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Theoretical IR Spectra for Water Clusters $(H_2O)_n$ ($n = 6-22, 28, 30$) and Identification of Spectral Contributions from Different H-Bond Conformations in Gaseous and Liquid Water

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The vibrational IR spectra in the O−H stretching region are computed for water clusters containing 6−22, 28, and 30 molecules using quantum-chemical calculations (B3LYP and an augmented basis set). For the cluster with 20 molecules, several different structures were studied. The vibrational spectrum was partitioned into contributions from different molecules according to their coordination properties. The frequency shifts depend on the number of donated/accepted H-bonds primarily of the two molecules participating in the H-bond, but also of the surrounding molecules H-bonding to these molecules. The frequencies of H-bonds between two molecules of the same coordination type are spread over a broad interval. The most downshifted hydrogen-bond vibrations are those donated by a single-donor 3-coordinated molecule where the H-bond is accepted by a single-acceptor molecule. The H-bonded neighbors influence the downshift, and their contribution can be rationalized in the same way as for the central dimer. Single donors/acceptors cause larger downshifts than 4-coordinated molecules, and the least downshift is obtained for double donors/acceptors. This result is at variance with the conception that experimental liquid water spectra may be divided into components for which larger downshifts imply higher H-bond coordination. A mean spectral contribution for each coordination type for the donor molecule was derived and fitted to the experimental liquid water IR spectrum, which enabled an estimation of the distribution of H-bond types and average number of H-bonds (3.0 ± 0.2) in the liquid.

1. Introduction

The experimental IR spectra of liquid water can to a good approximation be described by three Gaussian components in the O−H stretching region.[1] Brubach et al.[2] and Czarnik-Matusewicz et al.[3] assigned these components to water molecules with different numbers of hydrogen bonds. The most downshifted frequencies were assigned to molecules that participate in the largest number of hydrogen bonds. The conjecture was that in this way information could be obtained about the H-bond coordination and thereby the structure in liquid water. Buch et al.[4,5] performed molecular dynamic simulations using analytical potential models and computed vibrational spectra for water clusters of increasing sizes[4] and for liquid water.[5] The spectra were split into the contributions from water molecules with different kinds of coordination. It was found that the most downshifted frequencies correspond to H-bonds where the donor molecule is 3-coordinated and donates only this hydrogen. Ohno et al.[6] calculated frequencies for clusters with up to 8 molecules using quantum-chemical B3LYP/6-311++G(d,p) calculations and studied the downshift dependence on the coordination of the donor and acceptor molecule, which followed the same trend as seen in the study by Buch.[5] For dodecahedron-shaped water clusters, the OH-vibrational frequencies can be analyzed in a similar way.[7] Several other quantum-chemical studies of vibrational spectra of larger water clusters have been performed.[8−12]

In the present study, we study vibrational spectra of large water clusters of different sizes and investigate which kind of H-bond configurations contribute to the different features in the spectra. IR spectra for clusters with 6−22, 28, and 30 molecules are computed using quantum chemical methods. For the clusters with 20 molecules, several oxygen frameworks as well as H-bond topologies are studied. The vibrational modes are analyzed with respect to the coordination of both donator and acceptor molecules participating in the hydrogen bond. From extrapolation of the variation of spectral appearance with respect to increasing cluster size, conclusions are drawn also regarding the spectral shape and H-bond coordination, such as average number of H-bonds, of the liquid.

2. Method

IR spectra are calculated for clusters with 6−22, 28, and 30 water molecules using the Gaussian 03 program,[13] the B3LYP[14,15] method, and an augmented split-valence basis set. This basis set is equivalent to the aug-cc-pVDZ basis set[16,17] except that the diffuse p-functions on the hydrogen atoms have been removed. The 6−22 initial structures are taken from our earlier study[18] of clusters with up to 22 molecules. In the present study, we use the reoptimized structure with the lowest aug-cc-pVDZ energy (this structure is lowest also with the present basis set).

