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Fingerprints in IR OH vibrational spectra of H₂O clusters from different H-bond conformations by means of quantum-chemical computations

Yuan Liu and Lars Ojamäe

Department of Chemistry, IFM, Linköping University, SE-58 183 Linköping, Sweden

Abstract:

The thermodynamic stabilities and IR spectra of the three water clusters (H₂O)₂₀, (H₂O)₅₄, and (H₂O)₁₀₀ are studied by quantum-chemical computations. After full optimization of (H₂O)_{20,54,100} structures using the hybrid density functional B3LYP together with the 6-31+G(d, p) basis set, the electronic energies, zero-point energies, internal energies, enthalpies, entropies, and Gibbs free energies of the water clusters at 298 K are investigated. Furthermore, the OH stretching vibrational IR spectra of water molecules in (H₂O)_{20,54,100} are simulated and split into sub-spectra for different H-bond groups depending on the conformations of the hydrogen bonds. From the computed spectra the different spectroscopic fingerprint features of water molecules in different H-bond conformations in the water clusters are inferred.

1. Introduction

Water is a necessary substance for the origin and sustainability of life, and plays an important role in numerous biological processes, as well as being the foremost solvent in chemical experiments and manufacturing.[1] Clusters of water molecules are subject to many scientific studies due to their importance in atmospheric chemistry, cloud and ice formation, and biochemical processes.[1-8] The exploration of structural and binding properties of water clusters may provide a route to understand bulk water in its liquid or solid phase.[1, 9] Thus many studies have been presented on the structure of water clusters from small to large sizes both experimentally and theoretically.[10-20] For small clusters with up to ten water molecules, most computational *ab initio* investigations predict approximately the same geometries, which are consistent with experimental results.[1, 2, 4, 7, 10, 14] However, for a large cluster, it is still a challenge to obtain the structure that corresponds to the global minimum energy since the conformational space grows exponentially as the size of cluster increases.[1, 5, 21]

Infrared vibrational spectroscopy is often employed in the studies of water both experimentally and theoretically. Experimentally, the IR spectra are being used to identify the geometrical structure of small clusters.[10, 11, 13, 22, 23] At the same time, theoretical IR spectra of water clusters are frequently simulated based on quantum-chemical computations to help determine the molecular structure of water clusters through comparing with experimental results.[5, 6, 24-26] Regarding quantum-chemical studies of vibrations of larger clusters, the IR spectra of different (H₂O)₂₀ isomers were calculated by Fanourgakis et al. at the level of MP2 theory, where they demonstrated the different spectral features for the isomers and that these features could be related to the spectra of their constituent fragments.[25] Lenz and Ojamäe studied the evolution of IR spectra with increasing cluster size for various clusters containing up to 30 molecules by B3LYP hybrid density functional theory, and the contributions to the spectrum from different types of H-bond donor and acceptor configurations were analyzed.[6] Also in that study the spectra of different isomers of (H₂O)₂₀ clusters were compared. Similarly, Li et al. investigated the IR spectra of different structural patterns of the larger cluster (H₂O)₄₂ by BLYP density functional theory calculations.[5] The O-H stretching vibrational frequencies of H₂O are sensitive to the conformations of H-bonds of which the water molecule is a participant, and the IR spectra of bulk water or water clusters depends on the specific H-bond topology in the system.[3, 6] Thus the arrangement of water molecules in bulk water or water clusters can be explored through the spectral fingerprints of water molecules bonded in different H-bond conformations.

In the present study, the IR spectra of the three clusters (H₂O)₂₀, (H₂O)₅₄, and (H₂O)₁₀₀ which we here refer to as a small-, medium-, and large-sized water cluster, respectively, are simulated using quantum-chemical computations at the B3LYP level of theory. Furthermore, the IR spectra are divided into several parts according to the

specific contribution of water molecules connected by the H-bonds with different types of conformations. Then, the different spectroscopic fingerprint features of water molecules bonded by different conformational types of H-bonds in $(\text{H}_2\text{O})_{20,54,100}$ are identified and discussed.

