

# Supporting Information:

## Slowing Down of the Molecular Reorientation of Water in Concentrated Alkaline Solutions

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This file contains: 6 pages, 3 figures and 1 table.

### Spectral decomposition

We measured transient absorption spectra for solutions of different concentrations of sodium deuterioxide in HDO/D<sub>2</sub>O. The excitation-induced changes of the absorption are recorded both in parallel and perpendicular polarization configuration of the excitation and the probing pulses.

To analyze the vibrational relaxation mechanism and to identify the different spectral components contributing to the signal, we first construct the free-of-rotation (isotropic) transient signal:

$$\Delta\alpha_{\text{iso}}(\omega, t) = \frac{\Delta\alpha_{\parallel}(\omega, t) + 2\Delta\alpha_{\perp}(\omega, t)}{3}. \quad (1)$$

We assume that the relaxation process consists of a linear combination of discrete relaxation steps between different energy levels  $i$ , where each level is characterized by a transient

absorption spectrum,  $\sigma_i(\omega)$  and a population,  $N_i(t)$ . We write:

$$\Delta\alpha_{\text{iso}}(\omega, t) = \sum_i^n N_i(t) \cdot \sigma_i(\omega), \quad (2)$$

where  $n$  represents the total number of energy levels that the relaxation mechanism possesses.

The population dynamics are given by the following equation:

$$\frac{dN_i(t)}{dt} = K_{ij}N_j(t), \quad (3)$$

with  $K_{ij}$  matrix of rate constants representing the vibrational relaxation mechanism. The mechanism is discussed in the main text of the manuscript:

$$K_{ji} = \begin{bmatrix} -k_{\text{bulk}} & 0 & 0 & 0 \\ 0 & -k_{\text{ion}} & 0 & 0 \\ +k_{\text{bulk}} & +k_{\text{ion}} & -k_* & 0 \\ 0 & 0 & +k_* & 0 \end{bmatrix}. \quad (4)$$

To obtain the spectral components  $\sigma_i(\omega)$  and the decay rates, we perform a least-squares minimization process using the following weighted  $\chi^2$  function:

$$\chi_{\text{iso}}^2 = \iint \left( \frac{\Delta\alpha_{\text{iso}}^{\text{exp}}(\omega, t) - \sum_i N_i(t, \mathbf{k})\sigma_i(\omega)}{\xi(\omega, t)} \right)^2 dt d\omega, \quad (5)$$

with  $\Delta\alpha_{\text{iso}}^{\text{exp}}(\omega, t)$  the experimentally measured transient absorption signal with standard deviation  $\xi(\omega, t)$ . In order to reduce the fitting parameters, the transient spectrum of the heated state is set equal to the measured transient absorption spectrum at late delay times. In addition,  $k_{\text{bulk}}$  and  $k_{\text{ion}}$  are treated as global parameters, meaning that they are assumed to be the same for all solutions with different concentrations  $\text{OD}^-$ . A global least square fit over the whole concentration range delivers the relaxation time constants  $T_{\text{bulk}}(= 1/k_{\text{bulk}})$  and  $T_{\text{ion}}(= 1/k_{\text{ion}})$ , with values of  $0.78 \pm 0.05$  and  $0.29 \pm 0.05$  ps, respectively. These time

constants have the following covariance matrix:

$$\text{cov}(T_{\text{bulk}}, T_{\text{bulk}}) = \begin{bmatrix} 0.0013 & -0.0007 \\ -0.0007 & 0.0010 \end{bmatrix}. \quad (6)$$

In Figure S1 we show a 3D plot of the residuals of the fit as a function of  $T_{\text{bulk}} (= 1/k_{\text{bulk}})$  and  $T_{\text{ion}} (= 1/k_{\text{ion}})$ .

