SI. Table 1 – chemical composition of the samples studied.

Added H_2O (vol. fraction)	Added H_2O (wt. Fraction)	H_2O mole fraction in equilibrium	D_2O mole fraction in equilibrium	HDO mole fraction in equilibrium
0.05	0.045	0.002	0.912	0.086
0.1	0.094	0.009	0.821	0.17
0.15	0.1375	0.019	0.744	0.237
0.2	0.1842	0.034	0.666	0.3

Time-zero determination from XPM zero-crossing and chirp correction procedure:

The problem of chirped supercontinuum (white-light) probing in pump-probe methods (initially it transient absorption then also in FSRS) was probably most exhaustively studied theoretically and experimentally by Kovalenko et al. [1] They show therein that the time resolution as good as 10 fs can be achieved in the experiment with the chirped supercontinuum probing providing that the wavelength dependence of the supercontinuum was properly characterized. Having characterized the wavelength – dependence of the supercontinuum chirp (shown in the our Supplementary Figure 1) we may perform the time-zero correction of both cross-correlation signal and the and SRS data (Suppl. Figure 2).
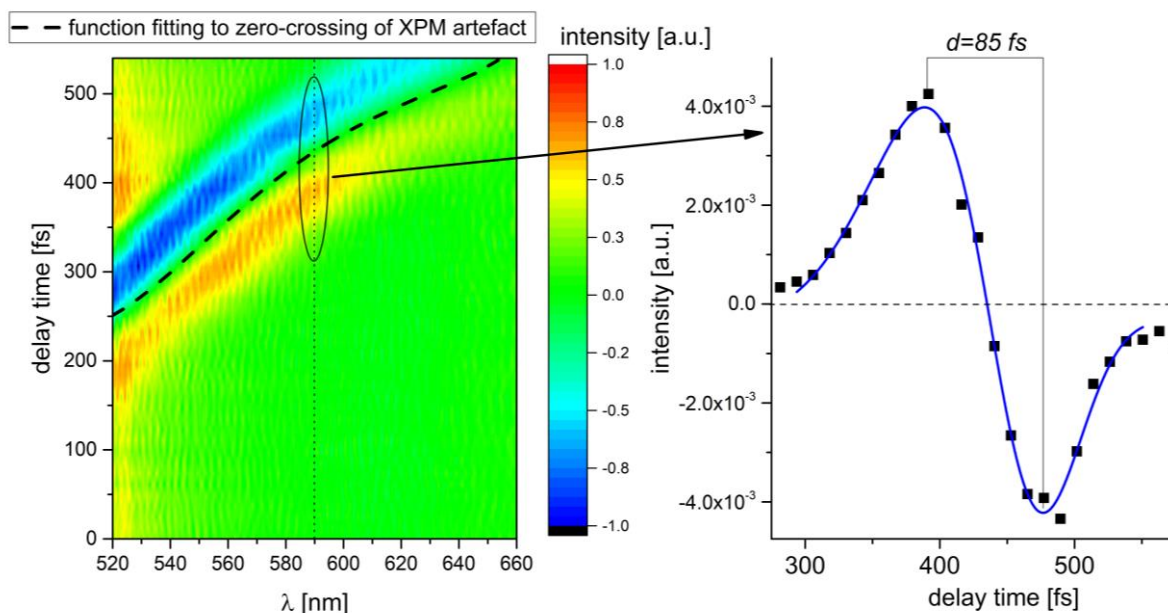
Supplementary Figure 1 – Determination of t=0 between white light and an infrared pulse based on the time of zero – crossing of a signal related to cross-phase modulation artefact (XPM). The dashed line shows a function fitted to zero crossing of an XPM signal. Right panel – determination of the time between extrema of XPM for evaluation of cross-correlation time of fs-IR-SRS experiment.
