Vibrational Spectroscopy and Modeling of the Surface and Subsurface of Ice and of Ice−Adsorbate Interactions

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FT-IR spectroscopic results in conjunction with simulations show that ice nanocrystals, formed at 70 K and annealed at 140 K, consist of a crystalline core, a highly irregular (though relatively smooth) crystalline surface, and a slightly distorted subsurface region connecting the surface and bulklike interior ice. Adsorbates on the nanocrystalline surface can be divided into three classes in terms of their effect on the three regions of the nanocrystals: weak adsorbates that influence the surface only; strong adsorbates that reverse the restructuring of the ice surface and thereby increase the order of the subsurface region; penetrating strong adsorbates that completely convert the nanocrystals to hydrates at cryogenic temperatures. To the extent that these properties of crystalline nanoparticles reflect the characteristics of the surface region of bulk ice, they must be recognized in attempts to understand chemistry at the ice surface.

Introduction

This paper considers (a) the structure and dynamics of the surface of ice nanocrystals, (b) the interaction of non-H-bonding small molecules with the surface sites of ice, and (c) the influence of H-bonding molecules on the ice surface, subsurface, and interior. The experimental spectroscopic results, in combination with a variety of computer simulation studies, have led to a definite concept of the structure and dynamics of the ice surface/subsurface and the response of the surface/subsurface to the presence of molecular adsorbates.[1−5] Within that concept, an annealed ice nanocrystal is viewed as being composed of a core region (with a structure identical to that of bulk cubic ice) surrounded by surface and subsurface regions, each of which has a unique vibrational spectrum that can be differentiated from that of the core.

The surface is imagined as a nonperiodic outer bilayer of water molecules forming ring structures of a broad size distribution (Figure 1b). Surface relaxation with respect to the crystal appears to be driven by the fact that there are many more disordered surface structures than ordered ones and that the disordered ones can be accessed at a small energy cost due to the greater freedom of motion of surface molecules. The energy cost is decreased by a reduction in the number of unsaturated H-bonding surface sites (i.e., dangling-hydrogen and dangling-oxygen coordination sites) that accompanies disordering. This reduction occurs with the formation of strained H-bonds, at the expense of loss of surface periodicity.

The existence of the seriously disordered ice surface bilayer foretells the presence of a subsurface region in which the disorder is attentuated in the direction of the crystalline core of the particles.[1] Spectra and simulation results suggest that, for the (111) face of cubic ice nanocrystals, this transition region consists of roughly two bilayers of water molecules. Beyond these bilayers, the dynamic dipolar forces, for which ice is notorious, couple the internal vibrational modes of the water molecules to form resonant delocalized (cooperative) modes characteristic of bulk ice.[7]
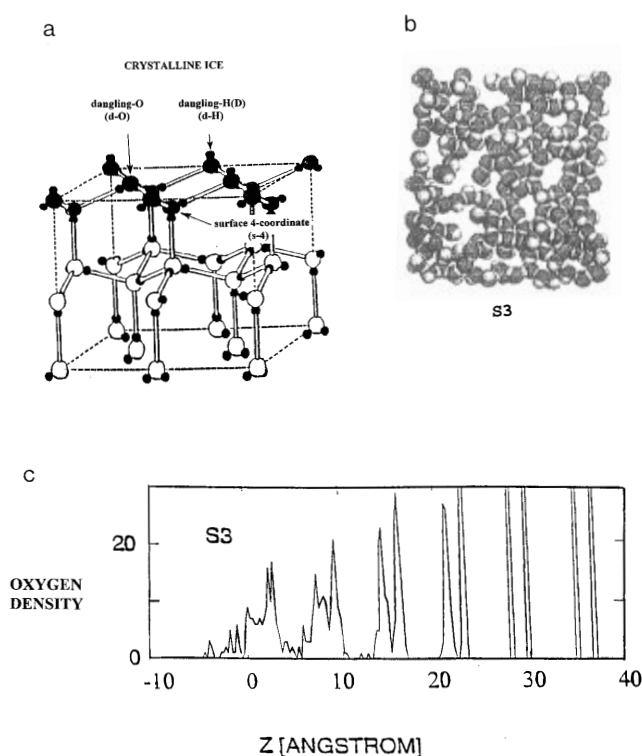

Figure 1. (a) Representation of the unreconstructed ice surface, (b) the S3 model of the reconstructed topmost bilayer of the ice surface (as described in the text), and (c) the density distribution along the vertical coordinate of O atoms of the S3 model.

