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Quantifying Hydrogen Bond Cooperativity in Water: VRT Spectroscopy of the Water Tetramer

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Measurement of the far-infrared vibration-rotation tunneling spectrum of the perdeuterated water tetramer is described. Precisely determined rotational constants and relative intensity measurements indicate a cyclic quasi-planar minimum energy structure, which is in agreement with recent ab initio calculations. The O–O separation deduced from the data indicates a rapid exponential convergence to the ordered bulk value with increasing cluster size. Observed quantum tunneling splittings are interpreted in terms of hydrogen bond rearrangements connecting two degenerate structures.

The quest for a genuine molecular description of bulk-phase water has motivated two lines of research. The first entails a convergence of theory and experiment in determining an accurate six-dimensional intermolecular pair potential hypersurface (IPS). As a central element of this effort, several of the intermolecular vibrational modes of the water dimer have been characterized by far-infrared vibration-rotation tunneling (FIR-VRT) spectroscopy (*1*). The second direction involves investigation of the structures and dynamics of larger water clusters, with the principal goal of quantifying the nature of cooperative (many-body) effects in hydrogen bonding (*2*). Detailed observation of the water trimer with tunable FIR-VRT spectroscopy confirmed that the equilibrium structure of the trimer is cyclic and quasiplanar, as predicted by many theoretical calculations (*3, 4*). Subsequent spectroscopic observations (*5, 6*) and several theoretical studies (*7–9*) have elaborated on this work.

Here we report measurement of the FIR-VRT spectrum of the fully deuterated water tetramer. The structure of this molecule, as deduced from its spectrum, is in agreement with most theoretical predictions (*4, 10–12*), which indicate that the minimum energy structure should be cyclic and quasi-planar (Fig. 1A). From these new data, we can begin to quantify the four-body terms in the interaction potential of bulk water.

The tunable FIR spectrometers used in this work have been described previously (*12–14*) (Fig. 2). Forty VRT transitions were measured to ±1.5 MHz in the spectral region near 68.0 wave numbers (cm^{-1}) and assigned to a parallel band of a symmetric rotor molecule. Table 1 lists the rotational constants obtained by nonlinear regression from the energy expression

$$E(J,K) = BJ(J+1) + (C-B)K^2 - D_J J^2(J+1)^2 + D_{JK}J(J+1)K^2 \quad (1)$$

where B and C are the symmetric top ($A = B$) molecular rotational constants, D_J and D_{JK} are centrifugal distortion parameters, and J and K are the assigned rotational quantum numbers. Each vibration-rotation transition was observed as a doublet of lines with approximately equal intensity and a constant (no change with J or K) average spacing of 5.6 ± 0.1 MHz (Fig. 2). Each datum in the fit is the numerical average of the two doublet frequencies.

Because a distribution of cluster sizes and species is present in a supersonic expansion, several tests were undertaken to identify the carrier of the spectra. Identical spectra were observed in expansions of Ar, Ne, and He; hence clusters containing carrier gas atoms were ruled out. As outlined in (*13*), the number of D_2O molecules in the cluster was determined by measurement of the intensity of several spectral features as a function of the mole fraction of D_2O in an H_2O-D_2O mixture. The amount of D_2O in the gas mixture can be varied while the total number of water molecules available for clustering is conserved. In this model, isotopic effects on the rates of cluster formation are assumed to be negligible. Five isotopic mixtures were tested and the resulting data were fit to the relation $\ln(I) = 2n \cdot \ln(\chi_{D_2O})$, where I is the relative signal intensity, χ_{D_2O} is the mole fraction of D_2O, and n is the number of D_2O molecules in the cluster. The results (Fig. 3) yield $n = 4.14 \pm 0.22$ at the 95% confidence level. Because no signal increase was observed with the use of any of the isotopic mixtures, clusters containing mixed water isotopes were ruled out as well. Additionally, the rotational constants, determined to a precision of about one part in 10^4, cannot be accounted for by consideration either of pure D_2O clusters containing more or less than four monomers or of other clusters containing any obvious contaminants.

Parallel transitions ($\Delta K = 0$) do not allow absolute determination of the C rotational constant in either state from the spectral line positions. Only the relative difference between C constants in the upper and lower states could be determined from these data, which precludes a rigorous rotational structural determination. Relative transition intensities, however, can yield an approximate value for the C rotational constant, because they arise from the absolute energy level positions in the lower vibrational state, which depend on that parameter. Comparison of careful relative intensity measurements in the compact Q-branch ($\Delta J = 0$) region with simulated intensity profiles as the C constant was varied between limits that would yield spherical ($A = B = C$) and planar oblate ($A = B = 2C$) structures (Fig. 2B) showed that the most consistent value was for a near-planar structure ($C = 1500 \pm 250$ MHz).

