# Direct Evidence of Angular Jumps During Water Reorientation Through Two-Dimensional Infrared Anisotropy

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ABSTRACT   Water reorientation was recently suggested via simulations to proceed through large angular jumps, but direct experimental evidence has so far remained elusive. Here we show that both infrared pump−probe and photon echo spectroscopies can provide such evidence through the measurement of the two-dimensional anisotropy decay. We calculate these two-dimensional anisotropies from simulations and show they can be interpreted as a vibrational frequency-resolved orientation time-correlation function. We develop a frequency-dependent extended jump model to predict the nature of the angular jump signature in these anisotropies. This model provides a rigorous and unambiguous connection between ultrafast infrared experimental results and the presence of angular jumps in bulk water, and calls for new experiments.

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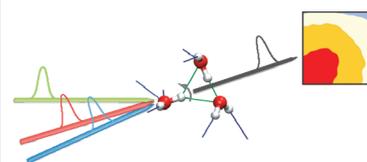
L iquid water forms a labile hydrogen-bond (HB) network, which constantly rearranges by breaking and forming HBs. This reorganization dynamics plays a key role in a wide range of fundamental processes, such as S_N2 and proton transfer reactions[1,2] together with proton transport[3] in aqueous solutions, where it enters in the rate-limiting step, and protein activity, where the labile water HB network facilitates the conformational transitions.[4] On the basis of molecular dynamics simulations, the reorientation of water was recently suggested to occur mainly through large angular jumps between HB acceptors.[5,6] This jump mechanism strongly contrasts with the previously assumed picture of Debye rotational diffusion through very small angular steps.

Experimentally, an indirect support of the jump picture comes from ultrafast infrared spectroscopy,[7] which evidences the transient character of non-HB states; this is fully consistent with the jump mechanism[5,6] where HB acceptor exchange occurs through the concerted breaking and forming of HBs. However, direct experimental evidence showing the existence of the angular jumps has so far remained elusive. The second-order reorientation time measured by NMR and ultrafast infrared spectroscopies cannot readily discriminate between the diffusive and jump models, and its ratio with the first- or third-order times is needed.[5,6] Unfortunately, these times are presently not directly accessible experimentally.[8] Additional indirect evidence in favor of the jump picture comes from quasi-elastic neutron scattering, which is sensitive to both the first- and second-order reorientation times. The surprising 2-fold difference between the second-order reorientation times obtained through neutron scattering and the values from NMR and ultrafast infrared spectroscopies

disappears when the angular jump model[5,6] is used in place of the rotational diffusion assumption to interpret the spectra.[9]

Molecular dynamics (MD) studies[5,6] suggest that the jump transition state is a bifurcated HB structure where the reorienting water OH donates two weak HBs to two acceptors, resulting in a blueshift of the OH stretch vibrational frequency.[6,10] These changes in the OH frequency during the jump thus make ultrafast infrared spectroscopy an exquisite technique to investigate the presence of angular jumps in water. In particular, two-dimensional infrared (2D IR) spectroscopy can selectively follow systems with given initial and final vibrational frequencies and has already proved to be extremely successful in the investigation of other aspects of water HB dynamics.[7,11−15]

However, water molecules close to the jump transition state cannot be selectively excited using a blue-shifted infrared excitation because most ($\simeq$80%) blue-shifted OHs only experience a transient HB break and quickly return to their initial HB acceptor and initial orientation without any jump,[6] while the jumping OHs represent a minor ($\simeq$20%) fraction. Because the OH frequency dynamics is similar for a successful jump forming a new HB with a different water acceptor and for an unsuccessful jump (i.e., a large amplitude libration) reforming an HB with the same initial acceptor, the frequency dynamics measured by 2D IR photon echo spectra cannot separate the contribution of jumps from that of librations. This was recently confirmed by the great similarity between the

