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LETTERS

Vibrational Spectroscopy of the $Cl^-(H_2O)_n$ Anionic Clusters, $n = 1-5$

Jong-Ho Choi,[†] Keith T. Kuwata, Yi-Bin Cao, and Mitchio Okumura*

Arthur Amos Noyes Laboratory of Chemical Physics, Mail Code 127-72, California Institute of Technology, Pasadena, California 91125

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The hydrogen-bonded and free OH stretch modes of $Cl^-(H_2O)_n$ ($n = 1-5$) have been observed by vibrational predissociation spectroscopy in the 2.6−3.2 μm region. Besides demonstrating that all clusters form strong ionic hydrogen bonds, the spectra provide clear evidence of water−water hydrogen-bonding networks in $n =$ 4 and $n = 5$, with the broad spectrum of $n = 5$ resembling that of large neutral water clusters. No water−water hydrogen bonding is seen in $n = 2$ and $n = 3$, but these clusters appear to be solvated asymmetrically. While the data suggest that Cl^- ion is solvated on the surface of water clusters, there are discrepancies between the observed spectra and ab initio predictions. This disagreement may stem from either zero-point motion or high cluster temperature, which tend to disrupt hydrogen bonding among the waters.

I. Introduction

The structures that water molecules form about the chloride ion Cl^- in gas-phase clusters reflect the competition between solvation of the ion vs hydrogen bonding among the waters. If hydrogen bonding to the ion dominates, the ion will move to the interior of a solvation shell. If hydrogen bonding among the waters dominates, Cl^- ion will move to the surface of a neutral water cluster. Molecular dynamics simulations[1−7] and ab initio calculations[8,9,10a,11c] both predict that surface states dominate in $Cl^-(H_2O)_n$ even at large n. However, the effects of temperature and zero-point energy leave open the possibility of interior structures.[3d,6,8b,10b]

Recent systematic ab initio studies of $Cl^-(H_2O)_n$ clusters have been performed at the SCF level by Jortner and co-workers[8] and Okuno.[9] Xantheas[10a] has performed the most definitive study to date, reporting MP2 geometries and vibrational frequencies for $n = 1-4$.

All previous ab initio calculations[8b,9,10a,11c,12] on $Cl^-(H_2O)$ suggest that Cl^- forms a nearly linear hydrogen bond with H_2O (Figure 1, **Ia**). However, the ion−dipole interaction alone would lead to a bridged structure (Figure 1, **Ib**) in which the Cl^- is equally shared by both H atoms. When a second H_2O is added, the key issue is its relationship to the first H_2O. SCF calculations by Jortner and co-workers[8b] indicate that the two waters may bind either to the same side (Figure 1, **IIa**) or to nearly opposite sides (resembling Figure 1, **IIb**). However, the MP2 calculations of Xantheas[10a] indicate that only **IIa** corresponds to a minimum on the global potential. While the minimum is expected to have a water−water hydrogen bond,[8b,9,10a,11c] large amplitude motions may greatly weaken this bond.[3d,4g,6]

Both SCF[8,9] and MP2[10a] calculations predict that all $n = 3$ isomers are surface structures. The ground state is C_3 pyramidal with all waters equivalent. Each H_2O donates one OH to the base of the pyramid, and the other OH to Cl^-. In the ring isomer,[9,10a] two waters bind to the Cl^- (each has one free OH bond), and the third forms a second solvation shell, binding to the first two waters.

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* Corresponding author. E-mail: mo@cco.caltech.edu. FAX: (626) 568-8824.

[†] Present address: 313 Department of Chemistry, College of Science, Korea University, Anam-1-dong, Seougbuk-ku, Seoul, Korea 136-701.

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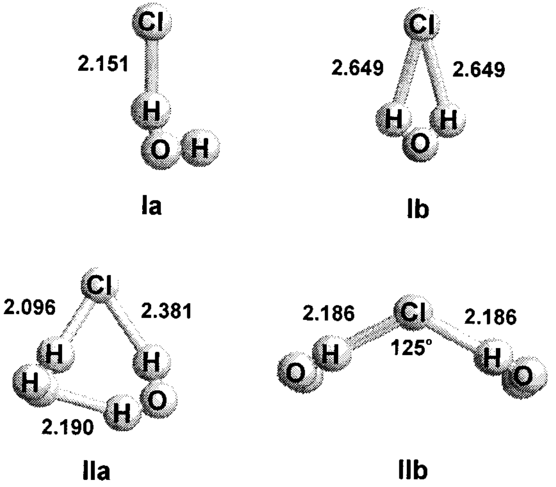

