Infrared Spectroscopy of Perdeuterated Protonated Water Clusters in the Vicinity of the Clathrate Cage

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We report infrared predissociation spectra of size-selected $D^+(D_2O)_n$ clusters in the size range $n = 18-24$ for comparison to previous studies of the corresponding $H^+(H_2O)_n$ species (Shin, J.-W.; Hammer, N. I.; Diken, E. G.; Johnson, M. A.; Walters, R. S.; Jaeger, T. D.; Duncan, M. A.; Christie, R. A.; Jordon, K. D. *Science* **2004**, *304*, 1137). For $n = 18-20$, two "free" OD stretch bands are observed and assigned to D_2O molecules in acceptor−acceptor−donor (AAD) and acceptor−donor (AD) hydrogen bonding arrangements. Only the AAD band is observed for the $n = 21$ perdeuterated species. This behavior is identical to that observed previously for the corresponding $H^+(H_2O)_n$ clusters. Similar to the all-H protonated species, the AD "free" OD stretch band is also absent for the perdeuterated $n = 22$ cluster but returns for clusters larger than $n = 22$. Like the $H^+(H_2O)_n$ systems, the perdeuterated clusters have no spectral band in the lower frequency range where the signature of the hydronium cation is predicted. These observations shed new light on the intriguing spectroscopy and dynamics of large protonated water clusters.

Introduction

Small protonated water clusters, $H^+(H_2O)_n$, have been shown both theoretically[1−3] and experimentally[4−7] to play a central role in the mechanism of proton transport in biological systems. Advances in theoretical and experimental tools for studying protonated water clusters have allowed for an increasingly more detailed microscopic understanding of this mechanism. Spectroscopic studies of size-selected protonated water clusters in the gas phase[8−18] have explored the evolution of structural motifs that are implicated in the structural diffusion mechanism of proton transport in bulk water.[19−26] Small protonated water clusters have open structures, but beyond the size of about $n = 14$, three-dimensional cage structures begin to form. A particularly intriguing cluster is the $n = 21$ species, which has an enhanced abundance in many mass spectrometry experiments[27−33] and is believed to have a symmetric cage structure like that known for the clathrates of natural gas hydrates. Infrared spectroscopy was recently reported for the $H^+(H_2O)_{21}$ species and other clusters in this size range, providing evidence for a high symmetry structure.[10,11] However, the details of these spectra raised many questions about the specific structure of these clusters and their dynamical behavior under various experimental conditions. In the present report, we present infrared spectra for the corresponding perdeuterated species to further investigate these issues.

Infrared spectroscopy of protonated water clusters, $H^+(H_2O)_n$, has now been reported for sizes up to $n = 100$, showing a trend from open structures for $n < 14$[8,9,12,14,18] to cage structures[10,11,15,16] that evolve to larger closed net structures for sizes up to and presumably beyond $n = 100$.[16] The net structures of the larger clusters are driven by the amphiphilic nature of the hydronium

ion[34−36] and its preference for three-coordinate bonding, as opposed to the four-coordinate bonding observed for neutral water molecules in the liquid state. The $n = 21$ cluster is a "magic number" in the mass spectra of protonated water clusters generated by a variety of methods,[27−33] and this intensity anomaly has been attributed to the high symmetry and thermodynamic stability of this species relative to other clusters in this size range. Although some early work proposed a structure having a 20-water cage with an internal hydronium cation,[31,32] all modern *ab initio* calculations predict the lowest energy $n = 21$ structure to be a distorted pentagonal dodecahedron with the hydronium ion in a three-coordinate surface site and a single *neutral* water molecule occupying the interior of the cage.[11,34,37−39] IR laser spectroscopy of the gas phase $H^+(H_2O)_n$ clusters in the size range around $n = 21$ was reported recently in independent studies by the group of Mikami and co-workers[10] and by our group in a collaboration with Johnson, Jordan, and co-workers.[11] Both groups found similar spectra, with distinctive band patterns in the "free" OH stretch region. For $n = 18-20$ cluster sizes, two "free" OH stretch bands were observed and assigned to H_2O molecules in acceptor−acceptor−donor (AAD) and acceptor−donor (AD) hydrogen bonding arrangements. However, at the $n = 21$ species, only the AAD band was observed,[11] consistent with the high symmetry structure predicted for this cluster by theory. Surprisingly, a similar spectrum with only the AAD band was also observed for the $n = 22$ species,[11] perhaps suggesting that it also has a high symmetry structure, although this cluster size had not been recognized to have such a structure previously. After $n = 21$ and 22, the larger clusters ($n = 23, 24,...$) again have both the AAD and AD bands. This data, which has also been reproduced by others,[15,17] suggests that the $n = 21$ (and 22) species have higher symmetry structures than other clusters in this size range, with more complete coordination for the surface water molecules. However,

