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SUPPORTING INFORMATION

Dielectric Response of Light, Heavy and Heavy-Oxygen Water: Isotope Effects on the Hydrogen-Bonding Network's Collective Relaxation Dynamics

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Supporting Tables and Figures for the experimental dielectric spectra and fitted parameters

Table S1 Dielectric parameters for the cooperative (c) and fast (f) relaxation modes of light water, $H_2{}^{16}O$, taken from literature:[S1] static (ε_s) and infinite-frequency (ε_∞) permittivities, relaxation amplitudes (S_c and S_f) as well as relaxation times (τ_c and τ_f). Also shown is the triple standard deviation of each parameter, obtained by fitting 12–16 spectra individually using Eq. 2 (main text).

T / K	ε_s	ε_∞[a]	S_c	S_f	τ_c / ps	τ_f / ps
278	85.77 ± 0.37	3.95	79.53 ± 0.25	2.29 ± 0.14	14.60 ± 0.36	0.50 ± 0.15
288	81.90 ± 0.40	3.66	75.92 ± 0.25	2.32 ± 0.15	10.80 ± 0.29	0.33 ± 0.16
298	78.17 ± 0.08	3.48	72.30 ± 0.06	2.39 ± 0.04	8.32 ± 0.04	0.26 ± 0.05
308	74.42 ± 0.12	3.06	68.96 ± 0.12	2.40 ± 0.04	6.53 ± 0.02	0.18 ± 0.06
318	71.29 ± 0.07	2.68	65.96 ± 0.07	2.65 ± 0.07	5.31 ± 0.01	0.15 ± 0.05
328	67.99 ± 0.07	2.59	62.69 ± 0.06	2.71 ± 0.09	4.38 ± 0.02	0.16 ± 0.05
338	65.32 ± 0.12	2.62	60.03 ± 0.15	2.67 ± 0.19	3.70 ± 0.03	0.13 ± 0.09

[a] In the present work, ε_∞ was fixed to literature data of $H_2{}^{16}O$.[S1]

Table S2 Dielectric parameters for the cooperative (c) and fast (f) relaxation modes of heavy-oxygen water, $H_2{}^{18}O$, determined in the present work by fitting 12–16 spectra individually, using Eq. 2 (main text): static (ε_s) and infinite-frequency (ε_∞) permittivities, relaxation amplitudes (S_c and S_f) as well as relaxation times (τ_c and τ_f). Also shown is the triple standard deviation of each parameter.

T / K	ε_s	ε_∞[a]	S_c	S_f	τ_c / ps	τ_f / ps
278	85.72 ± 0.26	3.95	79.46 ± 0.22	2.30 ± 0.09	15.18 ± 0.25	0.56 ± 0.09
288	81.88 ± 0.28	3.66	75.96 ± 0.22	2.26 ± 0.08	11.23 ± 0.25	0.31 ± 0.12
298	78.12 ± 0.08	3.48	72.34 ± 0.07	2.31 ± 0.03	8.65 ± 0.02	0.22 ± 0.03
308	74.49 ± 0.05	3.06	69.08 ± 0.04	2.35 ± 0.03	6.83 ± 0.01	0.12 ± 0.03
318	71.44 ± 0.08	2.68	66.27 ± 0.09	2.48 ± 0.06	5.52 ± 0.02	0.05 ± 0.04
328	68.21 ± 0.07	2.59	62.81 ± 0.09	2.81 ± 0.08	4.53 ± 0.02	0.28 ± 0.05
338	65.55 ± 0.08	2.62	60.07 ± 0.10	2.86 ± 0.04	3.89 ± 0.01	0.13 ± 0.09[b]

[a] In the present work, ε_∞ was fixed to literature data of $H_2{}^{16}O$.[S1]

[b] τ_f was fixed to that of $H_2{}^{16}O$.[S1]

Table S3 Dielectric parameters for the cooperative (c) and fast (f) relaxation modes of heavy water, $D_2{}^{16}O$, determined in the present work by fitting 12–16 spectra individually using Eq. 2 (main text): static (ε_s) and infinite-frequency (ε_∞) permittivities, relaxation amplitudes (S_c and S_f) as well as relaxation times (τ_c and τ_f). Also shown is the triple standard deviation of each parameter.