Figure 1. Ab initio stationary points predicted at the MP2/6-311++G** level for $Cl^-(H_2O)$ and $Cl^-(H_2O)_2$. Hydrogen bond lengths are given in Å. **Ia** is the C_s minimum. **Ib** is the C_{2v} transition state with $\Delta E_0 \sim 1.2$ kcal/mol. **IIa** is the C_1 minimum with three hydrogen bonds. **IIb** is a C_s stationary point similar to the interior state predicted by Jortner and co-workers.[8b] It is a transition state with $\Delta E_0 \sim 0.6$ kcal/mol. The H atoms obscured in **IIb** are pointing into the plane of the page.

The two $n = 4$ MP2 isomers identified by Xantheas[10a] are surface structures. The ground state is C_4 pyramidal with a structure analogous to the C_3 pyramidal isomer. In the "3+1" isomer, three waters form a pyramid and the fourth H_2O forms a bridge between the base of the pyramid and Cl^-. Jortner and co-workers[8] also find an interior isomer at the SCF level with a ring of three waters on one side and an ion-bound H_2O on the other side.

Experiments have yet to provide detailed cluster structures as a function of n. Mass spectrometry[11] reveals no breaks in the stepwise hydration enthalpies of $Cl^-(H_2O)_n$ ($n \leq 4$) that may indicate the closing of solvation shells. Cheshnovsky, Jortner, and co-workers[8,13] have tried to differentiate surface and interior solvation states by assigning experimental ionization potentials (IP) with ab initio predictions. However, the small differences in the ab initio IPs of surface and interior isomers make assignments ambiguous. On the basis of a decrease in the reactivity of $Cl^-(H_2O)_n$ at $n = 6$, Viggiano and co-workers[14] suggest a transition to an interior state at $n = 6$, but this shell closing is not predicted by either simulations or ab initio calculations.

Vibrational spectroscopy is a sensitive, size-specific probe of hydrogen bonding in both ionic[15-17] and neutral[18] solvated clusters. For example, the predissociation spectrum of $I^-(H_2O)$ has established that the structure contains one strong ionic hydrogen bond.[15a,16a] Here we report the infrared spectra of $Cl^-(H_2O)_n$ ($n = 1-5$). We consider cluster structures for $n = 1-4$ with the aid of Xantheas' calculations.[10a] We also report new MP2 predictions of $n = 2$ transition states and repeat MP2 calculations of previously identified $n = 1$ and $n = 2$ stationary points to provide a consistent set of geometries and vibrational frequencies.

II. Experiment and Calculations

Details have been given elsewhere,[15] and only a brief account is presented here. A mixture of H_2O and CCl_4 vapor seeded in CH_4 at a stagnation pressure of ~1500 Torr was pulsed into vacuum through a 1 mm nozzle. $Cl^-(H_2O)_n$ and $Cl^-(H_2O)_n(CCl_4)_m$ clusters were formed in the expansion by crossing the jet with a continuous 750 eV electron beam. The plasma was skimmed and entered a TOF mass spectrometer, where the ions were pulse-extracted and mass-analyzed. Parent ions, selected by a mass gate, were excited by the 3−5 mJ IR beam from a Nd:YAG-pumped $LiNbO_3$ OPO. Photofragment ions were separated from the parent ions using a reflectron and then detected by a MCP detector. Spectra were obtained by measuring ion signal as a function of the laser frequency, subtracting the background due to dissociation of metastable parent ions, and normalizing with the laser fluence.

Optimized geometries, harmonic frequencies, and absolute IR intensities of $Cl^-(H_2O)$ and $Cl^-(H_2O)_2$ stationary points were calculated at the MP2/6-311++G** level using the Gaussian 92 system of programs.[19] The calculations neglected the correlation of core electrons.

III. Results and Discussion

The only photofragment channel observed upon IR excitation of $Cl^-(H_2O)_n$ was loss of a single water molecule. Excitation of $Cl^-(H_2O)(CCl_4)$ gave loss of CCl_4 only. The $Cl^-(H_2O)_n$ mass spectrum peaked at $n = 0$, indicating a hot cluster distribution.

