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LETTERS

A Cluster Study of Anionic Hydration: Spectroscopic Characterization of the $I^-{\cdot}W_n$, $1 \le n \le 3$, Supramolecular Complexes at the Primary Steps of Solvation

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By isolating $I^-{\cdot}W_n$ clusters in the gas phase, we eliminate the fluctuations and heterogeneity present in solution, allowing us to follow how water molecules (W) sequentially lock into position and form supramolecular complexes at the early stages of hydration. We report vibrational predissociation spectra of the $I^-{\cdot}W_n$, $1 \le n \le 3$, complexes quenched close to their minimum energy configurations by complexation with argon. Structures are extracted from these spectra by comparison with the band patterns expected for the various geometries.

I. Introduction

Ionic hydration, a central theme of physical chemistry since the time of Arrhenius,[1,2] is presently undergoing a renaissance as ab initio methods[3−11] and experimental cluster techniques[12−21] are finally equal to the challenge of unraveling the molecular-level details of solvation. In the bulk, of course, we discuss the structure of the liquid in the context of coordination spheres,[22] where some water molecules are directly hydrogen-bonded to the ion[23] while more distant molecules gradually adopt positions in the ambient (fluctuating) H-bonding network.[24] In this paper, we use size-selected cluster ions, $I^-{\cdot}W_n$, to sequentially assemble this solvation "sphere" around the iodide ion and follow how each water locks into position via the structures of the $I^-{\cdot}W_n$ species.

In treating ionic hydration, perturbation methods are challenged because ionic[14−16,18−21] and interwater[25−31] H-bonding are of comparable magnitudes and, more importantly, the water molecule itself undergoes significant intramolecular relaxation upon engaging either type of bond. As a result, when only a few solvent molecules are present, one generally treats the entire ion−water cluster as a "supermolecule" with ab initio methods[3−11] to directly calculate intramolecular distortions, intermolecular topology, and harmonic vibrational frequencies.[14,15,19,20] Of course, the properties of the global minimum are of only limited utility in characterizing weakly bound van der Waals clusters,[32,33] where the observables arise from averaging over very floppy zero-point motion. In the case of ionic hydration, however, ionic and interwater H-bonds (especially when several of these are networked) are so strong that partially hydrated ions should be much more rigid (as well as quite stable, if kept in isolation). As such, the properties of their equilibrium geometries should be more directly reflected in the experimental spectrum. For example, the neutral W_n ($n \ge 3$) networks are surprisingly robust,[34−37] and the $n = 8$ and 10 clusters even occur as intact structural units binding organic moieties together in self-assembled supramolecular complexes.[38,39] In isolation, the W_n clusters yield simple band patterns in their OH stretching vibrational spectra, and because the OH oscillator frequencies are highly dependent on the H-bonding environment,[40] these patterns directly encode the cluster structures.[34−37] Our goal here is to study the ionic $I^-{\cdot}W_n$ supramolecular complexes in isolation by cooling the first three waters sequentially around the iodide anion and comparing their vibrational spectra with those of the corresponding W_n neutrals. We use the term "supermolecule" advisedly, and by it we imply that the ion−solvent complexes are governed by potential surfaces with

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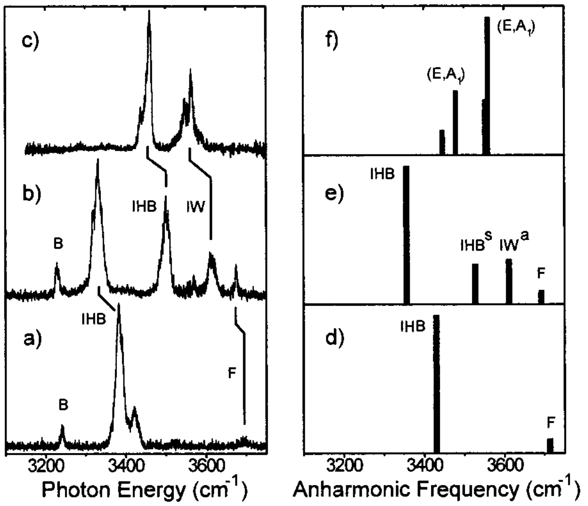

