Site-specific vibrational spectral signatures of water molecules in the magic $H_3O^+(H_2O)_{20}$ and $Cs^+(H_2O)_{20}$ clusters

Joseph A. Fournier^a, Conrad T. Wolke^a, Christopher J. Johnson^{a,1}, Mark A. Johnson^{a,2}, Nadja Heine^b, Sandy Gewinner^b, Wieland Schöllkopf^b, Tim K. Esser^c, Matias R. Fagiani^{b,c}, Harald Knorke^{b,c}, and Knut R. Asmis^{c,2}

^aSterling Chemistry Laboratory, Department of Chemistry, Yale University, New Haven, CT 06520; ^bFritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany; and ^cWilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, D-04103 Leipzig, Germany

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Theoretical models of proton hydration with tens of water molecules indicate that the excess proton is embedded on the surface of clathrate-like cage structures with one or two water molecules in the interior. The evidence for these structures has been indirect, however, because the experimental spectra in the critical H-bonding region of the OH stretching vibrations have been too diffuse to provide band patterns that distinguish between candidate structures predicted theoretically. Here we exploit the slow cooling afforded by cryogenic ion trapping, along with isotopic substitution, to quench water clusters attached to the H_3O^+ and Cs^+ ions into structures that yield well-resolved vibrational bands over the entire 215- to 3,800-cm⁻¹ range. The magic $H_3O^+(H_2O)_{20}$ cluster yields particularly clear spectral signatures that can, with the aid of ab initio predictions, be traced to specific classes of network sites in the predicted pentagonal dodecahedron H-bonded cage with the hydronium ion residing on the surface.

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ver the last decade, the cooperative mechanics underlying the microhydration of simple ions has undergone a renaissance due to rapid advances in experimental and theoretical methods. On the experimental side, it is routine to capture and study size-selected species cooled to cryogenic temperatures (1-5), and theoretical techniques are now capable of handling tens of atoms with all-electron, "supermolecule" approaches, where complex hydration networks are treated in the ansatz of polyatomic molecular physics (6). A dramatic example of the new insights afforded by this combined approach is the recent elucidation of the spectral signature associated with the hydronium ion when it is accommodated on the surface of a pentagonal dodecahedral cage formed by the "magic" $H_3O^+(H_2O)_{20}$ cluster (7). The theoretical structure proposed earlier (8) (denoted I) is illustrated in Fig. 1, and the recently reported D₂ predissociation spectrum of the cryogenically cooled, D_2 tagged $H_3O^+(H_2O)_{20}$ cluster is compared with that observed for the $H_3O^+(H_2O)_3$ Eigen cation (9, 10) in Fig. 1 A and B, respectively. The key bands derived from the OH stretching motions of the surface-embedded hydronium (denoted $\nu^a_{H_3O^+}$) were assigned (7) to the broad features in the experimental spectrum about 500 cm⁻¹ below the corresponding bands in the free Eigen cation. The intramolecular HOH bending and OH stretching modes of the surface water molecules are not strongly shifted by introduction of the ion, however, where the latter appear as a broad envelope spanning the 3,000- to 3,700-cm⁻¹ range typical of liquid water. An interesting aspect of the D2 tagged spectrum obtained with cryogenic cooling (as opposed to that reported on the same ion generated under the more rapid quenching conditions at play in a supersonic jet ion source) (8, 11) is that distinct features begin to emerge above the continuous background absorption in the OH stretching region above 3,400 cm⁻¹

This observation of sharp OH stretching structure in a moderately large water cluster is significant in the context of the ongoing, often controversial discussion regarding the origin of the diffuse OH stretching spectrum displayed by neat liquid water (12-14), as well as by dilute acids (15, 16). Indeed, over the last decade, intensive experimental (17, 18) and theoretical (19-21) efforts have addressed the underlying mechanics of this broadening, resulting in significant differences of opinion regarding the role of excitonic band structure, excited state dynamics, and Fermi resonances (22–25). Cluster behavior is highly relevant in this discussion as they allow one to isolate microscopic assemblies with well-defined H-bonding configurations and thus directly address the spectral signatures associated with the various network morphologies. In this paper, we contrast the behavior of the n = 20 hydrates of the H₃O⁺ and Cs⁺ ions, both of which are preferentially generated in the $M^+(H_2O)_n$ cluster ion distributions (i.e., are magic numbers) and are thought to be based on a pentagonal dodecahedron motif (12 interconnected H-bonded pentagons). An important difference between these ions is that H_3O^+ is predicted to reside on the surface of the cage (6, 8, 26), whereas Cs⁺ is sequestered in its interior (27, 28). We follow the evolution of the bands in the perdeuterated isotopologues, $Cs^+(D_2O)_{20}$ and $D_3O^+(D_2O)_{20}$, and find strong support for the earlier assignment of the spectral signature of the embedded H₃O⁺ ion. Of most importance here, however, is the observation that the perdeuterated isotopologues yield