T=0.25 ps   T=1 ps   T=3 ps

(a)
(b)
(c)
(d)
(e)
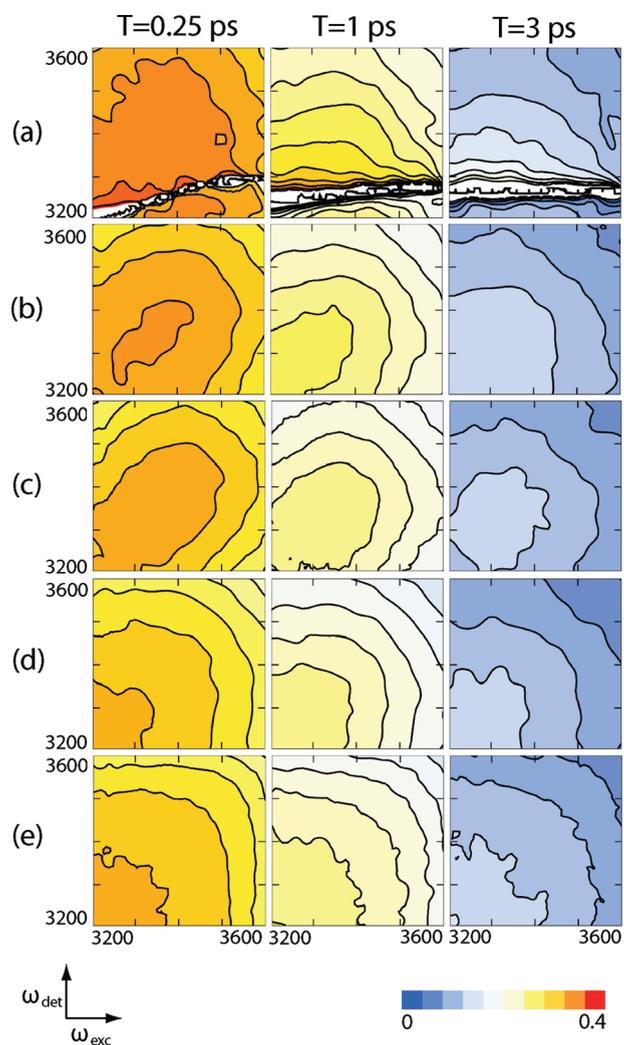
ω_{det}
ω_{exc}

0   0.4

Figure 1. 2D IR anisotropy (eq 1) calculated as a function of excitation and detection frequencies (in cm^{-1}) (a) including the 1−2 vibrational transition, (b) without the 1−2 transition, (c) without the 1−2 transition and the non-Condon effects, and (d) without the 1−2 transition, the non-Condon effects, and any reorientation contribution during the coherence periods. (e) Frequency-resolved orientational correlation function C_2 (eq 2). All quantities are represented at three different delays T.

calculated 2D IR spectra of water with and without the angular jumps respectively.[16]

The key difference between successful jumps and failed jump attempts is that only the former lead to a stable, long-time reorientation. A frequency-dependent reorientation study through spectrally resolved anisotropy measurements is therefore a promising way of specifically revealing the angular jumps. These can be performed, for example, by polarization-resolved pump−probe[17−22] or photon echo correlation[7,11−15] spectroscopies. Here we present 2D anisotropy decays calculated from MD simulations and develop a frequency-dependent version of the extended jump model previously suggested to describe the water jump reorientation time.[5,6] This new model specifically evidences which contribution to the 2D anisotropy originates from the angular jumps.
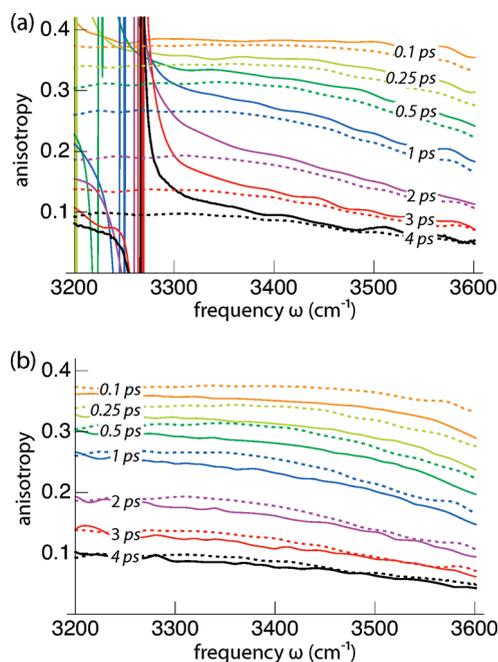

Figure 2. Cuts in the 2D surfaces shown in Figure 1 for $\omega = \omega_{exc} = \omega_{det}$ at different delays T, (a) comparing the anisotropy R (eq 1) with (solid line) and without (dots) the 1−2 vibrational transition, and (b) comparing C_2 (eq 2; solid line) and the anisotropy R without the 1−2 transition (dots).