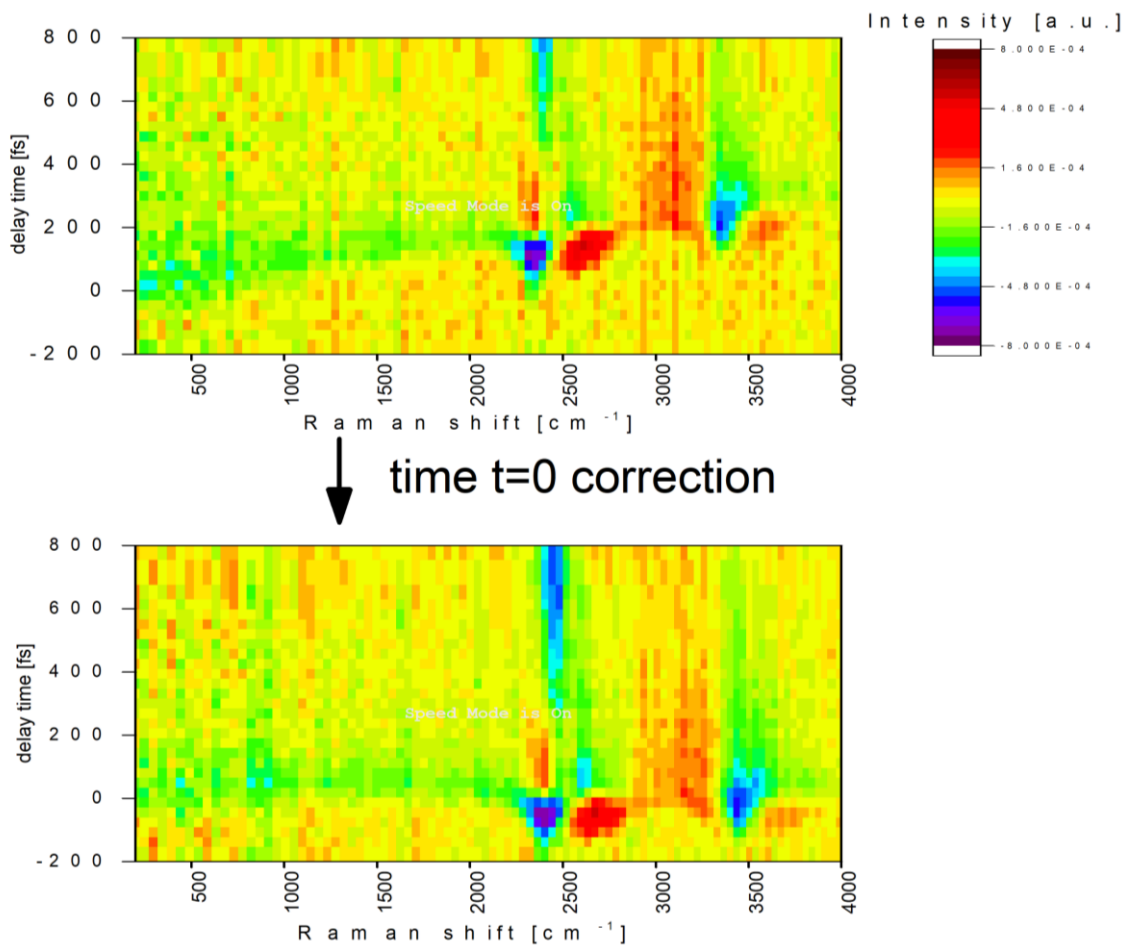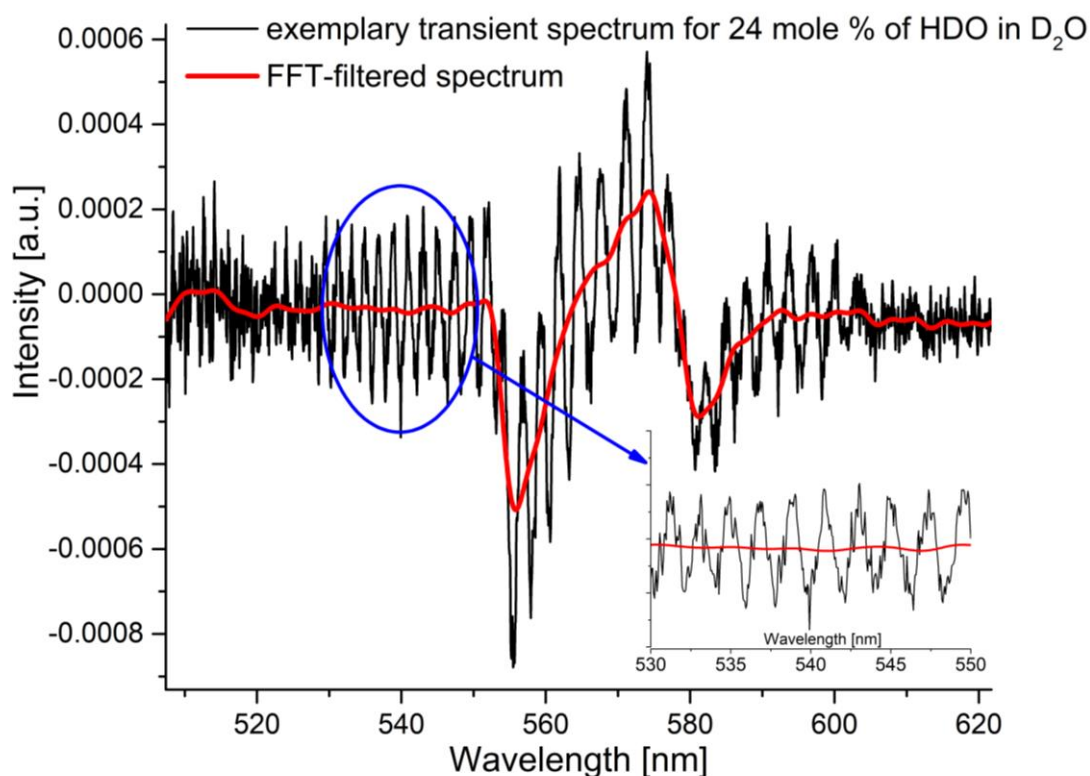
Supplementary Figure 2 – an example of the time t=0 zero correction of transient stimulated Raman signal after infrared pump based on the "true" time t=0 between white light and infrared pulse determined from XPM measurement in a sample.

Correction of oscillations on SRS spectra

W observed the most intense oscillation on a spectrum on a sample containing 24 mole % of HDO in D_2O (see. Supplementary Figure 3) The data after FFT filtration are presented with red line. The period of oscillation (2.1 nm at around 540 nm, see inset to SI Fig.) corresponds to sample thickness of around 52 μm.

For the sample presented in the manuscript (17 mole % of HDO in D_2O) the period of oscillation on a spectrum (2.2 nm at around 540 nm) correlates with sample thickness of around 50 μm. For 4600/cm cross-section of H_2O @ 3000 nm and given concentration of OH oscillator in the sample, the 50 μm thick sample should transmit around 1 % of the infrared light @ 3000 nm.

Supplementary Figure 3 - An example of a fs-IR-SRS transient spectrum with oscillations coming from WL oscillation (black) on a liquid jest and FFT filtered spectrum (red). Inset: spectral range used for determination of the oscillation frequency for estimation of the sample thickness. The transient spectrum refers to sample containing around 24 mole % of HDO in D_2O at the delay time of 250 fs.