2. Computational details

The coordination geometries in the clusters $(\text{H}_2\text{O})_{20,54,100}$ are the same as those used in previous studies.[2, 3, 6, 7, 17, 27, 28] The widely used dodecahedral water cluster model $(\text{H}_2\text{O})_{20}$ (Figure 1(a)), which notably only contains 3-coordinated (3c) water molecules, is a cavity motif in clathrate hydrates.[8] The water cluster of medium size, i.e. $(\text{H}_2\text{O})_{54}$ (Figure 1(b)), was likewise constructed from a clathrate structure, but six water molecules were added to the interior of the cage so that both 3c and 4-coordinated (4c) water molecules are represented.[7] As for the smaller cluster it lacks symmetry when the hydrogen positions are taken into account. The large $(\text{H}_2\text{O})_{100}$ cluster (Figure 1(c)) also contains both 4c and 3c water molecules.[7] The oxygen framework in the $(\text{H}_2\text{O})_{100}$ cluster is present in reality in the cavity of a polyoxomolybdate crystal structure.[29] As constructed [7] it is of C_i symmetry, which facilitates the computations.

The geometries of water cluster $(\text{H}_2\text{O})_{20,54,100}$ are fully relaxed to find the energy-minimized structures using the hybrid density functional B3LYP [30,31] together with the 6-31+G(d,p) [32] basis set in the Gaussian09 program.[33] Normal-mode computations of the vibrational frequencies and dipole derivatives were performed for the optimized structures. The electronic energies (E) with and without zero point energy corrections (ZPE), internal energies (U), enthalpies (H), entropies (S) and Gibbs free energies (G) at $T=298$ K are computed. Then, the binding energy (ΔE), etc., of water clusters formed from gas-phase water molecules are calculated according the following formula, where $X = E, U, H, S$ or G :

$$\Delta X = (X_{(\text{H}_2\text{O})_n} - n \cdot X_{\text{H}_2\text{O}}) / n. \quad (1)$$

IR spectra of $(\text{H}_2\text{O})_{20,54,100}$ are constructed from the quantum-chemical normal-mode results. Due to both deficiencies in the level of theory used and the neglect of anharmonicity in the normal-mode calculations the computed and experimental frequencies will differ, and generally for larger frequencies the computed frequencies will be red-shifted compared to the experimental.[34] The computed OH stretching vibrational wavenumbers are therefore scaled according to the following formula, which was obtained from least-squares fitting to the experimental [35, 36] versus computed frequencies for small water clusters $(\text{H}_2\text{O})_{2-6}$:

$$\tilde{\nu}_{\text{scaled}} = -472.02 + \tilde{\nu}_{\text{calc}} \cdot (1.4244 - 8.9176 \cdot 10^{-5} \cdot \tilde{\nu}_{\text{calc}}). \quad (2)$$

Since this expression was fitted to experimental frequencies that all were larger than 3100 cm^{-1} , the formula might be less reliable outside of this interval, i.e. for frequencies smaller than about 3000 cm^{-1} .

Each of the three IR spectra in the OH stretching region is split into sub-spectra

for different groups of hydrogen bonds, depending on their local conformations. The groups are defined from the arrangement of H-bonds around the molecule that donate the H-bond, the donor, and around the molecule that accepts the H-bond, the acceptor. More specifically, each group is defined by the number of H-bonds that the donor and acceptor molecules accept or donate. As shown in Figure 2, the H-bonds can be classified as 9 different groups according to specific donor-acceptor cases: (a) SD-SA, (b) SD-DA, (c) DD-SA, (d) DD-DA, (e) SD-4c, (f) DD-4c, (g) 4c-SA, (h) 4c-DA, (i) 4c-4c. The designation “xD-yA” is used for 3-coordinated water molecules and indicates the number of H-bonds x that the donor donates and the number of H-bonds y the acceptor accepts (SD: single donor, SA: single acceptor, DD: double donor, DA: double acceptor). The designation “4c” refers to a 4-coordinated water molecule, either as a donor or as an acceptor. In addition, there is one special group, which is the non-H-bonded hydrogens (referred to as “Free H”).

As each vibrational mode in principle has contributions from all the atoms in a system, the contribution of each atom to the vibrational mode can be quantified by the ratio of the square of the amplitude of the normal-coordinate of that atom to the sum of amplitudes squared of all atoms. This enables us to project out the contribution to the intensity of a given normal mode from atoms of a specific type:

$$I_i^X = \frac{\sum_{j=\text{atom} \in X} C_{x,j,i}^2 + C_{y,j,i}^2 + C_{z,j,i}^2}{\sum_{k=1, \text{all atoms}} C_{x,k,i}^2 + C_{y,k,i}^2 + C_{z,k,i}^2} \cdot I_i. \quad (3)$$

