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Argon Predissociation Spectroscopy of the $OH^{-}\cdot H_2O$ and $Cl^{-}\cdot H_2O$ Complexes in the 1000−1900 cm^{-1} Region: Intramolecular Bending Transitions and the Search for the Shared-Proton Fundamental in the Hydroxide Monohydrate

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We present argon predissociation vibrational spectra of the $OH^{-}\cdot H_2O$ and $Cl^{-}\cdot H_2O$ complexes in the 1000−1900 cm^{-1} energy range, far below the OH stretching region reported in previous studies. This extension allows us to explore the fundamental transitions of the intramolecular bending vibrations associated with the water molecule, as well as that of the shared proton inferred from previous assignments of overtones in the higher energy region. Although the water bending fundamental in the $Cl^{-}\cdot H_2O$ spectrum is in very good agreement with expectations, the $OH^{-}\cdot H_2O$ spectrum is quite different than anticipated, being dominated by a strong feature at 1090 cm^{-1}. New full-dimensionality calculations of the $OH^{-}\cdot H_2O$ vibrational level structure using diffusion Monte Carlo and the VSCF/CI methods indicate this band arises from excitation of the shared proton.

I. Introduction

Over the past 5 years, argon predissociation vibrational spectroscopy and electronic structure calculations have combined to yield a detailed picture of how water molecules bind to atomic and molecular anions.[1,2] Most of these studies have been carried out in the high-energy region of the OH stretching fundamentals, so that information on the HOH intramolecular bending vibration and the ion−molecule soft modes had to be inferred from overtone and combination bands involving interactions with the OH stretches. Recently, however, the spectra of many molecular ions and a few ion−molecule complexes have been reported for excitation energies below 2000 cm^{-1} using free electron lasers.[3−5] This region is especially important for strongly bound systems such as $OH^{-}\cdot H_2O$ and $H_5O_2^{+}$, where the motion of the shared proton is thought to yield very low energy fundamentals. In this report, we survey the low-energy region (1000−1900 cm^{-1}) of the $Cl^{-}\cdot H_2O$ and $OH^{-}\cdot H_2O$ complexes using a tabletop laser system based on nonlinear conversion in $AgGaSe_2$.[6,7] These results dramatically extend the spectral coverage for both complexes and allow us to identify the signatures associated with the intramolecular bending vibration, as well as the motions associated with the shared proton. This information is particularly important for the characterization of the hydroxide monohydrate, as this complex is key to understanding defect transport in water.[8,9]

The Cl^{-} and OH^{-} hydrates were chosen because they represent two different extremes of hydration behavior. In the case of the $Cl^{-}\cdot H_2O$ complex,[10−12] although strongly bound to the ion, the water molecule is clearly intact and is attached to the ion in a single ionic H-bond (SIHB) motif. This arrangement is readily apparent in the OH stretching region of the spectrum where the bound proton stretch occurs at 3130 cm^{-1}, far below the stretching fundamental of the free OH at 3698 cm^{-1}.[10] The strong SIHB band is accompanied by a weaker feature at 3283 cm^{-1}, which was assigned to the $2 \leftarrow 0$ overtone of the intramolecular bending vibrational transition (ν_2) of the intact water molecule. The assignment was made on the basis of the evolution of the bands in the $X^{-}\cdot H_2O$ (X = Cl, Br, I) complexes.[1,10] This $2 \leftarrow 0$ overtone was also explored extensively through its Fermi-resonant interaction with the bound OH stretch fundamental, where it appeared as a sharp band and displayed very little perturbation upon attachment of either argon atoms or CCl_4 molecules.[13] Thus, in the 1000−1900 cm^{-1} region, the $Cl^{-}\cdot H_2O$ spectrum is anticipated to be dominated by the bending fundamental close to 1642 cm^{-1} [i.e., $^{1}/_{2}(2\nu_2)$].

In contrast to the simple situation expected for the largely charge-localized chloride monohydrate, the $OH^{-}\cdot H_2O$ case is much more interesting as the very basic hydroxide ion is expected to disrupt the fabric of the attached water molecule, so as to yield a truly shared-proton configuration, $[HO\cdots H\cdots OH]^{-}$.[14−18] Recent calculations[18−20] indicate that, although the potential surface for the motion of the shared-proton has a small barrier, the vibrational zero-point motion effectively averages the ground state to a symmetrical structure. In a

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previous paper[24] reporting predissociation spectra of the $OH^-\cdot H_2O\cdot Ar_{1,2}$ complexes in the OH stretching region, we assigned sharp vibrational transitions at 3653 and 3672 cm^{-1} to the free OH stretching bands, where the higher-energy feature was found to quench upon addition of a second argon atom. The observation of a single OH stretching band immediately supports the symmetrical arrangement, as partial localization in the $OH^-\cdot H_2O$ form would split the stretches into two distinct features, one higher in energy close to the OH stretch in bare HOD,[22] and the other lower in energy approaching the OH stretch in the isolated hydroxide ion (3556 cm^{-1}).[23] Note that the persistent (3653 cm^{-1}) band origin in $OH^-\cdot H_2O$ is significantly red-shifted from the typical free OH stretch position (~3700 cm^{-1})[1], consistent with significant charge delocalization over both "free" OH groups.