The consensus of most ab initio quantum chemistry studies is that the minimum energy structure of the water tetramer is similar to that shown in Fig. 1A, which is best described by the S_4 point symmetry group. Recent high-level ab initio calculations by Xantheas (9) have yielded the rotational constants $A = B = 3149$ MHz and $C = 1622$ MHz for the S_4 structure, with an O–O separation of 2.74 Å. Assuming an S_4 structure in the present case and scaling for the experimentally determined rotational constants yield approximate average O–O separations of 2.78 and 2.79 Å in the lower and upper states, respectively. This result is consistent with the observed trend in O–O separations of 2.976, 2.90, and 2.76 Å in the water dimer (*15*), trimer (*8*), and pentamer (*16*) and indicates that this property is converging rapidly to the ordered bulk value with cluster size. Figure 4 shows that the experimental O–O separations follow the trends predicted by Xantheas's Hartree-Fock (HF) and second-order Möller-Plesset (MP2) calculations (9).

Spectral splittings, such as the doublets observed in this work, have been observed in the spectra of many small clusters, in-

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cluding $(H_2O)_2$ and $(H_2O)_3$ and their deuterated isotopomers, wherein they arise from quantum tunneling among permutationally distinct equivalent minima on the IPS. Tunneling splittings are observable when barriers (saddle points) between potential energy minima are low enough to allow the molecular wave function to sample more than one minimum at a time. Dynamically, quantum tunneling splittings imply that interconversion between structurally equivalent but uniquely labeled frameworks occurs within the frequency resolution of the experiment (10^6 s^{-1} in this work).

Permutation-inversion (PI) group theory (*17*) has been an invaluable tool for rationalizing these splittings in terms of degenerate structural rearrangements. The smallest possible molecular symmetry group for the water tetramer is that which describes a rigid (nontunneling) molecule, $S_4(M)$. Because tunneling is observed, larger subgroups of the complete PI group that include operations that interconvert degenerate structures must be considered in order to rationalize the data. Figure 1B schematically illustrates one such rearrangement pathway described by one PI operation, a simultaneous "flipping" of each of the unbound deuterons from one side of the O–O–O–O plane to the other. In the trimer, flipping is thought to occur through a potential energy barrier sufficiently low that it is best to describe the resulting eigenstates as a vibrational (pseudorotational) manifold (*5–7*). The barrier to unbound deuteron flipping in an S_4 water tetramer is calculated to be much higher than that in the trimer (*18*), and for the tetramer, simultaneous flips of all four unbound deuterons are required to produce a degenerate structure and thereby induce tunneling splittings. If this simultaneous flipping motion is responsible for the observed splittings, then the subgroup $C_{4h}(M)$ of the complete PI group is sufficient to describe the observed spectra. Under this group, each rovibrational level of the molecule is split into two levels labeled variously by the irreducible representations of the group: A_g, B_g, E_g, A_u, B_u, and E_u. Electric dipole selection rules allow transitions $A_g \leftrightarrow A_u$, $B_g \leftrightarrow B_u$, and $E_g \leftrightarrow E_u$ only, and nuclear spin restrictions on the molecular wave functions predict that the ratio of observed doublet intensities should be roughly unity for H_2O and D_2O tetramers. Therefore, this motion is adequate to explain the observed spectrum because it predicts transitions to occur in tunneling doublets with nearly equal intensity. However, Schütz and co-workers (*19*) have identified several low-energy minima and rearrangement paths in their recent ab initio study, which indicates that the tunneling dynamics are probably much more complicated.