We then relate these results to already or soon to be available experimental results to provide direct evidence of angular jumps in water.

In analogy with the conventional one-dimensional polarization anisotropy R, the spectrally resolved 2D anisotropy is recovered from pump−probe or photon echo signals collected with parallel and perpendicular polarizations (respectively $S_{\parallel}$ and $S_{\perp}$),

$$R(\omega_{exc}, \omega_{det}; T) = \frac{S_{\parallel}(\omega_{exc}, \omega_{det}; T) - S_{\perp}(\omega_{exc}, \omega_{det}; T)}{S_{\parallel}(\omega_{exc}, \omega_{det}; T) + 2S_{\perp}(\omega_{exc}, \omega_{det}; T)} \quad (1)$$

where ω_{exc} and ω_{det} are, respectively, the excitation and detection frequencies. In photon echo experiments, $S_{\parallel,\perp}$ are the $S_{XXXX,XXYY}$ 2D IR spectra, and T is the population time, while in pump−probe measurements,[21,22] $S_{\parallel,\perp}$ are the $\Delta\alpha_{\parallel,\perp}$ absorption changes, and T is the pump−probe delay. In the following, we adopt the 2D IR photon echo perspective, but the same analysis and discussion apply to pump−probe signals since 2D IR and transient hole burning pump−probe spectra are related through Fourier transformation.[23]

The resulting 2D IR anisotropy maps (Figure 1a) for different delays T and the associated cuts in the 2D surface along the diagonal for $\omega_{exc} = \omega_{det}$ (Figure 2a) show that the anisotropy is lower for initial or final OH frequencies on the blue edge ($\omega > 3400$ cm^{-1}) than for frequencies in the center of the band. This implies that water reorientation is faster for blue-shifted initial or final OH frequencies, in agreement with previous pump−probe spectroscopy results obtained for specific excitation and detection frequencies.[17,20−22]

The nodal line in the 2D IR spectra between the positive peak due to the 0−1 transition and the negative peak due to

the 1−2 transition causes the anisotropy to diverge in this spectral region. To assess how far this divergence affects the 2D anisotropy surface, the calculations were repeated without any excited-state absorption (Figure 1b). The 2D IR spectra and therefore the anisotropy are now rigorously symmetric with respect to a permutation of ω_{exc} and ω_{det},[23] as illustrated by the calculated anisotropy (Figure 1b). Similar results were reported recently.[12] Cuts in the 2D surface for $\omega_{exc} = \omega_{det}$ (Figure 2a) show that the experimentally available anisotropy map including the 1−2 transition is noticeably distorted by this divergence for red-shifted detection frequencies (≤ 3400 cm^{-1}), but that the blue-edge region where one expects the jump reorientation to contribute most is much less affected. This also demonstrates that it is preferable to focus on the OH rather than OD stretch because of its greater anharmonicity, i.e., of the greater difference between the 0−1 and 1−2 vibrational transition frequencies; the study of dilute HOD in D_2O rather than in H_2O is thus a better choice to investigate the 2D anisotropy decay, notwithstanding the shorter OH vibrational lifetime.[22]

The conventional, one-dimensional anisotropy decay is usually considered to be proportional to the second-order Legendre polynomial orientational time-correlation function (tcf)[24] $R(t) = 2/5 \langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$, where $\mathbf{u}$ is the orientation of the water OH bond.[25] We now examine whether the 2D anisotropy can be related in the same manner to the frequency-resolved orientational tcf:

$$C_2(\omega_{exc}, \omega_{det}; T) = 2/5 \langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(T)]$$
$$\delta[\omega(0) - \omega_{exc}]\delta[\omega(T) - \omega_{det}]\rangle \quad (2)$$

