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# Comparative FTIR Spectroscopy of HX Adsorbed on Solid Water: Ragout-Jet Water Clusters vs Ice Nanocrystal Arrays

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In addition to revealing the stretch-mode bands of the smallest mixed clusters of HCl and HBr (HX) with water, the ragout-jet FTIR spectra of dense mixed water−acid supersonic jets include bands that result from the interaction of HX with larger water clusters. It is argued here that low jet temperatures prevent the water-cluster-bound HX molecules from becoming sufficiently solvated to induce ionic dissociation. The molecular nature of the HX can be deduced directly from the observed influence of changing from HCl to HBr and from replacing $H_2O$ with $D_2O$. Furthermore, the band positions of HX are roughly coincidental with bands assigned to molecular HCl and HBr adsorbed on ice nanocrystal surfaces at temperatures below 100 K. It is also interesting that the HX band positions and widths approximate those of HX bound to the surface of amorphous ice films at <60 K. Though computational results suggest the adsorbed HX molecules observed in the jet expansions are weakly distorted by single coordination with surface dangling-oxygen atoms, on-the-fly trajectories indicate that the cluster skeletons undergo large-amplitude low-frequency vibrations. Local HX solvation, the extent of proton sharing, and the HX vibrational spectra undergo serious modulation on a picosecond time scale.

## Introduction

Because of the importance to atmospheric chemistry and the broad basic interest in solvation and ionic dissociation of common strong acids, there have been numerous studies of the interaction of HCl and HBr (HX) with ice surfaces and water clusters during the past dozen years. Such systems offer a level of control of the solvation process not available in aqueous solutions. A specific question that has provided a basis for several recent investigations is the level of solvation/ionization of HX when exposed to water confined to clusters, surfaces, or particles at temperatures below 100 K.

Early FTIR data were interpreted as evidence of kinetic stabilization of molecular HX below ∼60 K on amorphous ice films[1] and ice nanocrystals.[2] However, results of a molecular mechanics calculation suggested that HCl should ionize spontaneously on an ice surface.[3] Other computational results are in general agreement that a cluster of four water molecules will dissociate a single adsorbed HX[4,5] (and other references in ref 6), but the system must first assume a favorable coordination geometry, requiring mobility that may be missing at surfaces of clusters, ice particles, and ice films at low temperatures. Recently, detailed reports suggesting the retention of a high fraction of molecular HCl for dilute coverage of ice films (refs 7 and 8, reactive ion scattering) and ice nanocrystals (ref 6, FTIR spectra) up to 90 K seemed to establish rough limits to the kinetic stabilization of molecular HX at an ice surface. By contrast, FTIR studies of HCl molecular beams condensed on ultrathin ice films on a metal substrate gave no indication of the presence of molecular HCl, even at 10 K.[9]

Meanwhile, ragout-jet FTIR spectra have become available for dense supersonic jets containing both HX and water at ∼20 K,[10,11] with the temperature estimated from the HX−monomer rotational line intensities. The approach yielded novel spectra of the 1:1 and 2:1 small water−HX clusters. Further, the spectra of the denser jets, particularly those rich in HX, contain information about the interaction of HX and larger water clusters at these low temperatures. This letter considers the spectra of these larger clusters as they relate to the question of solvation/ionization of HX in water systems at low temperatures. Combined spectral evidence is presented, from ragout jets and nanocrystals,[6] of the existence of adsorbed molecular HCl. The interpretation of both types of spectra is also advanced through pertinent computational results.

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## Experimental Section

The two experimental approaches, ragout-jet cluster FTIR[10,11] and ice-nanocrystal 3D-array FTIR spectroscopy,[6,12] have been described in detail. The cluster jets were characterized by a high density of comparable amounts of HX and water, with helium as the carrier gas. Because water nucleates at a much higher temperature than HX, it is presumed that water clusters form initially and adsorb HX. However, some incorporation of HX in growing water clusters is possible. The spectra show that much of the HX and water remain as monomers or in pure and mixed small clusters, while bands are also indicated for larger water and pure $(HX)_n$ clusters. Data were collected for both HCl and HBr with $H_2O$, as well as for HCl with $D_2O$. Here, the focus is on sampling with the highest HX−water ratios.

