Electronic Supplementary Information

Reconsideration of the relaxational and vibrational line shapes of liquid water based on ultrabroadband dielectric spectroscopy

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Theory of the stochastic frequency modulation (SFM) model

The complex susceptibility $\tilde{\chi}(\omega)$ can be expressed as the Fourier-Laplace transform of the response function $\phi(t)$,

$$\tilde{\chi}(\omega) = \Delta\chi \int_0^\infty e^{-i\omega t}\phi(t)dt \tag{S1}$$

where $\Delta\chi$ is the strength. In the high temperature limit, the Kubo's theorem allows us to introduce the relaxation function $\psi(t)$ to eqn (S1) as follows:[1]

$$\tilde{\chi}(\omega) = \Delta\chi\left(1 - i\omega\int_0^\infty e^{-i\omega t}\psi(t)dt\right) \tag{S2}$$

Following a stochastic theory of line shape developed by Kubo *et al.*,[2] in which the frequency of the system is assumed to result from stochastic frequency modulation (SFM), the randomly perturbed oscillating frequency $\omega(t)$ is described as

$$\omega(t) = \omega_0 + \delta\omega(t) \tag{S3}$$

where ω_0 is the homogeneously oscillating frequency of the system and $\delta\omega(t)$ is the instantaneous frequency shift. If frequency modulation is assumed to be Markovian, a stationary process $\langle\delta\omega(t)\rangle = 0$ is

satisfied.[2] Since the fluctuation frequency for liquids can be treated classically, we can make the following semiclassical approximation to the relaxation function.[3,4]

$$\psi(t) = \left\langle exp\left[-i\int_0^t \delta\omega(t')dt' \right] \right\rangle e^{-i\omega_0 t} \tag{S4}$$

Given that the cumulant expansion of the angular bracket term is given by

$$\left\langle exp\left[-i\int_0^t \delta\omega(t')dt' \right] \right\rangle = exp\left[-i\int_0^t \langle\delta\omega(t')\rangle dt' - \frac{1}{2}\int_0^t dt'_1 \int_0^t dt'_2 \langle\delta\omega(t'_1)\delta\omega(t'_2)\rangle + \cdots \right] \tag{S5}$$

For a stationary process, only the second term is non-zero. Eventually, $\psi(t)$ is represented in the form

$$\psi(t) = exp\left[-i\omega_0 t - \int_0^t dt'(t-t')\langle\delta\omega(t')\delta\omega(0)\rangle \right] \tag{S6}$$

If Markov type frequency modulation is considered, the time-correlation function of the fluctuation frequency $\delta\omega$ is expressed with the Doob's theorem,[5]

$$\langle\delta\omega(t)\delta\omega(0)\rangle = {\omega_\Delta}^2 e^{-\Gamma|t|} \tag{S7}$$

where, ω_Δ is the amplitude and Γ is the rate of the frequency modulation process. According to the law of equipartition of rotational kinetic energy, the amplitude is related with the temperature T and the moment of inertia I, via a relation $I\omega^2/2 = k_B T/2$. Given that the modulation process is rotational, this relation is reduced to ${\omega_\Delta}^2 = k_B T/I$.[6] Furthermore, Γ is characterized by the inverse of the correlation time of modulation. Substituting eqn (S7) into (S6), the final form of the relaxation function $\psi(t)$

$$\psi(t) = exp\left[-i\omega_0 t - \left(\frac{\omega_\Delta}{\Gamma}\right)^2 \left(e^{-\Gamma t} + \Gamma t - 1\right) \right] \tag{S8}$$

is obtained.[2] As practical examples of the SFM, let us consider the *continuous* (i.e. Gauss-Markov) and *discrete* (i.e. two-state jump) processes below.

