensities were calculated for each of the water molecules of the three models: int-ice, surf-H, and surf-O (without charges). The histogram of the resulting bending frequencies, weighted by the intensities, is shown in Figure 7 (bottom). It is seen that intermolecular coupling results in intensity transfer to the lower frequencies. A similar result was obtained in past ab initio studies of water clusters $(H_2O)_n$, for $n = 3-10$.[36,37] Stronger asymmetry of the experimental band, for larger clusters than small ones, may reflect a smoother, more ordered surface[9] with more extended collective surface vibrations.

The most surprising result of the calculations, in apparent disagreement with experiment, is the relatively small frequency shift of the 4-coordinated molecules. The calculated shift for int-ice ("interior ice"), +77 cm^{-1}, is substantially lower than the measured one for H_2O isolated in D_2O ice[17,20] (140 cm^{-1}). Some of the discrepancy may be due to Fermi resonance between the (separated) bending fundamental of the isolated H_2O and the libration overtone at ~1570 cm^{-1}, which is expected to blue shift the bending frequency, and which is not included in the calculation. However, the relative magnitudes of the *calculated* surface mode frequencies (Table 1) are quite striking. The frequency of the 4-coordinated surface molecule (surf-4) is only slightly higher than that of the 3-coordinated surf-H and substantially lower than that for surf-O. Thus, addition of a fourth bond to the dangling-O molecule of the model lowers the frequency substantially.

While hydrogen bonding via H is expected to blue shift the H_2O bending frequency, the effect of bonding via O is not obvious. In another pertinent study[35] ab initio calculations of bending frequencies are presented for small cyclic water clusters, mostly with 1- and 2-coordinated molecules in different bonding configurations. These calculations yielded a blue shift of ~12 cm^{-1} with respect to $H_2O(g)$ in single acceptor molecules and blue shifts in the range 7−21 cm^{-1} for double acceptor molecules. Thus addition of the second acceptor bond does not necessarily increase the shift. More generally, the variation of intramolecular H_2O frequencies with coordination is not necessarily smooth; as another example, one may note that the hydrogen-bonded OH stretch of 3-coordinated d-H molecules is characterized by a significantly larger frequency shift than the OH stretch in 4-coordinated ice molecules.[4,8,38] On the other hand, one should keep in mind limitations of the present reduced-dimensionality model, as the apparently large discrepancy with respect to experiment is worrisome.

Discussion

Large-Cluster Spectra. The computational results for the bending modes of surface water molecules, using a reduced-dimensionality model, provide substantial guidance to interpretation of the large-cluster surface bending-mode spectra. The spectra of Figure 7 show that, with increasing cluster size, the spectra converge on the published surface bending-mode spectrum of larger ice nanocrystals. However, the present computational results strongly suggest a somewhat different interpretation of the band shape.[15] While the dangling-OH molecules are still identified as a primary source of intensity on the low-frequency side of the band complex, the calculated frequencies and intensities indicate that the d-O molecule bend dominates the high-frequency side with the s-4 molecules contributing more weakly to the intermediate region of the band system.

Though somewhat surprising, in view of the high bending frequency (1735 cm^{-1}) of the 4-coordinated H_2O molecules isolated in the interior of D_2O crystalline ice, this s-4 assignment is supported by new spectra of HDO isolated in D_2O ice large clusters (Figure 8). Adsorbed ammonia is expected to interact most strongly with the 3-coordinated surface molecules of these clusters, increasing their coordination number to 4 or higher.[39] The result (Figure 8c) is a loss of intensity on both the low- and high-frequency edges of the HDO bending band, with a gain in the band middle, consistent with the computational results that place the s-4 absorption in the midrange.

The computations further suggest that the dominant low-frequency component of the surface bending band (1650 cm^{-1}, H_2O; 1213 cm^{-1}, D_2O[15]) is accentuated by intermolecular bend−bend coupling. This view is affirmed by the band shape and peak intensity position for D_2O semiisolated in a large cluster (curve e of inset Figure 8). Relative to the spectrum (d) of pure D_2O, the prominence of the low-frequency component is strongly diminished and the peak blue shifted by ~4 cm^{-1}, as anticipated from the computational results.

Finally, consistent with earlier speculation,[15] the computational results suggest that the bending mode intensity is strongly reduced for 4-coordinated surface molecules, as well as int-ice. Since there are substantially more s-4 molecules than the combined d-H and d-O populations,[8,38] such a reduction makes clear why the s-4 molecules of intermediate frequency do not dominate the observed bending-mode band complex (Figure 7).