T / K	ε_s	ε_∞[a]	S_c	S_f	τ_c / ps	τ_f / ps
278	86.18 ± 0.12	3.40	80.43 ± 0.10	2.35 ± 0.03	19.68 ± 0.18	0.35 ± 0.04
288	81.81 ± 0.32	3.23	76.29 ± 0.27	2.29 ± 0.06	13.60 ± 0.24	0.22 ± 0.10
298	77.76 ± 0.10	3.13	72.27 ± 0.10	2.36 ± 0.03	10.52 ± 0.04	0.25 ± 0.04
308	74.11 ± 0.09	2.95	69.04 ± 0.08	2.12 ± 0.02	8.22 ± 0.03	0.29 ± 0.04
318	71.02 ± 0.08	2.70	66.23 ± 0.08	2.09 ± 0.06	6.59 ± 0.02	0.37 ± 0.05
328	67.72 ± 0.12	2.46	63.13 ± 0.14	2.04 ± 0.15	5.37 ± 0.03	0.69 ± 0.09
338	64.91 ± 0.13	2.25	60.48 ± 0.21	2.18 ± 0.29	4.47 ± 0.04	0.67 ± 0.18

[a] In the present work, ε_∞ was fixed to literature data of $D_2{}^{16}O$.[S1]

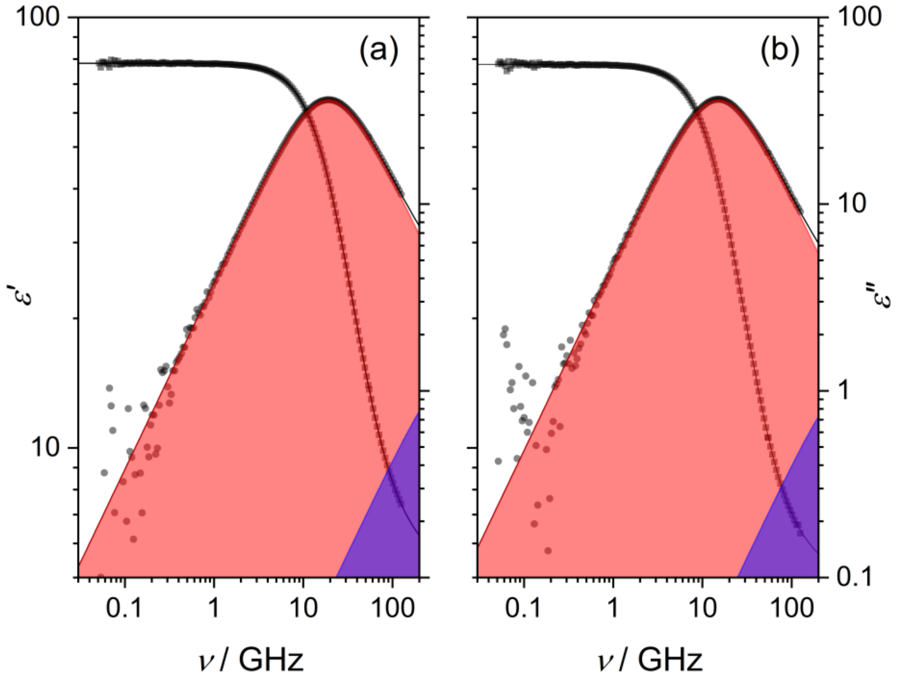

Figure S1 Relative permittivity (*ε'*, left axis) and dielectric loss (*ε''*, right axis) spectra of $H_2^{16}O$ (a) and $D_2^{16}O$ (b) at 298 K. Squares and circles represent the experimental *ε'* and *ε''* data, respectively; the black solid lines show the fits using Eq. 2. Red and purple shaded areas depict the contribution of the cooperative and fast relaxation modes to *ε''*, as obtained from the fit. For visual clarity, the last term of Eq. 2 was subtracted from *ε''*.