In addition, the $C_{4h}(M)$ group predicts parallel-type transitions, such as the one

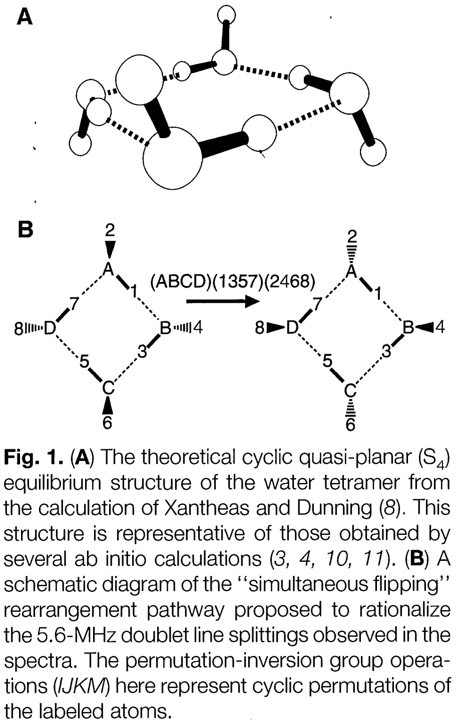

Fig. 1. (**A**) The theoretical cyclic quasi-planar (S_4) equilibrium structure of the water tetramer from the calculation of Xantheas and Dunning (*8*). This structure is representative of those obtained by several ab initio calculations (*3, 4, 10, 11*). (**B**) A schematic diagram of the "simultaneous flipping" rearrangement pathway proposed to rationalize the 5.6-MHz doublet line splittings observed in the spectra. The permutation-inversion group operations (*IJKM*) here represent cyclic permutations of the labeled atoms.

Table 1. Rotational constants (in megahertz) derived from a nonlinear least-squares fit of the averaged doublet frequencies to Eq. 1. ν_0 is the vibrational band origin. The root-mean-square residual of the fit was 1.18 MHz. Numbers in parentheses indicate one standard deviation. The magnitudes of the upper and lower *C* constants were determined, as described in the text, to be 1500 ± 250 MHz, which corresponds to a nearly planar oblate rotor.

Constant	MHz
ν_0	2,032,688.37 (33)
$A'' = B''$	3,079.512 (03)
D_J'''	0.0089 (04)
D_{JK}''	−0.0178 (07)
$A' = B'$	3,091.726 (31)
D_J'	0.0092 (03)
D_{JK}'	−0.018 (06)
$C' - C''$	−3.4771 (67)

