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An infrared study of the competition between hydrogen-bond networking and ionic solvation: Halide-dependent distortions of the water trimer in the $X^-(H_2O)_3$, ($X=Cl, Br, I$) systems

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Vibrational spectra of the water trimers solvating the halide anions (Cl^- , Br^- , I^-) have been acquired in the OH stretching region by predissociation spectroscopy of the $X^-(H_2O)_3 \cdot Ar_3$ complexes. These “wet” ions display two groups of bands assigned to normal modes of the (C_3) pyramidal structure. We interpret the evolution of the spectra down the halogens in the context of the rings closing up toward the structure of the bare $(H_2O)_3$ neutral. This trend is discussed in terms of the disruptive effect of the ionic H bonds on the water network. © 1999 American Institute of Physics. [S0021-9606(99)02115-7]

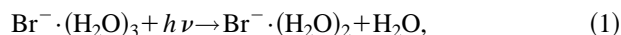
I. INTRODUCTION

It is well established that the local structure of water in the vicinity of an ion¹ results from the competition between ion–water hydrogen bonds^{2–4} and the cooperative forces^{5–8} binding the solvent. It is therefore remarkable that, in spite of the manifest importance of halide ion hydration in nature, we still have only a crude picture of the first coordination sphere. This arises due to the fluctuational nature of the liquid⁹ and the strong (orientation-dependent)¹⁰ intramolecular distortions of a water molecule when it is engaged in H bonding. In a previous paper,¹¹ we reported vibrational spectra of the isolated (gas phase) iodide hydrates, $I^-(H_2O)_n$, ($n = 1–3$), in the OH stretching region and, with the aid of *ab initio* calculations, assigned the simple doublet pattern in $I^-(H_2O)_3$ to fundamentals in the pyramidal C_3 structure.¹² In this paper, we establish how $(H_2O)_3$ responds as the ionic H bonds are systematically strengthened in going up the halogen series from iodide to chloride. The halide dependence of the bands also provides a valuable tool for establishing their coarse vibrational assignments to either ionic or interwater H-bonded OH stretches, respectively.

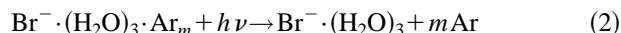
II. EXPERIMENT

We report the photodissociation spectra of size-selected anionic clusters using a tandem time-of-flight strategy described previously.¹³ Cluster ions are formed by electron impact ionization of a supersonic expansion containing trace amounts of an alkyl halide (CCl_4 , CH_2Br_2 , CH_3I) and water vapor seeded in several atmospheres of argon. Here, we are specifically interested in obtaining one-photon (i.e., linear) vibrational spectra corresponding to the minimum energy configurations of the $X^-(H_2O)_3$ complexes. This task is complicated by the large internal energy content of these strongly bound clusters when, as is the case here, they are formed by association reactions. The sequential water con-

densation energies onto halide ions are available from thermochemical measurements,^{2–4} and generally fall close to the energy range of the OH stretching fundamentals ($3000–3700\text{ cm}^{-1}$). These condensation energies are much larger than the strengths of typical interwater H bonds ($D_0 \sim 1500\text{ cm}^{-1}$),¹⁴ with the consequence that kinetically stable clusters (i.e., governed by the evaporative ensemble model)¹⁵ should generally display largely disrupted networks.¹⁶ This, in turn, complicates the spectra^{17–19} since the (adiabatic) high frequency OH stretching quanta strongly depend on the relative dispositions of water molecules due to the directionality of the H bonds.¹⁰ This situation is illustrated by the $Br^-(H_2O)_3$ spectra presented in Fig. 1. The lower trace displays the one-photon action spectrum from bare $Br^-(H_2O)_3$.¹⁹



while the upper two traces are recorded by argon atom predissociation:



from the $m = 1$ and 3 complexes. The argon predissociation spectra display much sharper bands than that of the bare complex, and yet are quite similar to each other. The similarity of the $m = 1$ and 3 argon spectra [Figs. 1(b) and (c)] implies that the observed features are not due to motions of the argon atoms. Much more likely, the difference arises from a profound reduction in the internal energy content of the parents.¹⁶ The argon atom is much more weakly bound than water (the ΔH_{assoc} values for Ar^{20} and $H_2O^{2–4}$ onto Br^- are ~ 400 and 4000 cm^{-1} , respectively), and an evaporative ensemble including at least one argon atom limits their internal energy content to values much less than that required to break up the water network (i.e., $E_{\text{int}} \sim 400\text{ cm}^{-1} \ll 1500\text{ cm}^{-1}$). At the same time, predissociation of the weakly bound “spy” atom²¹ enables the detection of one-photon spectra for excitation energies less than that required to dissociate a water monomer.

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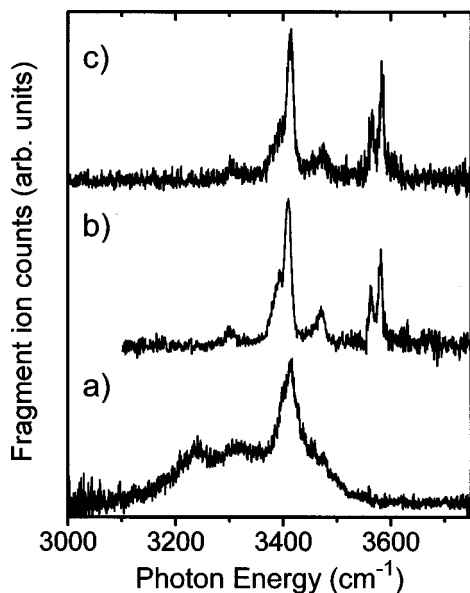


FIG. 1. Vibrational spectra of the $\text{Br}^-\cdot(\text{H}_2\text{O})_3\cdot\text{Ar}_m$ clusters: (a) $m=0$ recorded by evaporation of a water molecule [Eq. (1)], (b) $m=1$, and (c) $m=3$ recorded by argon predissociation into $\text{Br}^-\cdot(\text{H}_2\text{O})_3$ [Eq. (2)].

III. RESULTS AND DISCUSSION

A. Assignment and evolution of the OH stretching bands in the context of perturbed cyclic trimers

Argon predissociation spectra of the $\text{X}^-\cdot(\text{H}_2\text{O})_3\cdot\text{Ar}_3$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) complexes are reported in Fig. 2. Each spectrum is dominated by two groups of bands, centered around a gap at 3500 cm^{-1} , with more complex structure appearing in the lower energy group for the lighter halogens. Band positions are collected in Table I. Perhaps the most readily interpreted aspect of these spectra is the *absence* of bands in the region associated with a free OH group ($3707\pm 10\text{ cm}^{-1}$).^{17–19,22–29}

The absence of such a feature in all of the $\text{X}^-\cdot(\text{H}_2\text{O})_3$ systems rules out open structures such as the chain motif. Calculations^{11,12,17,30} indicate that the $\text{X}^-\cdot(\text{H}_2\text{O})_3$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) clusters adopt the (C_3) pyramidal structure, where a cyclic water trimer is bound to the ion with all “free” hydrogens pointing toward the ion. Apparently, the three strong ionic H bonds overcome the unfavorable arrangement of quasiparallel OH dipoles (recall that the neutral trimer has only two H’s on the same side of the O–O–O plane).^{31–34}

The infrared signature of the C_3 structure has only been calculated for the $\text{Cl}^-\cdot(\text{H}_2\text{O})_3$ system, which consists of the open doublets³⁰ reproduced in Fig. 2(d). Interestingly, this pattern is actually recovered for $\text{I}^-\cdot(\text{H}_2\text{O})_3$ [Fig. 2(a)], confirming its pyramidal structure,¹¹ while the observed $\text{Cl}^-\cdot(\text{H}_2\text{O})_3$ spectrum [Fig. 2(c)] is much more complex. In the context of the C_3 geometry, the higher energy ($\sim 3560\text{ cm}^{-1}$) doublet in the $\text{I}^-\cdot(\text{H}_2\text{O})_3$ spectrum occurs near the position of the ring modes in the neutral trimer ($\sim 3530\text{ cm}^{-1}$),^{25,35} and is assigned¹¹ to them, while the lower energy ($\sim 3460\text{ cm}^{-1}$) bands result from the dramatic redshift of the free OH’s when they engage in strong ionic H bonds.

