

(22). Typical results, for the pyridine-quinine pair, are shown in Fig. 4. The absorption spectra for 0.5 mM quinine and for 0.5 mM pyridine are shown in Fig. 4A. Pyridine shows a characteristic peak at ~ 252 nm. Quinine shows a much more intense band centered at 225 nm and two other bands at ~ 280 and ~ 330 nm.

The absorption spectrum for the feed solution used in the permeation experiment is shown in Fig. 4B. Although both molecules are present in solution at the same concentration, the higher absorbance of the quinine nearly swamps out the 252-nm peak of the pyridine. The absorption spectrum of the permeate solution after 72 hours is shown in Fig. 4C. In spite of the higher absorbance of the quinine (larger molecule), only the peak for the pyridine (smaller molecule) is seen in this spectrum. The very intense quinine band centered at 225 nm is absent. To our ability to make the measurement, this bottleneck nanotubule membrane has filtered these two molecules on the basis of molecular size (Fig. 4C).

To verify this point, we used a much more sensitive analytical method, fluorescence (23), to search for traces of quinine in the permeate solution. The magnitude of the absorbance in Fig. 4C indicates that the pyridine concentration in the permeate is 7×10^{-5} M. With fluorescence analysis (23), it is possible to detect 5×10^{-9} M quinine in the presence of 7×10^{-5} M pyridine. However, no quinine fluorescence could be detected from the permeate solution. These data show that, to our (now much more sensitive) ability to make the measurement, this membrane has cleanly separated these two molecules and that if any quinine is present in the permeate solution, its concentration is less than 5×10^{-9} M.

These analytical data can be used to calculate a minimal selectivity coefficient, $\alpha_{\min}$. Because the concentration of the smaller molecule in the permeate solution was 7×10^{-5} M and the concentration of the larger molecule (if present at all) must be less than 5×10^{-9} M, the minimal selectivity coefficient for the pyridine-quinine pair is $\alpha_{\min} = 15,000$. Minimal selectivity coefficients obtained in this way (24) for the other pairs are shown in Table 1. In all three cases, the larger molecule was undetectable in the permeate solution.

Nishizawa *et al.* have demonstrated that these Au nanotubule membranes can show charge-based transport selectivity (9), and we have shown here that these membranes can also have molecular size-based selectivity. It seems likely that chemical transport selectivity can also be introduced. Hence, these nanotubule membranes hold promise for the development of highly selective membranes for chemical separations.

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13. We approximated the IDs of tubules using a gas permeation method (9).
14. In our earlier studies, we used a plating bath at pH = 10 (9, 11). Higher plating rates can be achieved with the same plating bath at pH = 12.
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16. Such single-molecule permeation experiments are used routinely. See, for example, R. V. Parthasarathy, V. P. Menon, C. R. Martin, *Chem. Mater.* **9**, 580 (1997).
17. We determined the flux by continuously monitoring the ultraviolet (UV) absorbance of the permeate solution while passing the permeate through a UV detector.
18. The subscript "i" is for "ideal" and signifies that these coefficients were obtained by single-molecule permeation experiments. See (16).
19. D values are from Z. Prat, Y.-M. Tricot, and I. Rubinstein [*J. Electroanal. Chem.* **315**, 225 (1991)] (MV^{2+}) and C. R. Martin, I. Rubinstein, and A. J. Bard [*ibid.* **115**, 267 (1983)] [$[Ru(bpy)_3]^{2+}$].
20. Similar sieving was observed in radiotracer self-diffusion experiments on lightly etched films prepared by the track-etch process [T. K. Rostovtseva *et al.*, *J. Membr. Biol.* **151**, 29 (1996)]. However, molecular filtration of the type described here could not be observed.
21. Although α_i , in general, increased with decreasing tubule ID, an interesting anomaly was observed for two membranes with tubule IDs between those in Fig. 3, C and D. The α_i values for these membranes were lower than the $\alpha_i = 172$ observed in Fig. 3C. We are now exploring the genesis of this anomaly.
22. Because of the nonuniform shape of the bottleneck tubules (Fig. 1B), it is difficult to extract an ID with the gas-flux method (9). All bottleneck membranes were plated from pH = 12 bath for a duration of 8 hours.
23. Quinine was excited at an excitation wavelength (λ_{ex}) of 308 nm and detected at an emission wavelength (λ_{em}) of 403 nm.
24. The minimal quantity of $[Ru(bpy)_3]^{2+}$ that could be detected was determined by fluorescence: $\lambda_{ex} = 286$ nm; $\lambda_{em} = 594$ nm. The concentration of MV^{2+} was determined by UV absorbance (258 nm). We determined the minimal quantity of rhodamine B that could be detected from its extremely intense absorbance at 555 nm. The concentration of anilinium was determined from its absorbance (254 nm).
25. This work was supported by NSF and the Office of Naval Research.

