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Direct Absorption Spectroscopy of Water Clusters[||]

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Fourier Transform infrared spectrometry has been used to study the vibrational spectroscopy of water clusters prepared in a supersonic expansion. The clusters are assigned as being composed of 10−100 waters based on consideration of the free OH and bound OH vibrations and the experimental conditions used. Four vibrational features were observed simultaneously including the bend, free OH stretch, bound OH stretch, and an unresolved group of intermolecular vibrations. No absorption features were observed between 4000 and 8000 cm^{-1}. This is the first observation of the bending vibration for any size gas-phase water cluster.

Introduction

Water plays a major role in solar absorption in the atmosphere in the mid- and near-infrared, particularly at altitudes of less than 15 km. The earth's atmosphere also acts as an insulator by trapping up-welling radiation. This phenomenon is known as the greenhouse effect, and water vapor is a major contributor through its mid- and far-infrared absorption.[1] A question to be addressed is the effect that water clusters might have in these radiative transfer processes distinct from effects due solely to the H_2O molecule. Addressing the role of water clusters in the radiative balance of the atmosphere requires information on the position, width, and strength of the absorption features. Some of the required parameters have been measured experimentally, and some have been calculated with ab initio methods. This paper reports experiments undertaken to address some of the missing spectroscopic information.

A water cluster is a gas-phase species composed of some number of water molecules held together by hydrogen bonding interactions. A hydrogen bond involves the electron pair on an oxygen atom interacting with a hydrogen atom on another molecule. This is the same interaction that holds H_2O together in the liquid phase. The binding energy for the water dimer is ∼5 kcal/mol[2].

Significant effort has been expended using ab initio calculations to determine the structure and binding energies of small clusters.[2−38] The structures of these clusters are well established and can be checked against experimental information. Saykally et al. have used vibration−rotation-tunneling (VRT) spectroscopy to investigate the tunneling and derive structures for a number of small clusters in the far-IR region.[19,21,39−53] The features investigated spectroscopically correspond to some of the intermolecular vibrations, but not all of these intermolecular vibrations have been observed for any arbitrary sized cluster.

The mid-IR vibrational spectroscopy of $(H_2O)_n$ is less well characterized.[54−60] In contrast to the VRT spectra, which have narrow, resolvable lines, the mid-IR spectra obtained do not have resolvable rotational structure and are not well separated with cluster size. Mass specific information in the mid-IR has typically been obtained by conventional mass spectrometry which requires ionization of the cluster and measurement of the mass-to-charge ratio. For neutral species such as $(H_2O)_n$, this involves assumptions about ionization pathways. There has been considerable confusion about the assignment of observed spectroscopic features to cluster size and vibrational mode. The work of Huisken et al.[54] has sorted out these complications by using a size selective technique based on scattering rather than assumed ionization pathways. Two types of vibrations are observed for $n = 2-5$. The first is the stretching vibration of free OH bonds or those not involved in a hydrogen bond. These show relatively small shifts to the red with increasing n. The other vibration is the stretching vibration of a bound OH bond, referring to an OH which is participating in a hydrogen bond, and shows larger shifts to the red with increasing n.

In contrast to the far-IR and the fundamental stretching region of the mid-IR, there are several other regions where observations of cluster vibrational spectra have not been reported. The bending vibration in the gas-phase monomer occurs at 1600 cm^{-1},[61] and no observations of gas-phase water clusters have been reported in this region. In addition, intermolecular vibrations extend higher in energy[16] than Saykally's VRT spectra at ∼150 cm^{-1}. No observations have been reported between ∼250 and 1000 cm^{-1} where additional intermolecular vibrations are predicted by ab initio calculations[16] to occur. Combinations and overtones of the stretching vibrations as well as combinations of stretches with bends and intermolecular vibrations have not been reported for gas-phase clusters either.

