

Absorption spectra of liquid water and aqueous buffers between 0.3 and 3.72 THz

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I. INTRODUCTION

Water exhibits strong frequency-dependent terahertz absorption with attenuation lengths on the order of tens of micrometers. To access this spectral information, previous experimental investigations have employed femtosecond time domain transmission¹ and reflection² spectroscopies, reflection dispersive Fourier transform spectroscopy,^{3,4} optically pumped far infrared (FIR) laser transmission spectroscopy,⁵⁻⁷ and FIR grating transmission measurements.⁸

Below ~ 1.5 THz, these studies provide a well-documented absorption spectrum for liquid water, at approximately room temperature. At higher frequencies the published data⁴⁻⁸ are comparatively sparse, and the agreement is less satisfying. In particular, there are wide discrepancies among the transmission measurements with optically pumped FIR lasers.⁵⁻⁷ Analysis by Vij⁵ suggests that multiple reflections between the sample cell windows (standing wave or etalon effect⁹) can contribute significantly to uncertainties in measured terahertz absorption coefficients and may account for the observed scatter.

Here we have eliminated the standing wave effect and measured the terahertz absorption of distilled de-ionized water over the frequency range of 0.3–3.72 THz (10 – 124 cm^{-1}) with improved accuracy. We have also measured the terahertz absorption spectra of aqueous potassium phosphate buffers at pH 3 and 8.

II. METHODS AND MATERIALS

A. Methods

We have developed a terahertz absorption spectrometer suitable for studying strongly absorbing liquids such as water. Our spectrometer combines kilowatt-power terahertz radiation from the UCSB free-electron lasers with an ultrasensitive cryogenic detector, and is able to withstand attenuation of more than five orders of magnitude. A reference pyroelectric detector is employed to monitor the fluctuations in incident laser power. A precision variable path-length cell,^{1,10} accurate to ~ 0.5 μm , allows for reproducible control of the sample thickness. The cell windows are made of high-

density polyethylene, which is highly transparent and has an index of refraction that closely matches that of liquid water over the frequency range of interest.¹¹

We precisely determined the absorption coefficients of water using linear fits of the change in absorbance, ΔA , with changing path length, Δl ,

$$\Delta A = \Delta \left(- \ln \left[\frac{I_t}{I_{\text{reference}}} \right] \right) = \alpha \cdot \Delta l,$$

where I_t is the transmitted intensity, and $I_{\text{reference}}$ removes fluctuations in the incident radiation. We carefully choose the shortest path length employed at each frequency to ensure at least three orders of magnitude of attenuation. This, together with the closely matched indices of refraction of cell window and liquid water, eliminates the standing wave artifacts that have apparently contributed to uncertainties in some of the previous measurements.⁵⁻⁷ This approach also obviates the need to precisely characterize the optical properties of the cell window, and the need for precise determination of the absolute path lengths.

B. Materials

Water samples were prepared at 22 °C using distilled de-ionized water, and distilled de-ionized water buffered at pH 3 and 8 with 50 mM potassium phosphate.

III. RESULTS AND DISCUSSION

We measured the change in the terahertz absorbance of water with changing path length (Fig. 1). At each wavelength, we examined nine distinct path lengths, with increments ranging between 2–20 μm depending on the attenuation strength of the sample, and repeated the absorbance measurements approximately eight times to estimate confidence limits.

The approach we have adopted here does not require the precise knowledge of either the absolute path length or the optical properties of the sample cell, both of which are difficult to access and can contribute to error in final absorption measurements. Instead we employ only two variables, ΔA and Δl , which are readily obtained with high precision with the detectors and translation stage we have chosen. Standing

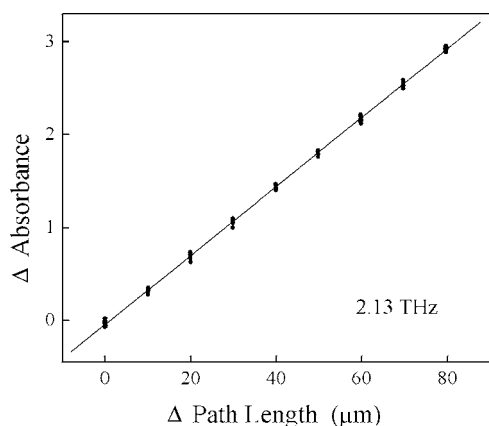


FIG. 1. The absorption coefficients of water are precisely determined from linear fits of the change in absorbance with changing path length. We repeat the absorbance measurements approximately eight times to estimate our confidence level. We need not consider the absolute path length, or the intrinsic optical properties of our cell window. Standing wave artifact is not present in our measurements, allowing for accurate determination of absorption coefficients.

wave artifacts that may have contributed to uncertainties in previous investigations^{5–7} are not observed in our measurements, allowing us to precisely determine the absorption coefficients from least-squares fits of the change in absorbance observed with changing in path length (Fig. 1).

