Supporting information for

Vibrational Relaxation Dynamics of the Core and Outer Part of Proton-Hydration Clusters

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1. Impact of the coherent effects on the measured pump-probe signal.

The change of the transient absorption signal around zero delay time, which is shown in Figure 4 of the main text is not a specific property of the studied $TfOH/H_2O/CD_3CN$ system. It is more general artifact which can be found in any pump-probe experiment. For example, we also observe it in the pump-probe experiment on vibrational relaxation of OH-stretch vibration in HDO/D_2O solution. Within the cross-correlation time the signal is strongly dependent on the probe pulse (Figure S1). However, no ultrafast relaxing excited state is expected for the OH-stretch vibration in HDO molecule.[1]
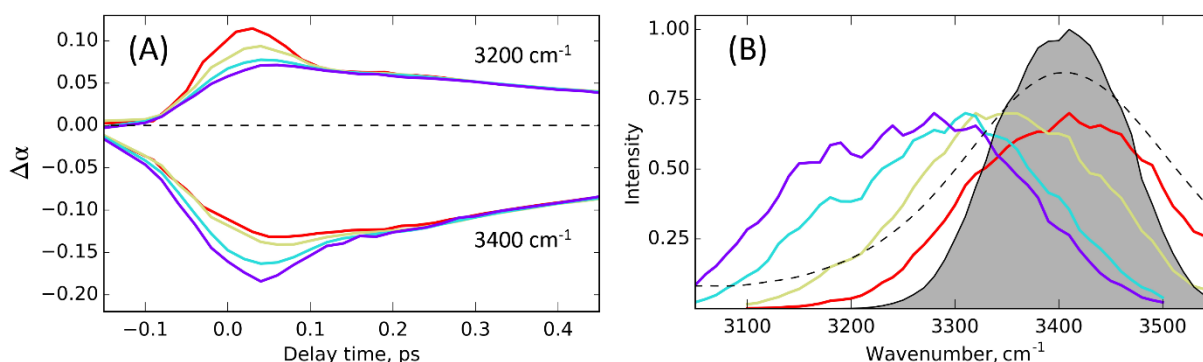

Figure S1. (A) Transient absorption change upon the excitation of OH-stretch vibration of HDO measured at 3200 cm^{-1} and at 3400 cm^{-1} with different probe pulses. (B) Pump (grey) and probe pulses (color coded with respect to A) used in the experiment; dashed line represents the linear absorption spectrum of HDO in D_2O.

In the transient absorption measurements it is usually assumed that the result is independent on the probe pulse. Indeed if the time dynamics of measured transient signal is slow enough, than we can assume, that the excited state population is constant during the probe pulse. In this case probe can be seen as a delta-pulse. However, finite broadness of the pulse can significantly distort pump-probe signal. Here we will model the transient absorption spectra and show their dependence on the probe pulse.

We calculate the third order polarization with the response functions derived from the density matrix formalism for a three level system.[2] The result can be written as a sum of 12 terms corresponding to 12 double-sided Feynman diagrams.[3] Two of them account for the stimulated emission, two – for the ground state bleaching and two – for the excited state absorption. Other six terms (diagrams) with a "wrong" electric field sequence, where probe field comes in time before or between the pump fields correspond to the artifacts known as perturbed free induction decay

and resonant grating. We do not include other 4 terms since they involve $0\rightarrow 2$ coherence. With this representation we can calculate selectively either "artifact-free" or only the pure artifacts. For the transient absorption signals shown here we set transition frequencies to be $\nu_{01}=3400$ cm^{-1} and $\nu_{12}=3200$ cm^{-1} with the dephasing times T_2 corresponding to 200 cm^{-1} broad (FWHM) Lorentzian shaped absorption bands. Pump was taken as 100 fs broad Gaussian pulse centered at 3400 cm^{-1}.