In the first example of the *continuous* SFM process, we assume a Gaussian probability distribution $P(\delta\omega)$ such that that the fluctuation frequency $\delta\omega$ can take *continuous* values. If we define the standard deviation as the amplitude of modulation, $P(\delta\omega)$ is expressed as:[4]

$$P(\delta\omega) = \frac{1}{\sqrt{2\pi}\omega_\Delta} e^{-\frac{\delta\omega^2}{2{\omega_\Delta}^2}} \tag{S9}$$

By substituting eqn (S8) into (S2), the complex susceptibility of the *continuous* SFM, $\tilde{\chi}_{cSFM}(\omega)$, can be expressed by the continued fraction.[2,7]

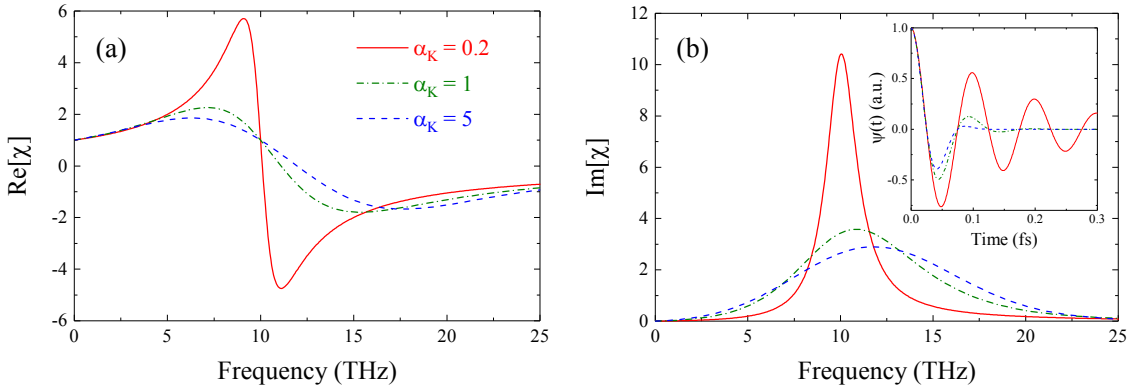

Figure S1 Oscillatory-type model complex susceptibilities of a *continuous* SFM process with the fluctuation frequency $\omega_\Delta/2\pi =$ 5 THz. α_K dependence: $\alpha_K =$ 0.1, $\alpha_K =$ 1 and $\alpha_K =$ 10. The inset shows the relaxation functions of the corresponding susceptibilities.

$$\tilde{\chi}_{cSFM}(\omega) = \Delta\chi\left\{1 - i\omega\frac{1}{i(\omega-\omega_0) + \frac{\omega_\Delta{}^2}{i(\omega-\omega_0)+\Gamma+\frac{2\omega_\Delta{}^2}{i(\omega-\omega_0)+2\Gamma+\ldots}}}\right\} \tag{S10}$$

Aiming to quantitatively characterize the impact of the stochastic modulation process, it is useful to introduce the modulation degree α_K as,[7-9]

$$\alpha_K = \frac{\omega_\Delta}{\Gamma} \tag{S11}$$

This quantity is otherwise known as the Kubo number. In the fast modulation limit, where random modulation is fast such that $\alpha_K \ll 1$, the relaxation function of eqn (S8) can be rewritten as

$$\psi(t) \approx exp\left[-\frac{\omega_\Delta{}^2}{\Gamma}t\right]e^{-i\omega_0 t} \tag{S12}$$

indicating that the random frequency modulation part decays as the single exponential characterized by the correlation time of $\tau = \Gamma/\omega_\Delta{}^2$.[4,7,8] Such a single exponential $\psi(t)$ is reduced to the Debye relaxation ($\omega_0 = 0$) and damped harmonic oscillator ($\omega_0 \neq 0$) line shapes in the frequency domain counterpart $\tilde{\chi}_{cSFM}(\omega)$. Now assume the slow modulation limit (i.e. $\alpha_K \gg 1$), the relaxation function can be re-expressed by truncating expansion of the exponential term of eqn (S8) up to the second-order:

$$\psi(t) \approx exp\left[-\left(\frac{\omega_\Delta}{\Gamma}\right)^2\left\{\left(1-\Gamma t+\frac{\Gamma^2 t^2}{2}\right)+\Gamma t-1\right\}\right]e^{-i\omega_0 t} = exp\left[-\frac{\omega_\Delta{}^2 t^2}{2}\right]e^{-i\omega_0 t} \tag{S13}$$

Fourier transform of eqn (S13) yields an inhomogeneous Gaussian line shape in the imaginary part of $\tilde{\chi}_{cSFM}(\omega_0 \neq 0)$, projecting the probability distribution $P(\delta\omega)$. The α_K dependence of the SFM resonances is modeled in Fig. S1. It is clear that the transition from fast modulation (i.e. $\alpha_K =$ 0.2) to slow modulation (i.e. $\alpha_K =$ 5) gradually shifts to the symmetric and broad dispersion, accompanying gradual blue shifts.[10]

Between these limits, the resonance grows motional narrowing as α_K increases.