All $Cl^-(H_2O)_n$ clusters have strong infrared bands in the 3200−3500 cm^{-1} region (Figure 2) which dominate the spectra. We assign these bands to OH stretches of ionic hydrogen bonds. A single band in $n = 1$ splits into an asymmetric doublet in $n = 2$, with the blue band being more intense. The higher frequency band blue-shifts 30−40 cm^{-1} with the addition of each water, indicating a weakening of the ionic hydrogen bonds. Adding more waters also makes the blue band progressively more intense than the red band. By $n = 4$, only one distinct band persists.

The $n = 4$ and $n = 5$ spectra have an additional band in the 3500−3650 cm^{-1} region, which we assign to the OH stretch of water−water hydrogen bonds. This band red-shifts by ~40 cm^{-1} from $n = 4$ to $n = 5$. Other bands that appear further to the red are also likely due to cooperative hydrogen bonding among the waters, but we cannot assign them definitively. The spectra of $Cl^-(H_2O)(CCl_4)$ and $Cl^-(H_2O)_n$ ($n = 2-5$) all possess a weak band appearing at ~3700 cm^{-1}, which we assign to the free OH stretch.

A. $n = 1$. Our spectrum (Figure 2a) demonstrates that H_2O forms one strong hydrogen bond to Cl^- (Figure 1, **Ia**). This agrees with all previous ab initio results (Figure 3a).[8b,9,10a,11c,12]

The intense band at 3285 cm^{-1} is clear evidence of a strong, nearly linear ionic hydrogen bond. The observed frequency agrees well with the prediction (3266 cm^{-1}) for the ionic OH stretch of **Ia**. The first bending overtone of H_2O at 3156 cm^{-1} is close to the free H_2O monomer frequency[20] of 3151 cm^{-1}. The H_2O bending mode has significant oscillator strength, and the overtone may gain further intensity through a Fermi resonance interaction with the 3285 cm^{-1} band. We tentatively assign a weak feature at ~3440 cm^{-1} to a combination of the OH bonded stretch and the Cl^-−H intermolecular stretch. The frequency of the intermolecular stretch, ~155 cm^{-1}, is somewhat less than the ab initio harmonic value of 184 cm^{-1}.

We observe the free OH stretch at 3698 cm^{-1} by loss of CCl_4, which we assume only weakly perturbs $Cl^-(H_2O)$. We do not see this band for $Cl^-(H_2O)$ itself. This may be due to the predissociation mechanism. Since the complex is bound by ~15 kcal/mol,[11] it dissociates by a stepwise-resonant two-photon process. A large anharmonicity in the free OH stretch shifts the second step out of resonance by ~200 cm^{-1} and could greatly reduce the Cl^- photofragment yield. In contrast, one-photon excitation of the broad ionic OH stretch band may couple

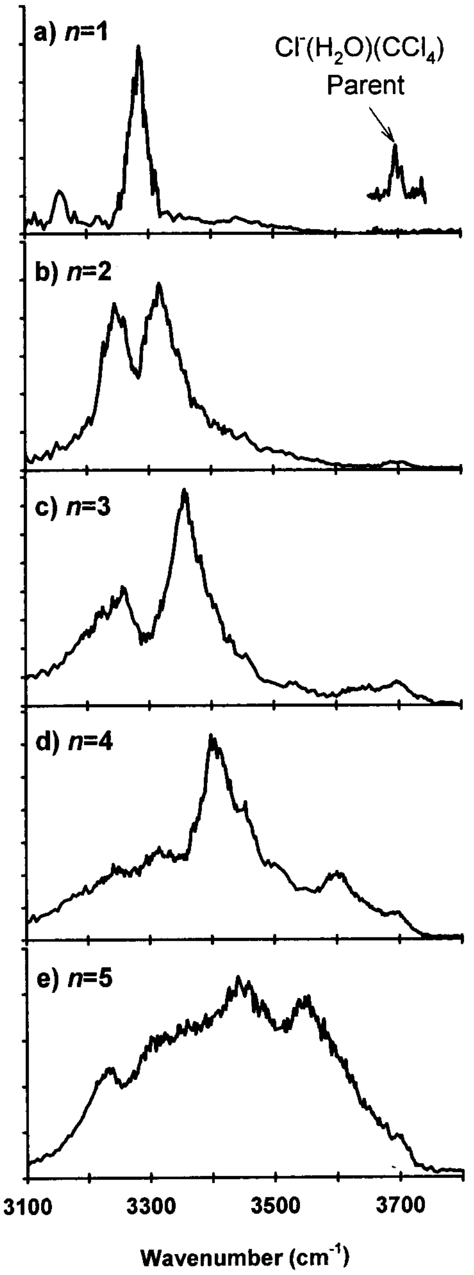

Figure 2. Infrared spectra of $Cl^-(H_2O)_n$ recorded by vibrational predissociation with loss of H_2O. The $n = 1$ inset shows loss of CCl_4 from the $Cl^-(H_2O)(CCl_4)$ parent. The intensity of the inset peak is arbitrary.

