Electronic Supplementary Information

Table of contents:

1. Samples preparation

All salt solutions were prepared in a solvent containing 5% (w/w) of D2O and 95% of H2O. The solvent was isotopically diluted in order to decrease the optical density of the samples in the spectral region of the OD vibration and to prevent the anisotropy data being affected by Förster energy transfer.

Formate salts (HCOOLi, HCOONa, HCOOK, HCOONH4, HCOOCs) and iodide salts (NaI, KI, LiI) were purchased from Aldrich and were of a purity of at least 98%. D_2O (Aldrich) contained over 99.99 % of D atoms. H_2O was purified with the use of a MiliQ system (Millipore). For the spectroscopic measurements the samples were placed between two parallel CaF_2 windows with a 25 µm Teflon spacer in between. Linear spectra of the solutions were measured with an FTIR spectrometer (Bio-Rad).

2. Experimental Setup

The source of the femtosecond laser pulses was a Ti:Sapphire laser (Hurricane, Spectra-Physics) which produced 800 nm pulses with a duration of 110 fs and a pulse energy of 0.9 mJ. Part of the light (60%) was used to pump an Optical Parametric Amplifier (OPA, Spectra-Physics) that generates 2000 nm pulses. These pulses were then frequency-doubled in a beta-barium borate ($Ba(BO_2)_2$) crystal. The thus obtained 1000 nm pulses are combined with the remaining 40% of the 800 nm beam to produce 4000 nm pulses via difference-frequency generation in a $LiNbO_3$ crystal.

The 4000 nm pulses are resonant with the 0->1 transition of the OD stretch vibration of HDO. Most of the pulse energy (~4 µJ) was used to excite a significant fraction of the HDO molecules. This excitation leads to a bleaching of the fundamental absorption of the OD stretch vibration. This bleaching is anisotropic because the pump will preferentially excite ODs that are oriented parallel to the pump polarization. This anisotropy decays due to the reorientation of the excited OD groups. We probed the bleaching signal with a weak (200 nJ) pulse delayed from the pump pulse by a time τ. The polarization of this probe pulse is rotated 45° with respect to that of the pump. A polarizer located behind the sample reflected the component that is oriented parallel ($\alpha_{//}$) and transmitted the component that is oriented perpendicular ($\alpha_{\perp}$) to the polarization of the pump. The parallel and perpendicular parts of the absorption spectra are detected simultaneously on two different arrays of a Mercury-Cadmium-Telluride (MCT) detector. Every second pump pulse was blocked by a 500 Hz chopper to obtain both the pumped and the unpumped absorption spectra, from which we obtained the transient absorption spectra $\Delta\alpha_{//}$ and $\Delta\alpha_{\perp}$. With these two signal components, we constructed the isotropic signal $\Delta\alpha_{iso}$ which is not sensitive to the molecular reorientation and only contains information about the vibrational lifetime of the OD oscillators:

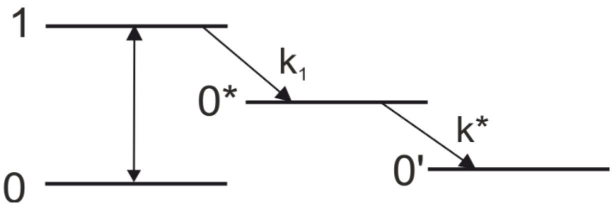
$$\Delta\alpha_{iso}(\omega,\tau) = \frac{1}{3}\left(\Delta\alpha_{\parallel}(\omega,\tau) + 2\Delta\alpha_{\perp}(\omega,\tau)\right) \tag{S1}$$

We also constructed the anisotropy parameter R:

$$R(\tau) = \frac{\Delta\alpha_{\parallel}(\omega,\tau) - \Delta\alpha_{\perp}(\omega,\tau)}{\Delta\alpha_{\parallel}(\omega,\tau) + 2\Delta\alpha_{\perp}(\omega,\tau)} \tag{S2}$$

in which the effect of vibrational relaxation is divided out. The decay of R(ω,τ) only represents the orientational relaxation of the HDO molecules.

3. Modeling of the pump-probe data



Scheme S1. Model used to describe the vibrational relaxation dynamics of the excited HDO molecules. The OD stretch oscillators that are excited to the v=1 state by the pump pulse decay with a rate constant $k_1=1/T_1$ to an intermediate state 0* that has no spectral signature in the probed region. This state subsequently decays to a thermalized ground state 0' with a rate constant $k^*=1/T^*$.

