IR spectroscopy of the Cesium Iodide–Water Complex

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ABSTRACT: There has been much interest inI-(H2O) as a simple model for a hydrated iodide ion. Here we explore how this fundamental ion-solvent interaction is modified by the presence of a counter ion, specifically Cs+. This has been achieved by forming the CsI(H2O) complex in superfluid helium nanodroplets and then probing this system using infrared spectroscopy. The complex retains the ionic hydrogen bond between the I- and a water OH group seen inI-(H2O) but the Cs+ ion substantially alters the anion-water interaction through formation of a cyclic Cs+-O-H-I- bonding motif. As with I-(H2O), the OH stretching band derived from the hydrogen bonded OH group shows sub-structure, splitting into a clear doublet. However, in contrast to I-(H2O), where a tunneling splitting arising from hydrogen atom exchange plays a role, the doublet we observe is attributed solely to an anharmonic vibrational coupling effect.

## I. INTRODUCTION

Solvated ions are a common component of most biological systems and the pairwise association can lead to the formation of salt-bridge structures, which play roles in protein folding and molecular recognition.1-3 During the creation of such anion-cation contacts, water molecules are desolved from the interacting charges, illustrating the importance of competing ion-ion and ion-water interactions.

Alkali metal-halides, MX, are prototypical salts that can be used as model systems to gain an understanding of the microsolvation of ions and the association of ion pairs in solution.4-7 However, experimental data remains sparse for small complexes consisting of a single water molecule attached to a cation-anion pair, MX(H2O). Examples include microwave spectroscopy of NaCl(H2O) in a pulsed molecular beam8,9 and IR spectroscopy of NaCl(H2O) embedded in superfluid helium nanodroplets.10 The former method is particularly well-suited to determining the three-dimensional structure of gas phase molecules and small complexes via analysis of the measured rotational constants. However the second method is also appealing because helium nanodroplets provide a low temperature (0.4 K) environment in which molecular complexes are readily formed following the statistical pickup of the respective species, which can subsequently be probed using IR spectroscopy to gain structural information.11,12 This is possible because the droplets do not absorb in the IR and the vibrational motion of the embedded species is only weakly perturbed by the surrounding helium.13-15

CsI differs from NaCl in having much larger cation and anion constituents. Solvated complexes of CsI have received relatively little attention in comparison with NaCl. However, in an Ar matrix isolation study performed over 40 years ago, three IR spectral features were identified for CsI(H2O).16 The IR band at 401 cm-1 was assigned to a hydrogen deformation mode, while those at 3164 and 3280 cm-1 were attributed to the two OH stretching modes of a nonplanar complex.

More recently, photoelectron spectra have been measured for the related charged species, CsI-(H2O),17 and IR spectra have been reported for I-(H2O)18-24 and Cs+(H2O).25,26 In the case of I-(H2O), one of the water OH groups interacts with the anion via an ionic hydrogen bond (IHB), whilst the other OH group remains free. This results in a large red-shift (~300 cm-1) in the bound OH stretching frequency, νOH(b), relative to the free OH stretching vibration, νOH(f), because the OH(b) group is weakened by the hydrogen bond.26 For Cs+(H2O), the cation interacts with the lone pairs on the oxygen atom of the water, such that both OH groups remain free and the OH stretching frequencies are red-shifted by <45 cm-1 relative to an isolated water molecule. Thus, IR spectroscopy is capable of probing the environment around water molecules and revealing how they interact with a solute in a microsolvation complex.

One of the more intriguing observations in the IR spectrum of I-(H2O) is a doublet observed for νOH(b) in Ar- and N2-tagged I-(H2O),19 when only one peak is anticipated. A detailed theoretical study on the untagged I-(H2O) complex,27 which used a recently developed many-body energy functional (MB-nrg),28 was able to closely replicate the experimental band positions (3393 and 3422 cm-1) of the doublet. From this analysis, the two bands were assigned to the symmetric and anti-symmetric tunneling splitting partners of νOH(b), which arise from quantum tunneling of the hydrogen atoms through a barrier between two equivalent global energy minimum structures.27