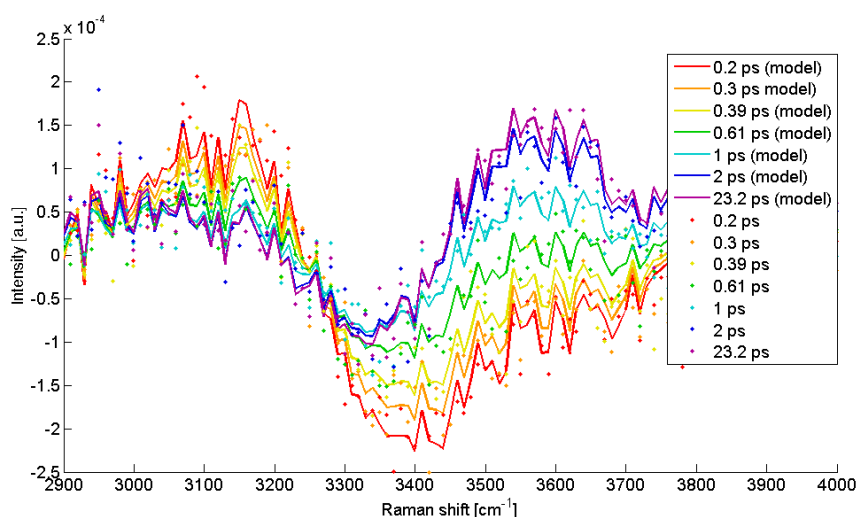

Supplementary Figure 4 – version of Figure 5 from the manuscript with oscillation present on the spectra (without FFT filtration of the data). Transient fs-IR SRS spectra registered between 0.2 ps and 23.2 ps in the OH stretch range after the OH excitation. Curves fitted to the experimental points with global kinetic model are shown as solid lines.
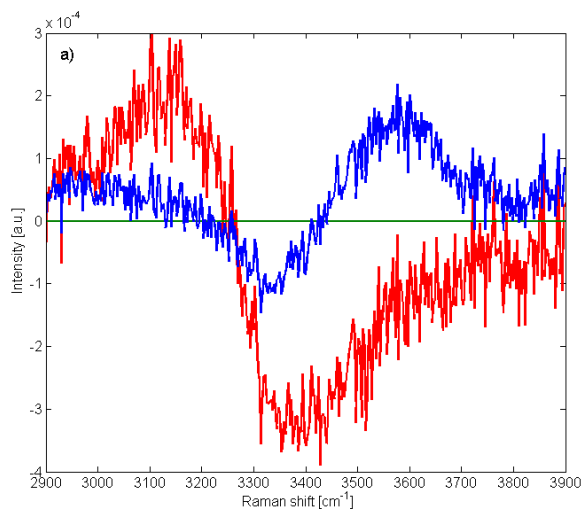
Supplementary Figure 5 – the version of Figure 6a from the manuscript without filtering out the oscillations from the transient spectra; fitted spectral components - vibrationally excited state (red) and thermalized ground state (blue) in the kinetic model of vibrational relaxation process in the sample containing 17 mole % HDO in D_2O.

## Model of the vibrational relaxation processes
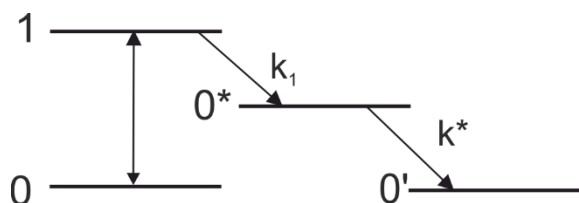
Supplementary Figure 6 Schematic presentation of the relaxation model used to describe the vibrational relaxation dynamics of the excited HDO molecules. The OH stretch oscillators that are excited to the v=1 state by the pump pulse first decay with a rate constant $k_1=1/\tau_1$ to an intermediate state 0* that has no spectral signature in the registered spectra. This state subsequently decays to a thermalized ground state 0' with a rate constant $k*=1/\tau*$.