Figure 1. (Left) Vibrational spectra of the $I^-\cdot W_n\cdot Ar_3$ clusters (recorded via predissociation into $I^-\cdot W_n$): (a) $n = 1$, (b) $n = 2$, and (c) $n = 3$. (Right) Ab initio simulations of the $I^-\cdot W_n$ OH stretch fundamentals (corrected for anharmonicity) for (d) $n = 1$, (e) $n = 2$, and (f) $n = 3$. Labels correspond to IHB = ionic H-bonded, F = free, IW = interwater H-bonded, s = symmetric OH stretches, and a = asymmetric OH stretches while B = bend overtone ($2\nu_2$). Symmetry labels are assigned to the (C_3) vibrations of the pyramidal $I^-\cdot W_3$ cluster in f.

sufficiently deep global minima that higher isomers are not explored at the zero-point level (i.e., they are not fluctional on the time scale of the experiment). As a result, the complexes yield vibrational spectra associated with the curvature at the equilibrium geometry, just as is the case in "normal" molecules. With the aid of ab initio calculations to define the properties of the global minima, we deduce the structures at the heart of ionic hydration and discuss them in the context of simple zero-order pictures of hydration.

II. Experimental Section

Spectra are recorded by predissociation of the argon-solvated clusters[20,21,41,42]

$$I^-\cdot W_n\cdot Ar_m \xrightarrow{h\nu} I^-\cdot W_n + m\text{Ar} \qquad (1)$$

for $1 \leq n \leq 3$ and $0 \leq m \leq 3$, upon excitation in the range 3000−4000 cm^{-1}. Each species is isolated using a tandem time-of-flight photofragmentation spectrometer described in detail previously.[43] Photoexcitation in this energy range can evaporate up to six argon atoms,[41,44] so the small argon clusters used here are degraded down to the more strongly bound[45−49] bare $I^-\cdot W_n$ complexes (eq 1). Excitation is carried out with a KTP-based optical parametric oscillator (Laser Vision) with fluences on the order of several mJ/cm^2 per 8 ns pulse and a bandwidth of about 3 cm^{-1}. Spectra are corrected for laser power fluctuations during the scan.

Of course, it is possible that argon is not only serving to cool the system, but is actually changing the structures of the ionic complexes.[50,51] We have, therefore, carried out detailed studies of how the extent of argon solvation affects the $I^-\cdot W_n$ spectra[20] and reached the general conclusion that the sharp features, usually embedded into bare cluster spectra, emerge as the dominant bands with the first argon and display sequential shifts of about 5 cm^{-1}/Ar for the first four argon atoms before tapering off. This shift is in line with that expected from matrix isolation studies,[34,52−57] and we therefore conclude that the primary effect of argon solvation is to cool the clusters.[20] The spectra of the $I^-\cdot W_n\cdot Ar_3$, $n = 1$−3, complexes are displayed in Figure 1. Spectra of the $I^-\cdot W_{1,2}$ complexes have been reported previously[20,21] and are included here in the context of their interpretation with ab initio theory as well as to follow the evolution of the bands in going from $I^-\cdot W$ to $I^-\cdot W_3$.

TABLE 1: Comparison of the Experimental Frequencies (±3 cm^{-1}) for the $I^-\cdot W_n\cdot Ar_3$ and W_n[25,26] Complexes[a]

assignment	$I^-\cdot W_n\cdot Ar_3$	W_n	assignment
	$n = 1$		
$O-H_{IHB}$	3385	3657[c]	ν_s
$O-H_F$	3695	3756[c]	ν_a
	$n = 2$		
$O-H_{IHB}$ (DA)	3331	3655−3660[b]	ν_s (A)
$O-H_{IHB}{}^s$ (DD)	3500	3735	$O-H_F$ (D)
$O-H_{IW}{}^a$ (DD)	3616	3601	$O-H_{IW}$ (D)
$O-H_F$ (DA)	3675	3745	ν_a (A)
	$n = 3$		
$\left.\begin{matrix}O-H_{IHB}\\O-H_{IHB}\end{matrix}\right\}$E,$A_1$	~3440 3462	3726	$O-H_F$
$\left.\begin{matrix}O-H_{Ring}\\O-H_{Ring}\end{matrix}\right\}$E,$A_1$	3548 3565	3533	$O-H_{Ring}$