Molecular Bending and Lattice Librational Modes of Condensed Water Phases. An important concept of the present study, based on the appearance of the molecular bending mode infrared absorption, is that different condensed phases of pure water can be usefully divided into two classes. In the first class, the infrared absorption of the bending mode is clearly visible, appears more or less independently of the librational overtone band, and assumes a moderate bandwidth consistent with an H-bonded system. In the second class, the bending mode is so thoroughly mixed with the librational overtone that, for the pure H_2O phase, it is not useful to speak of the bending mode fundamental; the mixed-mode absorption becomes a broad (~300 cm^{-1}) nearly structureless band.

The first class of substances includes liquid water, the large water clusters, and microporous amorphous ice, as is clear from the top three spectra of Figure 1. (In the case of the clusters, we have shown that only the surface component falls in this class.) The lead member of the second class is low-temperature crystalline ice I, represented by cubic ice at 12 K with the very broad featureless band of the bottom spectrum of Figure 1, and by the interior of large water clusters (Figure 6). The spectrum of ASW at 12 K (Figure 1b) also shows a broad relatively structureless absorption that becomes progressively less structured with further annealing near 130 K.[2]

The water bend-mode frequencies range from the liquid value of 1645 cm^{-1} to the cubic ice value of 1735 cm^{-1} at 90 K; meanwhile, the librational frequency blue shifts from below 600 cm^{-1} for liquid water[18] to 835 cm^{-1} for cubic ice at 10 K.[25] These values suggest that the frequency of the overtone of the bending mode, which is best viewed as the broad band near 1560 cm^{-1} in the spectrum of cubic ice of Figure 1c, increases with H-bond strength more rapidly than does that of the molecular bending mode. This factor is a critical one in understanding the full range of behavior depicted in Figure 1. It is the reason that the bend fundamental is fully mixed with the librational overtone only for the condensed phases of the second class.

It is worth noting that *warm* crystalline ice actually falls into the first rather than the second class of systems. Near 140 K the band of crystalline ice assumes the appearance of ASW, with a high-frequency protrusion (e.g., see Figure 4 of ref 2) that increases with further warming. This seems at least partly because, upon warming, the ice librational band and its overtone decrease in frequency,[25] reducing the overlap with, and diffusion of, the bend-mode band intensity. However, the mixing of the bend mode with the librational overtone is through a Fermi resonance with a symmetry-matching requirement that may also be less fully met for warm ice that experiences large amplitude lattice vibrations.

As noted earlier, the positions of the H_2O bending fundamental for cold crystalline ice (1735 cm^{-1})[16,17] and ASW (1711 cm^{-1})[14] have been observed in studies of D_2O ice containing isolated intact H_2O molecules. These observations were made feasible by a dramatic (factor of 3) narrowing of the librational mode (see Figure 1f and ref 40) and thus of the first overtone, which accompanies the isolation of one isotopomer in the matrix of the other. As a result, the bending fundamental bands stand clear of the overtone, so their absorption assumes a form like that of molecules in the first class.

However, the high frequency of the cubic ice band (1735 cm^{-1}) relative to the computed value for int-ice (1708 cm^{-1}) is a concern demanding some analysis (the discrepancy is larger if one considers the shift with respect to experimental/computed gaseous frequency, which is 140 vs 77 cm^{-1}). The bend-mode frequencies of HDO, isolated in both D_2O and H_2O ice I, have been noted previously.[16] It is interesting that the peak position differs in the two cases, being 1510 cm^{-1} in D_2O ice and 1490 cm^{-1} in H_2O ice. This difference may indicate a Fermi resonance between the HDO bend and ice-matrix librational overtones with shift magnitudes of ~10 cm^{-1} in each case. This is despite a sizable average separation of the bend and librational band positions and the intermolecular nature of the interaction.

This displacement of the HDO bend frequency, for an H_2O vs D_2O ice matrix, may help to rationalize the much higher bend frequency observed for H_2O isolated in D_2O ice than predicted for the int-ice of the reduced-dimensionality quantum computation. The isolated H_2O bend may be pushed to higher frequency by two closely related factors, neither of which are included in the computation: a Fermi resonance with the D_2O ice matrix librational overtone and an intramolecular resonance of the bending mode of isolated H_2O with its librational overtone. In the absence of these resonances, the decoupled bend mode of crystalline ice might be near the extrapolated value from the Falk plot (1708 cm^{-1}) and more consistent with the computed int-ice value of Table 1.