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Femtosecond Mid-IR Pump-Probe Spectroscopy of Liquid Water: Evidence for a Two-Component Structure

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A femtosecond mid-infrared pump-probe study of the vibrational and orientational dynamics of the OH-stretching mode of HDO dissolved in D_2O is presented. The orientational relaxation of the HDO molecules was observed to occur on either a very slow or a very fast time scale, with associated time constants of $\tau_R = 13$ picoseconds and $\tau_R = 0.7$ picosecond. It was observed that strongly hydrogen-bonded water molecules only relax through the slow orientational relaxation process, whereas the fast process dominates for weakly hydrogen-bonded molecules. This suggests that, with respect to orientational dynamics, two distinct molecular species exist in liquid water.

Knowledge about the orientational dynamics of water is essential for understanding the (bio)chemical and physical processes that take place in this liquid, notably chemical reactions and solvation. Therefore, the reorientational motion of molecules in liquid water has been extensively studied for over half a century, in particular by such methods as dielectric relaxation (1, 2), terahertz spectroscopy (3, 4), optical

and Raman-induced Kerr-effect spectroscopy (5, 6), and nuclear magnetic resonance (7). However, all of the experimental techniques employed to date have probed the orientational motion indirectly or as averaged over all the molecules in the liquid. In contrast, polarization-resolved pump-probe spectroscopy yields unambiguous information about the dynamics of orientational relaxation of small molecules in the liquid phase (8, 9). By developing a laser setup that generates intense femtosecond mid-infrared (mid-IR) pulses, we could study for

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the first time the orientational motion of vibrationally excited O–H groups of HDO molecules dissolved in liquid D₂O. The frequency tunability of the IR pulses made it possible to study specific subensembles of the water molecules. In a previous time-resolved IR pump-probe study (10), the pulses were too long to resolve the dynamics of the vibrational and orientational relaxation. It was shown that the results obtained in (10) could be well described by both a three-component and a continuum model (10, 11) and thus did not provide conclusive information on the hydrogen-bonded structure of liquid water.

Our setup consists of a commercial, tunable, femtosecond Ti:sapphire laser system, which is used to pump an optical parametric generation and amplification stage. In this way, nearly transform-limited IR pulses of 250 fs and 30 μ J are obtained in the wavelength region from 2.8 to 3.2 μ m (12). With these pulses, both one- and two-color pump-probe experiments have been performed. In one-color experiments, the IR pulses are split into an intense pump pulse (~ 20 μ J) that excites a significant fraction of the HDO molecules and a weak probe pulse (~ 1 μ J) that monitors the induced relative transmission change $\ln(T/T_0)$ as a function of the delay τ between the pump and probe pulses, where T_0 denotes the equilibrium probe transmission (no pump pulse). In two-color experiments, the probe pulse is generated separately from the pump pulse and can have a different center frequency. This makes it possible to monitor the pump-induced transmission changes at arbitrary frequencies, in particular at the $\nu_{\text{OH}} = 1 \rightarrow 2$ transition frequency, which is the absorption frequency of the vibrationally excited HDO molecules created by the pump pulse. The pulses are focused (focal length, 100 mm) and overlap in the sample.