Unless the system is involved in the overdamped limit, eqns (S12) and (S13) hold for the long-time ($t \gg \Gamma^{-1}$) and short-time ($t \ll \Gamma^{-1}$) limits, respectively. The physical meaning of this coincidence is that the somewhat inertial decay behavior turns to exponential after a time scale that is determined by Γ.[11] Eqn (S13) conveys that a smaller ω_Δ leads to more significantly inertial behavior at short times.

As the second example, let us consider a *discrete* two-state jump process in which the fluctuation frequency takes the *discrete* values, namely $\delta\omega = \pm\,\omega_\delta$, so that the perturbed frequency of the system realizes only $\omega_0 + \omega_\delta$ and $\omega_0 - \omega_\delta$ with equal probabilities. If further assume a process composed of *discrete* N-independent frequency modulation, in which the fluctuation frequency $\delta\omega$ can take discrete values such as $\delta\omega = \pm\,\omega_\delta,\ \pm\sqrt{2}\omega_\delta, \ldots, \pm\sqrt{N}\omega_\delta$ (N is integer), the quantity ω_δ is associated with the amplitude ω_Δ as:[7]

$$\omega_\Delta{}^2 = N\omega_\delta{}^2 \tag{S14}$$

According to eqns (S8) and (S14), the relaxation function of the *discrete* N-independent SFM process is given by

$$\psi(t) = \left\{\cosh\left(\frac{\Gamma t}{2a}\right) + a\sinh\left(\frac{\Gamma t}{2a}\right)\right\}^N exp\left[-i\omega_0 t - \frac{N\Gamma t}{2}\right] \tag{S15}$$