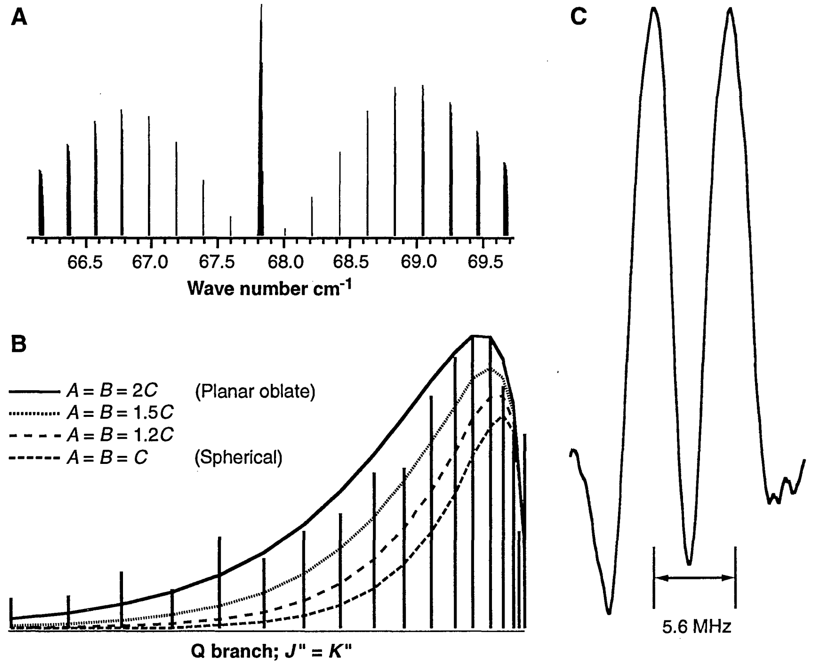

Fig. 2. (**A**) The observed FIR-VRT spectrum with calculated intensities if a rotational temperature of 5 K is assumed. We formed water clusters by bubbling Ar, Ne (70% with He), or He gas through D_2O (99.96%) and then forming a supersonic expansion with the mixture. This technique has the advantages that high concentrations of clusters are formed in a collision-free environment and that only the lowest few eigenstates are thermally populated, leading to greatly simplified absorption spectra. Two supersonic beam nozzles were used in this work: one a continuously operated slit-shaped nozzle (10 cm by 0.001 cm) and another of similar dimensions operated in a pulsed mode at 1 to 5 atm of backing pressure. Peak signal-to-noise ratios of 20:1 were obtained with the continuous wave source, and ratios better by a factor of 10 were obtained with the pulsed nozzle, even with the commensurate reduction (a factor of 100) in the detection duty cycle. (**B**) The measured $J = K$ Q-branch transitions (stick spectrum) are superimposed on expected Q-branch intensity profiles for values of the *C* constant stepped by 500 MHz from the planar oblate top value (top trace). By such an analysis, the magnitude of the lower state *C* rotational constant was bracketed to within ~250 MHz of the planar oblate value. The apparent intensity fluctuations are due to changes in laser power. (**C**) The $R(5_5)$ transition shows the doublet splitting and near-equal–intensity pattern exhibited by all transitions observed.

reported here, to occur only if the upper vibrational state can be labeled by the $C_{4h}(M)$ irreducible representations A_u or B_g. Schütz and Klopper (*19*) have recently given vibrational symmetry assignments for some predicted low-lying intermolecular vibrations of $(D_2O)_4$, including a B_g vibration at 77.1 cm^{-1} and an A_u vibration at 142.4 cm^{-1}. These harmonic vibrational frequencies are expected to be considerably higher than the measured frequencies; therefore, it is unlikely that the present spectrum corresponds to the 77.1 cm^{-1} vibration. Xantheas (*9*) has calculated the relative intensities of these transitions and predicts the A_u vibration to be roughly 20 times stronger than the B_g mode. In light of these calculations, it seems reasonable to conclude that the observed transition corresponds most closely to the 142 cm^{-1} A_u transition predicted by theory.

Of the large body of theoretical calculations on the water tetramer structure, the overwhelming consensus indicates an S_4 minimum energy structure (*3, 4, 10, 11*). Owicki *et al.* (*4*) and Kim *et al.* (*10*) have located several other local minima on empirical potential surfaces, some lying within 0.5 kcal mol^{-1} or about 10% of one hydrogen bond stabilization energy of the S_4 minimum. No recent high-level ab initio calculation has yielded a similar result. Most recently, Head-Gordon and Head-Gordon (*20*) have performed exhaustive ab initio and reaction coordinate calculations on alternative geometries, finding rapid relaxation of most alternative structures to the S_4 minimum.

Xantheas (*9*) has recently examined the convergence of several structural and energetic properties of water clusters as large as the hexamer as a measure of the cooperative (many-body) effects. The three-body interaction accounted for as much as 30% of the total stabilization energy of the water trimer, or about 4.5 kcal mol^{-1}, whereas the four-body interaction accounted for considerably less stabilization of $(H_2O)_n$ complexes with $n > 3$. Of the manifestations of many-body effects on cluster properties, hydrogen bond length is the simplest to monitor experimentally; therefore, a reliable estimate of the hydrogen bond length or O–O separation in the water tetramer provides a critical test of the calculated many-body effects. Xantheas (*9*) predicts a trend in contraction of the O–O separation, with that value exponentially decreasing to the bulk limit as the importance of larger terms in the many-body potential energy expansion decreases. The O–O separation of $(D_2O)_4$ derived from the present data (Fig. 4) is consistent both with theoretical values at the HF and MP2 levels and with our measured values of water clusters as large as the pentamer (*16*). Caution must be observed in interpreting the present data, however, because the observed rotational constants do not supply adequate information to fix all intermolecular coordinates and are likely to be "contaminated" by the large-amplitude dynamics apparent in the spectrum.

Our estimation of the O–O separation from the available data is consistent with an exponentially decreasing hydrogen bond distance with increasing cluster size. Observation of a parallel-type spectrum near 68 cm^{-1} is consistent with theoretical predictions of vibrational frequencies, intensities, and symmetries. Measurement of a perpendicular ($\Delta K = \pm 1$) transition will be necessary to establish precise values of the constants for rotation about the symmetry (C) axis and to thereby make a more rigorous determination of the structural parameters of the cluster. Nevertheless, rigorous dynamics calculations of the ground-state properties of the tetramer, with the adjustment of an empirical potential to agree with our VRT data, can now yield a quantitative estimate for the four-body terms operating in bulk-phase water, much as was recently demonstrated by Gregory and Clary (*21*) for the three-body effects in the water trimer.