There remain long-standing puzzles to consider. For example, how can the band in the bend-mode/librational overtone region be at a higher frequency for amorphous ice than for crystalline ice when both the bend and the librational fundamentals of the latter are of higher frequency? Also, how can this band move to lower frequency as the H-bond strength increases upon cooling of crystalline ice?[2] There is now a single straightforward answer to both puzzles. The bend-mode fundamental has a higher frequency than the librational overtone in all cases; therefore, when it is observed, it appears as a *high-frequency* protrusion on the broad underlying overtone absorption (curves c, d, and e of Figure 1, and warm crystalline ice[2]). However, for the second class of systems this absorption “disappears”, in part because of considerably reduced oscillator strength (as implied by the computed intensity of int-ice), and partly through increased mixing with the librational overtone with which it is more nearly coincident for the systems of the second class. As a consequence, the overall absorption in the bend-mode region moves to lower frequency during annealing, or crystallization of amorphous ice (Figure 1). An analogous explanation applies to the mysterious downshift in frequency of the absorbance in this range when either ASW or crystalline ice is cooled.

A second puzzle concerns the origin of the broad band near 2200 cm^{-1} in each of the spectra of Figure 1. The apparent progression of the three broad bands of cubic ice, from 835 to 1560 and finally 2255 cm^{-1} (ref 2 and Figure 1a), makes an assignment as the second overtone of the librational mode appear obvious.[3,41] It is also known that the 2200 cm^{-1} band moves to higher frequency with increased H-bonding[2], as expected for this overtone. However, a recurring assignment of this band for these condensed phases of water has been to a combination of the bending and librational fundamentals.[42,43] While the latter assignment may be valid for the liquid ($1645 + 570 = 2215$ cm^{-1}, as compared to the observed 2100 cm^{-1}), it appears unlikely for crystalline ice or ASW. With the cubic ice librational frequency established as 835 cm^{-1} and the bending frequency near 1700 cm^{-1}, the uncorrected combination frequency of ~2535 cm^{-1} appears much too high for such an assignment. On the other hand, application of the standard anharmonic energy-level formula ($E_n/h = (n + 1/2)w_e - (n + 1/2)^2 w_e x_e$) to the libration fundamental and first overtone of 835 and 1560 cm^{-1} results in a second overtone frequency of 2175 cm^{-1}, much closer to the observed value.

A fully satisfactory analysis of the 2255 and 1560 cm^{-1} bands of ice I presents a formidable theoretical challenge, since these excitations correspond to highly anharmonic collective motions that involve both librational and intramolecular bending degrees of freedom and which have remarkably large oscillator strengths. An ongoing analysis of these bands will be aided by librational fundamental spectra for the various isolated isotopomers of water presently under study (such as the narrow band of HDO isolated in D_2O ice of Figure 1f).

Summary

Large H_2O cluster infrared spectra *as a function of size*, for average diameters in the 2−12 nm range, are reported for the first time. Results for the OH stretch modes parallel those reported previously for D_2O large clusters: the spectra indicate the presence of a crystalline core, a disordered surface, and a strained subsurface that joins the surface and core regions, with the primary size effect being the diminution of the fraction of crystalline core with decreasing size. Both the simulated spectra, for a relaxed 4 nm ice cluster, and the experimental results are consistent with the core vanishing near 3 nm (while the strained but crystalline subsurface is retained). Near 2 nm the cluster subsurface region assumes an amorphous form. A satisfactory match of the simulated O−H stretch spectra with the observed spectra allows assignment of the regions of the surface spectrum to water molecules of the three classes: d-H, d-O, and s-4 molecules (Figure 4).

The simulated spectra of the bending-mode region have also permitted a new assignment of the subbands of the observed absorption to the three categories of surface molecules. Unexpectedly, comparison of the simulated and observed spectra identify the high-frequency side of the absorption (near 1700 cm^{-1}; Figure 7) with the d-O surface molecules, while the s-4 molecules apparently contribute only weakly to the midrange of the band. As expected,[15] the d-H molecules are identified as the source of the dominant low frequency band component.

Finally, the new information, from the large clusters, has been combined with existing data for various condensed phases of water to arrive at an internally consistent interpretation of the 6 μm (1650 cm^{-1}) region of the infrared spectra. The new results suggest the identification of two classes of condensed water phases: one in which the bend-mode absorption lies above that of the librational overtone and therefore appears as a normal infrared band; a second in which the bend-mode absorption is fully depleted by a combination of overlap/mixing with the librational overtone and a reduced inherent intensity that accompanies strong tetrahedral H-bonding of the water molecule.

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