In particular for the cluster with 20 molecules four dodecahedral clusters, two fused-prism clusters and one cluster derived from a liquid water simulation are analyzed (Figure 1). The dodecahedral clusters are the proposed non-symmetric energy minimum (for that particular oxygen skeleton) structure[19] and structures with symmetries C_i,[19] C_5,[20] and S_{10}.[19] A cluster with an oxygen framework shaped as a fused prism is probably the global energy minimum structure[21] for clusters comprised of

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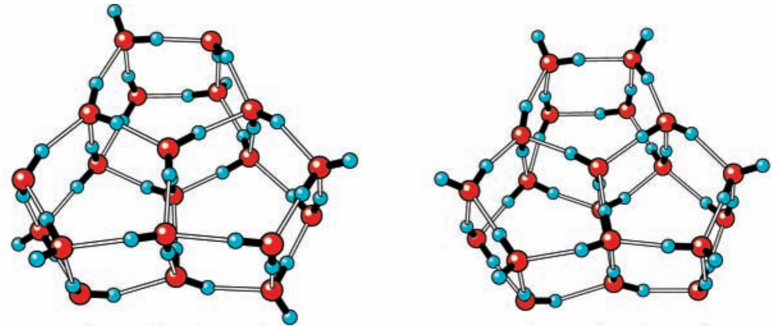
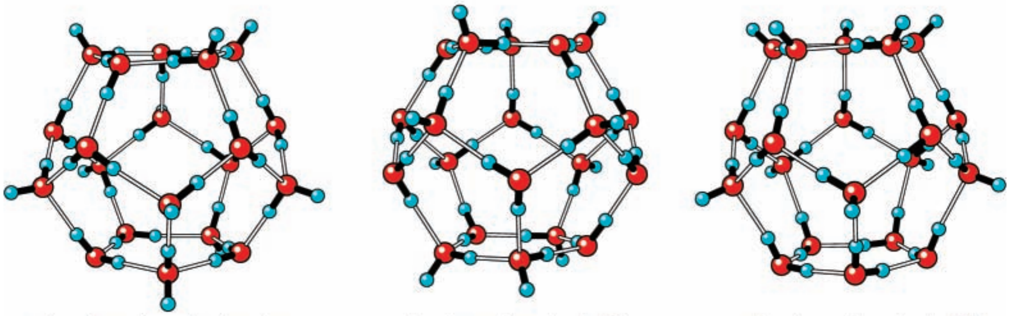
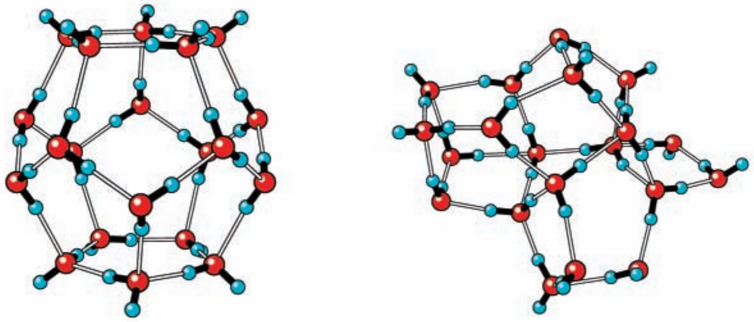


fused prism 1 fused prism 2



dodecahedral min dodecahedral Ci dodecahedral C5



dodecahedral S10 "liquid" cluster

Figure 1. The seven structures with 20 water molecules. For the geometries for the clusters with 6−22 molecules, see ref 18.

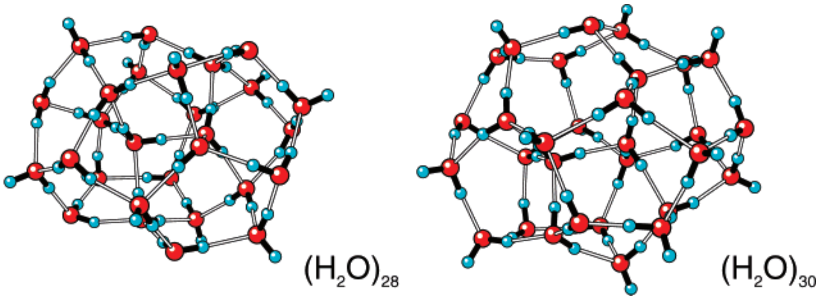


Figure 2. The structures for the $(H_2O)_{28}$ and $(H_2O)_{30}$ clusters.

