2015.7.27 PF研究会

「共鳴軟Ｘ線非弾性散乱と振動分光」

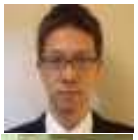
東京大学物性研究所
原田慈久

謝辞（敬称略）

東大（物性研・応化・放射光機構）


丹羽秀治（PD，筑波大8/1～）


小林正起（PD，現KEK-PF）


宮脇　淳（助教）


木内久雄（D3）


中島淳貴（修士,現シャープ）


小瀬川友香（技術補佐員）


尾嶋正治（東大放射光）

理研励起秩序研究チーム


徳島高


堀川裕加


辛　埴

東北大学


折茂慎一


高木成幸

JASRI/SPring-8


仙波泰徳


大橋治彦

広島大学


高橋　修

筑波大学


関場大一郎


栗田圭輔

EPFL(École Polytechnique Fédérale de Lausanne)


Marco Grioni

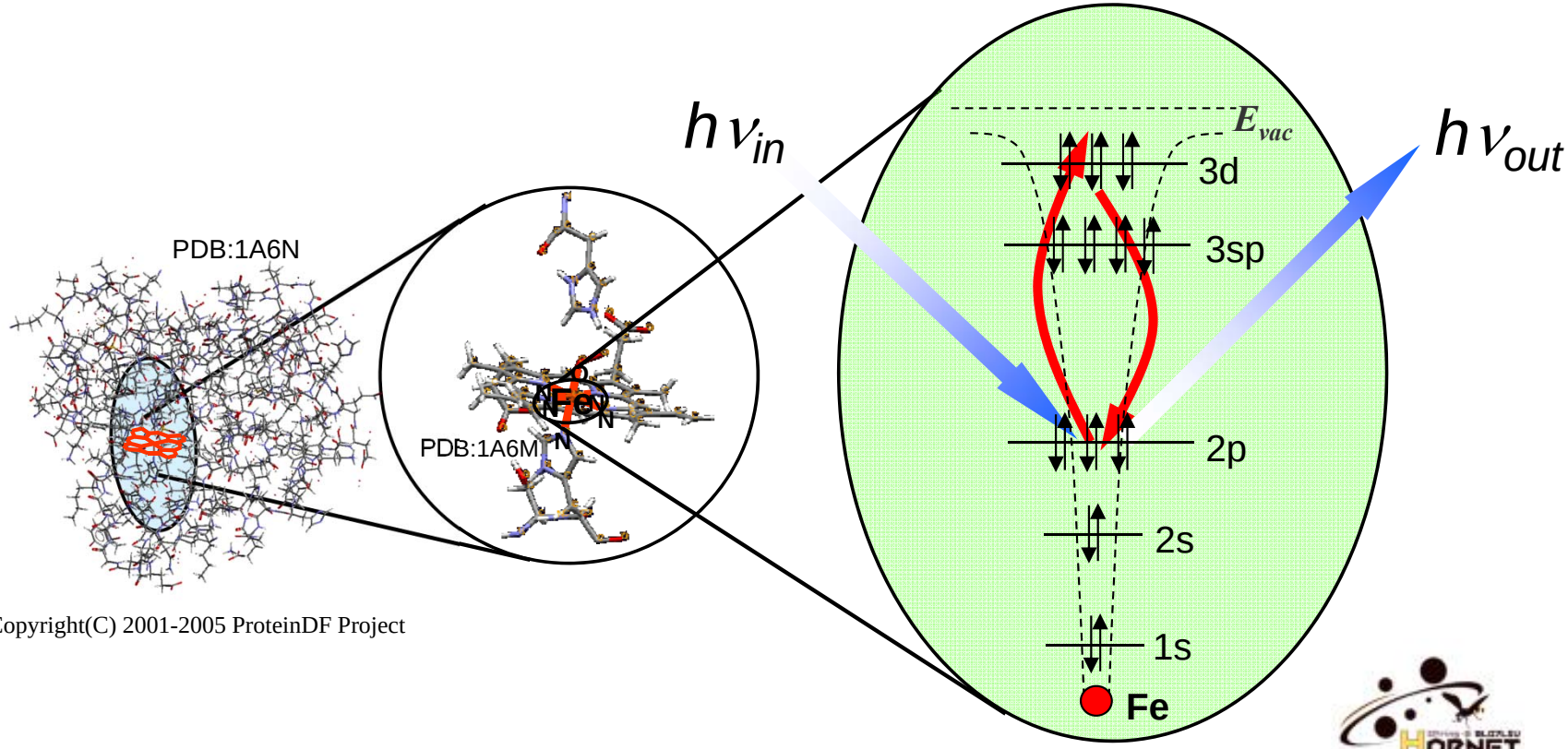

Moser Simon

SLAC, Stanford/Stockholm Univ.


Lars G.M. Pettersson


Anders Nilsson

軟X線発光分光とその特長



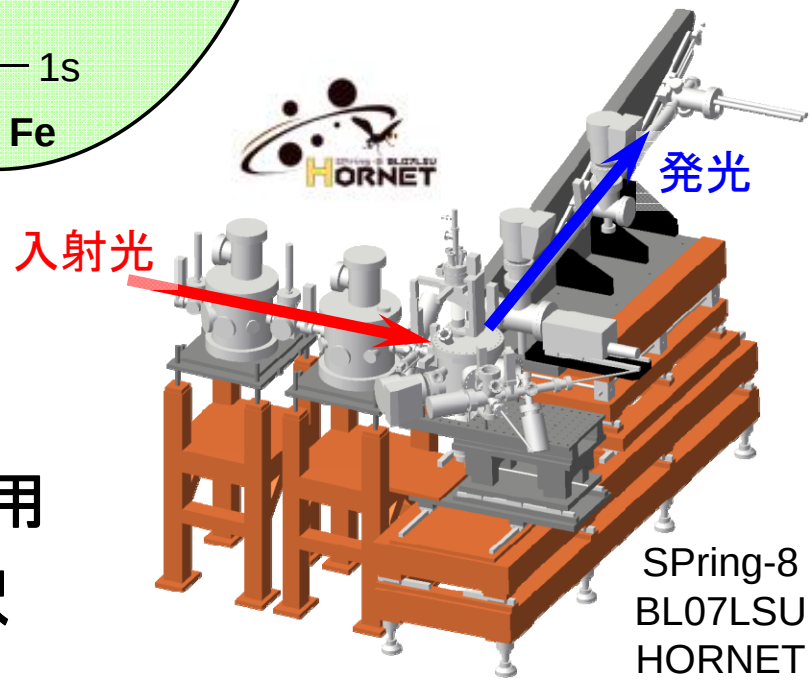
■内殻励起　⇒元素選択性

■双極子遷移　⇒軌道選択性

■軟X線-in/out　⇒深い侵入長(~1μm)

⇒絶縁体、溶液、ガス等への応用

■偏光利用　⇒結晶の異方性, 角運動量選択



SPring-8
BL07LSU
HORNET

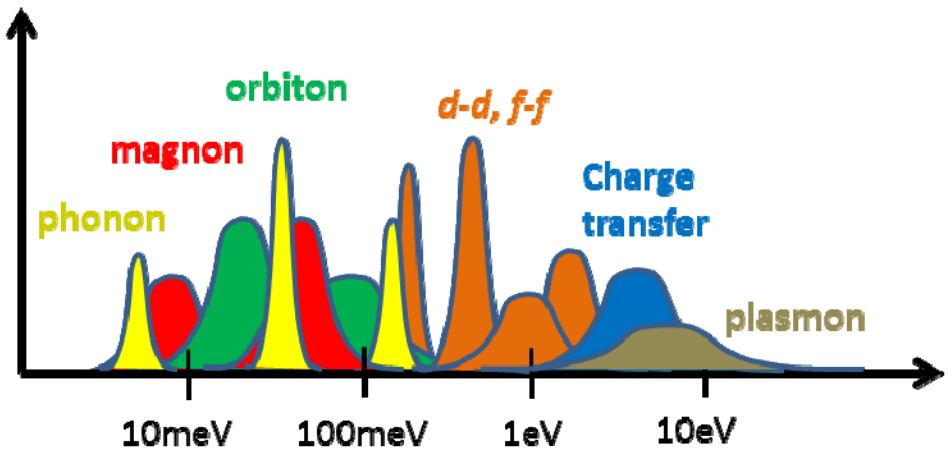
共鳴軟X線発光分光と素励起

超高分解能化 ⇒ 100 meV オーダーの素励起

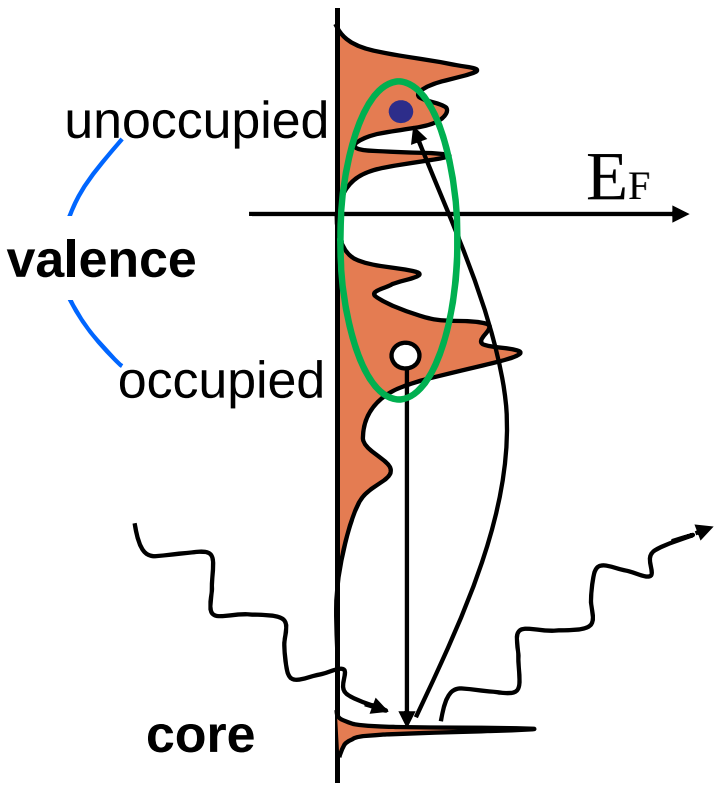
<u>element-specificity +</u>

- crystal field excitations
- vibrational(or phonon) excitations
- spinon or magnon excitations
- orbiton excitations

etc.



RXES or RIXS

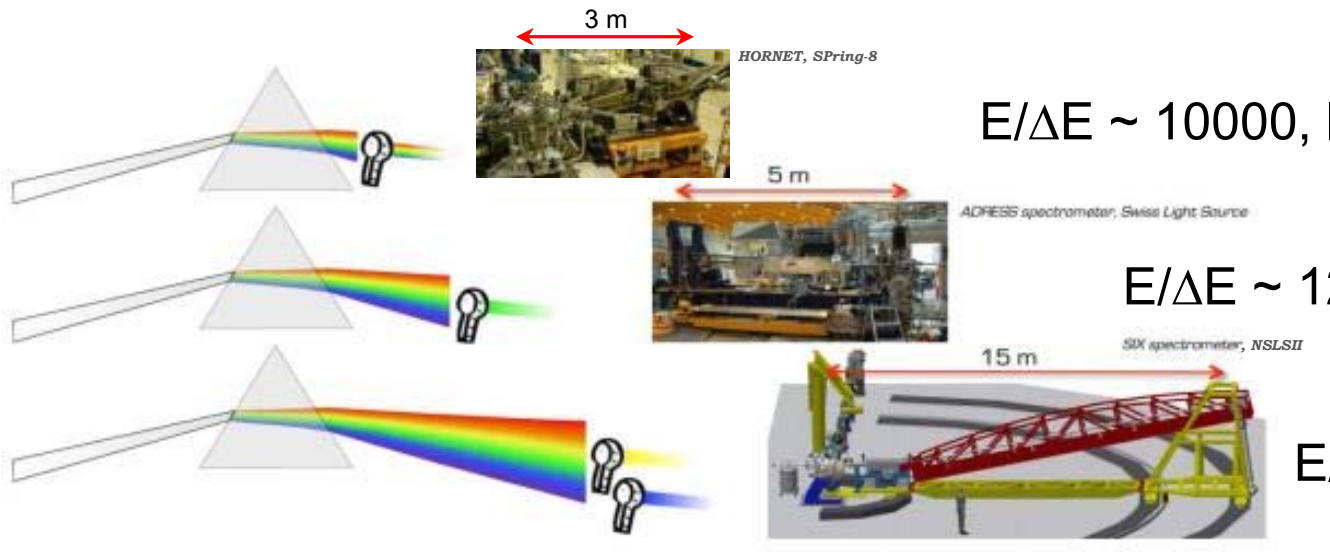


内殻正孔寿命で制限されない分解能

⇩

素励起の寿命幅 （~ 1meV）で制限

究極の分解能を目指す軟X線発光分光



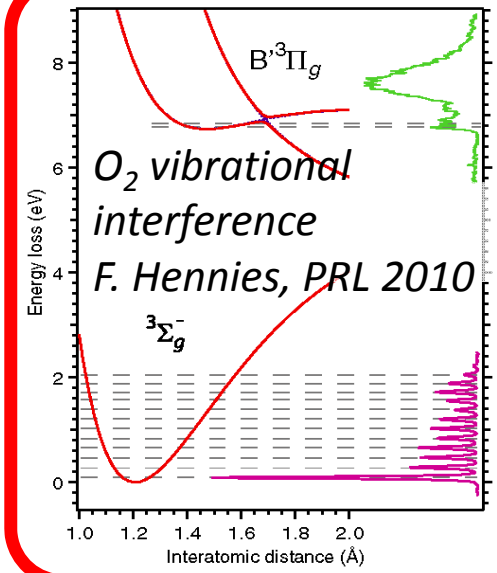
E/ΔE ~ 10000, liquid/operando, (角度分解)
Y. Harada, 2010

E/ΔE ~ 12000, 角度分解
G. Ghilingelli, 2008

E/ΔE ~ 100000, 角度分解
J. Ignace, 2017～?

liquids & gases - solution chemistry, batteries, photocatalysts, water etc..

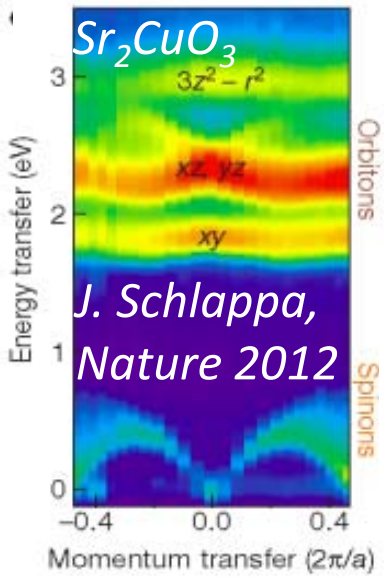
solids - superconductor, insulator, multiferroics, topological materials etc..



