0.15–3.72 THz absorption of aqueous salts and saline solutions

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It has recently been suggested that near-field terahertz ionic contrast microscopy can be employed to image subtle changes in ionic concentrations arising from neuronal activity. To do so, however, requires that solvated ions exhibit significant absorbance at terahertz frequencies. The authors have investigated this issue and find that, at room temperature, the molar extinctions of both sodium chloride and guanidine hydrochloride are approximately two orders of magnitude below some previous measurements and are, therefore, too low to support the proposed imaging application.


Recent advances in terahertz sources and detection methods have stimulated experimental researchers to employ absorption spectroscopy to directly probe the collective dynamics in both biomolecules and inorganic materials ranging from water to explosives. Unlike near infrared spectroscopy, which measures the local vibrations of individual bonds, or visible/ultraviolet spectroscopy, which monitors electronic transitions, terahertz resonances are sensitive to the global distributions of charge, mass, and force in a molecule or molecular assembly. For this reason terahertz spectroscopy has the potential to provide unique and distinguishing spectral “fingerprints” and may provide a noninvasive technology for applications in areas such as defense, security, biology, and medicine (reviewed in Refs. 26 and 27).

A novel biological application of terahertz absorption, ionic contrast terahertz near-field microscopy, has recently been proposed as an in situ imaging technique. This imaging modality would depend on the extent to which ionic solutes modulate the terahertz absorption of water solutions and is suggested to provide a real time image of functionally relevant variations of ion concentrations in biological samples. Using this approach, Masson et al. have reportedly observed physiologically relevant changes in the intra- and extracellular concentrations of potassium and sodium chloride in and around living neurons. They reported that the terahertz absorption of a solution is highly sensitive to its salt content, and that concentration variation as small as 10 mM can be readily measured using incident radiation between 0.1 and 2 THz.

Achieving a reasonable signal via ionic contrast terahertz near-field microscopy requires that the salt solutes significantly alter the dielectric properties of water. Consistent with this assessment, Masson et al. reported that the intensity molar extinction of sodium chloride (NaCl) in solution is ~1 mM−1 cm−1 at 0.5 THz (the reported amplitude absorption is scaled here by a factor of 2 to obtain intensity absorption), which increases the observed extinction from 150 cm−1 for distilled, de-ionized water to ~250 cm−1 for physiological NaCl concentrations (~100 mM). Previously, however, we have found that the terahertz absorption of dilute (~50 mM) potassium dihydrogen phosphate buffers (50 mM KH2PO4 solution titrated with either KOH or H3PO4 to obtain the desired pH) is experimentally indistinguishable from the spectrum of pure distilled, de-ionized water over the frequency range of 0.3–3.72 THz (experiments performed at 22 °C). We infer from these measurements that the molar extinction for aqueous KH2PO4 is at least two orders of magnitude below those reported by Masson et al. for aqueous NaCl or KCl. In support of our observations, both existing double Debye model and 0.035–0.09 THz measurements of the complex dielectric constants for sea water (~600 mM NaCl solution) indicate that there is no appreciable difference in absorption strength between dilute salt solutions and pure water below ~0.09 THz. In this letter we measure the terahertz absorption of concentrated solutions of both NaCl (5 M) and guanidinium chloride (GuHCl, 6 M) in order to explore this issue in more detail.

Employing the radiation output from an ErAs:GaAs photoconductive mixer, we have carefully measured the extinctions of concentrated NaCl solution (5 M) and dilute KH2PO4 buffer (50 mM, pH of 3) between 0.15 and 0.69 THz at 21 °C (Figs. 1 and 2). Consistent with our previous report, we find that the terahertz extinction of dilute KH2PO4 buffer is statistically indistinguishable from that of...
de-ionized water from previous reports.\textsuperscript{15–18} The terahertz extinctions of both dilute KH\textsubscript{2}PO\textsubscript{4} buffer (this study) and de-ionized water\textsuperscript{15–18} are well fitted by two existing double Debye models\textsuperscript{29,32} (Fig. 1). The Debye relaxation frequencies \( \nu_1 \) and \( \nu_2 \) are 17.4 and 217.9 GHz and the dielectric constants \( \varepsilon_0 \), \( \varepsilon_1 \), and \( \varepsilon_\infty \) are 78.3, 5.64, and 4.25, respectively.\textsuperscript{32} For comparison, for “single Debye” model (Fig. 1) the Debye relaxation frequency is 17.5 GHz and the dielectric constants \( \varepsilon_0 \) and \( \varepsilon_\infty \) are 79.7 and 5.26, respectively.\textsuperscript{32}