Significance

Understanding the mechanics underlying the diffuse OH stretching spectrum of water is a grand challenge for contemporary physical chemistry. Water clusters play an increasingly important role in this endeavor, as they allow one to freeze and isolate the spectral behavior of relatively large assemblies with well-defined network morphologies. We exploit recently developed, hybrid instruments that integrate laser spectroscopy with cryogenic ion trap mass spectrometry to capture the H_3O^+ and Cs^+ ions in cage structures formed by 20 water molecules. Their infrared spectra reveal a pattern of distinct transitions that is unprecedented for water networks in this size range. Theoretical analysis of these patterns then reveals the intramolecular distortions associated with water molecules at various sites in the 3D cages.

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¹Present address: Department of Chemistry, Stony Brook University, Stony Brook, NY 11794. ²To whom correspondence may be addressed. Email: mark.johnson@yale.edu or knut. asmis@uni-leipzig.de.

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Fig. 1. Vibrational predissociation spectra of (A) $H_3O^+(H_2O)_{20}$ and (B) the $H_3O^+(H_2O)_3$ Eigen cation. Bands attributed (7) to the antisymmetric H_3O^+ stretches, $\nu_{H_3O^+}^a$, and H_3O^+ umbrella bending mode, $\nu_{H_3O^+}^{umb}$ of the embedded hydronium ion are indicated by the red lines. The antisymmetric stretches of remote ADD type waters (circled in turquoise in A) were assigned (6, 7) to band A, whereas the free OH stretches from the AAD waters are circled in orange. The symmetric (s) and antisymmetric (as) OH stretches of the water molecules solvating the Eigen cation (circled in blue) are expected (7) to red shift into the broad continuum near position B in $H_3O^+(H_2O)_{20}$. The $H_3O^+(H_2O)_{20}$ structure, denoted I, was the lowest energy structure identified in a search using the B3LYP method (6, 8).

significantly better resolved fine structure in the lower energy OD stretching manifold than was evident in the $H_3O^+(H_2O)_{20}$ spectrum. Comparison of this pattern with harmonic predictions yields compelling assignments of the strongest transitions to four classes of water molecules, which, in turn, allows us to refine the $H_3O^+(H_2O)_{20}$ structure I suggested earlier. Special aspects of the n = 20 structures are further investigated in a study of the low frequency (<1,000 cm⁻¹) librational motions over the size range n = 17-27, where significantly sharper structure is observed in the n = 20 spectrum relative to those displayed by nearby cluster sizes. The origin of these bands is considered in the context of harmonic spectra predicted for the geometries identified through assignment of the OH/OD stretching band pattern. Features associated with frustrated rotations of the trapped H_3O^+ moiety, as well as of water molecules in four-coordinated network sites, are thus identified for the first time.

Results and Discussion

Comparison of the D₂ Tagged H₃O⁺(H₂O)₂₀ and Cs⁺(H₂O)₂₀ Spectra and Evolution of the Bands in the Perdeuterated Isotopologues. Fig. 2 presents the evolution of the D₂ tagged H₃O⁺(H₂O)₂₀ and Cs⁺(H₂O)₂₀ vibrational predissociation spectra on deuteration. The bands assigned to the antisymmetric hydronium OH stretch ($\nu_{H_3O^+}^a$) near 2,000 cm⁻¹ (Fig. 24, highlighted in red) are indeed observed to shift in the heavy isotopologue (Fig. 2*B*) to a location close to 1,600 cm⁻¹, as expected for the change in reduced mass. Moreover, the corresponding features are absent in the spectra of Cs⁺(D₂O)₂₀ and Cs⁺(H₂O)₂₀ displayed in Fig. 2 *C* and *D*, respectively. The OD stretching regions of both hydrates display very strong, well-resolved features just below the sharp free OD fundamentals (denoted AAD). In fact, the OD stretching spectrum of Cs⁺(D₂O)₂₀ is striking in that sharp features appear throughout the entire H-bonded OD stretching range, whereas the lower energy part of the corresponding feature in the $D_3O^+(D_2O)_{20}$ spectrum is more congested.

