Structure and Spectra of Three-Dimensional $(H_2O)_n$ Clusters, $n = 8, 9, 10$

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The vibrational OH stretch spectra have been measured for size-selected pure water clusters $(H_2O)_n$, in the size range $n = 8-10$. Comparison between experiment and calculations suggests that the spectra originate from a small number of "microcrystalline" structures, based on the cubic octamer. The $n = 8$ spectra are caused by two isomers of D_{2d} and S_4 symmetry. The proposed lowest energy nonamer and decamer structures are derived from the octamer by insertion of one and two two-coordinated molecules, respectively, into the cube edges. [S0031-9007(98)05604-X]

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Water clusters have been the focus of intense interest during the last several years. One of the objectives is to understand how the properties of $(H_2O)_n$ evolve towards condensed phase behavior. One may ask, for example, at which size a cold cluster starts displaying attributes of a small crystal. The initial stages of the evolution as a function of n have been largely understood. Recently, an elegant series of far-infrared vibration-rotation-tunneling [1,2] and infrared [3] laser spectroscopic studies demonstrated conclusively a cyclic structure for $n = 3-5$, and a transition towards a three-dimensional cage structure at $n = 6$ [4]. Similar conclusions were drawn from the double resonance ion-dip infrared experiments on water clusters connected to a benzene molecule [5]. At present, the challenge is to understand the evolution in the "cage" regime $n \geq 7$. A number of theoretical studies addressed this problem [6–9]. The only pertinent experimental results focus on the OH stretch spectroscopy of larger clusters without size selection [10,11] and $n = 7, 8$ clusters attached to benzene [5,9].

The present Letter reports the first measurement of the infrared spectroscopy of the OH stretch mode of *pure* water clusters in the size range $n = 8-10$. The OH stretch spectra of hydrogen bonded H_2O, which are redshifted by hundreds of cm^{-1} with respect to gaseous H_2O, are known to be strikingly sensitive to hydrogen bond coordination and to bonding geometry [7,12]. Thus they can be used to probe the cluster structure. Moreover, the spectroscopy of clusters can serve as a benchmark for the calibration of *flexible* force fields for studies of condensed H_2O and H_2O surfaces.

The experimental method which we apply is a combination of size selection by momentum transfer in a scattering experiment with atoms, with the infrared depletion technique [13,14]. This technique has been developed in our laboratory in Göttingen and mainly applied to cluster sizes $n \leq 6$. In the first step the different clusters are dispersed into different angles according to their masses and detected by a mass spectrometer. Then the OH stretch vibrational mode of the water molecules is excited by infrared laser radiation. The detector records the depletion in the cluster signal caused by the clusters which are dissociated by the absorbed radiation.

The experimental setup consists of a crossed molecular beam apparatus with an angular dependent detection of the scattered beam with a resolution of 0.1° using electron impact ionization and mass selection in a quadrupole mass filter [15]. The water clusters are generated by an adiabatic expansion of a dilute mixture of water vapor at 338 to 361 K with helium as carrier gas at 2.3 bars through a conical nozzle (opening angle: $2\alpha = 30°$; diameter: 90 μm; length: 2 mm). For the size selection, the water cluster beam is deflected by a helium beam [13]. The detector is set on the largest possible scattering angles Θ_n of the clusters $n = 8$, 9, and 10, which are in our experimental arrangement 4.1°, 3.7°, and 3.3°, respectively. Clusters smaller than these sizes are excluded by means of the mass spectrometer operated at the masses of the corresponding protonated $(H_2O)_{n-1}H^+$ ions. In this way complete size selection is achieved. For the excitation of the OH stretch mode a homebuilt optical parametric oscillator was used as coherent light source [16]. The tuning range is between 2400 and 3800 cm^{-1} at an average output energy of 2 mJ/pulse, a resolution of 0.2 cm^{-1}, and a repetition rate of 20 Hz. Because of water impurities in the crystal, our arrangement has an intensity gap between 3460 and 3500 cm^{-1}.

The results are shown in the upper parts of Figs. 1, 2, and 3, respectively. The dissociated fractions are fitted to Lorentzian profiles according to $P_{\mathrm{diss}} = 1 - \exp[-\sigma(\nu)F/h\nu]$. Here, $\sigma(\nu)$ represents the dissociation cross section, F the laser fluence, and $h\nu$ the photon energy. The solid line in the figures is the envelope of several such Lorentzians. The results for all three cluster sizes are characterized by three spectral bands at 3700, 3550, and 3100 cm^{-1}, and a large gap between 3152 and 3528 cm^{-1}.