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another key aspect of the infrared spectrum predicted by theory for the 21-mer was a band corresponding to the stretching mode of the surface-bound hydronium cation near 2500 cm^{-1}.[11] This region of the spectrum was only covered by the work done in our lab and that of Johnson.[11] Surprisingly, this key signature for the hydronium ion was completely missing in the experimental spectra from both laboratories.[11]

This anomalous spectral behavior for the $n = 21$ cluster has raised many questions and stimulated many theoretical and simulational investigations of the dynamical behavior of this cluster. It is essential to consider that, at the temperature of the experiment (estimated to be 100−150 K),[11] many isomeric structures are likely populated, and the spectroscopy is representative of an ensemble average over the thermally accessible conformations of the system rather than one single structure. Indeed, Wales and co-workers predicted 31 isomers of the 21-mer to lie within 1 kcal/mol of the global minimum structure.[40] For comparison, the $n = 21$ ions generated in the gas phase experiments have approximately 35 kcal/mol of residual internal energy.[11] Moreover, the zero-point motion of the cluster may render many of the low-lying isomers to be isoenergetic. Indeed, Voth and co-workers have shown in an atom-centered density matrix propagation (ADMP) simulation that, at the experimental temperature, the ensemble average over structural isomers is sufficient to "wash out" the distinction between the limiting Eigen ($H_9O_4^+$) and Zundel ($H_5O_2^+$) structural motifs.[35] In their study, the IR spectrum obtained from the dipole−dipole autocorrelation function does not have the strong bands near 2500 cm^{-1} indicative of the hydrogen-bonded OH stretches of the hydronium cation. Kim and co-workers have shown with Carr−Parrinello molecular dynamics (CPMD) simulations that the Eigen spectral signature only reappears when the temperature is reduced to about 50 K.[41]

Another consideration for these clusters is the dissociation yield and its energy dependence. Because we measure photodissociation and not absorption, the fragmentation dynamics may also influence our ability to detect a signal. The binding energy for the $n = 21$ species has been determined to be $\Delta G = 5.56$ kcal/mol ($\sim$2100 cm^{-1}).[31d] It is conceivable that the rate of dissociation on the time scale of our experiment (2−3 μs available for dissociation before reacceleration out of the interaction zone) at the energy of the predicted 2500 cm^{-1} band might lead to a decrease in the detectable dissociation yield here. It is furthermore possible that the rate of intramolecular vibrational relaxation (IVR) might be different for excitation of the hydronium moiety in the wall of the cluster than for a water molecule containing a free OH because of the higher connectivity. If energy dispersal is more rapid here, the rate of dissociation may be slower upon excitation of this chromophore, again reducing our ability to detect a signal.

Because of the predicted and demonstrated[11,15,17] sensitivity of the spectroscopy of these clusters to temperature, and the additional possibility of energetic/dynamical influences on fragmentation sensitivity, we have chosen to investigate the perdeuterated protonated water clusters near the $n = 21$ size. Stace and co-workers have shown previously that the $D^+(D_2O)_{21}$ clusters exhibit the same magic number behavior as the $H^+(H_2O)_{21}$ species.[42] The spectra of these species can address the role zero-point energy plays in determining the structures of these systems at finite temperature, and the lower frequencies of O−D stretches will shift the spectrum to a different energy range, perhaps influencing dissociation rates. We present here the corresponding spectra of the perdeuterated protonated water clusters in the $n = 18−24$ size range. In the only previous

spectroscopic work on isotopically substituted clusters, Johnson and co-workers have reported the IR spectra of the partially deuterated protonated water dimer.[43] Our group has investigated IR spectra of perdeuterated clusters in the $n = 3−10$ size range,[18] but there has been no previous report of deuteration in the larger clusters. Furthermore, we have expanded the spectral coverage of both the $H^+(H_2O)_{21}$ and $D^+(D_2O)_{21}$ species to search for other vibrational bands predicted below 2000 cm^{-1} that correspond to the bending motion of the surface hydronium cation. As shown below, the IR spectra of these perdeuterated clusters exhibit many of the same characteristics seen previously for the corresponding all-H species.

