Hydration dynamics in Deoxyribonucleic acid using an extended MHz-THz spectroscopy

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Abstract—**Dynamics of water molecules within hydration shells of deoxyribonucleic acid were studied by employing a high precision and an extended megahertz to terahertz frequency-domain spectroscopy. Three additional relaxation times longer that bulk water relaxation time of 8.27 ps were observed by analyzing dielectric spectrum using the Debye model. Total 64 ± 8 water molecules per base pair were observed to be influenced kinetically by the presence of DNA in the aqueous solution.**

I. INTRODUCTION

Aqueous solution of a bio-molecule is a complex system composed of several relaxation processes from sub-microseconds to picoseconds of timescales. The development of megahertz to terahertz spectroscopy in the recent decades has made it possible to observe the hydration dynamics of bio-molecules in the solution, such as protein and DNA. A number of studies probed the slow dynamics as well as ultra-fast dynamics of bio-molecules and their aqueous solutions. However, studies in the crucial frequency region from 1 GHz to 1 THz are scarce. In this study, using a frequency-domain based megahertz to terahertz (MHz - THz) spectroscopy, we could precisely determine the dynamics of water molecules within the hydration shells of DNA.

II. METHODS

A frequency-domain dielectric setup covering a broad spectral range of electromagnetic spectrum from 100 MHz to 1.12 THz has been used. Simultaneous measurements of refractive index and absorbance have been performed for 60 GHz - 1.12 THz band. The spectrometer consists of a commercial vector network analyzer (VNA) from Agilent, N5225A PNA, that covers a frequency range from 10 MHz to 50 GHz. Frequency extenders from Virginia Diodes, Inc. (Charlottesville, VA), were used to produce terahertz waves. Seven rectangular waveguides (WR) modules have been used to cover a frequency range of 60 GHz – 1.12 THz [1]–[6].

III. RESULTS

The absorption coefficients and refractive indices of water and an aqueous DNA solution ($13.04\,\mu$M) are shown in Fig. 1. Having information of refractive index and absorption coefficients, the dielectric dispersion and loss can be estimated (Fig. 2). The dielectric response of aqueous DNA solution consists of contributions from the bulk water, hydration water, hydrated DNA and counter ions. The total complex dielectric function can be represented as,

$$\epsilon_{sol}^*(\nu) = [n^2(\nu) - (c\alpha(\nu)/4\pi\nu)^2] + \iota[2n(\nu).c\alpha(\nu)/4\pi\nu + \sigma/2\pi\nu\epsilon]$$

(1)

where ϵ and σ are the permittivity of free space and electrical conductivity of the solution, respectively.
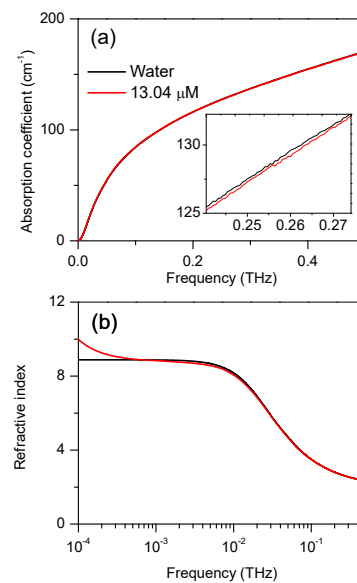

Fig. 1. (a) Absorption coefficients and (b) refractive indices for water and 13.04 μM aqueous DNA solution is shown, at 25 °C, for the frequency region of 100 MHz - 0.5 THz.

Addition of DNA macro-molecules in an aqueous solution decreases the aggregate absorption of the DNA solution with respect to bulk water. As a consequence, the dielectric loss corresponding to peak around 19 GHz is suppressed (Fig 2b). This behavior can be attributed to two factors: (a) DNA induced dilution. As bio-molecules, including DNA, show low absorption at terahertz frequencies [7], addition of DNA into water decreases the aggregate absorption of the aqueous solution with respect to bulk water. (b) A significant fraction of water molecules get kinetically retarded as compared to bulk

water due to DNA-water interaction. These water molecules are no longer relaxing via the bulk water orientational relaxation mode with the timescales of 8.27 ps, resulting in a decrease of the main loss peak at 19 GHz.
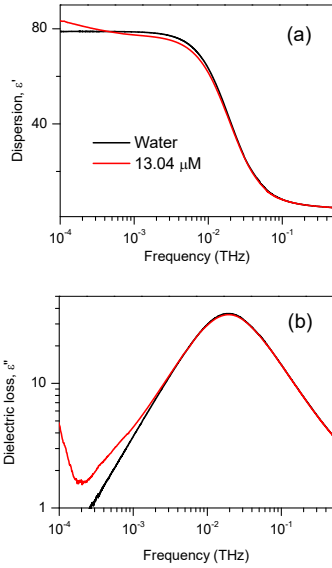

Fig. 2. (a) Dielectric dispersion and (b) loss for water and 13.04 μM DNA solution is shown at 25°C, for 100 MHz - 0.5 THz frequency region.

The spectral features of DNA hydration shells were heterogeneous over a few hydration layers around DNA surface. The low frequency MHz - GHz spectra were analyzed using the four-Debye model [1]–[6] in the form,

$$\epsilon^*_{sol}(\nu) - \epsilon_\infty = \frac{\epsilon_s - \epsilon_1}{1 + \iota 2\pi\nu\tau_1} + \frac{\epsilon_1 - \epsilon_2}{1 + \iota 2\pi\nu\tau_2} + \frac{\epsilon_2 - \epsilon_3}{1 + \iota 2\pi\nu\tau_3} + \frac{\epsilon_3 - \epsilon_4}{1 + \iota 2\pi\nu\tau_3}$$

(2)

where numerators of each term on the right hand side are dielectric strengths and τ's are the relaxation times. Three longer relaxation times $\sim$ 1 ns, $\sim$350 and $\sim$40 ps for the hydration water molecules were observed. Having an estimation of water molecules not participating in bulk water dynamics, we can extract total number of water molecules per solute macro-molecule, which are retarded in the relaxation time, referred typically as "hydration number", can be estimated. The number of water molecules in the hydration shell per base pair of DNA is given as [2]–[5],

$$N_{hyd}(c) = \frac{c_W - \frac{\Delta\epsilon_W}{\Delta\epsilon_{pure}} c_{pure}}{nc}$$

(3)

where c_W is the molar concentration of water in the aqueous solution, c_{pure} = 55.35 M is molarity and $\Delta\epsilon_{pure}$ = 73.25 is the dielectric strength of pure water at 25 °C, and n is number of base pairs. Using the above formula, the number

of water molecules kinetically influenced by the presence of DNA molecule was estimated, as $N_{hyd} = 64\pm8$ per base pair.

IV. CONCLUSION

In this work, using the extended megahertz to terahertz spectrometer, we have been able to adequately describe spectral features of DNA hydration dynamics. A total of 64 ± 8 water molecules per base pair was affected kinetically by the presence of DNA. The water molecules around DNA could be categorized by three longer relaxation times in addition to the bulk water relaxation time of 8.27 ps.

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