



Evaluation of the hydration state of saccharides using terahertz time-domain attenuated total reflection spectroscopy

Keiichiro Shiraga^{a,*}, Yuichi Ogawa^a, Naoshi Kondo^a, Akiyoshi Irisawa^b, Motoki Imamura^b

^a Bio-Sensing Engineering Laboratory, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

^b ADVANTEST Corporation, Aoba-ku, Sendai-shi, Miyagi 989-3124, Japan

ARTICLE INFO

Article history:

Received 3 October 2012
Received in revised form 22 January 2013
Accepted 18 February 2013
Available online 27 February 2013

Keywords:

Hydration
Saccharides
Complex refractive index
Dielectric loss
Terahertz time-domain attenuated total reflection spectroscopy (THz TD-ATR)

ABSTRACT

Despite intensive studies regarding the hydration state, experimental investigations have not fully explained the global hydration state. Terahertz (THz) spectroscopy is an emerging technology that has the potential to evaluate global hydration. This is because THz waves are very sensitive to picosecond water dynamics and, as such, effectively measures the state of water that is weakly bound to solute molecules by observing slowed down water dynamics. THz time-domain attenuated total reflection (THz TD-ATR) spectroscopy allowed to determine the complex refractive index of saccharide solutions and to experimentally characterize the global hydration state. Our result indicates the global hydration state is closely related to the number of hydrophilic groups and steric configuration of hydroxyl groups in saccharide molecules. This new tool to investigate the global hydration state will provide new knowledge about water dynamics around solutes that couldn't have been elucidated with the conventional techniques.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The hydration state of saccharides in aqueous solution is a subject of keen interest, with both practical and scientific importance, for it is involved in the reception of sweetness and environmental stress tolerance (Birch & Shamil, 1986; Magazù, Migliardo, & Telling, 2008; Starzak & Mathlouthi, 2006). Thus, various details of the hydration states of saccharides have been investigated. For instance, the hydration number of various saccharide molecules has been experimentally estimated using calorimetric, viscosity and ultrasound techniques (Branca et al., 2001; Furuki, 2002; Galema & Høiland, 1991). X-ray scattering and neutron scattering have given structural information about water molecules strongly bonded to the solute. On the other hand, nuclear magnetic resonance (NMR) and dielectric spectroscopy in the microwave region (Heugen et al., 2006; Nandi, Bhattacharyya, & Bagchi, 2000) have shed light on hydration dynamics (i.e. rotational relaxation of hydration water). Such dynamics are evaluated based mainly on relaxation times, which represent the temporal aspects of molecular mobility and rotational performance. These conventional techniques measure the dynamics of water directly bound to the solute, which have nanosecond relaxation times.

Fig. 1 illustrates a simplified hydration model toward a biomolecule, such as saccharides, nucleic acids and proteins (Otting,

Liepinsh, & Wuthrich, 1991; Tanaka, Arikawa, Yada, & Nagai, 2007). Layer A is a water monolayer directly bound to the hydrophilic portion of the solute by hydrogen bonding. The water molecules in this layer have much slower relaxation times, as slow as hundreds of nanoseconds (10^{-7} s), than bulk water (i.e. water that has no bonds with a solute). Water molecules in layer B are water weakly perturbed by the dipole of hydration water in layer A. NMR and microwave spectroscopy studies have in fact shown that water molecules, in the hydration sphere around the solute, have slower relaxation times in the order of 10^{-9} – 10^{-10} s. Water in layer C represents bulk water, which isn't influenced by the solute molecules and has the same physical properties as pure water.

For such bulk water the dynamics, the hydrogen-bonding network between bulk water molecules, where the hydrogen bonds are being formed and broken, are occurring on a time scale of picoseconds (Nagai, Yada, Arikawa, & Tanaka, 2006). The importance of understanding such picosecond dynamics of water has recently been pointed out, as they strongly influence the activity of enzymes (Pal, Peon, & Zewail, 2002). Thus, it is necessary to consider the dynamics of those water molecules in the hydration network that are located further away from the solute, but are still weakly bonded to the biomolecule. At present, molecular dynamics (MD) simulations are the main means of exploring the picosecond dynamics of such water molecules, as no effective methods have been available that can measure these dynamics at this time scale.