Experimental Section

Perdeuterated protonated water clusters are produced in a pulsed electric discharge source described previously.[44] A supersonic expansion of D_2O seeded into argon is produced with a general valve operating at 10 Hz. Two ring electrodes are concentrically positioned about the expansion with the high voltage electrode positioned 1 cm from the nozzle opening. A -1 kV pulse 5 μs in duration is applied to the high voltage electrode, while the other is held at ground potential. The high voltage pulse is timed so that a discharge is created in the temporal center of the pulsed nozzle expansion. The expansion is skimmed with a 2 mm skimmer, and the cations generated in the discharge are pulse-extracted into a specially designed reflectron time-of-flight mass spectrometer. In the first flight tube of this instrument, pulsed deflection plates are employed to size select a particular $D^+(D_2O)_n$ cluster. The tunable output from an IR OPO/OPA/AgGaSe$_2$ system (LaserVision) is timed to intersect the size-selected ion packet in the turning region of the reflectron field. Resonant vibrational excitation of the parent cluster ion leads to the loss of D_2O molecule(s). The parent and fragment ions are reaccelerated and separated in the second flight tube. The IR spectrum of the size-selected ion is obtained by monitoring the production of fragment ions (loss of one D_2O molecule) as the laser system is tuned from 1000 to 4000 cm^{-1}. Throughout this frequency range, the output pulse energy of the laser was adjusted to produce $\sim$1 mJ/pulse.

Results and Discussion

The mass spectrum of $D^+(D_2O)_n$ clusters produced by our source is shown in the Supporting Information for this paper. It contains mass peaks out to beyond $n = 30$. The $n = 21$ mass peak is not particularly prominent in this spectrum, but rather is one of many peaks in a smoothly varying profile. This behavior is consistent with our previous observation that this peak only becomes prominent as a "magic number" when the cluster distribution is warm and undergoing preferential evaporative loss of other cluster sizes.[11] The infrared predissociation (IRPD) spectra of the $D^+(D_2O)_{18−24}$ clusters are shown in Figure 1. These spectra contain sharp bands near 2700 cm^{-1} where the isolated D_2O molecule has its symmetric and asymmetric stretch (2671 and 2788 cm^{-1}, respectively),[45] and then at lower frequency, there is a broad structure assigned to hydrogen bonded O−D stretches. Except for the shift to lower frequency, the qualitative appearance of these spectra is remarkably similar to that measured previously for the corresponding $H^+(H_2O)_n$ species.[11] The free OD stretch region shows two distinct bands between 2700 and 2780 cm^{-1} that can be assigned on the basis of the previous $H^+(H_2O)_n$ studies[10,11] to AAD and AD D_2O molecules, as indicated in the figure. The structure in this region is expanded in Figure 2. The AAD band has a constant position at 2731 cm^{-1} for all cluster sizes, while the AD band appears