where $\omega(t)$ is the 0−1 vibrational transition frequency at time t. Figure 1e shows that C_2 qualitatively reproduces the frequency dependence of the 2D anisotropy R, especially the faster decay on the blue side. However, the two functions are not identical, as indicated by the contour lines, which are elliptic for R at short T (Figure 1b) but "corner shaped" for C_2 (Figure 1e). This is not due to the frequency dependence of the transition dipole moment included in the optical response functions entering in R (non-Condon effects[26]) but neglected in C_2: as presented in Figure 1c, the frequency-dependent anisotropy R is not dramatically affected by the neglect of these effects. The difference between R and C_2 is actually due to the (first-order) reorientations occurring between the first two interactions and between the last two interactions with pulses in the third-order nonlinear spectroscopy experiment (usually called coherence times t_1 and t_3[23]). Removing these contributions to the reorientation in the calculation[27] leads to an anisotropy surface (Figure 1d) that is very similar to C_2 (Figure 1e), with corner-shaped contours. The diagonal cuts (Figure 2b) show that the discrepancy between R and C_2 is greatest at short delays T, where the reorientation during t_1 and t_3 becomes comparably non-negligible. At longer delays ($T > 1$ ps), R and C_2 are very similar and exhibit the same frequency dependence. One can thus legitimately interpret the experimental R as a frequency-dependent C_2 orientational tcf, and in the following, we will focus on understanding the frequency dependence of the C_2 decay and its connection to angular jumps.

Our frequency-dependent model for C_2 is based on the extended jump model (EJM) recently developed to connect the angular jump mechanism to the experimentally accessible orientational tcf and reorientation time.[5,6] Within this picture, water reorientation is suggested to occur along three independent pathways.[5,6] First, a fast (sub-ps) but partial reorientation due to OH librations within a cone centered on the donor−acceptor HB axis; the second and most important contribution comes from the exchange of HB acceptor, where, once the environment has reorganized to offer a new viable HB acceptor, the water OH bond suddenly executes a large-amplitude angular jump from its former HB partner to this new acceptor; a third, minor, contribution is the slower diffusive tumbling of the intact HB axis (frame) between successive jumps. The analytic EJM associated with this mechanism successfully describes the bulk water reorientational dynamics, reproducing both the experimental and simulated reorientation times[5,6,9] and has been extended to aqueous solutions containing ions, amphiphiles, and amino-acids.[16,28−30]

We now examine the frequency dependence of each of these three contributions. The librational reorientation is well-known to be sensitive to the OH frequency.[10,17,20−22,31] Blueshifted frequencies correspond to more weakly bonded OHs, which reorient in a wider librational cone. Since the C_2 decay within the first few hundred femtoseconds is essentially due to librations, reorientation is thus more pronounced for blueshifted initial and/or final frequencies, as illustrated in Figures 1 and 2. For longer delays, the librational cone is fully sampled. The librational contribution to C_2 is thus constant and determines the frequency-dependent initial amplitude $C_2^{lib\infty}$ of the subsequent long-time decay.

Concerning the diffusive frame contribution due to the HB axis tumbling, the OH frequency is not sensitive to this motion, and this reorientation is thus independent of the OH frequency. This is confirmed by the calculated frequency-resolved C_2 between successive jumps,[5,6] whose long-time decay τ_2^{frame} is independent of the initial and final frequencies (data not shown).

We now turn to the key frequency dependence of the jump reorientation. The free energy barrier to reach the jump transition state was shown to be mostly due to the concerted elongation of the initial HB and penetration of the new partner within the first shell of the rotating water.[6] While the OH frequency is sensitive to the weakening of the initial HB, it does not report on the arrival of a new HB partner. Within a simplified picture,[10] the jump rate constant is thus expected to be frequency-independent, since a blueshifted OH frequency does not guarantee the presence of a new partner to stabilize the new orientation. However, the overall free energy barrier for the asymmetric translational motion of the initial and final partners is approximately 1.6 kcal/mol, with similar contributions ($\simeq 0.8$ kcal/mol) from each of the elongation and approach components.[6] The barrier to the new partner's approach is thus comparable to the thermal energy at 298 K ($\simeq 0.6$ kcal/mol). Independently of the initial HB strength, the thermal probability to find a new partner available is thus small but always non-negligible[32] because of the few second-shell waters that penetrate the first shell due to thermal
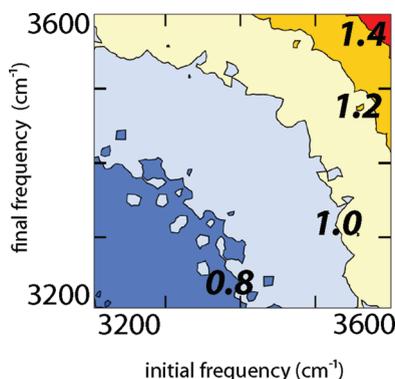
Figure 3. Contour plot of the average number of jumps between HB acceptors $N(\omega_{exc}, \omega_{det}; T)$ experienced by a water OH over a $T = 3$ ps period (close to the 3.3 ps frequency-averaged time between two jumps[6]), as a function of the initial and final frequencies.

