Nov. 26.'16 Aquaphotomics @ Kobe

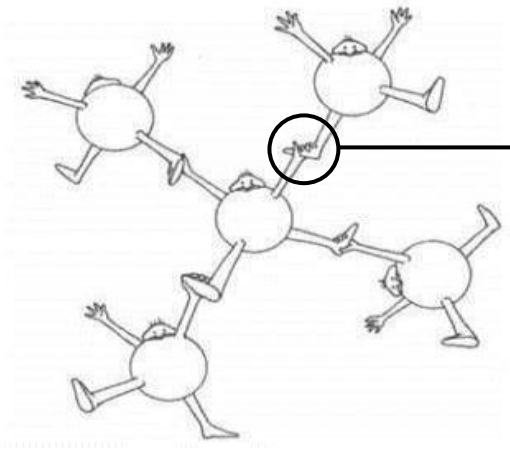
Electronic and vibrational structure in liquid water probed by soft X-ray resonant inelastic scattering and modeling

ISSP / Univ. of Tokyo / Japan

Yoshihisa HARADA

Hydrogen bonding of water

local structure of water

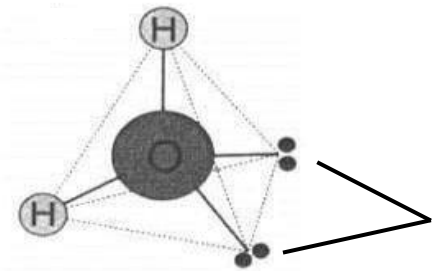


hydrogen bond

body = oxygen

hand = electron

leg = hydrogen



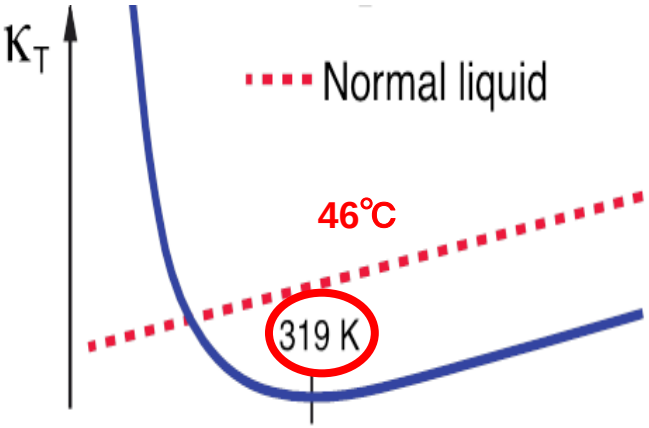
lone pair electrons

P. Ball, "*H_2O: The Biography of Water*"
Newton Press (1999)

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

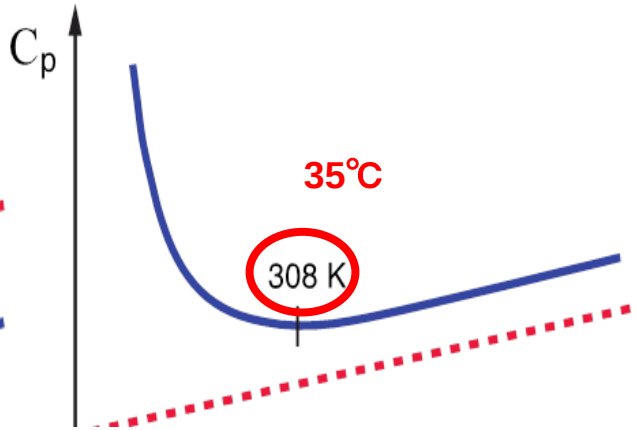
Thermodynamic anomaly of water

isothermal compressibility



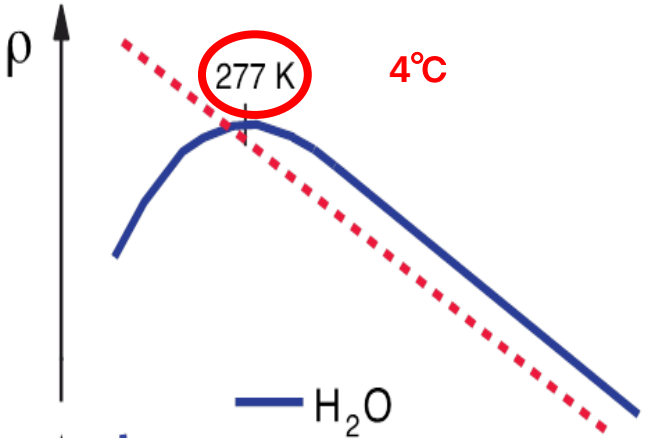
→density fluctuations

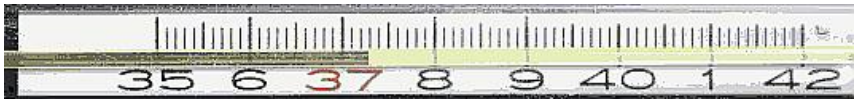
specific heat at constant pressure



→entropy fluctuations

density



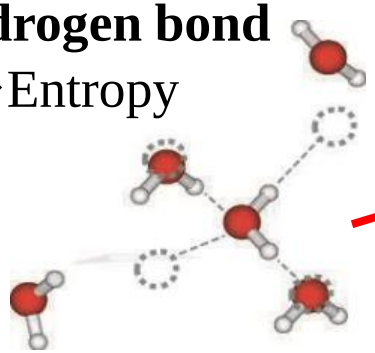


Beginning of water anomaly around your body temperature?

Water phase diagram

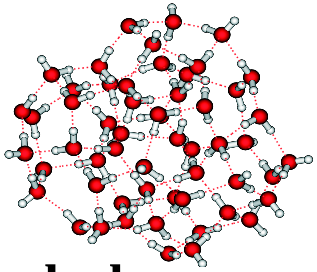
O. Mishima J. Chem. Phys. 123, 154506 (2005)