In the calculations, structures were minimized using the conjugate gradient algorithm, from random initial conditions. The calculation employed a modified empirical

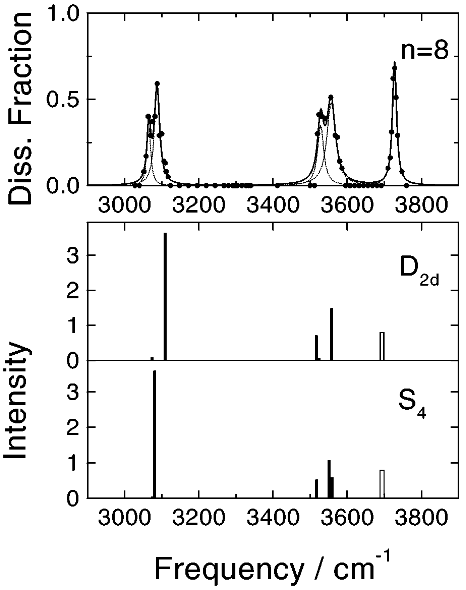

FIG. 1. Top: Experimental spectrum for $n = 8$. Bottom: Calculated, using the EMP potential for the two cubic isomers. The minimum energies are -71.32 and -71.27 kcal/mol for S_4 and D_{2d}, respectively. The intensity of the free OH stretch at 3700 cm^{-1} is multiplied by 5.

polarizable water potential proposed in [17] (henceforth EMP). The modified parameters are $r_s = 1.25$ Å, $b_{oo} = 2.65$ au; also, the polarizability center was shifted down the bisector of H_2O, 0.48 Å from O towards the H atoms. This potential provides a reasonable description of the different water phases (solid, liquid, and clusters) [18]. The EMP potential is rigid, so a scheme to translate minimum energy structures to spectra was needed. The OH bonds were treated as a collection of coupled local Morse oscillators; the stretch Hamiltonian was diagonalized in the Morse exciton basis. The bond frequency ω was assumed to be determined by the electric field component $E_{\|}$ at the H atom along the OH bond, as suggested by *ab initio* studies of [19]. To construct the function $\omega(E_{\|})$ we employed experimental IR frequencies for $n = 3-5$ [3], the experimental 3085 cm^{-1} IR peak of $n = 8$, and an additional lowest frequency point from second order many body perturbation (MP2) results for the $n = 6$ prism [20]. Other details of the calculation (such as the treatment of the intermolecular and intramolecular coupling and of the IR intensities) were adopted from [12]. Energy ordering of different cluster structures can be affected by the zero-point energy [4]. The intermolecular contribution to the zero-point energy was calculated using rigid body diffusion Monte Carlo [21], while the intramolecular component was estimated as a sum of zero-point energies of bond Morse oscillators.

In addition, *ab initio* calculations were carried out on the lowest energy cluster minima. The EMP minimum structures were used as input for *ab initio* optimizations at several levels: Hartree-Fock ($n = 8-10$) and MP2 ($n = 8$ only) employing double zeta Dunning basis plus polarization functions with exponents 0.9 for O and 1.0 for H (DZ1P basis [22]). The qualitative structural features

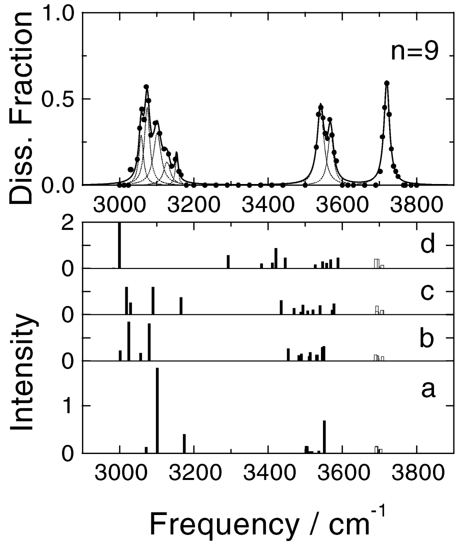

FIG. 2. Top: Experimental spectrum for $n = 9$. Bottom: Calculated, using the EMP potential, for four minima with the minimum energies from -80.54 (a) to -78.63 kcal/mol (d). For clarity, the lowest minimum spectrum at the bottom (a) is enlarged. The intensity of the free OH stretch at 3700 cm^{-1} is multiplied by 5.

