

Ice Surface Reactions with Acids and Bases

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Previous Fourier-transform infrared spectroscopic studies of adsorbates on the surface of ice nanocrystals have considered two categories of molecular adsorbates: (a) weak adsorbates that desorb rapidly into a vacuum at $T < 100$ K and that influence the vibrational modes of only the surface molecules of ice and (b) adsorbates that form significant H bonds to the unsaturated surface groups resist desorption at temperatures below ~ 120 K and, without penetrating the ice, alter the subsurface ice spectrum. Here, we consider a third category of adsorbates which is characterized by molecules that form strong H bonds with the ice surface, penetrate the ice, and form hydrates. It is shown that above some minimum temperature of adsorption strong acids and Lewis base molecules, including ethers and amines, penetrate the ice and ultimately form known crystalline hydrates of the adsorbate. Results are reported for HCl, ethylene oxide, and ammonia as representative of these three subclasses of penetrating/reacting adsorbates. Ethylene oxide is shown to convert nanocrystals of ice to nanocrystals of the type I clathrate hydrate at 130 K. Similarly, nanocrystals of ice, exposed to NH_3 at 120 K, convert slowly to nanocrystals of the monohydrate of ammonia by a *molecular* reaction mechanism. By contrast, HCl, following adsorption in the 60–125 K range, converts ice nanocrystals to the amorphous *ionic* monohydrate which crystallizes upon warming above 135 K. However, below 50 K, adsorbed HCl exists primarily as the molecular adsorbate with a behavior similar to that observed for adsorption on amorphous ice. Disorder associated with the surface reconstruction of bare ice and the presence of strained H bonds between water molecules of the relaxed surface are likely critical factors in the interaction/reaction with adsorbates, such as atmospherically important HCl. However, the ability of strong proton donor/acceptor molecules to break and replace stable H bonds to water molecules is considered a prerequisite for the observed complete conversion of ice nanocrystals to hydrates at cryogenic temperatures.

Introduction

The manner in which certain molecules interact with the surface of ice remains of keen interest in several areas of science. Gas–ice reactions that lead to clathrate hydrate formation are of particular interest in cometary research,¹ while more general adsorbate–ice interactions are apparently pervasive in interstellar space.² The interaction of acid molecules with the ice surface is a particularly pressing concern of atmospheric scientists. In this latter case, basic questions include how the ice surface can sufficiently solvate an adsorbed acid molecule, such as HCl, to stabilize the ionized form ($\text{H}_3\text{O}^+\text{Cl}^-$) and to what degree and with what rate the ionization reaction can penetrate beyond the ice surface region at a given temperature.

Early reports indicated that, at temperatures above about 80 K, adsorbed HCl ionizes quite readily on the surface of either crystalline or amorphous ice,^{3–5} but that ionization is (kinetically) limited at temperatures below about 50 K.⁵ More specifically, crystalline nanoparticles of ice convert to the amorphous monohydrate (or higher hydrates) of HCl when exposed to low levels of HCl(g) near 80 K, while DCl adsorbed on the surface of amorphous D_2O ice retains a molecular form indefinitely at temperatures below 40 K.

Both experimental and high-level quantum chemical results suggest that at least four water molecules are required to ionize HCl within a cluster such as $(\text{HCl})(\text{H}_2\text{O})_n$.^{6,7} The results of another theoretical study support the view that HCl embedded in the ice surface does ionize but did not fully answer the question of how the HCl becomes embedded.⁸ It was speculated that the mechanism involves a high diffusional mobility of water molecules near the surface. However, such a mechanism is not

acceptable in general, since HCl adsorbed on ice nanocrystals converts quickly to the *ionic* amorphous acid hydrate at 80 K,⁵ a temperature well below the onset of either volatilization or diffusional motion of water molecules at the ice surface.