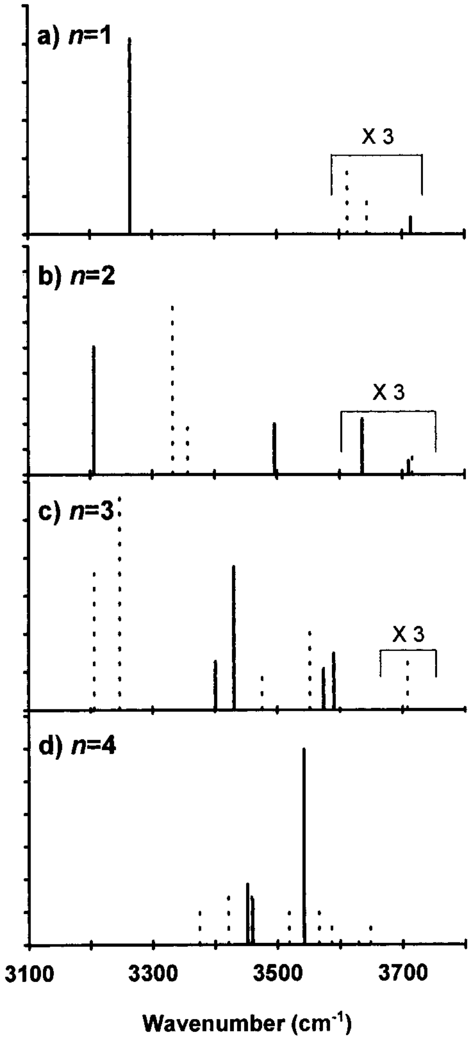

Figure 3. Ab initio vibrational stick spectra of $Cl^-(H_2O)_n$ stationary points. Results for $n = 1$ and $n = 2$ are from this work; results for $n = 3$ and $n = 4$ are adapted from the work of Xantheas.[10a] The frequencies are scaled by the average of the experimental stretches of H_2O, and all infrared intensities are on the same scale for a given cluster size. In each spectrum, the solid lines correspond to the global minimum; the dotted lines, to the less stable minimum or transition state. (a) C_s minimum and C_{2v} transition state. (b) C_1 minimum and C_s transition state. (c) C_3 pyramidal global minimum and C_s ring minimum with $\Delta E_e = 2.6$ kcal/mol. (d) C_4 pyramidal global minimum and C_1 "3 + 1" minimum with $\Delta E_e = 2.1$ kcal/mol.

to a quasi-continuum, allowing for facile dissociation with a second photon. A similar mechanism may account for intensity anomalies in the spectrum of $NO^+(H_2O)$.[15c]

We find no spectroscopic evidence for the C_{2v} isomer **Ib** (Figure 1), which is predicted[10a,12b] to be a transition state with two highly bent hydrogen bonds. While the barrier to H atom exchange ΔE_0 is only ~1 kcal/mol, both OH stretches of **Ib** are red-shifted by only 60−90 cm^{-1} (Figure 3a). However, we observe no bands in the 3500−3650 cm^{-1} region.

B. $n = 2$. The spectrum (Figure 2b) demonstrates that Cl^- ion is solvated by two nearly equivalent and independent waters. The dominant doublet with maxima at 3245 and 3317 cm^{-1} provides clear evidence of two strong ionic hydrogen bonds.[21] The absence of peaks from 3500 to 3650 cm^{-1} indicates that the waters do not hydrogen bond to each other.

We report two new MP2 stationary points. **IIb** (Figure 1) is a nonplanar C_s transition state for the exchange of the two waters of **IIa**, with a barrier height ΔE_0 of ~0.6 kcal/mol. Rotation of the waters into the H−Cl−H plane gives rise to a W-shaped C_{2v} second-order transition state (not shown) with ΔE_0 only ~0.02 kcal/mol above **IIb**. The gradients of both structures were minimized to $\leq 1 \times 10^{-8}$ hartree/a_0.