20 water molecules, and one of the fused-prism clusters used here is that of energy minimum H-bond topology.[21] An alternative H-bond topology for the fused-prism cluster was constructed by switching the direction of some H-bonds (see Figure 1). The "liquid" cluster was obtained by extracting a cluster of 20 molecules from a CPMD[22] liquid water simulation[23] followed by geometry-optimization of the cluster to the nearest local energy minimum.

The clusters with 28 and 30 molecules (Figure 2) were constructed to have two 4-coordinated molecules inside a cage of 26 and 28 molecules, respectively; that is, 8 of the molecules are 4-coordinated whereas the others are 3-coordinated,[24] and their H-bond network was chosen approximately to give as low energy as possible according to the rules in ref 18.

The O−H vibration IR spectra are divided into contributions according to the coordination of the water molecules participating in the H-bond. The O−H vibrations of the cluster molecules are divided into five groups, those involving: (1) non-H-bonded hydrogens (hereafter referred to as "free hydrogens"); (2) the H-bonded hydrogen in 2-coordinated molecules; in the present clusters, all 2-coordinated molecules are single donors; (3) hydrogens in 4-coordinated molecules; (4) hydrogens in 3-coordinated molecules where both hydrogens are donated (double donor, "DD"); and (5) the donated hydrogen in a 3-coor-

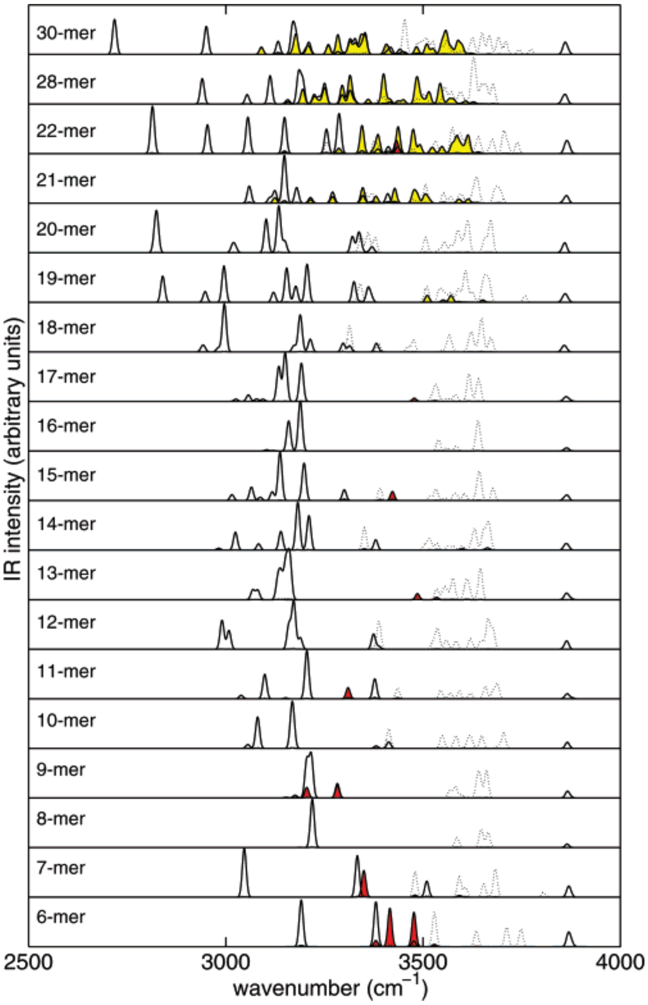


Figure 3. IR spectra for clusters with 6−22, 28, and 30 molecules (using the energy minimum dodecahedral structure for the cluster with 20 molecules). The spectra are split into contributions from free hydrogens, at ~3900 cm^{-1}, 3-coordinated double donors (dotted line), 2- and 4-coordinated molecules (filled red/yellow for 2/4-coordinated, respectively), and 3-coordinated single donor molecules (solid line) at the lowest frequencies.

dinated molecule where the other is a free hydrogen (single donor, "SD").