In Figure S2 we show the pump-probe spectra of the excited state with $T_1=0.5$ ps obtained using 10 fs broad probe pulse and with $T_1=0.2$ ps with 70 fs broad probe. As we see, the narrow probe pulse indeed can be seen as a delta-pulse and the resulting spectra are represent just the sum of the negative and positive Lorentzian bands centered at 3400 and 3200 cm^{-1} respectively. However, in the second case probe cannot be considered a delta-pulse, since the variation of the excited state population during the probe pulse is significant. As a consequence, pump-probe spectra become distorted, which can be found as an increased amplitude of the bleaching part, or a shift of the zero-cross frequency. If the character of the population dynamics does not vary on the time scale of the probe pulse (e.g. exponential decay over all the delay times), the relative time dependence of signal at each frequency will be measured correctly (giving correct time constant).
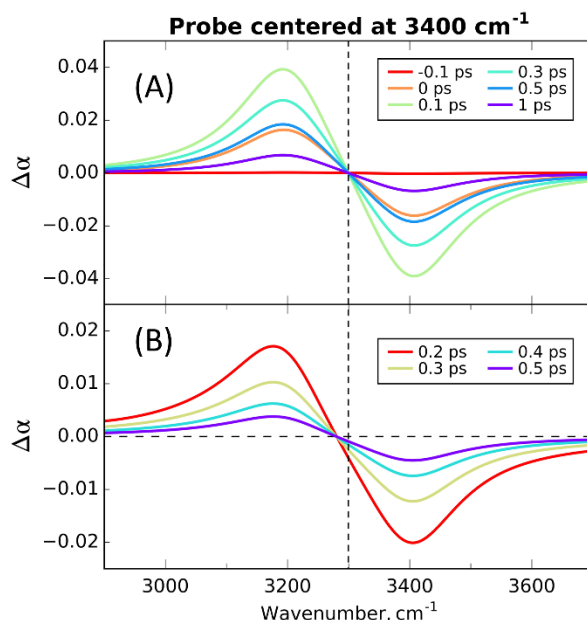

Figure S2. Pump-probe spectra modeled with 10 fs broad probe and $T_1=0.5$ ps (A) and 70 fs broad probe and $T_1=0.2$ ps (B).

The rapid growth of the excited state population around 0 ps distorts the spectra probed by the same 70 fs pulse much stronger (Figure S3). The character of this distortion depends on the center frequency of the probe. The effect can be phenomenologically explained by the time dependence of the complex refractive index, which modifies the pulse.
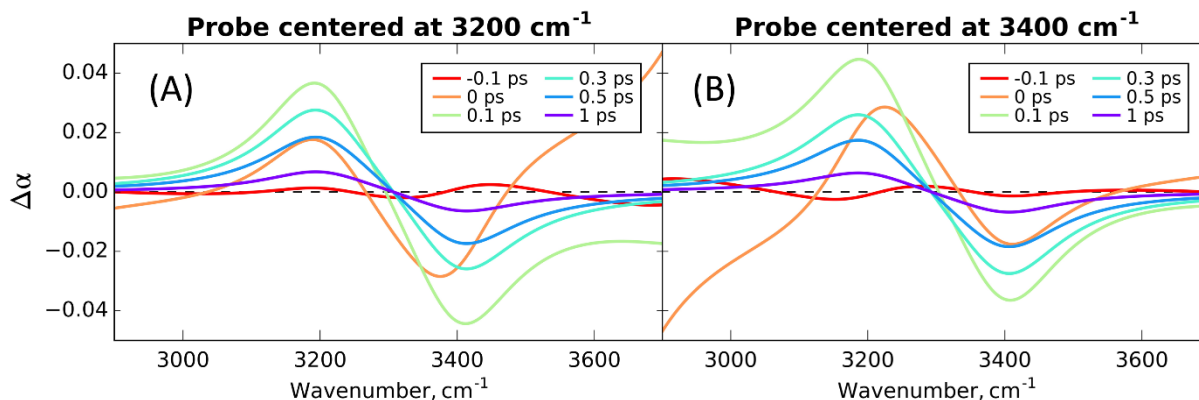
Figure S3. Pump-probe spectra modeled with 70 fs broad probe centered at 3200 cm^{-1} (A) and 3400 cm^{-1} (B).

