

*Research Article*

## **Terahertz time domain spectroscopy studies in liquids and solutions**

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### **Abstract**

Understanding solvent motion and solvent–solute interaction in solution is a central issue to elucidate solvent effects on chemical reactions and various relaxation processes in liquids and solutions. The intermolecular interaction often shows its characteristic frequencies in the region below  $100\text{ cm}^{-1}$ . In this low-frequency region various motions such as librational motion, intermolecular vibration, collective motions of associated liquids and reorientational relaxation have specific spectral components. Terahertz time-domain spectroscopy (THz-TDS) has been proven to be a powerful technique for studying these spectral components in low frequency regions. Different theoretical and analytical models may be used to get an insight of the experimental THz-TDS data.

**Key Words:** Liquids, Solutions, Dynamics, Low Frequency, Terahertz time-domain spectroscopy

### **Introduction**

The THz regime is sandwiched between the microwaves and the infrared, bridging the gap between electronics and optics. For a long time, the THz regime was also referred to as the “THz gap” as neither optical nor microwave devices could fully conquer this shadowy domain with its many hidden scientific treasures.<sup>1, 2</sup> Little commercial emphasis was placed on the development of THz systems as the available sources, such as synchrotrons, backward wave oscillators, Smith-Purcell emitters or free electron lasers, were very costly components.

But in the past two decades dramatic progress has been made in the generation and detection techniques of freely propagating THz radiation based on femtosecond pulsed laser which is cheaper compared to the previously mentioned instruments.<sup>1</sup> Because the pulse

duration of the THz radiation is in a sub-picosecond time region, it is possible to measure the electric field of the radiation by coherent detection methods, which consequently allows to conduct THz-TDS. The refractive index and extinction coefficient of a medium can be easily obtained by measuring the phase and amplitude of the THz radiation. This technique is a type of transmission spectroscopy and is suitable for studying the properties of the liquids and also the characteristics of solute molecules in solutions since the contribution of the solvent can be subtracted from the spectrum of the solution.<sup>2</sup> Thus, THz-TDS is an attractive method for the detection of low frequency spectra and also for studying dynamics with time scales of sub-picoseconds and picoseconds of various kinds of material, such as liquids and mixtures of liquids,<sup>3,4</sup> solutions of organic solvents,<sup>2,5-8</sup> biological molecules,<sup>9-11</sup> and ionic liquids and their mixtures with other solvents<sup>12-13</sup>.

There has been considerable interest in both the experimental and theoretical investigation of the low-frequency motion associated with molecules and molecular aggregates in condensed phases. Vibrational motions with resonance frequencies in the terahertz (THz; 1 THz =  $10^{12}$  Hz) frequency range are characterized by weaker potential forces and/or larger reduced masses, which are in sharp contrast to vibrations localized within a molecule with resonance frequencies in the mid infrared (IR) region.<sup>14-15</sup> In this article the special emphasis will be given to discuss the studies of condensed phases such as solutions and liquids namely water and methanol by THz-TDS technique.

## Discussion

### (a) Liquids:

Hydrogen bonding liquids such as water and methanol form characteristic network structures, which dynamically fluctuate by making and breaking hydrogen bonds. The structural fluctuation of the network has a great influence on chemical reactions and relaxation processes.<sup>1,16</sup>

Water shows a tremendous absorption in the low frequency domain. Water can form a three-dimensional network structure. Low frequency spectra of water show two distinct regions in the low frequency region, one around  $60\text{ cm}^{-1}$  and other around  $170\text{ cm}^{-1}$ .<sup>16</sup> The lower region may be attributed to the frustrated translations due to the local structure around a given molecule that produces the so-called cage effect. The librational motion of the molecules in a cage may affect this kind of band. On the contrary, the frequency band around  $170\text{ cm}^{-1}$  is absent in the spectral densities of non-associated liquids, which is consistent with the attribution of this band to the stretching of hydrogen-bonded molecules.<sup>16</sup> Thus for the liquid water, the low frequency band should not be associated with the existence of hydrogen bonding. The experimental

observations have been supported by different theoretical interpretations reported earlier also.<sup>17-18</sup> The low-frequency dynamics of water is also characterized by a distribution of the time scale of dynamics. Actually in water there are different kinds of hydrogen bonding networks with different sizes and conformation. Each network has its own characteristic time scale of dynamics.<sup>1</sup>