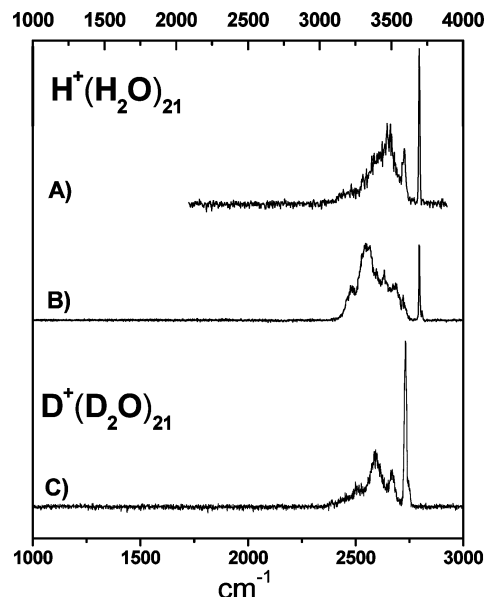Letters

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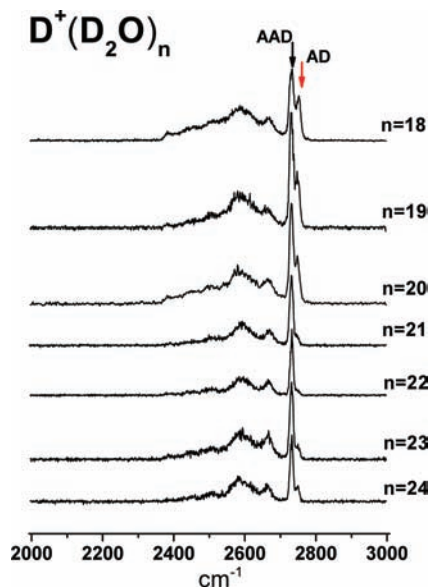
Figure 1. IRPD spectra of $D^+(D_2O)_n$ ($n = 18-24$) clusters measured in the loss of one D_2O fragmentation channel. The labels AAD and AD indicate the "free" OD stretch bands of D_2O molecules involved in acceptor−acceptor−donor and acceptor−donor hydrogen bonding arrangements, respectively.
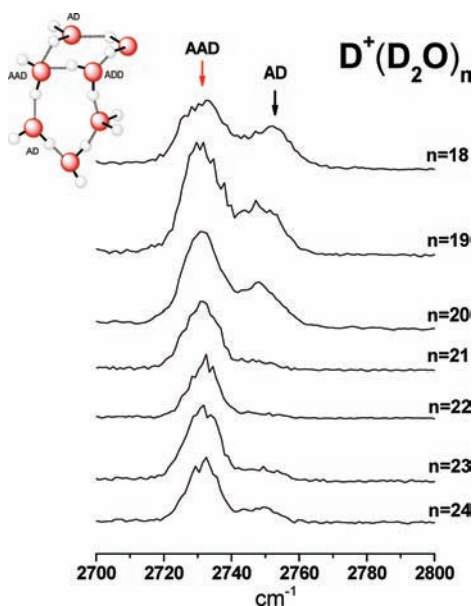
Figure 2. Expanded view of the free OD stretching region for $D^+(D_2O)_n$ ($n = 18-24$) clusters measured in the loss of one D_2O fragmentation channel. The labels AAD and AD indicate the "free" OD stretch bands of D_2O molecules involved in acceptor−acceptor−donor and acceptor−donor hydrogen bonding arrangements, respectively.

Figure 3. IRPD spectra of the $H^+(H_2O)_{21}$ clusters measured with the colder laser spark source (A) and with the present ring discharge source (B) compared to the spectrum of the $D^+(D_2O)_{21}$ (C) clusters, also measured with the ring discharge source. The deuterated species are measured between 1000 and 3000 cm^{-1}, and the $H^+(H_2O)_{21}$ spectrum is recorded over the range 1000−4000 cm^{-1}.

at 2752 cm^{-1} for the $n = 18$ species but shifts to a constant position at 2749 cm^{-1} for the other sizes. Below 2700 cm^{-1}, the broader features are attributed to D_2O molecules in the cluster that are donating both OD bonds to hydrogen bonds. Again, similar to $H^+(H_2O)_n$,[11] a broad but reproducible band occurs below the sharp free OD structure on the higher energy side of the hydrogen bonding region. This band, which occurs at 2664−2665 cm^{-1} for the $n = 19, 20, 23$, and 24 species, and slightly higher frequency at 2667−2668 cm^{-1} for $n = 21$ and 22, is assigned to "double-donor" DDA D_2O molecules that are bound to three AAD molecules. The signature of the onset of the high symmetry clathrate structure in the spectroscopy of $H^+(H_2O)_n$ clusters was the sudden disappearance of the band