Distorted hydrogen bond
→Entropy

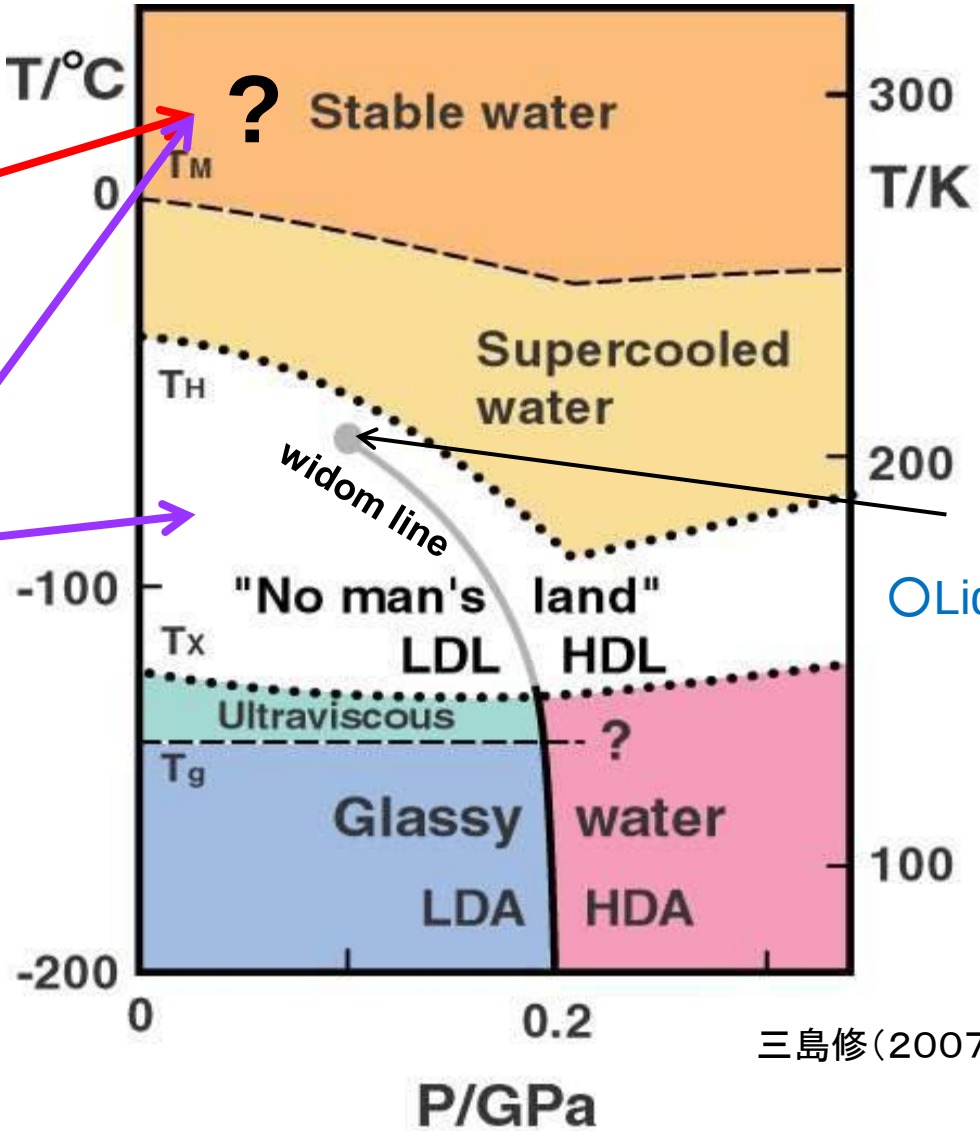


HDL

LDL



tetrahedral hydrogen bond
→Enthalpy



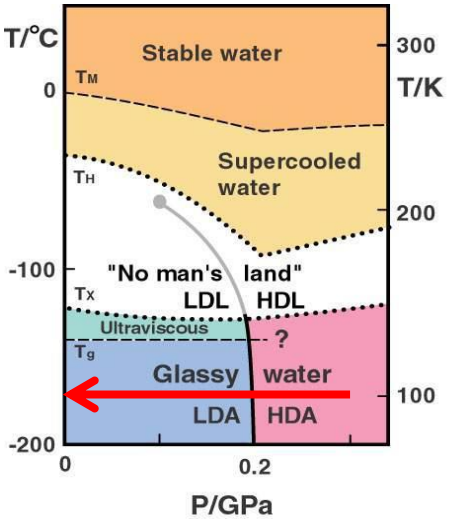
2nd critical point

○Liquid-liquid critical point

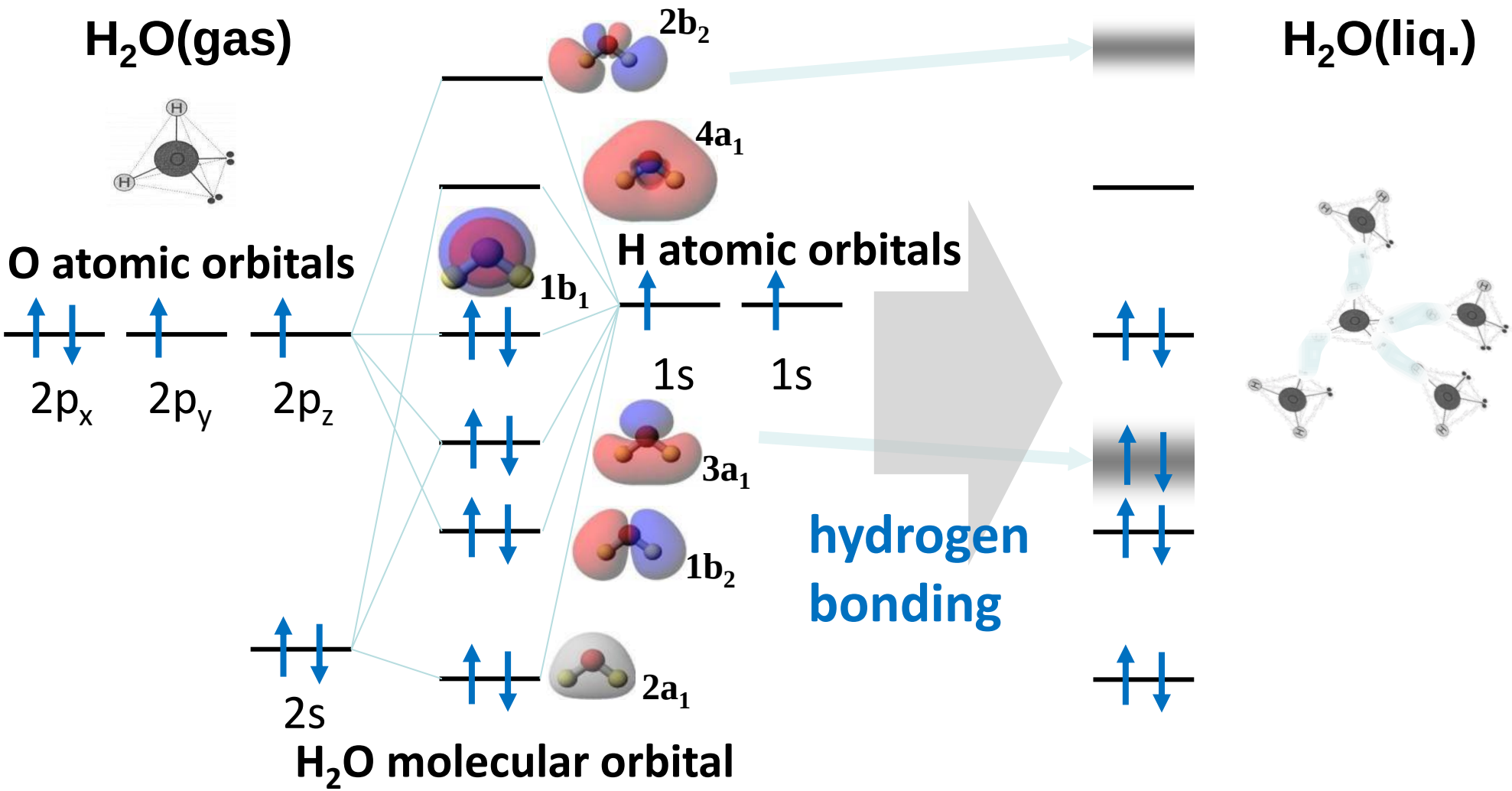
三島修（2007）

Two amorphous states of water

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

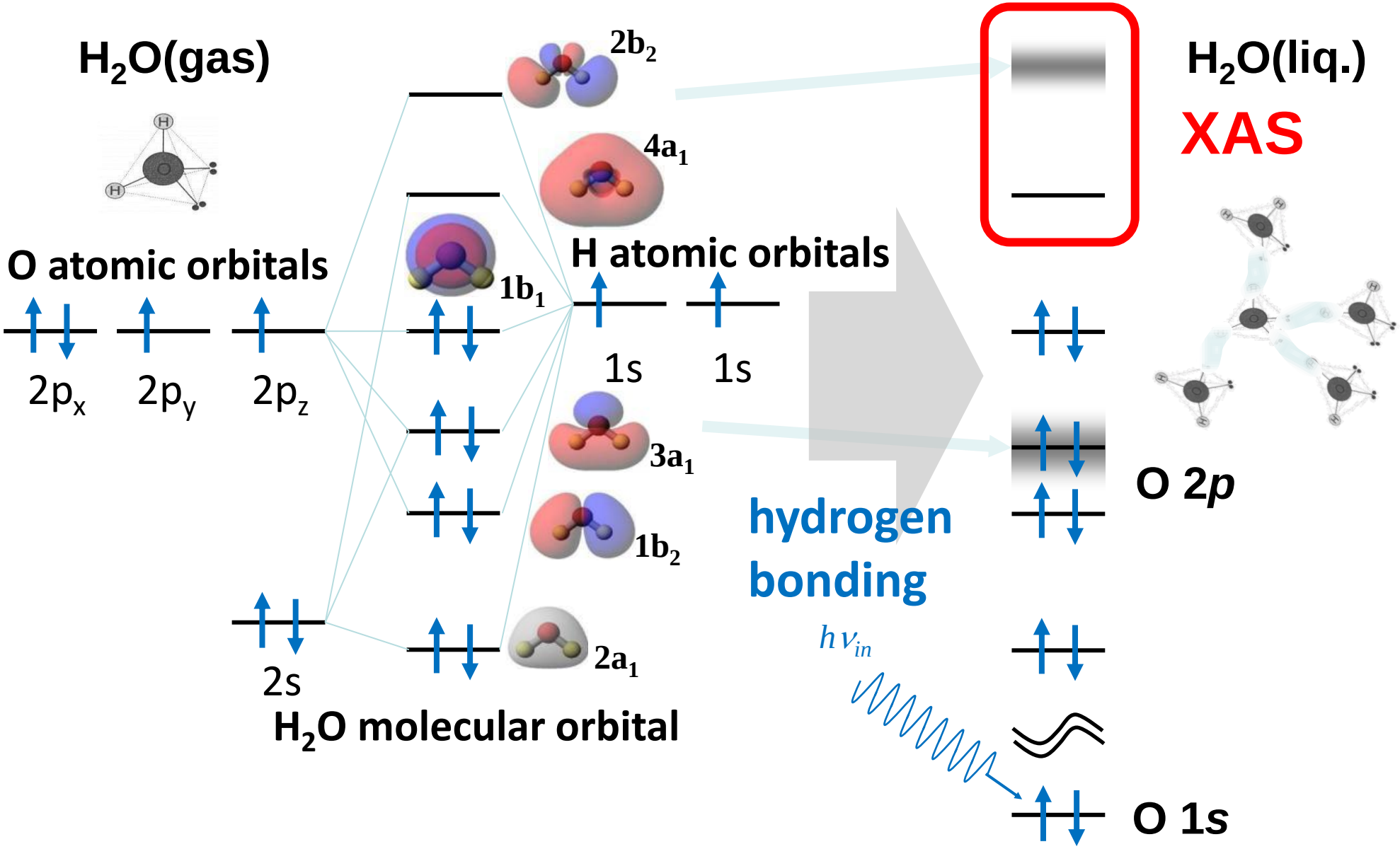


Electronic structure of water and Hydrogen bonding

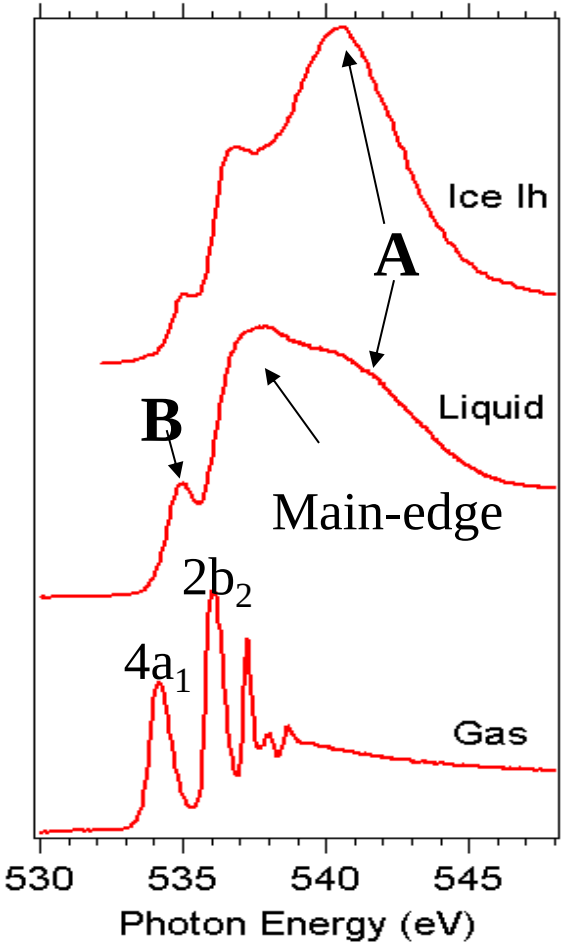


Electronic structure is a marker of hydrogen bond !