The sample was 200 μ m thick and contained a 1 mol/liter solution of HDO in D₂O, prepared by mixing appropriate amounts of H₂O (high-performance liquid chromatography grade) and D₂O (>99.9 atom% D). During the measurements, the water is rapidly circulated to ensure that for every laser shot a fresh part of the liquid is in the focus. Figure 1 shows the IR absorption spectrum of the sample in the OH-stretching region, measured with a conventional IR spectrometer.

We recorded pump-probe scans at excitation frequencies of 3320, 3400, and 3500 cm^{-1} . The power spectra of the pulses at those frequencies are shown in Fig. 1. The intensity of the pump pulse is sufficient to excite a significant fraction of the HDO molecules to the $\nu_{\text{OH}} = 1$ state. Because of the large anharmonicity of the ν_{OH} mode [270 cm^{-1} (10)], these molecules no longer

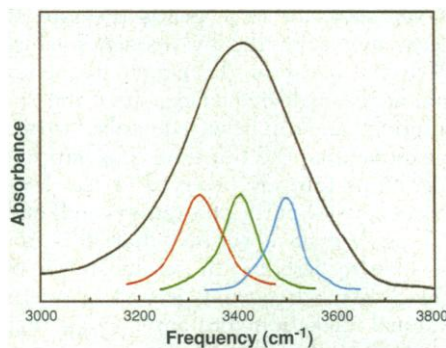


Fig. 1. Infrared absorption spectrum of the OH-stretching mode of HDO in D₂O (1 mol/liter solution in a 200- μ m sample), corrected for the D₂O background absorption (black curve); and normalized power spectra of the laser pulses, centered at 3320 (red curve), 3400 (green curve), and 3500 cm^{-1} (blue curve), respectively.

absorb at the frequency of the pump pulse. In the one-color experiments, this results in a transmission increase of the probe pulse for positive delays. The decay of the relative transmission changes of the probe pulse components polarized parallel and perpendicular to the pump pulse [$\ln(T/T_0)_{\parallel, \perp}$] is determined by both vibrational relaxation and rotational reorientation of the excited molecules.

In order to study the orientational relaxation of the excited molecules, we used the method described in (8): The polarization of the probe pulse is rotated 45° with respect to that of the pump pulse, using a zero-order $\lambda/2$ -plate, and the transmission changes $\ln(T/T_0)_{\parallel}$ and $\ln(T/T_0)_{\perp}$ are monitored by means of a polarizer placed behind the sample. If the pump field is polarized along the z axis, the $\nu_{\text{OH}} = 0 \rightarrow 1$ transition probability of a HDO molecule is proportional to $\cos^2 \theta$, where θ is the angle between the molecular transition dipole moment (directed along the OH bond) and the z axis. Because the molecular transition dipole moments are randomly oriented at thermal equilibrium, the excitation by the pump field results in an orientational distribution of the OH bonds of the excited molecules given by $f(\theta) = 3/4\pi \cos^2 \theta$. As a consequence, initially the transmission change for $\ln(T/T_0)_{\parallel}$ is three times larger than for $\ln(T/T_0)_{\perp}$ (8). As rotational reorientation of the molecules takes place, the difference between the $\ln(T/T_0)_{\parallel}$ and $\ln(T/T_0)_{\perp}$ components decreases, and in the limit of complete orientational scrambling, [$f(\theta) \rightarrow 1/4\pi$] vanishes.