Just as there are three parts of an ice nanocrystal (surface, subsurface, and interior), there are three classes of adsorbate molecules, based on their differing effects on these three regions of an ice crystal. The influence of weak adsorbates, such as CF_4, H_2, N_2, and CO, is apparently limited to the ice surface, being reflected exclusively in frequency shifts of the surface-localized modes. The members of a class of stronger adsorbates, which includes HCN, SO_2, H_2S, and acetylene, form significant H-bonds to the dangling coordination sites of the ice surface,

reduce the disorder of the surface bilayer by partially reversing the surface reconstruction, and as a direct result, reduce the extent of the subsurface region and increase the amount of interior ice.

Members of the third category, also H-bonding adsorbates such as ammonia and ethylene oxide (and probably HCl), have similar surface effects but are sufficiently strong proton acceptors (or donors) to "clip" the normal H-bonds of ice. Thus, with sufficient exposure they penetrate ice to form either amorphous or crystalline hydrates at cryogenic temperatures. This great range in the strength of the adsorbate interactions with the ice surface sites is also apparent from the induced shifts of the vibrational frequencies of surface-localized modes of ice (e.g., the shift of the dangling O−D(H) stretch vibration varies from 7 (10) cm^{-1} for CF_4 to over 500 (700) cm^{-1} for NH_3).

Measured and simulated spectra of the ice surface also indicate that a water molecule of the ice surface bilayer can usefully be assigned to one of three categories. As for the unrelaxed bilayer of a freshly cleaved surface represented in Figure 1a, these categories are 3-coordinated molecules with either a dangling-H or a dangling-O coordination and 4-coordinated molecules with coordination shells distorted with respect to tetrahedral symmetry.[1,2] Recognition of these three categories of surface molecules, denoted here as d-H, d-O, and s-4, is useful primarily because the (six) surface-localized O−H-stretch vibrations of ice divide into modes that, though generally not localized on a single molecule, can be recognized as having large amplitudes for molecules within one of the three categories.

Preparation of Networks of Nanoparticles of Ice (and Other Volatile Substances). A variety of successful studies of the surface properties of icy substances has followed the development of techniques that permit spectroscopic observations of ice (and of volatile molecular substances in general) in a form having an exceptionally high surface area.[1] The experimentation has made exclusive use of aerosols formed in small static infrared cold-cluster cells that are modeled after an original larger cell of Ewing .[8] A principal innovation has been based on recognition that some of the aerosol particles assemble into surprisingly stable networks of nanoparticles on the infrared-transparent end windows of the cells. In the case of ice nanocrystals, the formation and assembly occur during the (repeated) rapid loading of the cell with a 1.0% mixture of water vapor and $N_2(g)$ to a pressure of 300 Torr at ∼70 K.

The nanocrystal assemblies have many desirable characteristics that the corresponding aerosols lack. In the case of ice, these properties include: stability over periods of weeks at temperatures below 100 K, surface stability with time and to adsorption and desorption of nonreactive small molecules, and the retention of a "constant" number of water molecules during annealing at temperatures in the 120−140 K range. Though the precise influence of annealing on the nanostructured assemblies has not been determined, it is presumed that the growth of larger particles and disappearance of smaller ones, driven by the greater chemical potential of particles with a high surface-to-volume ratio, is the dominant effect. This Ostwald ripening allows very useful difference spectra to be determined for samples with the "same" total amount of ice but greatly differing surface areas. Difference spectra, from comparison of the FT-IR spectra of small with large nanocrystals of ice, or the spectra of bare nanocrystals with nanocrystals coated with monolayers of adsorbate molecules, have been used extensively in characterizing the bare ice surface and subsurface as well as adsorbate effects.

Model of the Ice Surface from Molecular Dynamic Simulation. To study surface properties, including the patterns of the uptake of the adsorbate CF_4 in particular, we generate ad hoc ice surface models of different structures, use them to evaluate observable properties, and employ comparison with experiment to assess the validity of the models. A family of models was generated by starting with a crystalline slab of six hexagonal (111) cubic ice layers (six bilayers) with O atoms at perfect crystalline positions as in Figure 1a, while the H atoms were distributed at random between pairs of neighboring O atoms following the well-known ice rules. Then, the disordered surface models, such as S3 of Figure 1, were obtained by heating to 200−300 K using molecular dynamics with a TIPS2 potential while keeping the bottom two layers rigid. Finally, the structure is recooled to the experimental temperature. By varying the maximal temperature and the duration of the heating and cooling runs, one can obtain models of different extents of surface crystallinity. The S3 surface model has proven quite successful in several comparisons with experimental data.