Electronic structure of water and Hydrogen bonding

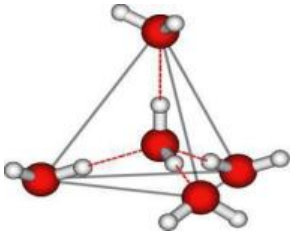


Soft X-ray absorption spectroscopy of water

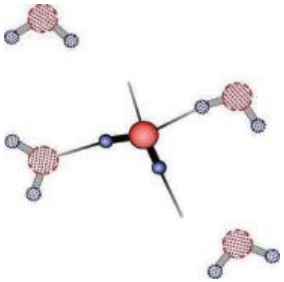


Myneni *et al. J. Phys.* 14 (2002) 213

Wernet *et al, Science* 304 (2004) 995



A : 4 HB→ice



B : 2HB→liquid？

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

R. Car et al., J. Chem. Phys. **120**, 8632 (2004)
R.J. Saykally et al., Science **306** (2004) 852
G. Galli et al., Phys. Rev. Lett. **96**, 215502 (2006)
T. Head-Gordon et al., PNAS **103**, 7973 (2006).
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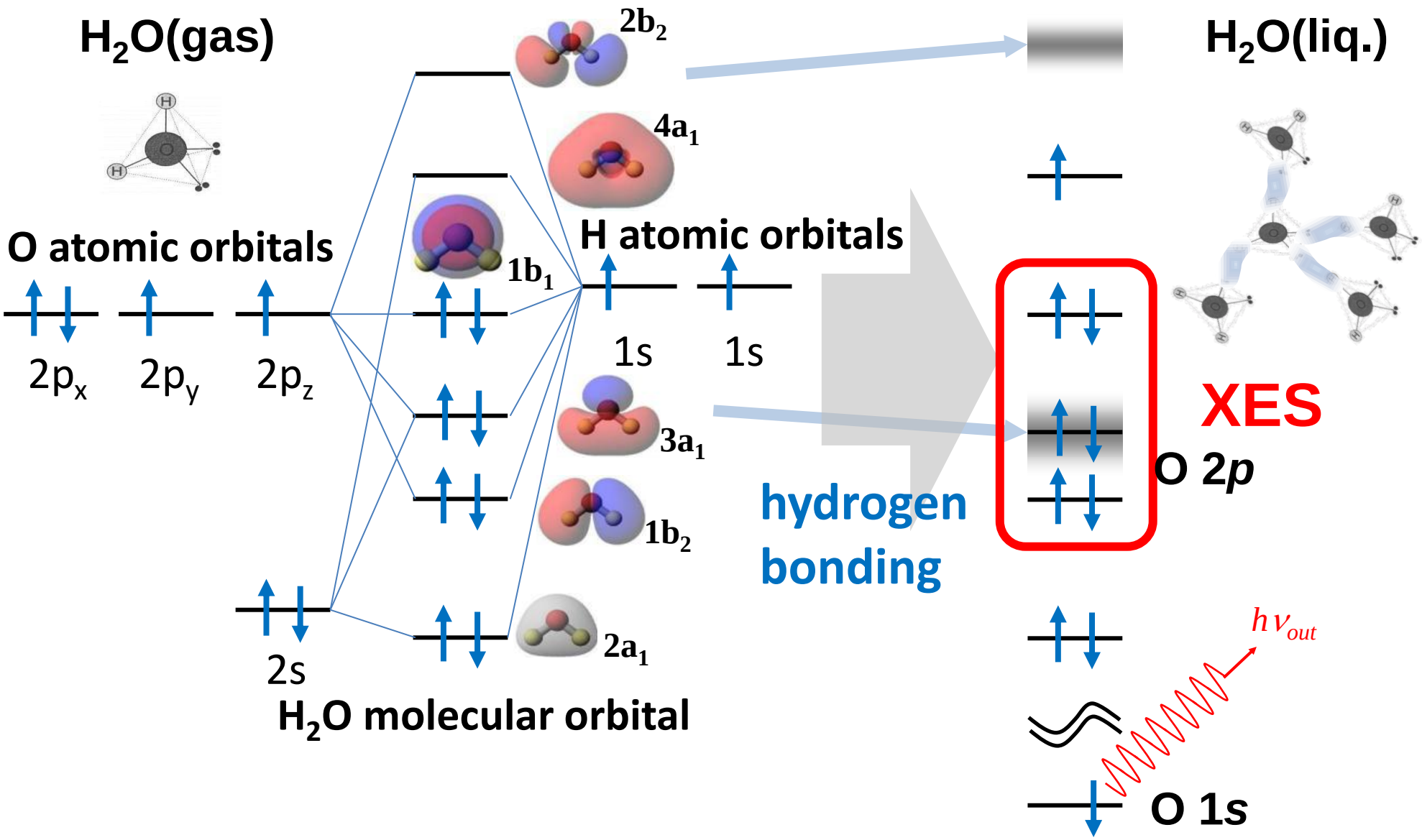
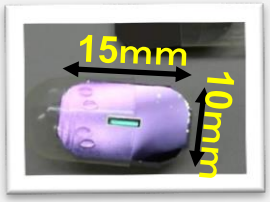
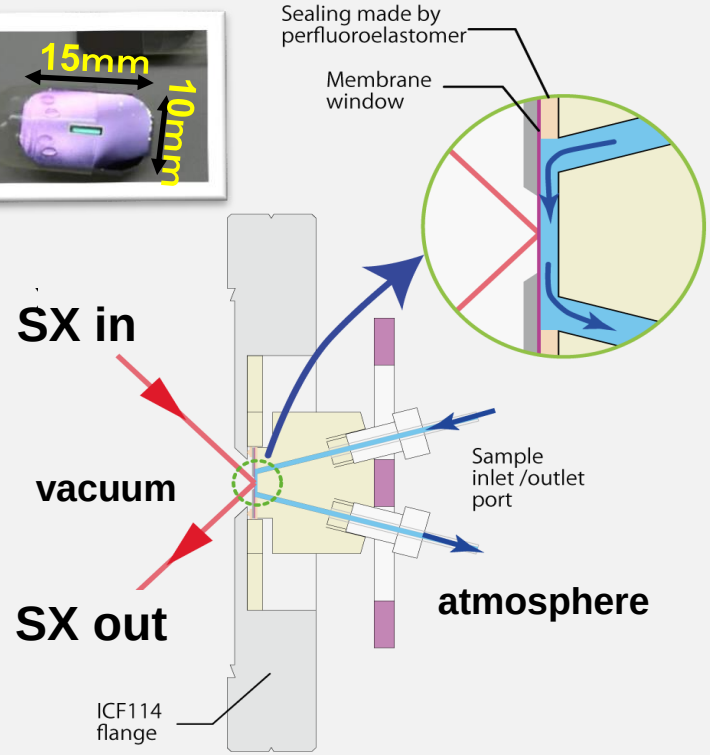
Electronic structure of water and Hydrogen bonding



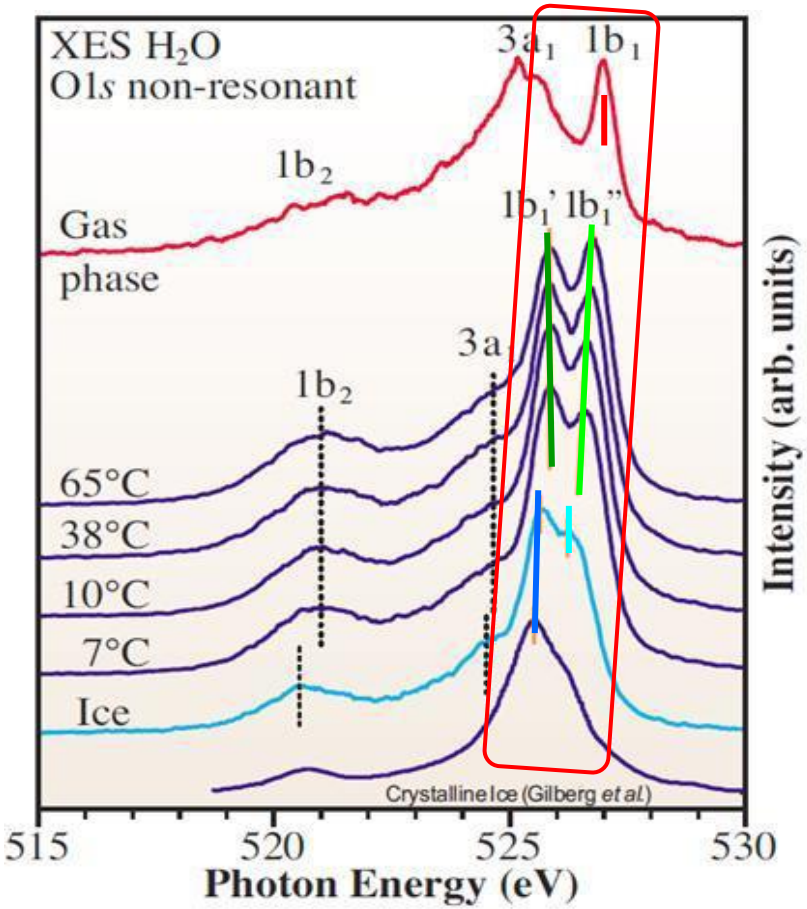
SPring-8 BL07LSU HORNET station

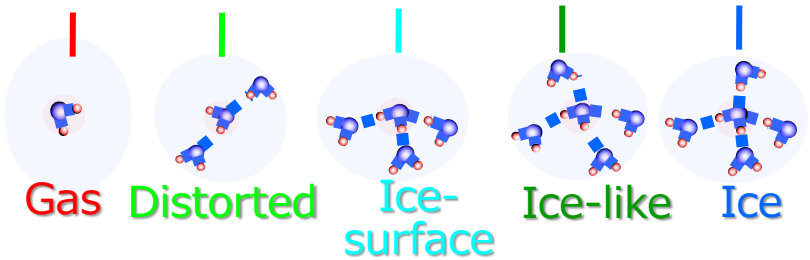




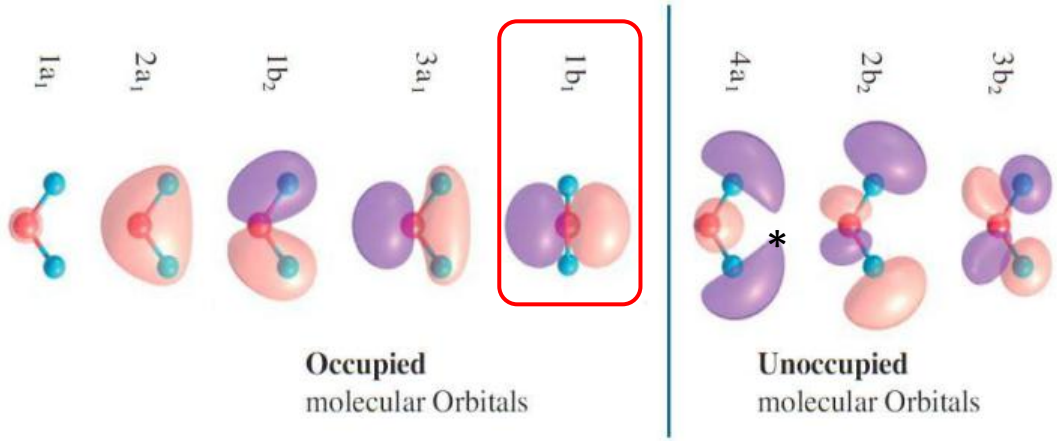
O 1s RIXS of liquid water

T. Tokushima *et al*. CPL **460**, 387 (2008).
T. Tokushima *et al.*, J. Electron Spectrosc. **177**, 192 (2010).





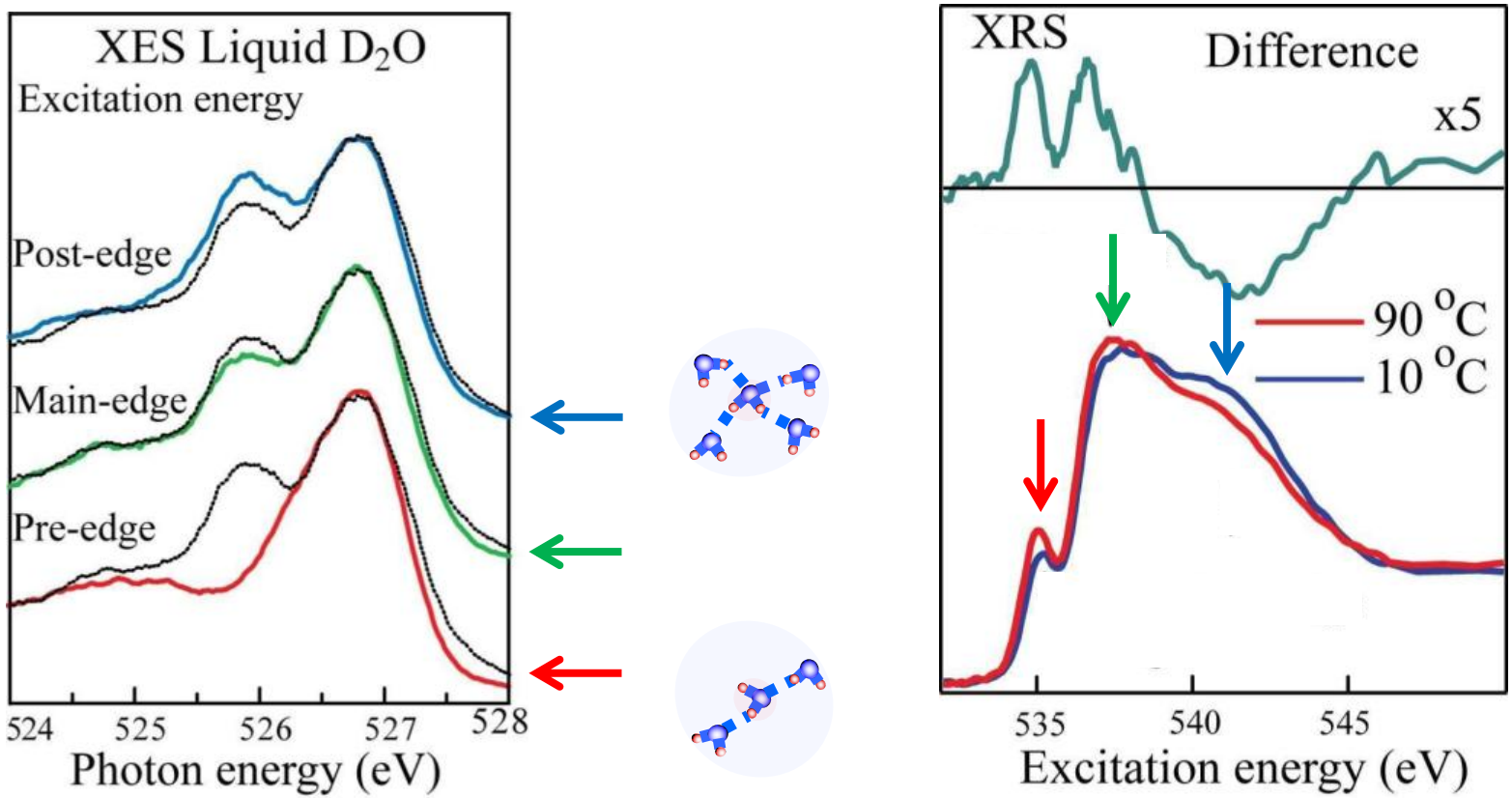
$1b_1$ position may be an effective marker of hydrogen bond asymmetry.



