Supporting Information

Vibrational Energy Relaxation of Thiocyanate Ions in Liquid-to-Supercritical Light and Heavy Water. A Fermi‘s Golden Rule Analysis.

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Experimental details

FTIR spectra were recorded with a commercial spectrometer (Nicolet 5700, Thermo Fisher) with a spectral resolution of 1 cm^{-1}. For the time resolved measurements, the output pulses (800 μJ, 220 fs, 775 nm, 1 kHz) of a femtosecond Titan Sapphire chirped pulse regenerative amplifier system (Clark MXR, CPA 2001) were used to pump two independently tunable optical parametric amplifiers (OPAs) based on type-I barium β-borate. The Signal and Idler outputs were used for difference frequency generation (DFG, type-I $AgGaS_2$) to create femtosecond pulses in the mid-IR spectral region (center frequency 2065 cm^{-1}, spectral bandwidth 150 cm^{-1} (FWHM)). One of the OPAs served as the pump pulse source, whereas the other served as the detection pulse source. The output of the detection OPA was split into probe and reference pulses. The probe pulses were temporally and spatially overlapped with the pump pulses inside the sample cell. Probe and reference pulses were focused onto the entrance slit of a 0.2 m monochromator and detected with 2 x 32 pixel HgCdTe array enabling the frequency resolved measurement of the pump induced change of the optical density (ΔOD) with a resolution of about 7 cm^{-1}. The relative polarization of pump and probe pulse was set to 54.7° (magic angle condition) to eliminate signal contributions from the reorientational dynamics. The time resolution was determined to 150 fs (FWHM) as derived from a measurement of the heavyside response of a thin silicon substrate. Pulse energies directly in from of the sample cell were 0.9 μJ for the pump and 0.2 μJ for the probe. All femtosecond data were recorded with the relative pump-probe polarization set to the magic angle (54.7°)

The samples were prepared using KSCN (Sigma Aldrich, purum p.a.) without further purification and dissolving it in H_2O (doubly deionized, 18 MΩ·cm) or D_2O (Deutero, 99.9 %) to receive 0.15 M solutions. The aqueous solutions were contained in a home-built high-temperature/high

pressure cell equipped with sapphire windows and an optical path length of 50 μm. The temperature of the sample could be controlled with an accuracy of 1 K and the pressure was set to 500±5 bar.