Our spectrum is not consistent with the predictions for **IIa**.[10a] The spectrum of the ab initio minimum (Figure 3b) contains four distinct bands whose intensities decrease monotonically with increasing frequency. The experimental spectrum contains only three bands, and the two red-shifted bands are of comparable intensity. The structure probed by our experiment cannot be the asymmetric isomer **IIa** (Figure 1).

For **IIb**, although the absence of a water-bound OH stretch and the small splitting in the ion-bound OH stretches are consistent with the experimental data, the red band (the antisymmetric linear combination) is nearly four times more intense than the blue band (Figure 3b). The structure probed by our experiment is considerably more bent than isomer **IIb**. Although we could not find an ab initio minimum lacking water−water hydrogen bonding, our spectrum is consistent with a very bent structure with two nearly equivalent ionic hydrogen bonds and no water−water hydrogen bonds.

The discrepancy between experiment and theory may be due to large amplitude motions. The small differences in the energies of the ab initio stationary points reveal a very flat potential. Either zero-point motion or high cluster temperature could make the complex less rigid. Using classical simulations, Asada et al.[6] find that when $Cl^-(H_2O)_2$ is warmed to ∼100 K, the cluster undergoes a phase transition that breaks the water−water hydrogen bond. Quantum simulations by Dang and co-workers[3d] indicate that the H atoms in $Cl^-(H_2O)_n$ are highly delocalized for $T \leq 100$ K, weakening the hydrogen bonding between the waters. A more dynamical simulation of the spectrum with explicit treatment of the large-amplitude motions appears to be necessary.

Our results suggest that $Cl^-(H_2O)_2$ is asymmetrically solvated in the absence of water−water hydrogen bonds. This has also been observed for $I^-(CH_3CN)_2$ by Johnson and co-workers.[16b] The stability of this geometry may be due not only to residual water−water interactions but also to a cooperative effect in which the binding of one water to the polarizable Cl^- ion induces a dipole that favors and is enhanced by the binding of a second water to the same side of the ion. The role of ion polarizability in asymmetric solvation has been simulated for $Cl^-(H_2O)_3$ by Sung and Jordan[2a] and calculated for $Ca^{2+}(H_2O)_2$ by Bauschlicher et al.[22]

C. *n* = 3−5. The spectra of larger clusters (Figure 2c−e) differ from the $n = 2$ spectrum in two ways. First, the intensity of the water-bound OH stretch increases with *n*. The $n = 3$ spectrum may contain peaks at ∼3530 and ∼3630 cm^{-1} barely discernible above the background. For $n = 4$, we observe a peak at 3590 cm^{-1} with an intensity ∼20% of that of the ion-bound OH stretch. In $n = 5$, this band red-shifts to 3548 cm^{-1} and is almost as intense as the Cl^--bound OH stretch. Second, all three spectra contain an underlying broad absorption. At $n = 4$, the red band of the ionic OH stretch doublet merges into this continuum. A number of peaks appear besides the main Cl^--bound OH stretch band. By $n = 5$, the spectrum is dominated by this broad absorption.

The increase in the red-shift and intensity of the water-bound OH stretch is consistent with the trends predicted by Xantheas[10a] for the ground-state isomers (Figure 3c,d). However, no $n = 3$ or $n = 4$ ab initio isomer by itself fully accounts for the spectra we observe. As a result, we cannot assign explicit structures for the $n = 3$ and $n = 4$ clusters.

For $n = 3$, a mixture of the pyramidal and ring isomers (Figure 3c) may account for the strong ion-bound OH stretches at 3257 and 3357 cm^{-1} (Figure 2c). However, any water-bound OH stretches are weak at best, while Xantheas[10a] predicts that for either isomer this band has an intensity ≥40% of that of the ion-bound OH stretch. It is possible that in $Cl^-(H_2O)_3$ three equivalent waters form hydrogen bonds to Cl^- but not to each other. The splitting of the ionic OH stretches would then be due to modes of A and E symmetry of a C_{3v} complex. Observation of the totally symmetric stretching mode means that $Cl^-(H_2O)_3$ is not internally solvated in a planar complex. Our spectrum is consistent with a pyramidal-like structure as predicted by ab initio theory[8,9,10a] but without water−water hydrogen bonding. Quantum or temperature effects in $n = 3$ may account for the same discrepancy between theory and experiment seen for $n = 2$.