Distinct splitting of the $1b_1$-derived orbital → Evidence of micro heterogeneity in liquid water?

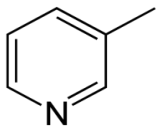
A lot of debates on the interpretation of the RIXS spectra

Interpretation of liquid water O 1s XES

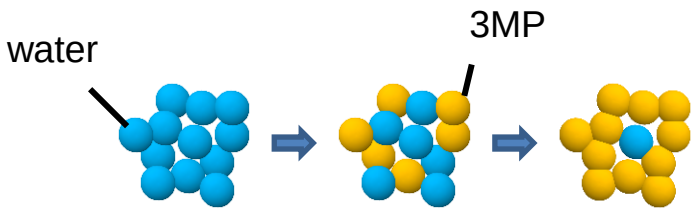


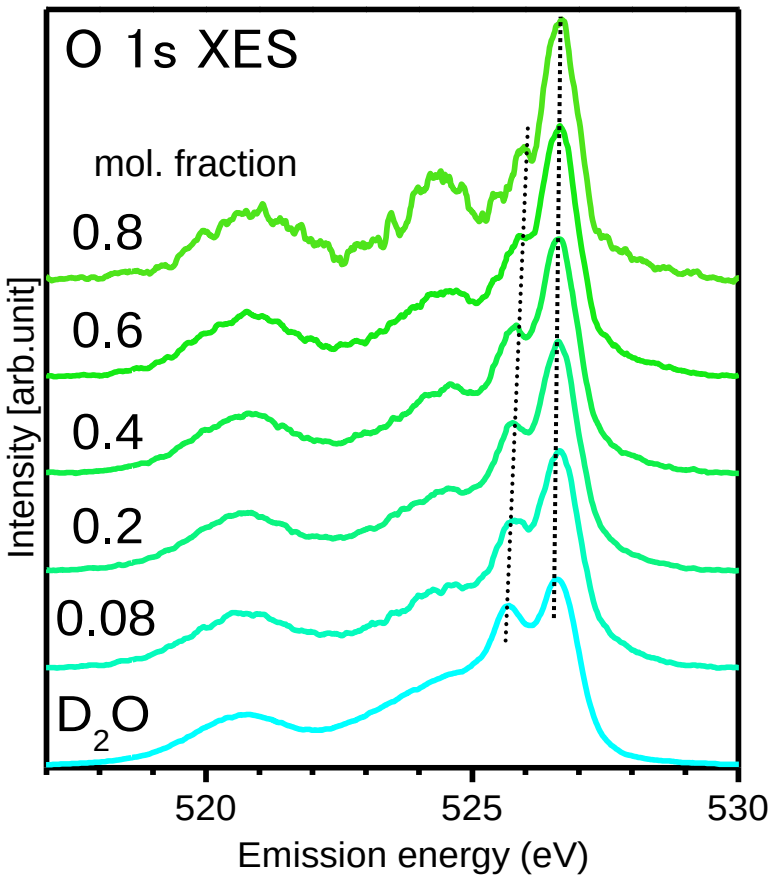
Two $1b_1$ components well correspond to pre- and post- edge excitations

Water mixed with 3-methyl pyridine



3-methyl pyridine (3MP) / D_2O





H. Arai *et al*. PCCP **14** (2012) 1576.

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

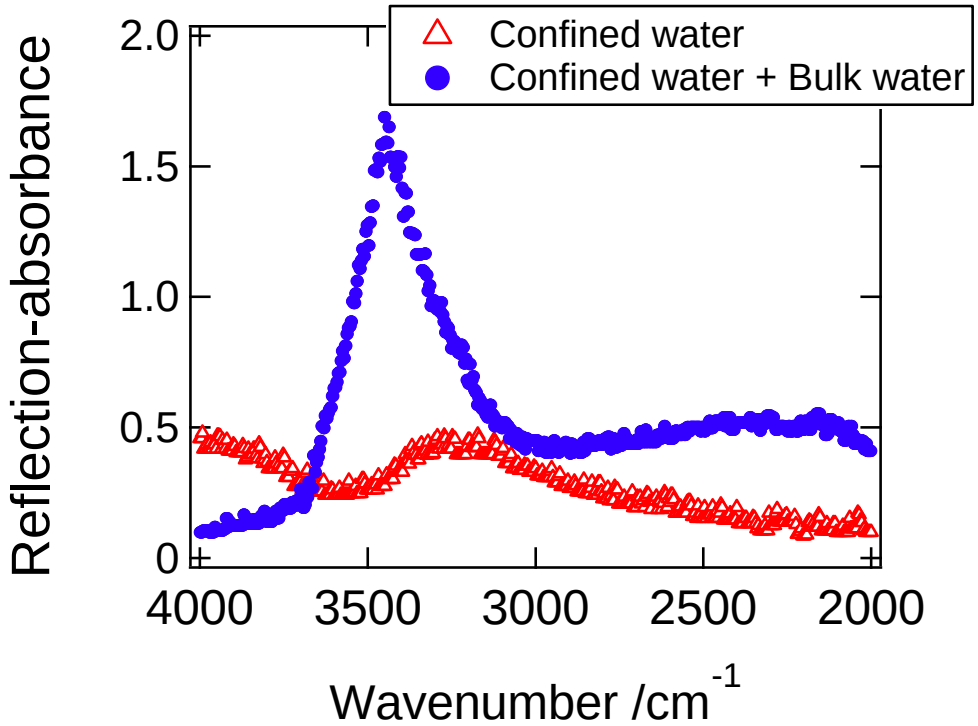
&

Only one $1b_1$ ($1b_1$”) peak was observed

Each $1b_1$ peak may reflect different HB configuration**

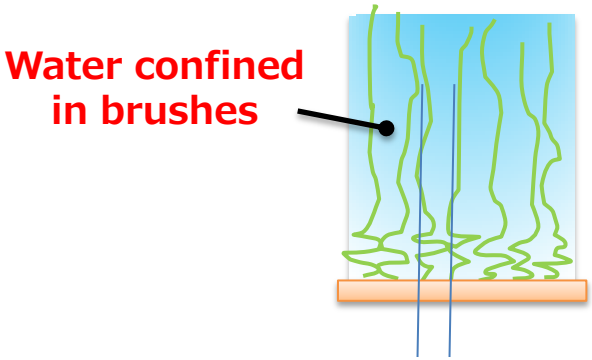
**K.M.Lange, R.Könnecke, M.Soldatov, R.Golnak, J.-E.Rubensson, A.Soldatov and E.F.Aziz, Angew. Chem. (2011)

Liquid water structure in a polymer brush



D. Murakami *et al*., Langmuir **29**, 1148 (2013).

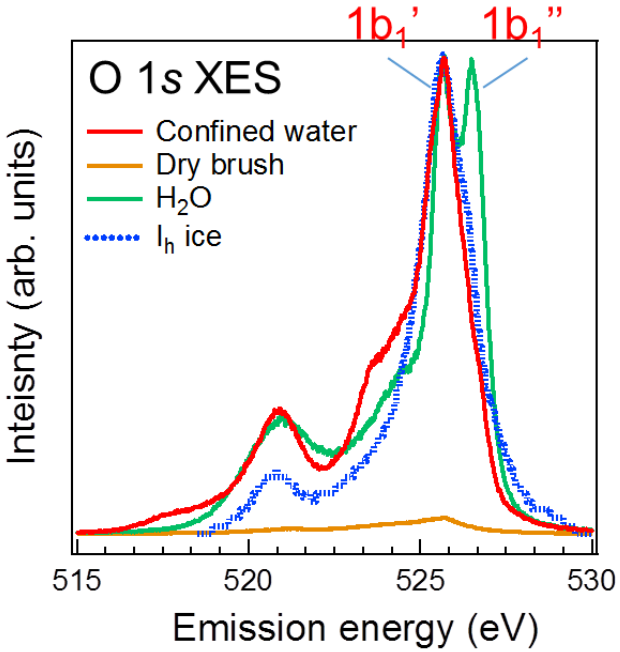
PMTAC on SiC
superhydrophillic

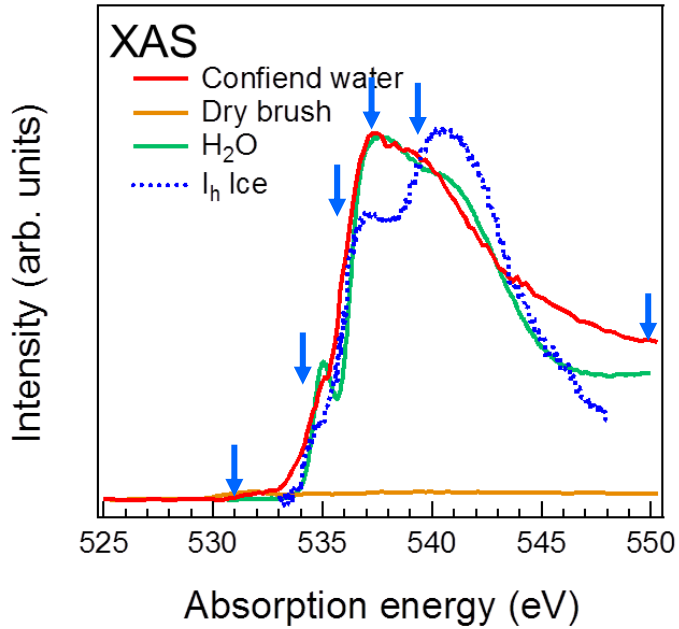


average spacing 1.3nm

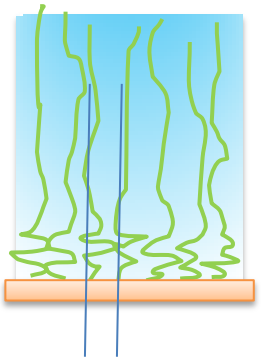
Structuring of water in a polymer brush?

XAS/XES of liquid water in a polymer brush

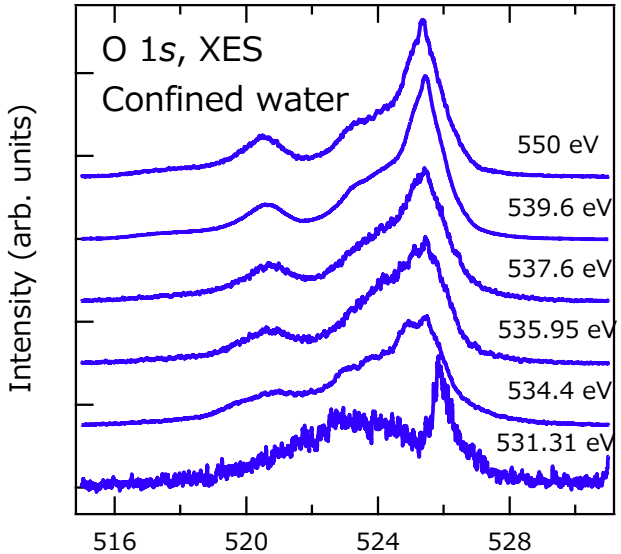




PMTAC on SiC superhydrophillic



ave spacing 1.3nm

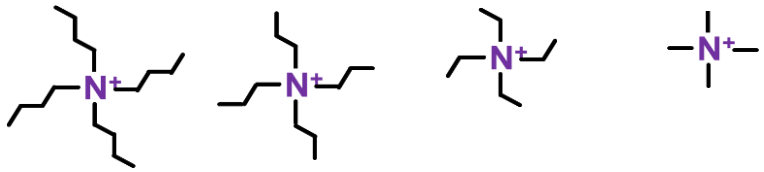


XAS/XES of fully (but slightly distorted) hydrogen bonded water in a polymer brush

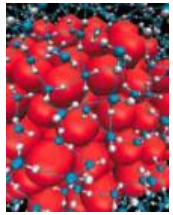
K. Yamazoe, YH *et al*. to be submitted.