The appearance of isolated and intense bands in the high energy OH/OD stretching regions of both the Cs⁺ and hydronium cluster spectra is of great interest, as such simple patterns likely signal rather symmetrical structures, i.e., those in which many water molecules reside in similar network sites. One of these bands (A near $3,580 \text{ cm}^{-1}$) was evident in the spectra reported a decade ago (8) and was assigned to the water molecules circled in turquoise in Fig. 1A, which adopt ADD network sites (A denotes an H-bond acceptor and D a donor) in structure I. Note that these sites are near the bottom of the cage, rather removed from the H_3O^+ charge center at the top. More recently, Xantheas revisited the theoretical structures expected for the $H_3O^+(H_2O)_{20}$ system in a systematic survey of more than 50,000 locally stable structures (6). He identified the seven lowest energy arrangements, all of which occur with H₃O⁺ ions on the surface of pentagonal dodecahedra with subtle variations of the detailed donor/ acceptor configurations of the water molecules that make up each interconnected pentagonal H-bonded ring. The calculated patterns of harmonic OH stretching fundamentals were found to be sensitive to these local variations, and indeed based on this dependence, he concluded that the structure displayed in Fig. 3 (denoted II) was more consistent with the observed spectrum. Specifically, this arrangement does not display the strong (harmonic) low energy OH stretching transition near 2,800 cm⁻¹ that is predicted for the originally proposed structure I, but is missing in the experimental spectrum (Figs. S1 and S2). Interestingly, the key change between these structures involves a concerted flipping motion of three AADD type sites (including the central H₂O) along with a remote ADD site of the H-bonded network while maintaining the same number (9) of free OH groups.



Fig. 2. Composite vibrational predissociation spectra of D₂ tagged ions taken with the Berlin FEL (<1,000 cm⁻¹) and the Yale table top system (1,000–3,800 cm⁻¹): (A) H₃O⁺(H₂O)₂₀, (B) D₃O⁺(D₂O)₂₀, (C) Cs⁺(D₂O)₂₀, and (D) Cs⁺(H₂O)₂₀. Bands attributed to the hydronium ion in A and B are highlighted in red and are clearly absent in the Cs⁺(D₂O)₂₀ spectrum. All spectra display a sharp free OH/OD stretching band highest in energy arising from AAD type water molecules (orange).



Fig. 3. Color-coded $H_3O^+(H_2O)_{20}$ structures for the MP2 minimum (structure II, *Left*) (6) and the B3LYP minimum (structure I, *Right*) (8). The H_3O^+ ion is colored red at the top of both structures. There are two classes of ADD waters: three (blue, ADD¹) solvate the hydronium ion and three (turquoise, ADD²) are remote from the charge center. Colored in orange are the nine AAD type waters. Two classes of four-coordinate AADD molecules are colored pink: one in the interior (AADD¹) and four at the surface (AADD³). The structural differences result from the reorientation of three of the five AADD molecules including the interior water.

Comparison with Harmonic Predictions: Structural Implications of the OH/OD Band Patterns. To clarify the assignments of the bands, we color code the various water molecules in structure II suggested by Xantheas in Fig. 3 and include a rotatable 3D structure in the *SI Materials and Methods* (structure I in Fig. S3 and structure II in Fig. S4). This structure exhibits approximate threefold symmetry evolving from the hydronium ion (red), with the three ADD water molecules (blue, denoted ADD¹) integrating the Eigen structure into the surface of the cage. Each of these bridging water molecules donates an H-bond to an AADD (pink) and an AAD (orange) molecule such that these orange AAD sites in turn link to the three lower ADD water molecules (turquoise, denoted ADD²) farthest from the ion. Four of the four-coordinated AADD molecules reside on the surface (AADD^s) and one is sequestered in the interior (AADDⁱ).

