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THz-TDS of Liquids in a Temperature-Controlled Transmission Flowcell

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Abstract—Precise temperature-control is necessary for many spectroscopic measurements. We present the temperature-dependent complex THz refractive index of liquid samples measured in a flowcell, analysed by a numerical method that allows simultaneous extraction of the sample’s thickness to verify the temperature-stability of the cell.

I. INTRODUCTION AND BACKGROUND

TERAHERTZ-FREQUENCY-RANGE measurements of biomolecular systems in biologically-relevant environments are expected to reveal information about their orientation, relaxation, and hydration. However, functional biological systems are sensitive to temperature fluctuations, an effect that has been shown to be of critical importance in the terahertz frequency-range [1]. Thus precise temperature-control is essential during the spectroscopic measurement of sample parameters. We present here the temperature-dependent refractive index of liquid samples, measured by free-space THz-TDS in a variable-temperature transmission flowcell comprising two *z*-cut quartz windows, separated by a variable-thickness spacer layer. Sample refractive index was determined using a field-transmission model that incorporated the Fresnel coefficients of the multi-layered structure, and the Fabry–Pérot cavity formed by the plane-parallel quartz windows [2].

In this method, a LT-GaAs photoconductive antenna was patterned on a 500- μm -thick *z*-cut quartz substrate, as described in Ref. 3. Picosecond pulses were generated by exciting the emitter with a 100fs laser source while a 100V bias was applied across the electrodes. The terahertz field was detected with an electro-optic sampling technique comprising a 2-mm-thick ZnTe crystal and a pair of balanced photodiodes.

II. RESULTS

Reference measurements were first made of the cell containing dry air, $E_r(t)$, after which the analyte was inserted into the cell, and the sample-loaded pulse, $E_s(t)$, was recorded. An initial approximation of the sample index was made, based on the frequency-dependent phase and amplitude of the measured transfer function, $H(\omega) = E_s(\omega)/E_r(\omega)$, from which the complex refractive index, $\tilde{n} = n' - jn''$, was estimated [4]. A gradient-descent fitting algorithm, initialised with the sample index approximation, was then used to fit the full field-transmission model to the measured $H(\omega)$. The propagation model is highly-sensitive to error in the measured sample-thickness, d , and sinusoidal oscillations are produced in the extracted index when the error in d is large, as shown in Fig. 1.

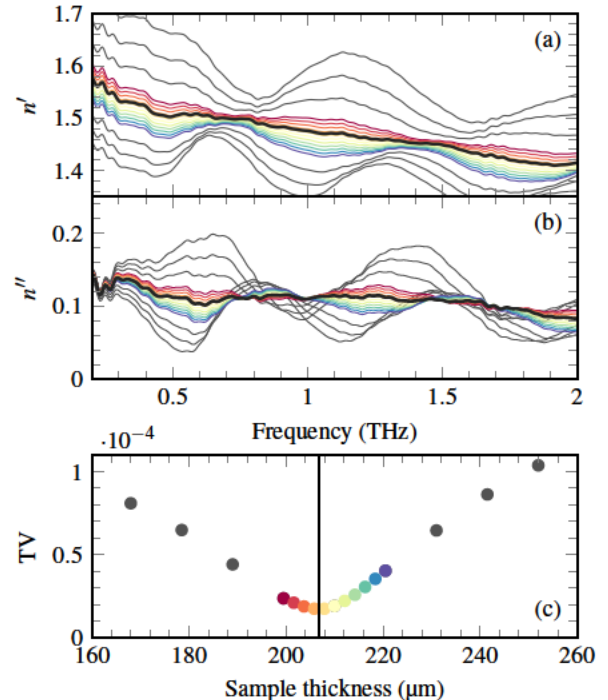


Fig. 1. The (a) real and (b) imaginary components of the refractive index of propan-2-ol measured at 20°C. The spacer was measured to be ~ 210 - μm -thick. (c) The TV was calculated for a coarse (grey) $\pm 20\%$ thickness-range and a high-resolution sweep was performed from -5% (red) to $+5\%$ (purple) of the coarse TV-minimum. Using this method, a sample-thickness of 206.9 μm was found, and the corresponding index calculated (black).

Accurate measurement of a spacer layer that is a few hundred microns thick is a non-trivial task; flexible materials such as PTFE can be compressed when the flowcell is constructed (thereby changing its thickness), and hard materials such as quartz are fragile, and therefore difficult to measure accurately without damage. Thus the sample-thickness, and corresponding refractive index, was determined *in situ* by minimising the total variation (TV) in \tilde{n} as a function of assumed d [5]. As shown in Fig. 1c, the TV in \tilde{n} was calculated for $d = \pm 20\%$ in 5% increments centred around an approximated spacer thickness (210 μm). A higher-resolution pass ($d = \pm 5\%$ in 1% increments) was then conducted around the coarse TV-minimum, and a peak-finding algorithm was used to extract the sample-thickness ($d = 206.9 \mu\text{m}$).

