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# Vibrational Spectroscopy of the Ionic Hydrogen Bond: Fermi Resonances and Ion−Molecule Stretching Frequencies in the Binary $X^-{\cdot}H_2O$ (X = Cl, Br, I) Complexes via Argon Predissociation Spectroscopy

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**Introduction.** While solvation of halide ions in water lies at the very foundation of aqueous chemistry, cluster techniques,[1−8] in combination with ab initio theory,[9−12] are only now available to elucidate the molecular level details of this important interaction. One of the most direct probes of the ionic H bond (IHB) is, of course, determination of the OH stretching spectrum, as the IHB acts to weaken the water OH bond in anticipation of the base hydrolysis reaction:

$$X^- + H_2O \rightarrow X^-{\cdot}H_2O \rightarrow HX + OH^- \qquad (1)$$

such that the strengths of the IHBs[13,14] reflect the p$K_a$ trends of the conjugate acids, HX (X = halide). The binary "complexes" are therefore trapped intermediates in the proton-transfer reaction,[15] and as such, they are characterized by a much richer interaction than that displayed by the ubiquitous ion−dipole complexes involving non H-bonding solvents.[16,17] Spectroscopy of the $X^-{\cdot}W$ (W = water) species allows us to determine how the intramolecular force field of the "solvent" water molecule is affected by the immediate proximity of the ion and to directly monitor the forces which mediate bulk effects such as dielectric saturation in ionic solutions.[18]

Previous spectroscopic studies[2−5,7,8] of $X^-{\cdot}W$ support the ab initio prediction[9−12] that the binary complexes adopt an asymmetric equilibrium structure where the water molecule is cocked with one OH bond elongated and pointing toward the halide and the other hydrogen free. In this paper, we report the first spectra of these clusters cooled into their potential minima, and use this information to deduce the intrawater distortions as well as the potentials governing the motion of the water molecule against the ion.

**Experimental.** In a cluster analogue of matrix isolation spectroscopy,[19,20] the $X^-{\cdot}W$ cluster ions are injected into moderately large argon clusters[5,21−23] to form the mixed $X^-{\cdot}W{\cdot}Ar_n$ ($0 \le n \le 10$) species after substantial evaporative cooling.[24] This strategy serves to quench the complexes into the global minima on their potential surfaces. Spectra are monitored in an action mode via predissociation of the argon "matrix":[5,21]

$$X^-{\cdot}W{\cdot}Ar_n + h\nu \rightarrow X^-{\cdot}W{\cdot}Ar_p + (n-p)Ar \qquad (2)$$

Infrared excitation was carried out by using a Nd:YAG-pumped, KTP-based, optical parametric oscillator (OPO, Laser Vision) to excite the mass selected ion beam at the transient focus of a tandem time-of-flight photofragmentation spectrometer.[25] We display predissociation spectra from the $X^-{\cdot}W{\cdot}Ar_3$ clusters because they yield the highest signal-to-noise ratio due to the fact that there is negligible metastable background in the $X^-{\cdot}W$ photofragment channel (eq 2; $n = 3$, $p = 0$). We have recorded spectra for different numbers of argon atoms to ensure that the conclusions regarding the nature of the $X^-$−W interactions are not influenced by the extent of argon solvation.

**Results. A. Observation of the (Halide Dependent) Ionic Hydrogen-Bonded and Free OH Stretching Bands.** The spectra from the three halide complexes are displayed in Figure 1. Each spectrum consists of an intense band (or bands) below 3400 cm$^{-1}$ (denoted IHB for ionic hydrogen-bonded OH) and a much weaker but sharper feature at 3690 cm$^{-1}$ (labeled F for free OH). The latter is very insensitive to the halide and occurs near the band in the bare water molecule (3707 cm$^{-1}$ for the average of $\nu_1$ and $\nu_3$). The intense $OH_{IHB}$ band, on the other hand, is strongly dependent on halide, displaying an increasing red shift of about 130 cm$^{-1}$ per halogen in going from I to Cl. This pattern is consistent with the ab initio expectation[9−12] that all the clusters adopt an asymmetric structure with one hydrogen engaged in the IHB and other free.