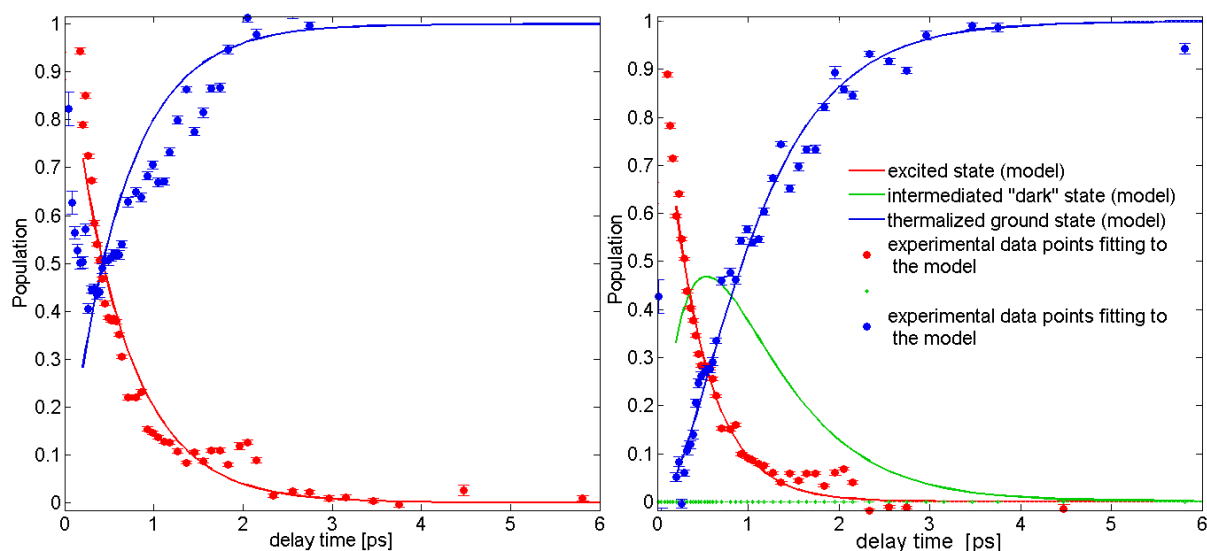
Supplementary Figure 7 – Comparison of the fitting of the scaled experimental data (strictly speaking, the points in the graphs refers to modelled spectral components scaled to match experimental data for a given delay time) to the kinetic cascade model for the two-state model (left panel) and the three state model with "dark" intermediated state (right panel). It is clear from the comparison that choice of model does not influence much fitting to the excited state decay (red), yet the satisfactory fitting to the ingrowth of thermalized ground state is only obtained with the delayed ingrowth of the thermalized ground state (blue), when energy is stored in the intermediated "dark" state (green).
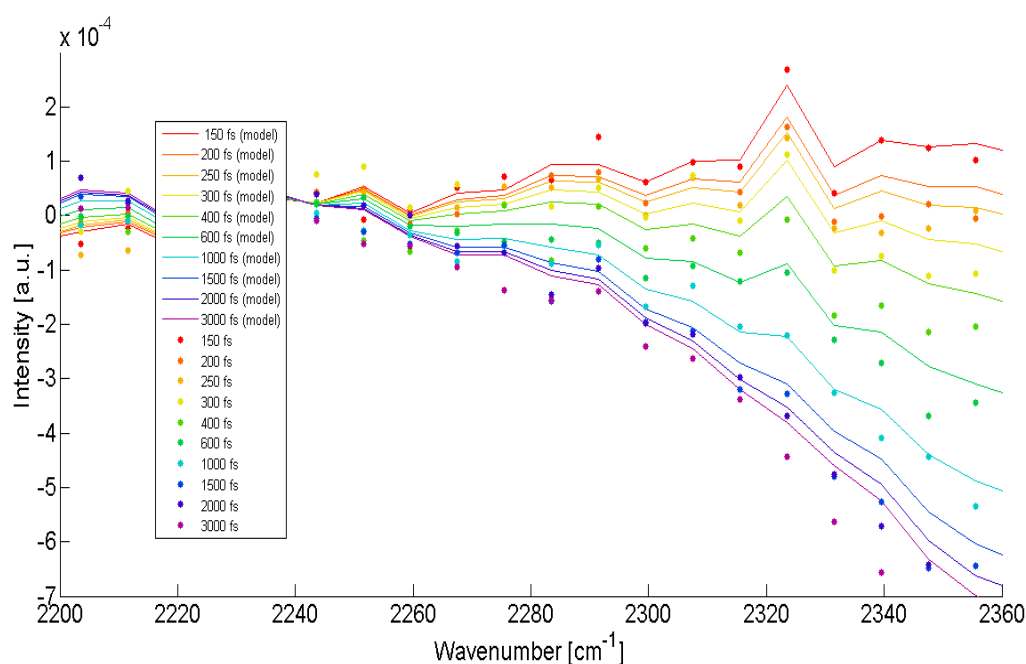
Supplementary Figure 8 – Transient fs-IR SRS spectra register between 0.15 ps and 3 ps in the OD stretch range (low wavenumber component) after the OH excitation. For clarity each 12 spectal points are averaged in the figure. Fitted curves to the experimental points with global kinetic model are shown in solid lines.