Significant progress has been made in recent years in devising an image of the ice surface that should be helpful in understanding ice–adsorbate interactions and the reactivity with HCl in particular.^{9–12} FT-IR spectroscopic studies, in close conjunction with molecular dynamic and Monte Carlo simulations, suggest that the ice surface is best imagined as a nonperiodic bilayer of water molecules with a broad distribution of ring sizes.^{9,13,14} The disordered bilayer includes strained H bonds that form during the reconstruction of the bare ice surface, so that the surface concentration of high-energy uncoordinated (dangling) groups is reduced. The existence of the seriously disordered surface foretells the presence of a transitional (subsurface) region in which the disorder is attenuated toward the interior ice. Consequently, ice nanocrystals are viewed as composed of a crystalline core surrounded by subsurface and surface regions, each of which has a unique vibrational spectrum that has been differentiated from that of the core.^{15,16} For nanocrystals of ~ 20 nm diameter, which have been the focus of the FT-IR spectroscopy, roughly 10% of the molecules are in the surface bilayer and 20% in the 2–3 bilayers of the subsurface, with the remainder a part of the crystalline core.

From the simulated structure and spectra, the molecules of the *surface bilayer* may be assigned to one of three categories: 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. The primarily 4-coordinated molecules of the *subsurface* experience a more limited distortion. The high percentage of

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molecules in the surface and subsurface regions allows the identification of detailed features of the corresponding spectra.^{14,15} This is possible through the use of two types of difference spectra: in one, Ostwald ripening is used to transform the nanocrystals to a larger average size without a change in the total amount of ice, so pronounced differences between spectra obtained before and after ripening reflect the loss of surface and subsurface and the gain of interior ice; in the second type of difference spectra, weak adsorbates, which selectively shift the modes of the water molecules of the surface bilayer, reveal the infrared bands of the three categories of surface water molecules,¹⁵ while stronger adsorbates permit identification of the infrared spectrum of the subsurface molecules.^{15,16}

The results, from comparison of spectra of bare ice with ice coated with adsorbates, have also shown that adsorbates that bond with medium strength to the surface convert much of the subsurface ice to interior ice, apparently through the replacement of strained bonds and a reduction of surface disorder.¹⁵ Here, using results for the interaction of HCl with the surface of annealed ice nanocrystals (in the 20–125 K range) and for the reaction of the ice surface with two other strongly H-bonding molecules, namely NH₃ and EO (ethylene oxide), it is shown that more strongly bound adsorbates readily penetrate the ice. These new data, for one strong proton-donor (HCl) and two strong proton-acceptor (NH₃; EO) molecules, in combination with the model of the relaxed ice surface derived from simulation and spectroscopic studies, suggest the outline of an alternate mechanism for the penetration of strongly H-bonding molecules into the ice surface at cryogenic temperatures.

Experimental Section

Assemblies of ice nanocrystals have been prepared as described previously¹⁴ by very rapid cooling of 1% mixtures of H₂O or D₂O in N₂(g) to temperatures in the 68–80 K range. A fraction of the nanocrystals that form in the gas phase assemble into a network of nanocrystals on the surface of the ZnS infrared windows of the cluster cell so that repeated loading of the cell permits the formation of stable samples with an optical density optimized for the particular study.

The individual nanocrystals, with average diameters in the 15–20 nm range, have been shown to have rough and irregular surfaces,¹³ while the O–D stretch band of ~1% HDO incorporated into the samples confirms that the interior of the particles is highly crystalline.¹⁴ During annealing the ice-particle surfaces apparently become smooth but remain irregular at the molecular level,¹³ while the average particle size increases as a result of Ostwald ripening. Unless otherwise noted, to assure the presence of a relaxed surface, the ice nanocrystals have been routinely annealed for an hour at a temperature (~140 K) at which amorphous ice is known to slowly crystallize and at which the vapor pressure of *bulk* ice is such as to cause surface renewal over a period of several minutes.^{17,18}

The annealed ice nanocrystals have been exposed to HCl (DCI) vapors while held at temperatures ranging from 20 to 125 K. At temperatures below 60 K a directed doser was necessary to facilitate contact of the HCl with the ice, so exposure to the acid was greatest for nanocrystals on the outer surface of the assemblies. Because NH₃ and EO are less volatile, temperatures in the 120–130 K range were used for their adsorption and reaction to allow uniform exposure of the nanocrystals to the vapors of the adsorbate. Several examples of reactions described in this paper are of ice nanocrystals exposed to the pure vapors of an adsorbate at a vapor pressure determined by equilibration with the coldest part of the inner section of a double-walled reaction cell. These vapor pressures

are referred to as saturation pressures. The related spectra are for nanoparticles on the cell windows, which are necessarily a few degrees warmer than the coldest part of the cell.