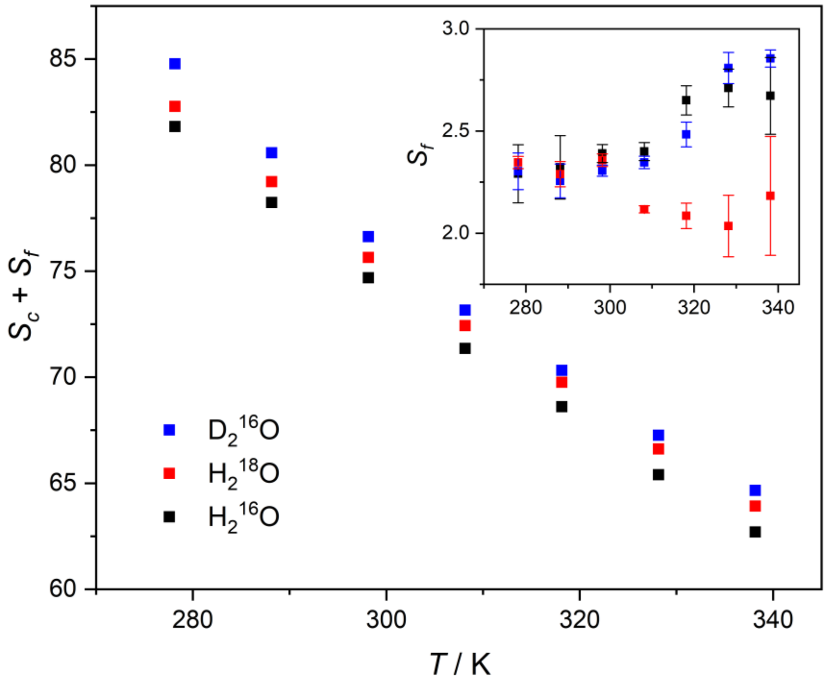

Figure S2 Total relaxation amplitude of the cooperative and fast relaxation modes ($S_c + S_f$) for $H_2^{16}O$, $H_2^{18}O$ as well as $D_2^{16}O$ as a function of temperature, as obtained by fitting Eq. 2 (main text) to the experimental complex permittivity spectra. The corresponding error bars are smaller than the size of the symbols. For visual clarity, the data of $H_2^{18}O$ and $D_2^{16}O$ are shifted by 1 and 2 along the vertical axis. Inset: relaxation amplitude of the fast mode (S_f). The error bars represent the triple standard deviations.