I_i denotes the amplitude of the vibrational mode i ; X represents a group of atoms of a specific type, in our case the hydrogens that participate in H-bonds in one of the H-bond conformation groups, i.e. $X = \text{SD-SA, SD-DA, DD-SA, DD-DA, SD-4c, DD-4c, 4c-SA, 4c-DA, 4c-4c, or Free H}$; $C_{x,j,i}$, $C_{y,j,i}$, and $C_{z,j,i}$ are the amplitudes of normal-mode i for atom j ; I_i^X is the contribution to the IR intensity of normal mode i from the atoms that belong to group X . From the contribution from the hydrogens (the contribution from the oxygens atoms is close to zero) in respective group, the IR spectra of OH stretching vibrational modes are in this way split into 10 individual spectra, similarly as in a previous study of fingerprints of H-bonds in IR spectra.[6]

3. Results and discussion

3.1 Geometric structures and thermodynamic stabilities.

The H-bonded O-O distance of water cluster $(\text{H}_2\text{O})_{20,54,100}$ were analyzed, and the minimum, maximum, and mean values in each cluster are listed in Table 1. The average O-O distance of the three water cluster are quite close, which are 2.76 Å for $(\text{H}_2\text{O})_{20}$, 2.77 Å for $(\text{H}_2\text{O})_{54}$, and 2.75 Å for $(\text{H}_2\text{O})_{100}$. The H-bonding network in $(\text{H}_2\text{O})_{54}$ is more irregular compared to the networks in $(\text{H}_2\text{O})_{20}$ and $(\text{H}_2\text{O})_{100}$, which is reflected by the larger difference (0.43 Å for $(\text{H}_2\text{O})_{54}$, 0.28 Å for $(\text{H}_2\text{O})_{20}$, and 0.32 Å for $(\text{H}_2\text{O})_{100}$) between minimum value and maximum value for that cluster. As listed in Table 1, all the molecules in $(\text{H}_2\text{O})_{20}$ are 3-coordinated, whereas there are 3- and

4-coordinated water molecules in both $(\text{H}_2\text{O})_{54}$ and $(\text{H}_2\text{O})_{100}$, and the mean coordination number of $(\text{H}_2\text{O})_{54}$ and $(\text{H}_2\text{O})_{100}$ are 3.33 and 3.40, respectively.

The absolute value of binding energy of the three water clusters increases when the coordination number or the size of the cluster increases, see Table 2. The ΔE can be taken as a measure of the stability: $(\text{H}_2\text{O})_{100}$, with the largest negative value of ΔE will be the most stable $(\text{H}_2\text{O})_{20}$ the least. The ZPE effect on ΔE can be accessed: it is 24.6% for $(\text{H}_2\text{O})_{20}$, 24.3% for $(\text{H}_2\text{O})_{54}$, and 23.3% for $(\text{H}_2\text{O})_{100}$. The decrease in ZPE probably reflects the lower ratio of non-H bonded hydrogens in the large cluster, since H-bonding lowers the OH stretching vibrational frequency.

The reaction enthalpies, internal energies, entropies, and Gibbs free energies of water clusters formed from isolated water molecules at 298 K were also calculated. The same trend as for ΔE is displayed, i.e. ΔH , ΔU , ΔS and ΔG all decrease as the size of clusters increase. Notably, ΔG is slightly positive for $(\text{H}_2\text{O})_{20}$ and $(\text{H}_2\text{O})_{54}$, but (slightly) negative for $(\text{H}_2\text{O})_{100}$. This could suggest that the $(\text{H}_2\text{O})_{100}$ cluster can be spontaneously formed from isolated water molecules at 298 K and 1 atm. However, the uncertainties in the interaction energies are rather large due to for example limitations of the basis set. In Ref. [3] the basis set effect was investigated for $(\text{H}_2\text{O})_{20}$ clusters and it was seen that using the present basis set compared to using larger basis sets resulted in an underestimation (i.e. too low values) of ΔG by about 1-1.5 kcal/(mol H_2O). The underestimation was about the same for smaller $(\text{H}_2\text{O})_{12}$ clusters. On the other hand, the B3LYP functional overestimated ΔG by about 0.5 kcal as compared to when MP2 was used, why about one kcal should be added to our calculated ΔG in order to get a “corrected” ΔG .

There are several low-frequency modes present in these clusters. Soft modes can in reality correspond to hindered rotations rather than vibrations, which would cause larger entropic contributions. For floppy water clusters this can be important, however in the present cases the cluster structures are quite rigid, where all water molecules are 4-coordinated or 3-coordinated. The low-frequency soft modes thus really are best described as vibrations.