Structure of Nanoparticle Surfaces Using CF_4 as a Probe Molecule. One of the critical tools in evaluating the ice surface structure (and that of other nanoparticles)[6] has been the pattern of the CF_4 asymmetric stretch-mode infrared band complex.[5] This triply degenerate vibration is characterized by a very large direction-independent dipole derivative. As affirmed by simulations, the oscillations of neighboring CF_4 molecules are always strongly dipole coupled to the extent that collective in-phase vibrations dominate the infrared spectra of the various condensed phases of CF_4, including monolayer and submonolayer adsorbate structures. In the limit of a monolayer, these collective modes are displayed as two strongly separated (∼80 cm^{-1}) prominent features attributable to dipole oscillations parallel (TO-mode) and perpendicular (LO-mode) to the adsorbate layer. The prominence of the usually silent LO-mode is a result of the largely off-normal incidence of the infrared probe beam at the nanoparticle surface.

These collective vibrational excitations of CF_4 adsorbate molecules are highly sensitive to the molecular-level structure of the underlying surface.[5] For smooth but disordered surfaces, such as model S3 (Figure 1), the most favorable binding sites identified for the CF_4 adsorbate are centers of (large) rings of water molecules. Just as these rings are distributed quite randomly on the ice surface, so are the CF_4 molecules at low molecular coverage. Such random distributions result in much different patterns in the CF_4 spectra than do 2-D islands of CF_4 that are favored by more cyrstalline surfaces. Comparisons of spectra, for submonolayer amounts of CF_4 on the ice surface with analogous spectra for crystalline and amorphous nanoparticles and for simulated spectra for surfaces with a great range of extents of crystallinity, suggest that surfaces of annealed ice nanocrystals are relatively smooth but with a high degree of lateral disorder.[5]

Assignment of the Surface-Localized Modes of Ice from IR Difference Spectra. The O−D-stretch absorption spectra of ice nanoparticle assemblies containing isolated HDO molecules indicate that the particles are dominantly crystalline when formed from 1% water in $N_2(g)$ in a 15 × 5 cm cylindrical cluster cell precooled to ∼70 K (see Figure 1 of ref 5). Nevertheless, the samples have been routinely annealed at temperatures in the 125−145 K range prior to investigation of surface-localized vibrational modes or of adsorbate−molecule infrared bands. Difference spectra of two types have been directly informative of the surface-localized ice modes.[1,2] Difference spectra that compare the small nanocrystals (<130 K annealed) with larger nanocrystals (annealed near 140 K) are dominated by three surface-localized-mode bands in the range 3450−3700 cm^{-1} (H_2O) or 2500−2750 cm^{-1} (D_2O).[1,2] From

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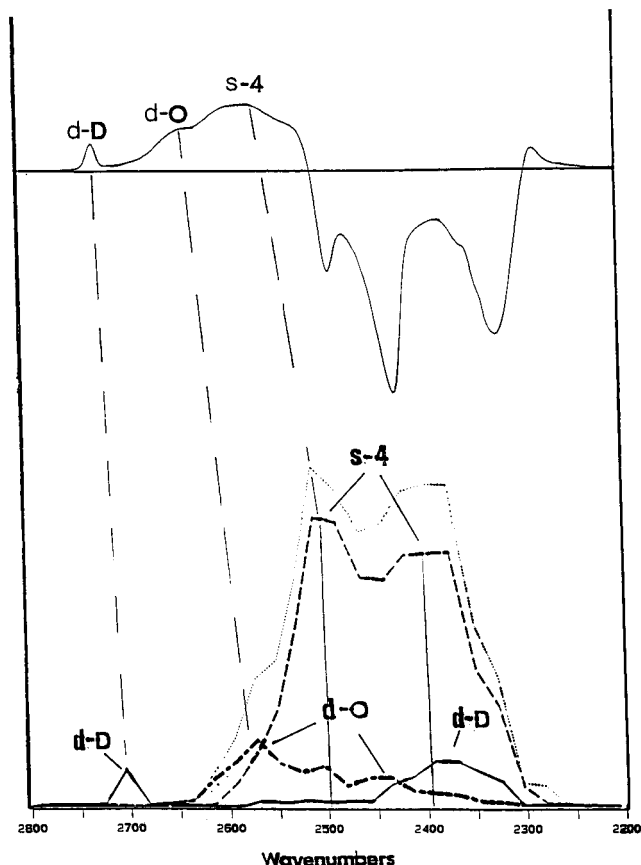*J. Phys. Chem. B, Vol. 101, No. 32, 1997* **6097**

Figure 2. Comparison of the band positions for the difference spectrum of small minus large nanocrystals with the simulated spectrum of the surface molecules of a thoroughly annealed $(D_2O)_{450}$ water cluster.