振動モードの完全分離

X線励起の振動分光で
電子状態・ポテンシャルと
構造の情報を統合

水への適用例:
Y. Harada et al. PRL 2013



角度分解の導入により
素励起のE-k分散を観測

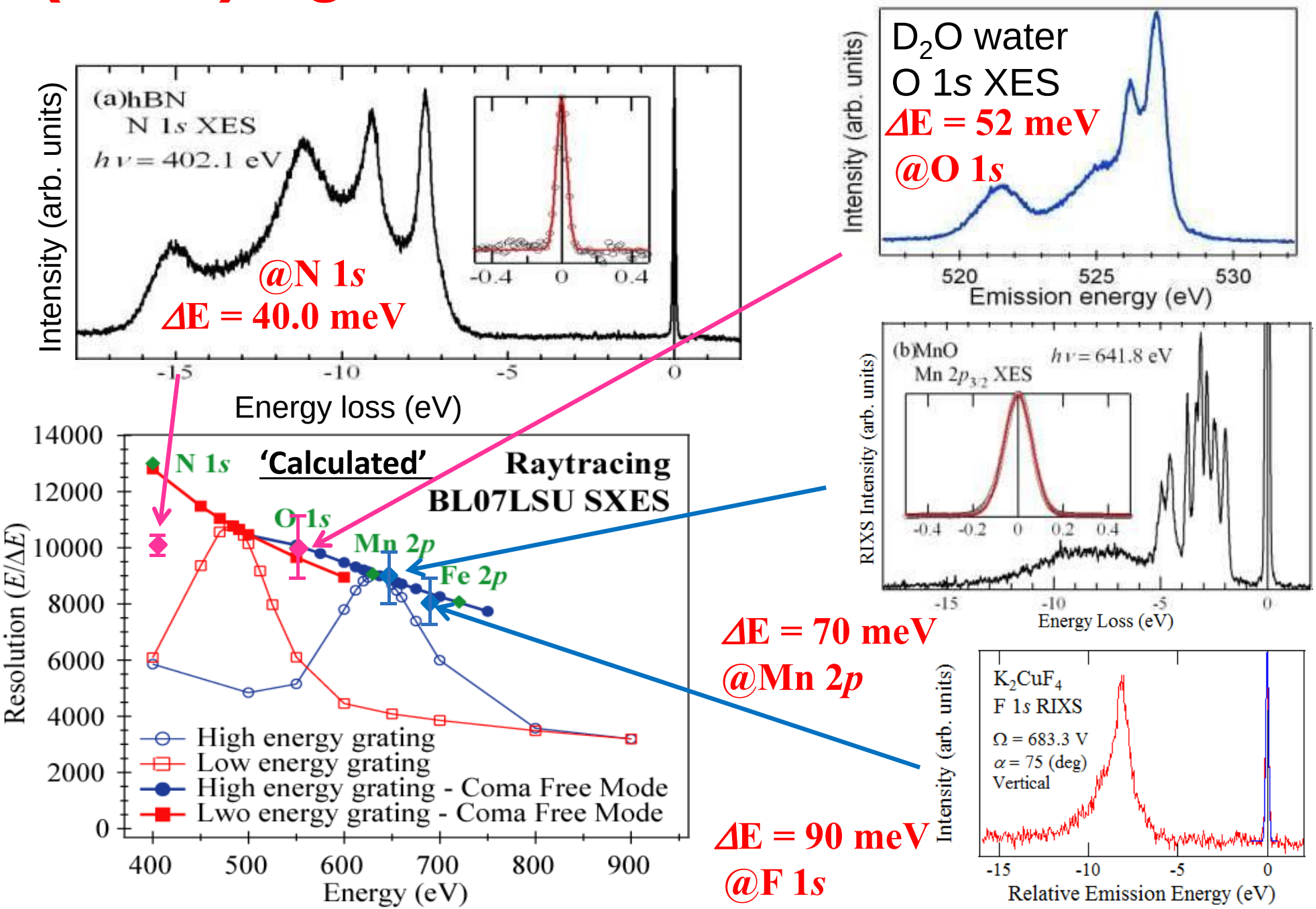
高分解能化＆偏光依存により、10meVオーダーの
マグノン・フォノン・オービトン
等の素励起を分離可能に

Experimental

Ultrahigh resolution soft X-ray emission spectroscopy @ SPring-8 BL07LSU HORNET station

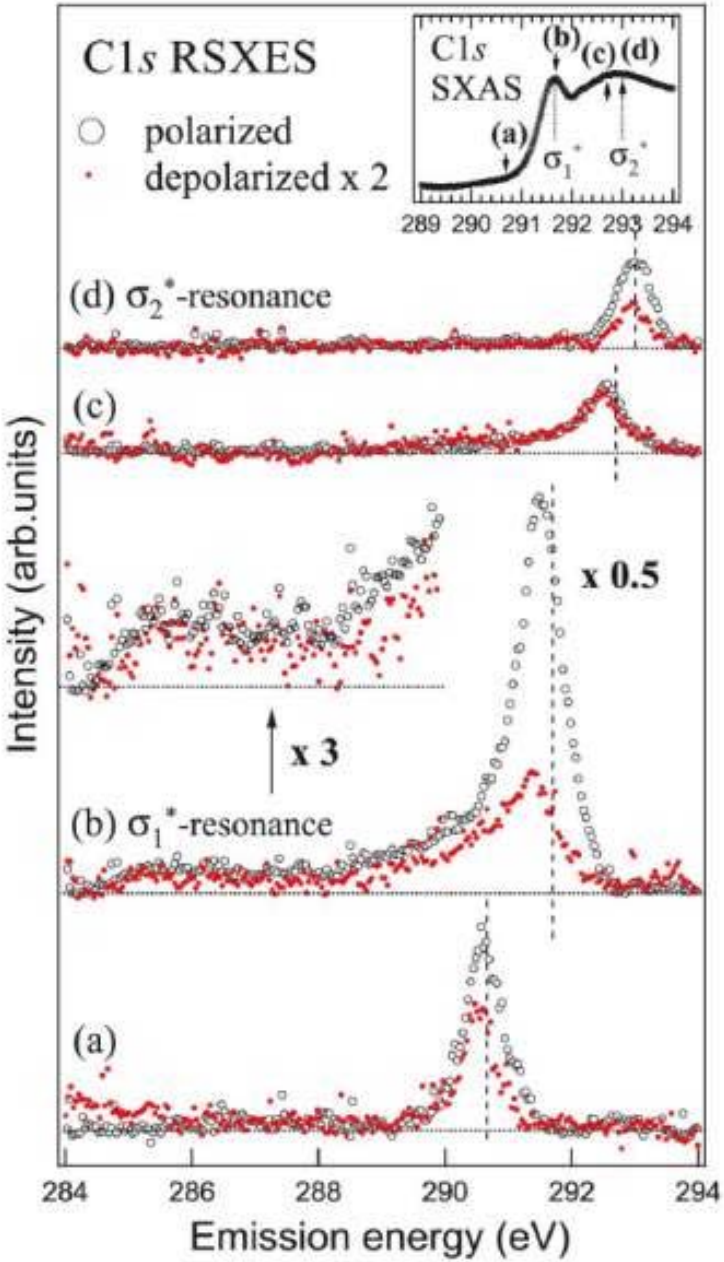
(Ultra)high resolution

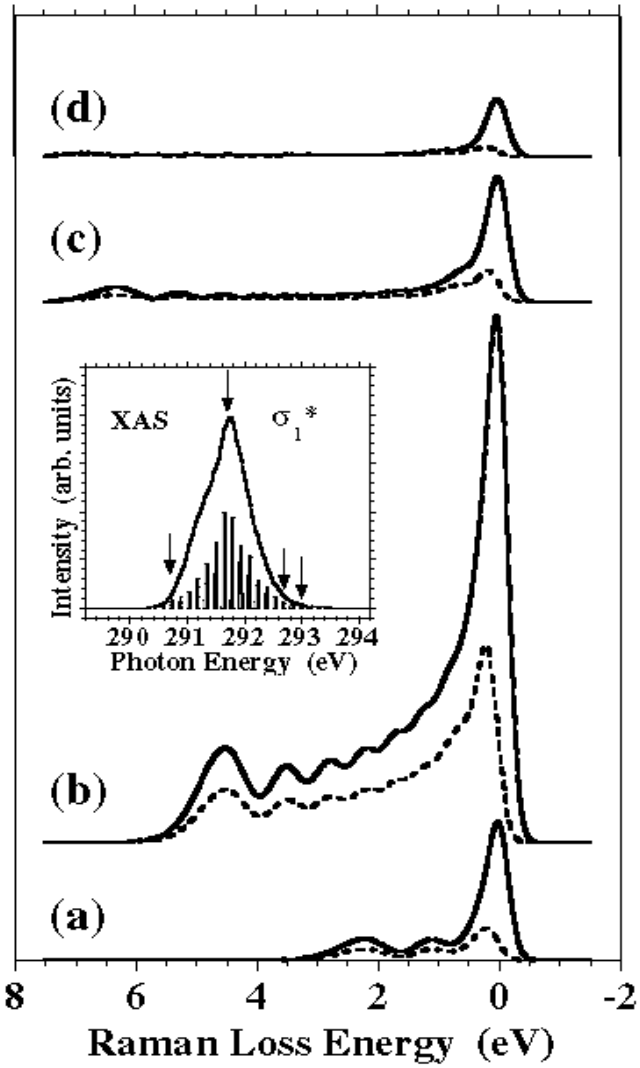
Y. Harada et al.,RSI ***83****, 013116. (2012)*

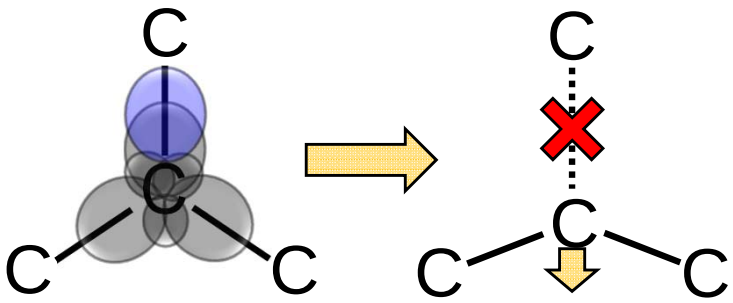


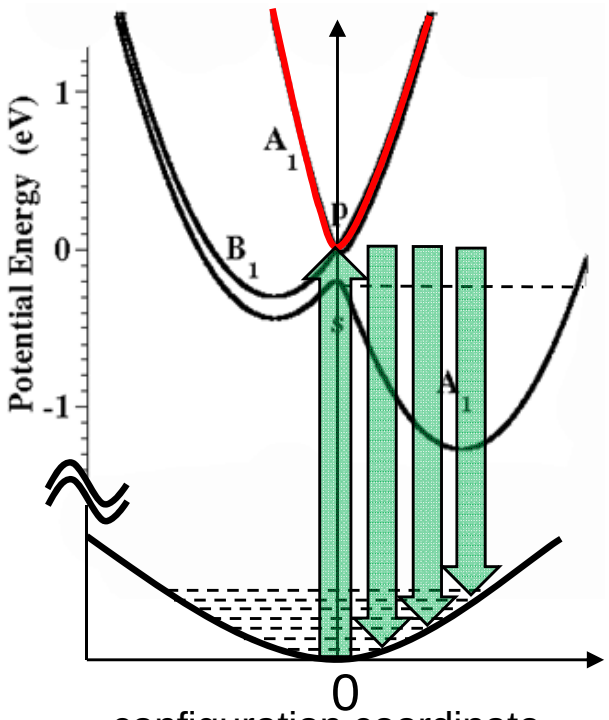
C 1s vibrational RIXS of graphite

Harada *et al*., PRL **93**, 017401 (2004)





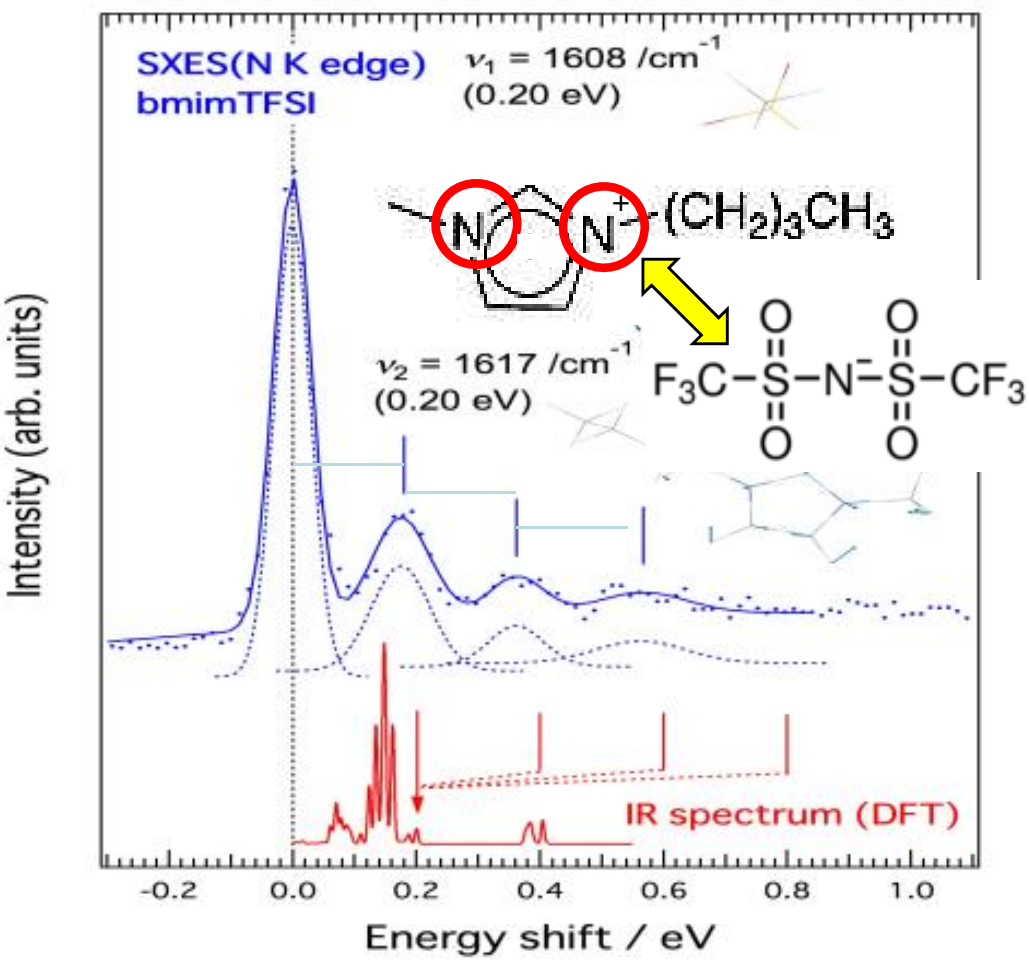


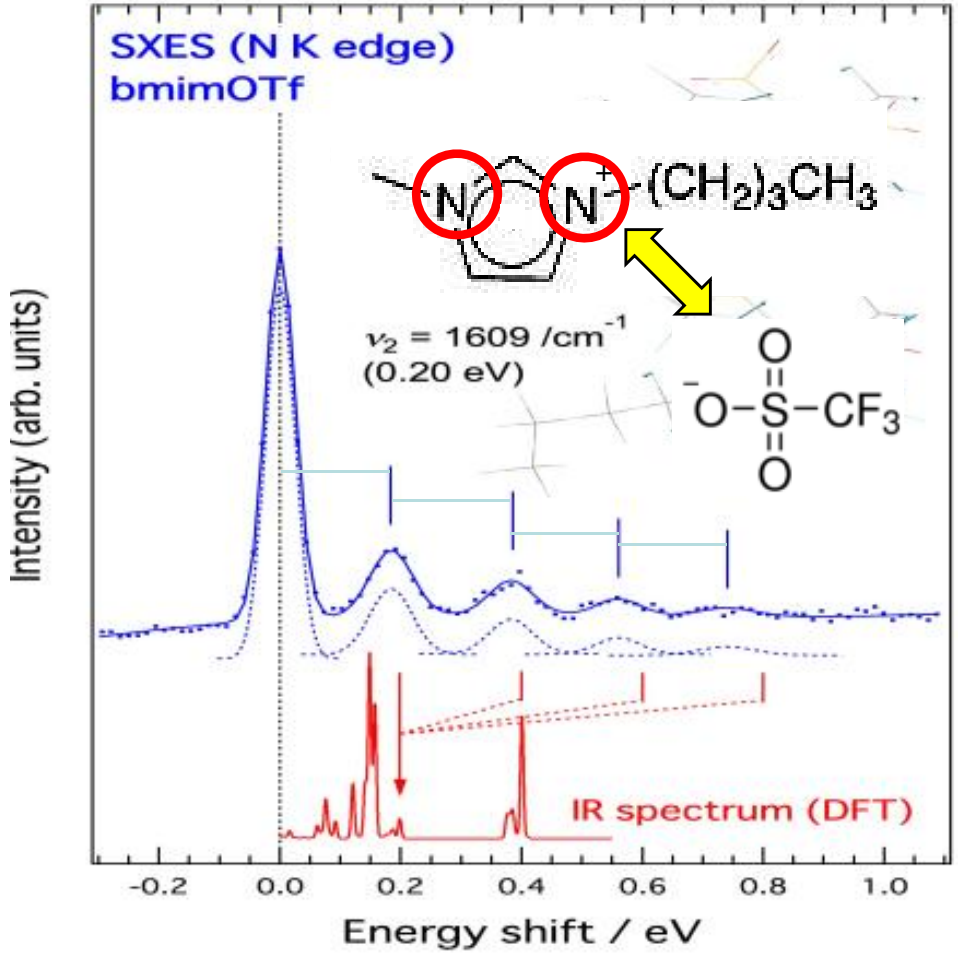


configuration coordinate
(C-C bond direction)