The harmonic spectra for structure II are included in Fig. 4 B (all-H) and D (all-D). The AAD molecules (orange) yield a group of closely spaced transitions highest in energy that together account for the single observed free OH peak at the rather modest experimental resolution (3 cm^{-1}). The least red shifted H-bonding feature (A) now appears as an asymmetrical, closely spaced doublet with a shoulder on the low energy side, fine structure that is remarkably consistent with the harmonic prediction for structure II. OH displacements within the remote ADD^2 molecules (turquoise) are calculated to make the dominant contribution to the A feature with their antisymmetric stretching modes and account for the observed doublet structure in a scenario where one of these ADD² molecules is further topologically distinguished by its orientation relative to that of the interior water molecule (AADDⁱ). The corresponding symmetric stretching modes of the ADD^2 sites, on the other hand, are calculated to fall lower in energy where they merge with a dense series of more delocalized vibrations. In this scheme, the third strong feature (B) is largely due to the antisymmetric stretch of the primary hydronium solvation shell provided by the ADD¹ (blue) molecules. The antisymmetric stretch of the surface (AADD^s class, pink) molecules is also calculated to reside nearby and likely contributes to the broadening of the B feature.

The plausibility of these OH stretching assignments is strengthened by comparison with the observed and calculated $D_3O^+(D_2O)_{20}$ spectra in Fig. 4 *C* and *D*, respectively. The highest energy free OD singlet and A doublet are similar to those features in the all-H case. The analog of feature B, however, at 2,588 cm⁻¹ emerges as a distinct band in the all-D spectrum [as opposed to blended with the blue edge of the continuous background absorption in the H₃O⁺(H₂O)₂₀ spectrum]. This behavior is also anticipated by the harmonic prediction in the context of increased separation of

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the antisymmetric stretches arising from the ADD^{1} (blue) molecules relative to the calculated symmetric stretches of the remote ADD^{2} (turquoise) molecules.

Although it is clear that anharmonic effects will undoubtedly complicate this simple picture, it is nonetheless compelling that the three strong free OH/OD, A, and B bands (especially evident in the OD stretching spectrum) can be traced to particular classes of water molecules at play in the pentagonal dodecahedron: nine AAD, three ADD¹ (blue), and three ADD² (turquoise). Only the transitions involving the motions of the remaining five AADD molecules are masked by overlap with the strongly coupled, more distributed motions.

Having considered the assignment of key bands in the $D_3O^+(D_2O)_{20}$ spectrum to particular network sites in the pentagonal dodecahedron, it is useful to compare its spectrum to that of the $Cs^+(D_2O)_{20}$ cluster. Two reported minimum energy structures (29) of the metal ion cage are displayed in Fig. 5 along with the corresponding harmonic predictions (note that nondodecahedral structures have also been shown to be nearly isoenergetic (27, 30) and high-level ab initio searches have yet to be performed on this system). Both arrangements have 10 AAD type molecules colored in orange. The remaining 10 ADD molecules are further differentiated into three classes according to the nature of the H-bond donor and acceptor molecules. The three ADD¹ sites (colored purple) are distinct because they accept



Fig. 4. Comparison of the experimental OH/OD stretching regions of (A) $H_3O^+(H_2O)_{20}$ and (C) $D_3O^+(D_2O)_{20}$ to the harmonic predictions for structure II in *B* and *D*, respectively. The top abscissa corresponds to the all-H spectra in *A* and *B*, whereas the bottom abscissa is associated with the all-D spectra in *C* and *D*. The spectra calculated for structure II are color-coded to identify sites whose displacements contribute most to the fundamental transitions. The free OH/OD stretches of AAD waters (orange) appear highest in energy, whereas feature A is traced to the antisymmetric stretches of the remote ADD water molecules (AAD², turquoise). The broad continuum near feature B in $H_3O^+(H_2O)_{20}$ resolves into a distinct band at 2,588 cm⁻¹ on deuteration. The calculations indicate feature B may be due to the antisymmetric stretches of the water molecules (AAD¹, blue) in the first solvation shell around the hydronium ion. All calculated spectra [B3LYP/6–31+G(d)] were scaled by 0.973 to bring the free OH/OD stretches into agreement with those observed.



Fig. 5. Overview of the $Cs^+(H_2O)_{20}$ harmonic predictions for two minimum energy structures reported in ref. 29 in traces *A* and *C* compared with the experimental spectrum in *B*. Both calculated structures are pentagonal do-decahedra with the Cs^+ located in the center of the cage. Colored in orange are the ten AAD type water molecules. The ten remaining water molecules make up three distinct ADD type sites which depend on the local H-bonding environment. These sites are labeled ADD¹ (purple), ADD² (turquoise), and ADD³ (green).

an H-bond from an ADD³ molecule (green) while donating both H-bonds to AAD type waters (orange). The three ADD³ sites (green) accept and donate an H-bond to AAD waters while donating the second H-bond to an ADD¹ water. The four ADD² (turquoise) waters are bound to three AAD molecules. A rotatable 3D model of structure I is given in Fig. S5.