**B. Assignment of Weak Features to Combination Bands and the Bending Overtone: Observation of Fermi Resonances.** While the assignment of the main pattern is clear,[2,3,5,7,8] we note that there are several weaker bands below 3500 cm$^{-1}$ in each spectrum, and that the $Br^-{\cdot}W$ case is dominated by an intense doublet (labeled IHB+B). The key to this puzzle lies in the pattern of $OH_{IHB}$ bands over the three halides. Note that one of the weak bands shifts along with the intense $OH_{IHB}$ (as displayed by brackets in Figure 1), displaced to the blue of the main band by about 150 cm$^{-1}$. Moreover, the $Br^-{\cdot}W$ complex displays two weak bands, split by the same amount as the main doublet. This trend indicates that these weak, shifting bands arise from combination bands involving the $OH_{IHB}$ stretch and a low-

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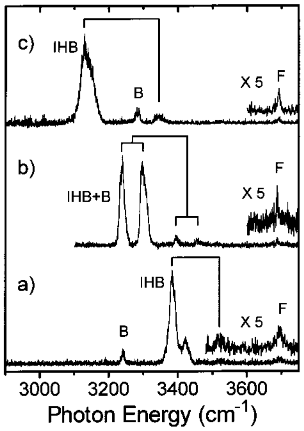

**Figure 1.** Vibrational predissociation spectra of $X^{-}\cdot W\cdot Ar_3$: (a) X = iodide,[5] (b) X = bromide, and (c) X = chloride. Labels show assignments to bending overtones (B), ionic H-bonded OH stretches (IHB), and free OH stretches (F). Brackets indicate combination bands involving the $OH_{IHB}$ stretch and the low-frequency ion−water stretch.

**Table 1.** Experimental (Theoretical Harmonic) Frequencies (±3 $cm^{-1}$) for the Binary $X^{-}\cdot W$ Complexes

| | $Cl^{-}\cdot W$ | $Br^{-}\cdot W$ | $I^{-}\cdot W$ |
|---|---|---|---|
| ion−water stretch | 210 (203)[11] | 158 | 135 (127)[7] |
| bend overtone (B) | 3283 (3340)[11] | 3264[a] | 3241 (3350)[7] |
| $OH_{IHB}$ stretch | 3130 (3338)[11] | 3270[a] | 3385 (3614)[7] |
| $OH_F$ stretch | 3690 (3894)[11] | 3690 | 3695 (3894)[7] |

[a] Unperturbed band position.

frequency mode of the complex. This splitting is much larger than the $I^{-}$−Ar stretch,[26] pointing toward a motion involving the water. Ab initio calculations[11,12] indicate that of the three (frustrated rotation) ion−molecule vibrations, the ion−water stretch is in the range of 150 $cm^{-1}$ and, like the bands in the spectra, increases in frequency with the strength[13,14] of the IHB. These bands are therefore assigned to the ion−water stretch in the vibrationally excited [$\nu(OH_{IHB}) = 1$] adiabatic surface. Note that the identification of the 3340 $cm^{-1}$ feature in $Cl^{-}\cdot W$ as a combination band (Figure 1c) is particularly compelling since the two linked bands display much larger widths than that of the interloper at 3283 $cm^{-1}$ (assigned shortly to the intrawater bending overtone).

Having assigned one of the weak bands to the low-frequency stretching motion, we are left with the more complex behavior of the $Br^{-}\cdot W$ system (Figure 1b) and a second weak band (B) occurring near 3250 $cm^{-1}$. The latter band was previously assigned to the intramolecular ($2\nu_2$) bend overtone[5,8] in $I^{-}\cdot W$ (3241 $cm^{-1}$) and occurs with about the same relative intensity in $Cl^{-}\cdot W$ (3283 $cm^{-1}$). Furthermore, it is interpolated to fall near the center of the doublet in $Br^{-}\cdot W$. It therefore appears that the $OH_{IHB}$ stretch in $Br^{-}\cdot W$ is accidentally shifting into a Fermi resonance with band B, whose position does not depend as strongly on the complex (Table 1). This behavior reinforces the assignment of the latter to the overtone of the intrawater bending mode which, since it largely involves the motion of the free hydrogen, does not change much for the different halides (since they all display asymmetric structures). Moreover, calculations anticipate that it should occur in this vicinity ($2\nu_2 = 3340$ $cm^{-1}$ at the harmonic level for $Cl^{-}\cdot W^{11}$), and slightly blue shifted with increasing H-bond strength, as observed in going from I to Cl (Table 1). The splitting in the $Br^{-}\cdot W$ case therefore *directly* records the matrix element (30 ± 5 $cm^{-1}$) for the Fermi-resonance type of interaction between the $OH_{IHB}$ stretch and bending overtone levels. This value is in line with analogous bend−stretch interactions in an isolated CH (for example, in $CHX_3$, $H_{int} = 20 \pm 10$ $cm^{-1}$).[27]