As can be seen from the values of ΔH and ΔS in Table 2, the fact that $(\text{H}_2\text{O})_{100}$ is thermodynamically more stable than the other two clusters is an energetic rather than an entropic effect, as could be expected.

3.2 IR spectra for different cluster sizes and for different groups of H-bonds.

The computed IR spectrum in the OH stretching region for the water cluster $(\text{H}_2\text{O})_{20}$ is shown in Figure 3a. Looking at the different conformations of H-bonds that occur in this cluster, the hydrogen bonds are divided into five groups: SD-SA, SD-DA, DD-SA, DD-DA, and Free H. The OH stretching frequencies of SD groups are generally lower than those of DD groups: the SD-SA group exhibits lower frequencies than the DD-SA group, and the SD-DA group lower frequencies than the DD-DA group. The OH frequencies for the SD-SA, SD-DA, DD-SA, DD-DA groups are located in the range of 2749 – 3098 cm^{-1} , 3263 – 3314 cm^{-1} , 3280 – 3321 cm^{-1} , and

3429 – 3573 cm^{-1} , respectively. Furthermore, if the acceptor of the H-bond is DA, the OH vibrational frequencies are higher than when the acceptor is SA, i.e. the DD-DA group exhibits higher frequencies than the DD-SA group, and similarly the SD-DA group higher frequencies than the SD-SA group. Thus, the OH stretching frequencies are sensitive to the conformations of the participating H-bonds in the water clusters. The OH stretching frequency depends on the strength of the H-bond: the greater the strength of the H-bond, the smaller the OH frequency. Therefore, the split spectra of different groups reflect the varying H-bond strengths. As the OH frequencies of SD-SA group can be found at the lowest-frequency part in the spectra, the strengths of SD-SA H-bonds should be stronger than those of other groups. It is consistent with discussions of how the topology effects the strength of H-bonds.[17] In addition, the free H group exhibits the highest OH vibrational frequencies, higher than 3700 cm^{-1} .

As $(\text{H}_2\text{O})_{54}$ and $(\text{H}_2\text{O})_{100}$ contains both 3c and 4c water molecules, the IR spectra (Figure 3b and 3c) are more complicated than that of $(\text{H}_2\text{O})_{20}$. Based on the types and numbers of participating H-bonds, the H-bonds are here divided into ten groups: SD-SA, SD-DA, DD-SA, DD-DA, SD-4c, DD-4c, 4c-SA, 4c-DA, 4c-4c, and Free H. Apparently, the OH stretching frequencies of free H group are the highest in the spectra, in the range of 3699 – 3712 cm^{-1} and 3698 – 3709 cm^{-1} for $(\text{H}_2\text{O})_{54}$ and $(\text{H}_2\text{O})_{100}$, respectively. For the bulk molecules (4c-4c), the O-H stretching frequencies are located in the middle part of the IR spectra between 3115 and 3475 cm^{-1} . Notably, for the molecules at the surface (SD-SA, SD-DA, DD-SA, DD-DA, SD-4c, DD-4c, 4c-SA, 4c-DA, and Free H), the OH stretching frequencies are spread over the whole stretching vibrational region from 2624 to 3712 cm^{-1} . Therefore, the OH frequency bands of bulk molecules and surface molecules overlap in the middle part of the IR spectrum. In addition, the OH frequencies of SD groups are lower than those of DD groups: the SD-SA group exhibits lower frequencies than the DD-SA group, the SD-DA group lower frequencies than the DD-DA group (in agreement with the results for the small cluster), and the SD-4c group exhibits lower frequencies than the DD-4c group. The OH frequencies for the SD-SA, SD-DA, SD-4c, DD-SA, DD-DA, and DD-4c groups are located in the range of 2752 – 3078 cm^{-1} , 3249 – 3317 cm^{-1} , 3178 – 3307 cm^{-1} , 3249 – 3317 cm^{-1} , 3416 – 3567 cm^{-1} , and 2955 – 3567 cm^{-1} , respectively. Furthermore, if the acceptor is a DA, the OH frequencies are higher than when it is a SA, i.e. the DD-DA group exhibits higher frequencies than the DD-SA group, similarly the SD-DA group higher frequencies than the SD-SA group, and the 4c-DA group higher frequencies than the 4c-SA group.