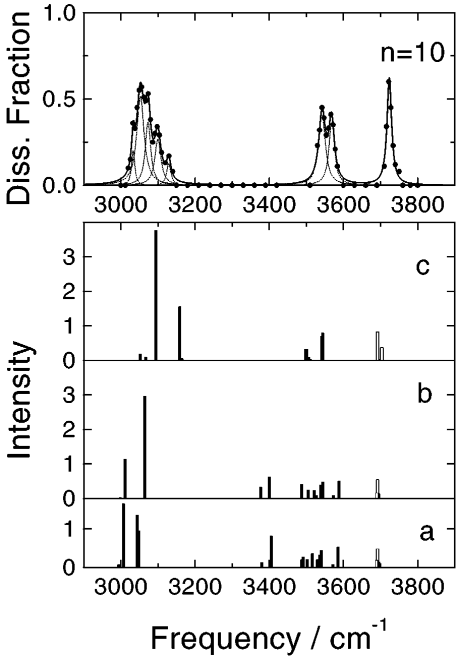

FIG. 3. Top: Experimental spectrum for $n = 10$. Bottom: Calculated, using the EMP potential, for three minima of the energies -92.01 (a), -91.93 (b), -89.67 (c) kcal/mol. The bottom two spectra (a) and (b) correspond to the two lowest cage structures, the top (c) to the butterfly structure. The intensity of the free OH stretch at 3700 cm^{-1} is multiplied by 5.

discussed below were obtained consistently in all *ab initio* calculations, and in EMP. Qualitatively reliable OH stretch spectra seem to require at least an MP2 level calculation in a polarized basis (see, e.g., [7,8,20,23]).

The general structural features are now discussed for the EMP potential minima. The numerous low energy minima obtained for $n = 8-10$ correspond to cage structures, dominated by three-coordinated water molecules. Such molecules come in two varieties (a) double proton donor-single proton acceptor (DDA), and (b) single proton donor-double proton acceptor (DAA). As already noted in the past, the $O \cdots O$ distances in hydrogen bonds emanating from DDA tend to be longer than bonds emanating from DAA, and the corresponding OH bond frequencies tend to be higher [5,7,8,12,20]. The lowest cluster minima can be loosely described as "crystal-like" (see Fig. 4), in the sense that one obtains two *well separated and distinct* groups of nearest neighbor $O \cdots O$ bond lengths, corresponding to DDA and DAA hydrogen bonds, respectively. As a result, the OH stretch spectrum contains two well separated DAA and DDA bands. In addition, a third band is obtained for the dangling OH bonds at the cluster surface. In higher energy minima of "more amorphous" structures, the range of $O \cdots O$ distances broadens for hydrogen bonds of both categories, the frequency gap between DDA and DAA spectral bands decreases, and infrared absorption features appear within the gap [see Figs. 2(b)–2(d)]. We then suggest the relative narrowness of the measured DDA and DAA bands and the clear separation between them as evidence for a small number of low energy minima of ordered structure.

Octamer.—The lowest energy minima obtained with EMP are two closely related and by now well known [6–9] cubic structures of S_4 and D_{2d} symmetry (see Fig. 4). The S_4 energy is lower by 0.05 kcal/mol (25 K; 70 K after the zero-point energy correction). Both structures contain only asymmetrically connected three-coordinated molecules; i.e., all DAA molecules are connected only to DDA, and vice versa. The three stretch bands are clearly visible both in the experimental and the calculated (EMP) spectrum in Fig. 1. The MP2/DZ1P calculations resulted in a qualitatively similar pattern. One should note the small splitting (30 cm^{-1}) between the symmetric and the asymmetric stretch of the DDA molecules in the experimental band at 3550 cm^{-1}, similar to the splitting for H_2O molecules isolated in the D_2O ice matrix [24] (45 cm^{-1}), and more than 3 times smaller than in gaseous H_2O value (99 cm^{-1}). Thus the intramolecular OH-OH coupling constant acquires a value close to ice already at $n = 8$ [7,12]. According to the calculations, each of the two lowest energy isomers has a single infrared active excitation mode in the vicinity of 3100 cm^{-1}, corresponding to a collective oscillation of the four hydrogen bonded OH bonds of DAA molecules. The observed doublet feature, split by about 20 cm^{-1}, suggests the presence of both isomers in the beam. The calculated splitting between the two isomers is 30 cm^{-1} (EMP) and 47 cm^{-1} (MP2/DZ1P rescaled harmonic *ab initio*). Spectroscopic evidence for two octamer isomers, was also reported in [9] for the water octamer bonded to benzene. One clear discrepancy between the computed and the measured spectra pertains to the relative intensities of the three OH bands. Whether this is a shortcoming of the calculation (neglection of intermolecular zero-point motion) or the experiment (absorption combined with dissociation, saturation effects) requires further studies.