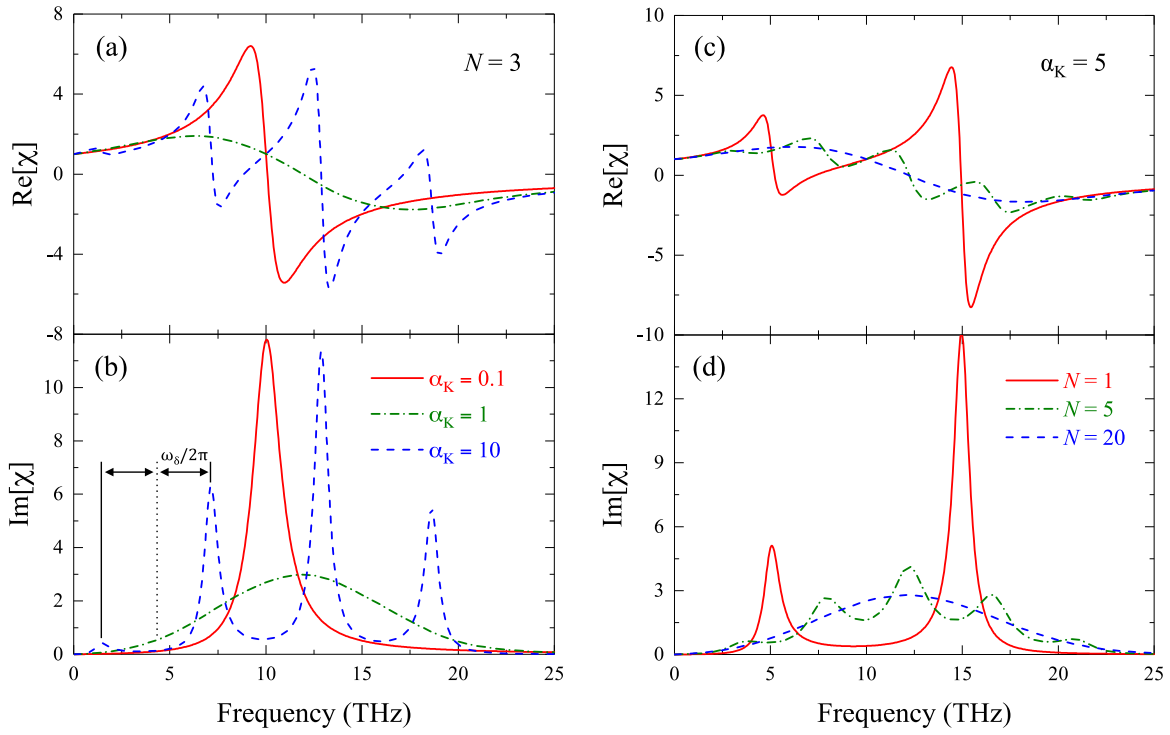

Figure S2 Oscillatory-type model complex susceptibilities of a *discrete* SFM process with the center frequency $\omega_0/2\pi =$ 10 THz and the fluctuation frequency $\sqrt{N}\omega_\delta/2\pi =$ 5 THz. (a,b) α_K dependence: $\alpha_K =$ 0.1, $\alpha_K =$ 1 and $\alpha_K =$ 10, with $N =$ 3 fixed. (c,d) Number of process dependence: $N =$ 1, $N =$ 5 and $N =$ 20, with $\alpha_K =$ 0.5 fixed.

where $a = \left(1 - 4{\alpha_K}^2\right)^{-1/2}$.[7,8] Note that the limit $N \to \infty$ of $\psi(t)$ corresponds to the *continuous* process. By substituting eqn (S15) to (S2), one can finally obtain the *discrete* SFM $\tilde{\chi}_{dSFM}(\omega)$ as follows,[7,8]

$$\tilde{\chi}_{dSFM}(\omega) = \Delta\chi\left\{1 - i\omega\frac{1}{i(\omega-\omega_0) + \frac{N{\omega_\delta}^2}{i(\omega-\omega_0)+\Gamma+\frac{2(N-1){\omega_\delta}^2}{i(\omega-\omega_0)+2\Gamma+\ldots\frac{N{\omega_\delta}^2}{i(\omega-\omega_0)+N\Gamma}}}}\right\} \quad \text{(S16)}$$

The simplest discrete process, namely the two-state jump process, can be achieved by setting $N = 1$. Its relaxation function is expressed as $\psi(t) = \{\cosh(\Gamma t/2a) + a\sinh(\Gamma t/2a)\}exp[i\omega_0 t - \Gamma t/2]$ and the resulting $\tilde{\chi}_{dSFM}(\omega)$ is reduced to,

$$\tilde{\chi}_{dSFM}(\omega) = \Delta\chi\left\{1 - i\omega\frac{1}{i(\omega-\omega_0) + \frac{{\omega_\delta}^2}{i(\omega-\omega_0)+\Gamma}}\right\} \quad \text{(S17)}$$

Fig. S2 shows the modeled complex susceptibilities of the resonant-type *discrete* SFM function at various α_K and N. From Fig. S2(a,b), it can be seen that the $N + 1$ sharp resonant dispersions appears at