Results and Discussion

The comparison of results subsequent to the adsorption of HCl, NH₃, and EO on the surface of crystalline ice is potentially useful because of similarities and differences in the behavior of these molecules. Above some minimum cryogenic temperature, each adsorbate is observed to attack the ice surface, ultimately converting the ice nanocrystals to crystalline monohydrates¹⁹ or, in the case of EO, to a type I clathrate hydrate. However, the hydrate of HCl is ionic while that of NH₃ and EO is molecular. As we will see, the mechanism of the formation of NH₃·H₂O from ice nanocrystals is also molecular in nature while the HCl hydrate forms as a consequence of ionization. Because of these similarities and differences, it is possible that the results for the more complex case of HCl can be viewed more clearly in terms of the results for NH₃ and EO.

Adsorption and Reaction of NH₃ at the Crystalline Ice Surface. *NH₃ Monolayer Coverage of D₂O Ice.* The behavior of ammonia adsorbed on the ice surface is strongly dependent on the level of exposure, the isotopic composition, and the temperature. Exposure of D₂O ice to NH₃ at levels *less than a monolayer* at 120 K results in strong hydrogen bonding of the ammonia to the dangling-deuterium (d-D) sites with more limited uptake at the dangling-oxygen (d-O) or 4-coordinated (s-4) surface sites. This preference to hydrogen bond as a proton acceptor is not surprising, as it is known that the O–H–N hydrogen bonds of the monohydrate and hemihydrate of ammonia result in a downshift of ~700 cm⁻¹ of the O–H stretch mode frequency,^{20,21} while NH₃ is a notoriously weak proton donor.

The strong bonding, to the ice surface d-D sites, is evidenced in part by a near coincidence of the infrared band frequencies of the adsorbed NH₃ molecules with those of the NH₃(II) molecules of the hemihydrate of ammonia. The NH₃(II) molecules, acting as proton acceptors, form a single strong H bond to water molecules of the hemihydrate network.²² Otherwise, the NH₃(II) molecules dangle into open channels of the crystalline 2NH₃·H₂O and thus serve as an obvious analogy to NH₃ molecules attached to the d-D groups of the ice surface. The comparative frequencies, in cm⁻¹, for NH₃(II) of the hemihydrate and adsorbate NH₃ are respectively 3402/3413, 3393/3386, 1631/1643, and 1104/1110, with assignments as in ref 21. These similarities of peak positions are apparently significant, since the corresponding vibrations of the NH₃(I) molecules, of the H-bonded network of the hemihydrate, are notably different.

Cooling stabilizes near-monolayer amounts of adsorbed ammonia, permitting a deliberate spectroscopic study. The results indicate that *adsorbed* ammonia influences the D₂O nanocrystals in a manner similar to that reported for the more weakly H-bonding molecules H₂S and acetylene.¹⁵ That is, a difference spectrum, such as in Figure 1b, shows that the adsorbed ammonia increases, by several percent, the amount of ice having a spectrum recognized as that of the interior ice. Thus, NH₃ joins a short list of molecules (including EO; vide infra) that are known to increase the order of ice in the surface/subsurface region.

This influence is demonstrated in Figure 1a,b by a comparison of the effect of the ammonia adsorbate with the effect of a monolayer of weakly adsorbed N₂. The difference spectra in Figure 1 are from the spectrum of bare ice nanocrystals minus the spectrum of the same nanocrystals with a near monolayer

