Terahertz Time-Domain Spectroscopy of D_2O

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***Abstract*—The dielectric spectrum of D_2O between 45 GHz and 1.7 THz is measured using Terahertz Time-Domain Spectroscopy. The data is modeled as a sum of Debye relaxations and Lorentzian oscillators. Similar to previous studies on H_2O, evidence is shown of anti-correlated effects in bulk D_2O. Work is being done to extend spectrometer bandwidth to 10 GHz to measure a possible low frequency oscillation at 11.2 °C, the temperature of maximum density.**

I. Introduction And Background

Although extensive research has been done on water, some of its properties are not truly understood; one of them being the density anomaly at 4 °C for H_2O and 11.2 °C for D_2O. To gain better insight into this peculiar behavior of liquid water, we use Terahertz Time-Domain Spectroscopy (THz-TDS) to measure the dielectric spectrum of D_2O from 45 GHz to 1.7 THz at 7 °C, 11.2 °C and 16 °C.

The pump probe experiment is done with a 100 fs Ti:Sapphire laser beam at 780 nm. The pump beam first passes through a delay stage that allows 1 ns of data acquisition, then is incident upon a GaAs photoconductive antenna which produces the THz pulse. The THz beam is collected and passed through the sample which is sandwiched between fused silica windows. The transmitted THz pulse is then focused on a ZnTe crystal where it is electro-optically detected by the probe beam.

The D_2O spectra exhibit similarities to previous THz-TDS data on H_2O in this same frequency range. The studies on H_2O have shown that a 21 GHz oscillator appears at 4 °C, and then diminishes at higher and lower temperatures. Since D_2O spectra have shown similarities to water, the current work is motivated by the possibility that D_2O has an analogous low frequency feature at 11.2 °C.

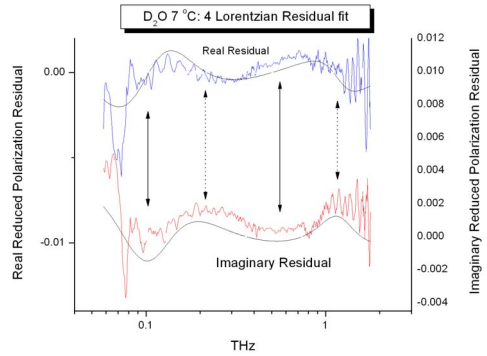
II. Results

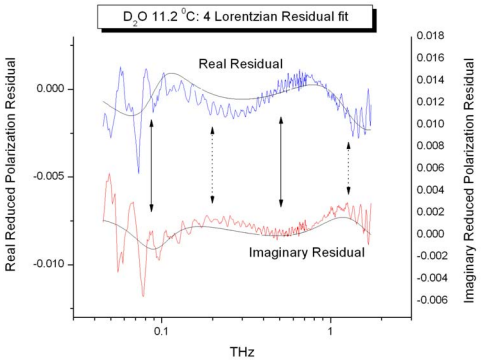
The D_2O dielectric spectrum is modeled as a sum of Debye relaxations and Lorentzian oscillators. To get accurate fits, microwave [1] and FIR [2] literature data were interpolated to the appropriate temperatures and joined at the ends of the data where noise is large. Frequencies below 45 GHz were set with a single Debye relaxation and FIR data was appended past 1.7 THz, providing data from 1 GHz to 18 THz. Using the reduced polarization formula, this complete set of data was then fit with the known 2 Debye relaxations and 4 Lorentzians.

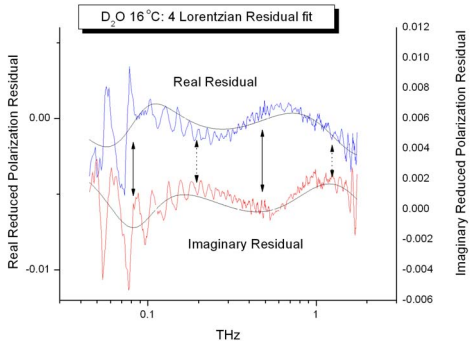
$$\frac{\left(\hat{\varepsilon}(\omega)-\varepsilon_\infty\right)\left(2\hat{\varepsilon}(\omega)-\varepsilon_\infty\right)\varepsilon_0}{\left(\varepsilon_0-\varepsilon_\infty\right)\left(2\varepsilon_0-\varepsilon_\infty\right)\hat{\varepsilon}(\omega)}=\sum_{j=1}^{2}\frac{f_j}{1+\left(i\omega\tau_j\right)}+\sum_{k=1}^{4}\frac{\omega_k^{\,2}f_k}{\omega_k^{\,2}-\omega^2+i\omega\Gamma_k}$$

This formula relates the microscopic dipole correlation function to the macroscopic polarization and makes for a more appropriate model for polar liquids since we eliminate long range dipole-dipole interactions.

The fits from the known relaxations and oscillations were then subtracted from the data to obtain residuals. These residuals exhibit oscillatory features previously not seen in the literature. We have fit the residuals to 2 positive and 2 negative Lorentzians. The solid arrows on the graphs denote the positions of negative Lorentzians, where dashed arrows point to positive Lorentzians.







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Similar negative Lorentzians were found in H_2O, thus providing the first evidence of anti-correlated effects in bulk water. Improvements are being made to extend the bandwidth of the spectrometer down to 10 GHz to acquire reliable fitting of low frequency residual features.

REFERENCES

[1] P.S. Yastremskii, J. Struct. Chem. **12**, 532, (1971).
[2] H.R. Zelsmann, J. Mol. Structure **350**, 95 (1995).