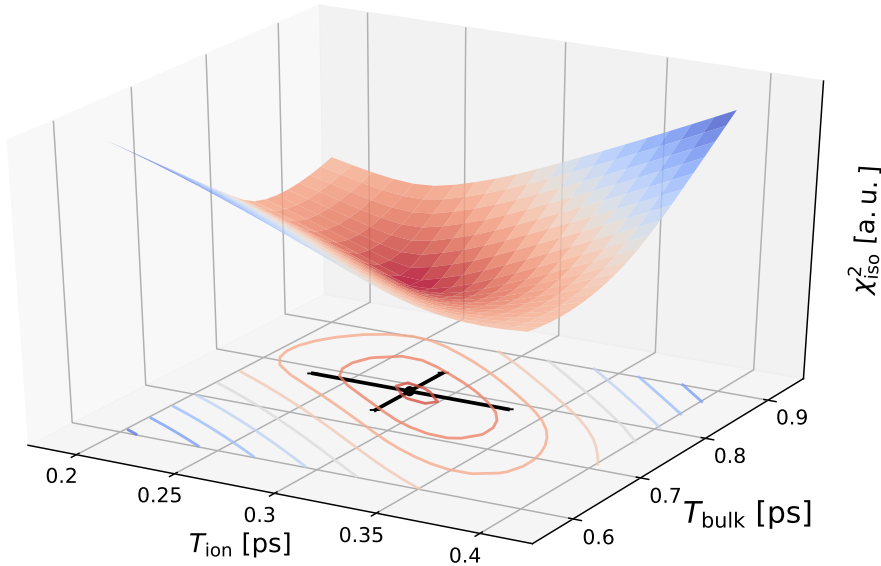


Figure S1:  $\chi_{\text{iso}}^2$  function in the space of  $T_{\text{bulk}} (= 1/k_{\text{bulk}})$  and  $T_{\text{ion}} (= 1/k_{\text{ion}})$ . The black point is located at the values that minimize the  $\chi_{\text{iso}}^2$  function with its corresponding variances.

As stated in the main text, the intermediate state has no associated transient spectrum,  $\sigma_i(\omega) \equiv 0$ , and its relaxation to the hot ground state only accounts for the delayed adaptation of the hydrogen-bond network to the energy that is dissipated by the relaxing OH vibrations. Table S1 shows the obtained values of  $T_*(= 1/k_*)$  at different  $\text{OD}^-$  concentrations.

Table S1: Ion concentration, M [mol/l], and lifetime of the intermediate relaxation step,  $T_*$  [ps], of the OH stretch band of HDO in NaOD:D<sub>2</sub>O solutions.

M	1.0	2.0	3.0	4.5	6.0	8.0
$T_*(= 1/k_*)$	0.79(4)	0.78(4)	0.84(4)	0.83(7)	0.93(5)	1.10(10)

The results of the fit are illustrated in Figure S2.