The lack of experimental information is related to the experimental techniques used previously in both the far-IR and mid-IR. Spectra of various sized water clusters using Fourier transform infrared (FTIR) absorption are reported here. The broad spectral coverage and accurate intensity information associated with FTIR spectrometry allows observation of all

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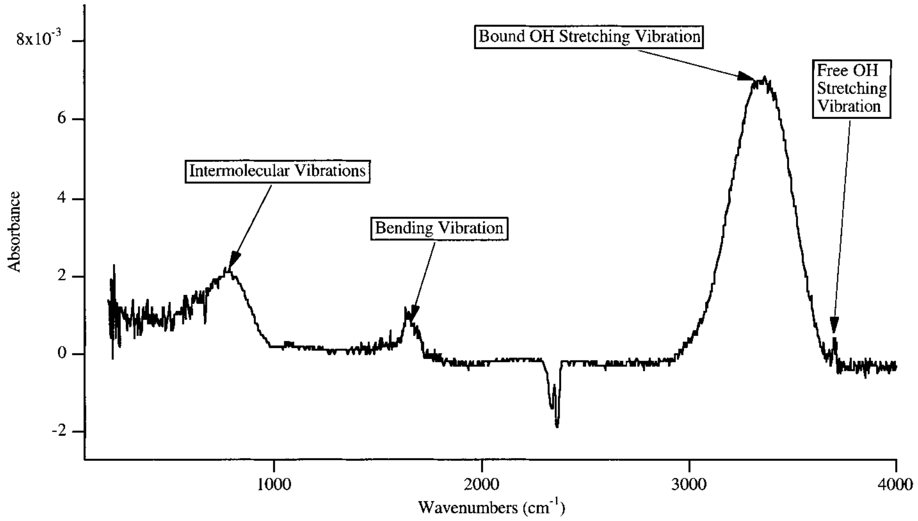

Figure 1. Observed spectrum of water clusters**.** The negative going peak at 2350 cm^{-1} is an artifact due to unpurged CO_2 in the spectrometer.

the fundamental bands while also allowing the intensities of vibrational overtones and combinations to be compared to those of the fundamentals. This new information can be used in modeling the atmospheric effects of water clusters.

Experimental Approach

Since only small numbers of clusters are present at ambient atmospheric conditions, supersonic expansion techniques were used to dynamically prepare cluster samples. Despite the fact that expansions are highly nonequilibrium environments with ill defined concentrations and path lengths, they are a powerful tool for preparing and studying clusters.[62−64] The high collision region at the opening of the nozzle and the low temperatures achieved by rotational and translational cooling both enhance cluster formation. Expansions can therefore be used to prepare relatively dense cluster samples and a variety of experimental techniques can be coupled to the expansion to probe the cluster sample.

These experiments were performed at the Pacific Northwest National Laboratories' High-Resolution IR Spectroscopy laboratory. The PNNL system has exceptional pumping throughput (600 Torr L per s at 0.1 Torr). The spectrometer used was a Bruker IFS120 with a maximum resolution of 0.0015 cm^{-1}. Sources included a quartz-halogen lamp or a globar with either a KBr or CaF_2 beam splitter. Detectors included either an InSb photodiode or a midrange MCT. The collimated light output of the interferometer is passed through a Gregorian type telescope to reduce the optical beam diameter and then sent through the expansion source sample chamber before being focused on the detector with an infrared compatible lens. The pumping system, housed in a separate room, has a pumping speed of 6000 L/s and consists of four Roots blowers in series backed by a large mechanical pump. Higher pumping speed results in the ability to achieve higher number densities of clusters or allows a lower rotational temperature to be achieved for an increased backing or stagnation pressure. In our case, signal was optimized by increasing the cluster number density at relatively low stagnation pressures. To this end, a 4 cm × 50 micron slot was used with the light being passed parallel to and through the long axis of the expansion gas.