[a] D = H-bond donor; A = H-bond acceptor; ν_s, ν_a = symmetric and a symmetric stretches. [b] Weak band not observed experimentally. [c] Reference 62.

TABLE 2: Structural Parameters (Distances in Å) of the Neutral (W_n) and Iodide-Bound ($I^-\cdot W_n$) Water Clusters from ab Initio Calculations[a]

ionic	$I^-\cdot W_n$	W_n	neutral[63,69]
	$n = 1$		
$O-H_F$	0.965	0.964	$O-H_F$
$O-H_{IHB}$	0.979	0.964	$O-H_F$
	$n = 2$		
$O-H_F$ (DA)	0.966	0.963	$O-H_F$ (D)
$O-H_{IW}$ (DD)	0.972	0.972	$O-H_{IW}$ (D)
$O-H_{IHB}$ (DD)	0.972	0.965	$O-H_F$ (A)
$O-H_{IHB}$ (DA)	0.982	0.965	$O-H_F$ (A)
O−O	3.002	2.917	O−O
	$n = 3$		
$O-H_{IW}$	0.976	0.977−0.978	$O-H_{IW}$
$O-H_{IHB}$	0.976	0.963−0.964	$O-H_F$
O−O	2.957	2.804−2.812	O−O

[a] D = H-bond donor; A = H-bond acceptor.

III. Results and Discussion

A. The First Water Molecule: Asymmetric Structure of the Binary Complex. The $I^-\cdot W$ spectrum (Figure 1a) is dominated by an intense band at 3385 cm^{-1} flanked by weaker features at 3695 and 3241 cm^{-1}. The $I^-\cdot W$ features can be reproduced (Figure 1d)[19] with the calculated (anharmonicity corrected) OH fundamentals from ab initio theory (Gaussian 94)[58] at the MP2 level using Truhlar's[59] (effective core) basis for I^- and the 6-31+G(2d, p) basis[60] recommended by Jordan[40] for neutral water clusters. The calculated spectra are displayed on the right side of Figure 1, with a few of the structural details collected in Table 2.

The binary complex adopts an asymmetric structure (Figure 2a), with one hydrogen preferentially bonding to the ion and the other free, in the double-minimum ground-state surface. The strong 3385 cm^{-1} band arises from the ionic H-bonded OH stretch (denoted IHB in Figure 1a, d),[61] while the weak 3695 cm^{-1} band is assigned to the free OH (F). The remaining low-energy band (B at 3241 cm^{-1} in Figure 1a) is due to the overtone of the intramolecular bending vibration ($2\nu_2$), which borrows intensity from the strong IHB band through a Fermi interaction with a matrix element of about 30 cm^{-1}.[21]

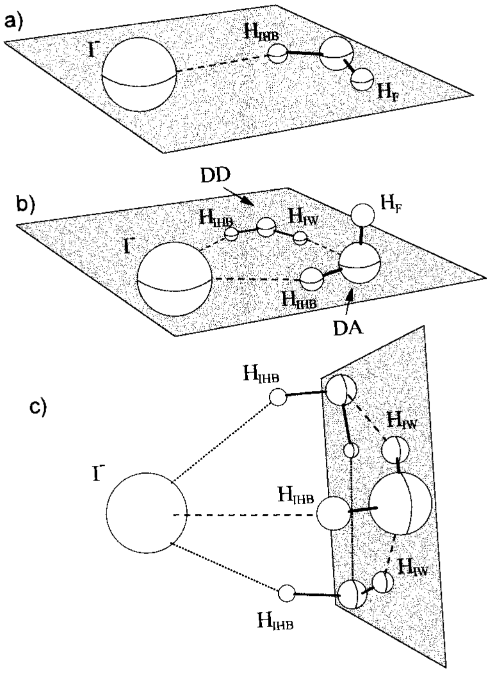

Figure 2. Ab initio structures of $I^-{\cdot}W_n$: (a) $n = 1$, (b) $n = 2$, and (c) $n = 3$ using 6-31G+(2d, p) for water[60] and SPV+ for iodide.[59]