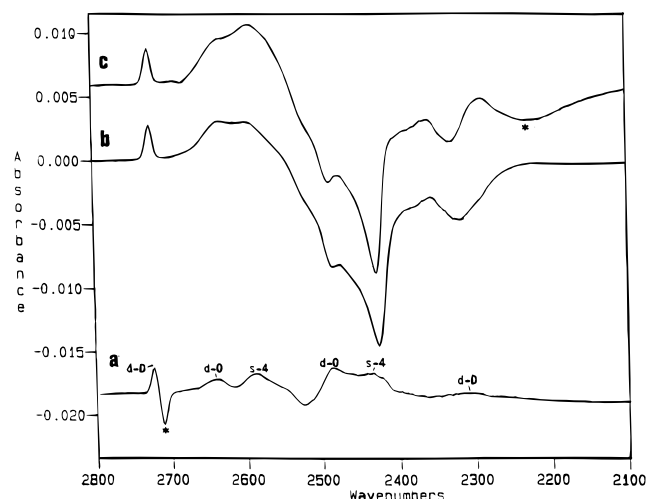


Figure 1. Difference spectra obtained by subtracting the spectra of adsorbate-coated D₂O ice nanocrystals from the spectrum of the same nanocrystals without adsorbate, using a subtraction factor of 1.000: the adsorbate was (a) N₂ (83 K), (b) NH₃ (120 K), and (c) NH₃ followed by acetylene (110 K). The spectra are vertically offset for clarity. Asterisks mark the shifted d-D bands.

of adsorbate. In the case of N₂, the adsorbate effect can be described as a shift in each of the six distinct surface-isolated modes of ice such that the difference spectrum shows a maximum near the labeled unshifted band positions and a minimum near the new positions.^{14,15}

By contrast, NH₃ (like H₂S and acetylene) causes the appearance of considerable new (negative) intensity in the difference spectrum below 2500 cm⁻¹ at precisely the frequencies where interior ice of the same temperature has strong discrete absorption bands. Adsorbate induced generation of new crystalline interior ice is recognized as an indirect effect of strong adsorbate interaction with the irregular ice surface. In addition to binding to the uncoordinated surface sites (d-H and d-O), the adsorbate molecules are thought to insert into the strained H bonds of the reconstructed bare ice surface. The resultant reduction in the strain at the ice surface is then reflected in a relaxation of the *subsurface* toward the interior ice structure and results in an increased amount of ice having the spectrum of interior (or bulk) ice.¹⁵

It was noted above that the ammonia molecules that associate with the ice surface as proton acceptors resemble the NH₃(II) molecules of the hemihydrate. If so, the O–D stretch mode frequency should shift from the bare ice value of 2724 cm⁻¹ to the hemihydrate position near 2200 cm⁻¹, producing a significant new (negative) band in Figure 1b. No such band is observed. However, a strong broad negative band does emerge in that region (2220 cm⁻¹), if the NH₃-coated ice is exposed to acetylene vapor (Figure 1c) or if the coating of NH₃ is increased to a complete monolayer. Since C₂H₂ is a relatively strong proton donor, the acetylene attaches at vacant d-O and s-4 sites of the surface. Such neighboring adsorbed acetylene molecules appear to stabilize a linear D-bonded structure of the NH₃ molecules at the d-D sites, strengthening the D bond to the NH₃ and causing the shifted d-D vibration to appear at the expected lower frequency. A corollary is that, at submonolayer coverage, the ammonia molecules at the d-D positions are stabilized by *multiple interactions* with the surface water molecules, interactions achieved by moving away from a linear hydrogen-bonded structure. (Simulation studies of adsorbates on the ice surface, such as of H₂ on amorphous ice²³ or of HCl on crystalline ice,²⁴ commonly show that adsorbate molecule positioning is influenced by the stabilizing effect of multiple interactions.)

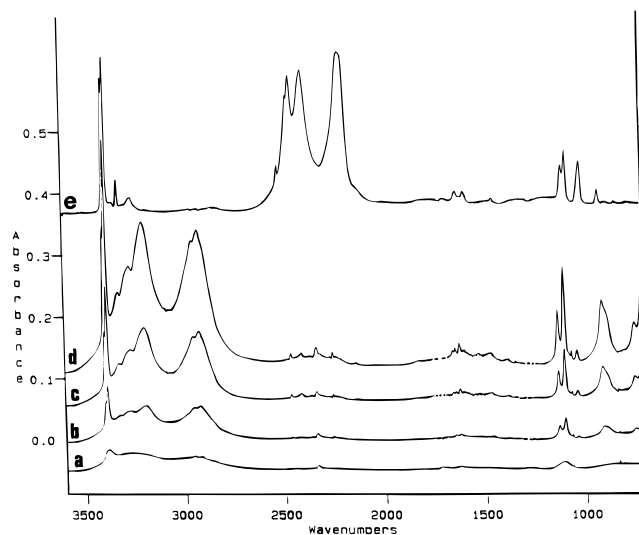


Figure 2. Infrared spectra showing the conversion of annealed ice nanocrystals to the (crystalline) monohydrate of NH₃ under the saturation pressure of ammonia at 120 K with the percent/time periods of conversion being (a) 15%/1.0 h, (b) 25%/2 h, (c) 40%/5 h, (d) 80%/10 h, and (e) spectrum of NH₃·D₂O from conversion of D₂O ice. The spectrum of the unconverted ice has been subtracted in each case, and the spectra are vertically offset for added clarity.