Because the spectrum of KH\textsubscript{2}PO\textsubscript{4} buffer is statistically indistinguishable from that of de-ionized water, we assume here that the absorption spectrum of the buffer is a good representative of the spectrum of water and compare our measurements of concentrated NaCl solution against it (Fig. 2). We find that below approximately 0.4 THz the absorbances of this dilute solution and 5 M NaCl are also indistinguishable. Above \( \sim 0.4 \) THz, the absorption strength of concentrated sodium chloride becomes somewhat greater than that of water and dilute buffer, indicating that the NaCl solute begins to contribute to the solution extinction more than the water it displaces in the solution. This effect, however, is very small and does not support the molar extinctions described by Masson \textit{et al.}, who reported an \( \sim 66\% \) increase in the solution absorption of 100 mM sodium chloride relative to that of de-ionized water at 0.5 THz.\textsuperscript{28}

In order to remove the dominating solvent base line and obtain the absorption spectrum of the dissolved salt we assume that the solution extinction is the weighted sum of solvent and solute absorptions by their respective molar concentrations (for detailed discussions see Ref. 20),

\[
\alpha_{\text{solution}} = \sigma_{\text{solute}}[\text{solute}] + \sigma_{\text{solvent}}[\text{solvent}],
\]

where \( \alpha_{\text{solution}} \) is the measured solution extinction, \([\text{solute}]\) and \([\text{solvent}]\) are the molarities, and \( \sigma_{\text{solute}} \) and \( \sigma_{\text{solvent}} \) the molar extinctions of the salt solute and water, respectively. We scale the water extinction spectrum by solvent concentration in the NaCl solution to obtain the solvent base line \( \sigma_{\text{solvent}}[\text{solvent}] \). Subtracting this from the total solution extinction allows us to measure the NaCl solute contribution to solution absorption and thereby determine its molar extinction (Fig. 3). We find that the thus determined terahertz absorption of aqueous NaCl is approximately two orders of magnitude below that reported by Masson \textit{et al.}\textsuperscript{28}
We have also extended our study to include a dramatically different salt guanidine hydrochloride (GuHCl, 6 M) by similarly extracting the molar extinctions of this salt in solution between 0.15 and 3.42 THz (Fig. 3). Measurements between 0.15 and 0.69 THz (at 21 °C) employed the ErAs:GaAs photomixer as radiation source, and between 0.6 and 3.42 THz (at 22 °C) the UCSB free-electron lasers. Despite very significant structural and molecular differences between NaCl and GuHCl, we observe no significant differences between their terahertz molar absorbance. The monotonic increase in terahertz absorption observed for both salts between 0.15 and 0.75 THz continues up to the highest examined frequency (3.42 THz) for GuHCl.

In conclusion, the molar extinctions of both NaCl and GuHCl in the terahertz spectral region, extracted using high concentration solutions (5 M and 6 M, respectively) at 21 °C, are approximately two orders of magnitude lower than those of aqueous salts (NaCl, KCl, and CaCl₂) reported recently by Masson et al.²⁸ (Fig. 3). Our findings suggest that the physiological concentration of a salt (~100 mM) will not significantly increase the terahertz (0.15–3.42 THz) absorption of the solution above that of pure water. This is consistent with both the modern double Debye model²⁹ and microwave measurements³⁰ of the complex dielectric constants for sea water (~600 mM NaCl solution) below 0.09 THz.

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