The temperature-stability of the cell when constructed with either PTFE or quartz spacer materials was investigated by

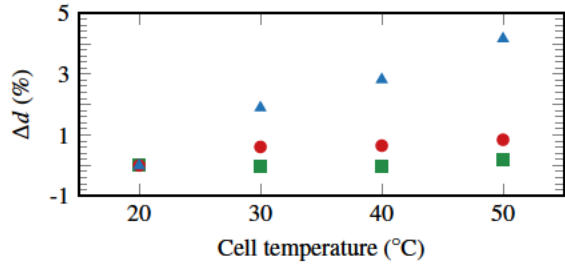


Fig. 2. The percentage increase in thickness of a 250- μm -thick PTFE spacer (▲), a 210- μm -thick quartz spacer (●), and a 360- μm -thick quartz spacer (■) as the cell was heated from 20 °C to 50 °C.

using the thickness-extraction method to determine the change in cavity length, Δd , as the temperature of a propan-2-ol sample was increased from 20 °C to 50 °C. As shown in Fig. 2, the thickness of the 250- μm -thick PTFE spacer increased by more than 4 % as the cell was heated (owing to its relatively large thermal expansion coefficient [6]), whereas both the 210 μm and 360- μm -thick quartz spacers changed by less than 1 % across the same temperature-range. As shown in Fig. 1, a 5 % thickness-error that is propagated through the system model, resulting in a substantial error in the extracted index. Therefore, Δd fluctuations were minimised with the use of quartz spacer materials for the following measurements.

Solutions of NaCl in deionised (DI)-H₂O were prepared with concentrations between 1.8 mol L⁻¹ and 5.1 mol L⁻¹, and the complex refractive index of the samples was measured as the temperature was increased from 20 °C to 30 °C. Fig. 3 shows the complex refractive index of the NaCl:DI-H₂O solutions when measured at 20 °C. As previously observed at microwave [7] and terahertz-frequencies [8], the real component of the refractive index was seen to increase with the addition of the salt, and little change in the extinction coefficient was observed beyond 0.5 THz. In contrast, as shown in Fig. 4, the imaginary component of the refractive index was found to be more strongly dependent on the sample-temperature than the real component.

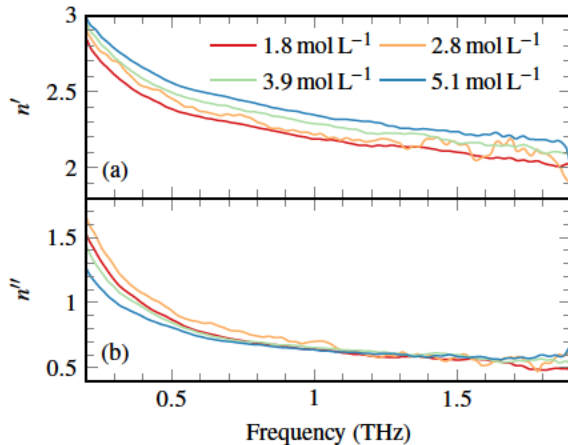


Fig. 3. The (a) real and (b) imaginary components of the refractive index of four NaCl:DI-H₂O solutions prepared with the concentrations given in the legend. All measurements made at 20 °C.

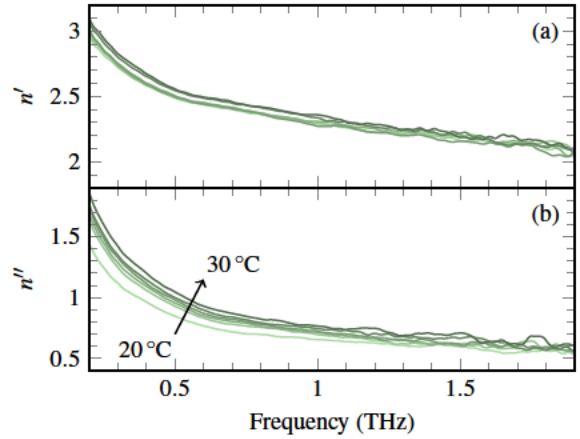


Fig. 4. The (a) real and (b) imaginary component of the refractive index of a 3.9 mol L⁻¹ NaCl:DI-H₂O solution measured as the sample temperature was increased from 20 °C to 30 °C.

III. CONCLUSIONS

We utilised a numerical method that enabled simultaneous extraction of the complex refractive index and thickness of a liquid sample contained between two windows. We then investigated the temperature-stability of a commercially available flowcell, and introduced the use of quartz spacer materials in order to prevent fluctuations in path-length as a function of temperature. NaCl:DI-H₂O solutions with concentration between 1.8 mol L⁻¹ and 5.1 mol L⁻¹ were measured as they were heated from 20 °C to 30 °C in 2 °C increments, and given the temperature-stability of the cell, we were able to accurately resolve small changes in the dielectric properties of the given samples.

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