It is also informative to compare the shift of the surface d-D mode, caused by bonding with NH₃, to the corresponding shift that occurs upon formation of the binary complex, HOD·NH₃, in an argon matrix. The observed shift of the O–D stretch mode for the complex²⁵ is only 176 cm⁻¹ compared to the shift of 500 cm⁻¹ observed in Figure 1c. Most of the difference in the magnitude of the shifts is attributed to the greater polarity of the dangling surface O–D bond caused by the cooperative effects of neighbor water molecules. This enhanced polarity has also been noted from the magnitude of the shift of the d-D mode caused by other adsorbate molecules, such as acetylene.²⁶

Conversion of Ice Nanocrystals to NH₃·H₂O and NH_{3-x}D_x·D₂O Nanocrystals. While NH₃ can be adsorbed on D₂O ice to near-monolayer amounts at 120 K with no evidence of reaction beyond a minor amount of isotopic exchange, the same is not true for NH₃ adsorbed on H₂O ice. Attempts to form a near monolayer of adsorbed NH₃ on H₂O nanocrystals have resulted in a reaction that is now recognized as the first step in the conversion of the ice to the monohydrate of ammonia. Since the spectra of the hydrates of ammonia have been well-characterized,^{20,21} the complete conversion of annealed nanocrystals of ice, exposed to the saturation pressure of ammonia vapor at 120 K, to the monohydrate of ammonia can be recognized with little chance of error. The spectra of Figure 2a–d represent the sequence of spectroscopic changes that occur during exposure to the ~2 μm pressure of NH₃(g) for times ranging up to 10 h. It is apparent from curves a and b that the reaction initially forms an amorphous hydrate, but after about 20% of the ice converts to hydrate, the crystalline monohydrate becomes the dominant product. A nanoparticle nature of the monohydrate product was established from the retention of surface area as reflected in the intensity of the infrared bands of a monolayer of adsorbed CF₄.

Though it is possible to coat D₂O nanocrystals with NH₃ without significant conversion to a hydrate (as noted above), exposure of deuterated ice to the saturation vapor pressure of ammonia at 120 K, over a period of several hours, does result in the formation of nanocrystals of NH_{3-x}D_x·D₂O. The spectrum of this deuterate is given in Figure 2e from which it is clear that the reaction occurs without exchange of the

deuterium atoms of the D_2O , since the O—H stretch bands of the monohydrate (Figure 2a–d) are fully shifted to the known positions for $ND_3 \cdot D_2O$ ²⁰ in the O—D stretch region. However, because ammonia has a nontrivial vapor pressure at 120 K, the NH_3 does undergo extensive exchange with D_2O nanocrystals in the warmer part of the cell (near the entry port) during the several hours of the reaction. This is clear from the appearance of the bands of NH_2D (1030 cm^{-1}) and NHD_2 (940 cm^{-1}) in Figure 2e. The failure of the sampled D_2O to undergo exchange is significant since this provides strong evidence that the conversion to the hydrate proceeds by a molecular mechanism. An ionic mechanism, based on ammonium and hydroxide ions, would produce extensive isotopic scrambling of the D_2O .

Adsorption and Reaction of EO at the Crystalline Ice Surface. *EO Monolayer Coverage of D_2O Ice.* Being an ether, ethylene oxide is a somewhat weaker Lewis base than ammonia. Thus, it is also expected to bind tightly at the d-D sites and to efficiently eliminate the strained H bonds of the surface of crystalline ice. For near-monolayer coverage at 125 K, this behavior is observed in the shifting of the d-D band by about 130 cm^{-1} to a new position near 2590 cm^{-1} . This shift is accompanied by a growth of the stretch-mode bands of the interior ice caused by a partial ordering of the surface. This growth, though not shown, is similar to that depicted in Figure 1b, for the adsorption of NH_3 ; so, not surprisingly, EO is also among the adsorbates known to increase the amount of the interior ice of the nanocrystals.