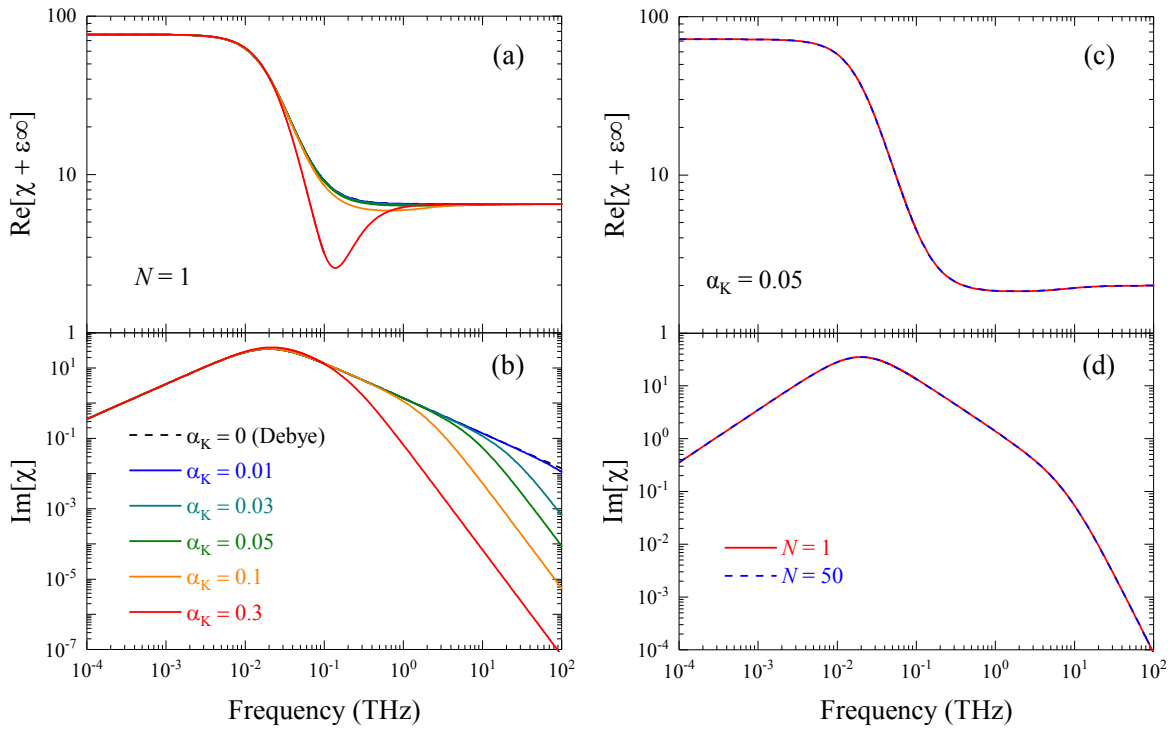

Figure S3 Relaxation-type model complex susceptibilities of a *discrete* SFM process with the fluctuation frequency $\sqrt{N}\omega_\delta/2\pi =$ 2.5 THz. (a,b) α_K dependence from $\alpha_K =$ 0 (Debye limit) to $\alpha_K =$ 0.3, with $N =$ 1 fixed. $\varepsilon_\infty =$ 6.5 is adopted for the real part. (c,d) Number of process dependence: $N =$ 1 and $N =$ 50, with $\alpha_K =$ 0.05 fixed. $\varepsilon_\infty =$ 2.0 is adopted for the real part.

regular frequency intervals of ω_δ/π in the case of slow modulation ($\alpha_K =$ 10). As the correlation with random frequency modulation is weakened until $\alpha_K \to 1$, the markedly sharp dispersions are broadened and eventually merge into a single peak. In fast modulation ($\alpha_K =$ 0.1), the resonant dispersion looks like homogeneous since the original resonant band shape is hardly affected by modulations. If $\alpha_K = 5$ is fixed, the results in Fig. S2(c,d) indicates that the increase in the number of process from $N = 1$ to $N = 20$ shows an increasing resemblance to the Gaussian band shape, because increasing N eventually goes into the *continuous* frequency modulation process. In the framework of the relaxation-type *discrete* SFM model, the α_K dependence (0~0.3) and the N dependence (1 and 50) are modeled in Fig. S3. The α_K dependence displayed in Fig. S3(a,b) shows that the deviation from the Debye model in the high-frequency tail becomes greater as α_K increases. On the other hand, under the fast modulation limit, we found the complex susceptibilities do not depend on N as depicted in Fig. S3(c,d). Therefore, it has no objection to fix $N = 1$ for simplicity as far as the fast modulation limit is satisfied. If we assume a $N = 1$ relaxation mode ($\omega_0 = 0$), eqn (S17) is further simplified to,

$$\tilde{\chi}_{dSFM}(\omega) = \frac{\Delta\chi{\omega_\delta}^2}{{\omega_\delta}^2 - \omega^2 + i\omega\Gamma} \tag{S18}$$

In the fast modulation limit where $\tau \approx \Gamma/{\omega_\delta}^2$ is held, we can approximate eqn (S18) as follows.

$$\tilde{\chi}_{dSFM}(\omega) \approx \frac{\Delta\chi}{1 - \left(\omega/\omega_\delta\right)^2 + i\omega\tau} \tag{S19}$$

This equation is nothing but the Rocard model, which considers small inertial effects of non-interacting ($1/\Gamma \ll 1$) rigid dipoles.[12]

In the *discrete* SFM model, further generalization of the model can be made to "unequal" probabilities by introducing an asymmetrical parameter σ: i.e. probabilities of the perturbed frequencies are $(1-\sigma)/2$ for $\omega_0 + \omega_\delta$ and $(1+\sigma)/2$ for $\omega_0 - \omega_\delta$.[13] Nevertheless, as is the case for the liquid water relaxations, the parameter σ is hardly affects the $\tilde{\chi}_{dSFM}(\omega)$ line shape under the fast modulation limit.[8]