Methanol is the simplest alcohol, and its hydrogen bond dynamics have been investigated by femtosecond laser spectroscopy such as time-dependent fluorescence Stokes shift and OKE spectroscopy. It has been observed that the deuterations on the hydroxyl and methyl groups have an influence on the solvation dynamics<sup>19</sup> and the OKE response of methanol.<sup>20</sup> The deuteration affects the hydrogen bond bending motion and libration, which have characteristic frequencies in the THz range between 10 and 100  $\text{cm}^{-1}$ . In recent years, dielectric properties of liquids have been investigated in this frequency range by THz-TDS. The low-frequency spectra of normal and deuterated methanols ( $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$ ) by THz-TDS to get an insight into the dynamics of the hydrogen bond network of methanol.<sup>4</sup> The spectra of the four methanols show two components around 20  $\text{cm}^{-1}$  and 60  $\text{cm}^{-1}$  which were assigned to an overdamped mode and an underdamped oscillation, respectively. Around 20  $\text{cm}^{-1}$  the absorption intensities of all the methanols are nearly the same, while around 60  $\text{cm}^{-1}$  the absorption intensity of  $\text{CH}_3\text{OH}$  is a little greater than those of deuterated methanols. This observation is due to the isotope effect on the change of the dipole moment along the coordinate of the normal mode. The hydrogen bonding networks of the shorter chain alcohol may be well developed compared to those of the longer chain alcohol. THz-TDS investigations also show that the shorter and longer alcohols roughly correspond to the biopolymers and amino acids, respectively.

#### **(b) Solutions:**

Dielectric relaxation of solvents in solution in the MHz and GHz regions are often dominated by the orientational motion of the molecules, which can be described by several theoretical models, including the Debye theory.<sup>3</sup> The Debye relaxation time characterizes the time scale of the orientational motion, which depends on the bulk viscosity of the system, which is in turn described by the Stokes-Einstein-Debye (SED) equation. The dynamics of the interaction in the solution are often characterized by time scales ranging between sub-picoseconds to tens of picoseconds, which correspond to the THz and GHz spectral ranges in the frequency domain, respectively. The high frequency (THz > GHz) response might be due to intermolecular vibration, librational motion, structural fluctuation of the hydrogen bonding network, as well as intramolecular large-amplitude motion. The high frequency dielectric response is especially important for understanding the ultrafast component in the solvation dynamics.<sup>1</sup> It has often been observed that the initial response of the solvation dynamics takes place in less than 100 fs, which

is due to the inertial motion of the solvent molecules.<sup>1</sup> In order to understand this ultrafast response of the solvent on a quantitative level, it is necessary to obtain accurate data regarding the dielectric response in the THz region. THz-TDS study actually provides the accurate experimental data in this region.

For a particular non-polar aromatic solute and polar solvent interacting system, there is a characteristic peak frequency of absorption in the THz region detected by THz-TDS. The peak wavenumber shifts towards higher wavenumbers with an increase in the chain length of the alkane solvent in the solution. The peak around 10-20 cm<sup>-1</sup> is possibly due to a librational motion in the solution. Smith and Meech interpreted this high-frequency component to be a result of the “librational motion in a cage model”.<sup>21</sup> In a simplified expression, librational frequency is given by  $(k/I_{\text{eff}})^{1/2}$  where  $k$  is the force constant of the harmonic potential surface, and  $I_{\text{eff}}$  is the effective moment of inertia of a molecule. Since the force constant depends on the strength of the intermolecular interactions, the librational frequency is expected to decrease with increasing dilution. The peak frequency is around 10–20 cm<sup>-1</sup>, which may be considered as a frequency at an infinite dilution limit. Thus, the shift in the peak frequency of  $\Delta\text{OD}$  could be explained according to the above relation. It is reasonable to assume that  $I_{\text{eff}}$  is independent of the type of solvent, which suggests that the peak frequency shift is due to a change in force constant caused by changing the solvent.