Ionic liquids (weak interaction with anions)

東京理科大　金井ら



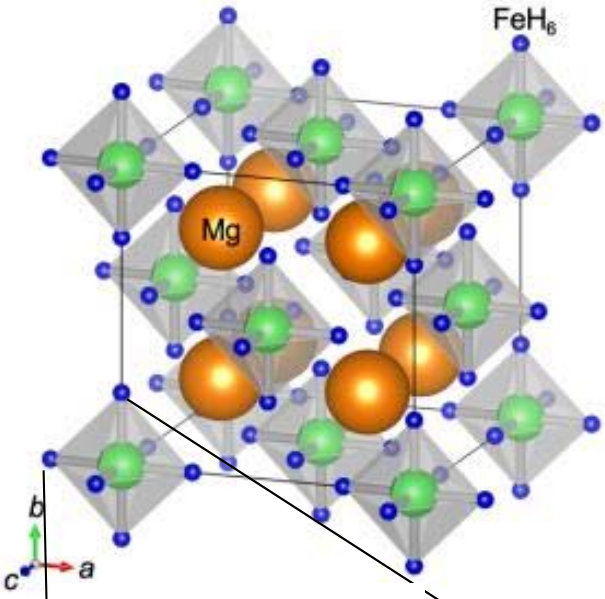


10 cm^{-1} (~1 meV) オーダーの分解能が必要
→ 既存のシステムではまだ難しい！

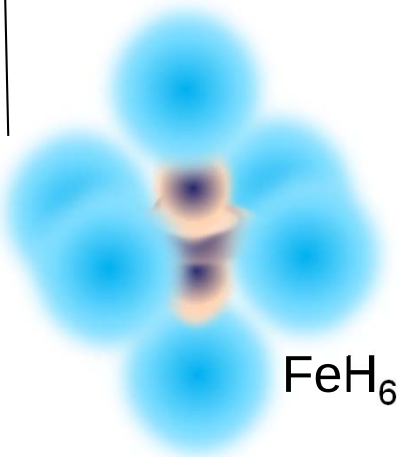
Hydrogen storage material (Very fast decay)

