

Covalent HCl at the Surface of Crystalline Ice at 125 K: The Stable Phase at Submonolayer Levels

Nevin Uras, M. Rahman, and J. P. Devlin*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

Received: August 26, 1998; In Final Form: October 1, 1998

FT-IR spectroscopy of ice nanocrystals, within micrometer thick assemblies, allows observation of the complete stretch-mode vibrational spectrum of the ice surface bilayer with a high level of signal-to-noise. For these high surface area samples, the influence of submonolayer quantities of DCl on the D₂O ice surface is clearly observable. The effects for DCl are analogous to those for strongly H-bonding *covalent* adsorbates in the following respects: (a) the extent of shifting of the ice surface-mode vibrational frequencies, (b) the induction of order at the ice surface followed by relaxation of the *subsurface* to oxygen-ordered interior ice, (c) the partial reversibility of the DCl adsorption upon exposure to a second strong adsorbate, and (d) the observation of the internal vibrational mode of the adsorbed DCl. These results identify covalently adsorbed DCl as the thermodynamically stable form for submonolayer exposures at 125 K.

Introduction

The interactions of strong acids with the ice surface is of particularly intense interest to atmospheric scientists. Experimental studies of crystalline ice exposed to HCl (DCl) have shown that results are sensitive to the sample temperature and the effective concentration of the acid.¹ Nevertheless, the known characteristics of the interaction can be stated fairly succinctly. At temperatures above ~60 K, the HCl can penetrate the ice, where it dissociates as ions and converts the ice to an amorphous (below ~140 K) or crystalline hydrate (at higher temperatures). In the presence of a limited amount of HCl at the interface, the preferred hydrate is the hexahydrate, while lower hydrates are favored by high rates/amounts of exposure and low temperatures.^{1,2}

The interaction of covalent HCl with the ice surface has been modeled in several theoretical studies,³ and there is experimental evidence that the covalent form is *kinetically stabilized* on ice below ~50 K^{1c,f} and is stable on the surface of its hexahydrate at higher temperatures.^{1d} It is generally recognized that HCl must *initially* adsorb as a covalent unit prior to dissociative ionization accompanied by hydration. In view of a deficiency of readily available water molecules for ion hydration at the crystalline ice surface, the possibility of long-term stability of a covalent adsorbed state has been recognized.³ However, we are not aware of previous experimental evidence for *stable* covalent HCl on the surface of pure ice, though the presence of HCl with a unique structure at the surface, for submonolayer exposures, has been observed.⁴ The purpose of this paper is to describe FT-IR spectroscopic studies of HCl on the surface of ice nanocrystals, near 125 K, that indicate that HCl is a *stable* covalent adsorbate on crystalline ice, provided exposure is limited to submonolayer quantities.

Experimental Section

The general methods of FT-IR spectroscopic study of nanoparticles, which have been used throughout the present investigation, have previously been described in some detail.⁵ Here, results have been obtained through the formation, at 140

K, of assemblies of D₂O nanocrystals of a standardized thickness. Formed at this temperature, the particles average ~60 nm in diameter and are immune to Ostwald ripening at any lower temperature. These standard assemblies were of a thickness to give an O–D stretch peak absorbance of 0.40 units at 125 K and a dangling-OD (d–D) stretch band of 0.0010 units. These assemblies were exposed to DCl vapors at 125 K with a pressure required to produce ~0.05 monolayer (ML) of adsorbate uptake per minute. However, exposure of the nanocrystals to DCl decreased significantly through the micrometer depth of the network of particles, so that, for an *average* exposure of 1 ML, the uptake varied through an assembly, from several monolayers (on the outer surface) to less than one.

Results and Discussion

The critical measurements of this study were difference spectra from a comparison of ice samples with less than monolayer coverages of DCl with the corresponding bare ice samples. An example, among similar spectra obtained for a few dozen samples, is given in the top curve of Figure 1 where the bare ice spectrum has been subtracted from a spectrum of the same ice assembly after the uptake of an average of 0.3 ML of DCl. The result has the appearance of a typical difference spectrum as observed for strong adsorbates such as NH₃^{1f} or SO₂.⁶ If we assume that this difference spectrum reflects strictly a loss of bare surface and replacement by the DCl-shifted surface, then, knowing the bare surface spectrum⁶ (middle curve of Figure 1), we can generate the spectrum of the ice surface with the DCl adsorbate present by merely adding the bare surface spectrum until the d–D band at 2725 cm⁻¹, unique to the bare surface, disappears.