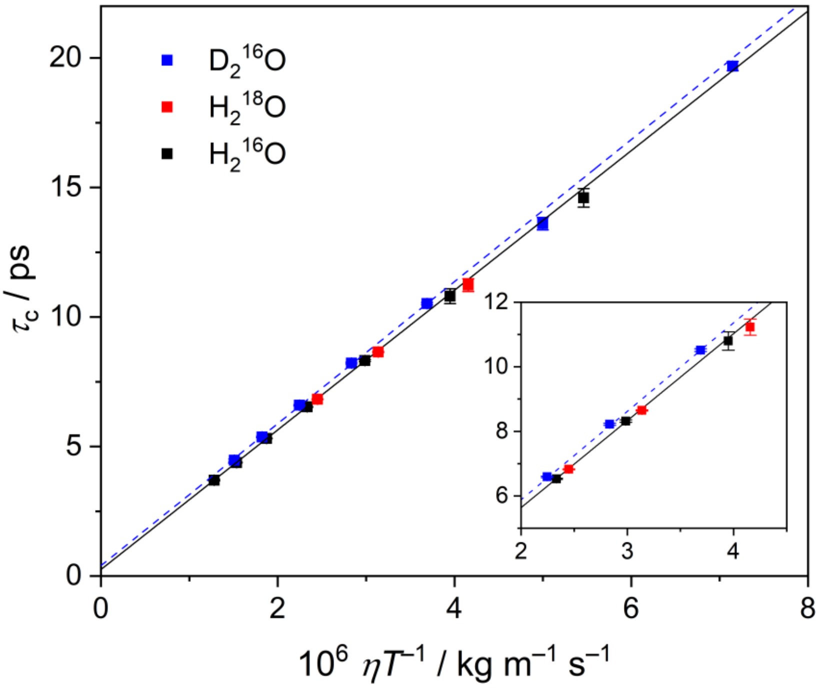

Figure S3 Relaxation time of the cooperative relaxation mode (τ_c) as a function of ηT^{-1}, (η: viscosity, T: temperature) for $H_2{}^{16}O$, $H_2{}^{18}O$ and $D_2{}^{16}O$. Inset: zoomed region of the same plot. Symbols represent experimental data, while the solid black ($H_2{}^{16}O$) and dashed blue lines ($D_2{}^{16}O$) are the results of the fits $\tau_c = a + b\cdot\eta T^{-1}$. The corresponding fitted parameters and triple standard errors: $a = (0.25 \pm 0.09)\cdot 10^{-12}$ s, $b = (2.70 \pm 0.06)\cdot 10^{-6}$ s$^2\cdot$m$\cdot$kg for $H_2{}^{16}O$ and $a = (0.40 \pm 0.24)\cdot 10^{-12}$ s, $b = (2.74 \pm 0.09)\cdot 10^{-6}$ s$^2\cdot$m$\cdot$kg for $D_2{}^{16}O$.

Modelling the isotope effect on the relaxation time upon H/D substitution

In the main text we use a translational mass factor, $\sqrt{M(\mathrm{D_2{}^{16}O})/M(\mathrm{H_2{}^{16}O})}$, and an apparent temperature shift, ΔT, to map the relaxation times of $D_2{}^{16}O$ onto those of $H_2{}^{16}O$ (see Eq. 7 of the main text), by assuming the same translational mass factor accounting for the classical mass effect for $D_2{}^{16}O$ and $H_2{}^{18}O$ as compared to $H_2{}^{16}O$. To determine ΔT (Eq. 7 of the main text), we determine the sum of their squared deviations, χ^2:

$$\chi^2 = \sum_{i=1}^{n}\left(\sqrt{M(\mathrm{D_2{}^{16}O})/M(\mathrm{H_2{}^{16}O})}\cdot\tau_c(\mathrm{H_2{}^{16}O}, T_i - \Delta T) - \tau_c(\mathrm{D_2{}^{16}O}, T_i)\right)^2 \qquad \text{(S1)}$$

as a function of ΔT. Here, we interpolate $\tau_c(\mathrm{H_2{}^{16}O}, T)$ using the fitting results described in the main text (Eqs. 3–5, Table 1). These deviations (Figure S4) show a minimum for $\Delta T = 7.16$ K.

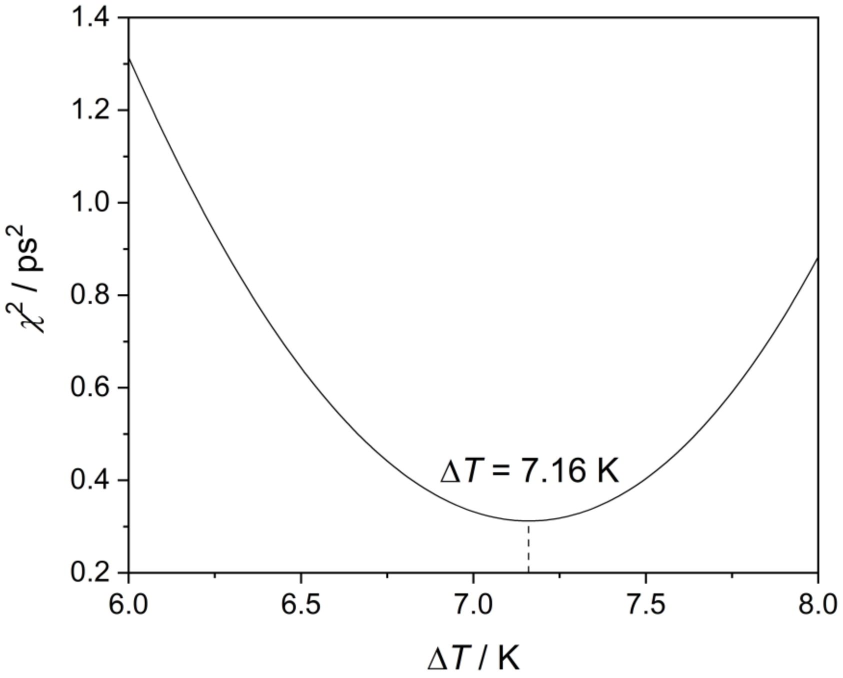

Figure S4 χ^2 (Eq. S1) as a function of the apparent temperature shift, ΔT. The value of ΔT at the minimum is labelled in the figure.