We have precisely measured the absorption spectra of distilled de-ionized water, as well as aqueous 50 mM phosphate buffers at pH 3 and 8, over the frequency range of 0.3–3.72 THz. We do not observe any statistically significant differences in the absorption of de-ionized water and the two aqueous buffers (both $R^2 > 0.985$, and both slopes within 1.00 ± 0.07 for linear fits of pH 3 buffer, and pH 8 buffer, versus de-ionized water). This statistical agreement may

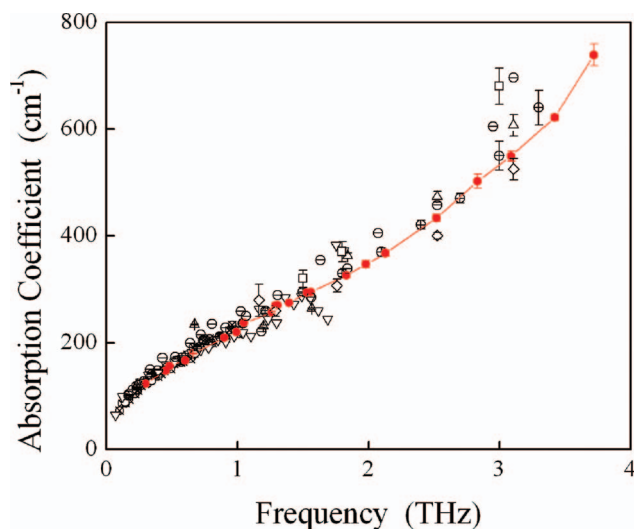


FIG. 2. (Color) Previously published water absorption spectra include measurements using femtosecond time domain transmission¹ (▽) and reflection² (⊗) spectroscopies, reflection dispersive Fourier transform spectroscopy^{3,4} (○ and ⊕, respectively), optically pumped FIR laser transmission spectroscopy^{5–7} (△, ◇, ⊖), and FIR grating spectroscopy⁸ (□). Our data are in excellent agreement with the published data below ~1.5 THz. Above this frequency, our measurements provide continuing and perhaps more accurate documentation for water absorption up to 3.72 THz.

TABLE I. The measured absorption coefficients of liquid water over 0.3–3.72 THz; errors are enclosed in parentheses.

Frequency (THz)	Absorption coefficients (cm ⁻¹)
0.30	123 (2)
0.45	148 (4)
0.48	156 (1)
0.60	167 (1)
0.66	180 (1)
0.90	210 (1)
0.99	220 (3)
1.05	237 (1)
1.26	256 (2)
1.29	269 (1)
1.31	271 (1)
1.40	275 (2)
1.53	294 (2)
1.56	295 (1)
1.83	326 (6)
1.98	347 (7)
2.13	367 (5)
2.52	433 (7)
2.84	502(13)
3.09	549(10)
3.42	622 (6)
3.72	739(21)

arise from the moderate ionic concentrations of the aqueous buffers (0.133M for pH 3 buffer, and 0.186M for pH 8 buffer). Nevertheless, our finding may prove to be a useful reference for solvent subtraction in future absorption study of buffered biomolecules in aqueous solutions.

Below ~1.5 THz our absorption data are in excellent agreement with previously published values.^{1–8} Above this frequency, however, we observe statistically significant discrepancies between our observations and those previously reported using optically pumped FIR laser transmission spectroscopy,^{5–7} and FIR grating measurements⁸ (Fig. 2). The discrepancies among the previous transmission measurements have been suggested to arise from the formation of standing waves between the sample cell windows.⁵ We have eliminated this potentially important artifact by maintaining a minimum path length that strongly attenuates the incident terahertz radiation (>1000 fold), and by closely matching the index of refraction of our cell windows with that of water. Thus, in addition to including several previously unexplored frequencies above 1.5 THz, our observations provide continuing and perhaps more accurate documentation for water absorption at higher terahertz frequencies up to 3.72 THz (Table I).

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