

Hydrogen Bond Breaking Dynamics of the Water Trimer in the Translational and Librational Band Region of Liquid Water

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Abstract: The effect of exciting each of the three classes of intermolecular vibrations on the hydrogen bond lifetime (τ_H) of the isolated water trimer is investigated by far-infrared laser spectroscopy. Single excitation of a librational vibration decreases τ_H by 3 orders of magnitude to $\tau_H = 1\text{--}6$ ps, comparable to the time scale of a number of important bulk water dynamical relaxation processes. In contrast, excitation of translational or torsional vibrations has no significant effect ($\tau_H = 1\text{--}2$ ns). Although such a dependence of τ_H on intermolecular motions has also been proposed for liquid water via computer simulations, these are the first experiments that provide a detailed molecular picture of the respective motions without extensive interpretation.

The hydrogen bond network and its fluctuations determine the unique properties of liquid water. Many different experiments have addressed these dynamics in terms of the underlying intermolecular motions, but they either were insensitive to the microscopic details or required extensive interpretation.^{1–8} Far-infrared vibration–rotation–tunneling (VRT) spectroscopy has proven to be a powerful experimental method for unraveling the molecular details of the structures and hydrogen bond rearrangement dynamics of small water clusters.^{9–13} However, none of the previous water cluster studies either sampled motions directly corresponding to those existing in the bulk or employed excitation energies relevant to ambient bulk processes. In this first detailed spectroscopic study of the translational and librational vibrations of a water cluster, we realize both ends

and exploit the water trimer as a model for the local hydrogen bond breaking dynamics of bulk water.

There are two strong intermolecular vibrational bands of liquid water, the “translational band”, centered at 180 cm^{-1} in H_2O , and the prominent “librational band”, extending from ca. 300 to 1000 cm^{-1} in H_2O . The internal motions giving rise to the “translational band” are essentially hydrogen bond stretching vibrations, while hindered rotational motions of water molecules give rise to the second absorption feature. The results of numerous experiments, e.g., neutron diffraction, dielectric relaxation measurements, and photon-echo spectroscopy, in conjunction with interpretation by theoretical models, have suggested that both the “translational” and the “librational” motions are directly involved in a number of dynamical processes, like the prototropic mobility and the solvation and relaxation dynamics of the liquid.^{3,4,6,7,14–18}

In recent femtosecond pump–probe experiments, Bakker et al. have studied the dependence of reorientational (librational) motion on the hydrogen bond stretching dynamics.¹⁹ They propose that excitation of translational motions facilitates the librations that are, in turn, responsible for hydrogen bond breaking through weakening of the hydrogen bond. Chandler and Luzar have examined the hydrogen bond dynamics of liquid water via computer simulations,^{6,15,16,20,21} postulating that librational motions play a central role in liquid-state dynamics because they are the dominant motion for the initial breaking of hydrogen bonds in the extended network, whereas translational motions themselves do not significantly lead to breaking of hydrogen bonds.^{6,15}

The above studies also show that the dynamics of one hydrogen bond are both uncorrelated with the fluctuations of

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neighboring bonds and surprisingly independent of the number of hydrogen bonds in which the water monomers are involved. The internal motions initiating hydrogen bond breaking remain the same even for water monomers making only two hydrogen bonds, although the absolute rate of bond breaking increases. Chandler and Luzar also conclude that under standard conditions, about half the water molecules use only three of the four tetrahedral bonding sites. The interpretation of recent dielectric relaxation measurements has even suggested that water molecules making only two hydrogen bonds are of special importance for bulk dynamics.⁸

The above results imply that the hydrogen bond breaking dynamics in liquid water are local and do not vary significantly with the hydrogen bond order. The free hydrogens in small water clusters—the main distinction between clusters and the bulk—are similarly predicted not to influence the translational and librational motions to a large degree.^{21,22} In support of this notion, recent low-resolution librational band spectra for water clusters containing 10–100 molecules rather closely resemble bulk spectra.²³ Although small water clusters are clearly not important as distinct constituents of liquid water, the above results show that they can provide a paradigm for elucidating the molecular details of specific local processes contributing to the liquid-state dynamics, viz., the hydrogen bond breaking dynamics.