K. Kurita *et al.*, JPSJ **84**, 043201 (2015).

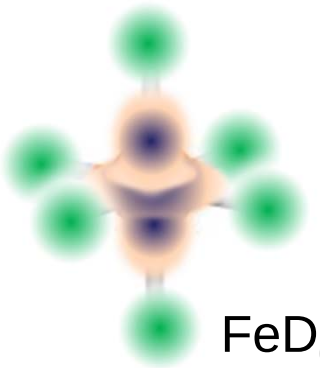
Mg_2FeH_6



FeH_6 cluster

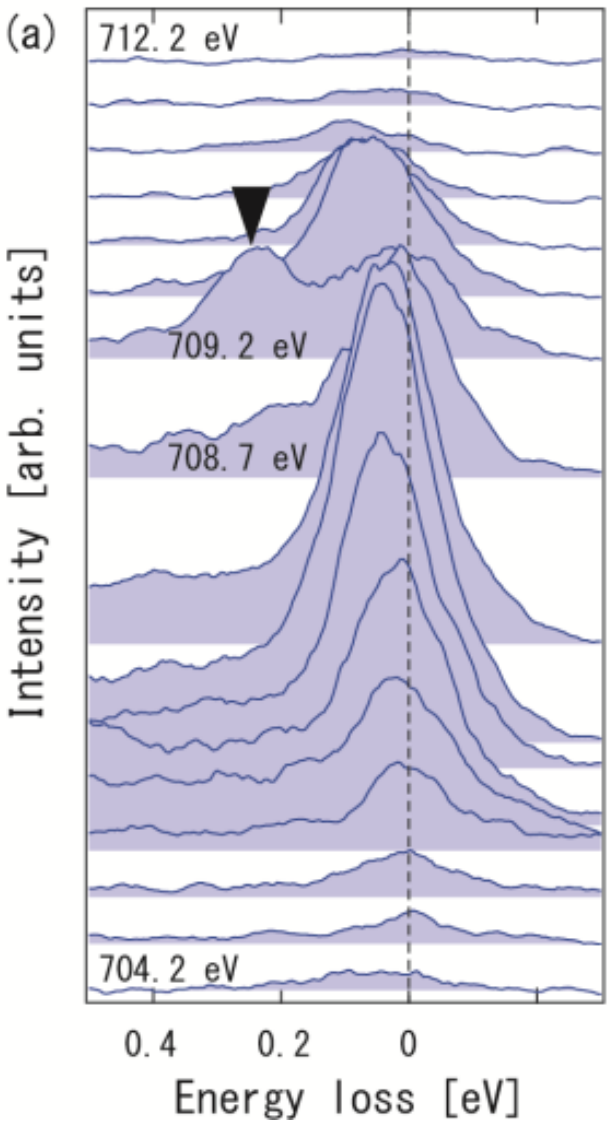


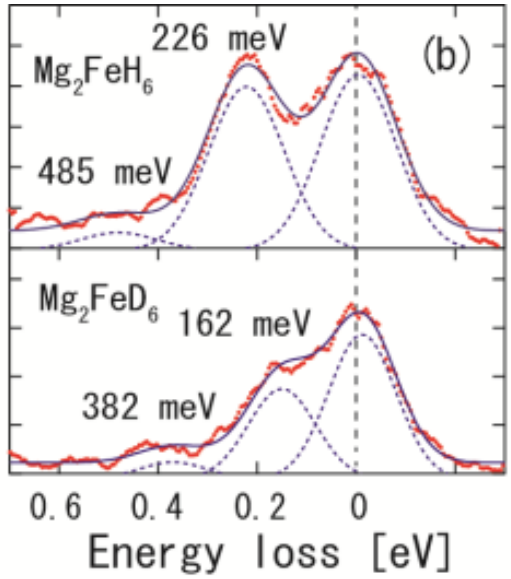
FeH_6

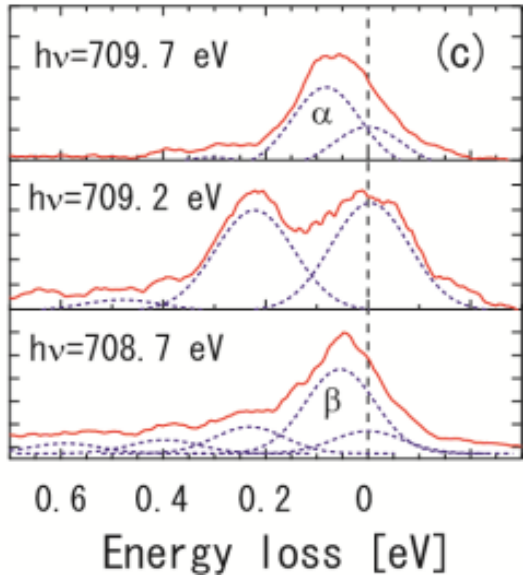


FeD_6

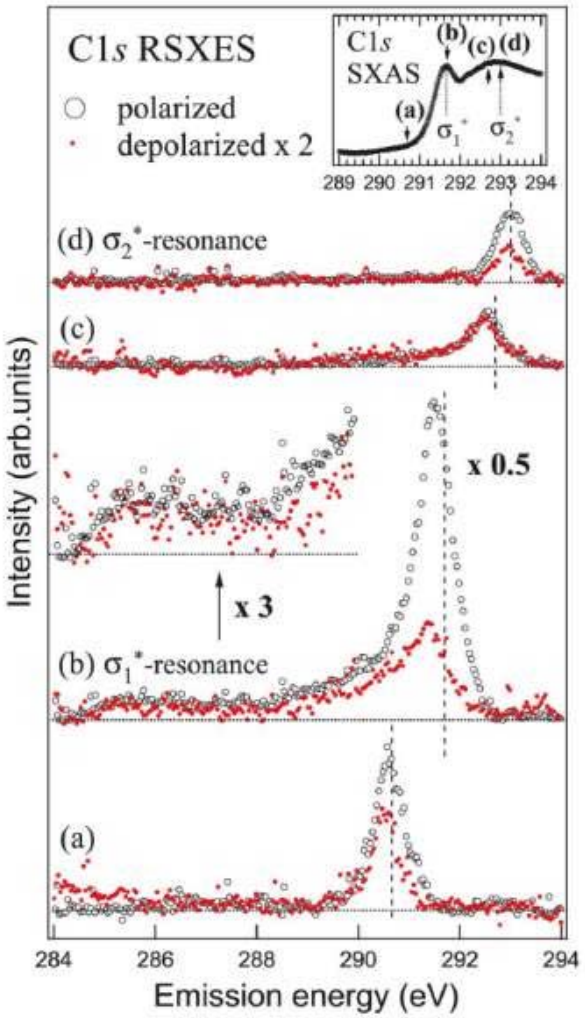
Fe 2*p* RIXS

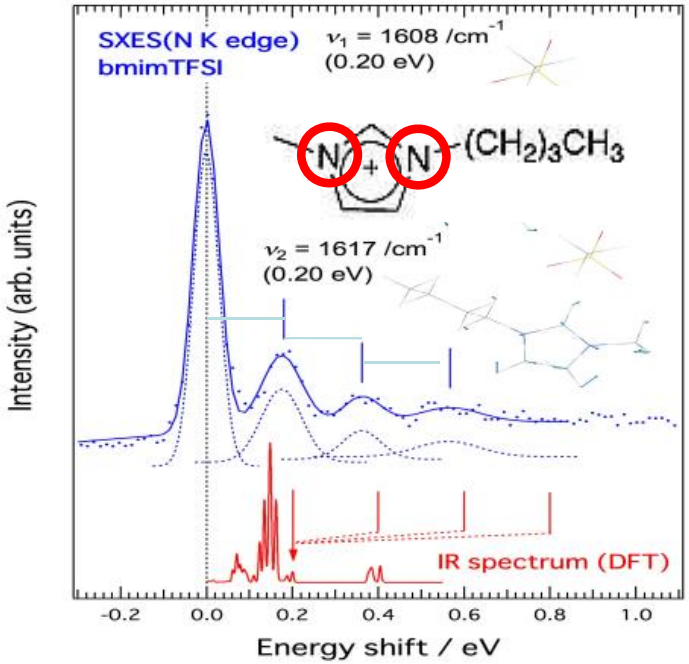


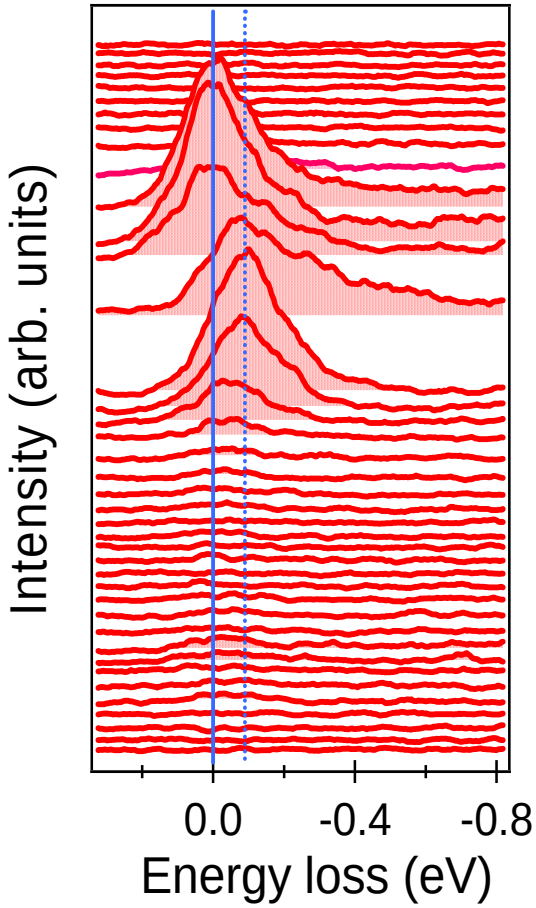




Vibrational RIXS at different timescales







graphite

C 1s ~ 10fs

ionic liquids

N 1s ~ 6fs

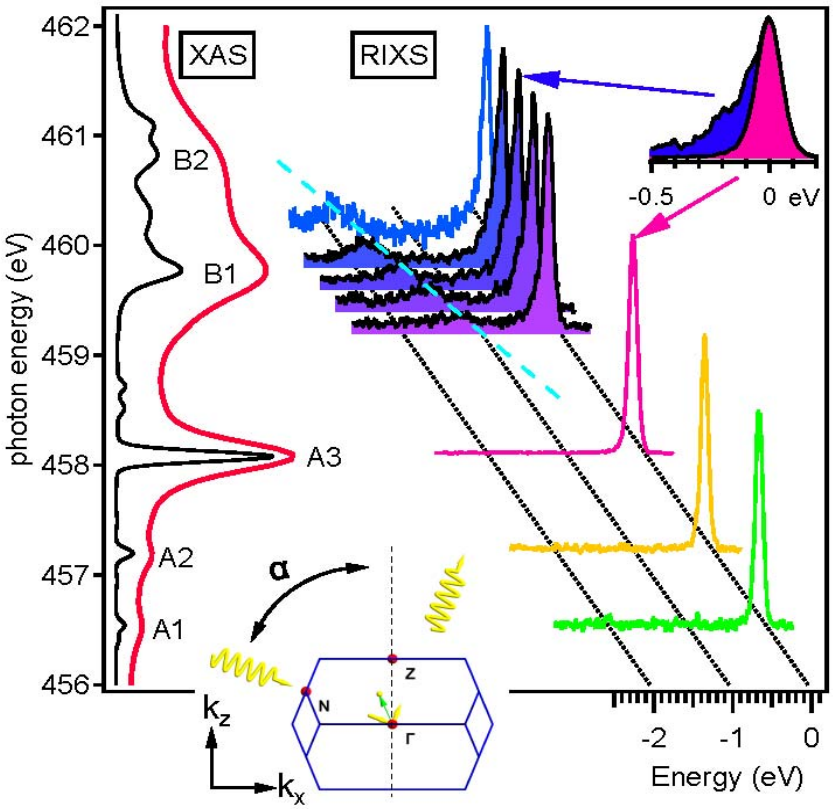
Mg_2FeH_6

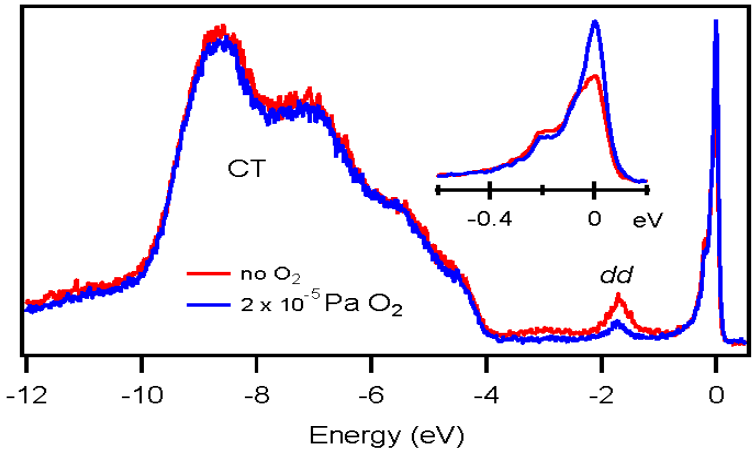
Fe $2p_{3/2}$ ~ 0.8fs

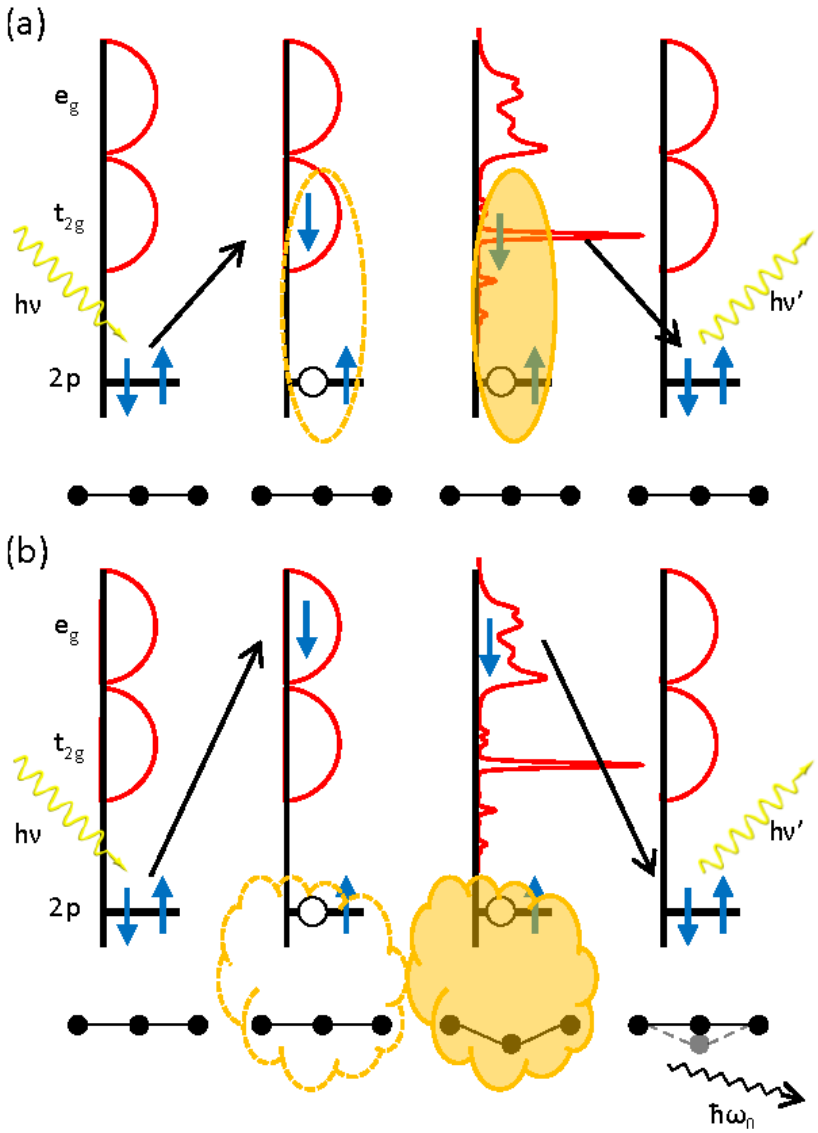
Phys. Rev. A, 22, 1615 (1980).

Anisotropic *e-ph* coupling in anatase TiO_2

S. Moser *et al.*, PRL, accepted.







Anisotropic *e-ph* coupling in anatase TiO_2

RIXS

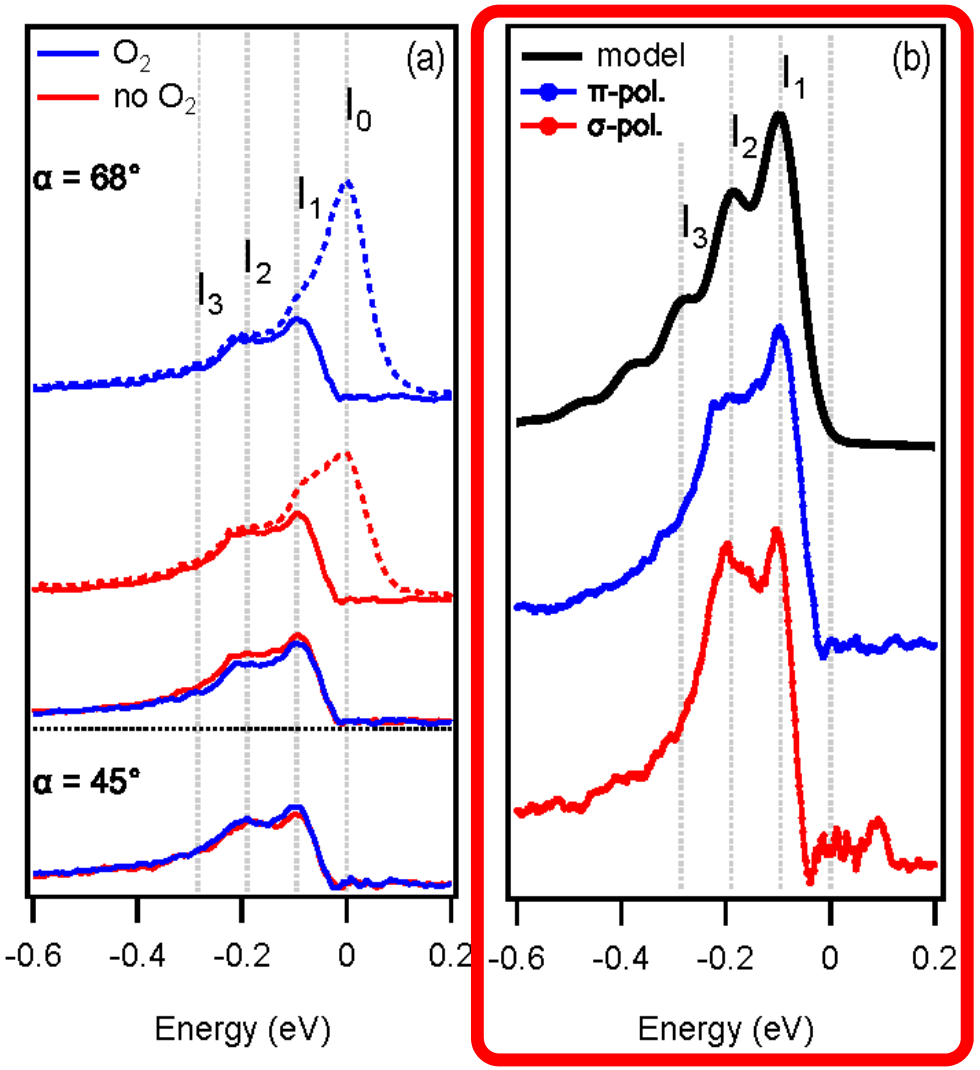
S. Moser *et al.*, PRL, accepted.

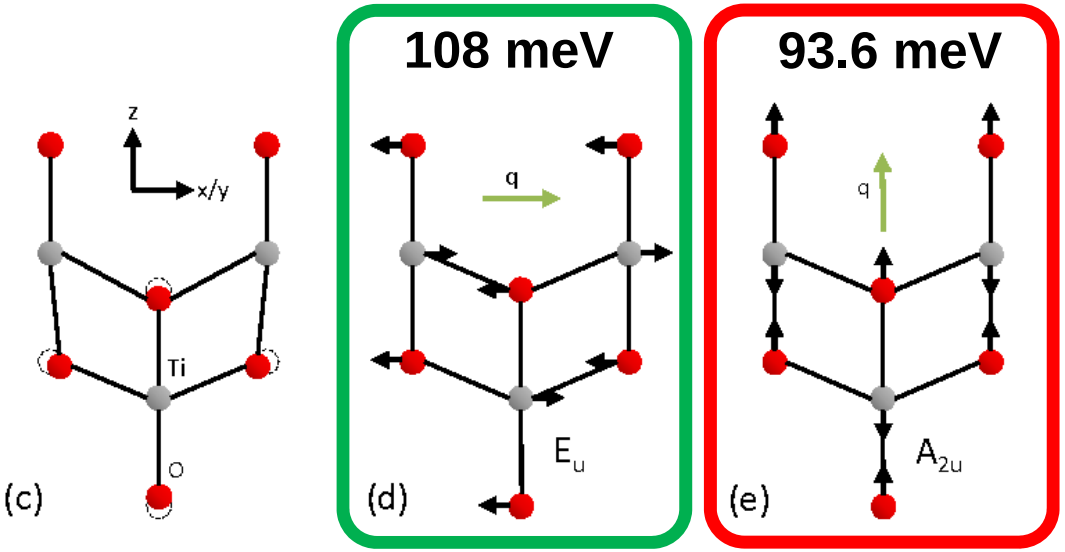
π-pol

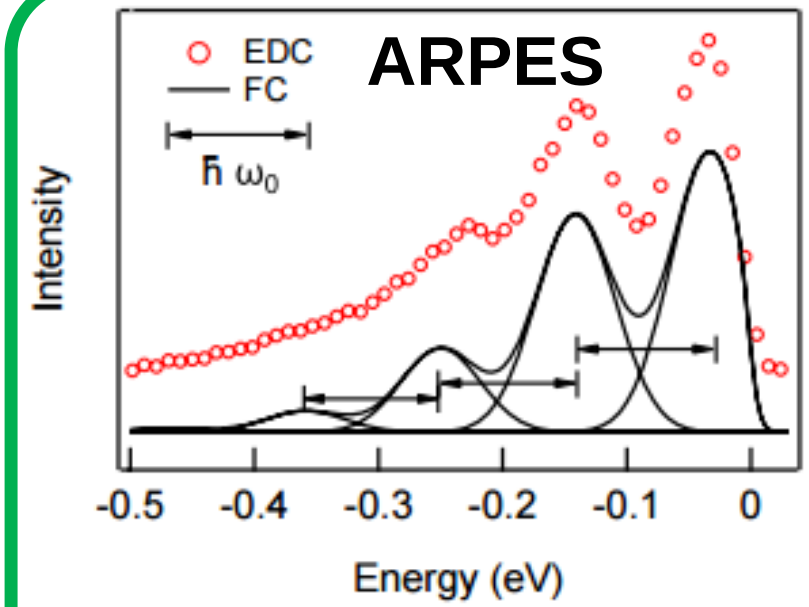
$$A_1 \otimes (E \oplus A_2)^2 = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \oplus E$$

σ-pol

$$A_1 \otimes E^2 = A_1 \oplus A_2 \oplus B_1 \oplus B_2$$





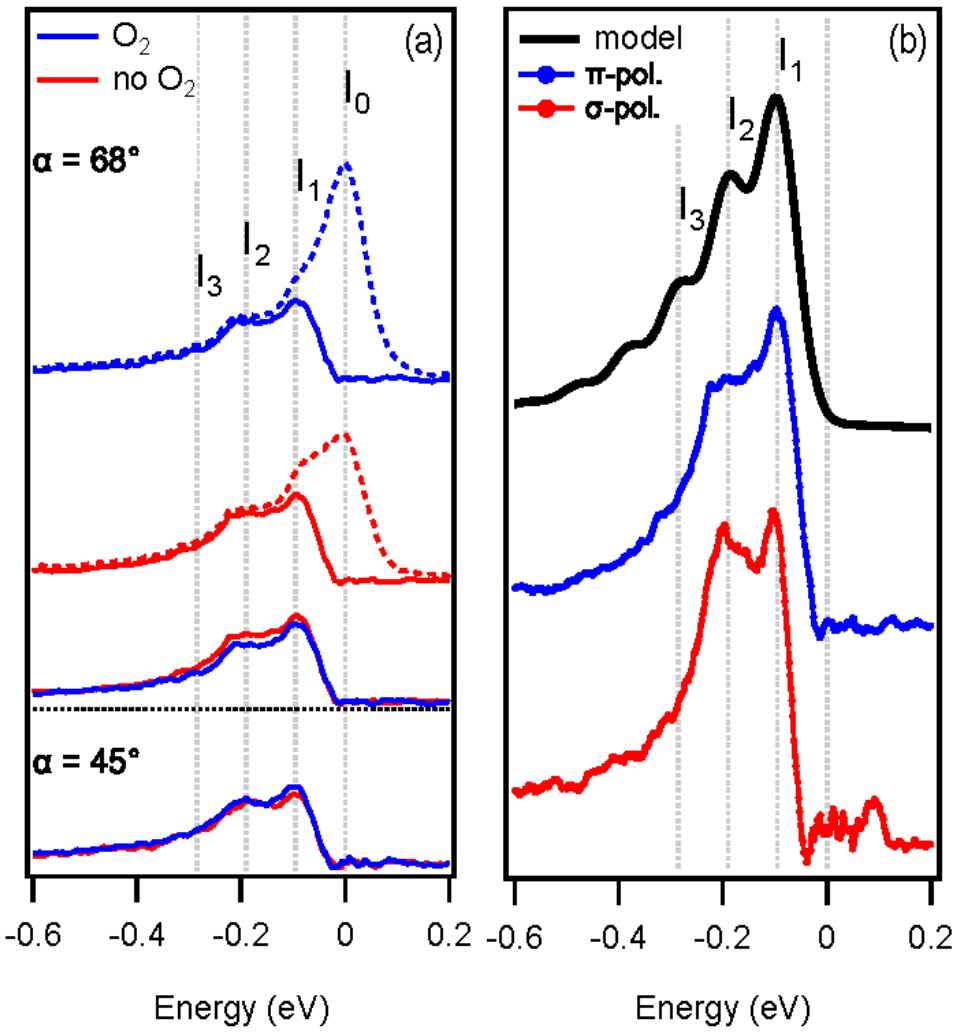


Moser *et al.*, PRL **110**, 196403 (2013)

