Supplementary Information for Isotope effect in a liquid-liquid transition in supercooled aqueous solution

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Cryostat Calibration

To increase the accuracy of the reported phase transition temperatures, we calibrated the cryostat by implementing a separate thermocouple in place of the sample. By this means, we could measure potential discrepancies between the temperature reported by the thermocouple attached to the brassholder of the cryostrat on the outside, and the actual temperature on the inside of the sample cell. Fig. S1 illustrates that in the range of interest, i.e. where the phase transition occurs, temperature discrepancies are negligible.

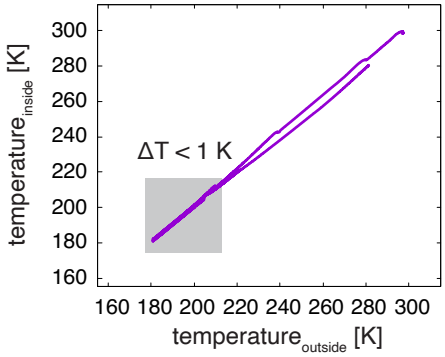

FIG. S1. Plot of the temperature inside the sample cell against the temperature read off the thermocouple on the brass holder outside the sample cell. Below $\sim$ 220 K, where we switched the cooling/heating rates to 1 K/min (grey area), the temperature discrepancy is negligible.

Singular Value Decomposition

Prior to the application of the multivariate curve resolution alternating least square (MCR-ALS) technique, we used singular value decomposition (SVD) to estimate the number of spectral components within the temperature range, where the liquid-liquid phase transition is observed. The spectral $m \times n$ data matrix $\mathbf{D}$ can be decomposed by factorization into its unitary matrices $\mathbf{U}$ $(m \times m)$ and $\mathbf{V^T}$ $(n \times n)$ and diagonal matrix Σ $(m \times n)$.

$$\mathbf{D} = \mathbf{U} \times \mathbf{V^T} \tag{1}$$

The singular values obtained from the diagonal matrix represent the magnitude of the individual components the data matrix $\mathbf{D}$ can be decomposed into. Table I shows the first five singular values for both OH in OD and OD in OH systems. In both cases, singular values beyond the first two only correlate with noise. We thus conclude that during the transition the system is composed of two components. Factorization of our spectral data was carried out using the open-source Python library SciPy [1].

TABLE I. Singular values

OD-rich	OH-rich
67.1077	4.95669
3.82967	0.10292
0.06931	0.00331
0.03291	0.00293
0.03027	0.00270

MCR-ALS

The MCR model we used to demix our spectral data is based on the following concept [2–4]. An algorithm decomposes a $m \times n$ data matrix $\mathbf{D}$ into its respective concentration $\mathbf{C}$ $(m \times k)$ and pure spectra $\mathbf{S^T}$ $(k \times n)$ profiles

$$\mathbf{D} = \mathbf{C} \times \mathbf{S^T} \tag{2}$$

The data matrix $\mathbf{D}$ contains the spectroscopic data table, comprising individual spectra for each temperature step (4 spectra/K) for the phase-transition regions of the OH and OD systems. MCR-ALS implements a constrained Alternating Least Squares (ALS) algorithm to extract the pure spectra of the systems. From the SVD calculations we surmised the presence of 2 components in both OH and OD systems. As an initial guess we took the first and the last spectrum in the transition range. Here, we