This procedure produces the bottom spectrum of Figure 1. Even with this low exposure of the ice surface to DCl, the gradation in exposure across our samples results in formation of a detectable amount of the DCl hexadeuterate, but at a level that does not noticeably affect this shifted surface spectrum. Thus, in the main body of Figure 2, this DCl-shifted surface spectrum is compared with similar spectra for other strong

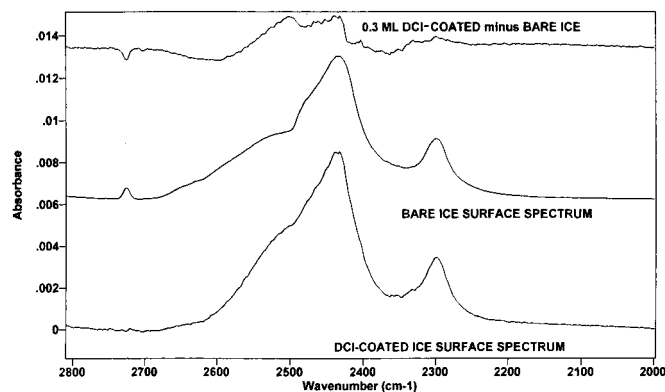


Figure 1. Infrared difference spectrum (top) from subtraction of the bare D₂O cubic ice spectrum from that of the same ice sample after adsorption of ~0.3 ML of DCI and (bottom) the same spectrum after addition of the bare ice spectrum (middle) to eliminate the bare surface component. The result is the DCI-shifted ice surface spectrum.

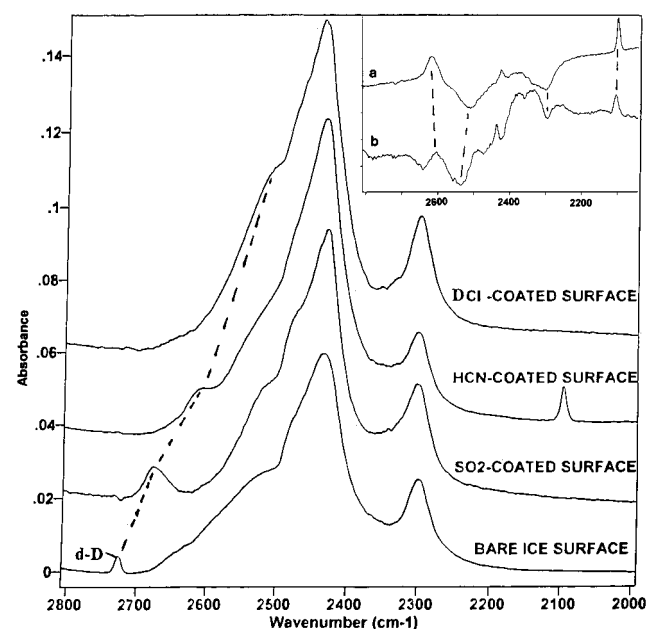


Figure 2. Spectra of the bare surface of D₂O cubic ice and of the ice surface coated with the strong adsorbates SO₂, HCN, and DCI. The dashed line joins the band for the d-D stretch mode for the different cases. The inset gives (a) the difference between these normalized HCN- and DCI-shifted ice surface spectra and (b) the directly observed difference spectrum caused by the partial replacement of adsorbed DCI by adsorbed HCN. The dashed lines join the four prominent features in (a) and (b) (see text).

(covalent) adsorbates. These spectra, obtained prior to subsurface relaxation for near monolayer adsorbate coatings on different ice samples, are very similar, differing primarily in the position of the shifted d-D band as indicated by the dashed line. On the basis of the procedure used in Figure 1, the shifted surface spectra have each been normalized to that of the bare surface.

The subtraction of the normalized DCI-shifted surface spectrum from the normalized HCN-shifted spectrum of Figure 2 is given as curve a in the inset. This difference should be dominated by the d-D band, since the shift of that mode with respect to the bare ice value is uniquely sensitive to the nature of the adsorbate (and is a good measure of the strength of the H-bond between the adsorbate and the d-D^{1f}). In fact, the two features (one positive and one negative) that appear above 2400 cm⁻¹ can be attributed to d-D-HCN (2620 cm⁻¹) and d-D-DCI (2510 cm⁻¹).