Figure 4 shows the evolution of the IR spectra going from the small cluster to the large cluster. The peaks in the spectra of $(\text{H}_2\text{O})_{54}$ and $(\text{H}_2\text{O})_{100}$ can be seen to locate at the middle part to a higher extent than for $(\text{H}_2\text{O})_{20}$, which originates from the contribution of four-coordinated water molecules. However, the spectrum for the $(\text{H}_2\text{O})_{100}$ cluster looks more distinct and ordered than for the $(\text{H}_2\text{O})_{54}$ cluster, due the higher symmetry of the present $(\text{H}_2\text{O})_{100}$ cluster.

4. Conclusions

In this work, the thermodynamic stabilities and IR spectra of the three water clusters $(\text{H}_2\text{O})_{20,54,100}$ have been studied using the quantum-chemical computations. The stability increases as the size of the water cluster increases. The change in Gibbs free energy when $(\text{H}_2\text{O})_{100}$ is formed from isolated water molecules is negative at 298K, which implies spontaneous formation from the monomers. The IR spectra in the OH stretching region of $(\text{H}_2\text{O})_{20,54,100}$ were simulated and split into different sub-spectra based on the contribution from different groups of H-bonds. The IR fingerprint of water molecules bonded by different conformations of H-bonds in $(\text{H}_2\text{O})_{20,54,100}$ were demonstrated. The OH stretching frequencies of the SD groups are lower than that of corresponding DD groups, i.e. the SD-SA/DA/4c group exhibits lower frequencies than the DD-SA/DA/4c group. If the acceptors of the H-bonds are DA, the OH vibrational frequencies are higher than when the acceptors are SA, i.e. the DD/SD/4c-DA group exhibits higher frequencies than the DD/SD/4c-SA group. Furthermore, the OH stretching vibration of bulk molecules and surface molecules overlap in the middle part of the IR spectrum. The OH vibrational frequencies of water molecules are sensitive to the conformations of the H-bonds, and the different groups of H-bonds have features that are located at different regions in the IR spectra. Thus the specific spectroscopic fingerprints can aid to identify the H-bond topology of water molecules in water clusters.

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Table 1. The H-bonded O-O distances in (H₂O)_{20,54,100}, and coordination number per water molecule. N3 and N4 denote the number of 3- and 4-coordinated molecules.

	H-bonded O-O distance/Å				Coordinate number		
	Min	Max	Mean	Standard deviation	N3	N4	Mean
(H ₂ O) ₂₀	2.60	2.88	2.76	0.10	20	0	3.00
(H ₂ O) ₅₄	2.54	2.97	2.77	0.10	36	18	3.33
(H ₂ O) ₁₀₀	2.56	2.88	2.75	0.08	60	40	3.40

Table 2. The binding energy (ΔE), internal energy (ΔU), entropy (ΔS), formation enthalpy (ΔH), and Gibbs free energy (ΔG) at T=298 K per water molecule. ZPE denotes the zero point energy correction. The unit is kcal/mol.

Cluster	ΔE	$\Delta E + \text{ZPE}$	ΔU	$T\Delta S$	ΔH	ΔG
(H ₂ O) ₂₀	-11.31	-8.53	-8.87	-9.59	-9.44	0.15
(H ₂ O) ₅₄	-11.99	-9.08	-9.43	-10.13	-10.01	0.12
(H ₂ O) ₁₀₀	-12.90	-9.90	-10.29	-10.40	-10.88	-0.48

Fig. 1 The structures of the water clusters: (a) $(\text{H}_2\text{O})_{20}$, (b) $(\text{H}_2\text{O})_{54}$, (c) $(\text{H}_2\text{O})_{100}$. The red sticks represent oxygen atoms, the white sticks represent hydrogen atoms, and the black dashed lines represent hydrogen bonds.

Fig. 2 The conformations of different donor-acceptor groups: (a) SD-SA, (b) SD-DA, (c) DD-SA, (d) DD-DA, (e) SD-4c, (f) DD-4c, (g) 4c-SA, (h) 4c-DA, (i) 4c-4c, (j) Free H. SD: single donor, SA: single acceptor, DD: double donor, DA: double acceptor, 4c: four coordinated water molecules. The green color denotes the OH stretching mode under study.

Fig. 3 The computed vibrational spectra for the a) 20-membered, b) 54-membered and c) 100-membered water cluster (top) and the contributions from different donor-acceptor conformations (bottom spectra). SD: single donor, SA: single acceptor, DD: double donor, DA: double acceptor, 4c: four coordinated water molecules.

Fig. 4 The computed vibrational spectrum for the 20-membered water cluster (top), 54-membered water cluster (middle), and 100-membered water cluster (bottom).