We compare the frequencies and bond lengths of the water in the binary complex relative to those in the neutral complex in Tables 1 and 2, respectively. Note that the free OH band (F) at 3695 cm^{-1} appears quite close to the centroid of the symmetric (ν_s) and asymmetric (ν_a) stretches in bare water (3707 cm^{-1})[62] while the IHB band occurs much farther to the red. The splitting between the F and IHB bands in the complex (310 cm^{-1}) is much larger than that of the bands in isolated water (99 cm^{-1}), a value which reflects the intrinsic coupling between the OH oscillators. The larger splitting in $I^-{\cdot}W$ indicates that the two oscillators are decoupled in the complex, becoming much more local in character.[4,9,15,19] At the same time, note the significant elongation (0.014 Å) of the OH_{IHB} bond length (Table 2) concomitant with the red shifting of this oscillator (following Badger's rule).[63] This indicates that the binary complex is itself not well described in terms of unperturbed H_2O and I^- components; $I^-{\cdot}W$ is already a distinct entity, a "supermolecule" in the context of our present discussion.

B. The Second Water: Solvation of the Binary Complex. The $I^-{\cdot}W_2$ spectrum (Figure 1b)[20] is more complex, consisting of five bands spread more-or-less evenly throughout the 3000–4000 cm^{-1} range. The ab initio global minimum structure is displayed in Figure 2b, indicating that the complex adopts an asymmetric structure[8] where each water binds to the ion as well as to each other. In this geometry, all four hydrogens are distinct (on the time scale of the experiment), and therefore, each contributes a unique band to the spectrum. The calculated pattern[20] of the four (anharmonicity corrected) OH stretching fundamentals is included as the stick spectrum in Figure 1e, providing a reasonable account of the observed spectrum.

It is instructive to consider the distortions of the neutral water dimer which occur upon complexation to the iodide, and we compare the frequencies and bond lengths of the two species in Tables 1 and 2, respectively. The basic structural motif of the neutral dimer[25,64] is distorted as it attacks the ion such that the interwater H-bond acceptor in the bare dimer forms a very strong donor H-bond to the ion. We denote this water as DA in light of its donor–acceptor configuration, and the bands associated with this molecule correspond to local OH oscillators,[20] much like those which occur in the binary complex.[4,9,15,19] In fact, the ionic H-bond formed by the DA water is *stronger* than that of the binary complex, as evidenced by the red shift in its OH_{IHB} band position[20] (relative to the OH_{IHB} band in $I^-{\cdot}W$) and further elongated OH_{IHB} bond length (0.979 and 0.982 Å in $I^-{\cdot}W$ and $I^-{\cdot}W_2$, respectively).[65]

The second water, on the other hand, adopts a double-donor (DD) configuration in $I^-{\cdot}W_2$ (see Figure 2b), with bands closer together (116 cm^{-1}) than the widely split pattern (344 cm^{-1}) associated with the DA water. As their splitting is similar to that of the bare water molecule (99 cm^{-1}),[62] the vibrations of the DD water remain more collective in character (and as such are labeled $OH_{IHB}{}^s$ and $OH_{IW}{}^a$ in Table 1 to emphasize their symmetric and asymmetric OH stretching contributions).[20] The band associated with the interwater OH stretch (IW) is, in fact, slightly blue-shifted (by 15 cm^{-1}) compared to its position in the neutral dimer (see Table 1). When the interwater bond completely breaks, this band will ultimately become local in character and shift back to the position of the free OH. Thus, the observed blue shift suggests a weakening of the W_2 bond[64,66-68] in the presence of the ion. This conjecture is born out in the calculations, which predict that the O–O distance is 0.085 Å larger in $I^-{\cdot}W_2$ than in W_2[63,64,69] (Table 2).