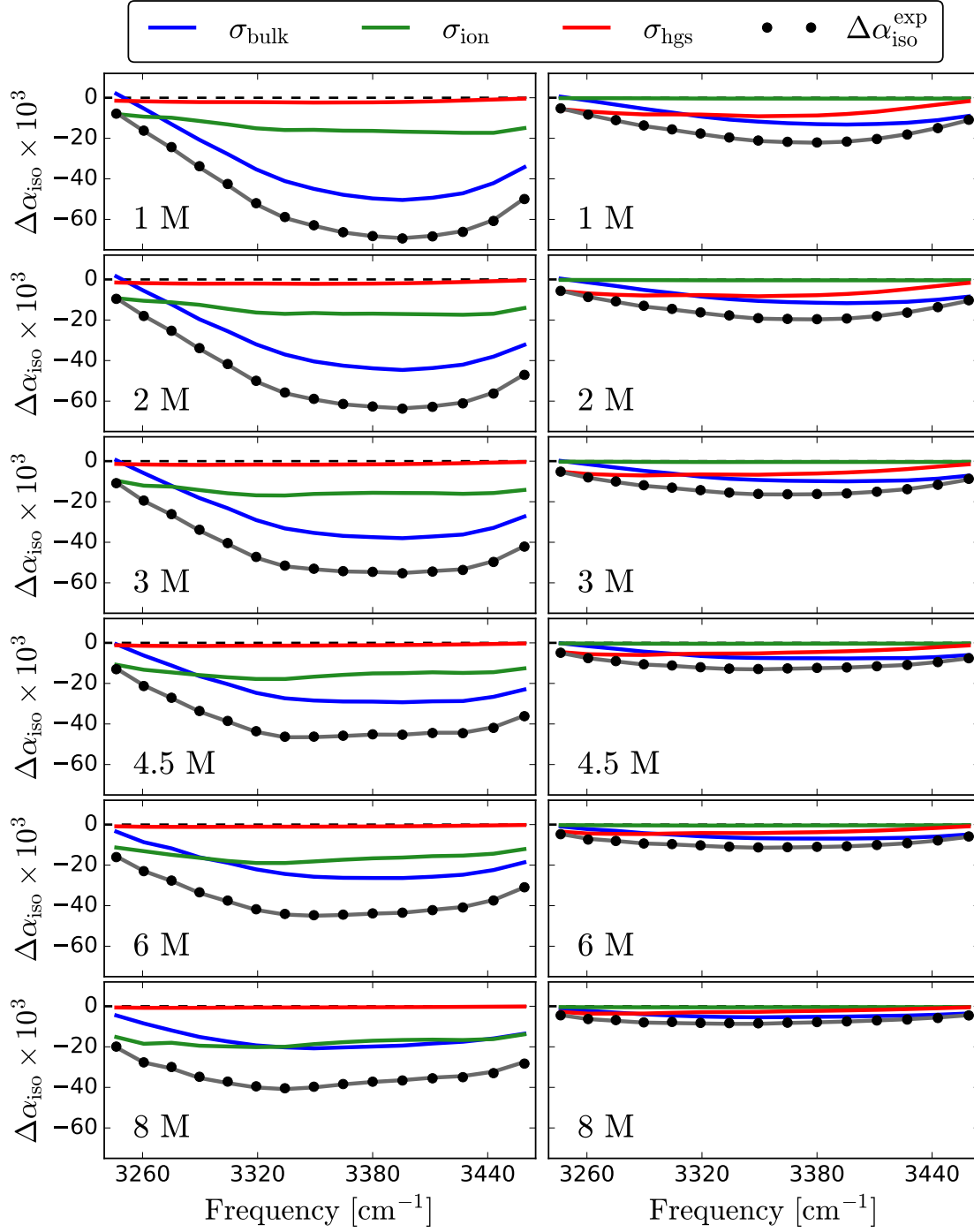


Figure S2: Spectral decomposition of the transient absorption spectra measured at 0.45 ps (left) and 1.5 ps (right). The solid circles represent the measured absorption changes, and the curves result from the least-squares fit described in the text.

## Reorientation dynamics

The transient absorption signal is measured with excitation and probing pulses in parallel and perpendicular polarization configuration. These signals are used to construct the anisotropy  $R$  of the transient absorption signal:

$$R = \frac{\Delta\alpha_{\parallel} - \Delta\alpha_{\perp}}{\Delta\alpha_{\parallel} + 2\Delta\alpha_{\perp}}, \quad (7)$$

which combined with equations 1 and 2 leads to

$$\Delta\alpha_{\parallel}(t, \omega) = \sum_{i=1}^n [1 + 2R_i(t)] N_i(t) \sigma_i(\omega), \quad (8)$$

$$\Delta\alpha_{\perp}(t, \omega) = \sum_{i=1}^n [1 - R_i(t)] N_i(t) \sigma_i(\omega). \quad (9)$$