Figure 3. Spectra (a–c) showing the difference between bare and adsorbated coated nanocrystals for the weak adsorbates H_2, N_2, and CO. Other (labeled) spectra show the combined surface/subsurface spectrum from small minus large nanocrystal spectra, and the result of resolving this spectrum into subsurface and surface spectra as described in the text. The top two spectra are of bulk cubic ice and amorphous solid water (ASW).

simulated spectra (Figure 2) each of these three O–D-stretch-mode bands have been assigned to the out-of-phase vibrations of one of the three classes of surface water molecules (i.e., the d-D, d-O, or s-4 molecules of Figure 1).

Such spectra show clearly the bands of the three surface-localized vibrations that occur at significantly higher frequencies than the bulk ice bands. However, since Ostwald ripening has three effects (a reduction of the amount of surface and subsurface and an increase of the amount of interior ice), such difference spectra are not useful in identifying surface modes in the region below 3500 (2500) cm^{-1}, which is dominated by reduced subsurface and enhanced interior mode absorption. Nevertheless, the other three surface-localized O–H(D)-stretch modes have been identified by comparing the simulated spectra (Figure 2) with difference spectra between bare ice nanocrystals and the same nanocrystals coated with a monolayer of a weak molecular adsorbate such as N_2, H_2, or CO (Figure 3a–c). Using the comparison with the simulated spectra, positive features in the 2100–2500 cm^{-1} range of Figure 3a–c are assigned to the in-phase vibrations of the three categories of surface water molecules.[6]

Subsurface Spectrum of Ice and Adsorbate-Induced Surface Ordering. The weak-adsorbate spectra of Figure 3a–c suggest, somewhat misleadingly, that the various surface-localized modes of ice have comparable peak intensities. This observation allows recognition of the general shape of the subsurface mode spectrum from difference spectra that compare small and large nanocrystals. The three intense relatively sharp (negative) features of the interior crystalline ice contribution to such a spectrum (Figure 2, top) can be removed by adding a percentage of the known spectrum of crystalline ice for that temperature.[3] When this is done the new spectrum is of the
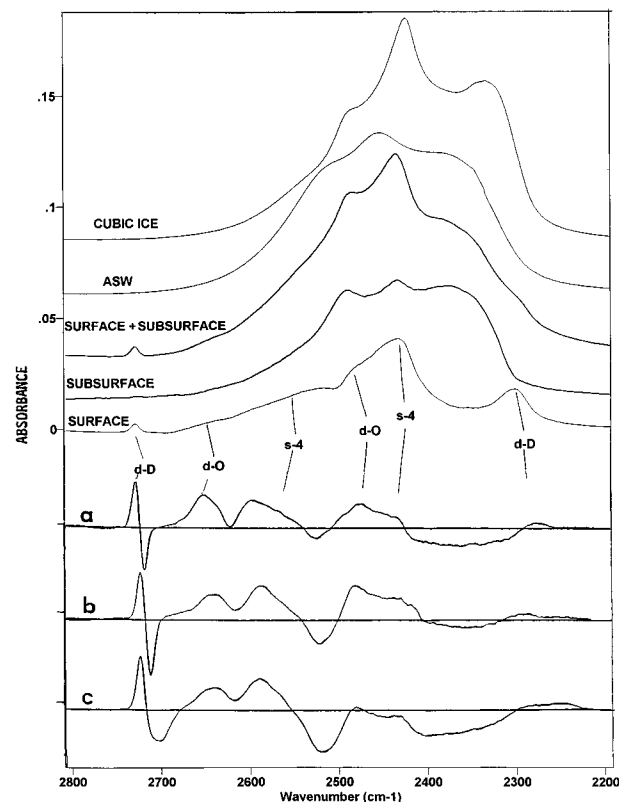
ice surface/subsurface lost by Ostwald ripening at ~140 K (third spectrum from the top in Figure 3). To the extent that the surface absorption is relatively weak, this new spectrum can be viewed as dominated by the spectrum of the subsurface ice that was lost (converted to crystalline ice) by annealation. Though this absorption is centered near that of the cubic ice (as expected since the subsurface is largely composed of distorted 4-coordinated molecules[1]), its shape is unique, being distinguished by bulges near 2500 and 2370 cm^{-1} and low intensity in the 2320 cm^{-1} region. The subsurface band intensity (~20% of the interior ice intensity for 20 nm particles) is consistent with a subsurface of roughly two bilayers, in agreement with the subsurface structure of a simulated slab of ice (Figure 1c).