The main challenge in the determination of spectra of HX on ice nanoparticle surfaces is to obtain a reasonable distribution of HX over the ice particles within an array. Vapor diffusion is not satisfactory, as the HX is soaked up by the particles near the front of the array, so that HX self-solvation promotes the release of protons. Even at 60 K, the resulting spectra are dominated by hydrated proton bands. This difficulty is overcome by mixing HX clusters among larger (∼12 nm) ice crystals during array formation. The HX moves to the ice particles upon warming in the 50−60 K range. This gives a more nearly even distribution of HX on the ice surface so that, with average HX coverage of ∼10% of a monolayer, the bands of the ionically dissociated acid (i.e., hydrated protons) are observed only very weakly. Despite the large surface-to-volume ratio provided by the nanocrystal arrays, adsorbed HX bands are generally not observed directly. Rather, subtraction of a spectrum of a comparable pure ice array is required.

## Results and Discussion

Spectra of the ragout jets containing HX and water are presented as the bottom three curves of Figure 1. The sharper features from monomers, dimers, trimers, and so forth. have been analyzed in previous publications.[10,11] Of greatest interest here are the broader bands labeled B2 and the response of the B2 bands to a change of acid or change of water isotopic composition. The broad B2 band, in the case of HCl with $H_2O$, is centered near 2570 $cm^{-1}$, which closely matches the position (but not the width; ∼150 vs ∼300 $cm^{-1}$) of the "hydrated proton" band of the amorphous HCl monohydrate (Figure 1 of ref 1). However, it also precisely matches, in both position and bandwidth, the absorption by HCl on an amorphous ice surface (Figure 5A of ref 1 and top curve of Figure 1) assigned to singly coordinated molecular HCl.[6]

Because it has been shown that the hydrated-proton band blue-shifts ∼40 $cm^{-1}$ when HCl is replaced by HBr in the ionic monohydrate,[1] the position of the B2 band in the (top) HBr/$H_2O$ spectrum of Figure 1 is particularly informative. The B2 band red-shifts ∼300 $cm^{-1}$ when HBr replaces HCl in the HX−water jet. This is similar to the red-shift (220 $cm^{-1}$) reported for the substitution of HBr for HCl adsorbed on the surface of ice nanocrystals[6] and matches the ∼310 $cm^{-1}$ shift reported for amorphous ice films (Figures 5 and 6 of ref 1). Such large chloride−bromide red-shifts are expected for *molecular* HX, considering the 330 $cm^{-1}$ lower gas-phase frequency of HBr. Furthermore, MP2 calculations[6] of a water cluster with a singly coordinated HCl molecule bound to a dangling O placed the HCl frequency within 50 $cm^{-1}$ of the observed band positions (2528 vs 2570 $cm^{-1}$ in Figure 1 and the nanocrystal value of 2480 $cm^{-1}$).

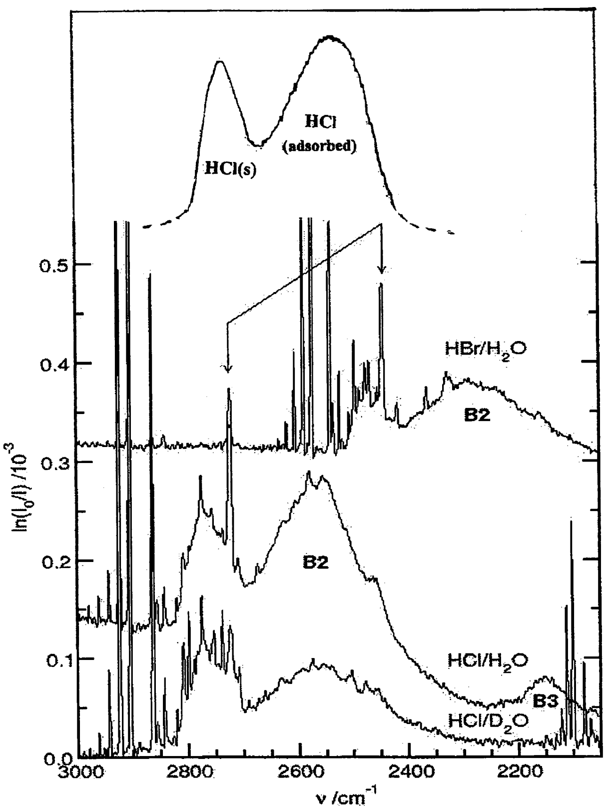

**Figure 1.** The bottom three curves are ragout-jet FTIR spectra of HX−water clusters adapted from ref 11. The molecular components within the supersonic jet are noted on each trace. The joined arrows indicate the corresponding mixed dimers. Other sharp bands are produced by monomers and small clusters. See the text for discussion of the broad bands labeled B2 and B3, and see refs 10 and 11 for details of the experimental conditions. The top spectrum is for HCl on amorphous ice at 60 K, as adapted from Figure 5 of ref 1.