Complete Conversion of Ice Nanocrystals to the EO Clathrate Hydrate. Ethylene oxide is also a member of a rather short list of small polar guest molecules known to facilitate the growth of clathrate hydrates,²⁷ particularly at cryogenic temperatures *in vacuo* from vapor phase deposits.^{28,29} EO apparently enables the clathrate growth by functioning as a proton acceptor that generates host–lattice defects. These defects are the source of solid-state mobility required for low-temperature structural rearrangement, as examined recently by Tanaka et al. in the simulation of lattice rearrangement processes of amine clathrate hydrates.³⁰

It follows that a likely molecular adsorbate, chosen to convert ice nanocrystals to nanocrystals of a clathrate hydrate at cryogenic temperatures, would come from a short list of Lewis base molecules, including EO, other small ether molecules, certain small amines, acetone, and formaldehyde. Special guest–molecule properties are required for this conversion, as nonpolar small molecules such as N_2 and CF_4 do not penetrate the ice nanocrystals at 120 K, even for long exposures at pressures in the range of 1 bar. Of the stable proton-acceptor molecules, EO was chosen, as it has the volatility required for diffusion to the ice surface of a nanocrystal assembly at $\sim 120\text{ K}$.

When the ice nanocrystals, coated with EO at 125 K, were warmed to 132 K in the presence of the saturation vapor pressure of the EO, the conversion to the crystalline type I clathrate hydrate of EO was initiated and completed in a period of 3 h. Evidence of this conversion, based on the well-known spectrum of the EO clathrate, is given in Figure 3. Part A shows the evolution of the D_2O stretch-mode spectrum (top) from that of ice to that of the clathrate hydrate (bottom curve). Simultaneously, the sharper band of the OH stretch mode of isolated HDO evolves to the broad band characteristic of the clathrate hydrate (Figure 3B), and the C—H stretch bands for EO in the large cage of the type I clathrate emerge.³¹ From the molecular mechanism for formation of the monohydrate of ammonia and the simulation results of Tanaka for clathrate rearrangement,³⁰ it is reasonable to assume that the formation of the clathrate

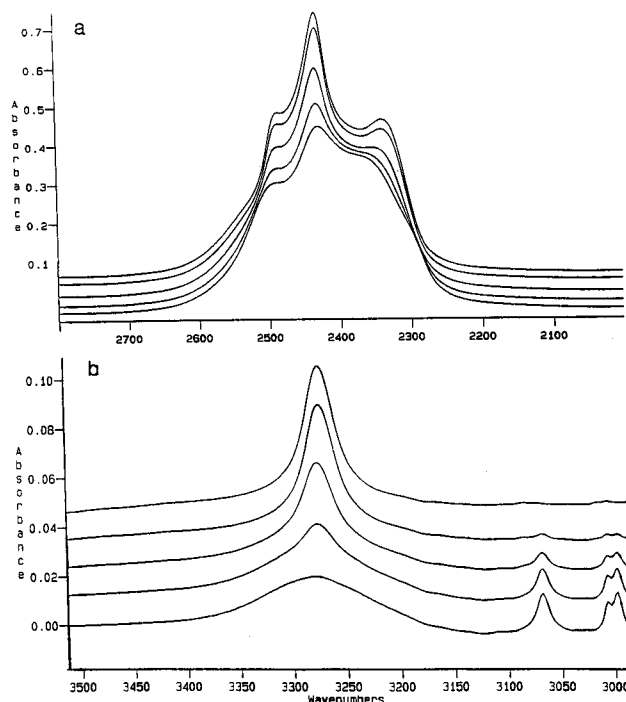


Figure 3. Infrared spectra showing the conversion of D_2O ice nanocrystals to the type I clathrate hydrate of EO over a period of 3 h at 132 K. The sequences from top to bottom show the changing pattern of (a) the O—D stretch region of D_2O and (b) the O—H stretch region of isolated HDO and the C—H bands of EO.

hydrate occurs by a molecular/defect mechanism that involves the breaking of old H bonds and the formation of new ones.

Other infrared absorption bands characteristic of enclathrated EO, such as the well-studied C—O stretch bands near 1270 cm^{-1} ,^{31,32} also mark the complete conversion to nanocrystals of the clathrate. Further, band intensities, of near-monolayer quantities of CF_4 adsorbed on the new icy phase, have shown that the clathrate nanocrystals retain a size similar to that of the original ice nanocrystals (i.e., $\sim 50\text{ nm}$ in diameter for particles annealed at 140 K).