Recently, a novel technology that can measure picosecond water dynamics, terahertz (THz) technology, has become available

* Corresponding author. Tel./fax: +81 75 753 6171.

E-mail address: k.shiraga@ky2.ecs.kyoto-u.ac.jp (K. Shiraga).

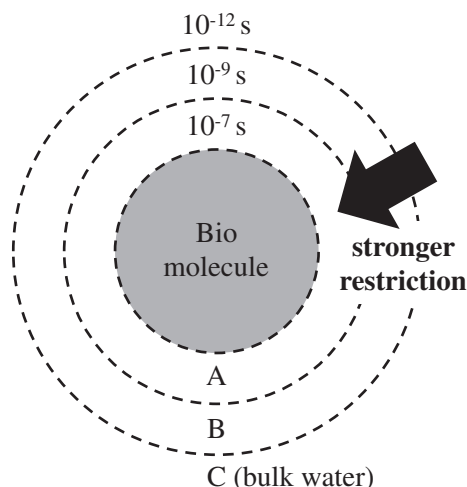


Fig. 1. Hydration model for biomolecule. Layer A and B represent hydration water restricted by the solute molecule. Phase C is bulk water in the hydrogen bonding network, which has picosecond order dynamics.

and is attracting considerable attention (Arikawa, Nagai, & Tanaka, 2008; Yada, Nagai, & Tanaka, 2008). THz waves are defined as those between 0.1–10 THz, whose periodic oscillating electric field is of the order of picoseconds. This makes THz waves ideal for investigating picosecond dynamics among bulk water molecules with high sensitivity. The global hydration state of aqueous solutions has been investigated based on the polarization and absorption in the THz region (Arikawa et al., 2008; Heugen et al., 2006). Furthermore, this technique of THz spectroscopy has been applied to studies of hydration states and the structure of phospholipid bilayer and surfactants (Arikawa, Nagai, & Tanaka, 2009; Hishida & Tanaka, 2011).

In this study, we determined the complex refractive index of various saccharides in solutions in order to precisely evaluate dynamics in the global hydration state. The hydration number was calculated using absorption in the THz region, since THz waves have much stronger absorption in bulk water with picosecond dynamics than water molecules in the global hydration state that have dynamics in the order of nanoseconds or sub-nanoseconds. In order to reduce the influence of the strong absorption of bulk water, THz time-domain attenuated total reflection (THz TD-ATR) spectroscopy was applied to obtain the complex refractive index of the saccharide solutions.

2. Experimental principle

With the advent of THz time-domain spectroscopy (THz-TDS), the application of THz spectroscopy has been rapidly accelerated. In this system, by using pulsed THz waves, with and without the sample in time domain, both time delay and amplitude decrease can be simultaneously measured. From this result complex refractive index $\tilde{n}(\omega)$ can be calculated (Smye, Chamberlain, Fitzgerlad, & Berry, 2001),

$$\tilde{n}(\omega) = n(\omega) - ik(\omega) \quad (1)$$

where, $n(\omega)$ and $\kappa(\omega)$ denote refractive index and extinction coefficient, respectively. In particular, refractive index indicates the slowness in propagating of the electromagnetic wave in the sample, while the extinction coefficient is a measure of the energy absorbed by the sample. This complex refractive index is a response of the electromagnetic wave to the sample, and thus it is influenced by hydration state, temperature, binding and conformational changes of the sample (Markelz, 2008). Complex refractive

index can be measured using THz-TDS with transmission geometry, when the sample has no strong absorption in the THz region. However, it is quite difficult to apply transmission measurements to aqueous solutions. This is because water absorbs 10^5 times stronger in the THz region than in the visible region (Møller, Cooke, Tanaka, & Jepsen, 2009).