The harmonic spectrum for the two calculated $Cs^+(D_2O)_{20}$ structures in Fig. 5 are presented in Fig. 6 *A* and *C*, respectively. The single feature highest in energy is accounted for by the nearly degenerate free OD stretches of the 10 AAD molecules (orange), whereas the ADD waters in $Cs^+(H_2O)_{20}$ are much less spectroscopically distinct compared with the two classes of ADD type molecules seen in $H_3O^+(H_2O)_{20}$ and lead to nearly overlapping transitions. Based on the calculated spectra, the sharp feature at 2,661 cm⁻¹ can be traced to the antisymmetric OD stretches of the three ADD¹ water molecules colored in purple. The broader feature centered at 2,630 cm⁻¹ then derives from the overlap of the antisymmetric OD stretches of the ADD² and ADD³ waters.

In essence, the most important aspect of this exercise is to emphasize that the structure in the spectra of the cryogenically cooled clusters is sufficiently well resolved to warrant such an attempt to identify the local sites responsible for the distinct bands. Unambiguous assignment will clearly require much more sophisticated theoretical treatment beyond the scope of this report, and it is indeed hoped that these results provide strong motivation for such efforts.

Survey of the Librational Bands from 200 to 1,000 cm⁻¹: Site-Specific H-Bonding Environments and Unique Behavior of $H_3O^+(H_2O)_{20}$. Our analysis of the $H_3O^+(H_2O)_{20}$ spectrum suggested that the fundamentals from the five AADD type (pink) molecules fall in a congested region of the OH/OD stretching manifold, and as such, are not expected to yield clear spectral signatures. Another aspect of the network environment of the AADD water molecules, however, is the strength of interaction with the

surrounding cage that is associated with their fully saturated H-bonding. It is anticipated that the bands in the low energy region (<1,000 cm⁻¹) would effectively report on this local H-bonding environment (31). The low energy portion of the spectrum associated with water librational motion has not been explored for these intermediate cluster sizes, but it is accessible with high power infrared free electron lasers as recently demonstrated by As mis and coworkers in a study of the $H^+(H_2O)_6$ ion (32). Here we survey the behavior of selected clusters in the n = 17-27range over the region 215–1,000 cm⁻¹, with the results collected in Fig. 7. The low binding energy of H₂ (300 cm⁻¹) (11) onto protonated water clusters ensures that single photon (linear) spectra can be obtained over nearly the complete spectral range investigated. All spectra in this size range display rather broad absorption envelopes with the exception of n = 20, which exhibits several distinct features throughout the range. The absorption peaks near 600 cm⁻¹ and resolves into a multiplet at n = 20before collapsing back to a single envelop at n = 27. The fine structure on the n = 20 spectrum strongly suggests that the ion ensemble is dominated by a single conformer class with rather high symmetry. This conclusion is consistent with the cage arrangement II depicted in Fig. 3, proposed based on the OH/OD stretching band patterns as described above.

To better gauge the types of motion involved in the low energy region of the spectrum, Fig. 8 A and D present the harmonic predictions for both n = 20 cations along with their experimental spectra from 215 to 1,800 cm⁻¹ (Fig. 8 B and C). Although it is clear that the calculated fundamentals lie higher in energy than the observed bands, it is nonetheless of qualitative interest to examine the normal modes yielding the most oscillator strength in this low-frequency region. Representative displacement vectors for several strong fundamentals contributing to the calculated H₃O⁺(H₂O)₂₀ spectrum are included in Fig. 8A. These modes are denoted 1–6 and colored according to the scheme outlined above according to the network sites most active in the calculated normal mode. Thus, feature 1 is associated mainly with the twisting motion of water molecules in AADD sites. Two modes arising from motions of the hydronium ion are colored red: one



Fig. 6. Harmonic vibrational spectra of (A) structure I and (C) structure II and that observed for $Cs^+(D_2O)_{20}$ in *B*. The highest energy feature is easily assigned to the free OD stretches of the AAD water molecules (orange). The ADD¹ water molecules (purple) are predicted to yield the narrower feature at 2,661 cm⁻¹, whereas the ADD² and ADD³ sites (turquoise and green) overlap to yield the broader band at 2,630 cm⁻¹.