Anisotropic *e-ph* coupling in anatase TiO_2

S. Moser *et al.*, PRL, accepted.

RIXS



Fröhlich Hamiltonian

electron phonon

$$H = M \sum_R d_R^\dagger d_R (b_R^\dagger + b_R) + \hbar\omega_0 \sum_R b_R^\dagger b_R$$

Kramers-Heisenberg

$$I(h\nu, h\nu') \propto \left| \sum_{n'=0}^{\infty} \frac{B_{\max(n,n'),\min(n',n)}(g) B_{n',0}(g)}{(g-n')\hbar\omega_0 + i\Gamma} \right|^2$$

$h\omega_0 = 93.6$ meV

$M = 130$ meV

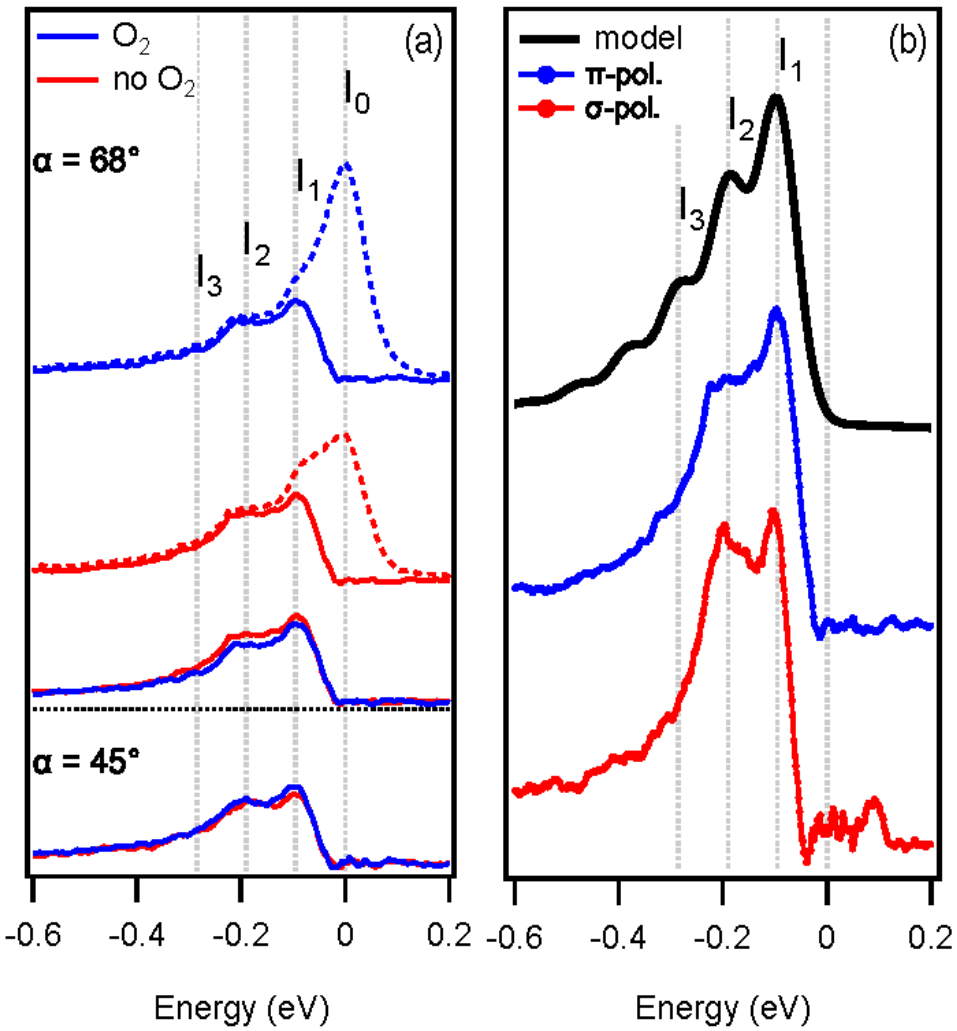
$g = M^2/(h\omega_0)^2 = 1.89 \pm 0.16$

intermediate coupling regime

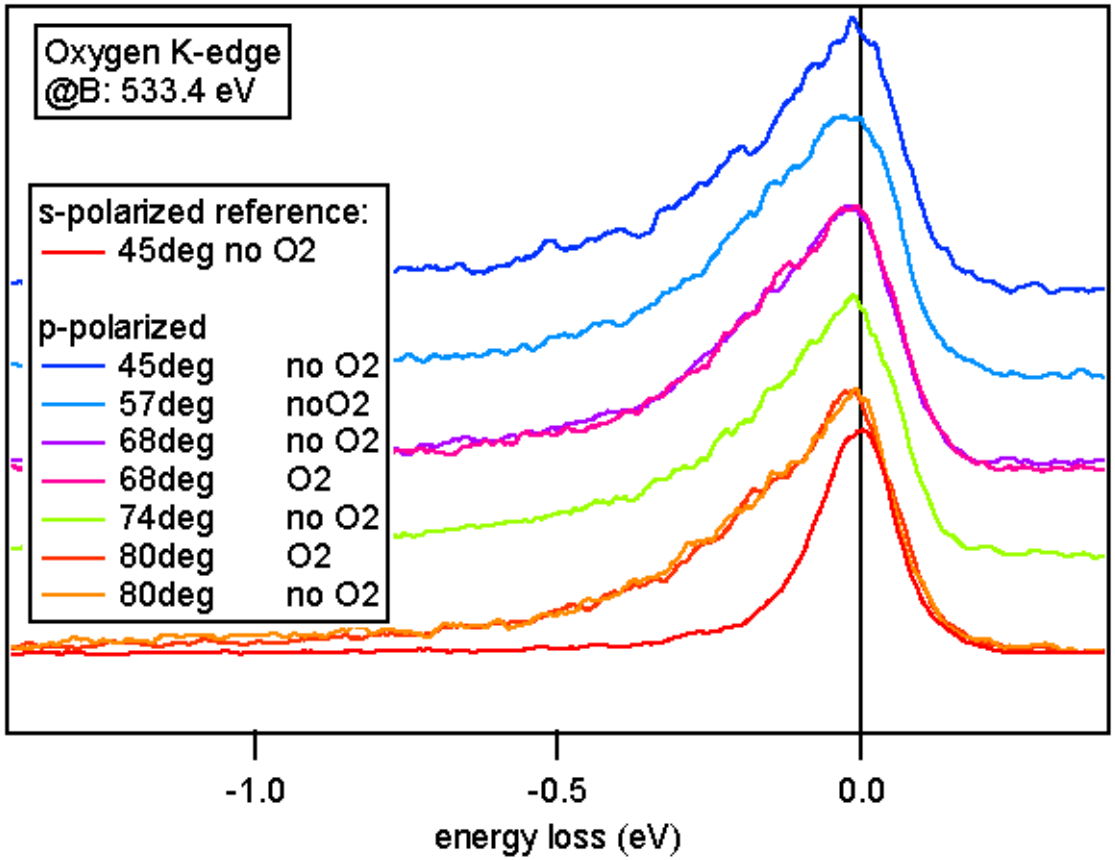
Anisotropic *e-ph* coupling in anatase TiO_2