Assignment of the 3241 $cm^{-1}$ feature in $I^{-}\cdot W$ (and 3283 $cm^{-1}$ in $Cl^{-}\cdot W$) to the bending overtone (B) therefore explains both the occurrence of the doublet (centered at 3267 $cm^{-1}$) in $Br^{-}\cdot W$ as well as the anomalous intensity of the nominally forbidden $2\nu_2$ bands in $I^{-}\cdot W$ and $Cl^{-}\cdot W$. In both of the latter cases, the $OH_{IHB}$ band is split from band B by similar amounts (153 vs 144 $cm^{-1}$ for $Cl^{-}\cdot W$ and $I^{-}\cdot W$, respectively), and so the 30 ± 5 $cm^{-1}$ matrix element is sufficient to enable the overtone to borrow intensity from the strong $OH_{IHB}$ transition (4% vs 5% for the calculated and observed intensity of the overtone relative to that of the $OH_{IHB}$).

Thus, the evolution of the bands throughout the halide series allows us to assign the observed bands to bending overtones (B), ionic H-bonded OH stretches, ($OH_{IHB}$), ion−water stretches and free OH stretches ($OH_F$), respectively. The only band left unassigned in this analysis is the shoulder on the high energy side of the main peak (3420 $cm^{-1}$) in $I^{-}\cdot W$ (Figure 1a). We have previously demonstrated,[5,7] however, that this feature is a vestige of the complex fine structure associated with the $OH_{IHB}$ band in bare $I^{-}\cdot W$. Unlike the other bands, this feature as been shown to completely quench with increasing Ar solvation ($n > 8$),[5] and so is not associated with a band origin. Therefore, all band origins are assigned and collected in Table 1, along with calculated values, where available.

We note that our assignment is at odds with an earlier report[2] of the $Cl^{-}\cdot W$ system, where similar features (at 3156 and 3285 $cm^{-1}$, respectively) were observed, but with intensities reversed from our argon solvated spectra. It seems likely that this discrepancy arises from the high bond energy of the $Cl^{-}\cdot W$ complex, which requires signficant internal energy to be present for the observation of linear action spectra.

The fact that the IHB substantially changes the frequency of the OH oscillator (and therefore the force field of the water molecule) provides a compelling rationalization for the observation that the intensity and frequency of the ion−water stretching combination band is markedly increased as the IHB gets stronger. In a physical picture, the intensity of this band is a manifestation of the microscopic dynamics where driving the $OH_{IHB}$ stretch provides a “handle” with which to initiate motion along the dissociation coordinate for the complex. Thus, it is clear why this mode, among the three low-frequency motions (one stretch and two wags), is predominantly excited along with $OH_{IHB}$. We are presently in the process of improving the signal-to-noise in these spectra to extract similar information for the other two low-frequency ion−water motions.

**Summary.** The mid-IR spectra of the $X^{-}\cdot W$ complexes, cooled close to their zero point energies by solvating them with several argon atoms, elucidate the distortion of the intrawater force field in the presence of the anions and reveal the occurrence of a strong Fermi interaction between the ($v = 1$) $OH_{IHB}$ level and the overtone of the intramolecular bend. Combination bands involving the soft ion−water stretching mode establish the force constants for motion along the ionic hydrogen bond (i.e. $X^{-}$−W) in the first $OH_{IHB}$ vibrational level. These empirical trends should be useful to benchmark further ab initio work on the ion−water interaction potential, and the band intensities will provide a direct probe of the dynamics on these surfaces.

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