For most experiments, argon was used as the carrier gas and regulated by an MKS mass flow controller. The flow controller was protected against backflow of liquid water by an empty bubbler. Water vapor was produced in a ~2 L metal boiler that was heated with heating tapes and powered by several Variacs. The transfer line and nozzle were also heated, and the nozzle temperature was monitored with a thermocouple. Other carrier gases tested included He and N_2. A wide variety of expansion conditions was examined using both the slot nozzle and a round nozzle of 1.2 mm diameter as well as backing pressures from 500 Torr to 3 atm. Spectra obtained with other sets of conditions showed the same features, but a 3:1 mixture of Ar/H_2O gave the largest signals in the 3000−4000 cm^{-1} region. Additional spectra obtained at other conditions with another experimental system are reported in ref 65 as well. None of these observations change the conclusions discussed below. Utilizing the FTIR spectrometer's wide spectral range, the 3000−4000 cm^{-1} region was first probed in order to characterize the fundamentals associated with water clusters and later compared to other spectral regions.

Results

A representative absorption spectrum is shown in Figure 1. This spectrum was taken with 8 cm^{-1} resolution and 200 coaveraged scans. The Ar backing pressure was 2.2 atm with a corresponding chamber pressure of 0.6 Torr. For this particular spectrum, the mid-band MCT, KBr beam splitter, and globar were used and allowed a useful range of 500−8000 cm^{-1}. Four features are observed simultaneously in this spectrum with no features observed between 4000 and 8000 cm^{-1}.

The two features at 3335 and 3703 cm^{-1} are assigned as the bound and free OH stretching vibrations, respectively, and are in agreement with Huisken et al.[54] The feature at 1658 cm^{-1} is assigned as the bending vibration. This vibration has not previously been observed in the gas phase and is consistent with the matrix cluster spectra as well as the gas-phase monomer spectrum. The feature at 779 cm^{-1} is assigned to an unresolved group of intermolecular vibrations by comparison with ab initio calculations of intermolecular vibrations at large n.[9,16,23−26]

The absence of combination and overtone vibrations in the 4000−8000 cm^{-1} region indicates that these are too weak to be observed for the clusters sizes in this sample. In the water monomer, the first combination is about 12% as strong as the stretching fundamental.[66] In liquid water, the first combination is only about 0.4% as strong.[67] The signal-to-noise ratio in Figure 1 can be used to calculate an upper limit on the relative strength of the first combination for the cluster sample in question. We estimate that the first combination is no more than

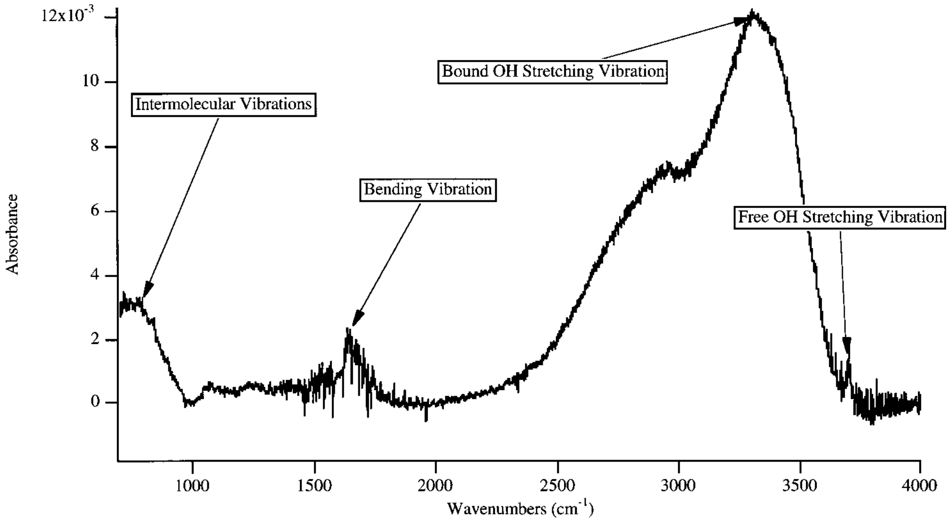

Figure 2. Observed high-resolution spectrum of water clusters. The sharp negative going lines at 1600 cm^{-1} are an artifact due to H_2O monomer in the unpurged portion of the spectrometer.