On the other hand, experimental IR spectra for bare I-(H2O) have revealed a spectral quartet for the IHB OH group rather than a doublet.18,19 The additional peaks were originally attributed to rotational fine structure,19 but were recently reassigned following the implementation of a sophisticated experimental technique involving two-color IR-IR double resonance spectroscopy, in combination with high level calculations using the MB-nrg functional.24 It was deduced that two mechanisms are responsible for the quartet; vibrational mode-dependent tunneling splitting and anharmonic coupling to combination bands containing low frequency intermolecular modes. However, only three of the strong quartet bands were closely replicated in the simulated spectrum, thus illustrating the limitations of even the most advanced calculations. This serves to exemplify the need for high quality experimental data, such as that measured by the Johnson group.23,24 Such studies remain essential to the advancement of our understanding of ion-water interactions and provide a valuable means of testing new theoretical methods.

In this work, we use IR spectroscopy to study the interaction between a single water molecule and a Cs+I- ion pair inside helium nanodroplets, thus revealing the influence of the Cs+ counter ion on the interaction between I- and water. We compare the experimental spectrum for CsI(H2O) with simulated spectra generated from anharmonic vibrational frequency calculations in order to evaluate the performance of several DFT functionals and the post Hartree-Fock MP2 method. Finally, we further investigate whether anharmonic coupling or hydrogen atom exchange is likely to be responsible for the spectral doublet observed in CsI(H2O).

## II. METHODS

### A. Experimental

Experiments were performed using a helium nanodroplet instrument that has been described previously.29-31 The nanodroplets were prepared by expanding helium gas at high pressure (32 bar) through the 5 μm diameter aperture of a cooled nozzle (16 K), resulting in a mean droplet size of ~5000 helium atoms. The continuous beam of droplets then passed through a skimmer and through the center of a cylindrical oven32 containing a powdered sample of CsI. The oven was maintained at 650 K, a temperature chosen to create a CsI vapor pressure which favored pick up of a single CsI molecule (the probability of multiple pickup events was estimated to be <4% under these conditions). A second pickup cell contained a variable pressure of water vapor, allowing water to be added to the helium nanodroplets in a controlled manner.

The doped droplets were overlapped with the counter-propagating tunable IR beam from a nanosecond optical parametric oscillator/amplifier (LaserVision) operating at a repetition rate of 10 Hz, with a bandwidth of ~4 cm-1. Upon reaching a quadrupole mass spectrometer (Extrel, MAX-1000), which is located at a distance of 60 cm from the second pickup cell, the doped droplets were ionized via electron impact at 90 eV and the resulting cations were detected. IR spectra were obtained by measuring the change in mass-selected ion signal as the laser wavelength was scanned. This change arises when resonant IR absorption by the neutral dopant leads to the evaporation of helium atoms and thus a reduction in droplet cross-section for the subsequent electron ionization process.

To determine the number of water molecules in the CsI-water complex responsible for the IR absorption features of interest, the ion depletion signal was also measured as a function of the water pressure within the second pickup cell at selected IR wavelengths. A comparison was then made between the measured pickup cell pressure (PUCP) curves and the normalized Poisson distributions expected for the statistical pick up of one and two water molecules by the droplets.

### B. Computational

Geometry optimization and harmonic vibrational frequency calculations for CsI(H2O) were performed using two different DFT functionals, LC-PBE and CAM-B3LYP, as well as the MP2 and CCSD post Hartree-Fock methods, within the Gaussian 16 software package.33 The aug-cc-pVTZ basis sets were used for the O and H atoms of the water molecule. For Cs and I atoms the aug-cc-pwCVTZ-PP basis sets34,35 were employed in combination with the ECP46MDF (for Cs) and ECP28MDF (for I) effective core potentials.36,37 We shall refer to this combination of basis sets as awCVTZ. Anharmonic vibrational frequencies were calculated using generalized 2nd order perturbation theory (GVPT2).38 Vibrational resonances were treated variationally for states containing up to three vibrational quanta39 and separated by up to 400 cm-1. Simulated spectra were obtained by Gaussian broadening (4 cm-1 FWHM) the calculated anharmonic vibrational frequencies in order to account for the laser bandwidth.