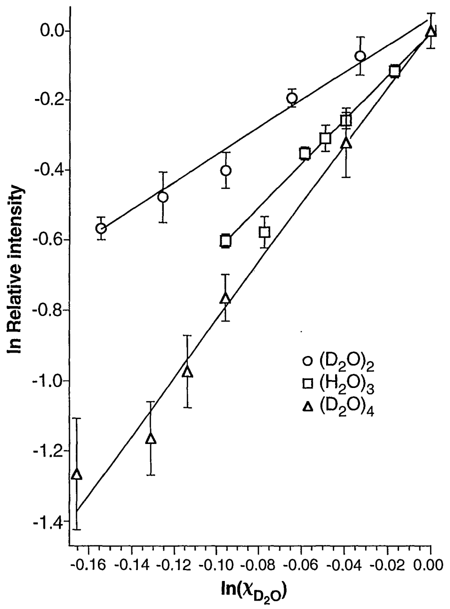

Fig. 3. Plots of ln relative intensity versus ln[mole fraction (χ) of D_2O or H_2O] for $(D_2O)_2$, $(H_2O)_3$, and the spectrum reported here. $(H_2O)_3$ transitions were selected over those observed for $(D_2O)_3$ for this comparison because of their strong signal intensity. Linear least-squares fits to the equation given in the text yield $n = 1.97 \pm 0.17$, 3.13 ± 0.14, and 4.14 ± 0.22 for the dimer, trimer, and tetramer, respectively, where n is the number of D_2O (H_2O) molecules in the cluster. Error bars indicate the 95% confidence interval. The principal uncertainty in this experiment arises from the irreproducibility of intensities, which worsens as the signal approaches the noise level. Each data point in the fit was therefore weighted by the reciprocal of the variance of 10 intensity measurements.

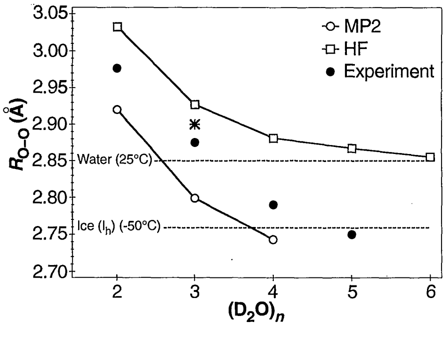

Fig. 4. Plots of R_{O-O}, the interoxygen separation for water clusters up to the pentamer. The traces represent the theoretical predictions in (*9*) for H_2O equilibrium R_{O-O} values. The solid circles denote experimental values for perdeuterated clusters. We obtained the R_{O-O} values of the trimer, tetramer, and pentamer by assuming the ab initio geometric details and varying the distances of the monomers from the cluster center of mass until agreement with the measured moments of inertia was obtained. This is a different approach than that used in an accompanying paper (*16*). Both methods are limited by the large vibrational averaging effects but produce a similar exponential convergence to bulk R_{O-O} values. The dimer value is due to Dyke and co-workers (*15*). The asterisk marks the vibrationally averaged R_{O-O} of the D_2O trimer recently calculated by Gregory and Clary (*21*). The bulk phase values were taken from (*22*) (liquid water) and (*23*) (ice I_h).

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Vibration-Rotation Tunneling Spectra of the Water Pentamer: Structure and Dynamics

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Far-infrared laser vibration-rotation tunneling spectroscopy was used to measure an intermolecular vibration (81.19198 wave numbers) of the isolated water (D_2O) pentamer. Rotational analysis supports the chiral, slightly puckered ring structure predicted by theory. The experimentally deduced interoxygen separations for the water clusters up to the pentamer showed exponential convergence toward the corresponding distance in bulk phase water.

The quasiplanar pentagonal structure formed from five doubly hydrogen-bonded water molecules appears to have a special role in chemical and biological systems. Whereas normal ice (I_h) consists of regular arrays of hexagons, molecular dynamics calculations (*1–3*) show the liquid (25°C) to be dominated by pentagons. The anomalous thermodynamic properties of liquid water have been rationalized in terms of fluctuations in the number of pentagons (*4*). Clathrate hydrate structures consist of water molecules organized in arrays of pentagons and hexagons around a central hydrophobe (*5*). A similar array of five-membered water rings occurs near the surfaces of proteins (*6*), DNA (*7*), and DNA-drug complexes (*8*). These latter examples reflect the ability of pentagons to form closed geometrical structures, which may be of general significance in the hydration of biological macromolecules.