Libration mode: $\tilde{\chi}_L(\omega)$

Aiming to confirm the validity of our best-fitted libration mode, $\tilde{\chi}_L(\omega) = \tilde{\chi}_{L1}(\omega) + \tilde{\chi}_{L2}(\omega)$, the fitted result is compared with the experimental one exposed by subtracting the other relaxation and vibration susceptibilities from the dielectric constant of water,

$$\tilde{\chi}_L(\omega) = \tilde{\varepsilon}(\omega) - \left(\tilde{\chi}_{slow}(\omega) + \tilde{\chi}_{fast}(\omega) + \tilde{\chi}_B(\omega) + \tilde{\chi}_S(\omega) + \varepsilon_\infty\right) \quad \text{(S20)}$$

where $\tilde{\chi}_{slow}(\omega)$: the slow relaxation, $\tilde{\chi}_{fast}(\omega)$: the fast relaxation, $\tilde{\chi}_B(\omega)$: the intermolecular bending, $\tilde{\chi}_S(\omega)$: the intermolecular stretching and ε_∞: the real part of the high-frequency limit. The obtained experimental result (gray circles) is compared with the best-fitted one (black dot line) in Fig. S4.

Fig. S4(a) shows the dual-DHO description under the Debye-type $\tilde{\chi}_{slow}(\omega)$ and $\tilde{\chi}_{fast}(\omega)$, i.e. eqn (1). It