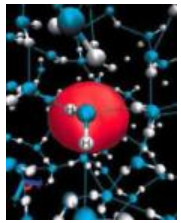
Structure making/breaking of water : hydration

TBA^+ **TPA^+** **TEA^+** **TMA^+**



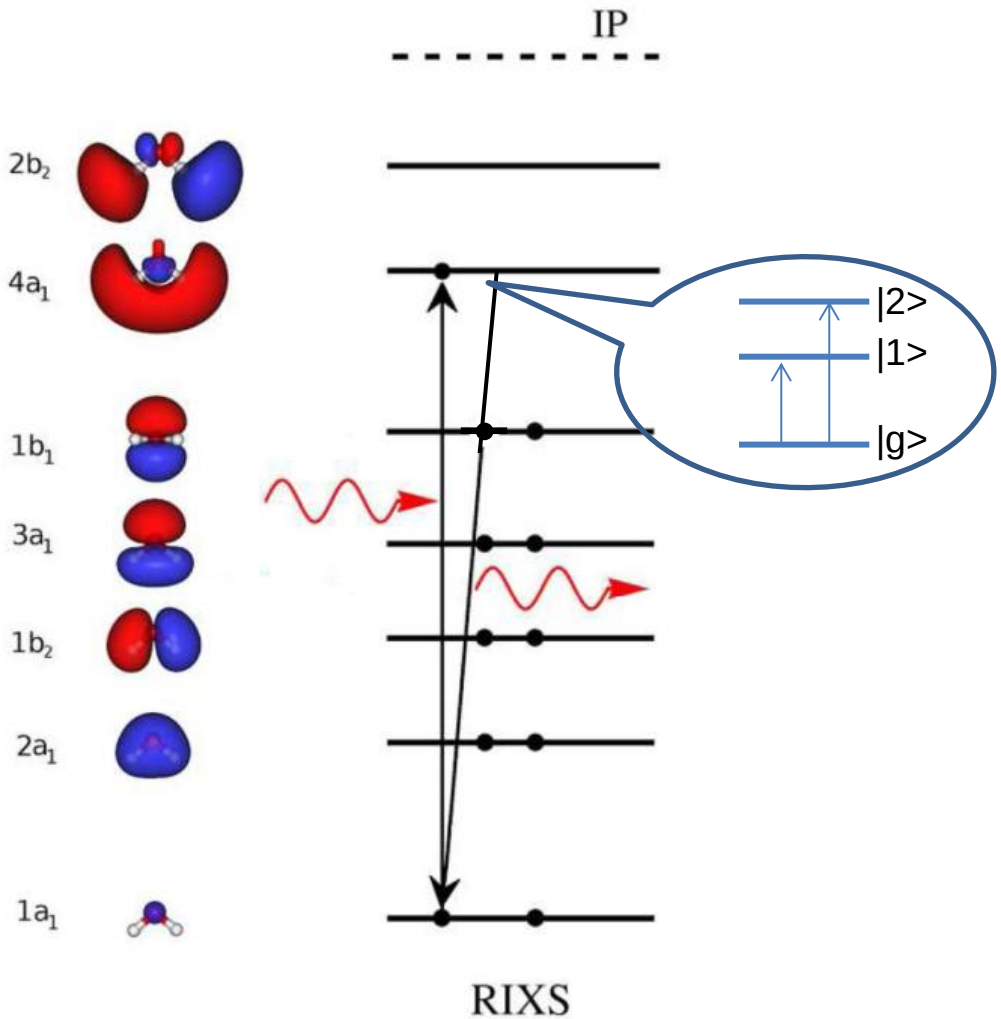
breaking → making

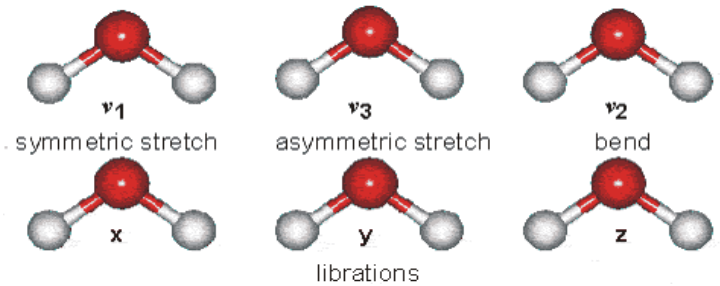




Chandler, Nature **437**, 640, (2005).

Gradual change from making to breaking under the influence of hydrophobic hydration and central charge



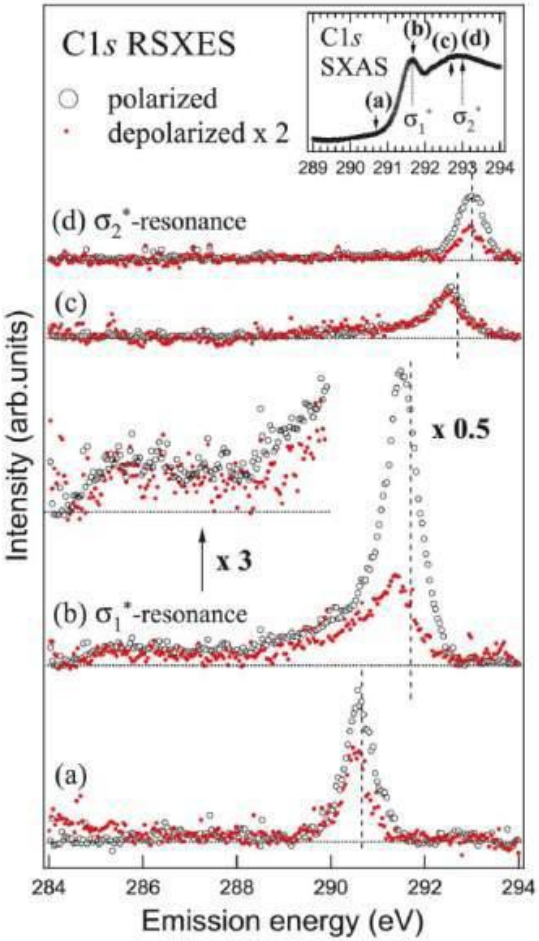


From http://www.lsbu.ac.uk/water/
Martin Chaplin, London South Bank University

Vibrational RIXS

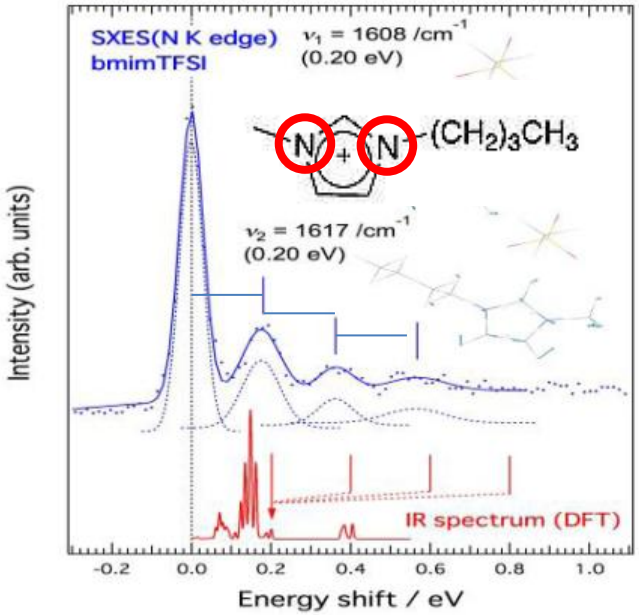
Vibrational RIXS at different timescales

Phys. Rev. Lett. 93, 017401 (2004).



graphite

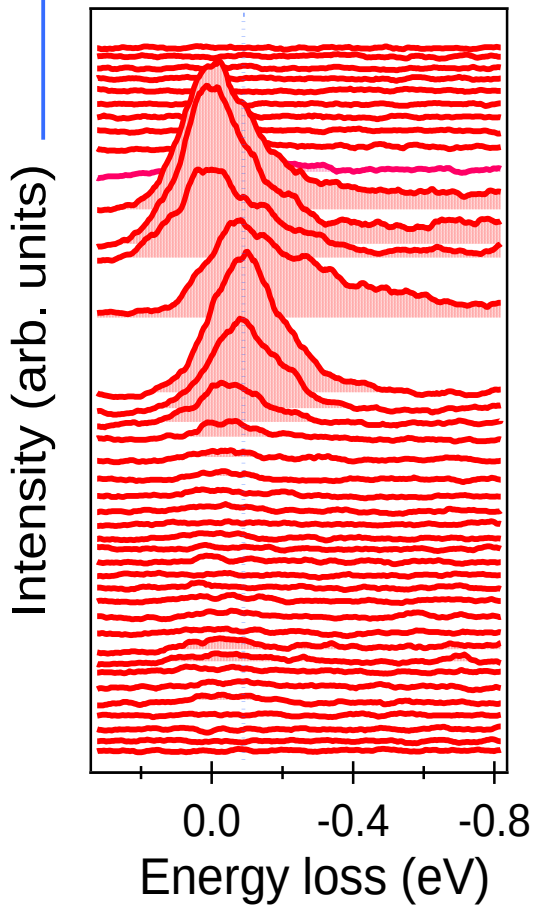
C 1s ~ 10fs



ionic liquids

N 1s ~ 6fs

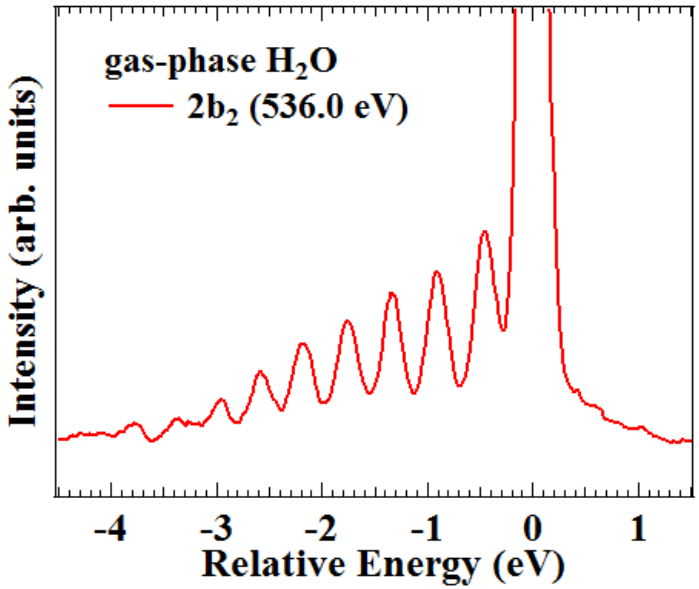
J. Phys. Soc. Jpn , 84, 043201 (2015).