Using the already obtained  $\sigma_i(\omega)$  and  $N_i(t)$  we determine  $R_i(t)$  by minimizing the following  $\chi^2$  function

$$\chi^2 = \int \int dt d\omega \left[ \left( \frac{\Delta\alpha_{\parallel}^{\text{exp}}(\omega, t) - \sum_i [1 + 2R_i(t)] N_i(t) \Delta\sigma_i(\omega)}{\xi_{\parallel}(\omega, t)} \right)^2 + \left( \frac{\Delta\alpha_{\perp}^{\text{exp}}(\omega, t) - \sum_i [1 - R_i(t)] N_i(t) \Delta\sigma_i(\omega)}{\xi_{\perp}(\omega, t)} \right)^2 \right], \quad (10)$$

In this optimization, we assume the anisotropy dynamics of each level to follow a single exponential:

$$R_i(t) = A_i e^{-t/\tau_{\text{or},i}} \quad (11)$$

where  $A_i$  cannot exceed the maximum theoretical anisotropy of  $R(0) = 2/5$ , and  $\tau_{\text{or},i}$  is the time constant of reorientation of level  $i$ .

The ion-associated component has a negligible influence on the total anisotropy due to its short vibrational relaxation time, and thus its reorientation time constant cannot be

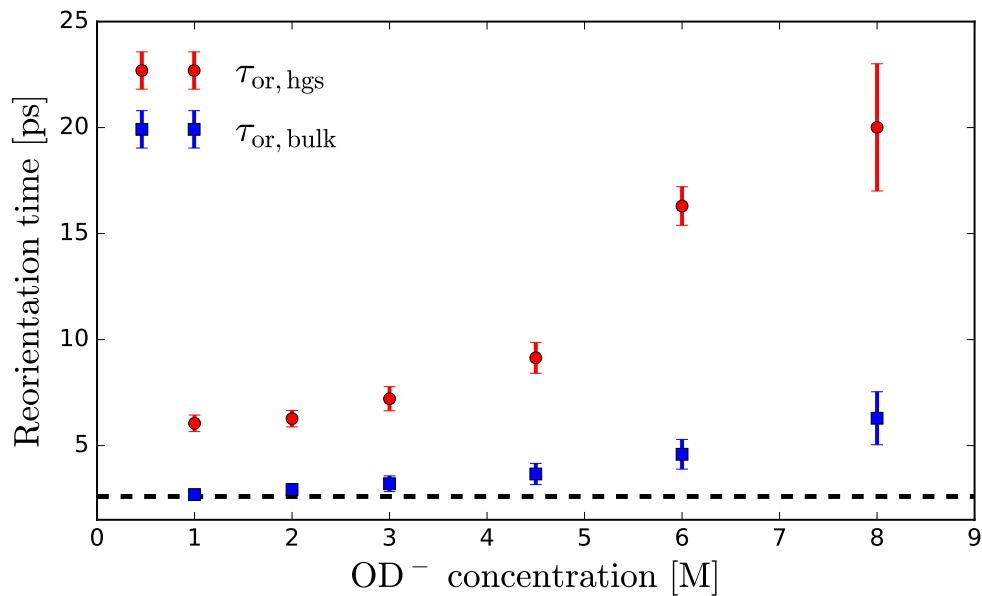


Figure S3: Reorientation time constants of the excited bulk-like OH oscillators (blue squares) and the hot ground state (red circles). The dashed black curve shows the molecular reorientation time constant of neat bulk water.<sup>S1,S2</sup>

determined. We find that the reorientation time constants associated with the excited bulk-like OH oscillators,  $\tau_{\text{or,bulk}}$ , and the hot ground state,  $\tau_{\text{or,hgs}}$ , are well defined, and increase with increasing the OD<sup>-</sup> concentration, as illustrated in Figure S3.

## References

- (S1) Rezus, Y. L. A.; Bakker, H. J. On the orientational relaxation of HDO in liquid water. *J. Chem. Phys.* **2005**, *123*, 114502.
- (S2) Rezus, Y. L. A.; Bakker, H. J. Orientational dynamics of isotopically diluted H<sub>2</sub>O and D<sub>2</sub>O. *J. Chem. Phys.* **2006**, *125*, 144512.