Electronic and vibrational structure in liquid water probed by soft X-ray resonant inelastic scattering and modeling
Hydrogen bonding of water

local structure of water

hydrogen bond

body = oxygen
hand = electron
leg = hydrogen

lone pair electrons

Directional bonding of water forced by hydrogen bonding → origin of the diamond-like structure of $I_h$ ice

Thermodynamic anomaly of water

- Isothermal compressibility
- Specific heat at constant pressure
- Density

→ Density fluctuations
→ Entropy fluctuations

Beginning of water anomaly around your body temperature?
Water phase diagram

Distorted hydrogen bond → Entropy

HDL

LDL

tetrahedral hydrogen bond → Enthalpy

2nd critical point

Two amorphous states of water

http://www.nims.go.jp/water/

real-time
Electronic structure of water and Hydrogen bonding

Electronic structure is a marker of hydrogen bond!
Electronic structure of water and Hydrogen bonding

$\text{H}_2\text{O}(\text{gas})$

$\text{H}_2\text{O}(\text{liq.})$

XAS

$\text{O atomic orbitals}$

$2p_x$

$2p_y$

$2p_z$

$\text{H atomic orbitals}$

$1b_1$

$1s$

$2b_2$

$4a_1$

$1s$

$3a_1$

$1b_2$

$2a_1$

$\text{H}_2\text{O molecular orbital}$

$\text{hydrogen bonding}$

$\text{hv}_{in}$

$\text{O 2p}$

$\text{O 1s}$
Soft X-ray absorption spectroscopy of water

XAS tells us that water forms asymmetric hydrogen bond, rather than making tetrahedrally coordinated diamond structures

Debates started on the X-ray spectroscopy of water

T. Head-Gordon et al., PNAS 103, 7973 (2006).

\[ \text{A: } 4 \text{ HB} \rightarrow \text{ice} \]
\[ \text{B: } 2\text{HB} \rightarrow \text{liquid?} \]
Electronic structure of water and Hydrogen bonding

H₂O(gas)

O atomic orbitals
2pₓ 2pᵧ 2p𝒛

H₂O molecule orbital
2s 2pₓ 2pᵧ 2p𝒛

H₂O(liq.)

H atomic orbitals
1s

O 2p

Hydrogen bonding

XES

hv_{out}

O 1s
SPring-8 BL07LSU HORNET station

Ultrahigh energy resolution SXE spectrometer

Liquids and wets (in situ experiments)

Solids X-rays at atmosphere vacuum SX in SX out

Sealing made by perfluoroelastomer

Membrane window

Sample inlet/outlet port

ICF114 flange

Vacuum
O 1s RIXS of liquid water

T. Tokushima et al., J. Electron Spectrosc. 177, 192 (2010).

Distinct splitting of the 1b₁-derived orbital → Evidence of micro heterogeneity in liquid water?

1b₁ position may be an effective marker of hydrogen bond asymmetry.
Interpretation of liquid water O 1s XES

Two 1b₁ components well correspond to pre- and post- edge excitations.
Water mixed with 3-methyl pyridine

3-methyl pyridine (3MP) / D$_2$O

Water surrounded by 3MP do not have H-accepting hydrogen bond

Only one 1b$_1$ (1b$_1$”) peak was observed

Each 1b$_1$ peak may reflect different HB configuration


Liquid water structure in a polymer brush

Structuring of water in a polymer brush?

XAS/XES of liquid water in a polymer brush

1b'  1b”

O 1s XES
- Confined water
- Dry brush
- H2O
- I_h ice

Intensity (arb. units)

515 520 525 530 535 540 545 550
Emission energy (eV)

528 524 520 516 512

534.4 eV 535.95 eV 537.6 eV 539.6 eV 550 eV 531.31 eV

Confined water

Intensity (arb. units)

O 1s, XES

516 520 524 528
Absorption energy (eV)

550 eV 539.6 eV 537.6 eV 535.95 eV 534.4 eV 531.31 eV

534.4 eV 535.95 eV 537.6 eV 539.6 eV 550 eV

PMTAC on SiC
superhydrophillic

ave spacing 1.3nm

XAS/XES of fully (but slightly distorted) hydrogen bonded water in a polymer brush

K. Yamazoe, YH et al. to be submitted.
Gradual change from making to breaking under the influence of hydrophobic hydration and central charge.