While water cluster VRT experiments do not contain dynamical information per se, as they measure transitions between stationary states, the tunneling splittings observed for vibration–rotation transitions characterize the feasible hydrogen bond rearrangements in the cluster. The magnitude of the tunneling splitting directly corresponds to the facility of such a hydrogen bond rearrangement, and it is straightforward to extract a time scale for a given tunneling motion (Figures 2–4).^{24,25} Among these rearrangements, the bifurcation pathway is uniquely suited for the study of the dynamics of the hydrogen bond in small water clusters, as it has been observed for all water clusters except the tetramer^{12,13} and corresponds to the lowest energy pathway for breaking and making a hydrogen bond. Furthermore, the potential barrier for the bifurcation pathway is similar for all water clusters studied so far, and it is a local process; hence, we can utilize this specific tunneling process as a probe of the hydrogen bond breaking dynamics and investigate the effect of both cluster size and excitation of various intermolecular vibrations on these dynamics.

Here we report the effect of exciting the torsional, translational, and librational vibrations on the hydrogen bond breaking dynamics of the water trimer. In the trimer, the bifurcation tunneling pathway (Figure 1) connects eight degenerate minima (Figure 2), and the interaction among the degenerate minima can be represented by a Hückel matrix (Figure 3). The bifurcation pathway splits each rovibrational transition into a quartet with a characteristic intensity pattern determined by nuclear spin statistics. From the experimentally determined magnitude of the tunneling splitting for a given vibrational state and the eigenvalues and eigenvectors of the Hückel matrix, we can extract the time scale for breaking and making a hydrogen bond, i.e., the hydrogen bond lifetime (τ_H) of that state (Figure 4). All previously observed bands of $(H_2O)_3$ ($<100\text{ cm}^{-1}$) arise

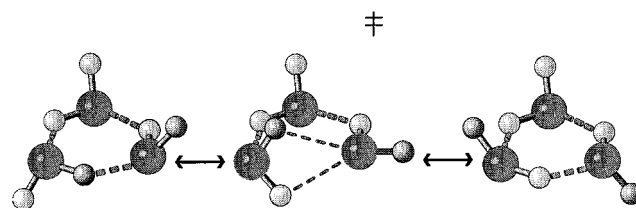


Figure 1. Bifurcation tunneling motion. The bifurcation tunneling pathway involves the exchange of the free and bound hydrogen of one water monomer, accompanied by a simultaneous torsional flipping motion of a neighboring water monomer.^{35,38,40} The tunneling pathway connects eight degenerate minima on the intermolecular potential energy surface and splits each vibration–rotation transition into a quartet (Figures 2 and 3). This tunneling motion has been observed for all water clusters except the water tetramer, for which the high symmetry inhibits this tunneling motion.¹³ This bifurcation motion represents the lowest energy pathway for breaking and making hydrogen bonds in small clusters and therefore may be of special importance for the dynamics of liquid water.

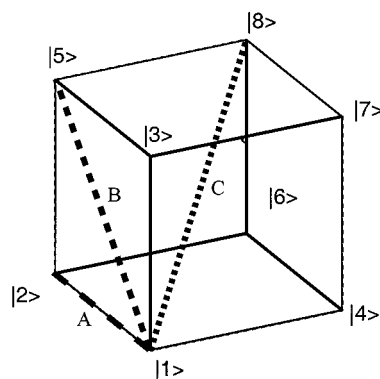


Figure 2. Bifurcation tunneling splitting. The connectivity of the eight degenerate minima by the bifurcation tunneling pathway is isomorphic to that of the corners of a cube with the edges *A* connecting minima via single tunneling events, face diagonals *B* via double tunneling events, and body diagonals *C* via triple tunneling events.

	1>	2>	3>	4>	5>	6>	7>	8>
1>	E0	A	A	A	B	B	B	C
2>	A	E0	B	B	A	A	C	B
3>	A	B	E0	B	A	C	A	B
4>	A	B	B	E0	C	A	A	B
5>	B	A	A	C	E0	B	B	A
6>	B	A	C	A	B	E0	B	A
7>	B	C	A	A	B	B	E0	A
8>	C	B	B	B	A	A	A	E0

Figure 3. Representation of the dynamics by a Hückel matrix with $E0$ as the diagonal element, A the first nearest neighbor interaction (NNI), B the second NNI, and C the third NNI. The eigenvalues are a singlet of energy $E_{A1} = E0 + 3A + 3B + C$, a triplet of $E_{T1} = E0 + A - B - C$, a triplet of $E_{T2} = E0 - A - B + C$, and a singlet of $E_{A2} = E0 - 3A + 3B - C$. In the high barrier limit valid in the ground state, only single tunneling events are important ($A \gg B, C$), and the tunneling results in an evenly spaced quartet with spacing $2A$. The barrier has been calculated to lie between 380 and 500 cm^{-1} , and the excited state therefore lies close to the top of the barrier, wherein all NNIs become important.^{35,36}

from torsional vibrations of the free hydrogen atoms. From a vibrational ground-state splitting of ca. 0.0033 cm^{-1} , the hydrogen bond lifetime of the ground state was determined to be $\tau_H(\text{GS}) = 1\text{--}2\text{ ns}$ for $(H_2O)_3$ (Figure 4).²⁵ The magnitude of the usually equally spaced tunneling splittings ranges from 0.003 to 0.007 cm^{-1} among states examined in the torsional manifold.²⁵ The very small dependence of the magnitude of the tunneling splitting on torsional energy confirms that the