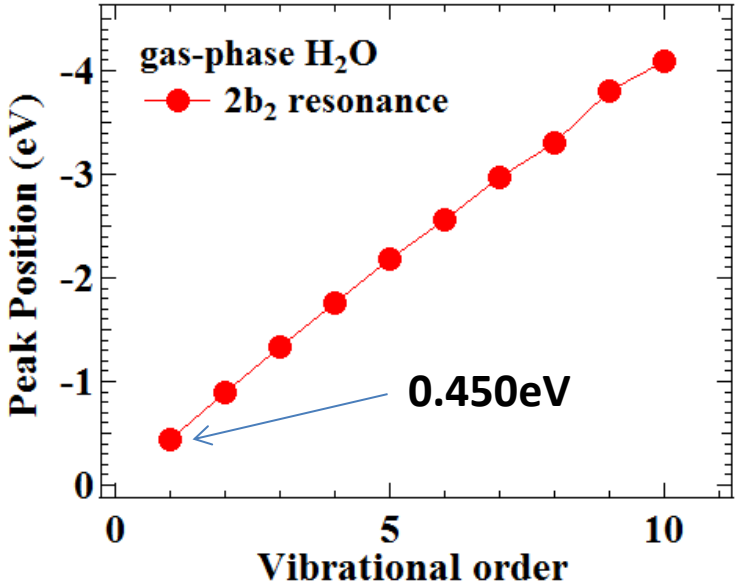


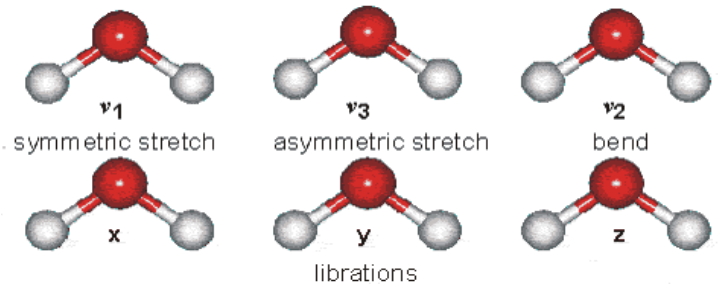
Mg_2FeH_6

Fe $2p_{3/2}$ ~ 0.8fs

O 1s vibrational RIXS of H_2O molecule







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

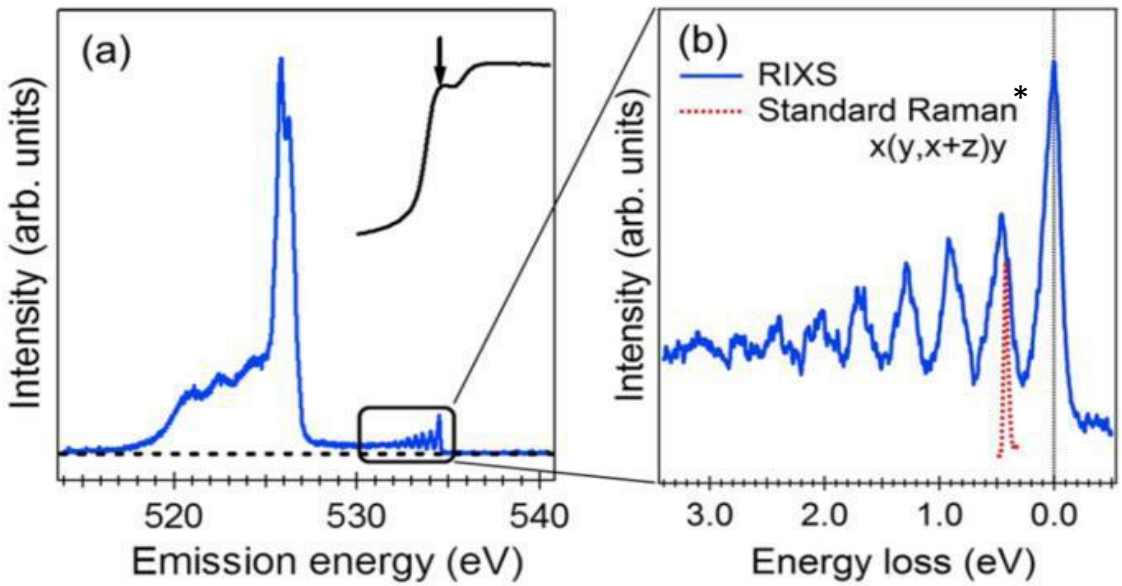
gaseous water

Vibration(s)	liquid H_2O (25°C)		liquid D_2O (25°C)	
	v, cm^{-1}	eV	v, cm^{-1}	eV
v_1	3657.1	**0.4530**	2671.7	0.3309
v_2	1594.7	0.1975	1178.4	0.1460
v_3	3755.9	**0.4653**	2787.7	0.3453

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

Vibrational RIXS in liquid water

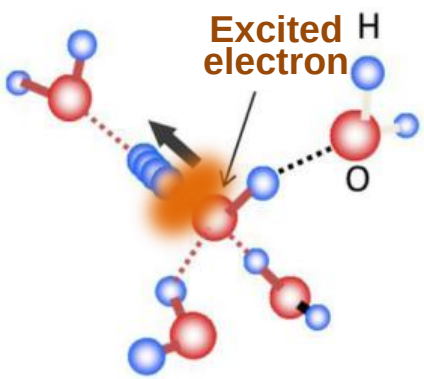
Y. Harada *et al*. PRL **111**, 193001 (2013).



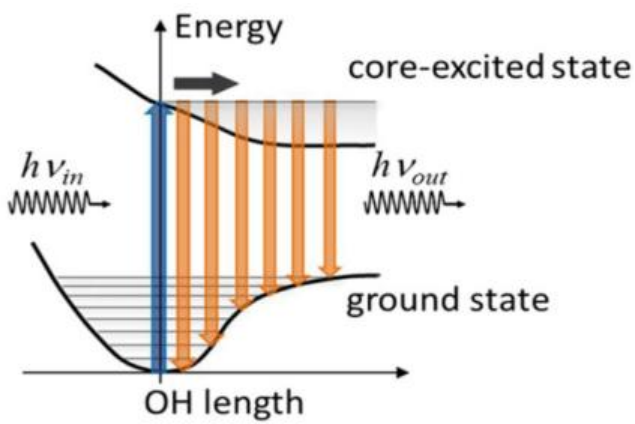
OH stretching mode is dominantly excited

Sensitive to the local hydrogen bond coordination selected by excitation energies

Excitation energy dependence of the vibrational RIXS



Real space



Energy space

*G. E. Walrafen *et al*., Chem. Phys. **85**, 6964 (1986).

Soft X-ray vibrational spectroscopy of water

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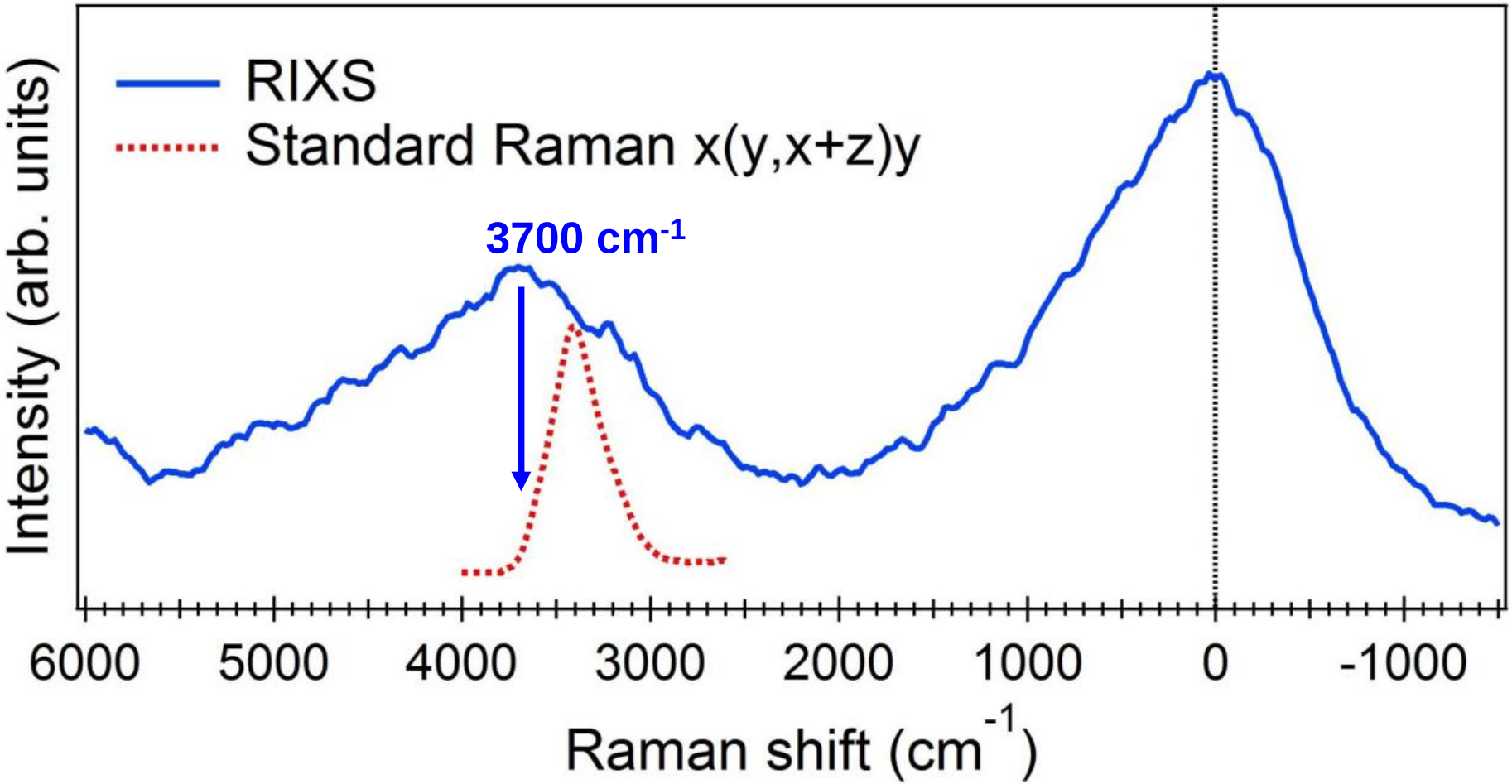
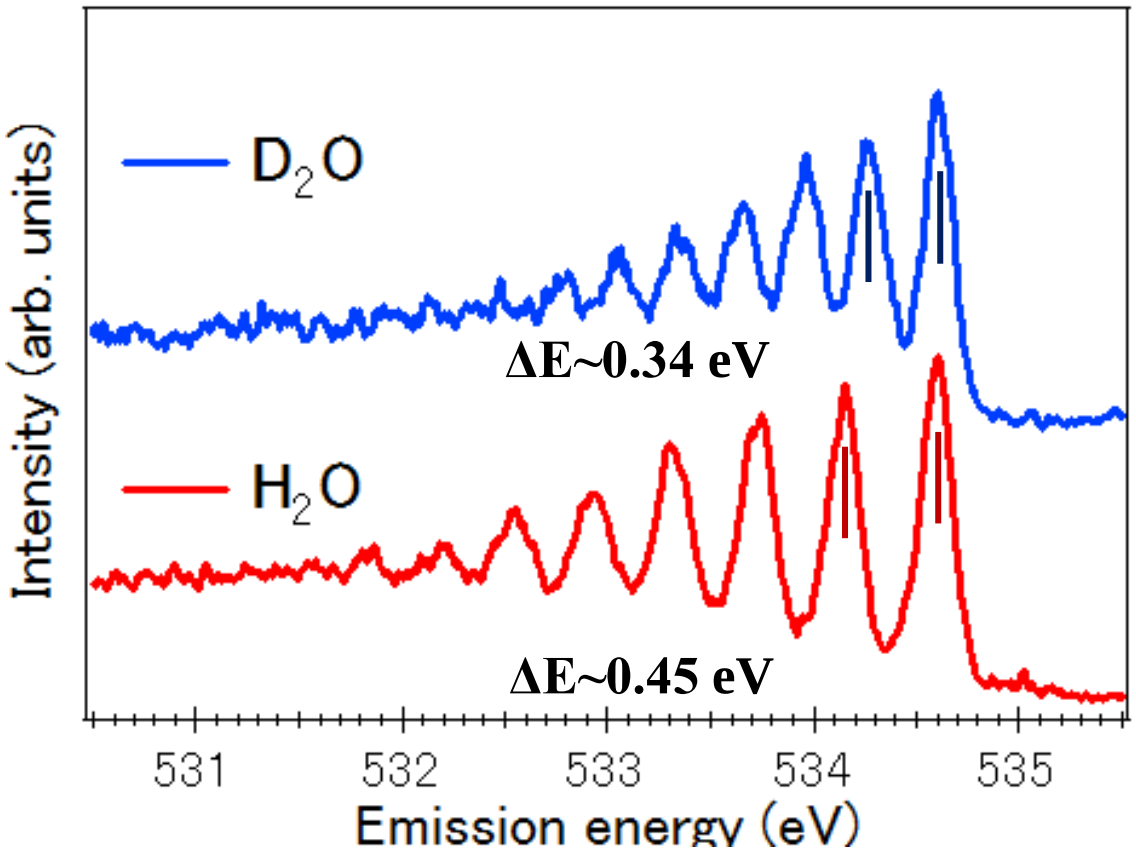
Y. Harada *et al*. PRL. **111**, 193001 (2013).