Figure 2 shows the results obtained by pumping at 3400 cm^{-1} , at the center of the absorption band, for the parallel and perpendicular components of the probe pulse. Vibrational relaxation leads to a population transfer from the $\nu_{\text{OH}} = 1$ to the $\nu_{\text{OH}} = 0$

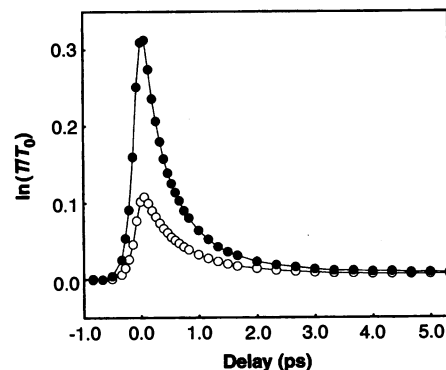


Fig. 2. Pump-probe scans recorded pumping and probing at an excitation frequency of 3400 cm^{-1} (the pulse spectrum is shown as the green curve in Fig. 1). The relative transmission change $\ln(T/T_0)_{\parallel, \perp}$ of the probe pulse is plotted versus the delay τ for the components polarized parallel (solid points) and perpendicular (open points) to the pump pulse.

state and thus to a decrease of the bleaching for both polarization components of the probe pulse, but does not change the ratio [$\ln(T/T_0)_{\parallel}/\ln(T/T_0)_{\perp}$]. It is easily shown that the rotation-free signal $\Delta\alpha_{\text{RF}}(\tau)$, which is defined as in (8)

$$-\Delta\alpha_{\text{RF}}(\tau) = \ln(T(\tau)/T_0)_{\parallel} + 2\ln(T(\tau)/T_0)_{\perp} \quad (1)$$

reflects only the excited-state population dynamics, whereas the rotational anisotropy $R(\tau)$, which is defined as in (8)

$$R(\tau) = \frac{\ln(T(\tau)/T_0)_{\parallel} - \ln(T(\tau)/T_0)_{\perp}}{\ln(T(\tau)/T_0)_{\parallel} + 2\ln(T(\tau)/T_0)_{\perp}} \quad (2)$$

reflects only the orientational dynamics (independent of the vibrational relaxation), with a value between 0 (complete orientational scrambling) and 0.4 (maximal anisotropy). It can be shown that the rotational anisotropy is proportional to the second-order rotational autocorrelation function of the transition dipole moment of the excited molecules (13):

$$R(\tau) \propto \langle P_2[\vec{\mu}_{\text{OH}}(0) \cdot \vec{\mu}_{\text{OH}}(\tau)] \rangle \quad (3)$$

where $P_2(x)$ is the second Legendre polynomial.

Monitoring the rotation-free signal as a function of the delay, we obtain the vibrational lifetime T_1 . This vibrational lifetime is found to be ~ 700 fs and shows a very weak excitation-frequency dependence, increasing slightly with the excitation frequency. The only previous time-resolved IR study on liquid water reported a much longer vibrational lifetime (10), probably because the pulses employed in that study were not sufficiently short to accurately determine this lifetime. We have also per-

formed a two-color experiment, exciting the HDO molecules at 3400 cm^{-1} and probing at 3150 cm^{-1} , where the $\nu_{\text{OH}} = 1 \rightarrow 2$ transition is located (10). An induced absorption was observed that decayed with a time constant equal to that with which the bleaching observed at 3400 cm^{-1} decayed, confirming that this bleaching is indeed caused by population of the $\nu_{\text{OH}} = 1$ state.

The observed rotational anisotropy as a function of delay is shown in Fig. 3, for three excitation frequencies within the broad absorption band. The power spectra are shown in Fig. 1 (the colors in Figs. 1 and 3 match). In contrast to the virtually frequency-independent vibrational relaxation rate, the rotational dynamics clearly depend dramatically on the excitation frequency. At the high-frequency side of the absorption band (blue points), the decay of the anisotropy occurs much faster than at the low-frequency side (red points; exponential decay with a time constant of 13 ps). It is well known that the O–H stretching frequency decreases with increasing hydrogen bond strength (14). Therefore, our results imply that for strongly hydrogen-bonded water molecules (low O–H stretching frequency), orientational relaxation takes place much more slowly than for weakly hydrogen-bonded molecules (high O–H stretching frequency). At the center frequency (green points) and the high-frequency side (blue points) of the absorption band, the decay does not occur with a single exponential decay constant but in a biexponential manner. For small delays the decay

is very fast; for large delays the rate of decay approaches the low-frequency value. Both the decay at the center frequency and at the high-frequency side of the absorption band can be well described with a biexponential, the two time constants being 13 ps (already observed at the low-frequency side of the absorption band) and 0.7 ps. We have verified that it is not possible to describe the results shown in Fig. 3 with a frequency-dependent orientational relaxation constant $\tau_R(\nu_{\text{OH}})$ that varies smoothly with the excitation frequency ν_{OH} . Apparently, for the orientational relaxation only two time scales exist in the liquid.