Adsorption and Reaction of HCl at the Crystalline Ice Surface. The conversion of ice nanocrystals to the hydrate of ammonia proceeds without any spectroscopic evidence of ionization. By contrast, interaction of HCl with ice nanocrystals reflects both the much greater volatility of HCl and the greater tendency of HCl to ionize in a water environment. Because of the greater volatility of HCl, it is possible to adsorb HCl onto the nanocrystals at a much lower temperature, but because of the greater reactivity, it is not possible to adsorb a full monolayer of HCl without reaction occurring. Adsorption using the HCl saturation pressure is possible on a reasonable time scale at temperatures down to about 60 K. However, it has already been shown that exposure of nanocrystals, suspended in an inert gas at 80 K, results in adsorption and rapid ionization of HCl,⁵ so it is not surprising that, in the present study, HCl adsorbed on ice nanocrystals at 60 K was observed in an ionized form rather than as a molecular complex with the ice surface sites.

Spectra that demonstrate the reaction of HCl with the ice surface at 125 K are presented in Figure 4. Exposure to the saturation pressure of HCl for 1 h converted the ice nanocrystals completely to the amorphous monohydrate, for which the infrared spectrum is well-known.⁵ Warming to 135 K caused the transition to crystalline nanoparticles of the ionic monohydrate of HCl, also of known infrared spectrum.⁵ The more rapid conversion of ice nanocrystals to the monohydrate of HCl, compared to the conversion to the monohydrate of NH_3 , does

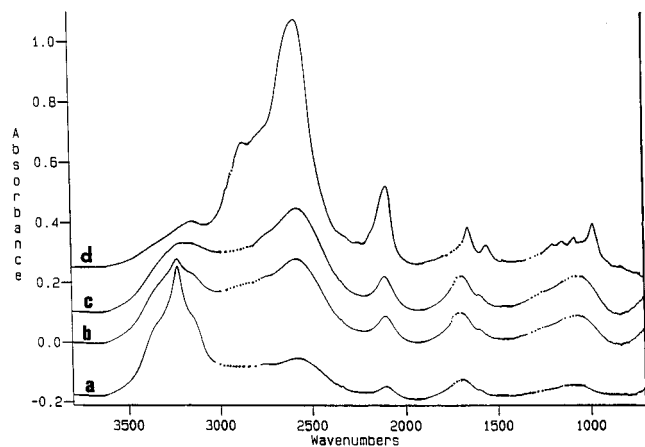


Figure 4. Infrared spectra showing the conversion of annealed ice nanocrystals to the (crystalline) monohydrate of HCl: (a) $\sim 30\%$ conversion after a few minutes at 125 K; (b) $\sim 90\%$ conversion after 45 min at 125 K; (c) complete conversion after 1 h at 125 K; (d) hydrate nanocrystals after warming to 145 K.

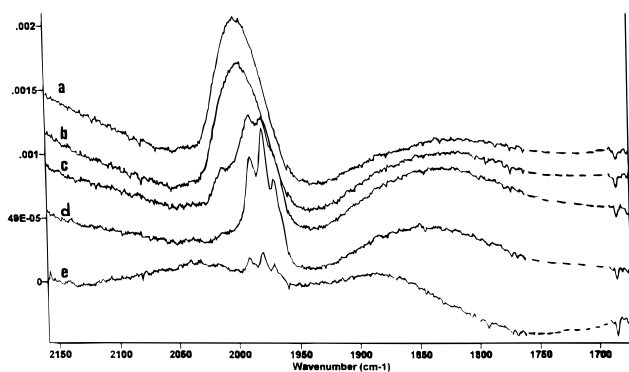


Figure 5. Infrared spectra for D_2O ice, annealed at 100 K, dosed with DCl at 20 K (a) and subsequently warmed to 30 (b), 40 (c), 50 (d), and 60 K (e). The acid-surface complex band ($\sim 1830\text{ cm}^{-1}$) and the emergence of the $D_3O^+ \cdot Cl^-$ band near 2050 cm^{-1} at 60 K are observed. Time at each temperature was ~ 30 min.

not necessarily imply an inherently greater reaction rate as the saturation vapor pressure of HCl is much greater than that of NH_3 .