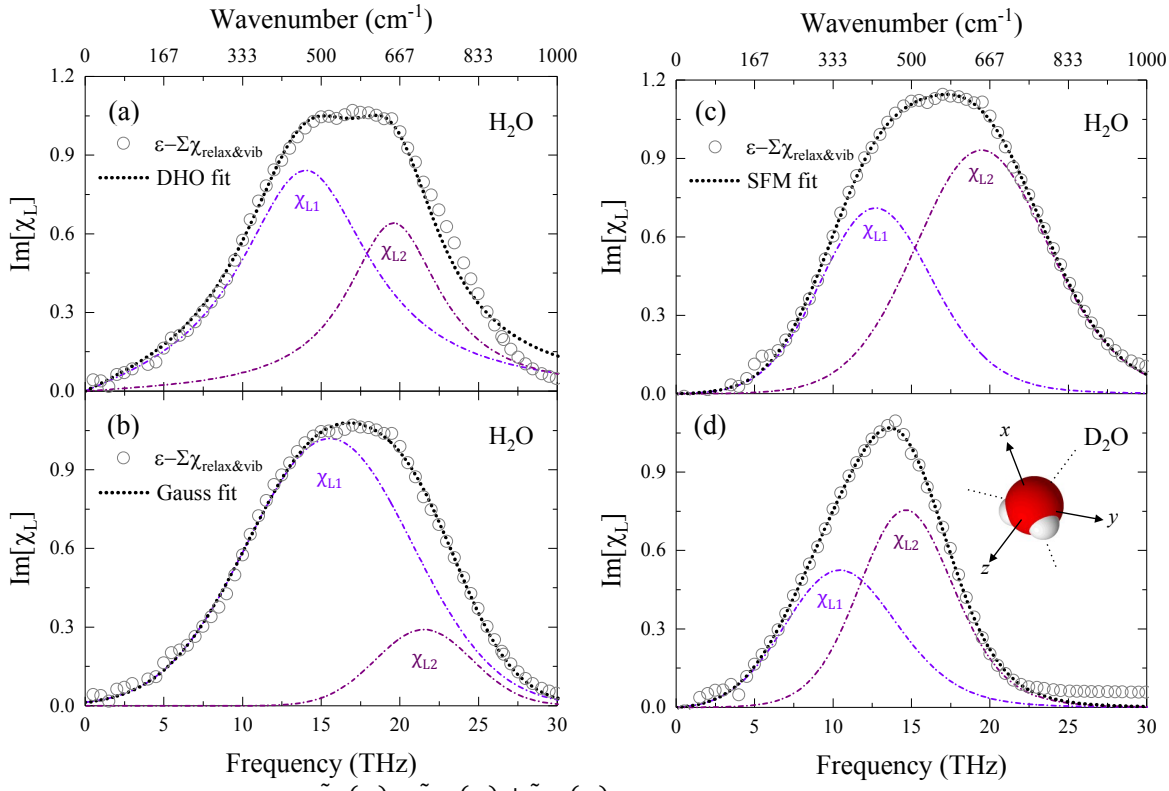

Figure S4 Imaginary part of $\tilde{\chi}_L(\omega) = \tilde{\chi}_{L1}(\omega) + \tilde{\chi}_{L2}(\omega)$. (a) Dual-DHO and (b) dual-Gaussian description under the Debye-type relaxation model (eqn.1). (c) H_2O and (d) D_2O libration mode described by the *continuous* stochastic frequency modulation model when the *discrete* relaxation model (eqn.4) is used as $\chi_{slow}(\omega)$ and $\chi_{fast}(\omega)$ modes. The inset in (d) shows the three inertial principal axes contributing to the libration.

Table S1 Best-fitted libration parameters of eqn (5) under the constraint of $\Gamma_{L1}/2\pi = \Gamma_{L2}/2\pi =$ 1.4 THz. Uncertainties are shown in parentheses.

	$\tilde{\chi}_{L1}$		$\tilde{\chi}_{L2}$	
	$\omega_{L1}/2\pi$ (THz)	$\omega_{\Delta}^{L1}/2\pi$ (THz)	$\omega_{L2}/2\pi$ (THz)	$\omega_{\Delta}^{L2}/2\pi$ (THz)
H_2O	11.66 ± 0.05	4.22 ± 0.03	18.52 ± 0.07	4.84 ± 0.03
D_2O	9.10 ± 0.04	4.27 ± 0.03	14.00 ± 0.05	3.60 ± 0.03

can be noticed that the dual-DHO shapes the ambiguously split peak around 18 THz (600cm^{-1}) and the high-frequency tail of the libration band (typically above 20 THz) is ill replicated. On the other hand, replacement of the dual-DHO function to the dual-Gaussian compensated for these deficiencies as shown in Fig. S4(b), suggesting that the water libration mode is composed of two sub-bands undergoing inhomogeneous broadening, as expected previously.[14] The continuous SFM fitting of the libration band by the use of eqn (5) is exhibited in Fig. S4(c,d). Please keep in mind that the exposed experimental $\tilde{\chi}_L(\omega)$ in Fig. S4(c) is not identical to that in Fig. S4(a), because the *discrete* SFM relaxation in eqn (5) differs from the Debye typically above 3 THz. The obtained best-fitted parameters are summarized in Table S1.

Hindered translation modes: $\tilde{\chi}_B(\omega)$ and $\tilde{\chi}_S(\omega)$

Although purely hindered translational motions in a system of non-polarizable molecules involves no direct fluctuations of the total dipole moment,[15] computational studies has revealed that modulation with the intramolecular H-O-H (or D-O-D) bend and the intermolecular charge flux provokes the IR intensities of the intermolecular bending and stretching, respectively.[16] Despite the very weak IR activity of the intermolecular bending $\tilde{\chi}_B(\omega)$, it is evident from Fig. 3(c) that the contribution of the bending mode is non-negligible so as to reproduce the dielectric responses in between the fast relaxation (~300 GHz) and the intermolecular stretching (~5 THz) region. Taking note of the isotope effect, its oscillator strength $f_B \propto \int \omega Im[\tilde{\chi}_B(\omega)]d\omega$ is found to be almost H/D independent within the margin of error. In contrast, the intermolecular stretching mode $\tilde{\chi}_S(\omega)$ exhibits a significant isotopic effect on the oscillator strength: $f_S(H_2O):f_S(D_2O) = 1:0.84$ with an accuracy of ± 0.01. Considering that the degenerated asymmetric stretching of the instantaneous tetrahedral structure is associated with the dipole moment changes,[17] $f_S(H_2O) > f_S(D_2O)$ is indicative of the greater degree of dynamical fluctuation involving distortion of the water structure of liquid H_2O compared to that of D_2O.[18] In addition, the damping ratio of the intermolecular stretch of H_2O ($\xi_S = \omega_S/\gamma_S =$ 0.82) is found to be significantly smaller than that of D_2O ($\xi_S =$ 0.90), pointing to a more quickly dismantled instantaneous tetrahedral HB structure of H_2O. These views are generally consistent with widely accepted knowledge that D_2O is a more structured liquid than H_2O, where the intermolecular O…O…O angle is more close to that of a regular tetrahedron and its

distribution is sharper for D_2O.[19-22]

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