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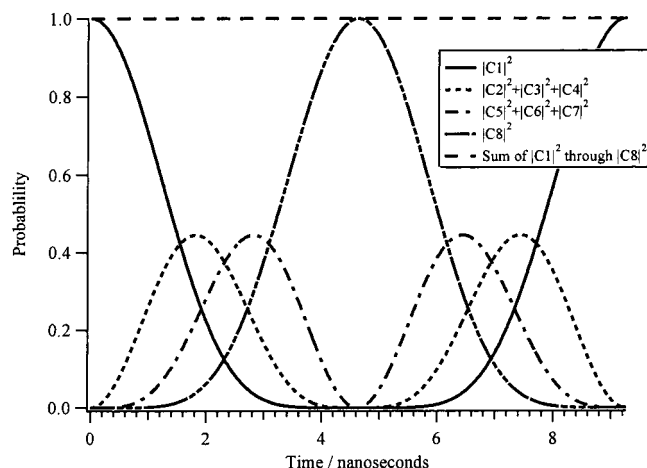


Figure 4. Knowledge of the magnitude of the splitting allows calculation of a tunneling time scale between degenerate minima. The graph shows the time evolution of the population $|C_n(t)|^2$ of the eight minima (the corners of the cube in Figure 2) with the starting condition $|C_1(0)|^2 = 1$ for the vibrational ground state ($2A = 100$ MHz) of $(\text{H}_2\text{O})_3$. We define the hydrogen bond lifetime τ_H as the time for a single tunneling event to occur, as this corresponds to breaking and making the hydrogen bond once. The time until the maximum in $|C_2(t)|^2 + |C_3(t)|^2 + |C_4(t)|^2$ is reached, 1.8 ns, corresponds to the time for a single tunneling event. The time until the maximum in $|C_8(t)|^2$ is reached, 4.6 ns, can be viewed as the time for three tunneling events. Therefore, a reasonable estimate for the hydrogen bond lifetime in the vibrational ground state is $\tau_H(\text{GS}) = 1\text{--}2$ ns,²⁵ which is identical with $\tau_H(\text{Trans})$ of the excited state of the translational vibration. With the two splittings of 6.7 and 1.4 cm^{-1} observed in the low barrier case of the 520 cm^{-1} bands, we can similarly extract a time scale of $\tau_H(\text{Lib}) = 1\text{--}6$ ps.

hydrogen bond lifetime does not change significantly upon excitation of torsional vibrations.²⁵

We have recently examined the frequency range corresponding to the translational and librational band region of liquid water utilizing the Berkeley tunable THz-VRT laser sideband and supersonic cluster/beam diode laser spectrometers. Experimental and spectroscopic details have been published elsewhere.^{26–32} The study of the translational band revealed a vibrational band of $(\text{D}_2\text{O})_3$ centered at 142.8 cm^{-1} (Figure 5). The band was assigned to a translational vibration (degenerate asymmetric stretch)³¹ and constitutes the first observation of a translational vibration for an isolated water cluster. The rovibrational transitions show no tunneling splittings within the experimental uncertainty (ca. 2 MHz).³¹ Therefore, the magnitude of the bifurcation tunneling splitting for the excited state of the translation has to be nearly identical to that of the vibrational ground state of the water trimer. $\tau_H(\text{Trans})$ therefore remains unchanged at $\tau_H(\text{Trans}) = \tau_H(\text{GS}) \approx 1\text{--}2$ ns upon excitation of the translational vibration.