Structures of the transition states associated with hydrogen atom exchange in CsI(H2O) and I-(H2O) were determined at the CCSD/awCVTZ level of theory. The atomic charge distribution for the global energy minimum structure in CsI(H2O) was calculated using natural population analysis at the same level of theory. BSSE-corrected energies for the global minima and transition states in CsI(H2O) and I-(H2O) were determined using CCSD(T)/awCVTZ at the geometries deduced at the CCSD/awCVTZ level of theory.

2D relaxed potential energy surfaces were created by performing a geometry optimization at each chosen combination of the I-O separation and the coordinate for hydrogen atom exchange, using the LC-PBE/awCVTZ level of theory. For this purpose, a dummy atom, X, was positioned midway between the two hydrogen atoms such that the I--O-X-H dihedral angle can be used to represent the exchange coordinate for CsI(H2O). Similarly, the I--O-X angle is representative of the exchange coordinate for I-(H2O). All other bond lengths and angles were allowed to relax.

## III. RESULTS & DISCUSSION

### A. Experimental spectra

Figure 1(a) shows a mass spectrum obtained using a CsI oven temperature of 650 K and a water vapor pressure of 4.8 × 10-6 mbar. Two series of peaks are observed. The peaks in the first series, which are most clearly seen on the left hand side of the mass spectrum and are relatively weak, are separated by *m*/*z* 4 and derive from He*m+* ions. The second and most prominent series shows peaks at *m*/*z* 133. 151, 169, 187, 205 and 223, which correspond to Cs+(H2O)*k* ions with *k* ranging from 0 to 5. These ions are formed by loss of the iodine atom, all of the helium atoms and possibly one or more water molecules from droplets containing embedded CsI-water complexes of various sizes, following electron impact ionization.

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**Figure 1.** (a) Mass spectrum derived from electron ionization of helium droplets doped with CsI and water. This spectrum was measured at a water vapor partial pressure of 4.8 × 10-6 mbar, which corresponds to an average pickup of ~2 water molecules per droplet. IR depletion spectra measured at mass channels and partial pressures of (b) *m*/*z* 133 and 4.8 × 10-6 mbar, and (c) *m*/*z* 133 and 0.8 × 10-6 mbar (pink trace), and *m*/*z* 151 and 1.3 × 10-6 mbar (blue trace). The difference between the two spectra in (c) is shown in (d), revealing the peaks attributed solely to CsI(H2O).

Figure 1(b) shows an IR depletion spectrum measured whilst gating on the mass peak at *m*/*z* 133 (Cs+), using the same oven temperature and water pressure that were used for recording the mass spectrum in Figure 1(a). The observed spectral features arise from IR absorption by neutral CsI-water complexes and, because of the detection of Cs+, no contributions from neutral H2O or its clusters are possible. The spectrum in Figure 1(b) shows considerable spectral structure arising from CsI-water complexes of various sizes, but much of the spectral congestion can be reduced by careful optimization of the experimental conditions.

Figure 1(c) shows a second IR depletion spectrum recorded at *m*/*z* 133 (pink trace), which was measured using a far lower partial pressure of water vapor in order to favor the formation of the smallest possible CsI-water complex inside the droplets. Here the most intense features are assigned to CsI(H2O). Minor contributions from larger complexes may still be present in the spectrum but these are readily identified by comparison with an IR spectrum measured at the next highest mass channel in the series, namely, at *m*/*z* 151. The blue trace in Figure 1(c) represents such a spectrum, and the intensity has been normalized to aid comparison with the *m*/*z* 133 spectrum. Because the IR peaks at 3315 and 3327 cm-1 are observed in both mass channels, they are assigned to a complex containing more than one water molecule, most likely CsI(H2O)2. In contrast, the strong peaks at 3266 and 3282 cm-1 are absent from the spectrum at *m*/*z* 151, suggesting that they arise from IR absorption by CsI(H2O).