Fig. 7. Vibrational spectra of the low energy librational modes collected using the FHI free electron laser for the indicated $H_3O^+(H_2O)_n$ clusters: (A) n = 17, (B) 19, (C) 20, (D) 21, (E) 23, and (F) 27. Interestingly, the librational modes for n = 20 (C) are more intense and better resolved compared with the other cluster sizes, perhaps due to the pentagonal dodecahedral symmetry. The positions of these modes should be indicators for the local H-bonding environment. The 341 (orange) and 842 cm⁻¹ (pink) features observed in each cluster, for example, likely result from lower and higher H-bond coordination sites within the 3D cage structures, respectively.

from frustrated rotation about the C_3 axis (feature 2) and one from rocking against the solvation shell (feature 3). Also in this energy range, and much weaker, are librational modes traced to motions of the bound hydrogens of AAD type waters (not labeled). With this in mind, we tentatively attribute the prominent feature (labeled † in Fig. 8*B*) near 850 cm⁻¹ to H₃O⁺ and fourcoordinate AADD librational modes. Interestingly, the activity near 900 cm⁻¹ in the Cs⁺(H₂O)₂₀ spectrum (Fig. 8*C*) appears much weaker and less resolved than in H₃O⁺(H₂O)₂₀, consistent with the absence of the H₃O⁺ and AADD motifs in the metal system. The weaker transitions in this range for the Cs⁺ cluster are mostly due to tortional motion of the AAD bound hydrogen as illustrated in Fig. 8*D*.

The strongest librational activity in the $H_3O^+(H_2O)_{20}$ spectrum (features 4 and 5 in Fig. 8A) is derived from the two classes of ADD molecules, with the waters directly solvating the hydronium (ADD^{1}) falling higher in energy than those (ADD^{2}) in the more remote site. The predicted envelope is in qualitative agreement with the observed multiplet spanning the range from 500 to 700 cm⁻¹. Interestingly, the corresponding ADD modes in Cs⁺(H₂O)₂₀ (Fig. 8D and Fig. S6) occur in the same range and would similarly account for the multiplet structure that dominates that spectrum near 600 cm⁻¹. Finally, the lowest observed band at 341 cm⁻¹ in $H_3O^+(H_2O)_{20}$ is in good agreement with predicted feature 6 (Fig. 8A), which is calculated to involve motions of the AAD free hydrogens, with the corresponding transition in $Cs^+(H_2O)_{20}$ appearing at 401 cm⁻¹. It is interesting to note that the librational modes of these free hydrogens are relatively sharp, isolated bands as was the case with the corresponding free OH stretches at 3,700 cm⁻¹. This localization of oscillator strength from a feature derived from so many oscillators [9 for $H_3O^+(H_2O)_{20}$ and 10 for $Cs^+(H_2O)_{20}$] is again easily

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rationalized by the relatively high symmetry of the pentagonal dodecahedron structures.

Conclusions

Cryogenic cooling of the size-selected $H_3O^+(H_2O)_n$ (17 < n < 27) cluster ions, in conjunction with D_2 tagging and isotopic substitution, yields unprecedented structure in their vibrational predissociation spectra, both in the higher-frequency region corresponding to OH stretching and the lower-frequency region arising from librational motions of water molecules trapped in various distinct network sites. The evolution of the H₃O⁺ (H₂O)₂₀ spectrum with H/D substitution, as well as on replacement of hydronium with Cs⁺, provides strong support for the earlier assignment (7) of the spectral signature associated with the $H_9O_4^+$ Eigen cation embedded on the surface of a pentagonal dodecahedron cage structure. The low energy librational motions are reported for this class of systems for the first time, to our knowledge, and reveal site-specific features based on the local H-bond coordination and strength. The observation of highly articulated band patterns for these hydrates opens the way for rigorous characterization of the structures at play at the elementary stages of ion hydration by explicitly including vibrational anharmonicity in the calculated band patterns.