The halide dependence of these bands [Figs. 2(a)–2(c)]

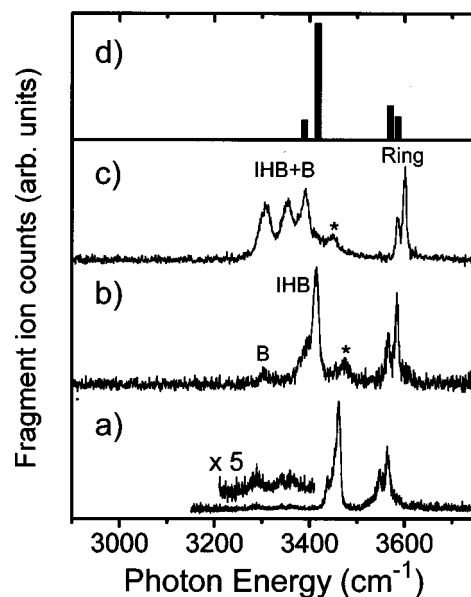


FIG. 2. Vibrational spectra of the $\text{X}^-\cdot(\text{H}_2\text{O})_3\cdot\text{Ar}_3$ clusters recorded by argon predissociation into $\text{X}^-\cdot(\text{H}_2\text{O})_3$: (a) $\text{X}=\text{I}$, (b) $\text{X}=\text{Br}$, (c) $\text{X}=\text{Cl}$, and (d) calculated—Ref. 30 (harmonic) OH stretch spectrum of pyramidal $\text{Cl}^-\cdot(\text{H}_2\text{O})_3$, corrected by -164 cm^{-1} to match the experimentally observed centroid of the ν_1 and ν_3 vibrations in H_2O . Bands are assigned to collective (normal) modes predominantly involving OH_{IHB} and OH_{ring} stretches or (0–2) bend overtones of the water molecules (B). The small bands labeled by an asterisk are tentatively assigned to combination bands involving the OH_{IHB} stretches and a soft mode of the cluster (possibly the ion–trimer stretch).

bears out their qualitative assignments to ring (OH_{ring}) and ionic H-bonded (OH_{IHB}) OH stretches. The similarity of the high energy doublet indicates that all three species indeed adopt the ring motif, while the low energy bands display a more complicated evolution (we will discuss the origin of this complexity shortly). Overall, however, the lower energy bands redshift up the halogen series as expected, reflecting the increased strength of the ionic H bonds.^{2–4} Interestingly, the ring modes *blueshift* as the ionic H bonds become stronger from iodide to chloride. An expanded view of this effect is displayed in Fig. 3.

The location of the IR active, (degenerate) E symmetry ring modes of the neutral trimer ($\sim 3530\text{ cm}^{-1}$)^{25,35} is displayed by the arrow in Fig. 3(a), and occurs very close to the observed bands in the iodide complex. In this context, the

TABLE I. Observed band positions in the $\text{X}^-\cdot(\text{H}_2\text{O})_3\cdot\text{Ar}_3$ complexes.