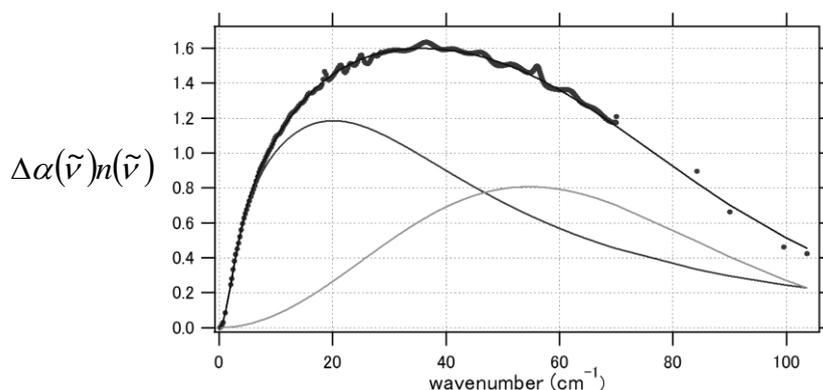
The low frequency spectra can be analyzed by different models.<sup>2,5-6</sup> The following equation (Eq.1) fits the experimental data (Figure 1) very well in the THz region considering the analytical model equation (Eq. 2)

$$\Delta[\alpha(\tilde{\nu})n(\tilde{\nu})] \propto \text{Re}[N_{\text{solute}} \tilde{\nu} \{1 - \exp(-hc\tilde{\nu}/kT)\} \times \int_{-\infty}^{\infty} dt \exp(-i2\pi c \tilde{\nu} t) \left( \langle \mu_k^{\text{solute}}(t) \mu_k^{\text{solute}}(0) \rangle + 2 \sum_i \langle \mu_i^{\text{solvent}}(t) \mu_k^{\text{solute}}(0) \rangle \right)], \quad (1)$$

$$\langle \mu_{\text{solute}}(t) \mu_{\text{solute}}(0) \rangle = \mu^2 \left[ a_1 \left\{ \frac{\tau_1}{\tau_1 - \tau_2} \exp(-t/\tau_1) - \frac{\tau_2}{\tau_1 - \tau_2} \exp(-t/\tau_2) \right\} + a_2 \exp(-(t/\tau_3)^2) + a_3 \exp(-(t/\tau_4)^2) \right], \quad (2)$$

where  $\Delta\alpha(\tilde{\nu})n(\tilde{\nu})$  is the change of the product spectra of the refractive index and the absorption coefficient between solution and solvent;  $N_{\text{solute}}$  is the number of solute molecules,  $\langle \mu_{\text{solute}}(t) \mu_{\text{solute}}(0) \rangle$  is time correlation function of solute in solution,  $a_i$  -amplitude of the time components,  $\tau_1$  denotes the reorientational relaxation time,  $\tau_2$  is the angular velocity

correlation time including the inertial effect,  $\tau_3$  is related to the mean time between collisions and  $\tau_4$  corresponds to the additional high frequency component with a Gaussian function.



**Figure 1:** Spectral fitting for the difference product spectra  $\Delta\alpha(\tilde{\nu})n(\tilde{\nu})$  with Eq. (1) for the TCF of the solute dipole moment. (Eq. 2)

Hydrogen bonds (HB) play an important role in structural formation of biological macromolecules. Since the strength of HB is between those of covalent bonds and van der Waals forces, it also results in structural flexibility. To deepen understanding on hydrogen bond, there have been efforts to study intermolecular vibrations of dimers in the liquid phases.<sup>8</sup> In solutions, the interaction with surrounding solvent molecules affect the intermolecular interaction and structural stability of the dimer.

## Conclusion

The accurate experimental findings in the low frequency region by THz–TDS study along with theoretical models having proper physical meanings help to understand different kind of motions like librational motion, intermolecular vibration, collective motions of associated liquids and reorientational relaxation etc. in the condensed phases. Numerous applications for THz–TDS exist and many industrial branches can benefit from its unique capabilities in future.

## References

1. Schmuttenmaer, C. A. Exploring dynamics in the far-infrared with terahertz spectroscopy. *Chem. Rev.* **2004**, *104*, 1759.
2. Dutta, P.; Tominaga, K. Obtaining Low Frequency Spectra of Acetone Dissolved in Cyclohexane by Terahertz Time-Domain Spectroscopy. *J. Phys. Chem. A* **2009**, *113*, 8235.