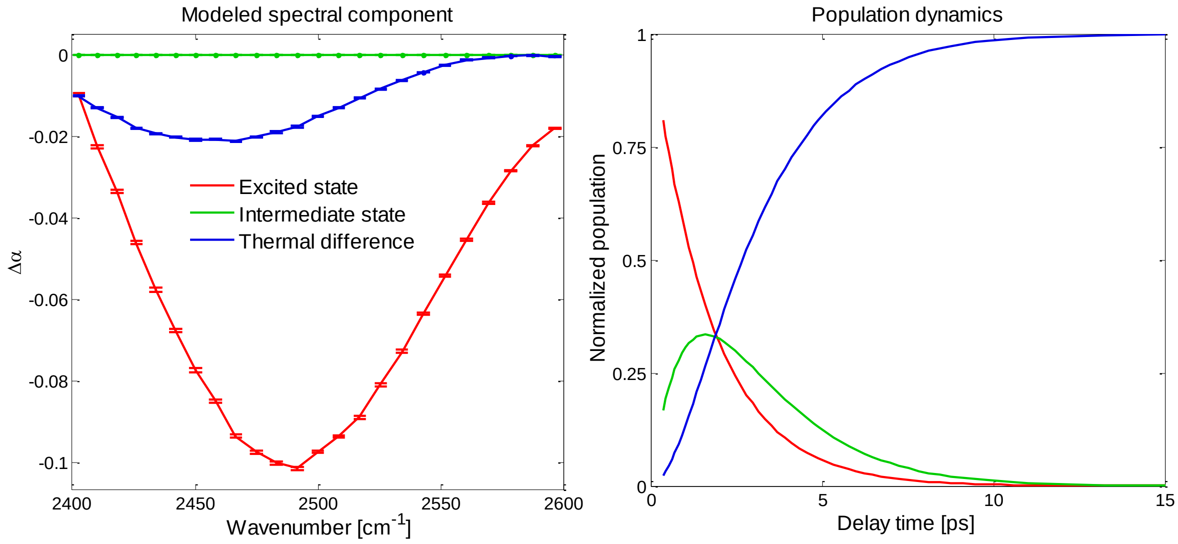


Figure S1. Left panel – Spectral components obtained from a fit of the kinetic model to the transient spectra of a 4m solution of HCOONa in 10% HDO/H_2O which are shown in Fig. 1b of the manuscript; Right panel – normalized populations of the different states of the kinetic model as a function of delay. The time-dependent populations of the different states are the weighing factors of the corresponding spectral components shown in the left panel, together forming the total transient spectrum at a given delay time τ.

From the transient spectra in Fig. 1b it is clear that after the complete decay of the vibrational excitation, there is a remaining bleaching signal which remains for over 100 ps after the excitation. This signal results from the heating of the sample due to the absorbed energy of the pump pulse [S1]. Heating of water leads to a weakening of the hydrogen bonds which in turn induces a blue-shift of the OD stretch frequency. Therefore, the heating effect leads to a bleaching signal in the red wing of the absorption band and to an induced absorption in the blue wing. In order to calculate the anisotropy of the signal of the excited OD oscillators, we need to subtract the heating contribution from the data. It has been observed [S1] that the ingrowth of the heating signal is somewhat delayed with respect to the decay of the excited state. Hence, to model the isotropic transient spectra we use a kinetic model in which the excited OD stretch vibration relaxes to an intermediate state with time constant $T_1=1/k_1$ that subsequently relaxes to a heated ground state with time constant $T^*=1/k^*$ (see Scheme S1). The transient spectrum of the intermediate state has no spectral signature in the measured spectral range, meaning that the absorption spectrum of this state closely resembles that of the ground state. Therefore, the delayed rise of the heating effect likely results from the relatively slow adaptation of the water hydrogen-bond network to the higher energy content of the low-energy degrees of freedom resulting from the relaxation of the excited OD stretch vibration.

Because the heat is observed to be isotropic, we subtracted its signal contribution equally from $\Delta\alpha_{//}$ and $\Delta\alpha_{\perp}$ to obtain signals that only represent the effect of the excitation of the OD stretch vibration. These signals were used to construct the delay-dependent anisotropy spectra according to Formula S1. Because the anisotropy shows no frequency dependence, we averaged the values of R in the frequency range 2480-2520 cm^{-1}.

4. References:

[S1] Y. L. A. Rezus, H. J. Bakker, *The Journal of Chemical Physics* **2005**, *123*, 114502.