Using the eigenvalues from the normal-mode calculations, the normal modes are projected onto the coordinates of the hydrogens belonging to each group (eigenmodes projected onto the oxygen atoms do not contribute to the spectra in the studied interval of 2500−4000 cm^{-1}). For the $(H_2O)_{21}$ cluster, in addition, a more detailed study was performed. The frequencies for the hydrogen bonds are classified according to characteristics of both the donor molecule (4-coordinated, 3_{DD} or 3_{SD}) and the acceptor molecule (4-coordinated or 3-coordinated single acceptor, "SA", or double acceptor, "DA"). A similar study of fingerprints of hydrogen bonds in IR spectra has been carried out for different geometrical shapes of water clusters with 12 and 20 molecules.[8] Note also the investigations of the influence from H-bond topology on the OO-distances described in ref 20.

3. Results and Discussion

3.1. Spectral Fingerprints of H-Bond Coordination.

3.1.1. Variation with Cluster Size. The IR spectra for clusters with 6−22, 28, and 30 molecules are shown in Figure 3. For the cluster with 20 molecules, the dodecahedral energy minimum cluster, rather than the fused-prism cluster, is displayed in Figure 3 to facilitate comparison with the 21-/22-mer, whose structures are based on the dodecahedral structure. For all clusters, the O−H stretching vibrations of the free hydrogens give rise to a spectral peak near 3870 cm^{-1}. This is in agreement with earlier studies of vibrational spectra of free hydrogens in clusters of several sizes.[25,26] The vibrations of hydrogens in 3-coordinated molecules correspond to vibrations in two regions. These can be related to 3_{SD}-vibrations at lower frequencies, 2700−3400 cm^{-1}, and 3_{DD}-vibrations at 3500−3700 cm^{-1}. The OH-frequencies from hydrogen bonds donated by 2- and 4-coordinated molecules lie between the frequencies of 3-coordinated molecules, 3100−3700 cm^{-1}. The liquid water MD study by Buch[5] shows the same order for donor molecules, from low to high frequencies: 3_{SD} (3180−3500 cm^{-1}), 2-coordinated (3250−3600 cm^{-1}), 3_{DD} (3400−3700 cm^{-1}), and free hydrogens around 3700 cm^{-1}. In that simulation, most molecules were 4-coordinated, and hence the peak for these molecules dominated for almost all frequencies. In a study of dodecahedral clusters by Anick,[7] the frequencies for 3_{SD}-, 3_{DD}-coordinated molecules found were 2000−3500 and 2700−3700 cm^{-1}, respectively, where the main part of the frequencies lies at higher wavenumbers. In the study by Ohno et al.[6] of small clusters with up to 8 molecules, the frequencies found were 3000−3400, 3500−3700, and 3100−3700 cm^{-1} for 3_{SD}-, 3_{DD}-, and 4-coordinated molecules, respectively. The most downshifted frequencies in clusters with 17−21 molecules have been assigned to vibrations of 3_{SD} molecules.[9,27]

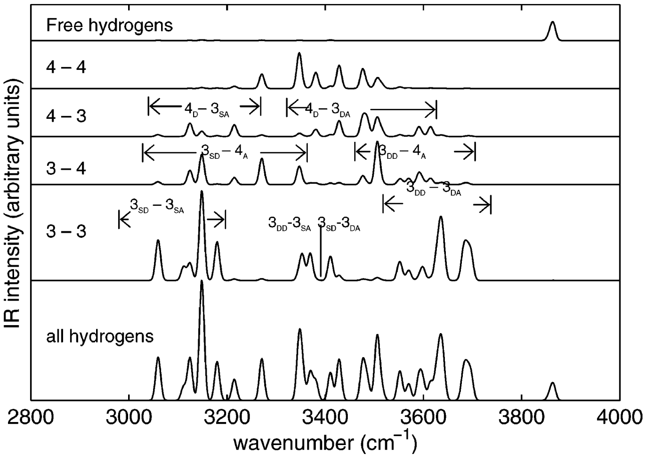


Figure 4. IR spectrum for the cluster with 21 molecules, which is split into the contributions from the different types of H-bond donor and acceptor configurations.

For the cluster with 21 water molecules, where a 4-coordinated water molecule resides in the interior of a distorted dodecahedral structure, the H-bond frequencies are also categorized with respect to the nature of the acceptor molecule (Figure 4). For a given donor type (4-coordinated, 3_{SD} or 3_{DD}), the bonds accepted by a 3_{SA} molecule give rise to the lowest frequencies, whereas H-bonds accepted by a 3_{DA} molecule give the highest frequencies. Hydrogen bonds accepted by a 4-coordinated molecule would have frequencies in between those accepted by 3_{SA} and 3_{DA} molecules.