This indication that the B2 bands of HX in Figure 1 have a molecular origin is confirmed by the lack of response of the *HCl* B2 band to the substitution of $D_2O$ for $H_2O$ in the ragout jet. The B2 band position and width are essentially unaffected by switching to $D_2O$ water, inconsistent with B2 originating from hydrated (deuterated) protons. The expected influence on spectra from deuteration can be judged by comparing the spectra for amorphous protiated hydrates (Figure 1 of ref 1) with those of the deuterated hydrates (Figure 13 of ref 6). For all water−acid ratios, the major bands are red-shifted by hundreds of reciprocal centimeters. In particular, the 2550 band of the HCl monohydrate shifts to 2000 $cm^{-1}$. So, should B2 have a protonic origin, a strong deuteration shift from 2570 toward 2000 $cm^{-1}$ should be observed. A similar lack of band shift accompanied the replacement of $H_2O$ with $D_2O$ ice nanocrystals at 50 K (Figure 8 of ref 6). In that case, the intense $D_2O$ ice band interfered with observation of the 2480 $cm^{-1}$ HCl band, but a second band, of dilute adsorbed HCl near 1740 $cm^{-1}$, was insensitive to deuteration of the ice. (This band, attributed to doubly coordinated, severely stretched molecular HCl, is outside the frequency range of the ragout-jet study.[10,11])

One of the more convincing signs that a band is caused by molecular HX is its disappearance during warm-up of an ice array while bands attributed to the hydrated proton emerge. This can be seen in Figure 11 of ref 6. Figure 2 is included to show that, for our lowest HCl dosage of $D_2O$ nanocrystals (∼10% of a monolayer resulting in a minimum level of HCl self-solvation), the 1740 $cm^{-1}$ HCl band retains significant intensity up to 100 K. Meanwhile, a band assigned to molecular HCl attached to

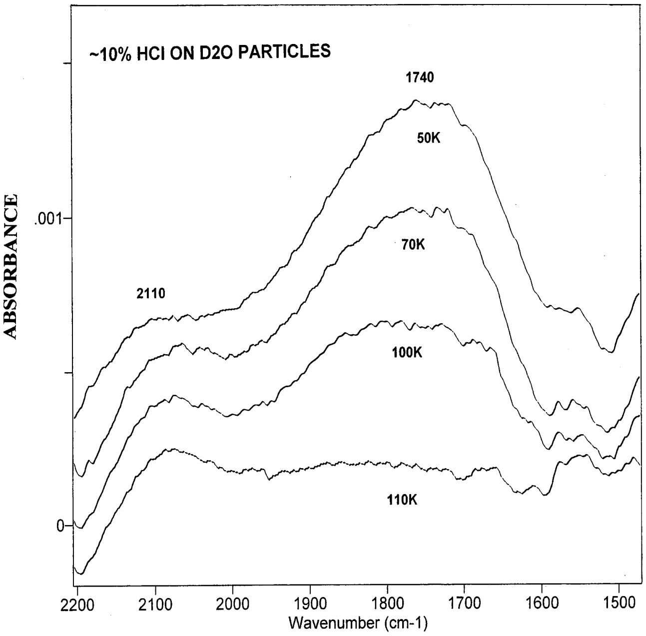

**Figure 2.** FTIR difference spectra for ∼10% of a monolayer of adsorbed HCl on $D_2O$ nanocrystals showing the temperature dependence of the 1740 $cm^{-1}$ HCl band.

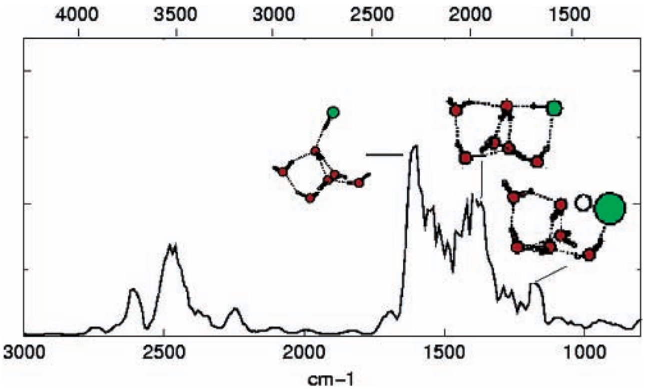

**Figure 3.** Infrared spectrum of a $DCl(D_2O)_6$ cluster from an on-the-fly 7 ps trajectory at 60 K. The different cluster structures (red—oxygen, black—hydrogen, and green—chloride), each identified with a DCl band component using sub-picosecond segments of the same trajectory, are described in the text. The larger chloride/hydrogen in the right structure signifies partial ionization. The frequency scale for protiated clusters (top) is also indicated. HCl frequencies are slightly underestimated at the present level of the calculation.