As mentioned, one of the effects of the presence of certain H-bonding adsorbates (e.g., H_2S, acetylene, NH_3, SO_2, and HCN) is the reduction of the disorder and strain energy of the bare relaxed ice surface. Spectroscopically, this is observed in the conversion of about 50% of the subsurface infrared absorption described above to the spectrum of interior ice, as the reduced surface disorder also reduces the extent of the subsurface transition region.[3] This effect is most apparent in the comparison of difference spectra, of bare minus adsorbate-coated ice. Only for strong adsorbates is there an obvious strong (negative) interior ice contribution generated through interaction with the adsorbate (see Figure 4 of ref 3).

SO_2-Promoted Subsurface-to-Interior Ice Relaxation (and the Spectrum of the Subsurface). The dominant infrared absorption by the ice subsurface is apparently contained in a broad band complex centered near 2420 cm^{-1}, in the region of the central peak of the interior crystalline ice band. This is

consistent with the simulated spectrum for the top three bilayers of the slab of cubic ice.[1] As for the subsurface, most of the molecules of these three bilayers are 4-coordinated with their coordination shells distorted with respect to tetrahedral symmetry. However, determination of the precise experimental spectrum of the subsurface requires a different approach that is based on very different rates of adsorbate-induced structural relaxation of the surface and subsurface.

When SO_2 is adsorbed at 125 K onto nanocrystals of ice preannealed at 140 K, there is initially a strong shifting of the surface-localized modes of ice. However, relatively little new interior ice is evident in the difference spectrum comparing the bare and SO_2-coated ice, (in contrast to the report for H_2S and acetylene at 100 K[3]). However, during the next several hours at 125 K the SO_2-coated nanocrystals relax, and there is a prolonged (but limited) period of increase in the crystalline interior ice absorption. The difference between the spectra obtained before and after this period of relaxation is a relaxation spectrum that is interpreted as reflecting the conversion of subsurface to interior ice. As such, the addition of a correct percentage of the interior ice spectrum to the difference spectrum should yield the spectrum of the subsurface ice that was converted to interior ice during this relaxation. The resulting surface spectrum is presented fourth from the top in Figure 3.

The correct amount of interior ice absorption to be removed from the relaxation spectrum was estimated by following the changes in the O−H-stretch-mode band of isolated HDO. The extra interior ice from relaxation is reflected in the difference spectrum by a sharp negative feature at 3275 cm^{-1}. At an intermediate stage of the addition of the interior ice spectrum, an irregular positive doublet appears, but eventually the anticipated smooth single broader feature of the isolated HDO mode of the ice subsurface emerges. Addition of interior absorption is stopped at that point, giving the D_2O subsurface spectrum of Figure 3. It is interesting to compare this subsurface spectrum with those of crystalline ice and amorphous ice (top 2 curves in Figure 3). This comparison shows that, as one would anticipate, the subsurface spectrum is intermediate to that of the two bulk forms of ice. It is perhaps notable that it more resembles the amorphous ice spectrum in shape but, at a common temperature, is more like crystalline ice in the position of the subbands.

In this manner, the fortuitous difference in the rates of adsorbate-induced relaxation of the surface and subsurface leads to a view of the subsurface spectrum. Confirmatory evidence includes a very similar subsurface spectrum obtained using either acetylene or HCN as the adsorbate. Though each adsorbate causes a unique rate (and extent) of subsurface relaxation, the rates of the surface saturation and subsurface relaxation can be separated by adjusting the temperature of the nanocrystals. Finally, using the subsurface spectrum, the combined surface and subsurface spectrum can be separated to obtain the surface spectrum of the ice nanocrystals (Figure 3). The relative intensity of the component surface and subsurface spectra are indicative of a subsurface of no more than two bilayers.

Adsorbate Penetration and Reaction with Ice Nanocrystals. Beyond some limiting H-bonding strength, adsorbates are capable not only of inserting into the strained H-bonds of the reconstructed ice surface but also of "clipping" other H-bonds and, thereby, moving through the ice structure even at cryogenic temperatures.[4,9] Such behavior is particularly apparent for the adsorbate ammonia,[4] which is a notoriously strong proton acceptor. Ammonia, at less than monolayer coverage on D_2O ice, preferentially bonds to the surface d-D groups, downshifts the d-D stretch mode by about 500 cm^{-1}, reduces the disorder of the ice surface, and, like H_2S, SO_2 etc., increases the amount of crystalline interior ice of the nanocrystals.[4] However, with time and increased exposure at 120 K, ammonia penetrates the ice surface and progressively converts the nanocrystals to the amorphous monohydrate and, ultimately, to nanocrystals of $NH_3 \cdot H_2O$. Other strongly H-bonding molecules, such as ethylene oxide and HCl, behave similarly.[4]

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