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Finding the accurate permittivity model for liquid water and heavy water at different temperatures in the Terahertz range

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Abstract— We present a study of liquid water and heavy water in the terahertz range at temperatures between 283K and 348K. We will fit our data with the fit@TDS software that provides a criterion to discriminate good models from others. We will present a comparison between the models proposed in the literature for liquid water and use this criterion to find the most accurate one.

I. INTRODUCTION

THE liquid state of water has a very unique structure, due to the specific arrangement of water molecules that form up to four hydrogen bonds with surrounding molecules [1]. It results in the formation of a complex hydrogen-bond (H-bond) network. Different methods have been used to study the properties of water but its dynamical behavior is still only partially understood. To retrieve information on molecular processes in water, and in particular intermolecular interactions, the study has to be conducted in the Terahertz range, which covers the H-bond response [2]. It makes Terahertz time-domain spectroscopy (THz-TDS) a perfect candidate for the investigation. The data collected during the experiment can be fitted with permittivity models in order to gain information on the microscopic dynamics in liquid water. Literature includes many studies of water with THz-TDS but there is still no consensus on the correct model to use or on the fitting process. Several models have been proposed, starting with the well-known Debye model (see equation 1) that works for frequencies below a few tens of gigahertz:

$$\tilde{\epsilon}(\omega) = \frac{\Delta\epsilon}{1 + j\omega\tau} \quad (1)$$

Most of the time, other models build on this first one when they extend to higher frequencies, the most popular containing two Debye terms and two Lorentz terms for the terahertz range. However, the fit is not fully satisfactory; specifically, around 1,5 THz and other versions have been proposed, such as replacing the Debye terms by *Havriliak-Negami* (see equation 2) or *Cole-Cole* models:

$$\tilde{\epsilon}(\omega) = \frac{\Delta\epsilon}{[1 + (j\omega\tau)^\alpha]^\beta} \quad (2)$$

Recent progress on the fitting process and the importance of taking experimental noise and its correlations into account [3, 4] is making it now possible to discriminate bad models from good ones, with the help of the *Akaike* criterion. We decided to analyze liquid water and heavy water, which has a different structure hence different dynamics, and their temperature dependence in the terahertz range. Using this new method, implemented in the fit@TDS software [5], we will be able to compare the proposed models and find the appropriate one.

II. RESULTS

The experiment was made with a Menlosystem Terasmart THz-TDS setup purged with nitrogen. The water sample was placed inside a microfluidic cell composed of z-cut quartz windows separated by a 100 μ m Teflon spacer. The temperature of the cell was regulated thanks to a thermocouple and a chiller operated by a PID controller. We made measurements between 10°C and 70°C with 10°C increments as well as an additional measurement at 75°C.

On figure 1, we traced the spectra of heavy water (D₂O) and water (H₂O) at each temperature, normalized by the spectrum of the reference, that is without any sample on the beam path.

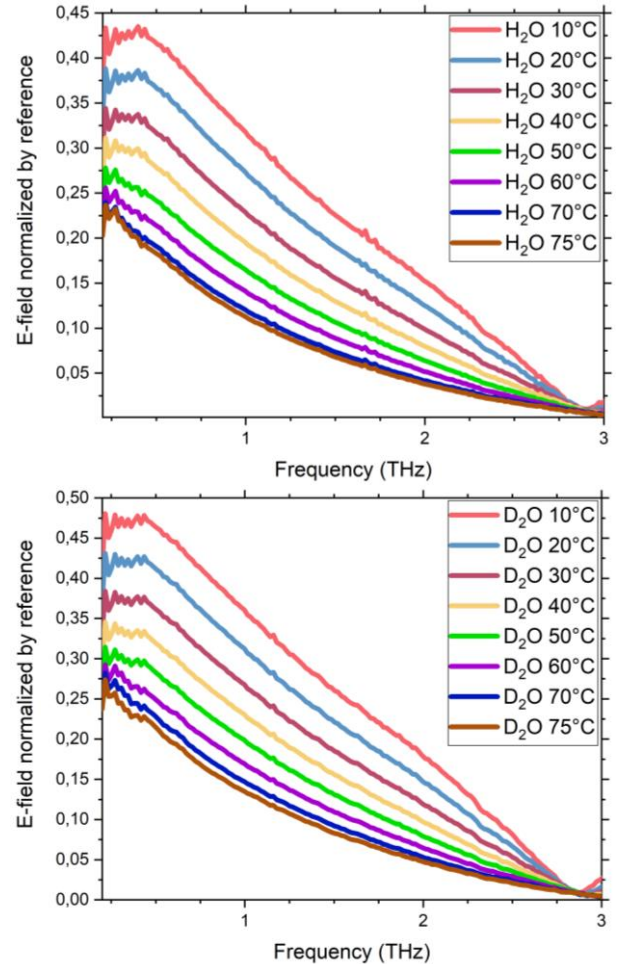
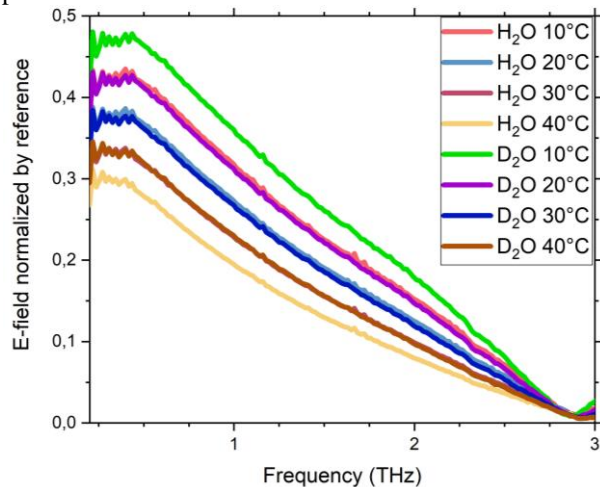


Fig. 1. Spectra of liquid water (top) and heavy water (bottom) normalized by the spectrum of the reference at temperatures between 10°C (283K) and 75°C (348K).

For both samples, their absorbance increases as the temperature increases, which is consistent with the fact that water becomes less viscous as the temperature increases.

However, we can note that the D₂O sample is less absorbing than the H₂O sample. This is showcased on figure 2, where some of the curves are compared (we only put the first temperatures for the sake of clarity). Thus, even if they are very similar in shape, the models, or at least their parameters, will be different. For the conference, we will complete the fit analysis of this result and advance further on the understanding on how the structure of the H-bond networks of both D₂O and H₂O compare.



III. SUMMARY

Liquid water is still one of the most discussed topics in THz-TDS and is the foundation of any biological related study. For instance, a deep understanding of the terahertz dielectric function or dynamics will bring knowledge on the biochemical reactions in water. This is why it is of utmost importance to characterize it precisely, which requires rigorous experimental and fitting procedures.

In this conference, we will show the result of the fitting process, made with the fit@TDS software. The model chosen as well as its parameters should lead the path to an answer to the discussion on liquid water in the terahertz range and to how it compares to heavy water.

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