In the delay time dependence it can appear as an enhanced or decreased transient absorption around zero time (Figure S4). It is more pronounced in the tails of the probe spectrum.
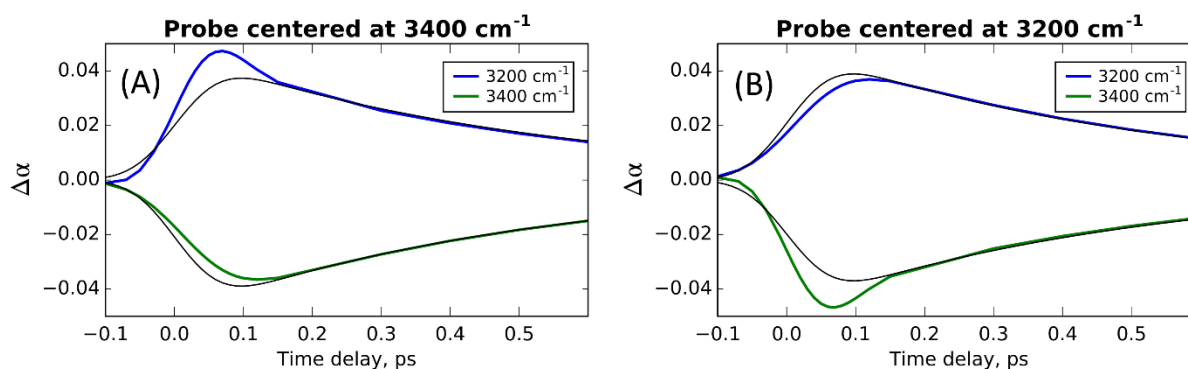

Figure S4. Transient absorption at 3200 cm^{-1} and 3400 cm^{-1} as a function of delay time with 70 fs broad probe centered at 3400 cm^{-1} (A) and 3200 cm^{-1} (B). Black lines represent the calculated dynamics of the excited state.

In addition to the distortion of transient absorption dynamics resulting from the strong variation of excited state population, the coherent artifacts due to the "wrong" electric field sequence can arise around zero time. Since they require an interaction of the probe field before the pump they contribute more at the negative delay times (Figure S5). As we see, these artifacts are significantly reduced around the center frequency of the probe.
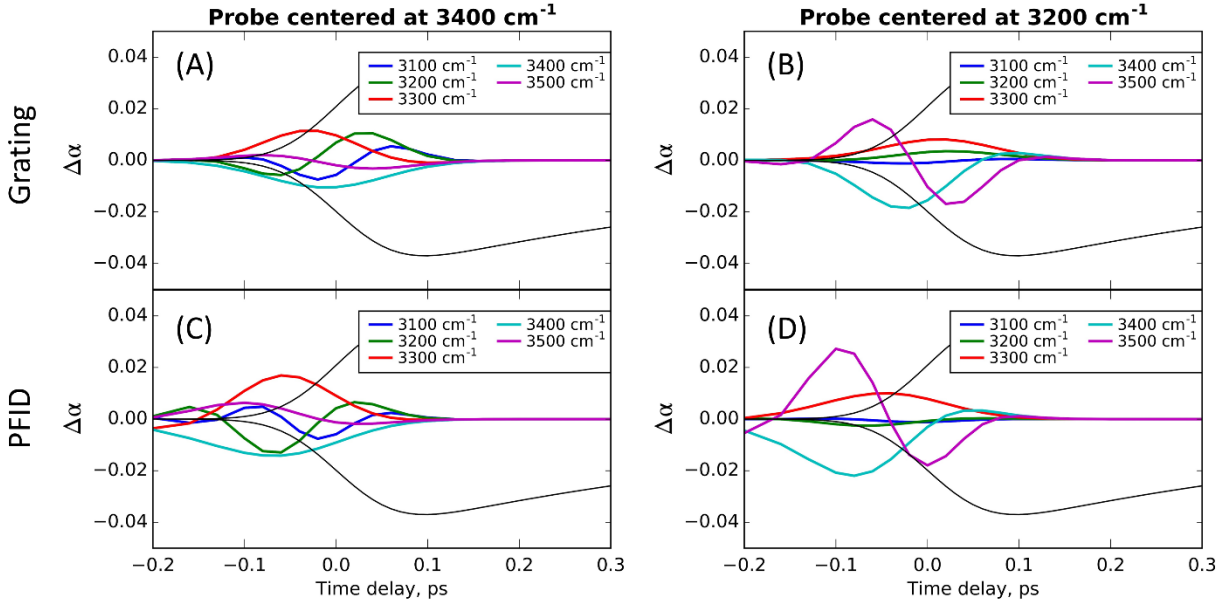
Figure S5. Pump-probe signal due to transient grating (A,B) and perturbed free induction decay (C,D) as a function of delay time.