The behavior of adsorbed HCl at 125 K can be contrasted with that of DCl adsorbed onto D_2O ice nanocrystals at a *much lower temperature* (Figure 5). Directed dosing of the D_2O nanocrystals with DCl(g) at 20 K resulted in a sample with the spectrum of Figure 5a. Here (and in the other curves of Figure 5), the narrower band near 2000 cm^{-1} is from a thin deposit of DCl on the front of the assembly of nanocrystals, while the band near 1830 cm^{-1} is assigned to the stretch mode of *molecular* DCl complexed with the ice surface. The latter assignment is based on a similar reported assignment for DCl adsorbed on microporous amorphous ice at 20 K.⁵ The *uncomplexed* DCl(s) film can be seen to convert from an amorphous to a crystalline form near 40 K and to nearly vanish by 60 K, the loss resulting from a combination of reaction and vapor transport.

When warmed from 20 to 40 K (Figure 5c), the amount of complexed molecular DCl can be seen to increase as the acid molecules better permeate the assembly of nanocrystals; but by 60 K (Figure 5e), a broad band appears in the region of the O-D stretch mode of $D_3O^+ \cdot Cl^-$ ($\sim 2050\text{ cm}^{-1}$).⁵ Not surprisingly, the molecularly adsorbed acid converts to the ionized form at 60 K, as signaled by the decrease of the 1850 cm^{-1} band intensity (Figure 5e) and the growth of the 2050 cm^{-1} broad band. This behavior of hydrogen chloride on the nanocrystal

surface is similar to that reported for the surface of microporous amorphous ice.

Summary

This study has demonstrated the unlimited conversion of ice nanocrystals to crystalline hydrates of three strongly H-bonding molecules, HCl, NH_3 , and EO, upon exposure to the saturation vapor pressures at cryogenic temperatures ($< 130\text{ K}$). It has also shown that the conversion to the crystalline ammonia monohydrate occurs by a molecular mechanism that can be envisioned as a result of the ability of the ammonia to compete successfully with water molecules as a proton acceptor. The lack of isotopic scrambling of D_2O during the formation of $NH_3 \cdot x D_2O$ requires the switching of H bonds from water-water to water-ammonia without an ionization stage. Since EO is less inclined to ionize than NH_3 , it is concluded that the formation of the crystalline EO clathrate hydrate from crystalline ice proceeds similarly, a behavior consistent with the molecular nature of the lattice rearrangements of amine clathrate hydrates.³⁰

On the other hand, it is clear that HCl readily ionizes following adsorption on the crystalline ice surface at temperatures above 50 K. This does not mean that the primary step in the conversion of ice to the monohydrate of HCl is ionic in nature. When the HCl first bonds to the dangling surface groups of the ice, it presumably is molecular in form, since the general perception is that HCl must interact with at least four water molecules to ionize.^{6,7} Rather, it is reasonable, based on the results for NH_3 and EO as proton acceptors, to presume that HCl, after being adsorbed, employs its power as a proton donor to disrupt/replace the H bonds of the ice surface. By so doing, it can penetrate the first bilayer of the surface and *then ionize* as it becomes embedded in the ice subsurface.

A lack of any qualitative difference between the observed reactivity of HCl with amorphous and crystalline ice may reflect the disordered surface structure of ice nanocrystals,¹³ and, presumably, of hexagonal and cubic ice in general. Although disordered, the surface of the ice nanocrystals is unquestionably different than that of the pores of microporous amorphous ice. This is evident from a 4 cm^{-1} downshift in the frequency of the stretch mode of the surface dangling O-H groups,¹⁴ a reduction of $\sim 30\%$ in the corresponding bandwidth, a much lower concentration of 2-coordinated surface water molecules, and the markedly different spectra of adsorbed CF_4 .¹³ Nevertheless, the surface resembles the amorphous-ice surface in some respects. One common feature that may be particularly important is the presence of strained H bonds that form during the surface reconstruction.¹³ Such H bonds would be particularly vulnerable to replacement by new H bonds to adsorbates, such as HCl, and likely have a role in the first step of penetration of the ice surface by strongly H-bonding adsorbates.

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