In addition to the free OH band, two broad, weak features near 3100 and 3380 cm^{-1} were also observed in the $OH^-\cdot H_2O\cdot Ar$ spectrum.[21,24] These were tentatively assigned as overtones of the intramolecular bending and shared proton (i.e., along the quasilinear O···H···O axis) vibrations, which were anticipated to be strongly coupled in the earlier calculations by Xantheas.[17] More recent calculations by Bowman and co-workers[18] have cast some doubt on this simplistic interpretation, instead placing the shared-proton vibration far below the energy implied by the harmonic frequencies at the global minima in the surface.[17] Here, we probe the fundamental region of the putative overtones to experimentally challenge these previous assignments.

II. Experimental Section

Spectra were obtained using the Yale tandem time-of-flight, double-focusing photofragmentation spectrometer described previously.[25,26] Argon-solvated cluster anions were prepared in a pulsed supersonic expansion (10 Hz) in which slow secondary electrons were introduced by ionization with a counterpropagating electron beam (1 keV). For the $Cl^-\cdot H_2O\cdot Ar_n$ study, an entrainment approach was employed[27] where trace amounts of $CHCl_3$ and H_2O were introduced just outside the nozzle with independently controlled pulsed valves. In the hydroxide case, the argon-solvated hydrates were generated by careful control of an ionized expansion of water vapor seeded directly in the argon carrier gas as described previously.[21] The $OH^-\cdot H_2O\cdot Ar_n$ beam was more difficult to prepare, and consequently, the parent-ion intensities were approximately a factor of 10 lower than those observed for $Cl^-\cdot H_2O\cdot Ar_n$.

A critical aspect of the present study was the generation of infrared radiation in the 1000−1900 cm^{-1} range (~9.8−5.3 μm). This was accomplished by nonlinear mixing of the 1.5- and 3-μm beams in a 5 × 5 × 10 mm $AgGaSe_2$ crystal. The two input beams were obtained from the usual output of the KTP/KTA OPO/OPA parametric converter (LaserVision). With a combined input energy of 20 mJ/pulse, about 250 μJ of output was obtained in the 1500 cm^{-1} region. This beam was directed into the laser interaction region through a 1-m CaF_2 lens and passed through the ion packet six times using a multipass mirror system located inside the high-vacuum chamber. The path of the laser beam leading to the chamber was carefully purged with dry N_2 to minimize modulation of the laser power due to absorption of ambient water vapor. Reported spectra arise from the summation of 30−40 individual scans and are normalized for variations in the laser output energy over the scan range.

III. Results and Discussion

Argon predissociation spectra of the $Cl^-\cdot H_2O$ complex in the water-bending region are presented in Figure 1 for the complexes with one (Figure 1a) and two (Figure 1b) attached argon atoms. The dotted arrow in Figure 1b indicates the bending fundamental in an isolated water molecule,[22] and the solid arrow denotes the expected location of the bending fundamental in the complex based on the previously assigned[10] 2 ← 0 overtone transition. Indeed, the observed band appears very close to the anticipated energy, with very little shift upon addition of a second argon atom (Figure 1b). This observation appears to support the conclusion that the potential describing the HOH intramolecular bending mode in the $Cl^-\cdot H_2O$ complex is quite harmonic.