Finally, we construct the total transient absorption signal (Figure S6). The signal we measure at the center of the probe spectrum is the least distorted one. The results of our simple modelling are in qualitative agreement with pump-probe experiments. The artifacts discussed and modeled here can be mistaken with an ultrafast relaxation processes. They are strongly dependent on the pulse characteristics and dephasing rates – parameters, which are usually not taken into account in experiments. Thus, analysis of the experimental data within pulse cross-correlation time can lead to wrong conclusions.
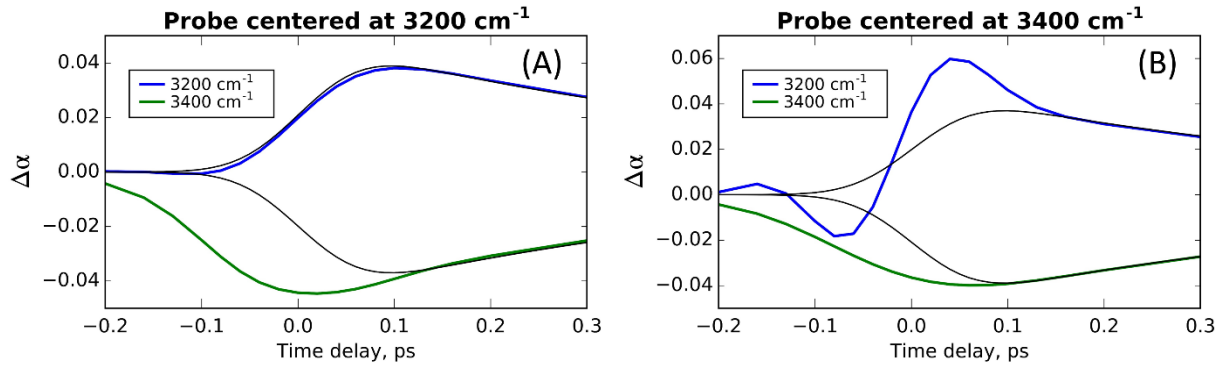

Figure S6. Total transient absorption signal at 3200 cm^{-1} and 3400 cm^{-1} as a function of delay time with probe centered at 3200 cm^{-1} (A) and 3400 cm^{-1} (B).

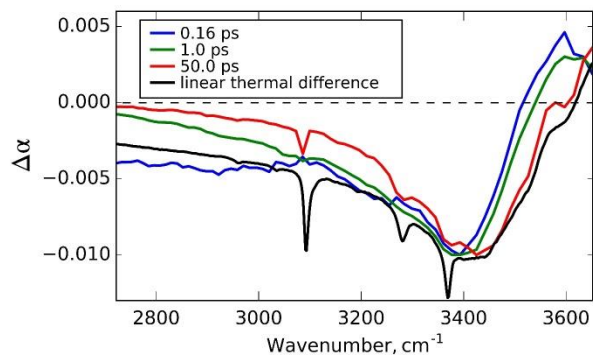## 2. Comparison of the linear thermal difference spectrum and the pump-probe spectra

Figure S7. Isotropic pump-probe spectra at different delay times (ν_{ex}=2900 cm^{-1}) and a linear thermal difference spectrum of the studied solution. All the spectra are scaled with respect to the pump-probe spectrum at 50 ps. The transient spectra at 1 ps and 50 ps are much more narrow than the linear thermal difference spectrum.

REFERENCES

(1)   Rezus, Y. L. A.; Bakker, H. J. Orientational Dynamics of Isotopically Diluted H2O and D 2O. *J. Chem. Phys.* **2006**, *125*, 144512.

(2)   Mukamel, S. (Shaul). *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press, 1995.

(3)   Hamm, P.; Lim, M.; Hochstrasser, R. M. Structure of the Amide I Band of Peptides Measured by Femtosecond Nonlinear-Infrared Spectroscopy. *J. Phys. Chem. B* **1998**, *102* (31), 6123–6138.