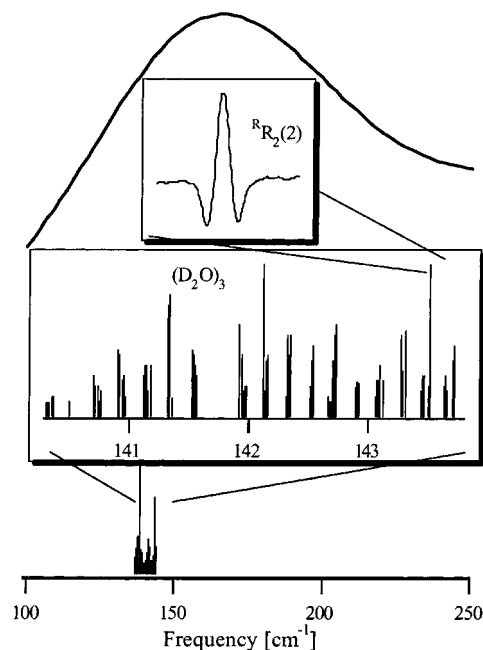


Figure 5. Translational band of $(\text{D}_2\text{O})_3$. An overview of the observed D_2O transitions with respect to the translational band of liquid D_2O shows that the 142.8 cm^{-1} band of $(\text{D}_2\text{O})_3$ lies well within the translational band of the liquid. The first inset shows a stick spectrum representation of the 142.8 cm^{-1} $(\text{D}_2\text{O})_3$ band, and the second inset is a scan of the $R_2(2)$ transition, representative of the strongest observed rovibrational transitions. The transition shows no tunneling splitting, indicating that the splitting in the lower and upper states have to be identical within the experimental uncertainty (ca. 2 MHz). The vibrational assignment and spectroscopic details have been discussed elsewhere.³¹ Methods: The Berkeley tunable THz spectrometers have been described in detail elsewhere.^{26,27,30,31} Tunable THz light is generated by mixing radiation from a line-tunable THz laser pumped by a CO_2 laser with continuously tunable microwave radiation in a 1T24 Schottky barrier diode. The resulting sidebands ($\nu_{\text{SB}} = \nu_{\text{THz}} \pm \nu_{\text{MW}}$) are separated from the carrier frequency and then multipassed 20–22 times through a planar supersonic jet. Water clusters were produced by expanding Ar bubbled through room-temperature D_2O in the supersonic expansion. The direct absorption signal is monitored by a liquid-helium-cooled unstressed Ga:Ge photoconductor.

The study of the librational band region revealed three parallel bands of $(\text{H}_2\text{O})_3$ at 517.2, 523.9, and 525.3 cm^{-1} (Figure 6). The very intense ($\sim 1\%$ absorption for Q-branch transitions) bands are located close to the center of the librational band of liquid H_2O and are assigned to the out-of-plane (oop) libration,³² predicted to be the most intense librational feature.^{33,34} In contrast to these 520 cm^{-1} bands, all previously observed $(\text{H}_2\text{O})_3$ bands are split into closely spaced quartets by the bifurcation tunneling motion (Figure 1). The oop libration couples to this bifurcation pathway very strongly, facilitating the tunneling motion in the excited state and resulting in dramatically increased spectral splittings. In fact, the splittings are so large that one actually observes isolated vibrational bands for each tunneling component, rather than a small splitting of each rovibrational transition within a single band. The three individual bands observed within 8 cm^{-1} correspond to these tunneling components, revealing that the bifurcation splittings in the excited librational state are nearly 3 orders of magnitude larger than those for the vibrational ground state. In the high barrier limit, valid for the previously observed low-energy states, the

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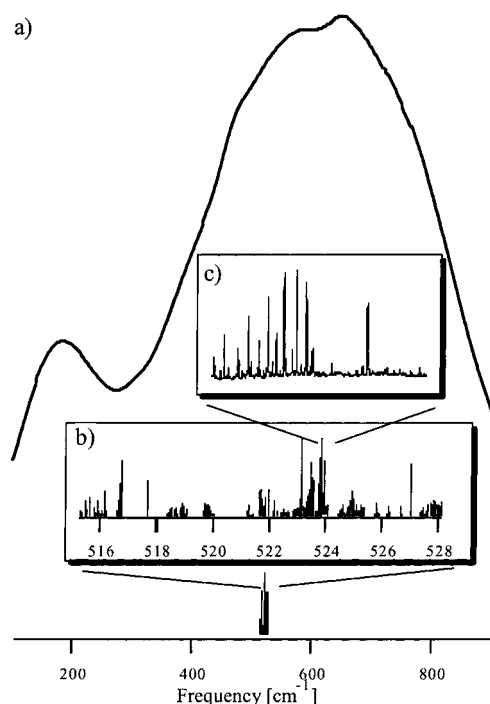