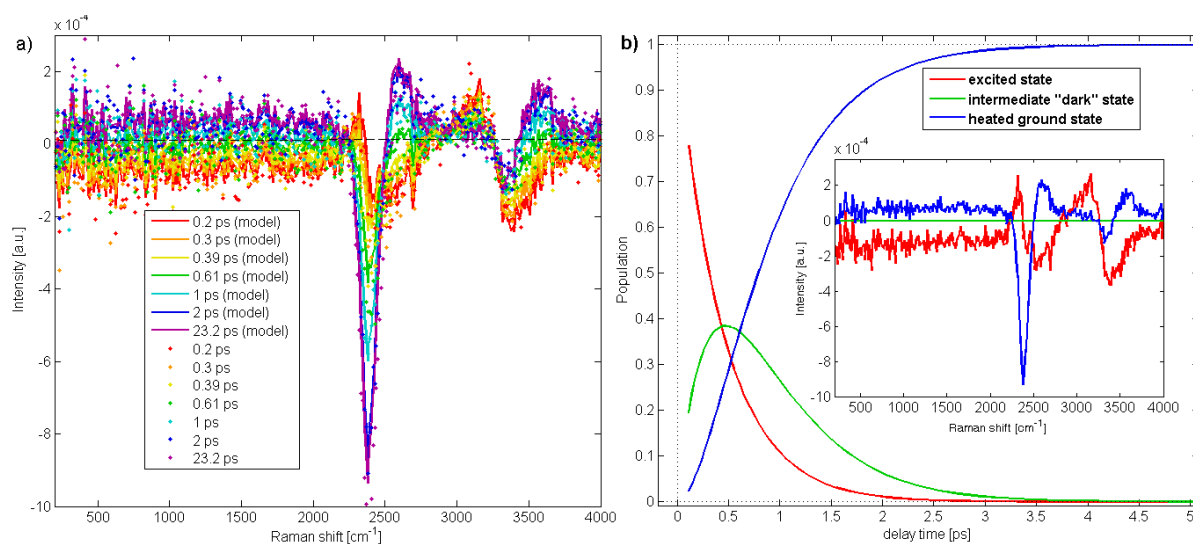
Supplementary Figure 9 – the version of Figure 9 from the manuscript without filtering out the oscillations from the transient spectra. Oscillations are present in the spectra in panel a) and they increase the noise in the modeled spectral components in the inset to panel b). Curves fitted to the experimental points with global kinetic model are shown as solid lines. (b) – Global kinetic model of the spectra in shown in panel a); fitted spectral components are shown in the inset and their population dynamics in the time-traces in the panel; vibrationally excited state (red) and thermalized ground state (blue), the intermediate dark state (green);

1.   S. A. Kovalenko, A. L. Dobryakov, J. Ruthmann and N. P. Ernsting, *Physical Review A*, 1999, **59**, 2369-2384.