Vibrational RIXS

From http://www.lsbu.ac.uk/water/
Martin Chaplin, London South Bank University
Vibrational RIXS at different timescales


C 1s ~ 10fs
N 1s ~ 6fs
Fe 2p_{3/2} ~ 0.8fs

graphite
ionic liquids
Mg_{2}FeH_{6}

O 1s vibrational RIXS of H$_2$O molecule

From http://www.lsbu.ac.uk/water/
Martin Chaplin, London South Bank University

The obtained vibrational energy well corresponds to symmetric ($v_1$) and asymmetric ($v_3$) OH stretching.

<table>
<thead>
<tr>
<th>Vibration(s)</th>
<th>liquid H$_2$O (25°C)</th>
<th>liquid D$_2$O (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>v, cm$^{-1}$</td>
<td>eV</td>
</tr>
<tr>
<td>3657.1</td>
<td></td>
<td>0.4530</td>
</tr>
<tr>
<td>2671.7</td>
<td></td>
<td>0.3309</td>
</tr>
<tr>
<td>$v_2$</td>
<td>v, cm$^{-1}$</td>
<td>eV</td>
</tr>
<tr>
<td>1594.7</td>
<td></td>
<td>0.1975</td>
</tr>
<tr>
<td>1178.4</td>
<td></td>
<td>0.1460</td>
</tr>
<tr>
<td>$v_3$</td>
<td>v, cm$^{-1}$</td>
<td>eV</td>
</tr>
<tr>
<td>3755.9</td>
<td></td>
<td>0.4653</td>
</tr>
<tr>
<td>2787.7</td>
<td></td>
<td>0.3453</td>
</tr>
</tbody>
</table>

From http://www.lsbu.ac.uk/water/
Vibrational RIXS in liquid water


OH stretching mode is dominantly excited

Sensitive to the local hydrogen bond coordination selected by excitation energies

Excitation energy dependence of the vibrational RIXS

*G. E. Walrafen et al., Chem. Phys. 85, 6964 (1986).
Soft X-ray vibrational spectroscopy of water

Y. Harada et al. PRL. 111, 193001 (2013).

Raman spectrum by
Isotope effect

The energy of the fundamental vibrational mode is close to that of gas phase water, rather than liquid water.

\[ \Delta E \approx 0.34 \text{ eV} \]

\[ \Delta E \approx 0.45 \text{ eV} \]

Y. Harada et al. PRL. 111, 193001 (2013).

Consistent with the interpretation of the O 1s XAS pre-edge peak.
Excitation energy dependence

Y. Harada et al. Unpublished

H$_2$O vib. progression

Relative intensity of vib. tail

Excitation energy (eV)

O 1s XAS

532.7 eV

533.9 eV

534.4 eV

534.9 eV

535.3 eV

535.5 eV

535.6 eV

535.7 eV

535.8 eV

536.9 eV

537.9 eV

539.9 eV

Intensity (a.u.)
Excitation energy dependence of vibrations

Heterogeneous hydrogen bond in liquid water

Competition between
Enthalpy ($\Delta H$) & Entropy ($\Delta S$)

\[ \Delta G = \Delta H - T \Delta S \]

Soft X-ray vibrational RIXS

CPL (2008)
PNAS (2009)
JESRP (2010)

PRL (2013) & unpublished
Microheterogeneity in liquid water

HDL
Distorted hydrogen bond

LDL
Tetrahedral hydrogen bond
Summary

#High resolution soft X-ray emission is powerful to investigate the hydrogen bond property of water.

#Vibrational information can be obtained by RIXS. Energy distribution against excitation energy has significant implications to interpret the XES/RIXS spectra.

#X-ray spectroscopic studies indicate the presence of microheterogeneity in liquid water, which might be important to understand the debated phase diagram of water in the T-P plane.
Acknowledgements

University of Tokyo

H. Niwa (→ Tsukuba U.)
M. Kobayashi (→ KEK)
J. Miyawaki
H. Kiuchi(D3)
J. Nakajima(→ Sharp)
Y. Kosegawa
K. Yamazoe(D1)
M. Oshima
K. Mawatari
T. Kitamori

RIKEN/SPring-8

T. Tokushima
Y. Horikawa
S. Shin
JASRI/SPring-8
Y. Senba
H. Ohashi

Stanford/Stockholm University

Financially supported by
CREST & Hikari-Ryoshi

Photon and Quantum Basic
Research Coordinated
Development Program by MEXT
Thank you for your attention!

LDL

HDL