C. The Third Water: Onset of a Symmetrical Solvent Network. Unlike the situation in the dimer, the $I^-{\cdot}W_3$ spectrum (Figure 1c) displays fewer bands than the number of hydrogens, an unambiguous signature of high symmetry. The spectrum consists of two groups of bands spaced by about 100 cm^{-1}, similar to the splitting in the bare water molecule. Both $I^-{\cdot}W_3$ bands appear red-shifted by about 50 cm^{-1} relative to the DD bands in the dimer (connecting lines in Figure 1), while the widely spaced bands associated with the DA water are missing (along with the weaker band assigned to its intramolecular bend overtone (B in Figure 1b)).

The simplicity of the $I^-{\cdot}W_3$ spectrum suggests that the three water molecules adopt identical binding motifs. However, the similarity of the $I^-{\cdot}W_3$ spectra with that of the DD water in the dimer complex rules out the open, propeller-type (planar) structures[3,4] with very high (C_{3h}) symmetry. Thus, on qualitative grounds, one anticipates a C_3, pyramidal structure where the waters form a cyclic trimer with each molecule having one hydrogen atom participating in a donor–acceptor (homodromic) interaction in the ring and its other hydrogen donated to the ion.

This C_3 structure has, in fact, been reported previously[8] for the $I^-{\cdot}W_3$ species, and we have carried out additional ab initio calculations to extract the vibrational pattern expected for this complex. The results are included in the stick spectrum in Figure 1f, which nicely anticipates the locations of the observed bands. Moreover, the fine structure within the main features is also explained as each subband is associated with closely spaced degenerate E and A_1 modes, accounting for the expected six OH bands grouped into two doublets. The character of the modes is intuitive, with the lower energy doublet associated largely with OH stretches toward the ion (all in phase (A_1) and piston-like, up–down (degenerate E) stretches)[7] and the upper band is associated with the collective ring motions.[63,69,70] This characteristic C_3 pattern has been predicted for related systems ($Cl^-{\cdot}W_3$,[4] $OH^-{\cdot}W_3$[7]), although the present study is the first to experimentally verify its spectral motif.

The bond lengths of the waters in $I^-{\cdot}W_3$ bear little resemblance to the H_2O moiety in the binary complex,[15,18,21] instead appearing most similar to the "solvating" DD water in $I^-{\cdot}W_2$ (Table 2). In fact, one can view the C_3 structure (Figure 2c) as being derived from that of $I^-\cdot W_2$ by simply locking a water molecule into the gap left in the $I^-\cdot W_2$ structure (Figure 2b). In closing the cycle, each water adopts a DDA (double-donor/acceptor) H-bonding configuration. The collective forces[28] binding the water trimer network appear to overcome the enhanced ionic H bond gained by the terminal water in a chain.

In Table 2, we also compare the structural parameters for the free and ion-bound water trimer. While the ring bears a close resemblence to its neutral cousin, the iodide-bound trimer displays a much longer O−O distance, indicating that the interwater interaction is reduced as the free OH's are bound to the ion. Consistent with this picture, the ring OH bond length shortens and the interwater (OH_{IW}, nominally ring) modes are slightly blue-shifted (by $\sim$20 cm^{-1} compared to the neutral cluster (Table 1)) as the waters relax back toward their free OH positions.

IV. Summary

The mid-IR spectra of $I^-\cdot W_n$ complexes characterize the distinct supermolecules which occur upon sequential addition of the first three water molecules to the iodide ion. These molecules display quite different intramolecular distortions of the water component in each subcluster, becoming more like unperturbed water with increasing size. The $I^-\cdot W_3$ cluster is particularly aesthetic, forming a pyramid with the ion on top of a symmetrical water trimer, an arrangement which yields a very simple vibrational spectrum in the OH stretching region.

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