S. Moser *et al.*, PRL, accepted.

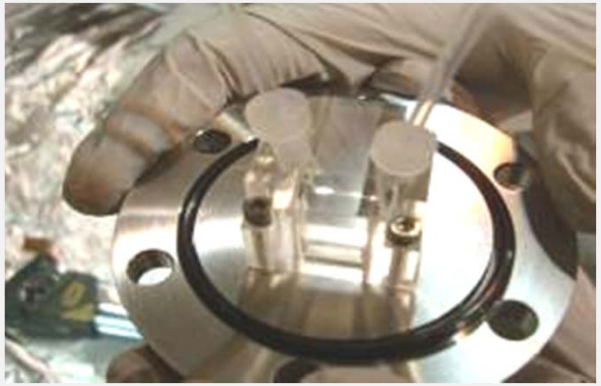
Ti 2p RIXS

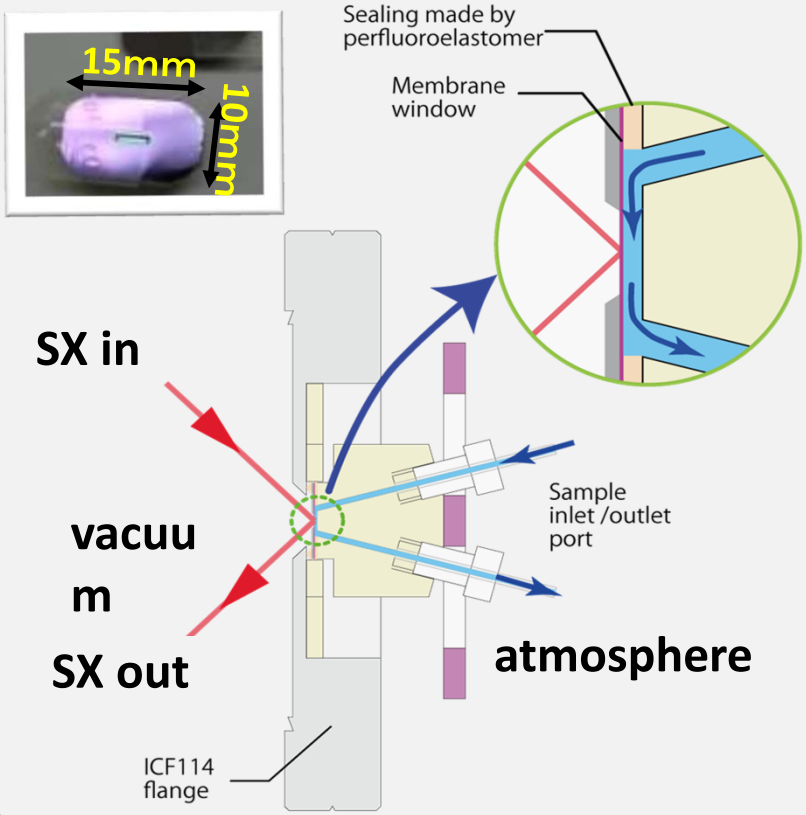


O 1s RIXS

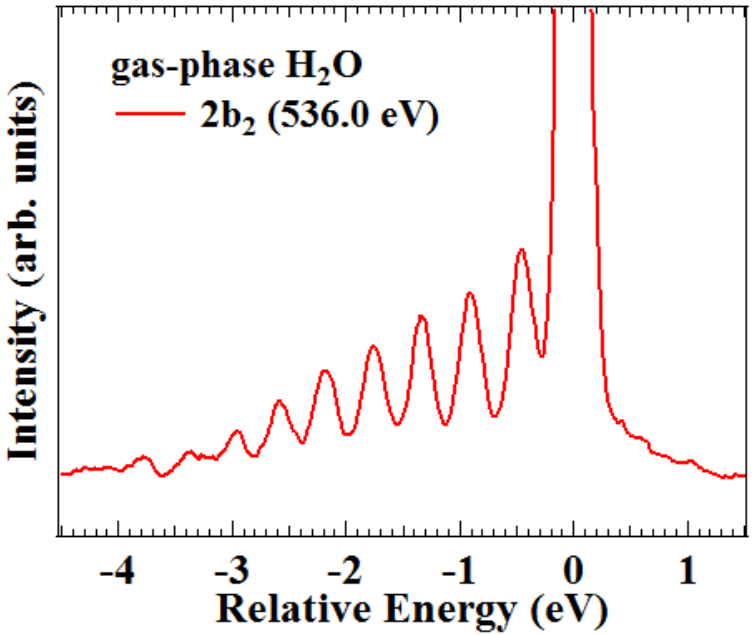


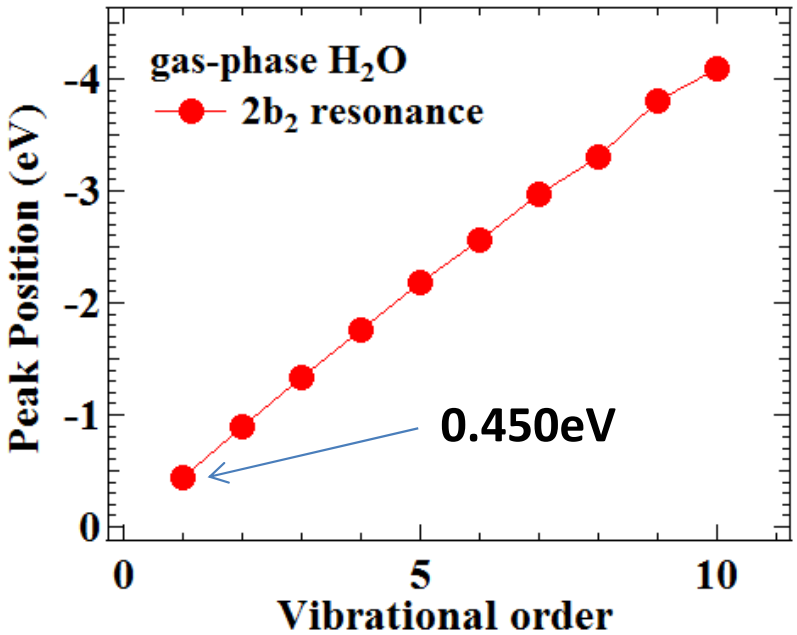
RIXS of water and wet materials

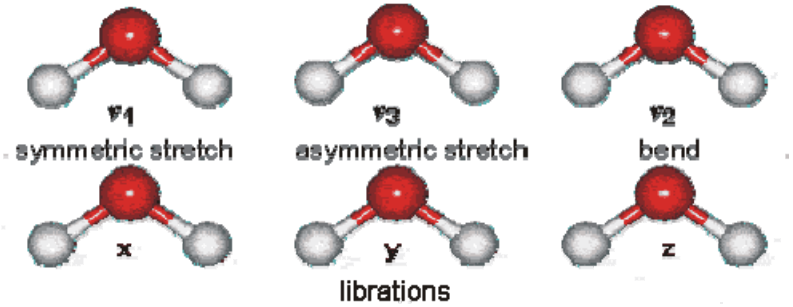




O 1s vibrational RIXS of H_2O molecule







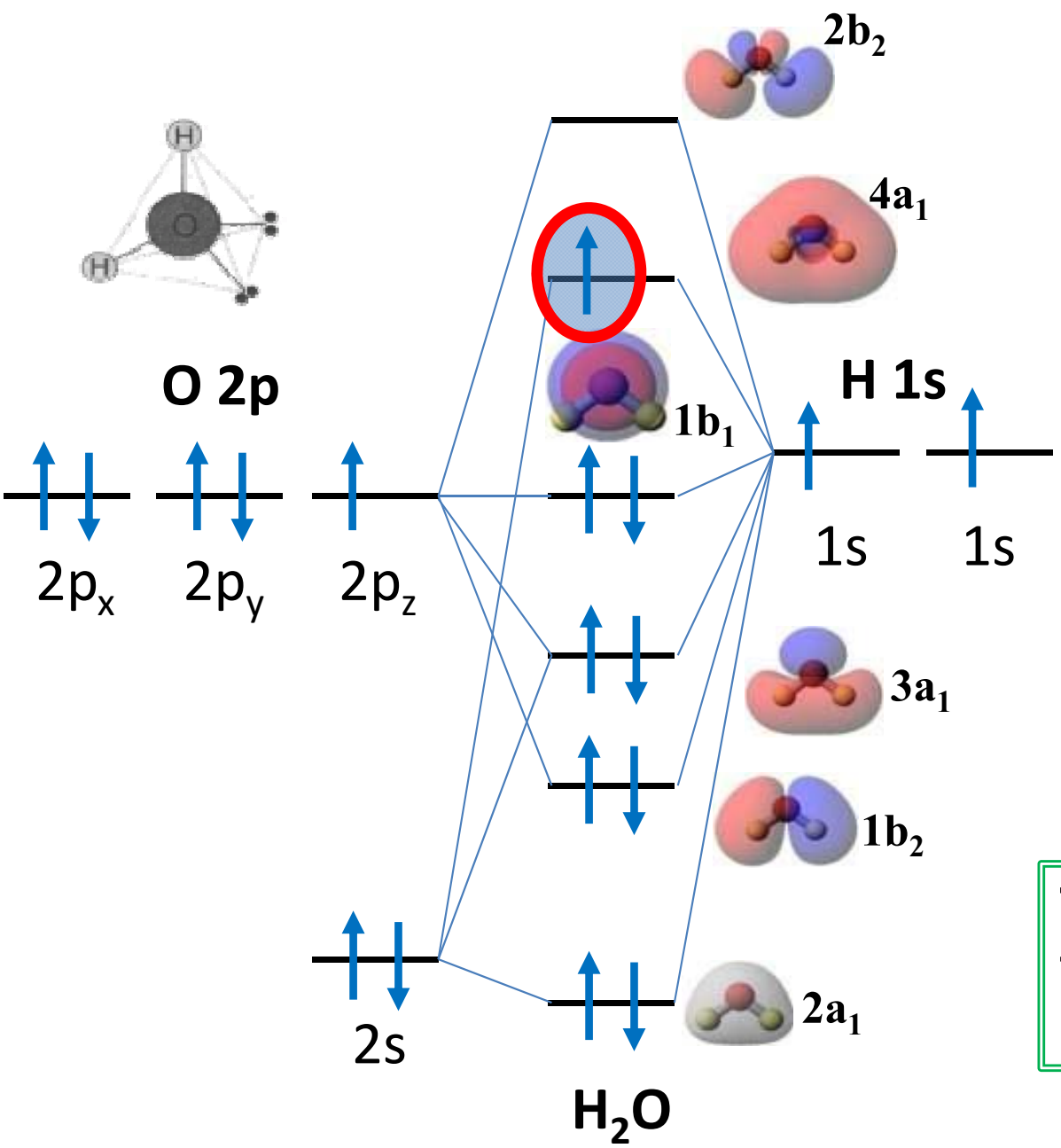
From http://www.lsbu.ac.uk/water/
Martin Chaplin, London South Bank University

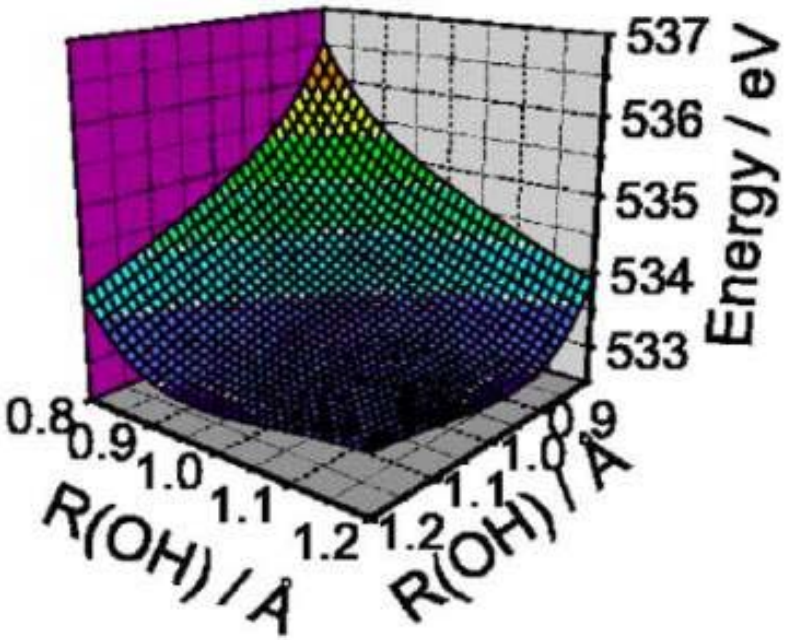
gaseous water

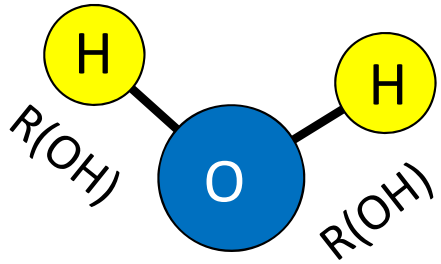
Vibration(s)	liquid H_2O (25°C)		liquid D_2O (25°C)	
	v, cm^{-1}	eV	v, cm^{-1}	eV
v_1	3657.1	**0.4530**	2671.7	0.3309
v_2	1594.7	0.1975	1178.4	0.1460
v_3	3755.9	**0.4653**	2787.7	0.3453

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

OH bond dissociation stimulated by resonant excitation



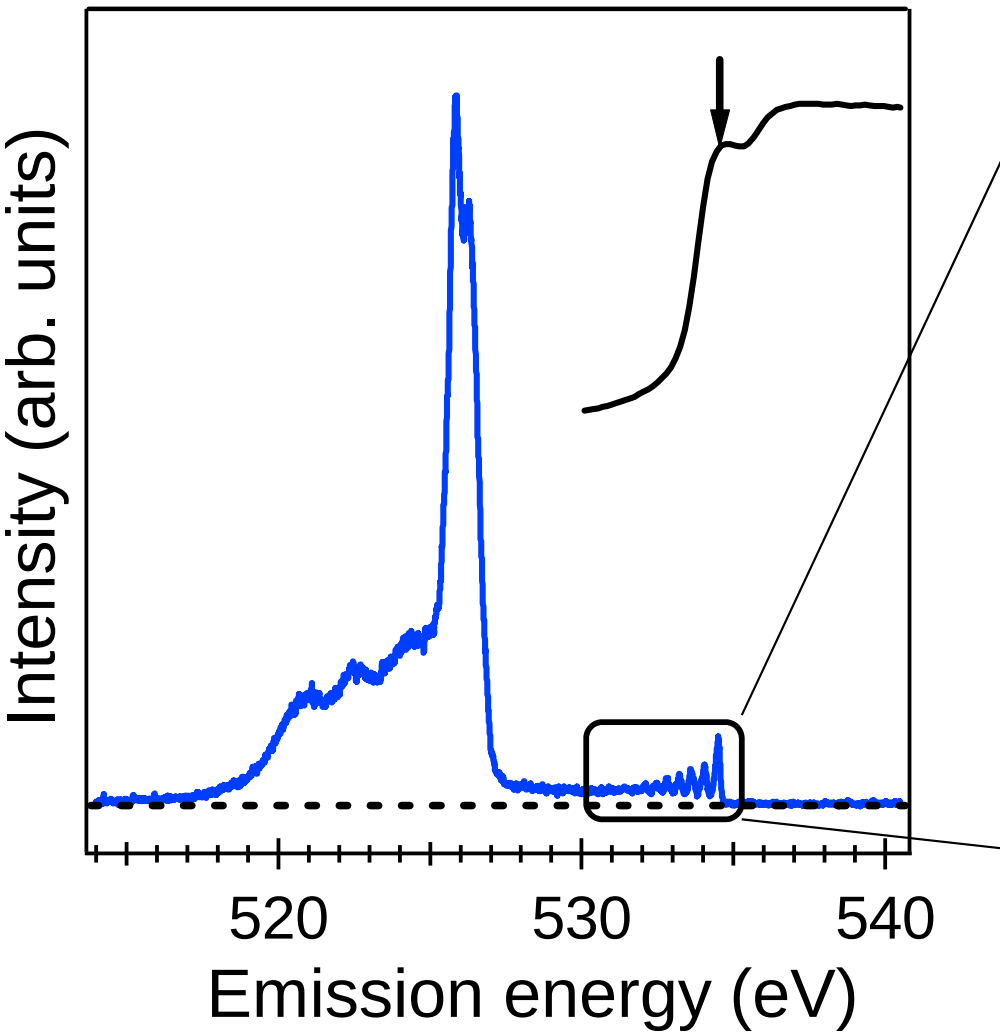


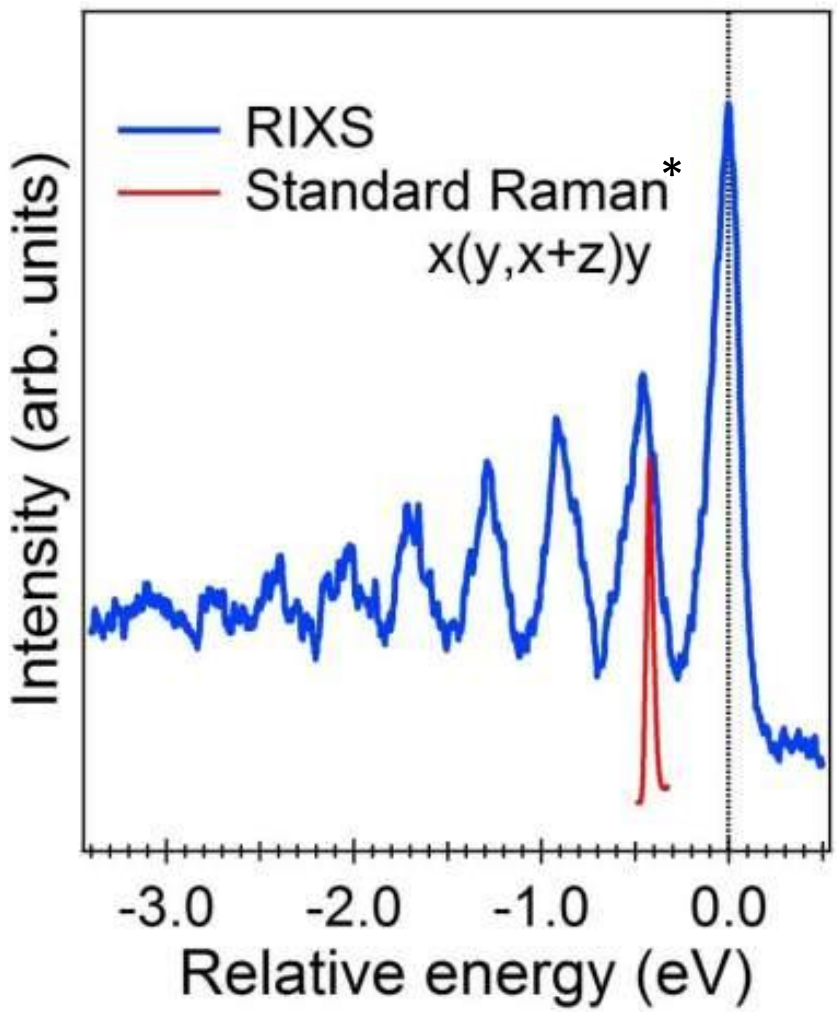


The presence of electron excited to the antibonding orbital is essential to the dissociation

O 1s vibrational RIXS of liquid H_2O

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

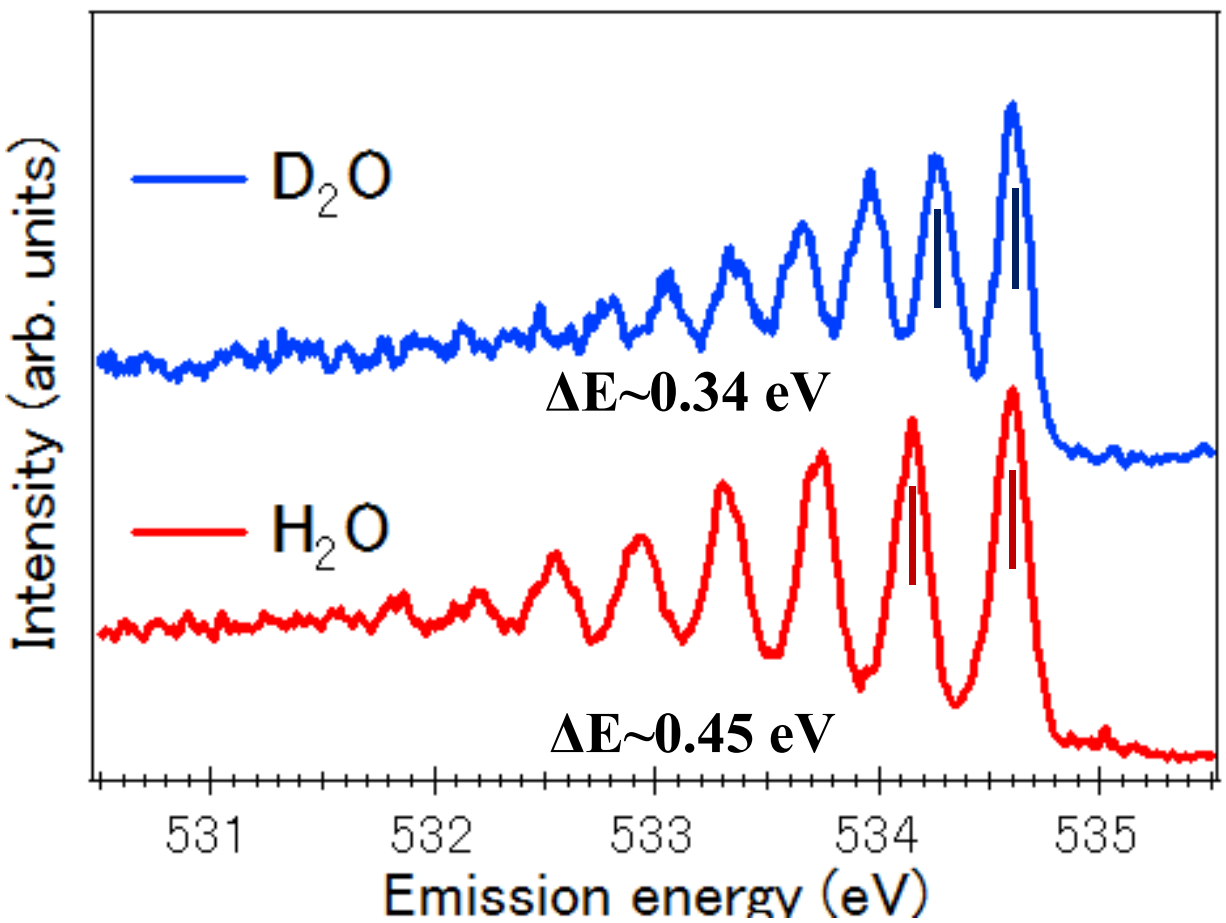




*G. E. Walrafen *et al*., Chem. Phys. **85**, 6964 (1986).