In order to get around this problem, THz-TDS was combined with an attenuated total reflection (ATR) technique (Hirori, Yamashita, Nagai, & Tanaka, 2004), hereafter referred to as THz TD-ATR spectroscopy. In this geometry, the incident THz pulse is totally reflected off the bottom of an ATR prism, and an evanescent field is created in the sample close to the sample-prism interface. As a consequence, there is an interaction with the sample, and the time delay ($\Delta\phi$) and amplitude decrease (ΔA) can be precisely measured (see Fig. 2). Fourier transformed spectra of both phase spectrum $\Phi(\omega)$ and reflectance $R(\omega)$ in the frequency domain can be experimentally determined by Eqs. (2) and (3).

$$R(\omega) = \left| \frac{\tilde{r}_{12}(\omega)}{r_{\text{REF}}(\omega)} \right|^2 \quad (2)$$

$$\Phi(\omega) = \text{Arg} \left[\frac{\tilde{r}_{12}(\omega)}{r_{\text{REF}}(\omega)} \right] \quad (3)$$

where, $\tilde{r}_{12}(\omega)$ and $r_{\text{REF}}(\omega)$ are the Fresnel's reflection coefficient of the prism-sample interface and of prism-air, respectively. Additionally, the theoretical Fresnel's reflection coefficient of the prism-sample interface is expressed as a function of the incident angle θ , and the (complex) refractive index of the ATR prism $n_1(\omega)$ and sample $\tilde{n}_2(\omega)$.

$$\tilde{r}_{12}(\omega) = \frac{n_1(\omega) \sqrt{1 - \left(\frac{n_1(\omega)}{\tilde{n}_2(\omega)}\right)^2 \sin^2 \theta} - \tilde{n}_2(\omega) \cos \theta}{n_1(\omega) \sqrt{1 - \left(\frac{n_1(\omega)}{\tilde{n}_2(\omega)}\right)^2 \sin^2 \theta} + \tilde{n}_2(\omega) \cos \theta} \quad (4)$$

The solution of the simultaneous Eqs. (2)–(4) gives the complex refractive index of the sample, if the other parameters are given. The process above ensures the complex refractive index of the sample is an optical constant, which is independent of instrumental functions such as the THz intensity and the penetration depth of the evanescent field (Hirori et al., 2004). In THz TD-ATR

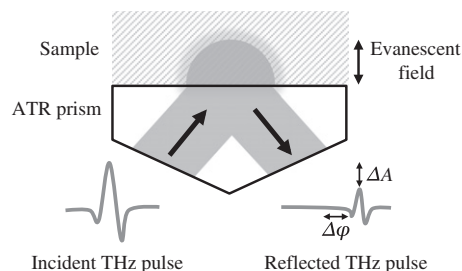


Fig. 2. Schematic illustration of THz TD-ATR spectroscopy. From the time delay ($\Delta\phi$) and amplitude change (ΔA), the refractive index and extinction coefficient of the sample can be determined.

Table 1

Sample solutions of monosaccharides and disaccharides with mol concentrations [M]. Mass percent [wt.%] converted is shown in the bracket.

Monosaccharides: $C_6H_{12}O_6$		
D(+)-Glucose	0.292–0.877 M	(4.83–22.16 wt.%)
D(+)-Galactose	0.292–0.877 M	(4.83–22.16 wt.%)
D(+)-Mannose	0.292–0.877 M	(4.83–22.16 wt.%)
Disaccharides: $C_{12}H_{22}O_{11}$		
Sucrose	0.292–1.754 M	(9.58–49.26 wt.%)
Maltose	0.292–0.877 M	(9.58–27.15 wt.%)

Download English Version:

<https://daneshyari.com/en/article/1184911>

Download Persian Version:

<https://daneshyari.com/article/1184911>

[Daneshyari.com](https://daneshyari.com)