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**Figure 2.** Pick-up cell pressure (PUCP) curves obtained by measuring the depletion in ion signal for a range of partial pressures of water at IR frequencies of 3266, 3282, 3315 and 3327 cm-1. The solid lines represent Poisson distributions for the statistical pickup of one and two water molecules by the helium nanodroplets.

Our assignment of a particular CsI(H2O)*n* complex to each of the IR features observed between 3250 and 3350 cm-1 in Figure 1(c) is supported by the experimental PUCP data shown in Figure 2, in which good agreement is observed between the experimental data points for IR peaks at 3266 and 3282 cm-1 and the Poisson distribution for pickup of a single water molecule. Furthermore, the experimental PUCP curves for the IR peaks at 3315 and 3327 cm-1 show good agreement with the Poisson distribution expected for the water dimer, indicating that these features arise from IR absorption by CsI(H2O)2. In this study we focus on CsI(H2O) and will discuss larger CsI(H2O)*n* complexes in a future publication.

The IR spectrum shown in Figure 1(d) represents a difference spectrum, which has been obtained by subtracting the normalized spectrum measured at *m*/*z* 151 from the spectrum measured at *m*/*z* 133 [see Figure 1(c)]. To a good approximation, the difference spectrum represents IR absorption by the CsI(H2O) complex only.

### B. Calculated structure and IR spectra

Prior to deducing the vibrational assignments for the IR spectral features observed for CsI(H2O), we first consider the structure and bonding motif for this complex, noting that only one structure has been identified in calculations.17,40 The optimized geometry deduced at the CCSD/awCVTZ level of theory is shown in Figure 3. It is apparent that the water molecule forms an IHB with the iodide ion, by virtue of the OH pointing towards the anion. The electronegative oxygen atom interacts with the cesium cation, which provides further electrostatic stabilization. This configuration leads to a cyclic Cs+-O-H-I- bonding motif and the remaining OH group points away from the ion pair, such that the resulting complex has a planar geometry. The atomic charges on the Cs and I are calculated to be +0.97*e* and -0.94*e*, respectively, confirming that they constitute an ion pair.

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**Figure 3.** (a) Bond lengths (in Å) and (b) angles (in degrees) calculated at the CCSD/awCVTZ level of theory for a complex consisting of a Cs+I- ion pair with one water molecule attached. The symmetry of this complex is Cs.

The IR spectrum in Figure 1(d), which is replicated in Figure 4(a), contains a weak peak at 3707 cm-1 that is readily assigned to the stretching fundamental of the free (dangling) OH group, νOH(f), from the water molecule within the complex. This peak lies approximately midway between the symmetric and antisymmetric OH stretching frequencies for an isolated water molecule. However, the most intense IR peaks lie at 3266 and 3282 cm-1 and this doublet is assigned to the stretching vibration of the OH group involved in hydrogen bonding, νOH(b). The source of the splitting will be discussed in Section III-C. The large red-shift of the νOH(b) bands relative to νOH(f) is a consequence of the weakening of the O-H bond when it interacts with the iodide anion.18-20,24 The spectrum also contains an absorption feature at 3181 cm-1. Through a comparison with previous studies on NaCl(H2O)*n* and I-(H2O) complexes,10,23,24 we tentatively assign this band to the 2νHOH overtone transition, where νHOH is the H-O-H water bending vibration. The 2νHOH transition presumably gains intensity through Fermi resonance with the νOH(b) bright state. We note that similar vibrational resonances have been observed for other molecules embedded in helium nanodroplets, such as formic acid and acetylene.13,31

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**Figure 4.** (a) Experimental IR depletion spectrum for the CsI(H2O) complex embedded in helium nanodroplets. Simulated IR spectra generated using (a) LC-PBE, (b) CAM-B3LYP and (c) MP2 methods with the awCVTZ basis set are also shown.

Simulated spectra obtained by GVPT2 calculations using the LC-PBE, CAM-B3LYP and MP2 methods are plotted below the experimental spectrum in Figure 4. Reasonably good agreement is observed between the experimental spectrum and the simulations using the DFT functionals, with frequency differences of <50 cm-1 for the νOH(b) fundamental band and the 2νHOH overtone transition, and <75 cm-1 for the νOH(f) band. Our calculations confirm a modest gain in the 2νHOH band intensity through Fermi coupling with the νOH(b) vibration. All remaining features in the LC-PBE and CAM-B3LYP simulations derive from relatively weak (≤35 km mol‑1) combination bands.