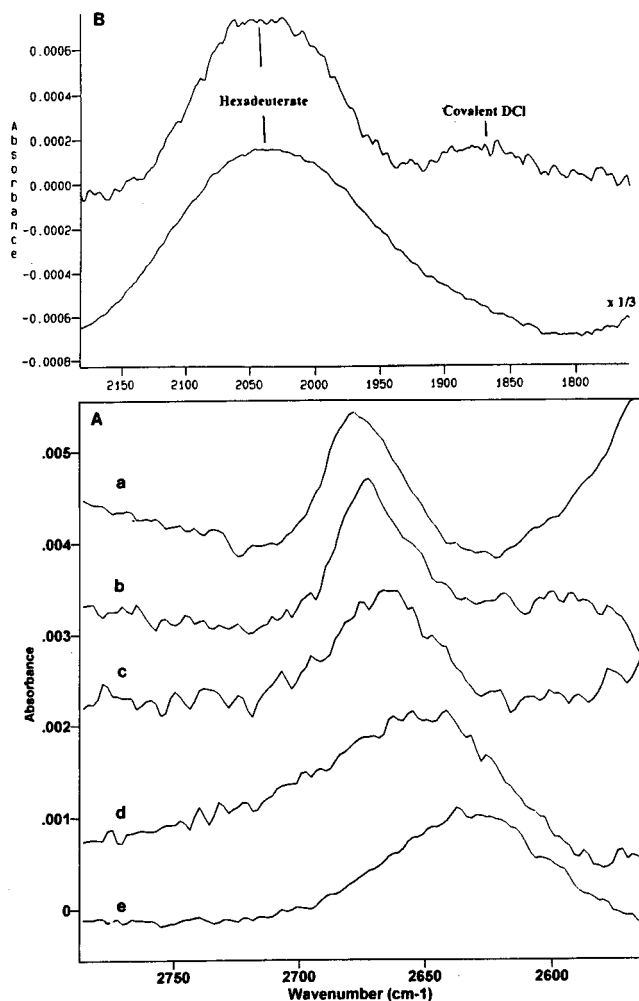


Figure 3. (A) Spectra (c-e) of the d-D-SO₂ O-D stretch-mode band, for samples coated with adsorbed DCI but then exposed to SO₂ vapor at 120 K for several hours, compared with this band for (a) SO₂ adsorbed on bare ice and (b) SO₂ adsorbed on an ice surface originally saturated with ND₃. Here, (c-e) are for samples with an increasing amount of the hexadeuterate present, with (c) ice with (primarily) a DCI monolayer coating and (e) largely a hexadeuterate sample. (B) Spectra in the DCI stretch-mode region for a sample with uptake of about 0.5 ML of DCI (top) compared with a sample with ~4 ML uptake of DCI.

This assignment is consistent with results from exposure of a DCI-coated ice sample to HCN vapor at 125 K, as shown in curve b of the inset. HCN replaces DCI on the ice surface as indicated by the emergence of the band near 2605 cm⁻¹, the accompanying loss of intensity near 2520 cm⁻¹, and the appearance of the CN stretch-mode band at 2096 cm⁻¹. A negative band also appears at 2300 cm⁻¹, caused by a reduced intensity of the d-D symmetric stretch band for HCN vs DCI. The slight offset in band positions, indicated by the slanted dashed lines, is attributed to the mixture of adsorbates present in curve b. The obvious displacement of DCI from the surface by HCN and the appearance of a band for the d-D mode shifted by DCI are both signs of the presence of covalent DCI.