3. Rønne, C.; Thrane, L.; Astrand, P.-O.; Wallqvist, A.; Mikkelsen, K.V.; Keiding, S.R. Investigation of the temperature dependence of dielectric relaxation in liquid water by THz reflection spectroscopy and molecular dynamics simulation. *J. Chem. Phys.* **1997**, *107*, 5319.
4. Kambara, O.; Kawaguchi, S.; Dutta, P.; Ponseca Jr., C. S.; Ikeshima, K.; Yamaguchi, S.; Hirai, S.; Banno, M.; Naito, S.; Tominaga, K. Low-Frequency Dynamics in Condensed Phases Studied by Terahertz Radiation Spectroscopy. *Proceedings of International Symposium on Terahertz between Japan and Sweden, TMU Symp. Ser.*, **2008**, *1*, 44.
5. Dutta, P.; Tominaga, K. Dependence of low frequency spectra on solute and solvent in solutions studied by terahertz time-domain spectroscopy. *Mol. Phys.* **2009**, *107*, 1845.
6. Dutta, P.; Tominaga, K. Terahertz Time-Domain Spectroscopic Study of the Low-Frequency Spectra of Nitrobenzene in Alkanes. *J. Mol. Liq.* **2009**, *147*, 45.
7. Oka, A.; Tominaga, K. Terahertz spectroscopy of polar solute molecules in non-polar solvents. *J. Non-Crystalline Solids* **2006**, *352*, 4606.
8. Yamaguchi, S.; Tominaga, K.; Saito, S. Intermolecular vibrational mode of the benzoic acid dimer in solution observed by terahertz time-domain spectroscopy. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14742.
9. Rungsawang, R.; Ueno, Y.; Tomita, I.; Ajito, K. Angle-dependent terahertz time-domain spectroscopy of amino acid single crystals. *J. Phys. Chem. B* **2006**, *110*, 21259.
10. Xu, J.; Plaxco, K.; Allen, S. J. Collective dynamics of lysozyme in water: terahertz absorption spectroscopy and comparison with theory. *J. Phys. Chem. B* **2006**, *110*, 24255.
11. Markelez, A. G.; Knab, J. R.; Chen, J. Y.; He, Y. Protein dynamical transition in terahertz dielectric response. *Chem. Phys. Lett.* **2007**, *442*, 413.
12. Koeberg, M.; Wu, C.-C.; Kim, D.; Bonn, M. THz dielectric relaxation of ionic liquid:water mixtures. *Chem. Phys. Lett.* **2007**, *439*, 60.
13. Chakraborty, A.; Inagaki, T.; Banno, M.; Mochida, T.; Tominaga, K. Low-frequency spectra of metallocenium ionic liquids studied by terahertz time-domain spectroscopy. *J. Phys. Chem. A* **2011**, *115*, 1313.
14. Möller, K. D.; Rothschild, W. G. Far-infrared Spectroscopy, Wiley, New York, **1971**.
15. Yarwood, J. Ed. Spectroscopy and Structure of Molecular Complex, Plenum Press, London, **1973**.

16. Padro, J. A.; Marti, J. An interpretation of the low-frequency spectrum of liquid water. *J. Chem. Phys.* **2003**, *118*, 452.
17. Ohmine, I.; Tanaka, H. Fluctuation, relaxations, and hydration in liquid water. Hydrogen-bond rearrangement dynamics. *Chem. Rev.* **1993**, *93*, 2545.
18. Sutmann, G.; Vallauri, R. Hydrogen bonded clusters in the liquid phase: I. Analysis of the velocity correlation function of water triplets. *J. Phys. Condens. Matter* **1998**, *10*, 9231.
19. Shirota, H.; Pal, H.; Tominaga, K.; Yoshihara, K. Deuterium isotope effect of salvation dynamics in methanol: CH<sub>3</sub>OH, CH<sub>3</sub>OD, CD<sub>3</sub>OH, and CD<sub>3</sub>OD. *J. Phys. Chem.* **1996**, *100*, 14575.
20. Shirota, H.; Yoshihara, K.; Smith, N. A.; Lin, S.; Meech, S. R. Deuterium isotope effects on ultrafast polarisability anisotropy relaxation in methanol *Chem. Phys. Lett.* **1997**, *281*, 27.
21. Smith, N. A.; Meech, S. R. *J. Phys. Chem. A* **2000**, *104*, 4223.