Raman spectrum by
GE Walrafen Chem. Phys. **85**, 6964

Isotope effect

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

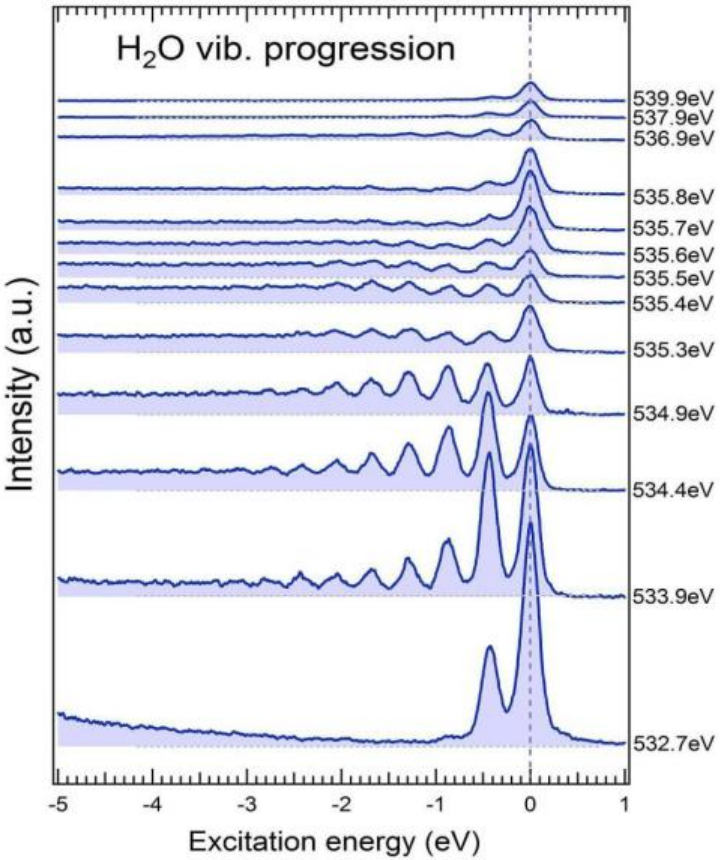


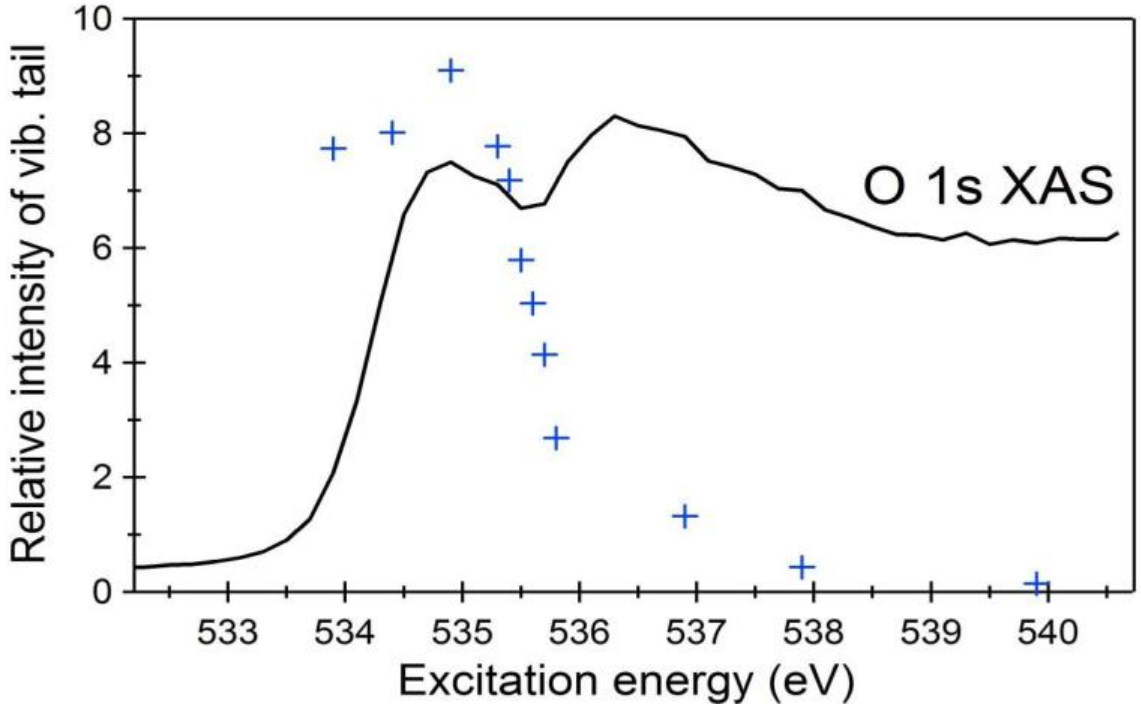
The energy of the fundamental vibrational mode is close to that of gas phase water, rather than liquid water.

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

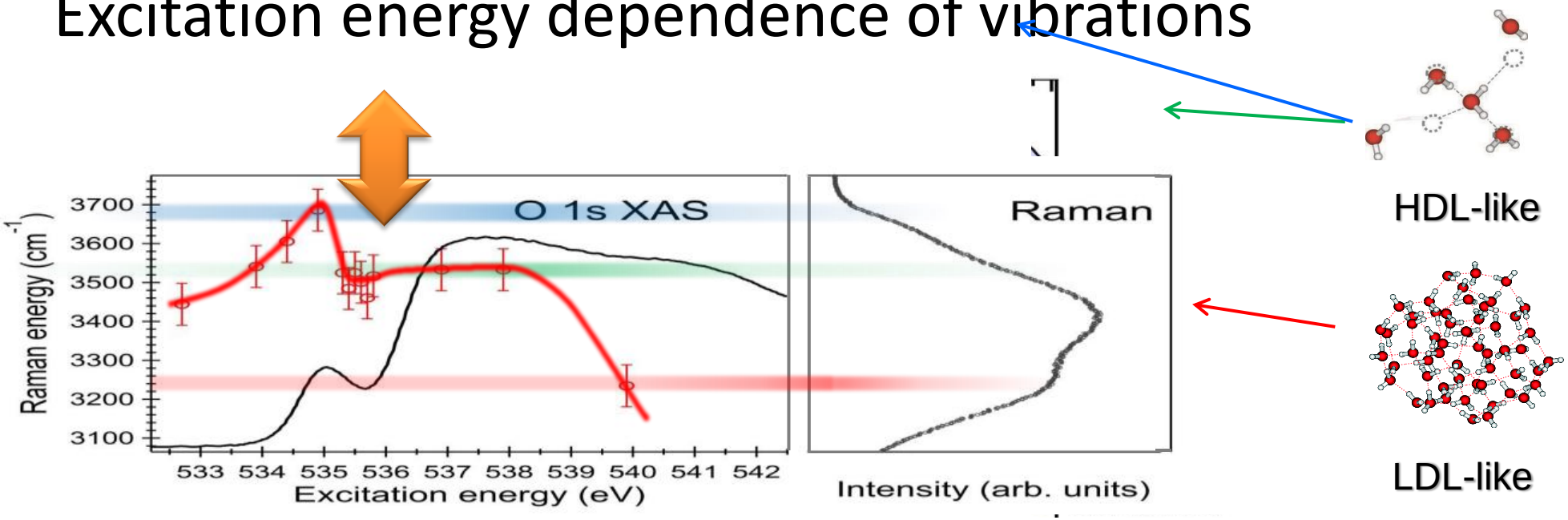
Excitation energy dependence

Y. Harada *et al.* Unpublished

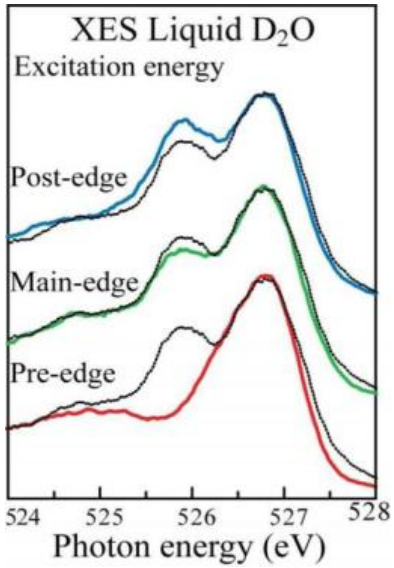




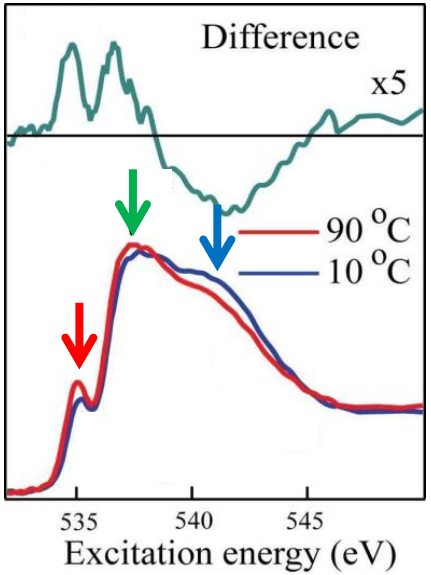
Excitation energy dependence of vibrations



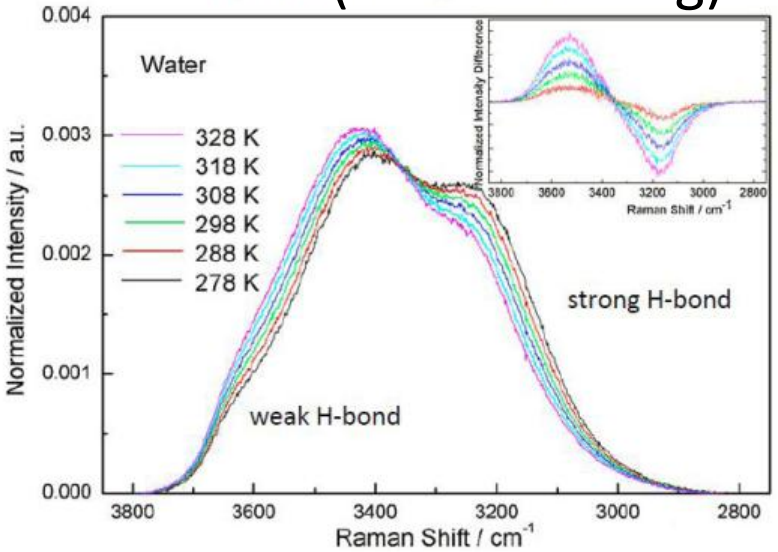
O 1s XES



O 1s XAS



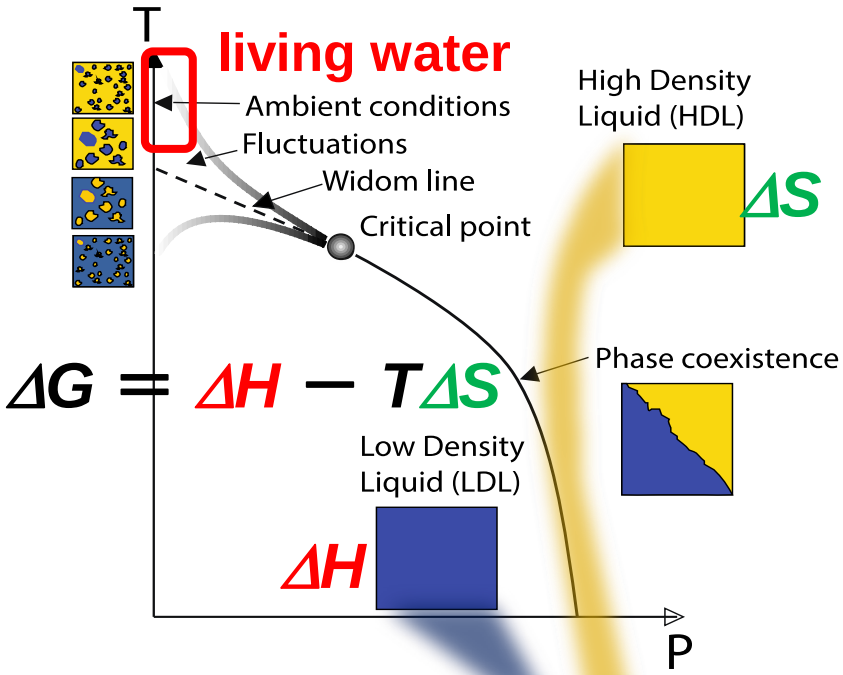
Raman (OH stretching)



