Terahertz spectroscopy for water dynamics and hydration effect

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1. Introduction

Water is the most basic solvent on the earth for soft materials including biomolecules. The physical properties of water molecules near the soft material in meso-scale have been attracting attention, since its hydration state strongly relate with the self-assemble mechanism of soft materials to various characteristic structures. Thus, the hydration states of soft materials have been studied for long with using NMR or neutron scattering from the viewpoint of the dynamics of a water molecule. However, these methods have observed only the strongly bound water molecules at the solute surfaces due to its observable time-scale (relaxation time $\tau \sim 10^{-9}$-10^{-11} s) of water dynamics, despite the rotational dynamics of pure water molecule lie in the ultrafast time scale ($\tau \sim 10^{-12}$-10^{-13} s). To know the hydration state of soft materials in detail including slightly perturbed water molecules, it is necessary to detect the delicate change of the water dynamics in the ultrafast time-scale. Therefore THz sensing and microscopy is a promising technique to identify hydration effect in soft materials and biological function of living tissues. Remarkable developments of femtosecond light sources have been promoting terahertz time-domain spectroscopy (THz-TDS), facilitating precise measurements of dielectric constants in the THz frequency region. In THz-TDS, temporal profiles of the electric field are detected with the optical sampling technique. This enables us to determine optical constants of the sample directly without Kramers-Kronig relations.

2. Terahertz attenuated total reflection (ATR) technique

We proposed a novel THz-TDS with attenuated total reflection (ATR) technique [1], which can access samples with various shapes and optical properties. In general, ATR technique provides information on the sample through the interaction between the sample and the evanescent wave that is generated by the internal total reflection on the prism surface. We applied THz-ATR technique to study surface plasmon mode [2], surface phonon mode [3], and dynamics of liquid water [4, 5]. Especially for liquid water, penetration depth of the THz wave is about 10 μm and is almost the same order as the extinction length of the evanescent wave. Therefore we can see dynamics of bulk water using THz-ATR.

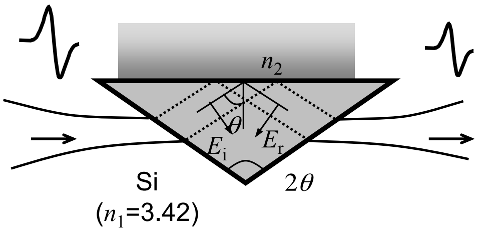

Fig. 1. The scheme of TD-ATR geometry using Dove prism

3. Terahertz spectroscopy of water

Figure 2 shows dielectric constants of liquid water obtained by THz-ATR method. Previous data by other groups are depicted in the same figure [6, 7, 8]. Dispersion of water in THz frequency region has extensively investigated and overall dielectric constant in the terahertz frequency region can be decomposed into three components as described in the following equation,

$$\tilde{\varepsilon}(\nu) = \frac{\Delta\varepsilon_1}{1+i(2\pi\nu\tau_1)} + \frac{\Delta\varepsilon_2}{1+i(2\pi\nu\tau_2)} + \frac{A_S}{\nu_S^2 - \nu^2 + i\nu(\gamma_S/2\pi)} + \varepsilon_\infty . \qquad (1)$$

The first and the second terms are the slow relaxation and the fast relaxation components with the relaxation strengths $\Delta\varepsilon_{1(2)}$, and the relaxation times $\tau_{1(2)}$, respectively. The slow relaxation mode is due to the structural relaxation of the hydrogen-bonding network [9], showing strong temperature dependence. However, the fast relaxation mode is originated from the collision process between the free water molecules without hydrogen bonding network and shows tiny temperature dependence [4]. The third terms are the intermolecular stretching vibration (V_S) with the amplitudes A_s, the frequencies ν_s, and the damping constants γ_s, respectively. Here we neglected the contribution of the libration mode (V_L). The intermolecular stretching vibration at 5 THz is well known as the experimental evidence for the hydrogen-bonding network with tetrahedral water structure in water [10]. This intermolecular stretching vibration mode has been extensively investigated by Raman spectroscopy for understanding disordering of water structure. This component shows strong isotope dependence [5]. The oscillator strength of the THz peak decreases when we make the isotopic substitution to heavy water (D_2O), whereas that of the Raman peak increases instead [11]. This behavior suggests that the hydrogen-bonding network is more solid in heavy water [5].

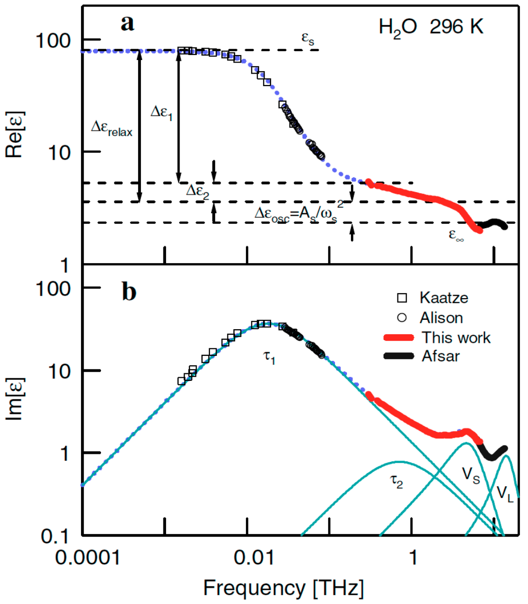

Fig. 2. (a) Real and (b) imaginary parts of the complex dielectric constant of liquid H_2O at 296 K [5]. In addition to our results (red lines), the results of microwave spectroscopy (open rectangles [6] and open circles [7]) and far-infrared spectroscopy (black lines [8]) are also depicted in the figure.

4. Hydration effect

We applied THz-ATR technique to analyze the hydration effect in solutions of bio-related molecules, such as sucrose [12, 13]. We successfully know how many water molecules are connected to the solute. We also applied THz-ATR technique for multi-lamellar vesicles of phospholipid (main constituent of biomembrane) and investigated the dynamical state of water between the lipid membranes (water layer thickness ~2.5 nm) [14]. The hydration state of lipid membrane has been believed to relate with biochemical reactions on the biomembrane and with the self-assembly of the membrane. THz-ATR results clearly show that the hydration number of fully hydrated lipid membrane is about 28 water molecules per a lipid. This indicates that the layer of hydration water at a lipid membrane is much larger than that expected in earlier studies and it reaches up to 1 nm from the surface, if we evaluate the hydration water including slightly perturbed water. In the result, most water molecules between membranes (over 75%) are regarded as the hydration water. This long-range hydration effect means that the water molecules at a phospholipid membrane surface have much different physical properties than bulk water in a large extent, and we need to reconsider the phenomenon took place through water layer at the lipid membrane in meso-scale, such as hydration repulsion between bilayers.

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