associated with the AD waters, leaving only a single band in the free OH stretch region.[11] For $H^+(H_2O)_n$, this signature is observed at $n = 21$ and $n = 22$ and the AD band reappears for clusters $n \geq 23$. Similarly, the IRPD spectra of $D^+(D_2O)_n$ show both an AAD and AD band for $n = 18, 19$, and 20. The intensity of the AD band drops off significantly for $n = 21$, remains absent for $n = 22$, and then reappears for $n = 23$ and $n = 24$. The relative intensities of the AAD and AD bands for the perdeuterated 21- and 22-mers are essentially identical to those observed previously for $H^+(H_2O)_{21,22}$. Apparently the zero-point energy difference has little effect on the spectroscopy in the high frequency OD/OH stretch region. Again, as observed for $H^+(H_2O)_{22}$, a single free OD stretch band is observed for the 22-mer, although Wales and co-workers have found that only three of the 31 lowest energy $n = 22$ isomers lack AD H_2O moieties.[40] More recently, Kim and co-workers have explained this experimental observation in terms of the dynamics of the 22nd water molecule bound to the surface of the $n = 21$ cluster.[41] They found in their simulations that the A and AD stretch bands of the dangling water are extensively broadened due to strong anharmonic coupling of the symmetric and asymmetric stretch vibrations as it undergoes wide amplitude motion on the cluster surface. If this is the correct explanation for the spectrum of the $H^+(H_2O)_{22}$ cluster, it remains upon deuteration.

Figure 3 shows a comparison of the $H^+(H_2O)_{21}$ (trace B) and $D^+(D_2O)_{21}$ (trace C) IRPD spectra measured in the present experiment over a broader frequency range. We also include a reproduction of the spectrum of $H^+(H_2O)_{21}$ published previously (trace A; from our lab),[11] which was generated using a pulsed laser spark source instead of the present pulsed ring discharge source. The present spectrum has significantly improved signal levels, and extends the infrared range for the $H^+(H_2O)_{21}$ species down to 1000 cm^{-1}, whereas the previous spectrum ended at the low frequency of 2000 cm^{-1}. As shown, there are qualitative similarities between the all-H and all-D spectra. Both have a sharp AAD band at high frequency, a broad range of signal in the hydrogen bonding region, and then no bands at lower

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frequency. The 2500 cm^{-1} band predicted by theory for the hydronium in the wall of the H$^+$(H$_2$O)$_{21}$ species was not detected previously in a similar experiment measuring the elimination of water from the clusters,[11] or when the Johnson lab employed argon tagging predissociation in this spectral range.[11] It is still not detected here with the improved sensitivity (2−3×) of the present experiment. Additionally, there are no other bands in the expanded lower frequency range of the spectrum for the H$^+$(H$_2$O)$_{21}$ species. Like the H$^+$(H$_2$O)$_{21}$ spectrum, the D$^+$(D$_2$O)$_{21}$ spectrum also has no bands at frequencies below the broad structure in the hydrogen bonding region. In particular, at 0 K, the hydrogen bonded OD stretches of the surface-bound hydronium ion would be located near 1750 cm^{-1} for the perdeuterated 21-mer, and there is clearly no band here. In fact, there are no bands for either isotopomer found below 2400 cm^{-1}. This is despite the fact that both Voth's ADMP[35] and Kim's CPMD[41] simulations (among others)[46,47] predict spectral features below 2000 cm^{-1}. Iyengar has predicted with ADMP simulations that there should be bands at 1050 and 1350 cm^{-1} corresponding to the coupled stretch and bending motion of the protonated water moiety in H$^+$(H$_2$O)$_{21}$.[47] Again, these features are absent in the experimental IRPD spectrum of H$^+$(H$_2$O)$_{21}$. This is perhaps surprising given that the ensemble averaging and proton dynamics associated with the zero-point motion of the cluster are included in the above-mentioned simulations.[35,41,46,47]

As we mentioned earlier, the lack of signal below 3100 cm^{-1} in our IRPD spectrum of H$^+$(H$_2$O)$_{21}$ remains to be explained. We noted above that dissociation energetics or the dynamical rate of dissociation at these lower energies might be the problem. The deuterated species studied here have effectively higher dissociation thresholds because of the lower zero-point energy. Because of the lower vibrational frequencies, the average density of vibrational states at any selected energy is greater for the deuterated species than it is for the all-H system, effectively improving the coupling for energy flow that would dissipate energy throughout the cluster. Both of these factors should make it more difficult to fragment the deuterated species on the time scale of our experiment. However, in spite of this, there is efficient fragmentation for the D$^+$(D$_2$O)$_n$ clusters in the hydrogen bonding region extending down to about 2400 cm^{-1}. This suggests that the absence of signal in the 2500 cm^{-1} region for the H$^+$(H$_2$O)$_{21}$ spectrum[11] was not due to unfavorable dissociation energetics or rates. Presumably, energetics would become more of a problem at lower energies, and this may explain the lack of fragmentation signal below 2000 cm^{-1}.