Figure 4. Cuts in the 2D anisotropy R with the $1-2$ transition for $\omega = \omega_{exc} = \omega_{det}$ at different delays T, divided by the red-edge value at 3400 cm^{-1}.

activation. In these few situations where a new partner is available, the jump is conditioned only by the initial HB strength, reflected by its OH frequency. The jump probability is thus slightly frequency-dependent. This is confirmed by the calculation of the number N of jump events, i.e., of HB acceptor exchanges during a given time interval, which exhibits a moderate increase with increasing initial or final frequency (Figure 3).

The frequency-dependent jump probability can be incorporated within the EJM,[5] where the jump reorientation component is described through the Ivanov jump model.[5] The latter relates the time between jumps τ_{jp} and the jump amplitude $\Delta\theta$ to the orientation tcf $C_2^{jp}(T) = \exp[-(T/\tau_{jp}) f_2(\Delta\theta)]$, where f_2 is an angular factor.[5] The ratio T/τ_{jp} is the number of jumps during the period T, and the frequency-dependent extension of the Ivanov model is therefore

$$C_2^{jp}(\omega_{exc}, \omega_{det}; T) = \exp[-N(\omega_{exc}, \omega_{det}; T) f_2(\Delta\theta)] \quad (3)$$

The jump amplitude $\Delta\theta$ is assumed to be frequency-independent since it is determined by the location of the new HB acceptor, to which the OH frequency is not sensitive. For delays longer than the initial subpicosecond librational decay, the frequency-dependent EJM, hereafter denoted as FD-EJM, incorporates the above-discussed librational, frame, and jump contributions and leads to the orientation tcf:

$$C_2(\omega_{exc}, \omega_{det}; T) = C_2^{lib\infty}(\omega_{exc}, \omega_{det}) \exp[-T/\tau_2^{frame}]$$
$$\exp[-N(\omega_{exc}, \omega_{det}; T) f_2(\Delta\theta)] \quad (4)$$

The key point here is that, beyond the librational decay, the C_2 decay rate dependence vis-a-vis the frequency is specifically due to the angular jumps whose number N is frequency-dependent.

We now return to the experimentally accessible R. Since we have shown that R can be interpreted as a C_2 tcf, a frequency dependence of its decay beyond the librational time scale would point unambiguously to the presence of angular jumps. This frequency dependence of R is most easily evidenced by dividing R at each delay by its value, for example, on the red edge to remove the frequency-independent decay. The frequency dependence then appears as a
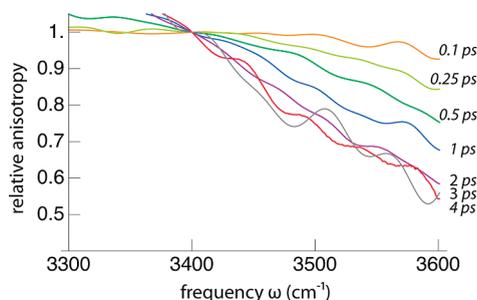
distortion with time of the normalized R. Cuts for $\omega_{exc} = \omega_{det}$ in the normalized R (Figure 4) clearly exhibit such distortion. While the faster decay on the blue edge is initially due to librations, it persists beyond the librational time scale (> 1 ps), leading to a growing distortion of the profile. This can only be explained by the angular jumps, which are slightly more probable for blueshifted frequencies and lead to a faster reorientation. For delays longer than twice the vibrational frequency dephasing time ($\simeq 2 \times 1.4$ ps[19]), the correlation between the number of jumps and the initial and final frequencies becomes negligible, and the anisotropy decay rate is the same at all frequencies, as previously observed;[10,21,31] the anisotropy profile along the frequency thus stops distorting (Figure 4).