surface $Cl^-$ from ionized HCl[6] gradually intensifies near 2100 $cm^{-1}$. This emerging band resembles in position (2110 $cm^{-1}$) and bandwidth (∼80 $cm^{-1}$) the B3 band of Figure 1, suggesting a low level of ionic dissociation of HX within the ragout jets. The B3 band does not appear in the HCl/$D_2O$ spectrum, which was recorded for a lower HCl concentration.

Results in Figure 3, from an on-the-fly QUICKSTEP study of a mixed HCl−water cluster,[13] help demonstrate qualitatively the type of vibrational dynamics that could lead to the observed HX spectra. A 60 K NVE (i.e., constant composition, volume, and energy) classical trajectory was calculated for a deuterated water hexamer with a single adsorbed DCl molecule (deuteration allows for larger time steps). The initial structure was adopted from Figure 6o of ref 6. The spectrum was determined from a 7 ps cluster trajectory, in the course of which the HCl intermittently probed an O-bonded singly coordinated molecular configuration, a doubly coordinated one, and occasionally, a proton-sharing configuration with a neighboring water molecule. The lifetimes of the different configurations, in the ∼0.1−1 ps range, included numerous HCl oscillations, and therefore, each produced a unique feature in the HCl spectrum, as marked in Figure 3. As expected, the highest-frequency feature originated from the singly coordinated configuration and the lowest from one with proton sharing. Many different but related HCl adsorbate configurations are sampled by experiment whether the HCl is adsorbed on a cluster or a particle surface, giving rise to an absorption continuum as in Figure 12 of ref 6, with maxima near 2570 $cm^{-1}$ (Figure 1) and 1750 $cm^{-1}$ (Figure 2). Ultimately, the solvation level and band positions are determined by factors such as the presence/absence of a second acceptor bond to the proton acceptor oxygen.[6,17]

While the present computational example is not designed to sample all possible HCl−particle surface configurations, the results of Figure 3 exemplify several principles. A water−acid cluster, while including a sufficient number of solvent molecules for ionization, may be kinetically stabilized in a “particle−molecular adsorbate” configuration presumably because of an activation barrier.[18] Rather, in the course of a trajectory, the cluster skeleton undergoes large-amplitude, low-frequency vibrations, which modulate the local solvation. The HX responds by transient adjustment of its vibrational frequency, resulting finally in a broad but structured infrared band. In this way, the same HCl molecule gives rise to three distinct spectroscopic features. Similar phenomena were observed in on-the-fly simulations of crystalline HX etherates.[19] One can view this physical behavior as a “generalized Zundel effect” extended to the molecular acid.

## Summary Conclusions

The presence of *molecular* acid adsorbate on icy particles at low temperatures is demonstrated in two independent experimental approaches. One pertains to water−acid clusters with tens of molecules at ∼20 K. The other probes dilute acid adsorbates on water nanocrystals from 60 to 100 K. Because excess water is available for ionization in both cases, the molecular acid form appears to be kinetically stabilized. This interpretation of the experimental results is supported by an on-the-fly trajectory from QUICKSTEP[13] for HCl bonded to $(H_2O)_6$.

However, the kinetic stabilization may have a quite different origin in the two cases. Only very dilute HX on ice nanocrystal surfaces resulted in dominant molecular bands at 60 K.[6] The colder ragout jets leading to Figure 1 were comparably rich in acid and water on a molar basis. There are other condensed-phase examples in the literature where HX−water ratios near unity have resulted in the presence of a significant fraction of molecular HX. Giguere reported Raman spectra of supersaturated HX in water solutions with bands of HCl (2600 $cm^{-1}$) and HBr (2320 $cm^{-1}$) attributed to molecular HX complexes with water.[20] Though HX self-solvation can contribute significantly to proton transfer,[6,19] it can be ineffective at high temperatures[20] and below ∼50 K as indicated by the ragout-jet results and the spectra of films of excess HX deposited on amorphous ice surfaces (Figure 1 (top) and ref 1).

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