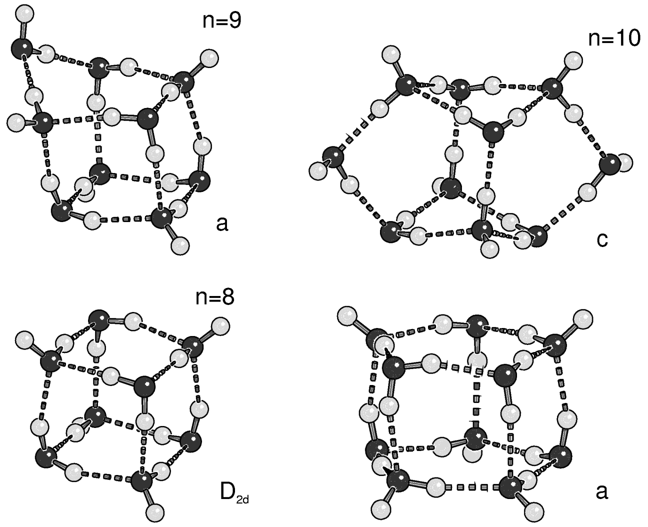

FIG. 4. Structures of water clusters for $n = 8$ (D_{2d}); $n = 9$ (a); $n = 10$, (a) and (c). The characters in parentheses refer to the spectra given in Figs. 1–3, respectively.

Nonamer.—The lowest minimum energy structure found can be viewed as two rings—a pentamer and a tetramer—fused by four hydrogen bonds (see Fig. 4). The OH bonds within the two rings are oriented in the opposite direction. A similar minimum, denoted "basket," was reported in an *ab initio* study of [8] and is also found in the simulation of $Cl^-(H_2O)_8$ clusters [25]. The clear separation to three spectral bands is still present, and is reproduced in the calculated spectrum for this structure. While the calculated spectrum does not match the experiment quantitatively, the qualitative agreement is significantly better than for the higher energy minima [see Figs. 2(b)–2(d)]; note especially the absence of peaks in the 3200–3500 cm^{-1} gap.

One can also view this $n = 9$ structure as a D_{2d} octamer, with an extra two-coordinated DA molecule inserted into one of the edges. One of the hydrogen bonds to this molecule emanates from a DAA molecule, and is accordingly short; the second DA bond adopts a similar bond length. The collective excitation of the two bonds is calculated just below 3200 cm^{-1}, in accord with experiment and in contrast to the octamer. Moreover, in the remaining "octamerlike" part of the nonamer, the DAA bonds are no longer equivalent, resulting in two

DAA bands near 3100 cm^{-1}, rather than in a single one, as in the octamer. The calculated DAA band covers roughly a correct spectral range; however, the measured spectrum includes more subpeaks, suggesting the presence of two or more structurally related isomers.

Decamer.—We are not aware of any other studies of the decamer structure. The two calculated lowest energy structures can be viewed as two fused pentamers (see Fig. 4), with the same and the opposite orientation of OH bonds in the two cycles, respectively. However, the spectrum calculated for these two minima does not match the experiment very well [see Figs. 3(a) and 3(b)]. The main discrepancy originates from the presence of a DDA-DDA-DAA-DAA bonding pattern in one of the "walls" of the cage, which contributes to the spectrum a pair of absorptions near 3400 cm^{-1}. Significantly better agreement [see Fig. 3(c)] was attained for another "butterfly" minimum energy structure, as shown in Fig. 4. This structure can be viewed as a D_{2d} octamer, with two two-coordinated extra DA molecules inserted at opposite edges. The resulting spectrum is similar to that of the nonamer, except for a slight shift to the red of the low frequency band in accord with experiment. The calculated energy of the butterfly minimum is 2.3 kcal/mol above the lowest cage minimum; however, inclusion of zero-point energy effects reduces the energy gap to only 0.34 kcal/mol (170 K), less then 0.5% of the well depth. One can easily imagine errors of this size in the EMP potential. The present experimental results suggest that the true energy of the butterfly structure is below that of the cage.

Summarizing, we have presented the first measurements of the OH stretch spectra of essentially three-dimensional water clusters for $n = 8$, 9, and 10. Calculations of cluster structures, energetics, and spectra were used to interpret the data. Based on the narrowness and the separation of the two hydrogen bonded OH stretch bands, it is demonstrated that the spectra originate from a small number of ordered crystal-like structures, derived from the octamer cube. The measured spectra will provide a valuable benchmark for calibration of flexible intermolecular potentials for H_2O. A first step towards constructing such a potential was taken in the present study. The presented experimental technique will allow us to extend the measurements to cluster sizes down to $n = 6$ and up to $n = 20$, by changing the carrier gas and the collision partner. Preliminary results for $n = 7$ suggest a hexamer prism structure [4], with an extra DA molecule inserted into one of the triangles. Furthermore, we anticipate investigation of higher and more disordered cluster minima by raising the cluster temperature. Filling of the frequency gap is predicted here as experimental evidence for the presence of such minima.

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