Pump−probe spectroscopy experiments have evidenced such faster anisotropy decays for blue-shifted frequencies beyond the librational time scale.[17,21] These measurements were done for specific pump and probe frequencies, thus corresponding to specific points in the 2D anisotropy surface. Our FD-EJM therefore provides a rigorous connection between this accelerated decay and the presence of angular jumps in water. This is direct experimental evidence that very strongly supports the existence of angular jumps in water.

However, these existing experimental results should still be complemented by more detailed frequency-resolved anisotropy experiments. Bakker and co-workers have presented pioneering hole-burning results for the OD stretch in H$_2$O corresponding to vertical cuts in the 2D anisotropy surface along the probe frequency for different fixed pump frequencies.[21] These results partly differ from the ones we report here, for example, with an increase of R along the probe frequency when pumped in the blue ($R_{blue-blue} > R_{blue-red}$), while we see the opposite (Figure 1a). Several concerns can be raised regarding these experimental results: (a) the long duration ($\simeq 150$ fs) of the pump pulses precludes any unambiguous interpretation of the results at short (< 500 fs) delays; (b) the observed asymmetric role of the pump and probe pulses ($R_{red-blue} \simeq R_{blue-blue} > R_{blue-red}$) is intriguing and points to an effect of the excited state absorption, since within a two-level picture one expects a symmetric behavior ($R_{red-blue} = R_{blue-red}$);[23] (c) the choice of the OD stretch in H$_2$O with a smaller anharmonicity than the OH stretch leads to non-negligible effects of the distortion due to excited-state absorption, even on the blue edge. This distortion very

probably masks the underlying changes of R with the probe frequency and explains the discrepancy with our results.

It would therefore be extremely interesting to repeat these hole-burning experiments on HOD in D_2O and also to measure the anisotropy from photon-echo 2D spectra, which have the great advantage of not being bandwidth duration limited. While a major difficulty in these latter experiments is the need for absolute value 2D IR spectra, promising preliminary results are already available (A. Tokmakoff, MIT, private communication).

In this contribution, we have developed a frequency-dependent extended jump model for water reorientation. This FD-EJM incorporates the slightly increased jump probability for blue-shifted OH frequencies and shows that a faster reorientation for blue-shifted initial or final frequencies at intermediate (approximately 500 fs to 3 ps) delays is direct evidence of angular jumps during water reorientation.[33] This model provides the first rigorous interpretation of this faster reorientation observed in pump−probe experiments and calls for new photon-echo 2D IR anisotropy experiments to provide direct evidence of the presence of angular jumps in water.

METHODS

We calculated the anisotropy corresponding to a dilute HOD molecule in D_2O from an MD trajectory with 500 SPC/E D_2O water molecules, propagated for 2.5 ns in the microcanonical ensemble, at an average temperature of 298 K and at the experimental 1.104 g/mL D_2O density. The parallel and perpendicular 2D IR spectra were calculated with XXXX and XXYY polarizations, respectively, based on the third-order optical response functions[23] without assuming Gaussian fluctuations and including non-Condon effects, following the procedure detailed in refs 16 and 26.

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(33) While the frequency-dependent reorientation evidences the existence of angular jumps in bulk water, it cannot provide the jump characteristics. For concentrated aqueous salt solutions, recent 2D IR studies have measured the water HB switching time between an anion and a water molecule (Moilanen, D. E.; Wong, D.; Rosenfeld, D. E.; Fenn, E. E.; Fayer, M. D. Ion–Water Hydrogen-Bond Switching Observed with 2D IR Vibrational Echo Chemical Exchange Spectroscopy. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 375–380) and the angular amplitude of the associated motion (K. J. Gaffney, SLAC, private communication).

Correction to "Direct Evidence of Angular Jumps During Water Reorientation Through Two-Dimensional Infrared Anisotropy"

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Preliminary two-dimensional (2D) IR polarization-dependent results were incorrectly mentioned in our Letter. The first full paragraph on page 1515 should read as follows:

"It would therefore be extremely interesting to repeat these hole-burning experiments on HOD in D_2O and also to measure the anisotropy from photon-echo 2D spectra, which have the great advantage of not being bandwidth duration limited. While Fourier transform 2D spectra remain technically challenging, promising preliminary results are already available for aqueous ionic solutions".

These results now appear in ref 1.

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