To support the assumption that classical mass effects for $D_2{}^{16}O$ can be accounted for by the same translational mass factor as for $H_2{}^{18}O$, we also test the analogous mapping by treating the mass factor, α, as an adjustable parameter:

$$\tau_c\left(\mathrm{D_2{}^{16}O}, T\right) = \alpha \cdot \tau_c\left(\mathrm{H_2{}^{16}O}, T - \Delta T\right) \tag{S2}$$

Here, we fit ΔT as a function of α by minimizing the following χ^2:

$$\chi^2 = \sum_{i=1}^{n}\left(\alpha \cdot \tau_c\left(\mathrm{H_2{}^{16}O}, T_i - \Delta T\right) - \tau_c\left(\mathrm{D_2{}^{16}O}, T_i\right)\right)^2 \tag{S3}$$

The results of this minimization (Figure S5) demonstrate that the parameters α and ΔT are correlated. The minimum of χ^2 at $\alpha = 1.054$ coincides with $\sqrt{M\left(\mathrm{D_2{}^{16}O}\right)/M\left(\mathrm{H_2{}^{16}O}\right)}$, which suggests that for the enhancement of the dielectric relaxation time upon H/D exchange the translational mass factor can account for classical mass effects, similar to $^{16}O/^{18}O$ substitution.

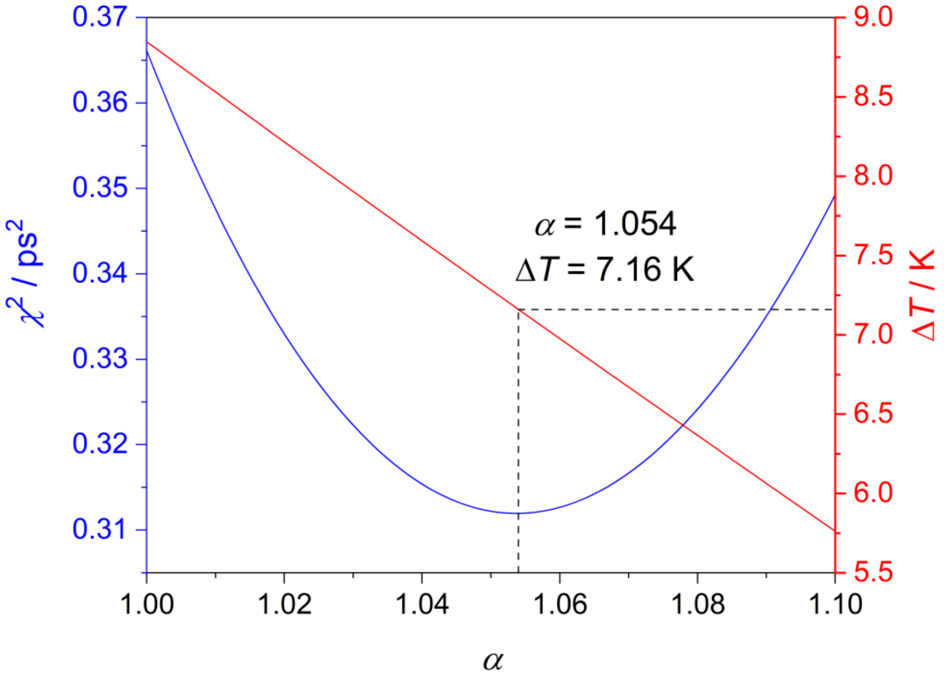

Figure S5 Minimized χ^2 (Eq, S3, left axis) and the fitted apparent temperature shift, ΔT, (right axis) as a function of α (see Eqs. S2 and S3). The values of α and ΔT corresponding to the minimum value of χ^2 are labelled in the figure.

Supporting References

S1. S. Schrödle, PhD thesis, University of Regensburg, 2005