3.1.2. Analysis of Spectral Band Features. In Figure 3, it is seen that the lowest-frequency peak becomes more downshifted when the cluster size increases. A notable deviation is seen for the cluster with 21 molecules. Here, the most downshifted peaks present in the 20 and 22 clusters are missing. Generally, the most downshifted peak corresponds to H-bonds from a 3_{SD} to a 3_{SA} molecule. To explain the variations in the low-frequency region in the clusters with 19−22, 28, and 30 molecules, one

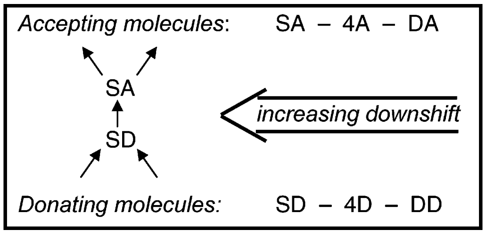


Figure 5. Illustration of the S-4-D series describing the downshift of an O−H vibrational frequency in the IR spectrum. The magnitude of the downshift correlates with the coordination of both the donor/acceptor molecules that participate directly in the H-bond and the H-bonded neighbors of these molecules. The larger is the number of molecules that are single (S) donors/acceptors, the more downshifted the frequency will be. Less downshift is observed for 4-coordinated, and the least is observed for double (D) donors/acceptors.

needs to study how the frequency is influenced by the molecules that donate H-bonds to the central donor molecule (3_{SD}) and by the molecules that accept H-bonds from the central acceptor (3_{SA}) molecule (the "central" dimer encompasses the H-bond whose OH-stretching frequency is studied). The frequency is most downshifted if the two molecules donating to the donor molecule in the H-bond are of type 3_{SD} and the two molecules accepting H-bonds from the acceptor molecule are of type 3_{SA}. The downshift will be less if the donor or/and acceptor molecules are 4-coordinated (4_D/4_A) and even less if those are 3_{DD}/3_{DA}.

These results can be summarized by a "S-4-D" rule (Figure 5), which states that increasing the proportion of single (S) donating/accepting molecules leads to a larger frequency downshift. The downshift is lower for 4-coordinated and smallest for double (D) donors/acceptors. In fact, the S-4-D-series works also for the central molecules participating in the H-bond (compare Figure 4). For the donor and acceptor molecules, the same trend has been seen in a study of smaller clusters.[6] Because downshifted frequencies correlate with shorter distances,[28] this result agrees with the relation between coordination and short H-bond lengths in ref 20. The numbers of (S, 4, D) types around the $3_{SD}-3_{SA}$ H-bonded pair responsible for the most downshifted peak are (2, 0, 2) for the 19-, 20-mers, (1, 1, 2) for the 21-mer, (1, 2, 1) for the 22-, 28-mers, and (2, 1, 1) for the 30-mer. This is in agreement with the 30-mer having the most downshifted peak and the 21-mer the least. The difference between the 22- and 28-mer is probably due to there being more S-donors/acceptors in the next-nearest neighbor shell for the 22-mer than for the 28-mer.

3.1.3. Hydrogen-Bond Energies. When the interaction energy per water molecule depending on the cluster size is plotted (Figure 6), it can be seen that the energy for the cluster with 21 molecules is lower than that for the nearby cluster sizes (−42.7 kJ/mol for the 21-mer and −41.7 and −41.3 kJ/mol for the 20- and 22-mer, respectively). In these three clusters, the number of hydrogen bonds changes.

Another way to present the energy is the interaction energy per H-bond, which depicts the mean strength of the H-bonds. This gives the energies −27.8, −26.4, and −26.0 kJ/mol for the 20-, 21-, and 22-mer, respectively. This means that the hydrogen bonds (on average) are most stable in the pure 3-coordinated 20-mer. The low-energy per water molecule for the cluster with 21 molecules is a result of the high average number of hydrogen bonds per water molecule that is 3.24, to be compared with 3.00 and 3.18 for the clusters with 20 and 22 molecules, respectively.