Fig. 8. Comparison of the 200- to 1,800-cm⁻¹ region of (*B*) $H_3O^+(H_2O)_{20}$ and (*C*) Cs⁺($H_2O)_{20}$ to those computed for the lowest energy structures in *A* and *D*, respectively. Displacement vectors are shown for the dominant $H_3O^+(H_2O)_{20}$ fundamentals indicated in *A*. The highest energy librational bands in $H_3O^+(H_2O)_{20}$ involve motion of the AADD type waters (feature 1, pink) and frustrated rotations of the hydronium ion (features 2 and 3, red). For Cs⁺($H_2O)_{20}$, the weaker and broader bands near 1,000 cm⁻¹ derive mostly from the bound AAD hydrogen. The dominant multiplets near 600 cm⁻¹ in both spectra are mostly due to torsional motions of the multiple ADD sites [features 4 and 5 for $H_3O^+(H_2O)_{20}$]. Lowest in energy are motions of the AAD free OH (orange).

Materials and Methods

Research carried out at Yale used the tandem time of flight photofragmentation mass spectrometer described previously (33) to acquire the vibrational spectra of the protonated water clusters cryogenically frozen close to their zero-point energies. Clusters were generated by electrospray ionization of 0.1% H₂SO₄ in a H₂O solution and D₂SO₄ in a D₂O solution for the all-H and all-D clusters, respectively. In the case of the Cs⁺(H₂O)₂₀/(D₂O)₂₀ cluster, Cs₂CO₃ in H₂O/D₂O was used as the electrospray solution. The generated clusters were guided using RF-only quadrupole and octopole guides into a 3D quadrupole Paul trap (Jordan) mounted to the second stage of a 4 K closed cycle Helium cryostat. The ions were stored for ~90 ms, during which they are collisionally cooled by helium buffer gas. The buffer gas was doped with about 10% D₂, which condensed onto the cluster of interest at these cold temperatures and acted as the spectroscopic messenger (34). The cold clusters were ejected from the trap into the extraction region of a Wiley-McLaren TOF mass spectrometer.

Mass-selected ions were photoexcited with the output from a Nd:YAG pumped (7 ns, 10 Hz) optical parametric oscillator and amplifier (OPO/OPA) infrared (IR) laser (LaserVision). The output of the OPA is tunable from 2,200 to 4,500 cm⁻¹, with a laser bandwidth of about 3 cm⁻¹. The lower energy 600- to 2,600-cm⁻¹ region was produced by difference frequency mixing of the signal and idler output of the OPA in AgGaSe₂. The action spectra were collected by monitoring the single photon-induced evaporation of the D₂ molecule with respect to photon energy and normalized to the laser pulse energy to take account for fluctuations in the laser power during the scan.

Infrared photodissociation experiments in the lowest energy region (215–1,000 cm⁻¹) were carried out using the Berlin 6-K ion-trap triple mass spectrometer (35) in combination with the widely tunable and intense IR radiation from the Fritz-Haber-Institute free electron laser (FHI-FEL) (36). Microhydrated ions were produced in a nanospray ion source. Protonated water clusters were generated as described above. $Cs^+(H_2O)_{20}/(D_2O)_{20}$

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clusters were generated from a CsCl/H2O/D2O solution. The continuous molecular beam was collimated using a He-filled RF-only octopole ion guide. After mass selection with a quadrupole mass filter, the ions were focused into a linear RF ring electrode ion-trap, which was kept at 13–14 K, to accumulate, thermalize, and D₂ messenger tag (37). Ion packets were extracted and focused in a 5-Hz cycle into the center of the extraction region of TOF mass spectrometer. Here, they were irradiated by the intense 5- to 8-µs-long IR pulse of the FHI-FEL. (See SI Materials and Methods for characteristics of the IR pulses.) Action spectra were recorded by averaging over 75-100 TOF mass spectra per wavelength step. Typically, a distribution of (D₂)_mtagged cations, peaking at m = 1, were produced in the ion trap (Fig. S7). However, the differences between the action spectra of cations with a single (m = 1) and with more than one tag (m > 1) were negligible (Fig. S8), and therefore the ion yields of all tagged cations were summed up. The photo dissociation cross section σ was then determined from the relative abundance of the fragment and parent ions (I_F/I_D) and the frequency-dependent laser fluence $F(\nu)$ using $\sigma(\nu) = -\ln\{[I_F(\nu)/I_P]\}/F(\nu)$. A comparison of spectra collected at Yale and FHI is given in Fig. S9.

All calculations were performed using the Gaussian 09 suite of programs (38) using the B3LYP/6–31+G(d) level of theory and basis. For the Cs⁺(H₂O)₂₀ calculations, the LANL2DZ pseudopotential was used for Cs.

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