	Assignment	Band position ($\pm 2\text{ cm}^{-1}$)
$\text{I}^-\cdot(\text{H}_2\text{O})_3\cdot\text{Ar}_3$	B	3289, 3342, 3360
	IHB	3462
	Ring	3547, 3564
$\text{Br}^-\cdot(\text{H}_2\text{O})_3\cdot\text{Ar}_3$	B	3302
	IHB	3410
	Ring	3565, 3584
$\text{Cl}^-\cdot(\text{H}_2\text{O})_3\cdot\text{Ar}_3$	IHB+B	3310, 3354, 3391
	Ring	3585, 3600

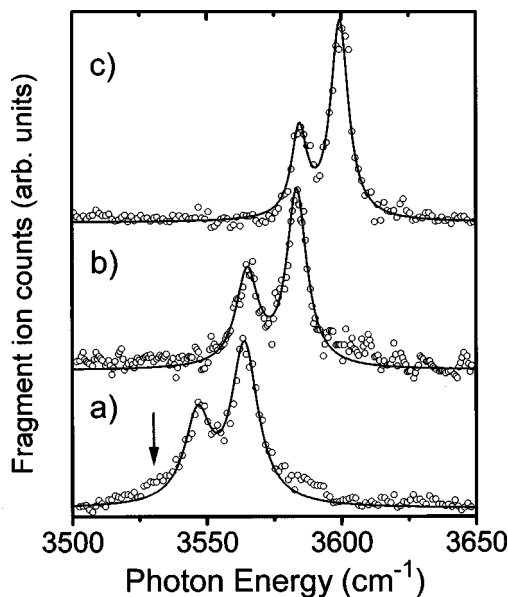


FIG. 3. Expanded view of the $X^{-}\cdot(H_2O)_3$ OH_{ring} modes: (a) $X=I$, (b) $X=Br$, and (c) $X=Cl$. The arrow indicates the position of the degenerate E symmetry ring mode observed for the neutral water trimer—Refs. 25 and 35.

likely reason for the blueshift of the ring modes is that, as the ionic H-bonded hydrogens are drawn closer to the ion, the ring hydrogens distort above the O–O–O plane. This less favorable O··H–O angle weakens the interwater H bonds,¹⁰ leading to ring opening and causing the OH_{ring} stretches to blueshift as their force constants relax back toward the larger values characteristic of the free OH.

This data set nicely complements very recent work on the $F^{-}\cdot(H_2O)_3$ system,¹⁸ where the mid-IR spectrum indicates complete insertion of the fluoride ion into the plane of the ring. In that case, the erstwhile ring modes blueshift all the way out to the position of the free OH.^{17–19,22–29} The heavier halides studied here anticipate this insertion effect at an earlier stage, where the ring partially opens and the bands appear at an intermediate value between the neutral trimer and the free OH.

With these assignments of the bands, it is interesting to revisit the spectrum of the “hot” $Br^{-}\cdot(H_2O)_3$ complex shown in Fig. 1(a). The ring modes ($\sim 3580\text{ cm}^{-1}$) are *completely absent*, establishing that this cluster has sufficient internal energy to break open the ring.

B. Fine structure of the bands

The band envelopes of the ring modes are remarkably similar in all three halides (Fig. 3), with the same doublet spacing ($\sim 17 \pm 2\text{ cm}^{-1}$) and approximate 2:1 intensity ratio. Given the modest resolution of these survey spectra ($\Delta\nu \approx 2\text{ cm}^{-1}$), we only interpret qualitative features of the envelopes in the context of the proposed pyramidal structures. In C_3 symmetry, the six OH fundamentals fall into two groups,^{11,17,34} with each group containing three closely spaced transitions. Each set of three arises from two fundamentals corresponding to the (degenerate) E and A_1 modes. In the cyclic neutral,^{32–34} the symmetric (A_1) transition lies

below that of the E modes, but is much weaker and has not been observed in the bare complex. Apparently, the $X^{-}\cdot(H_2O)_3$ complexes remove the effective planar symmetry of $(H_2O)_3$, and this perturbation induces intensity in the symmetric ring mode without breaking the degeneracy of the two out-of-phase modes.^{11,17,30} We caution, however, that at this resolution, we cannot be definitive about the (E , A_1) vibrational assignments within the high energy doublets.