The simulated spectrum in Figure 4(d), which was obtained using the MP2 method, shows less favorable agreement with the experimental IR spectrum [Figure 4(a)] than the LC-PBE and CAM-B3LYP simulations. Most notably, the νOH(b) fundamental lies >150 cm-1 below the experimental band and it has a lower frequency than the 2νHOH overtone transition in the MP2 simulation, which is the opposite of the band order observed in the experimental spectrum. We note that the νOH(b) bright state has the highest intensity in each spectrum in Figure 4, enabling the band order reversal to be easily discerned. The poor agreement indicates that the MP2 method is not able to accurately model the interaction between the Cs+I- ion pair and the water molecule. In particular, the excessive red-shift of the νOH(b) bands indicates that the MP2 method overestimates the strength of the IHB. This is reflected in the calculated value of 2.46 Å for the I­­--H separation, which is significantly smaller than the values calculated using the CCSD (2.53 Å), LC-PBE (2.54 Å) and CAM-B3LYP (2.56 Å) methods. This illustrates that the experimental spectrum provides valuable benchmarking data that can be used to critically assess the performance of quantum chemical calculations.

### C. Spectral doublet

Even though the agreement between experimental and calculated band positions in Figures 4(a)-(c) is reasonably good, there is an obvious discrepancy; only one band is expected in the νOH(b) region whereas two peaks separated by 16 cm-1 are actually observed in the experiment. Because a similar doublet has been observed for Ar- and N2-tagged I-(H2O), whilst a spectral quartet was observed for bare I-(H2O),18-24 it seems likely that a similar underlying mechanism is responsible for the doublet in CsI(H2O). Consequently, we consider whether (i) mode-dependent tunneling splitting arising from hydrogen atom exchange or (ii) anharmonic coupling to combination bands containing low frequency intermolecular modes might be the source.

To assist this process, we have calculated the transition state structure associated with hydrogen atom exchange in CsI(H2O). Images of the global minimum and transition state structures are shown in Figure 5(a). Intermediate stages of the hydrogen exchange reaction are illustrated in Figure S1 of the Supporting Information document. In Figure 5(a), the coordinate for hydrogen atom exchange is represented by an azimuthal angle, φ, which is measured about an axis passing through the O atom and the center of mass of the water molecule. Note that this axis changes direction relative to the Cs+-I- axis as the hydrogen exchange proceeds and we specify a value of φ = 0° for the transition state geometry. Figure 5(b) shows similar images for I-(H2O) for comparison and, in this case, the exchange coordinate involves an in-plane rotation about angle θ. The transition state energies relative to the global minima are calculated to be 1092 and 121 cm-1 [CCSD(T)/awCVTZ] for CsI(H2O) and I-(H2O), respectively, where the latter value is in reasonable agreement with those of 102 cm‑1 and ~200 cm-1 obtained from two recent studies27,24 that used an analytic MB-nrg functional developed for halide ion-water complexes.28

In Figures 5(c) and (d) we present plots of the 2D relaxed potential energy surfaces for CsI(H2O) and I-(H2O), obtained from DFT calculations with the LC-PBE functional. These plots represent the change in energy as the exchange coordinate and I-O distance are varied. It can be seen that the tunneling barrier between equivalent minima for CsI(H2O) is not only an order of magnitude higher than for I-(H2O), but it is also significantly wider in terms of the angle of rotation along the exchange coordinate. Consequently, tunneling splitting in the ground state of CsI(H2O) is anticipated to be small, most likely < 1 cm-1, where this upper limit has been approximated from a comparison of the computed barrier heights (2404, 475, 277 and 102 cm-1) and ground state tunneling splittings (0, 1, 6 and 27 cm-1) for F-(H2O), Cl-(H2O), Br-(H2O) and I-(H2O).27 Assuming that the tunneling splitting in the νOH(b) vibrationally excited state is also < 1 cm‑1, which seems highly probable, then transitions to these states would not be resolved in our experiments on account of the 4 cm-1 laser bandwidth. We therefore conclude that it is unlikely that hydrogen atom exchange can account for the doublet separation of 16 cm‑1 observed for CsI(H2O).