Similarly, theory seems to overestimate the extent of water−water association for $n = 4$ (Figure 3d). The pyramidal isomer, with its ring of four waters, has a water-bound OH stretch predicted by Xantheas[10a] to be at ∼3540 cm^{-1} which is more intense than the ion-bound OH stretch. However, the water-bound OH stretch we see (3590 cm^{-1}) is much weaker than the ionic OH stretch (3408 cm^{-1}) (Figure 2d). The smaller red-shift seen for the water-bound OH stretch may be due to a smaller ring of waters, as in the 3 + 1 isomer. This isomer has a series of peaks[10a] from 3375 to 3650 cm^{-1} which is consistent with the broad absorption underlying our spectrum. However, the 3 + 1 isomer cannot account for the free OH stretch at 3694 cm^{-1}. Our spectrum suggests a more open structure with at least one free OH bond. We cannot rule out a structure resembling the SCF interior state identified by Jortner and co-workers,[8] but MP2 theory[10a] indicates that the fourth H_2O is attracted to the remaining waters. The appearance of several weak peaks may indicate the presence of more than one isomer.

The $n = 5$ spectrum (Figure 2e) differs considerably from the others. It is dominated by a broad absorption from 3100 to 3750 cm^{-1} and has several distinct peaks. The spectrum resembles that of large neutral water clusters.[23,24] Experiments now in progress suggest that the spectra reported here were taken at high cluster temperatures. These conditions would produce a mixture of low-lying isomers that would broaden the spectrum as observed here.

Despite the breadth of the spectrum and the lack of ab initio calculations, we can assign the major features. The free OH stretch is clearly present at 3696 cm^{-1} and implies that not all OH bonds participate in hydrogen bonding. We assign the peak at 3441 cm^{-1} to the ion-bound OH stretch, on the basis of the blue-shift of this band with increasing *n*. We assign the peak at 3548 cm^{-1} to the water-bound OH stretch, assuming the red shift of this band with increasing *n*.

Of the remaining bands, the peak at 3233 cm^{-1} is most notable. Although the most red-shifted band of ionic cluster spectra is typically an ion-bound OH stretch, the 3233 cm^{-1} band does not follow the trend we see for smaller clusters. It is even more red-shifted than the ion-bound OH stretch in $n = 1$. Such a large red-shift could be caused by cooperative hydrogen bonding in cyclic $(H_2O)_n$ structures. Vernon et al.[23] and Huisken[24] have observed a similar band in the spectra of large neutral water clusters. Xantheas and Dunning[10c] have predicted that the water-bound OH stretch can red-shift by as much as ∼500 cm^{-1} in $(H_2O)_4$. Therefore, we assign the peak at 3233 cm^{-1} to the ring OH stretch of cyclic water structures within the cluster. From the red-shift we infer that the $n = 5$ cluster contains rings of at least four waters.

IV. Conclusion

The structures we infer from our spectra have less hydrogen bonding than predicted by theory. These discrepancies are most likely due to either to zero-point effects or high cluster temperature, which would favor large-amplitude motions and lead to the breaking of water−water hydrogen bonds. As a result, we would not observe the ab initio ground-state isomers, but rather a mixture of low-lying isomers, particularly for $n = 5$. Because the clusters are hot, we cannot tell if zero-point motion alone would cause the breaking of hydrogen bonds among the waters.

Despite the ambiguity from high temperature and multiple isomers, the current data provide strong evidence that Cl^- is surface-solvated for larger clusters. The $n = 4$ and 5 spectra reveal water−water hydrogen-bonding networks, and the $n = 5$ spectrum itself resembles that of large neutral water clusters. It is noteworthy that we observe surface solvation even at high temperature, which favors interior solvation states in molecular dynamics simulations.[6a] For $n = 2$ and 3 we observe that Cl^- ion is asymmetrically solvated without hydrogen bonding between the waters. This disagreement with the ground state ab initio structures may be due to temperature or zero-point energy effects that lead to breaking of the water–water hydrogen bonds. Further experiments with colder $Cl^-(H_2O)_n$ are ongoing.

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(21) Both harmonic and anharmonic terms should split the infrared bands of the ionic hydrogen bonds. Alternatively, one of the red-shifted bands may correspond to the bending overtone of one of the H_2O's. However, since the $n = 1$ bending overtone is only ~10% of the intensity of the $n = 1$ bonded OH stretch fundamental, it is unlikely that the $n = 2$ bending overtone could be of comparable intensity to the bonded OH stretch. Also, since the H_2O bending fundamental is predicted to blue-shift only ~20 cm^{-1} in going from $n = 1$ to $n = 2$, it is unlikely that the bending overtone will shift from 3156 to 3245 cm^{-1}.

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