Other strong adsorbates can also displace DCI from the ice surface. This is shown in Figure 3A for SO₂ where it can be seen that the SO₂-d-D band (c), which emerges when SO₂ replaces DCI, is very similar to that observed (b) for the displacement of NH₃ from the surface, both of which are similar to the band from direct loading of SO₂ onto bare ice (a). That the band of curve c is not caused by displacement of DCI from the surface of the hexadeuterate contaminant can be seen by

comparison with curve e obtained for primarily hexadeuterate nanoparticles.⁷

The strongest spectroscopic evidence that adsorbed DCI is covalent in nature must be based on the observation of a band for the DCI internal stretch mode,^{1b} like the one near 1850 cm^{-1} for DCI adsorbed on amorphous^{1c} and crystalline^{1f} ice at temperatures below 60 K. The observation of a similar broad band for covalent DCI adsorbed on ice at 125 K is complicated by the unavoidable formation of some hexadeuterate. However, such a band, of similar position, intensity, and bandwidth to that observed at low temperatures, and which does not grow with the increasing hexadeuterate content of a sample, is exemplified in Figure 3B.

Since DCI seems to form a *covalent* monolayer coat on the ice surface, then, like other strong covalent adsorbates, it is expected to insert into the vulnerable weak H-bonds of the disordered ice surface, reordering the ice surface and subsurface in the manner that has been described in detail for SO_2 .⁶ For DCI, the evidence for this insertion is an extensive relaxation of the subsurface, to form interior ice, that begins immediately with DCI exposure and is completed within $\sim 2\text{ h}$ at 125 K. This relaxation overrides any loss of interior ice from hexadeuterate formation, so, ironically, a monolayer coating of ice nanocrystals by DCI actually increases the amount of crystalline ice by as much as a few percent. Less extensive results indicate that this and the other DCI effects on the ice surface are closely matched by DBr. Further, the various results reported here are apparently unaffected by increasing the sample temperature to 145 K, considered the limiting practical temperature for study of the ice nanocrystals.

Five spectra are apparently needed to examine in great detail the progression of the reaction of DCI with the ice surface, subsurface, and interior at 125 K. These five spectra are now

available: the DCI-shifted ice surface spectrum (Figures 1, 2), the spectrum of the amorphous hexadeuterate (determined using film co-deposition techniques described in ref 1c, and the published spectra⁶ of the ice interior, surface, and subsurface. Difference spectra such as the top curve of Figure 1, but for DCI exposures ranging from 0.3 to 8.0 ML, can be zeroed-out with insignificant residual errors. The details of this use of these five spectra will be reported elsewhere.

Acknowledgment. We gratefully acknowledge support of this research through NSF Grant CHE-9617120 and the substantive suggestions from Prof. V. Buch of the Hebrew University, whose thoughts prompted this study.

References and Notes

- (1) See, for example: (a) Koehler, B. B.; McNeill, L. S.; Middlebrook, A. M.; Tolbert, M. A. *J. Geophys. Res.* **1993**, *98*, 10563. (b) Horn, A. B.; Chesters, M. A.; McCoustra, M. R. S.; Sodeau, J. R. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1077. (c) Delzeit, L.; Rowland, B.; Devlin, J. P. *J. Phys. Chem.* **1993**, *97*, 10312. (d) Graham, J. D.; Roberts, J. T. *J. Phys. Chem.* **1994**, *98*, 5974. (e) Horn, A. B.; Sodeau, J. R.; Roddis, T. B.; Williams, N. A. *J. Phys. Chem. A* **1998**, *102*, 6107. (f) Delzeit, L.; Powell, K.; Uras, N.; Devlin, J. P. *J. Phys. Chem. B* **1997**, *101*, 2327.
- (2) C. Pursell, Trinity University, private communication.
- (3) See, for example: (a) Kroes, G.-J.; Clary, D. C. *J. Phys. Chem.* **1992**, *96*, 7079 and other references in (b) Bussolin, G.; Casassa, S.; Pisani, C.; Ugliengo, P. *J. Chem. Phys.* **1998**, *108*, 9516.
- (4) D. Worsnop, (Aerodyne), J. Robinson, and B. Henson (Los Alamos), private communication.
- (5) Devlin, J. P.; Buch, V. *J. Phys. Chem.* **1995**, *99*, 16534.
- (6) (a) Delzeit, L.; Devlin, J. P.; Buch, V. *J. Chem. Phys.* **1997**, *107*, 3726. (b) Devlin, J. P.; Buch, V. *J. Phys. Chem.* **1997**, *101*, 6096.
- (7) It should be noted that the appearance of the band of curve e, from SO_2 displacement of DCI from the hexadeuterate surface, is consistent with the results of Graham and Roberts (ref 1d), which have recently been challenged (ref 1e), showing covalent adsorbed HCl on the hexahydrate surface.