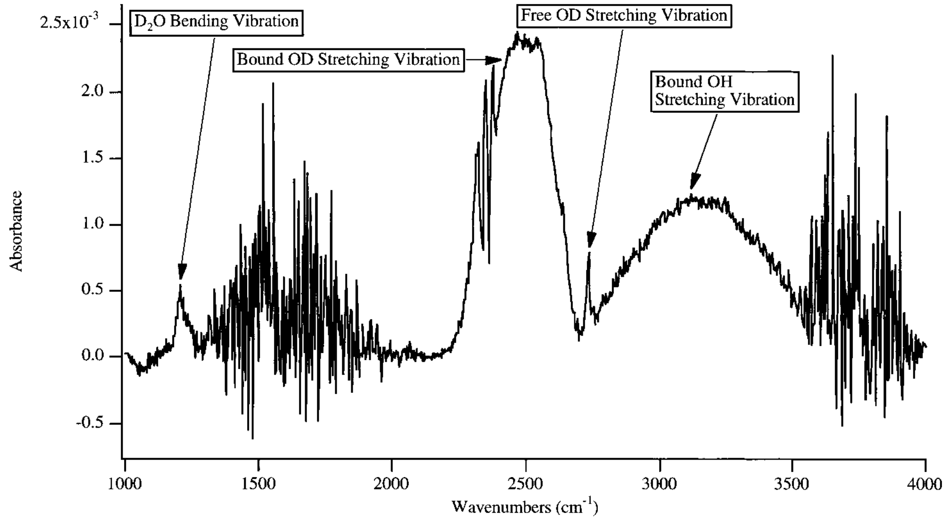

Figure 3. Observed spectrum of D_2O clusters. The negative going peaks at 2350 cm^{-1} and the sharp lines at 1600 and 3750 cm^{-1} are artifacts due to unpurged CO_2 and H_2O in the spectrometer.

2% as strong as the bound OH stretch. This is consistent with a cluster size between the monomer and liquid water.

The bending vibration and intermolecular vibrations are below the binding energy of the dimer (4.95 kcal/mol or ~1730 cm^{-1}) and thus are not expected to be dissociative with lifetime broadened lines. Figure 2 shows a spectrum obtained at 0.03 cm^{-1} resolution and conditions similar to those of Figure 1. While the general features of the spectra obtained do not vary, the existence of small shoulders, such as the one at 3000 cm^{-1} in Figure 2, varies with small changes in experimental conditions which lead to changes in the exact cluster distribution. There is no resolvable structure in either the 1658 or 779 cm^{-1} feature of Figure 2. This may be due to the specific cluster sizes being produced in our expansion or severe spectral congestion.

To eliminate complications due to tunneling, similar experiments were conducted using D_2O in place of H_2O. Figure 3 shows a representative spectrum at 8 cm^{-1} resolution. Higher resolution spectra at 0.03 cm^{-1} were also recorded, but no rotational structure could be observed and the features appeared diffuse like those of H_2O. If the cluster features were distinguishable with respect to cluster size and did not overlap, the mixed D_2O/H_2O technique used by Saykally et al.[19,40,43,45] could be used to establish the size of the clusters.

Discussion

The difficulty of assigning cluster sizes to our jet samples, which imposes limitations on the application of these results to atmospheric radiative transfer, will be discussed. A comparison to existing literature on the vibrational spectroscopy of clusters will be made. Finally, comparisons will be made to bulk solid and liquid H_2O as well as thin ice films.