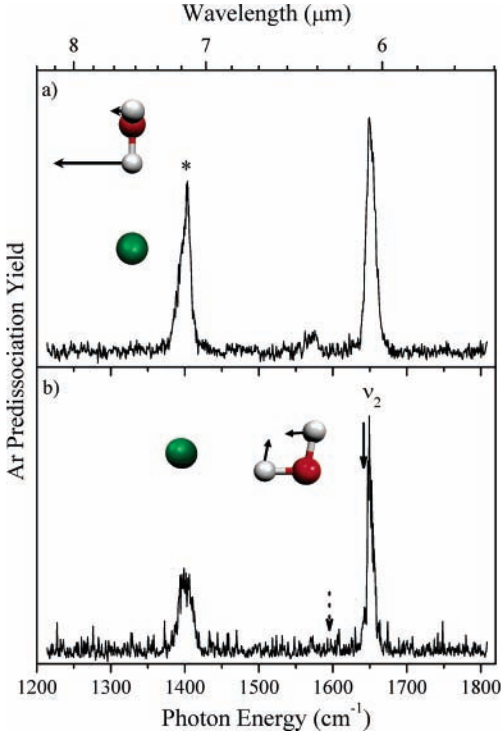

Figure 1. Argon predissociation spectra of the (a) $Cl^-\cdot H_2O\cdot Ar$ and (b) $Cl^-\cdot H_2O\cdot Ar_2$ binary complexes in the water bending region. The dotted arrow corresponds to the band origin of the bending fundamental in the free water molecule (ref 22). The vibrational band labeled ν_2 corresponds to the fundamental of the water bend in the complex, with the solid arrow in panel b indicating the expected position of this vibration based on the previous assignment of the bend overtone ($2\nu_2$). The displacement vectors for this normal mode are shown in the inset of panel b. The feature denoted by the asterisk (*) is tentatively assigned to the 2 ← 0 overtone of the out-of-plane wag vibration ($2\nu_3$; depicted in the inset of panel a) on the basis of the calculated fundamentals reported in refs 28−31.

In light of the fact that no additional fundamentals are expected in the 1200−1800 cm^{-1} region,[28] the appearance of a *second* strong band at 1402 cm^{-1} (labeled * in Figure 1a) is surprising. Although this feature could conceivably arise from a (0, 1) vibrational hot-band transition involving a soft mode with a 250 cm^{-1} quantum, the relative integrated intensity of this feature is not changed (it is rather broadened) by addition of a second argon atom, casting doubt on this hypothesis. Note that one would also expect a significant (1, 1) sequence member in such a scenario, whereas only a single peak is observed near the strong bending fundamental. We therefore favor its assignment to a combination or overtone transition arising from the ground state of the complex. As a tentative assignment, we note that recent calculations[28−30] indicate that the out-of-plane motion of the ion-bound proton (ν_3) occurs with a fundamental energy close to 700 cm^{-1}, leading us to suggest that the observed feature at 1402 cm^{-1} might be the 2 ← 0 overtone involving this motion.

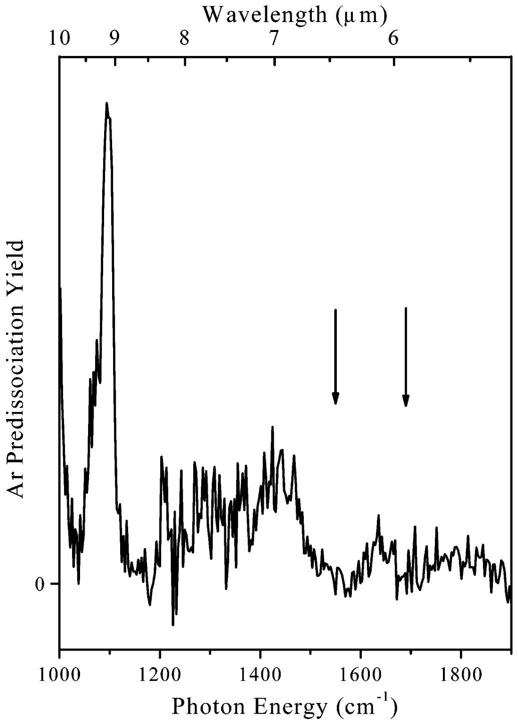

Figure 2. Argon predissociation spectrum of the $OH^-\cdot H_2O\cdot Ar$ complex. The arrows correspond to the expected fundamental transitions of the putative overtones tentatively assigned previously (refs 17, 21, and 24) in the OH stretching region.

The normal-mode displacements associated with this mode are indicated in Figure 1a. High-level vibrational calculations in full-dimensionality would certainly be helpful to address the plausibility of this assignment, as well as the interaction of this motion with that of the intramolecular bend. Interestingly, a very recent anharmonic vibrational calculation of the $Cl^-\cdot H_2O$ complex on a "morphed" ab initio potential surface predicted that the intramolecular bend would be strongly mixed with $2\nu_3$.[31]