Another important consideration for these systems is the role of finite temperature. The effect of temperature on the free OH stretching frequencies has been discussed previously by our group[11] and others.[15] The sharp preference for the single AAD band is only seen when clusters are quite cold; as clusters become warmer, the AD band corresponding to lower coordinate structures becomes more noticeable. Indeed, some H$^+$(H$_2$O)$_n$ spectra produced from some ion sources exhibit no noticeable reduction in the AD band intensity near the 21-mer.[10] At the temperatures in our experiment here (estimated to be 100−150 K),[48] perdeuteration of protonated water clusters has little effect on the IRPD spectroscopy, other than to shift the bands to lower energy, and all of the features observed for the H$^+$(H$_2$O)$_{21}$ cluster size are similarly observed for D$^+$(D$_2$O)$_{21}$. However, there are some subtle features of these spectra worth mentioning. Trace A shows the spectrum published previously by our group for H$^+$(H$_2$O)$_{21}$ using our laser spark source.[11] Because this source ignites a plasma only at the laser focus, a very small volume of hot gas is produced, and the supersonic expansion is then able

to collisionally cool the ions more effectively. Consistent with this, this source gives sharper spectra for several ions that we have studied, including the H$^+$(H$_2$O)$_{21}$ species that was studied in both our lab and that of Johnson.[11] For comparison to our coldest conditions shown in trace A, trace B shows the spectrum of H$^+$(H$_2$O)$_{21}$ measured in the present experiment with the pulsed ring discharge. We prefer to use the pulsed discharge because it makes larger ion signals, but the ions are not quite as cold (judged by linewidths and the ease of argon tagging in other experiments) as those produced with the laser spark. In trace B, the H$^+$(H$_2$O)$_{21}$ ions are cold enough to have the single AAD band and no AD feature, but the spectrum is somewhat different from that in trace A. The contour of the hydrogen bonding region is shifted toward lower frequency, and the ratio of signal in the free OH band is much smaller compared to that in the hydrogen bonding region. A possible explanation for this is that the ions from the ring discharge have more internal energy, which enhances the dissociation rate at the lower energy in the hydrogen bonding region, thus giving greater signals here. Additionally, the "colder" spectrum (A) has a more well-defined peak at 3600 cm^{-1} assigned to the double-donor moiety (DDA).[11] Trace B does not have this structure, again consistent with warmer ions. Interestingly, the spectrum of the perdeuterated 21-mer (C) has a contour like that of the H$^+$(H$_2$O)$_{21}$ species in trace A, with much greater intensity in the free O−D AAD band. It also has a narrower hydrogen bonding region and a well-defined DDA band at 2667 cm^{-1}. Although the perdeuterated species was produced with the same ring discharge used to obtain the H$^+$(H$_2$O)$_{21}$ spectrum in B, its spectrum looks *colder*. The colder spectrum for the perdeuterated species can be understood simply as an effect of its lower zero-point energy. This makes the dissociation energy higher than that of the all-H species, as noted above. However, the lower zero-point energy also affects barriers to structural rearrangement in the cluster framework. Effectively, the perdeuterated species is more rigid and thus colder, thus giving rise to the well-defined DDA feature. If this reasoning is correct, then the sharp DDA feature is a convenient indicator for cold clusters.

Of course, all of this discussion is necessarily very qualitative. We cannot measure temperature in our experiment, and the estimations of warm and cold are not quantitative. IR spectroscopy of clusters at a well-defined cold temperature would be extremely valuable, and these experiments are being attempted.[17] However, it is clear that temperature does affect the structural rigidity of these systems, and dynamical averaging of structures remains the most likely possibility for why the hydronium vibrational bands are not detected. Dissociation threshold energies and rates are not likely the cause of the missing bands near 2500 cm^{-1}, but these affects could influence bands predicted but not observed at lower frequencies.

Supporting Information Available: Figure showing the mass spectrum of the D$^+$(D$_2$O)$_n$ clusters produced by our source. This material is available free of charge via the Internet at http://pubs.acs.org.

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