

Reconsideration of the relaxational line shape of liquid water based on ultrabroadband dielectric spectroscopy

Keiichiro Shiraga

RIKEN Center for Integrative Medical Sciences (IMS), keiichiro.shiraga@riken.jp

Summary: Ultrabroadband dielectric spectroscopy of liquid water ranging from 500 MHz to 400 THz demonstrated that molecular inertia and intermolecular interactions should be considered to predict the line shape of the water relaxation peaked around 20 GHz.

Introduction: The Debye relaxation model is widely used to describe the large dielectric dispersion of ambient water around 20 GHz. However, from a theoretical point of view, this model is supposed to give incorrect predictions at high frequencies owing to the inappropriate assumption that inertial effects and intermolecular interactions do not affect the relaxation dynamics. In this work, we propose an alternative relaxation model to achieve a thorough understanding of the water relaxation dynamics.

Methods: Ultrabroadband dielectric spectra of liquid H₂O and D₂O at 300 K, over 500 MHz to 400 THz, were obtained by combining vector network analyzer, terahertz time-domain spectroscopy and infrared absorption spectroscopy systems. It should be emphasized here that this ultrabroadband spectra, completely covering the microwave to NIR, measured from the same water sample at the same temperature stands out as having been measured by a single workgroup: it is not a set of various measurements collected from different literatures.

Results and Discussion: The measured complex dielectric constants $\tilde{\epsilon}(\omega)$ of liquid H₂O and D₂O are shown in the left Figure. An intense mode around 20 GHz (for H₂O) is a well-known collective reorientation of hydrogen-bonded water molecules, which has been historically described by the Debye relaxation function. Nevertheless, as displayed in the right Figure, the present ultrabroadband spectroscopy revealed that the Debye function itself exceeds the actual imaginary part above 65 THz (or 2166 cm⁻¹ in wavenumber / 4.62 μm in wavelength). Such an unreliable prediction by the Debye model at high frequencies can be theoretically traced to neglected inertial effects and intermolecular interactions, which only influence the relaxation dynamics at short times. In order to overcome this issue, a discrete stochastic frequency modulation (SFM) relaxation model, assuming a stochastic process in which the dipole relaxation is subject to the Markovian frequency fluctuation ($\pm\omega_\delta$) with the correlation time of $1/\Gamma$, was used to describe the water relaxation, namely,

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

where $\Delta\chi$ is the relaxation strength.¹⁾ Unlike the Debye model, this SFM relaxation model was consistent with the experimental dielectric spectra up to 400 THz serving as a baseline of intramolecular bands in the infrared region. The SFM model starts to deviate from the Debye above 1 THz on account of small but non-negligible correlations with the environmental stochastic process (i.e. hydrogen bond dynamics represented by intermolecular vibrations). Transforming $\tilde{\chi}(\omega)$ into the time-domain, the SFM relaxation model clearly shows that the moment of inertia hinders the water reorientation with a persistence time of typically 25 fs.

¹⁾ K. Shiraga *et al.*, Phys. Chem. Chem. Phys., (accepted).

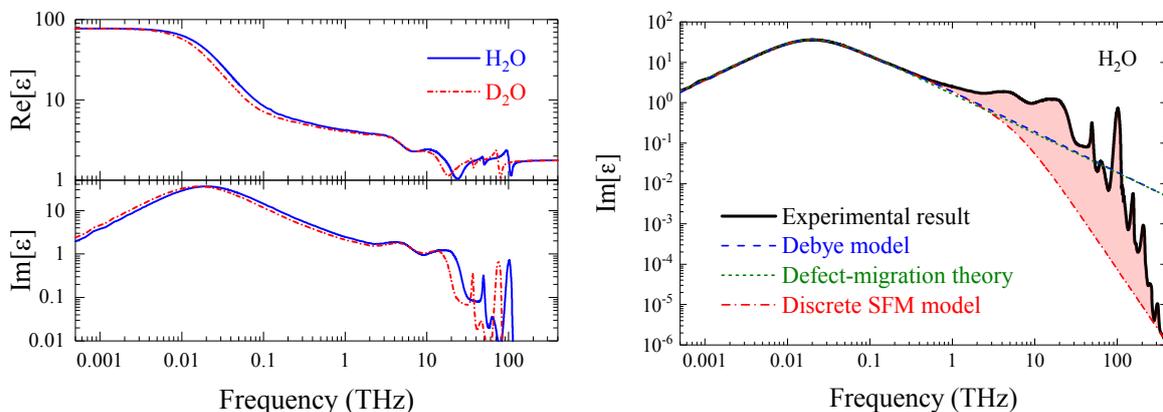


Figure. (Left) Ultrabroadband dielectric spectra of liquid H₂O and D₂O at 300 K, ranging from 500 MHz to 400 THz. (Right) Dielectric loss spectrum of H₂O compared with the representative relaxation models.