3.1.4. Variation with Cluster Conformations. To study more in detail the effect on the spectral shape of both the H-bond arrangement as well as the general oxygen framework, the 20-molecule cluster was put into focus, and a comparison of the energies and spectra of the seven different 20-molecule structures in Figure 1 was made.

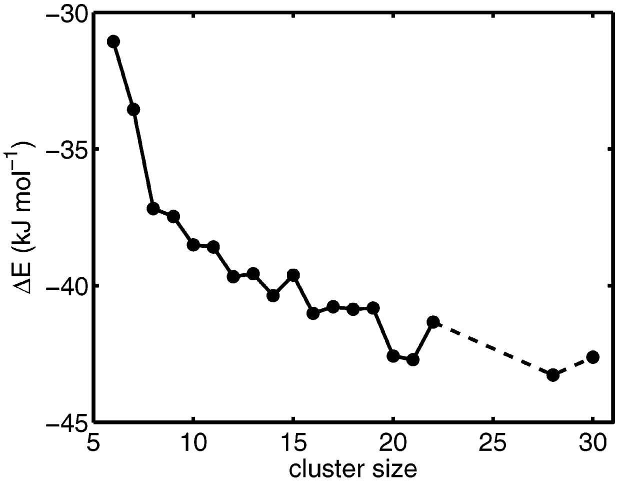


Figure 6. Interaction energies per water molecule for the clusters studied. (The 20-molecule cluster energy is that of the fused-prism energy minimum structure.)

The optimized energies are −41.7 and −42.6 kJ/mol for the energy minimum structure for the dodecahedral and fused-prism clusters, respectively. The energies for the dodecahedral clusters are −41.1 kJ/mol (C_i symmetry), −37.5 kJ/mol (C_5), and −36.5 kJ/mol (S_{10}), respectively. The energy of the fused-prism structure with the modified H-bond arrangement is −39.9 kJ/mol, 2.7 kJ/mol higher than for the minimum topology. The "liquid" cluster is slightly higher in energy, −39.1 kJ/mol, but is considerably lower in energy than the high-symmetry dodecahedral structures.

Studying the spectra for the different 20-molecule clusters, Figure 7, it is seen that the IR spectra for the two low energy dodecahedral clusters are similar, whereas the most downshifted frequencies are missing for the C_5 and S_{10} structures. The missing most downshifted 3_{SD}-frequencies in the C_5, S_{10}, and the second fused-prism spectra can be rationalized by that in these structures all 3_{SD} molecules are placed in adjacent positions, which gives rise to something similar to a sterical repulsion between the non-hydrogen-bonded hydrogens. This is also of relevance for the auto ionization phenomena in water clusters.[20] The S-4-D rule is valid also for these clusters.

3.2. Analysis of the Liquid Water Spectra. We have calculated vibrational spectra for increasing cluster sizes and it is interesting to use this information to extrapolate to the limit of infinite clusters, that is, the infrared spectrum of liquid water. The IR spectrum of liquid water has been deconvoluted into Gaussian-shaped contributions from three different H-bonding situations by Brubach et al.[2] and Czarnik-Matusewicz et al.[3] We note that the so-obtained frequency distribution with respect to molecules with varying number of H-bonds does not agree with the S-4-D rule obtained from our water clusters. We therefore try a simplistic approach to estimate the contributions to the liquid water spectra from the coordination types. Mean spectra for each coordination type of the donor molecule were derived using the frequencies from the energy minimum structures. These mean spectra were then fitted to the experimental liquid water spectra.[2] Thermal and disorder effects cause an intermediate bonding situation that will affect the frequencies. Fitting mean spectra from cluster calculations to the liquid water spectrum will thus be a crude model, but it constitutes an illustrative first-order approximation.