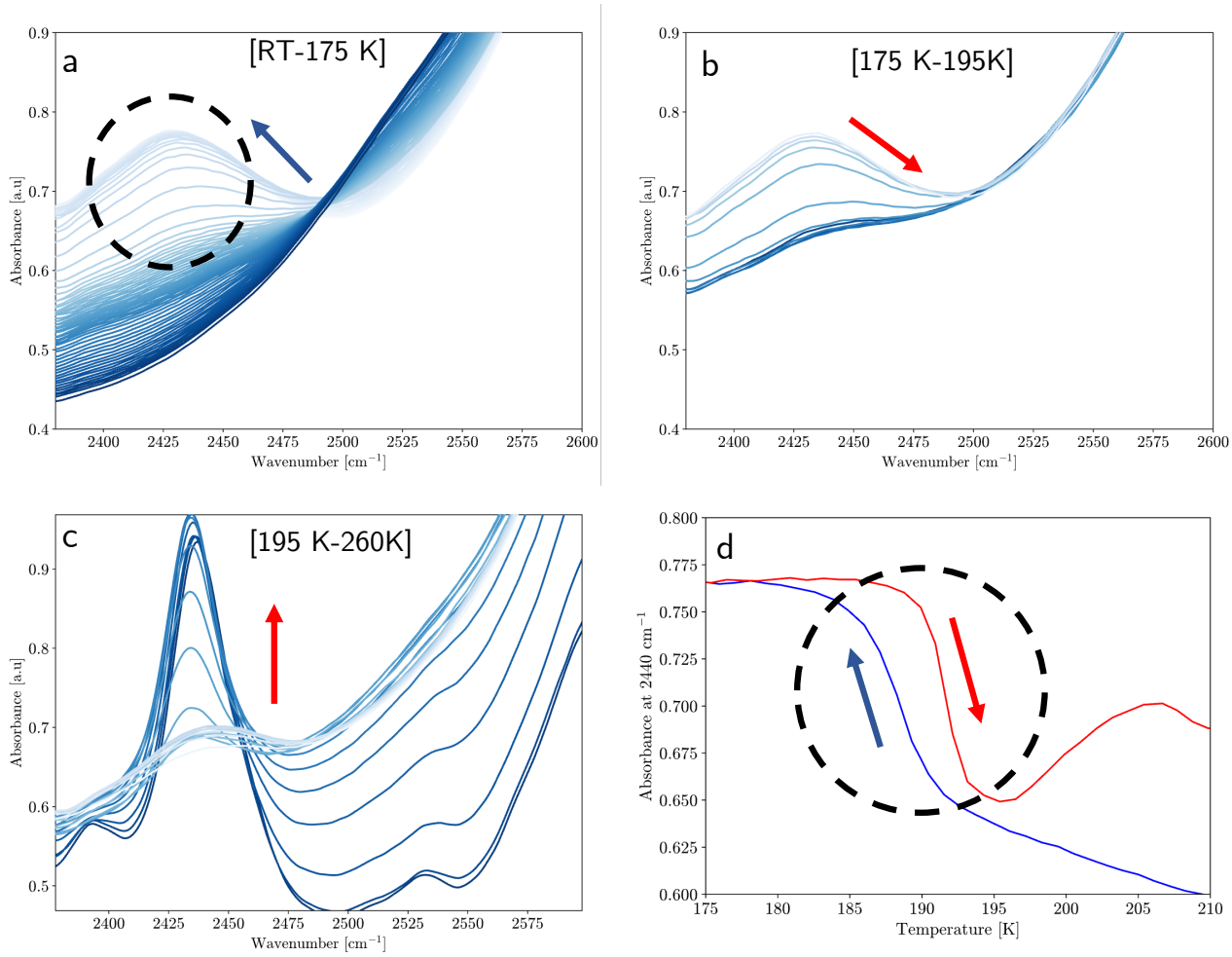

FIG. S2. Temperature-dependent infrared spectra of a isotopic mixtures of aqueous $N_2H_5 \cdot TFA$ solution, prepared with neutral pH. **a-d** Cooling down and reheating of the 3 % OD in OH system. The changes in the hydrogen-bond structure are probed using the the OD stretching mode. Arrows show the direction of the evolution of the spectra. At $\approx$ 192 K, the sample undergoes a liquid-liquid transition, indicated by a sudden jump to a new broad peak at $\approx$ 2440 cm^{-1} (dashed circle).

set non-negativity and normalization as constraints. We used the open-source Python library pyMCR to perform MCR-ALS calculations [5].

Liquid-liquid transition in a neutral aqueous solution

The studied hydrazinum-trifluracetate solutions (x_{water} = 0.84) are slightly acidic (pH $\simeq$ 3.4). To determine whether or not the observed phase transition was influenced by the pH, we prepared and investigated, using IR absorption spectroscopy, a neutral $N_2D_5 \cdot TFA$ solution (pH $\simeq$ 7). A thermal protocol similar to the one employed for the spectra shown in Fig. 1 of the main text was used, i.e., the sample was cooled down with a rate of 5 K/min down to 220K and of 1.5 K/min in the region between 180 K and 220 K. The temperature-dependent spectra are shown in Fig. S2 (a-d) and analogous features as for the acidic solution reported in the main text (see Fig. 1 (e-h)) can be clearly observed: the pH of the solution does not play a major role in phase transition.

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