Figure 6. Librational bands of $(\text{H}_2\text{O})_3$. Three VRT bands of $(\text{H}_2\text{O})_3$ were assigned in the frequency range from 515 to 529 cm^{-1} . The vibrational assignment and spectroscopic details have been discussed elsewhere.³² This corresponds to the highest energy intermolecular vibration and the first observation of a librational vibration for a water cluster. (a) The bands are close to the center of the librational band of liquid water. (b) Enlarged representation of all water cluster transitions observed in this region. (c) Q-branch of the 523.9 cm^{-1} band together with the P(3) clump of the 525.3 cm^{-1} band. The oop librational vibration (predicted at 697.1 cm^{-1} ³⁴) is expected to facilitate the bifurcation tunneling motion that it closely resembles. Further evidence for this is revealed in that the 525.3 cm^{-1} state is considerably more planar than the ground state, requiring torsional motion of a free hydrogen toward the oxygen ring plane. This further evidences the similarity of the observed vibration to the bifurcation tunneling motion. Method: The spectra were obtained using the Berkeley supersonic cluster/beam diode laser spectrometer described in detail elsewhere.^{28–30,32} It resembles the experimental setup described in Figure 5, with a commercial tunable diode laser as radiation source and a Si:B photoconductive detector.

bifurcation tunneling components are usually equally spaced in energy (Figure 3). Wales and Fowler calculated bifurcation barrier heights of 381 (at the DZP/MP2 level) and 523 cm^{-1} ((TZ2P+diff)/CCSD), including ZPE corrections.^{35,36} If the oop libration indeed couples strongly to this pathway, this implies that the excited state observed here is near the top of the bifurcation barrier. The calculation of the splitting pattern for this low barrier case is more complicated. Our calculations (Figure 3) show that instead of the four equally spaced tunneling components, we instead expect three components close in energy and one separated by a larger degree. The 523.9 and 525.3 cm^{-1} bands are two of the three closely spaced components, with the third not currently observed due to its low intensity, determined by nuclear spin statistics.³² The 517.2 cm^{-1} band corresponds to the single isolated “tunneling” component.

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Having assigned the three observed vibrational bands to individual tunneling components of the excited state of the oop libration, we can extract a hydrogen bond lifetime of $\tau_{\text{H(Lib)}} = 1\text{--}6$ ps, strikingly similar to the accepted hydrogen bond lifetime in liquid water (~ 1 ps) and also to the time scales of a number of important dynamical processes in bulk phases of water (attributed to single-molecule reorientation), e.g., dielectric relaxation ($\tau_{\text{D}} \approx 8\text{--}9$ ps, $\tau_{\text{D}_2} \approx 1$ ps),¹⁴ reorientation relaxation ($\tau_1 \approx 13$ ps, $\tau_2 \approx 0.7$ ps),³⁷ and prototropic mobility (~ 1 ps).¹⁴ Whereas the molecular details of the tunneling motions and vibrations we observe in small water clusters are well understood,^{35,38,39} none of the experiments used for measuring these bulk time scales are sensitive to the microscopic details of the dynamical processes, and accordingly any molecular interpretation is strongly model dependent. The value of our VRT results is that they clearly demonstrate the dramatic effect of exciting specific intermolecular motions on the hydrogen bond breaking rate. Therefore, rather than the perhaps coincidental similarities of $\tau_{\text{H(Lib)}}$ with those of the bulk relaxation processes, the most important result of our study is that we have confirmed the same dependence of the hydrogen bond breaking dynamics on intermolecular motions in the water trimer as postulated in theoretical models of liquid water. Specifically, we observe a dramatic increase ($\times 1000$) in the rate of hydrogen bond breaking compared to that in the ground state of the water trimer upon excitation of a single quantum in the librational mode, no change of τ_{H} upon single quantum excitation of a translational mode, and an insignificant change of τ_{H} on excitation of the torsional vibrations. Hence, libration is the dominant vehicle for breaking and making the hydrogen bond, whereas the torsions and translations do not facilitate hydrogen bond breaking, just as postulated to be the case for liquid water. The study of the hydrogen bond breaking dynamics of the water trimer has therefore shown that it is, indeed, possible to successfully employ small water clusters as models for specific aspects of local bulk dynamics. Clearly, water clusters cannot be used as models for long time bulk dynamics, e.g., diffusion, or dielectric friction, e.g., in solvation and electron-transfer processes, for which librational motions are also largely responsible. The excitation energies of the librational VRT bands correspond to temperatures of ca. 400 °C and thus mimic the high-energy Boltzmann tail of room temperature water molecules in rearranging the hydrogen bond network. Although these librational bands occur at energies that are significantly lower than those required to actually break the hydrogen bond, it is to be expected that, in the bulk, the full energy required for breaking the hydrogen bond is similarly not required, as partial formation of other hydrogen bonds and rearrangements of the surrounding hydrogen bond network are occurring simultaneously.

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