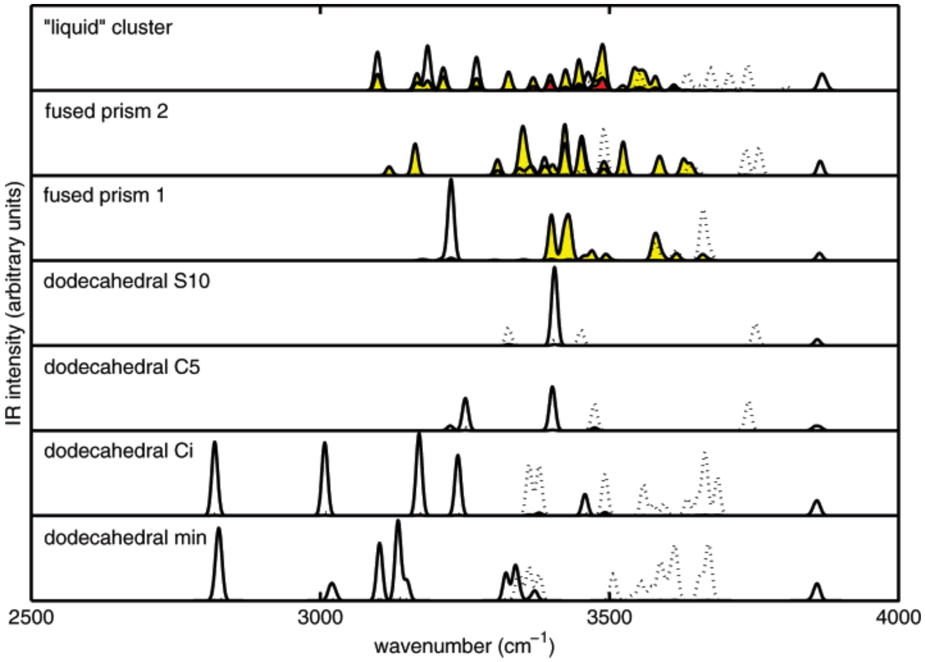


Figure 7. IR spectra for the different structures with 20 molecules. The spectra are split into contributions from free hydrogens, at ~3900 cm^{-1}, 3-coordinated double donors (dotted line), 4-coordinated molecules (filled yellow), and 3-coordinated single donor molecules (solid line) at the lowest frequencies.

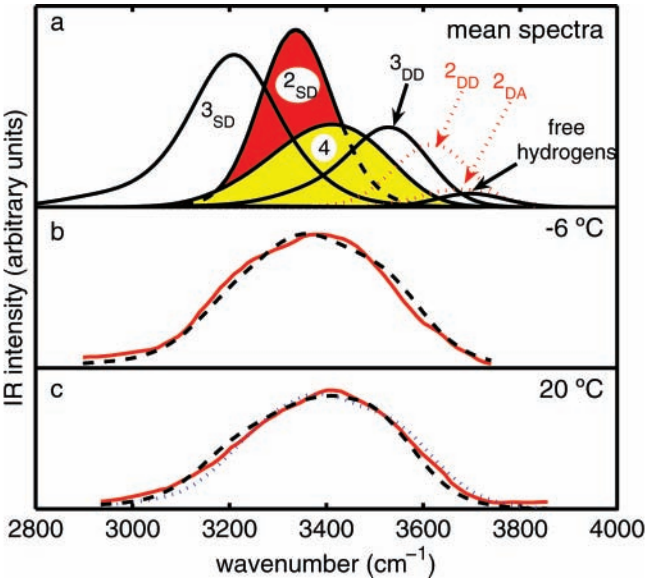


Figure 8. (a) IR intensity versus frequency distribution per OH oscillator, for the different coordination types. The wavenumbers are scaled using the formula $\nu_{\text{scaled}} = \nu_{\text{calc}}*(1.2630 - 7.9305*10^{-5}*\nu_{\text{calc}})$. (b) Experimental spectra[2] of liquid water (red line) and fitted spectra using the mean spectra for each coordination type with scaled frequencies (black dashed line) at −6 °C and (c) 20 °C. The downshifts of the mean spectra with the scaled frequencies were reduced by 10% in the fit shown as the blue dotted line at 20 °C.