Isotope effect

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

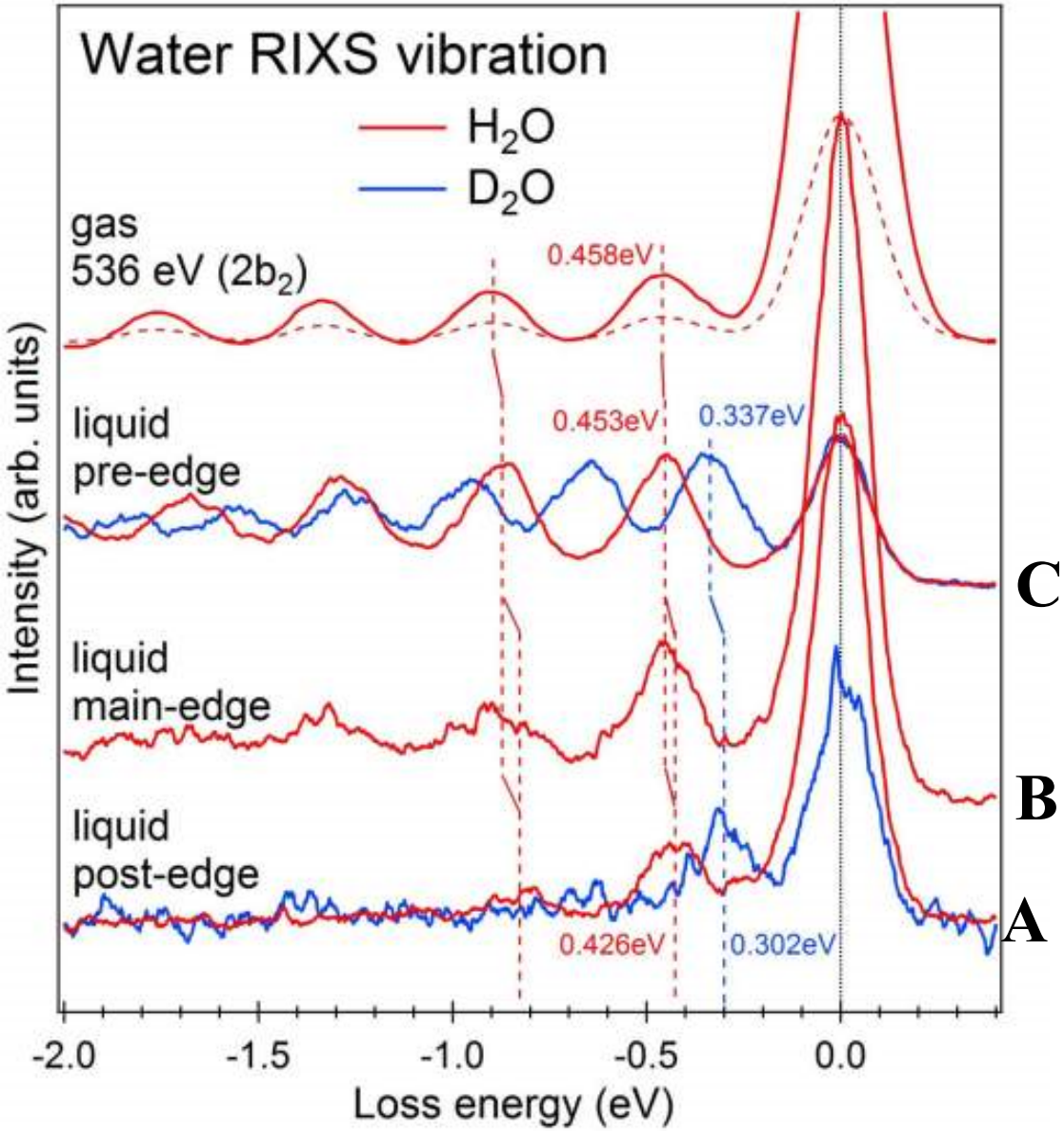


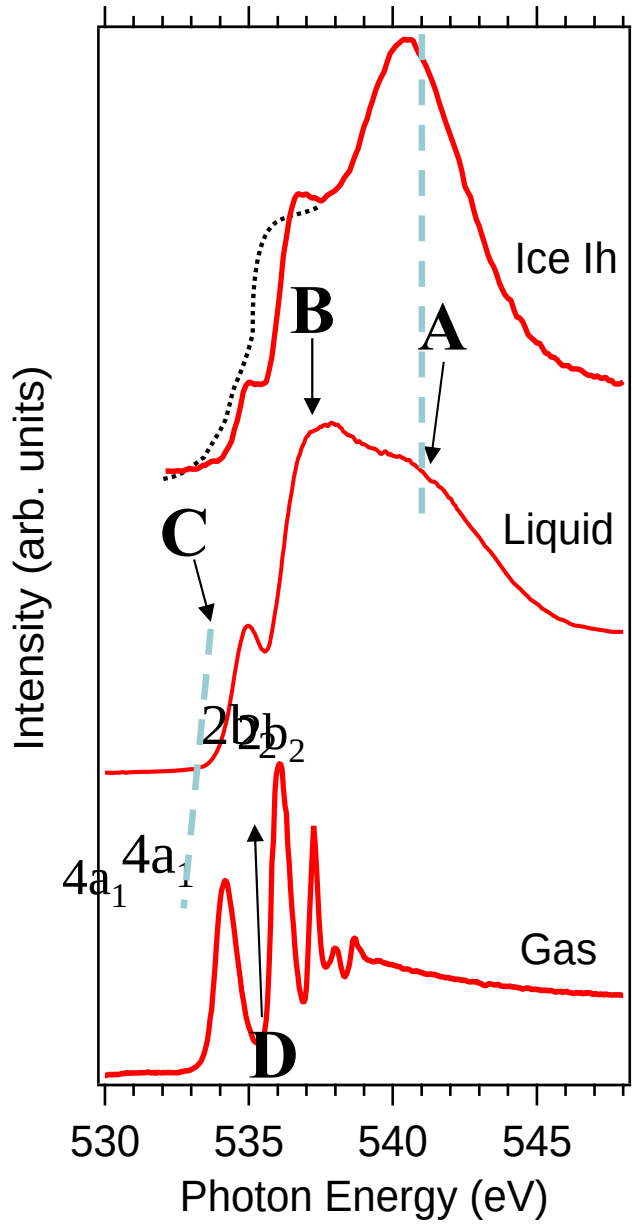
The energy of the fundamental vibrational mode is close to that of gas phase water, rather than liquid water.

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

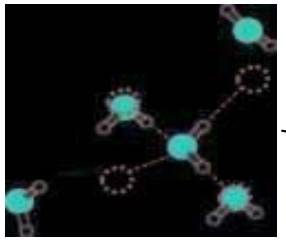
Soft X-ray vibrational spectroscopy of water