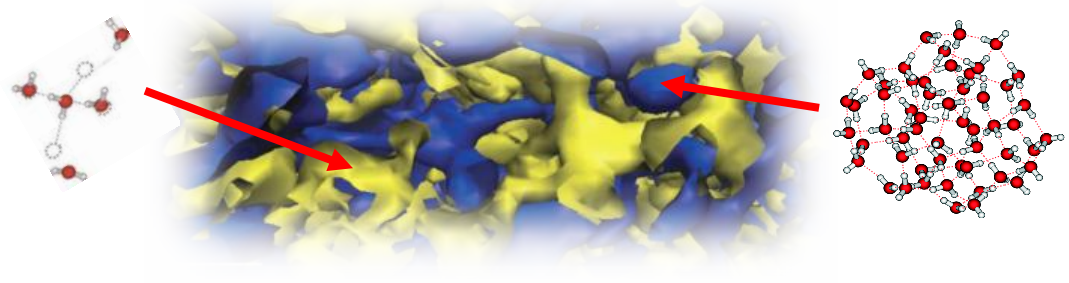
Q. Sun, Vib. Spectrosc. **62** (2012) 110.

Heterogeneous hydrogen bond in liquid water

Courtesy of Nilsson and Pettersson

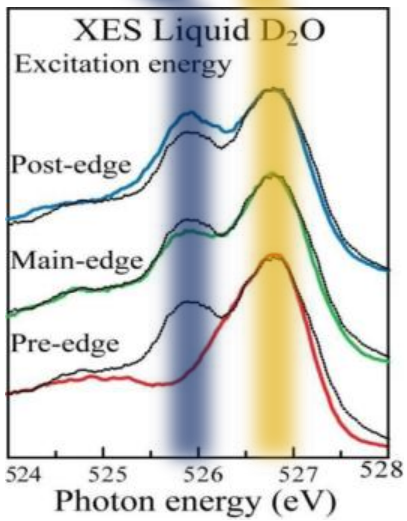


Competition between
Enthalpy (ΔH) & Entropy (ΔS)



soft X-ray valence RIXS

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



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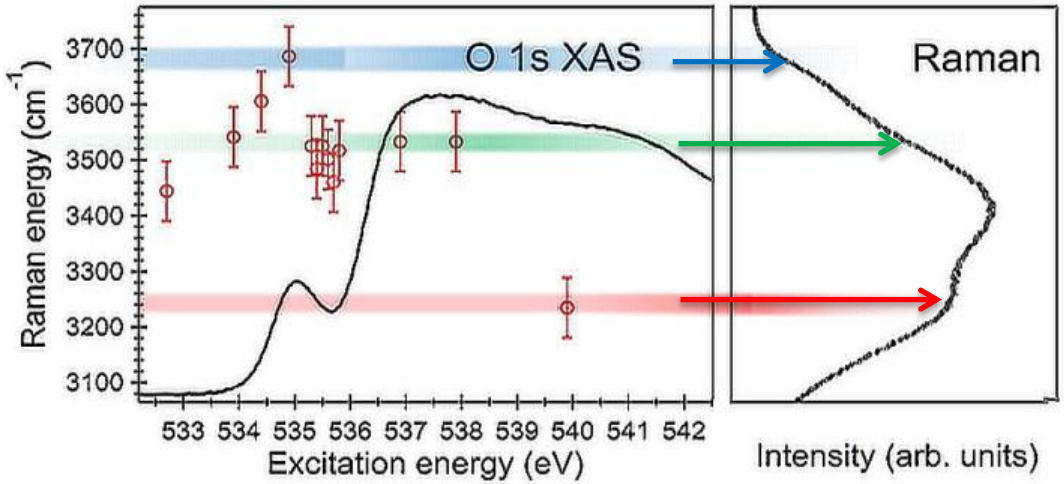
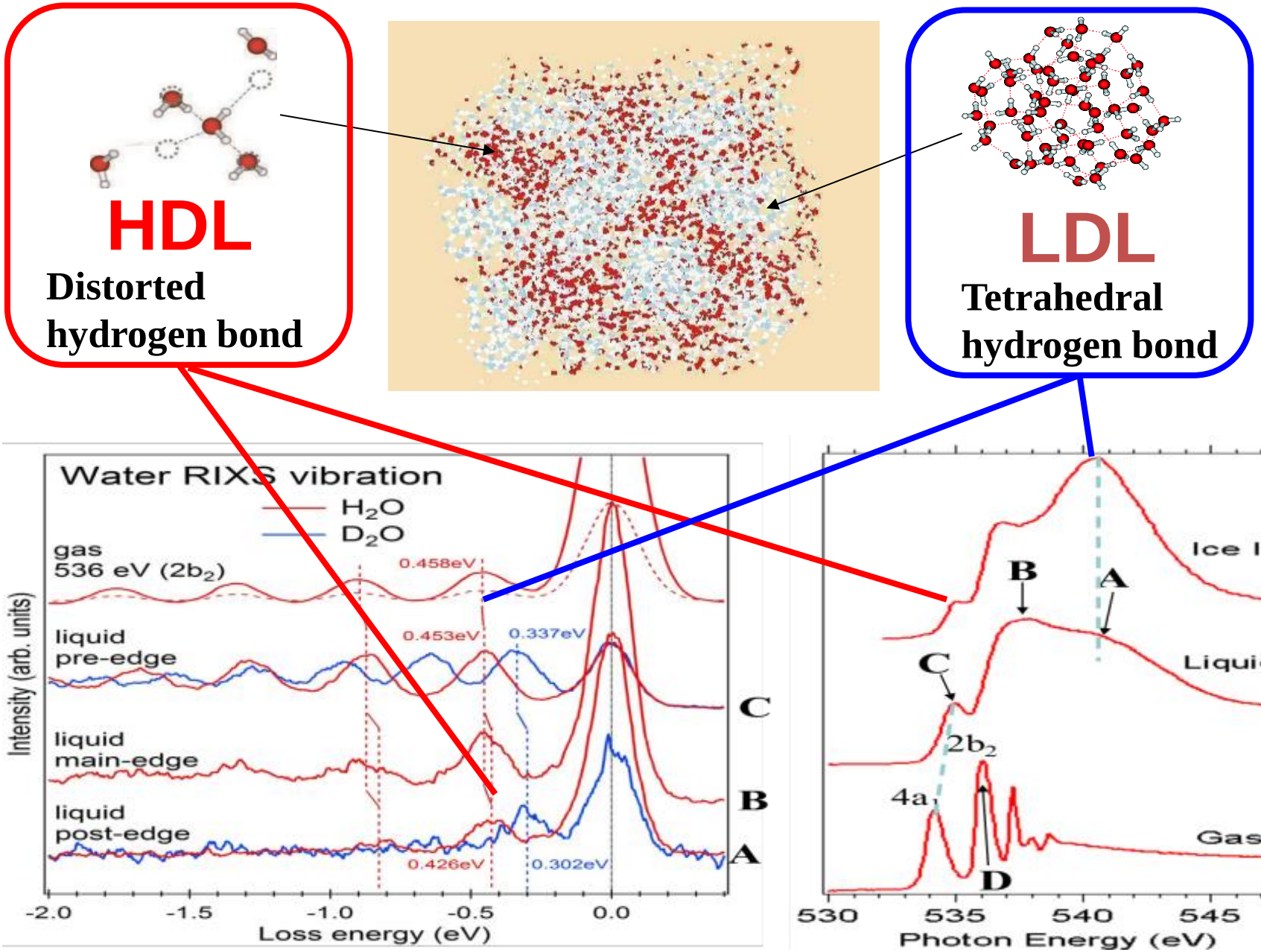


PRL (2013) & unpublished

Microheterogeneity in liquid water

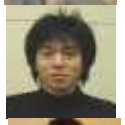


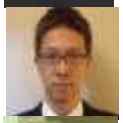
Summary

#*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

A. Takahara

Y. Higaki

M. Tanaka

H. Murakami

JASRI/SPring-8

Y. Senba

H. Ohashi

Stanford/Stockholm University

A. Nilsson

L. Pettersson

T. Wikfeldt

Financially supported by $$$$$$$

CREST & Hikari-Ryoshi

CREST
戦略的創造研究推進事業
Core Research for Evolutional Science and Technology

Photon and Quantum Basic Research Coordinated Development Program by MEXT

Thank you for your attention !

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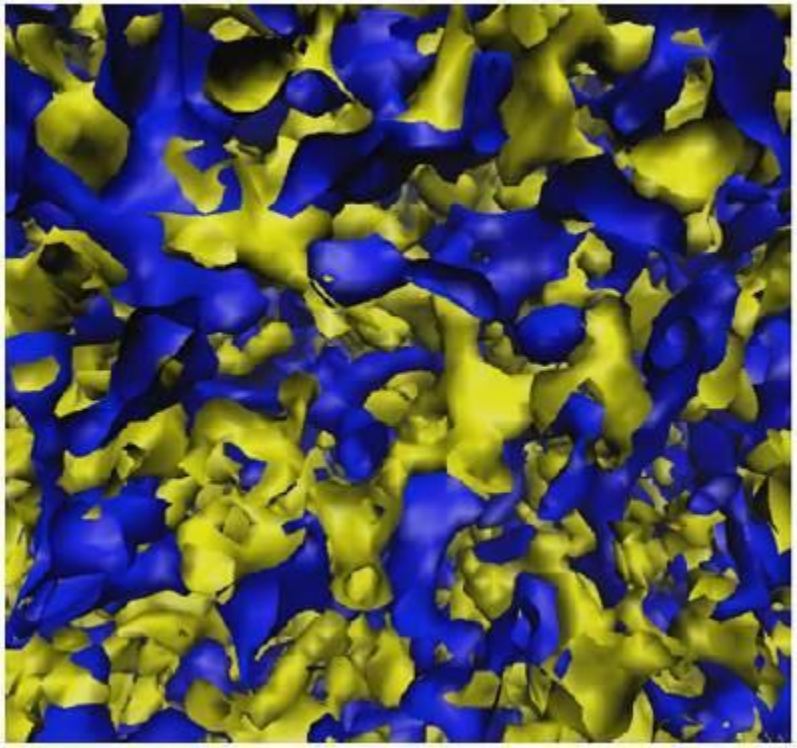

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