The mean spectra are constructed by summing intensities for each coordination type from the studied clusters and then normalizing them by division by the total number of OH oscillators (Figure 8). For the cluster with 20 molecules, the energy minimum structures for the dodecahedral and fused-prism clusters are used, and the results are compared to a calculation including all 20-mers. To get better statistics for the 2-coordinated molecules, frequencies for ring-shaped clusters with 6, 7, and 8 molecules were included in the mean-spectra calculations. The 2-coordinated molecules in all of these clusters are single donors. Therefore, additional computations on clusters with 9, 13, and 19 molecules (see Supporting Information) were made, and, from these, frequencies for 2_{DD} and 2_{DA} molecules were also included in the mean spectra. The calculated frequencies were scaled to agree with the experimental frequencies in the gas phase and the H-bonded OH-band for the $(H_2O)_6$ ring-shaped cluster.[6] Each frequency is convoluted by a Gaussian function, and the sum of these functions constitutes a peak for this coordination number. The width of the Gaussians (165 cm^{-1} at half-height) was adjusted to give the best fit to the experimental spectra from Brubach et al.[2] Thermal motion is likely to distort the H-bond geometries away from the optimal straight geometries present in our calculations. To minimize the influence from this complication, we fit to the experimental liquid spectrum at the lowest temperature available,[2] −6 °C. The fit is made under the restriction that all donated H-bonds are also accepted and that the ratio of each coordination type should be greater than or equal to zero.

From the fit in Figure 8, we get an estimation of the amount of molecules that are 2-, 3-, and 4-coordinated, and from this the average number of H-bonds can be calculated. The mean number of H-bonds in liquid water differs widely in different studies,[2,5,29−32] lying roughly between 1.5 and 3.6 H-bonds per molecule, depending on the measurement method used and on the definition of an H-bond. Using the scaled frequencies at −6 °C gives an average number of H-bonds per molecule of 3.1 ± 0.2 (20%, 53%, and 27% for 2-, 3-, and 4-coordinated molecules, respectively). All 2-coordinated molecules are 2_{SD} because the contribution from 2_{DD} and 2_{DA} molecules will be reduced to practically zero when fitting to the liquid spectra. At the higher temperature of 20 °C, thermal motion causes a larger amount of bent H-bonds that are not represented in our model, which is why our fitting procedure becomes cruder. For bent H-bonds, the downshift magnitude is likely to be lower, which agrees with that the frequencies for liquid water get less downshifted when the temperature is increased.[33] We note that the center at half-height of the experimental spectra in ref 2 is downshifted by ~10% in the 20 °C spectrum as compared to the −6 °C spectrum. For simplicity, we therefore assume that for all H-bond types the downshift is reduced by 10% due to the thermal motion.

Using these approximate reduced frequencies results in 3.0 ± 0.2 H-bonds on average (21%, 63%, and 17% for 2-, 3-, and 4-coordinated molecules, respectively) at 20 °C. Using the original mean spectra also at 20 °C would give 3.4 H-bonds in average. Including all studied clusters with 20 molecules instead of only the energy minimum structures gives almost the same results: the number of H-bonds is decreased with 0.05 at both −6 and 20 °C. In addition, the H-bond strain present in the small clusters is smaller in larger clusters or in liquid water.[4] Reduced strain implies larger downshift especially for the 4-coordinated molecules, which have energetically unfavorable geometries in the small clusters.[4] Compensating for this effect would probably increase the estimation of the average number of H-bonds in liquid water. These results point to the need for refined models for extracting information on H-bond configurations from vibrational spectra.

4. Conclusions

In the IR O−H stretching spectra of water clusters, hydrogen bonds between 3-coordinated single-donor and single-acceptor molecules are the most downshifted. Hydrogen bonds in 2- and 4-coordinated molecules are intermediate downshifted, whereas H-bonds donated by a double-donor to a double-acceptor give the highest frequencies. Also, the H-bonded neighbors to the donor and acceptor in the H-bond affect the downshift of the frequencies. These follow a general trend, which can be described by a S-4-D rule. If these results are valid also in the limit of infinite clusters, these results contradict the H-bond coordination of the molecules assigned to the three Gaussians fitted to the experimental spectra of liquid water.[2,3] Fitting a mean spectrum for each coordination type of the donor molecule gives a fair agreement with the experimental liquid water spectrum at −6 °C, resulting in 3.1 H-bonds on average per water molecule. At the temperature 20 °C where the H-bonds are further distorted due to thermal motion, an approximate model gives on average 3.0 H-bonds per molecule in liquid water.

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Supporting Information Available: A data file in Xmol format containing the structural coordinates (in angstroms) for the water clusters seen in Figures 1 and 2, and a data file containing the coordinates for the clusters with $2_{DD}/2_{DA}$ molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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