Cluster Size. In the absence of discrete assignable transitions, direct absorption spectroscopy does not allow an exact determination of the cluster sizes. This is the case for the spectra reported here, and the cluster sizes must be inferred by other means. If the clusters were large enough to show bulk liquid behavior, the free OH stretching vibration would not be observable. The ratio of free OH band strength to bound OH band strength for the dimer is calculated to be 0.96.[3] Similar ratios for the trimer and tetramer are 0.71 and 0.31.[9] The ratio for the clusters observed in Figure 1 is 7.6×10^{-3}. This clearly suggests that these clusters contain more than a few water molecules but not enough to show liquid behavior. Based on these considerations and the experimental conditions used, these clusters are assigned as being composed of 10−100 waters. There is evidence for enhanced stability of clathrate-type structures in water cluster ions (see, for example, refs 68 and 69). The size distribution of the clusters in these experiments may reflect the stability of these structures.

Comparison to IR Literature on Clusters. The existing literature on the vibrational spectroscopy of water clusters can be divided into two groups, covering mid-IR and far-IR. The features observed between 3000 and 4000 cm^{-1} here are similar to those observed by Huisken et al.,[54] Coker et al.,[55] and Vernon et al.[56] The excellent size-resolved spectra of Huisken et al. show the same two types of features: free and bound OH stretching vibrations.[54] The largest cluster observed by Huisken et al., the pentamer, has a bound OH feature at 3360 cm^{-1}. The extension of the bound OH feature to ~2815 cm^{-1} in Figure 1 is consistent with the presence of much larger clusters. Huisken et al. have also shown that the preceding literature has been contaminated by contributions from larger clusters[54] (as described in the Introduction). The shapes of the reported spectra can be compared to that observed in Figure 1 even if the size assignments are incorrect. The work of Coker et al. clearly demonstrates the effect of decreasing the percentage of H_2O in the expansion.[55] Figures 1 and 2 of Coker et al. show a narrowing of the bound OH feature and a moderate shift to the blue of the absorption maximum.[55] The relatively concentrated expansion of about 25% water probed in Figure 1 can be compared to spectrum 1B of ref 55. Spectrum 1B of ref 55 is truncated at 3000 cm^{-1}, and the signal, while decreasing, is not back to zero, suggesting that it extends to lower frequencies consistent with the spectrum reported here in Figure 1. The relative strengths of the features are clearly different, possibly because of expansion parameters such as throughput, nozzle geometry, height probed, etc. The spectra of Vernon et al.[56] show perhaps the least similarity in this region. Their bound OH features appears to have three distinct components of varying contribution for different mass signals. The work of Page et al. probes a smaller cluster size range than our spectra but is consistent with the presence of both bound and free OH which they observed at 3600, 3545, 3730, and 3714 cm^{-1}.[57]

There are no spectroscopic observations in the literature of gas-phase clusters of any size in the 1600−1700 cm^{-1} region. The spectrum shown in Figure 1 represents the first observation of the gas-phase bending vibration in a water cluster. Work involving the matrix isolation spectra of water has reported observations of the bending vibration in this region for N_2 and Ar matrices. Ayers and Pullin show how decreasing the matrix-to-absorber ratio (M/A) changes the absorption features[70] in the range of the free OH and bound OH stretching regions. Decreasing M/A gives a more concentrated matrix that is more likely to contain larger clusters. Observations over the same M/A range in the bend region clearly show that the effect on the bend is to broaden the features and fill in the spaces between but not to extend the range of the features to higher or lower energies.[70] Bentwood et al. show the same trends.[71] The position of the bending vibration is therefore not very sensitive to cluster size, consistent with ab initio calculations. This means that for a wide variety of experimental conditions, the position of the bending vibration does not change very much.

The intensity of the bending vibration with respect to the bound OH is relatively small for this (10−100) cluster size range. This is qualitatively consistent with differences in cluster structure. The matrix data of Ayers and Pullin[70] is the only quantitative data and suggests that this is not the case for the cluster sizes observed in those experiments. Qualitatively it appears that in the matrix spectrum of ref 70, the strength of the bending feature is closer to the strength of the stretching vibration. The ratio of the ab initio band strengths for the bend and bound OH stretch is 0.9 for the dimer,[3,5] 0.3 for the trimer, and 0.07 for the tetramer.[9] The corresponding ratio for the clusters in Figure 1 is 0.05.