The relatively simple spectra of the $Cl^-\cdot H_2O$ complex are useful in that they give us confidence in the experimental approach as well as confirm our previous assignment[10] of the intramolecular bending overtone. Such a check is important because the situation in the $OH^-\cdot H_2O$ complex is much more complicated, as indicated by its argon predissociation spectrum displayed in Figure 2. This spectrum displays only weak, broad vibrational structure in the typical location of the intramolecular HOH bend and, instead, is dominated by a strong transition at the very lowest energy presently available (~1090 cm^{-1}) in our spectrometer. Most importantly, the two arrows in Figure 2 indicate the locations of the "fundamentals" that would correspond to our earlier preliminary overtone assignments of the two broad bands in the OH stretching spectrum.[21,24] As these assignments originated from harmonic analysis at the two equivalent global minima,[17] it is clear that such a strategy is inadequate to understand this system. In fact, the harmonic analysis fails to recover any fundamentals within even 20% of the strong band at 1090 cm^{-1}. We will return to this assignment on the basis of the new full-dimensional calculations below, but first we briefly compare the $Cl^-\cdot H_2O$ and $OH^-\cdot H_2O$ spectra.

At a qualitative level, it is of interest to comment on the mechanics of how the intramolecular bending vibrational motion of a water molecule bound to an ion evolves with the strength of the ionic hydrogen bond. In the $Cl^-\cdot H_2O$ case, the bend is blue-shifted relative to the bare water molecule (1595 cm^{-1}, dashed arrow in Figure 1b),[22] and the spectrum displays a second feature that appears to be associated with the out-of-plane motion ($2\nu_3$) of the shared proton, perpendicular to the plane of the complex. In more strongly bound complexes, however, it is now clear that proton transfer becomes operative.[32] As such, when the shared proton is increasingly removed from the water molecule, one expects that the HOH force constant will be lowered as the complex evolves from an $X^-\cdot H_2O$ arrangement toward the proton-transferred $HX\cdot OH^-$ geometry. In the case of the hydroxide monohydrate, the ~50 cm^{-1} red shift in the single free OH stretching band (relative to bare HDO) indicates that the shared proton is dramatically delocalized over the double-well potential such that the two OH groups become equivalent. It therefore seems reasonable that the intramolecular bend will fall to lower energy, while the remnant of the out-of-plane shared-proton vibration evident in $Cl^-\cdot H_2O$ evolves toward higher energy in the more strongly bound $OH^-\cdot H_2O$ system.

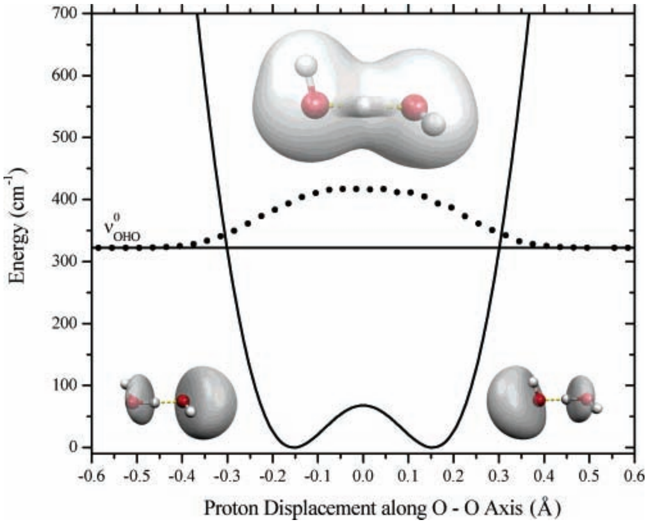

Figure 3. Relaxed potential surface, calculated from the nine-dimensional potential described in ref 18. The zero-point vibrational level and its corresponding wave function were obtained by projecting the DMC ground-state wave function onto the proton-transfer coordinate. The inset structures located near the bottom of the figure depict the two equivalent (i.e., eigen-) forms of the complex in which the shared proton is more closely associated with one of the oxygen atoms. The upper inset depicts the zero-point averaged structure with the proton equally shared by the two OH groups.