Next we consider whether the doublet can be explained by anharmonic coupling between νOH(b) and a combination band containing two quanta in νHOH and one quantum in a low frequency intermolecular mode, i.e., 2νHOH + νINTER. We note that two of the quartet peaks observed for I-(H2O) have been assigned to combination bands of this type.24 The anharmonic vibrational frequency calculations (GVPT2) that were compared with the experimental spectrum in Figure 4 already include contributions from 1-3 Darling-Dennison resonances, *i.e.*, coupling between zero-order states containing one and three vibrational quanta. Consequently, if one of the 2νHOH + νINTER dark states were to gain significant intensity via coupling to the νOH(b) bright state, then we would expect to see a doublet in the simulated spectra in Figures 4(b)-(c). No such doublet is observed. However, we note that the GVPT2 method is best suited to modelling vibrational modes with near harmonic character and therefore predictions for large-amplitude low-frequency modes should be treated with caution. Hence, it is possible that the GVPT2 calculations underestimate the coupling strength and therefore we shall restrict our comparison to the calculated frequencies rather than intensities.

We present selected results obtained from anharmonic frequency calculations at the LC-PBE/awCVTZ level of theory in Table 1. We specifically include the 2νHOH + νINTER bands in the table because two bands of this type were assigned to peaks in the spectral quartet feature in I-(H2O).24 The vibrational motion associated with each normal mode in CsI(H2O) is illustrated in Figure S2 in the Supporting Information document and the fundamental frequencies are given in Table S1.

Table 1. Calculated anharmonic frequencies for selected vibrational states in CsI(H2O) and the frequency shift (ΔνOH(b)) relative to the bound OH stretching vibration.

|  |  |  |
| --- | --- | --- |
| vibrational state | frequency / cm-1 | ΔνOH(b) / cm-1 |
| 2νHOH | 3132 | -136 |
| 2νHOH + νIOCs | 3260 | -8 |
| νOH(b) | 3268 | 0 |
| 2νHOH + νIO | 3328 | 60 |
| 2νHOH + νCsO | 3355 | 87 |
| 2νHOH + νIOH(f) | 3361 | 93 |
| 2νHOH + νIOH | 3615 | 347 |
| 2νHOH + νIOH(b) | 3731 | 463 |
| νOH(f) | 3778 | 510 |

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**Figure 5.** Images of the global minimum and transition state (TS) structures for (a) CsI(H2O) and (b) I-(H2O), illustrating the coordinates (φ, θ) for hydrogen atom exchange. 2D relaxed potential energy surfaces are shown for CsI(H2O) in (c) and I-(H2O) in (d), where the solid black contour lines represent energy increments of 500 cm-1.

We find that the predicted frequency for the 2νHOH + νIOCs combination band (3260 cm-1) lies within 10 cm-1 of the νOH(b) fundamental (see Table 1). All other 2νHOH + νINTER bands are predicted to lie at least 60 cm-1 to the blue of νOH(b). Calculations performed at the CAM-B3LYP/awCVTZ level of theory give similar results, including a calculated frequency of 3268 cm-1 for 2νHOH + νIOCs, thus providing further support for an accidental vibrational degeneracy. We therefore conclude that anharmonic coupling between the 2νHOH + νIOCs band and the νOH(b) bright state is most likely responsible for the doublet feature at 3266 and 3282 cm-1. The vibrational motion associated with each of the three contributing modes is illustrated in Figure 6. The low frequency mode, νIOCs, involves a translation of the water molecule towards the Cs+I- ion pair, which is accompanied by a Cs-I stretch. This motion resembles the insertion of a water molecule in between the two ions. Therefore, excitation of this mode can potentially induce partial ion pair separation.

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**Figure 6.** Vibrational motion associated with the νOH(b), νHOH and νIOCs normal modes for the global minimum structure of CsI(H2O).