The lower energy group of bands, nominally assigned to the OH_{IHB} stretches, are obviously more complex, with the $Cl^{-}\cdot(H_2O)_3$ cluster displaying a quartet structure in contrast to the predicted³⁰ asymmetric doublet [Fig. 2(d)]. Even in $Br^{-}\cdot(H_2O)_3$, however, smaller features are becoming significant on either side of the main OH_{IHB} bands. We emphasize that, like the $Br^{-}\cdot(H_2O)_3$ case presented in Fig. 1, all three systems were scanned with 1 and 3 argon atoms to ensure that the patterns are not affected by the degree of solvation.

A similar trend toward increasing complexity of the OH_{IHB} bands with the lighter halogens was observed and assigned in the $X^{-}\cdot(H_2O)$ monohydrates,³⁶ providing a clue to their origin in the trimer spectra. First and most important, a strong Fermi interaction ($H_F \approx 30\text{ cm}^{-1}$)³⁶ occurs when the OH_{IHB} stretches redshift into near resonance with the 0–2 overtones of the intramolecular bends (B). These overtones occur in the range $3200\text{--}3400\text{ cm}^{-1}$, and the interaction becomes more pronounced in the lighter halides because their stronger ionic H bonds^{2–4} redshift the OH_{IHB} stretch fundamentals into this region.

This mixing effect can be observed in the spectra displayed in Fig. 2, where very weak bands around 3300 cm^{-1} , barely evident in the $I^{-}\cdot(H_2O)_3$ spectrum, become progressively more intense as the OH_{IHB} stretches redshift directly over these features. Deconvolution of these mixed bands is not warranted without rotationally resolved spectra, and is clearly not amenable to the simple two-state model used to deperturb the binary complexes.³⁶ Moreover, we note that the separation between IHB and ring character, useful for qualitative discussion, is artificial as the ring- and ion-bound OH stretches should interact. This is especially true as the gap between the two groups approaches the matrix element ($\sim 100\text{ cm}^{-1}$) coupling the two oscillators in bare water.

The second cause for increasing complexity of the OH_{IHB} stretches in the $X^{-}\cdot H_2O$ spectra is the emergence of a combination band involving the ion–water stretch.³⁶ In the $X^{-}\cdot(H_2O)_3$ systems, a band (labeled with an asterisk) occurs about 70 cm^{-1} above the OH_{IHB} fundamentals, first appearing as a shoulder on the red side of the ring modes in $I^{-}\cdot(H_2O)_3$ [Fig. 2(a)] and splitting out as a distinct feature in the $Br^{-}\cdot(H_2O)_3$ [Fig. 2(b)] and $Cl^{-}\cdot(H_2O)_3$ [Fig. 2(c)] spectra. The increasing intensity of IHB-based combination bands with increasing ionic H-bond strength³⁶ is consistent with this assignment, while the observed $\sim 70\text{ cm}^{-1}$ shifts are qualitatively smaller than the calculated (harmonic) ion–trimer stretches ($\sim 100\text{ cm}^{-1}$).³⁰

IV. SUMMARY

Argon predissociation spectroscopy in the OH stretching region indicates that the $X^{-}\cdot(H_2O)_3$ ($X=Cl, Br, I$) species adopt pyramidal (C_3) structures. The spectra display two

groups of bands, one of which redshifts while the other blue-shifts as the strength of the ionic H bonds are systematically increased from iodide to chloride. The blueshifted bands are simple, and are assigned to predominantly ring OH's of the cyclic water trimer subcluster, which opens up as the ionic H bonds strengthen. The ring modes are absent in the spectrum of the bare $\text{Br}^-(\text{H}_2\text{O})_3$ complex, consistent with the rupture of the trimer ring due to internal excitation. The bands nominally arising from the OH's bound to the ion are significantly more complex than those of the ring due to Fermi interactions with the intramolecular bend overtones and the emergence of ion–water combination bands.

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