There is not necessarily a one-to-one correspondence between the two time scales and strongly and weakly hydrogen-bonded water molecules, because the possibility cannot be excluded that the weakly hydrogen-bonded molecules relax through both the fast and the slow process. It is clear however, that the strongly hydrogen-bonded molecules can only relax through the slow process. Hence, with respect to the orientational dynamics, there exist two distinct species of liquid water molecules that differ in showing the fast orientational relaxation process. At the center frequency and at the high-frequency side of the absorption band, a mixture of the two species is excited, leading to a biexponential decay of the rotational anisotropy. The very slow orientational relaxation observed at the red side of the absorption band shows that there is no rapid exchange (spectral diffusion) between the weakly and strongly hydrogen-bonded water molecules. Of course, the possibility cannot be excluded that the spectral diffusion is faster within each of the two components.

As yet, it is not possible to unambiguously relate the two orientational relaxation time scales to differences in local structure or hydrogen-bond lifetimes (15, 16). The slow orientational time scale possibly involves the breaking of a hydrogen bond and might be associated with a structural relaxation process. In fact, the value of the slow relaxation constant is quite similar to the Debye constant of liquid water observed in dielectric measurements (2). The fast orientational time scale observed for the weakly hydrogen-bonded OH groups could be associated with the motion of these molecules around the (possibly hydrogen-bond coordinated) O–D bond. This process probably does not involve the breaking of a hydrogen bond. This type of molecular relaxation due to intramolecular motions is denoted as β -type relaxation (17). Recently, a β -type relaxation process was also observed in the dielectric response of liquid 1-propanol but was interpreted differently (18).

We would like to note that in our experiments, we can selectively study either of the components by tuning to their respective O–H stretch absorption frequencies. This is a very important advantage when compared to dielectric relaxation measurements, which inherently measure an average over all molecules in the liquid and which might therefore only observe the relaxation process that contributes dominantly to the dielectric response. In the present case, this seems to be the slow process. Furthermore, the decay of the rotational anisotropy directly reflects the motion of the O–H groups, whereas in other methods, such as dielectric relaxation and Raman-induced Kerr-effect spectroscopy, it is often not clear to what kind of molecular motion the observed relaxation is related.

The development of a laser system that delivers intense, femtosecond mid-IR pulses has made it possible to study the orientational relaxation of selected molecules in liquid water. Our results suggest that a mixture model applies to liquid water and that, with respect to orientational dynamics, only two species exist in the liquid.

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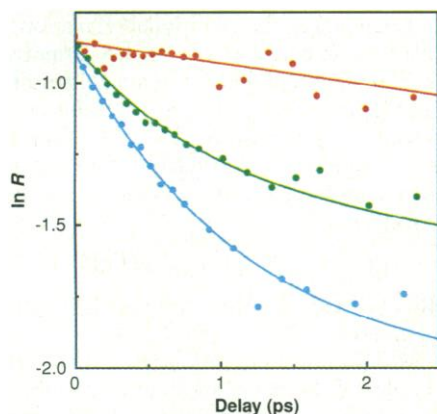


Fig. 3. Logarithm of the rotational anisotropy as a function of the delay between the exciting and probing pulse, at three excitation frequencies within the broad O–H stretching absorption band of water. The colors of the data points correspond to the laser power spectra shown in Fig. 1. The red curve represents a single exponential decay (decay constant $\tau_R = 0.7$ ps); the green and blue curves represent a biexponential decay ($\tau_R = 0.7$ ps and 13 ps).