The reason for the dominance of pentagons and hexagons in bulk water systems is that these are the smallest polygons that can produce O–O–O angles near the optimum (tetrahedral) value, which maximizes the hydrogen bond energy (*2*). There is consensus in the theoretical work as to the equilibrium structure of the water pentamer (*9–11*). The most stable form of the pentamer is a cyclic, slightly puckered ring (similar to the bent form of cyclopentane) in which each water molecule acts as both a single hydrogen bond donor and acceptor (Fig. 1).

Although numerous ab initio and semiempirical studies have addressed the water pentamer, it remained to be experimentally characterized. Vernon *et al.* (*12*) and Huisken *et al.* (*13*) observed the OH stretching bands by vibrational predissociation in a mass-selected molecular beam, and x-ray crystallography measurements established the basic structure of concatenated water pentagons in biopolymers (*6–8*). But these experiments lacked the precision required to establish definitively structure and properties. Here, we report the determination of the water pentamer structure. This work follows our recent studies of the water dimer (*14*), trimer (*15*), and tetramer (*16*) by far-infrared (far-IR) laser vibration-rotation tunneling (VRT) spectroscopy (*17*).

A total of 218 parallel ($\Delta K = 0$, where K is the quantum number of the rotational angular momentum component along the molecular symmetry axis) transitions were fit to a symmetric top Hamiltonian (Table 1). The composite data set, together with a simulated stick spectrum produced by the fitted molecular parameters, is shown in Fig. 2. The observed spectrum was assigned unambiguously to an exact oblate symmetric top, as no asymmetry splitting had been resolved. No quantum tunneling features were evident within the spectral resolution (~2 MHz) of our experiment. An attempt to measure a first-order Stark effect was not successful for the pentamer. The signal in this experiment was determined to result from pure water clusters (*18*).

The size of the cluster responsible for the observed transitions was determined through the isotope mixture test described in our previous study of the water trimer (*15*). A measurement of the line intensity as a function of the D_2O mole fraction in the sample yielded a cluster size of 5.14 ± 0.36 at the 95% confidence level. The pentamer transitions appear as featureless singlets, so the isotope mixture test was necessary to discriminate the pentamer signals from the absorptions of other clusters coexisting in the jet. The validity of this mixture test has also been established for VRT spectra of the water dimer, the pure and isotopically substituted trimer, and the tetramer (*16*).

Structural information is derived from an analysis of the observed spectral pattern. Because of the nature of a parallel transition for a symmetric top, the rotational constant about the unique symmetry axis cannot be determined by fitting the spectral line positions alone. Only the difference between ground and excited state values of this constant can be definitively established. Simulation of the intensity profile gave good agreement with the experimental profile only for a nearly planar ($A = B \sim 2C$) oblate top (see Fig. 2). The rotational constants thus obtained preclude assignment to a tetramer or hexamer.

On the basis of the measured rotational constants, the averaged interoxygen distances, R(O–O), estimated from a point-mass model for $(D_2O)_n$ [n = 2, 3, 4 (*16*), and 5], can be fit to a reasonable exponential function (Fig. 3), as noted by Xantheas and Dunning in their ab initio work on small cyclic water clusters (*9*). The similar R(O–O) contraction (toward the bulk values) apparent in both experiment and theory clearly shows the "cooperative" effects in the hydrogen bonding network. The discrepancy between them is primarily a result of the difference between the equilibrium and vibrational averaged structures, which can be significant for such fluxional systems.

The quantum tunneling dynamics in the water pentamer are responsible for the ob-

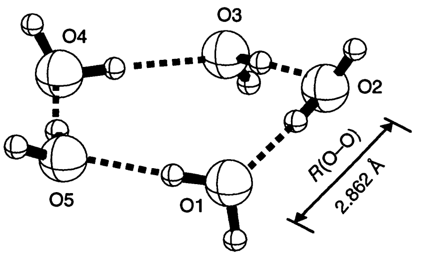

Fig. 1. Predicted equilibrium structure of the cyclic water pentamer. The coordinates used here are from the highest level available ab initio calculation, performed by Xantheas and Dunning (9). Other theoretical predictions give similar structural parameters. The dashed lines represent the hydrogen bonds. The calculated rotational constants *A*, *B*, and *C* for $(H_2O)_5$ structure are 1859, 1818, and 940 MHz, respectively. Because all five lateral distances are only slightly different, a typical *R*(O–O) is indicated here. The pentamer ring structure is puckered; the O1–O2–O3 plane bends about 20° from the O1–O3–O5 plane (O4 is approximately in this plane).

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