### D. Further insight

We compare our experimental IR spectrum for the CsI(H2O) complex embedded in superfluid helium nanodroplets [Figure 4(a)] with results obtained from an FTIR study of CsI(H2O) in a solid Ar matrix at 16 K.16 In the FTIR study, three bands were observed and those lying at 3164 and 3280 cm-1 were attributed to the two OH stretching modes of a nonplanar structure with a pyramidal geometry. We reassign these bands to the 2νHOH overtone and νOH(b) fundamental transitions of the planar structure that is shown in Figure 2. The difference in peak frequencies between the two studies is attributed to vibrational perturbation induced by the solid Ar matrix, which is much stronger than that imposed by superfluid helium. The presence of only one band at 3280 cm-1, rather than a doublet, is also attributed to the Ar matrix environment. This assertion is supported by evidence from an experimental study on Ar-tagged I-(H2O), in which one of the doublet peaks showed a decrease in intensity when additional Ar atoms were attached, until only a single peak was observed for 8 Ar tags.21 The matrix environment has also been shown to affect the positions and relative intensities of resonance multiplet peaks for propene embedded in helium nanodroplets and solid *para*-hydrogen.41

The influence of the Cs+ counter ion on the interaction between I- and H2O can be deduced by comparing our experimental IR spectrum for CsI(H2O) with one measured previously for I-(H2O).24 We find that upon binding of the Cs+, the νOH(b) multiplet band is red-shifted by ~142 cm-1, which brings it closer to the 2*ν*HOH dark state to which it is strongly coupled. The red-shift indicates that the Cs+ has a stabilizing effect on the anion-water interaction. This observation is supported by CCSD/awCVTZ calculations, which show a decrease in the IHB length from 2.64 Å to 2.53 Å following the attachment of Cs+ to I-(H2O).

A spectral doublet lying near 3300 cm‑1 has been observed in this work for CsI(H2O)2, as well as for CsI(H2O), as shown in Figure 1(c). As a result, it may be tempting to assign the CsI(H2O)2 peaks at 3315 and 3327 cm-1 to a 1-3 vibrational resonance similar to that identified for CsI(H2O). However, other explanations are possible. First, the peak pair could be attributed to the symmetric and antisymmetric stretching vibrations of the bound OH groups, arising from two water molecules symmetrically arranged about the iodide ion and each linked to it via a single IHB. Another possibility is that more than one structure contributes to the spectrum, since several structures have been predicted for the CsI(H2O)2 complex.17,40 The favored assignment will be addressed in a future publication.

## IV. CONCLUSIONS

An IR spectrum has been recorded for a complex consisting of a single water molecule attached to a Cs+I- ion pair, which is embedded inside superfluid helium nanodroplets. This has been achieved through optimization of the experimental conditions and subtraction of the residual signal from larger complexes. A comparison with anharmonic vibrational frequency calculations demonstrates that our experimental spectrum for CsI(H2O) can be used to benchmark the performance of various theoretical treatments. For example, the widely used MP2 method does a surprisingly poor job at describing the ionic hydrogen bond in this system.

A particularly striking feature in our spectrum is a doublet observed for the bound OH stretching vibration, when only one peak is expected. Quantum chemical calculations show that this doublet is not readily explained by a hydrogen exchange reaction and we therefore assign it to anharmonic coupling between νOH(b) and the 2νHOH + νIOCs combination band, where νIOCs is an intermolecular mode that can promote ion pair separation.

Finally, a comparison between the measured IR spectrum for CsI(H2O) with one previously measured for I-(H2O) has revealed that the Cs+ counter ion stabilizes the IHB interaction between I- and H2O. This is confirmed by our quantum chemical calculations, which indicate a shortening of the equilibrium IHB length when Cs+ and I- form an ion pair in the presence of a water molecule.

ASSOCIATED CONTENT

**Supporting Information**.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

Illustration showing the intermediate stages of the hydrogen atom exchange reaction in CsI(H2O). Vibrational motion and frequencies for each of the normal modes in CsI(H2O). Full bibliographic record for Ref. 33. (PDF)

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Notes

The authors declare no competing financial interest.

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