Ion effects on liquid structure of water monitored by terahertz time-domain spectroscopy

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THz light

Ionic hydration
1. Ionic hydration studied by THz spectroscopy
   M. Kondoh, Y. Ohshima, and M. Tsubouchi,

2. Liquid-sheet jet for THz spectroscopy
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1. Ionic hydration studied by THz spectroscopy

Ionic hydration

1) affects the chemical and biological properties of water, (Macroscopic)
2) induces rearrangement of the hydrogen bonding network. (Microscopic)

<table>
<thead>
<tr>
<th>Viscosity $\eta$ of ion solution</th>
<th>$\eta/\eta_{water}$ at 1 mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1.097</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>1.066</td>
</tr>
<tr>
<td>KOH</td>
<td>1.129</td>
</tr>
<tr>
<td>KCl</td>
<td>0.987</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>0.988</td>
</tr>
</tbody>
</table>

up

down
Frank and Wen model

H. S. Frank, W. Y. Wen, Discuss. Faraday Soc. 24, 133 (1957)

- Region A: Water molecules are tightly bound to the centric ion. → “Lower” mobility
- Region B: Hydrogen bonding structure is disrupted by “Structure breaking effect” → “Higher” mobility
- Region C: Normal water

In the last half century, this hydration model has been extensively examined by experiments and calculations.
Previous studies

  “Hydrogen bond structure partially modified by ion”

- Femtosecond mid-IR pump-probe (Omta et al., Science, 2003)
  “No measurable effect of dissolved ion”

Controversy!!

The hydration model has not been proven yet!

THz spectroscopy has been recently employed to investigate “structure breaking effect” in aquatic solution.

Orientational relaxation

Light is absorbed by orientational relaxation.

Water: Orientational relaxation is slow due to hydrogen bonding. (Microwave region)
THz spectroscopy on pure water


Dielectric spectrum of liquid water

Absorption spectrum

\( \varepsilon''(\nu) \)

\( \nu \) [THz]

\( \varepsilon''_{MW} \)

\( \varepsilon''_{THz} \)

Normal water

“Fast” water

Weak contribution to hydrogen bonding

→ “Higher” mobility
Frank and Wen expected “Structure breaking effect” induce high mobility of water molecules in hydrogen bonding network. This effect may increase the fraction of the “fast water”.

Ion hydration modify the $\varepsilon''_{\text{THz}}$?
Debye model

Model for dielectric relaxation for polar liquid.

\[ \varepsilon''(\nu) = \frac{2\pi\nu\tau S}{1 + (2\pi\nu\tau)^2} \]

- **S**: Amplitude (Fraction of fast water)
- **\(\tau\)**: Relaxation time (Mobility of fast water)

Change in direction of E-field

- **Small \(\tau\)**
- **Large \(\tau\)**
Recipe of our study

1. Measurements of the dielectric function of ion solution
   ✅ By changing ion species
   ✅ By changing ion concentration

2. Extraction of the $\varepsilon''_{\text{THz}}$ from the dielectric function

3. Comparing the $\varepsilon''_{\text{THz}}$ between pure water and ion solution

4. Evaluation of the **structure breaking effect**
Experimental setup

- THz light generation: Optical rectification with pulse front tilting
- THz light measurement: Electro-optic sampling

Ti:Sapphire REGEN (800 nm, 1 kHz, 120 fs, 0.8 mJ)
Cell and samples

Reference: *Pure water*

Quartz windows (1mm) 100μm

Absorption spectra: $\varepsilon''(\nu)$

Sample: *ion solution*

Sample: *LiCl, NaCl, KCl, and CsCl aq* (cation dependence)
*KCl, KNO$_3$, KBr, and KI aq* (anion dependence)

Concentration range: 0.5-1.5 mol/L
**Result 1: Anion vs Cation**

Anion dependence

- water
- KCl
- KNO$_3$
- KBr
- KI

Cation dependence

- water
- CsCl
- KCl
- NaCl
- LiCl

$\varepsilon''(\nu)$

$\nu$ [THz]

• Anion dependence $<<<$ Cation dependence
Hydration is parallel to dipole.

In this study, we have focused on the cation dependence.
Result 2: Cation dependence

Amplitude decreases as the ion radius decreases.
Comparison with MW data

Previous MW study

MW data

\[ \varepsilon''_{MW}(\nu) = \text{Im} \left[ \frac{S_{MW}}{1 - (2\pi\nu \tau_{MW})^{1-\alpha}} \right] \]

v [THz]

0.001 0.01 0.1

T. Chen et al. JPC. A, 107, 4025 (2003) etc.

KCl aq.

Our study

Our data

Extrapolation

THz component !!
Extraction of THz component

Debye model \[ \varepsilon''(\nu) = \frac{2\pi \nu \tau S}{1 + (2\pi \nu \tau)^2} \]

High frequency shift of \( \varepsilon''_{\text{THz}}(\nu) \)

- Shorter \( \tau \) than that of pure water
- Higher mobility
- Structure breaking due to ion hydration?
“Structure breaking effect” is true. Population of “fast” water should increase as the number of ions in solution increases.

Ion concentration dependence of $\varepsilon''_{\text{THz}}(\nu)$ should be one of the evidences of structure breaking effect.
Result 3: Ion concentration

As we expected, $\varepsilon''_{\text{THz}}$ increased in amplitude as the ion concentration increased.

Ion-induced “structure breaking effect.”
Similar concentration dependence of amplitude in all ion solutions

All ions have the structure breaking effect

Debye model

\[ \varepsilon''(\nu) = \frac{2\pi \nu \tau S}{1 + (2\pi \nu \tau)^2} \]
Evidences for “structure breaking effects“

THz spectroscopy can provide the new points of view for ion solvation

- Relaxation time of “fast water” becomes shorter by ion hydration.
- Population of “fast water” becomes larger as the ion concentration increases.
2. Liquid-sheet jet for THz spectroscopy

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Motivation

Problems in THz spectroscopy for solution

**Windows** in the sample cell

- Absorption and multiple reflections by window \( \rightarrow \textbf{Complicated analysis} \)
- Damage due to strong optical light (\textit{i.e.} Optical pump – THz probe)

Window-less measurements
It is difficult to change thickness in this nozzle

**Thickness:** $L = 5.7 \pm 0.3 \mu m$
Colliding jet nozzle


- By colliding two liquid jets, the liquid sheet can be produced.
- By changing the colliding angle $\theta$, the thickness can be easily controlled.

![Graph showing the relationship between crossing angle and sheet thickness](image)
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