Recent calculations[18] found that the shared-proton motions in $OH^-\cdot H_2O$ would occur with much lower energies than those derived from the harmonic frequencies at the global minimum and further established that the vibrational dynamics are, in fact, strongly anharmonic. Indeed, full-dimensional vibrational calculations on a full-dimensional potential indicate that the zero-point probability density is delocalized symmetrically over the two minima, as depicted in Figure 3. This concurs with the conclusion based on a previous one-dimensional analysis.[19] Prior to undertaking the present experimental study, we initiated a parallel theoretical effort to refine the earlier calculations[18] of the $OH^-\cdot H_2O$ dynamics. These involved the use of both diffusion Monte Carlo (DMC)[33-35] and VSCF/CI calculations implemented in both the single-reference and reaction-path (RP) versions of Multimode (MM)[36,37] approaches. These calculations employed the potential and dipole moment surfaces reported in ref 18. Full details of these calculations and results will be reported soon.[38] With these results in hand, however, it is useful to consider the assignment(s) of the 1090 cm^{-1} band observed in this work (Figure 2). We conclude (on the basis of vibrational energies and dipole moment considerations) that the relevant quantum states involve large displacements of the shared proton, along and/or perpendicular to the O−O axis. Using diffusion Monte Carlo simulations for excited states within the fixed-node[39] or ADMC[40] approach, we obtained wave functions for two states in the region of the experimental band, with energies of 1019 and 1102 cm^{-1}. Judging from an analysis of the wave functions, these two states involve large displacements of the shared proton perpendicular to the O−O axis and also significant displacements of the proton stretch, wag, and rock modes (compared to the ground vibrational state). Although the states were calculated to be the lowest-energy states that correspond to displacements of the shared proton perpendicular to the O−O axis, they might correlate to combination bands rather than the true fundamentals.

To further sort out the assignment of the strong 1090 cm^{-1} band, we also consider the results obtained by both single-reference and reaction-path MM simulations. Reaction-path MM simulations provide the more accurate energies of the two approaches, but at present, we are only able to obtain intensities using the single-reference MM approach. In the MM spectrum, we find intense peaks at 1308 and 1357 cm^{-1}. They are both mixed states and involve the shared-proton stretch as well as the wag mode and the O−O stretch. Although these assignments are consistent with the DMC wave functions, the MM energies for these states are not well converged. On the basis of the reaction-path MM calculations, we find mixed states with significant shared proton-stretch character in the 1000−1100 cm^{-1} region, in good agreement with the DMC results.

On the basis of the above analysis, we believe that the observed band, centered at 1090 cm^{-1}, arises from states that involve excitation of the shared proton. In terms of our zero-order, normal-mode basis, this motion is most easily described as a combination band involving the shared-proton stretch and the wag and rock motions of the complex. Such an assignment might at first seem surprising, but one must consider that, as the shared proton is displaced from the O−O axis, the system begins to more closely resemble the eigen form of $OH^-{\cdot}H_2O$ with the shared proton closer to one of the oxygen atoms. However, in the zero-point averaged structure, the proton is equally shared by the two OH groups. It is interesting to note that this motion is reminiscent of that involved in the assignment of the lower-energy transition observed in the $Cl^-{\cdot}H_2O$ spectrum (denoted by * in Figure 1), highlighting the enhanced role of such off-axis proton motions in low-frequency spectra. A more complete discussion of the approaches taken to reach the above conclusions, as well as further analysis of these and other states, will appear in a future publication.[38]

The DMC and both MM calculations all indicate that the band that corresponds to the lowest-energy excitation involving displacement of the proton *along* the O−O axis will occur in the range 650−720 cm^{-1}. This frequency is out of the range of the present experimental configuration, but judging from the intensities calculated using the traditional MM approach, this band should be stronger than the bands described above.

The assignment of the remaining weak, broad structure in the $OH^-{\cdot}H_2O$ spectrum near the expected location of the intramolecular bending mode likely involves combination bands and is presently unclear. Improvements to achieve an enhanced signal-to-noise ratio and extend the measurements below 1000 cm^{-1} are expected to reveal additional vibrational eigenstructure that will be critical in unraveling the molecular physics of this important cluster.

IV. Conclusions

Summarizing, we have used argon predissociation spectroscopy to observe the first vibrational spectra of the $Cl^-{\cdot}H_2O$ and $OH^-{\cdot}H_2O$ complexes in the 1000−1900 cm^{-1} region. This extension to lower energy allows us to probe the spectral signatures of the intramolecular bending fundamentals (ν_2) of the bound water molecule, as well as, in strongly bound systems such as $OH^-{\cdot}H_2O$, the motion of the shared proton. Surprisingly, two bands were recovered for the $Cl^-{\cdot}H_2O$ complex, one that arises from the expected bending fundamental and another that is tentatively assigned to an out-of-plane motion of the ion-bound hydrogen atom. The $OH^-{\cdot}H_2O$ spectrum is more difficult to analyze, being dominated by a strong feature at 1090 cm^{-1}, far below the typical region of the bending modes. We explore the origin of this band in the context of recently completed theoretical calculations that incorporate the full dimensionality of the potential surface. These calculations indicate that hydroxide monohydrate exhibits large charge delocalization effects and that they account for the dominant feature as resulting largely from the motion of the shared proton.

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