The observation of the intermolecular vibrations in Figure 1 is at a very different energy than the vibration−rotation-tunneling spectroscopy of Saykally et al.[41,43,44,46,50,72] and the matrix spectra of ref 71. A comparison can be made to ab initio calculations of positions for some of the larger clusters. The work of Xantheas[16] gives intermolecular vibrational energies for the hexamer that reach as high in energy as 990 cm^{-1} as calculated with density functional theory. By comparison, some energies for the tetramer calculated with density functional theory are larger than energies calculated at the MP2 level,[16] suggesting that this 990 cm^{-1} position for the hexamer may be somewhat high in energy. A position lower in energy would be more comparable to the upper limit of our observed intermolecular vibrations at 949 cm^{-1}. Cluster structural parameters such as the interoxygen distance converge to solid and liquid values at $n = 6$. It is thus reasonable to suggest the intermolecular vibrations will not go higher in energy for larger clusters since the hexamer has reached an interoxygen distance comparable to the bulk.[9]

Comparison to Bulk Liquid and Solid and Thin Ice Films. The spectrum in Figure 1 was compared to the bulk solid and liquid spectra of refs 67 and 73. The comparison between solid/liquid and observed clusters is easiest to make for the bend. The position of maximum absorption is very similar for all three, ~1640 cm^{-1}. The line widths are comparable for the liquid and observed cluster, ~80 cm^{-1}, but the ice is somewhat wider, ~200 cm^{-1}. The broad bound OH feature is also comparable for solid, liquid, and observed clusters, with a fwhm of 400 cm^{-1} and absorption maximum at ~3300 cm^{-1}. As expected, the bulk solid and liquid also show no free OH stretching vibration.

Thin films of ice, however, have been observed to have a low intensity free OH feature.[74] This is attributed to OH bonds that “dangle” off the surface,[74] analogous to the free OH bonds exposed in the gas-phase clusters. The larger the number of molecules, the fewer the number of free OH bonds compared to the total OH bonds. The clusters observed in Figure 1 represent an interesting intermediate point between thin films and small clusters. Schaff and Roberts have made a detailed study of the differences in surface properties between crystalline and amorphous ice films.[75] They concluded that the surface chemistry is different, probably because the crystalline surface has a poorer hydrogen bond donor ability. Zondlo et al. have also studied these dangling OH bonds and suggested that they are indicative of the surfaces of micropores present within amorphous ice.[76]

The region of the observed cluster spectrum between 500 and 950 cm^{-1} has been assigned to intermolecular vibrations. In the gas-phase monomer, only very high J rotational lines occur here. In the liquid and solid, diffuse librations occur in this region. The intermolecular vibrations of the observed clusters are motions of one or more molecules with respect to the others. Jung and Gerber calculate displacements for these vibrations.[77] They have probed the effects of anharmonicity of the fundamental vibrations and determined that the positions of these intermolecular vibrations are sensitive to the inclusion of the anharmonicity.[77]

Conclusions

Experiments have been reported that provide vibrational information on water clusters which is complementary to that already reported in the literature. The spectra reported are the only ones available for clusters of water where all fundamental vibrational features are obtained with accurate relative intensities. The wide frequency range of Fourier transform spectrometry has allowed simultaneous observation of four vibrations of water clusters, including two not previously observed. The relative strengths of these features have been measured.

While the spectra are not sufficiently sensitive to size for specific size assignments to be made, the size range for these samples is likely to be in the range of 10−100 waters. The cluster sizes in our samples preclude direct application of these results to the atmosphere. However, the data does constrain the range of intensities of water clusters that could be used to model this effect in radiative transfer. Examination of these vibrational features and comparison to similar features for solid and liquid water suggests that these clusters show behavior intermediate between small clusters such as the dimer and bulk condensed phase samples.

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