Y. Harada *et al.*, to be submitted.



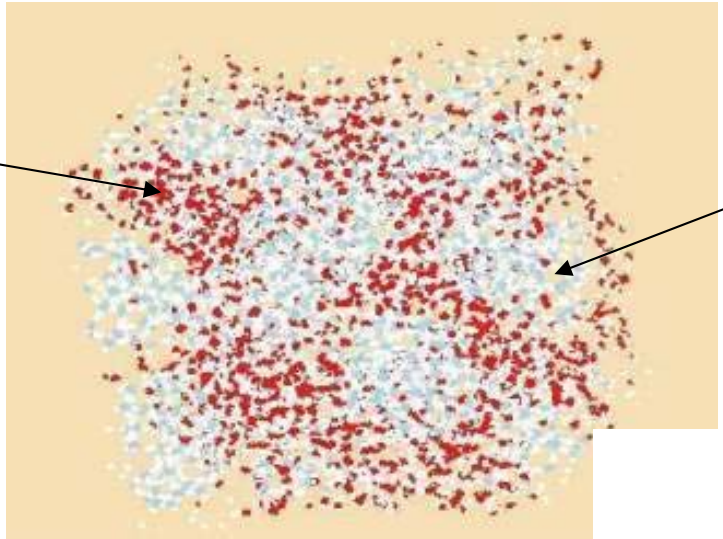


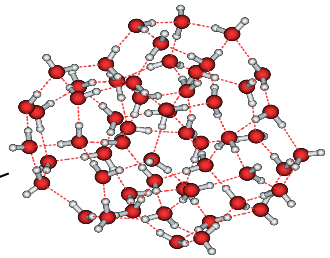
Microheterogeneity in liquid water



HDL

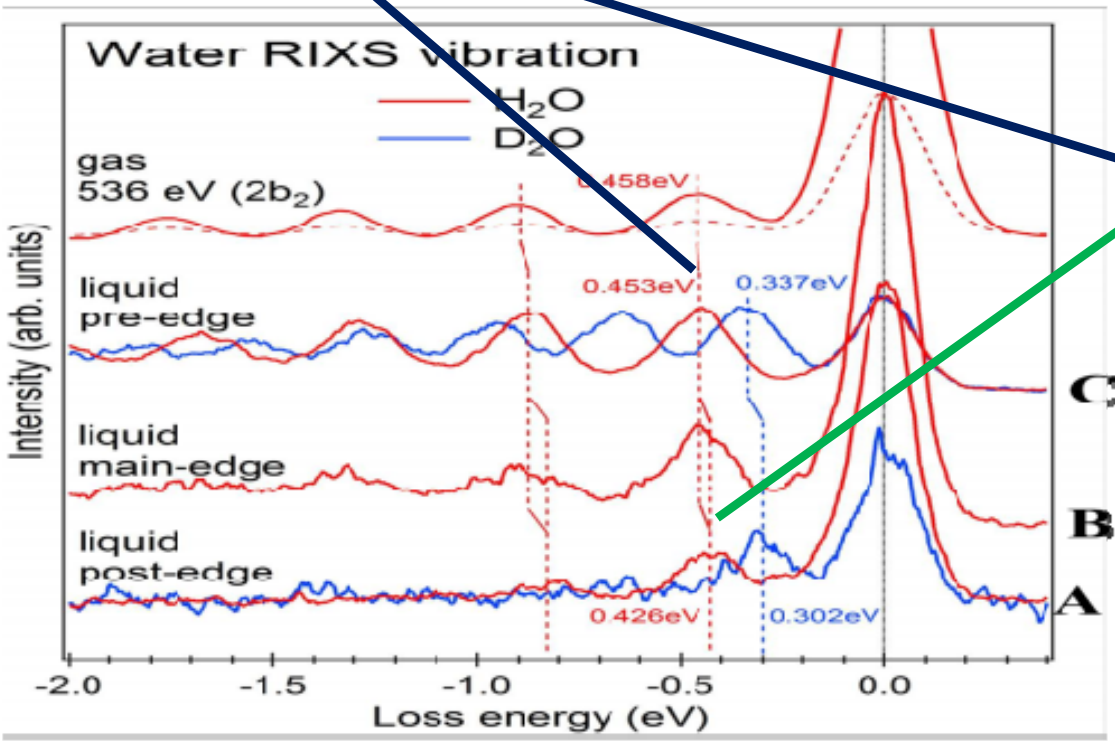
Distorted hydrogen bond

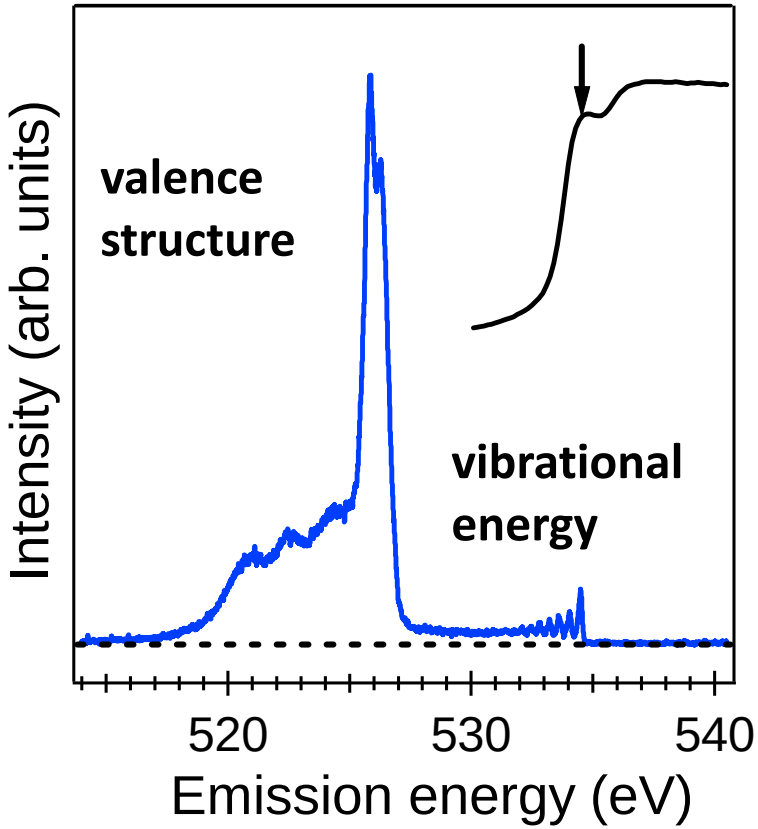




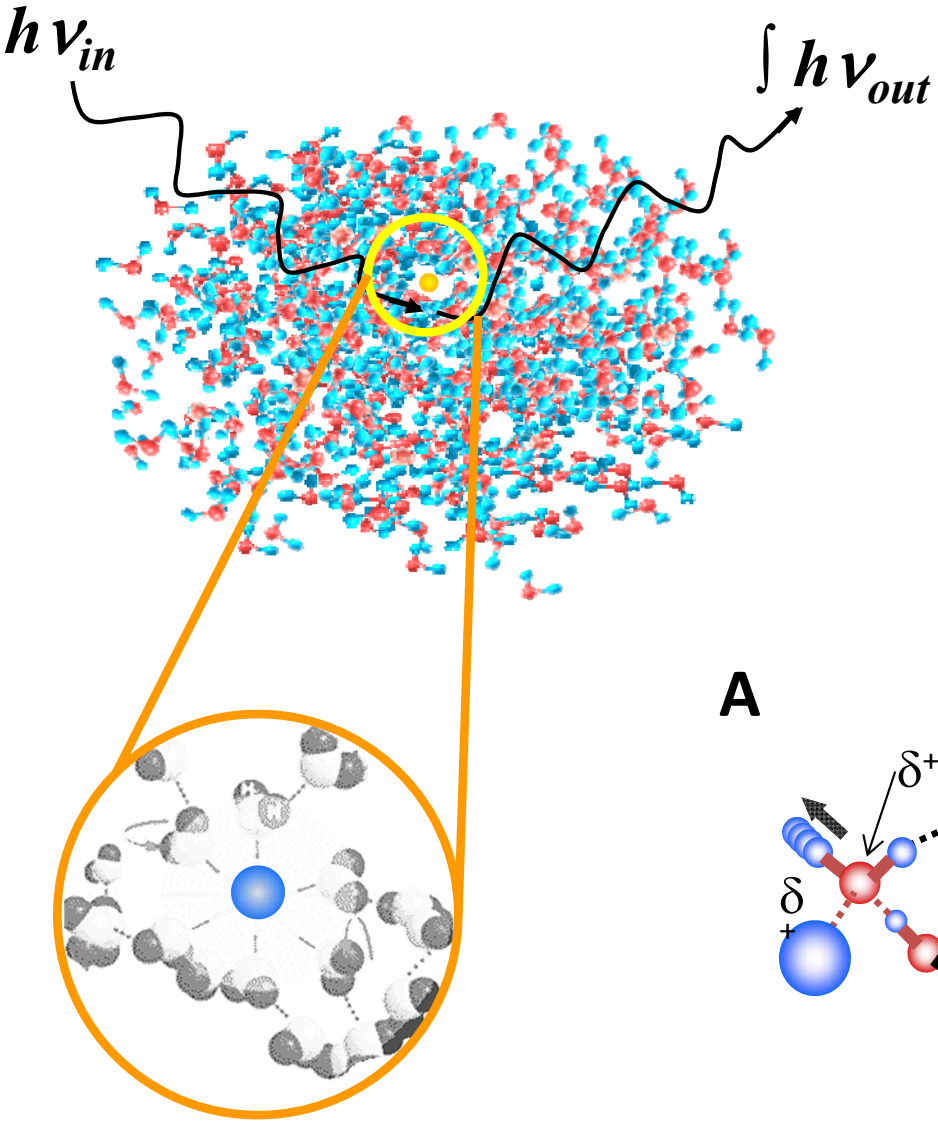
LDL

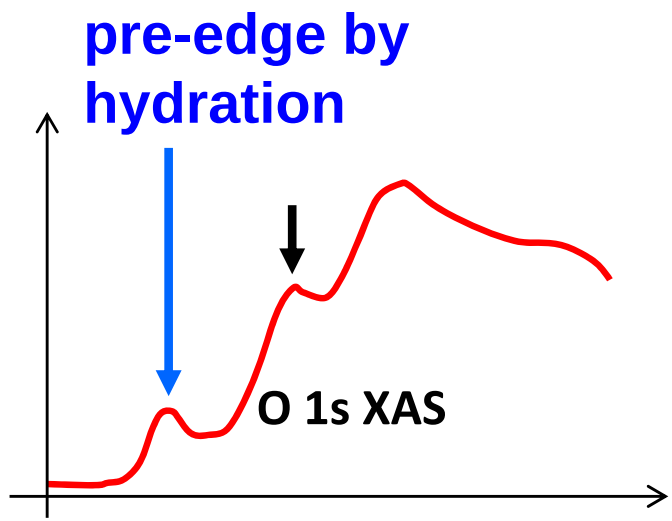
Tetrahedral

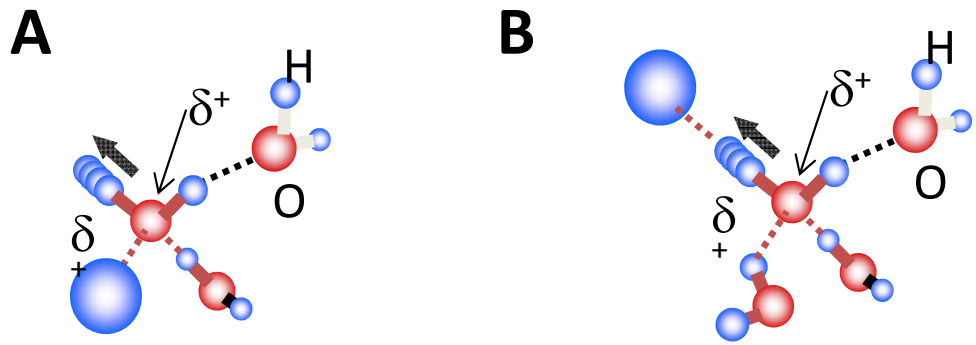




Future application of vibrational RIXS to hydration

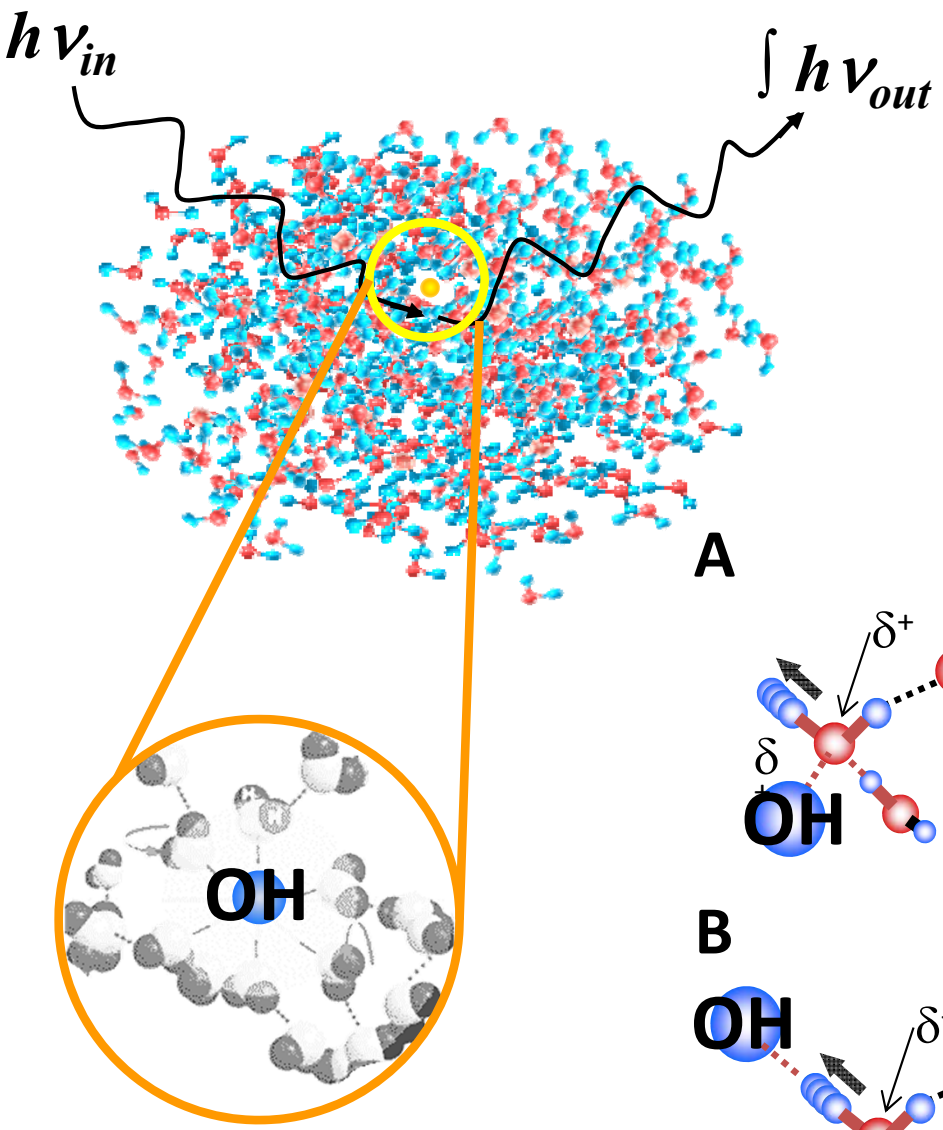


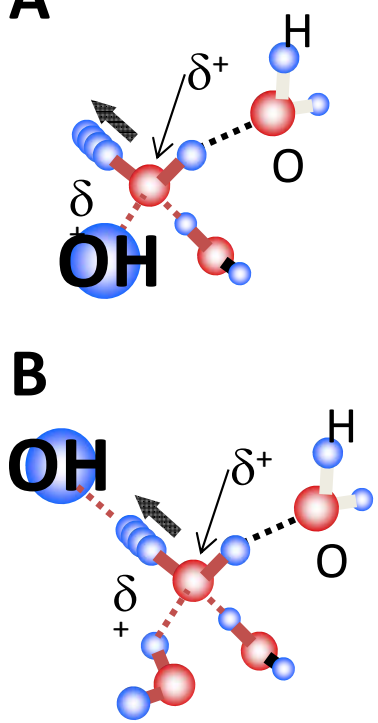


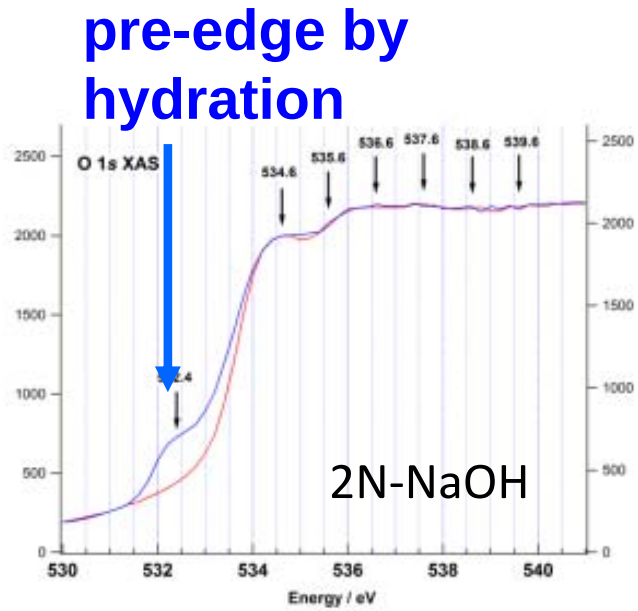


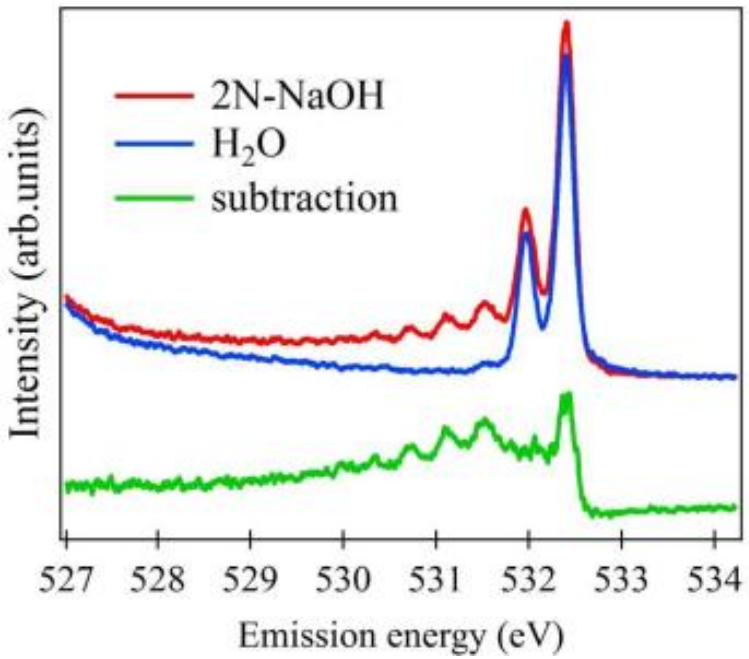
Selective vibrational spectroscopy of hydrated water

Application of vibrational RIXS to hydrated OH



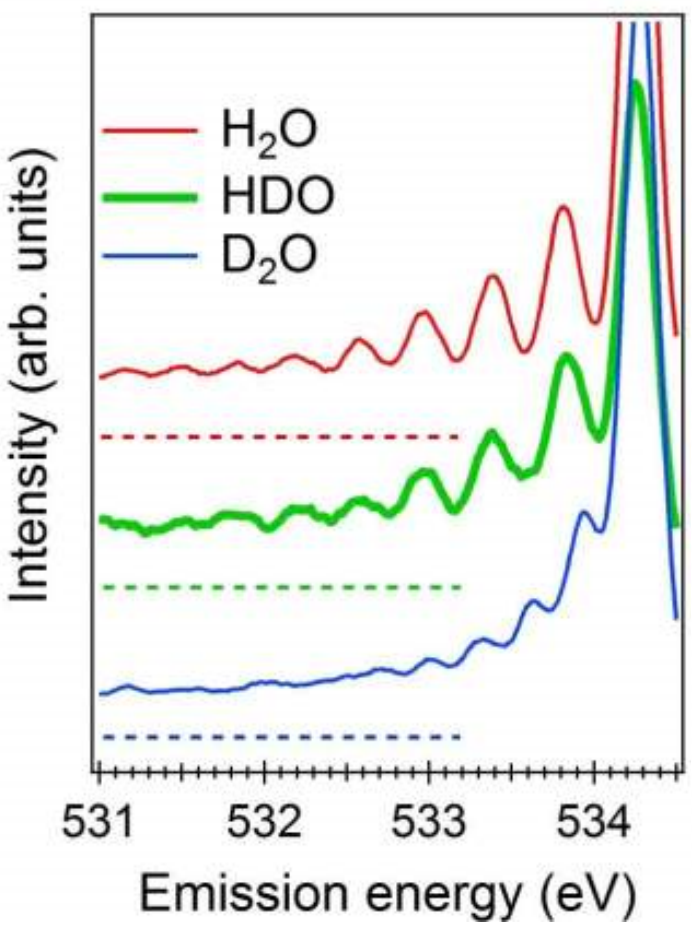


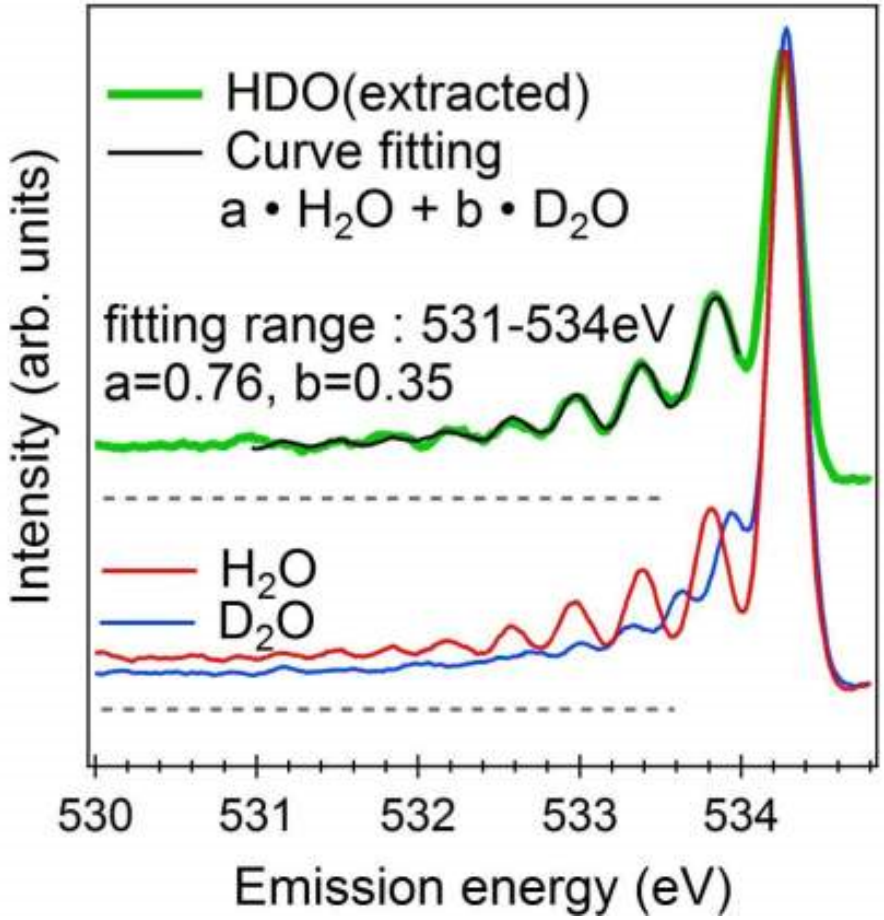


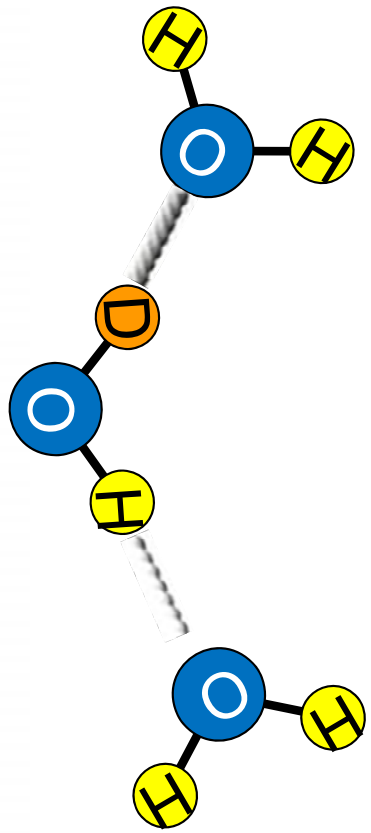


Isotope effect

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





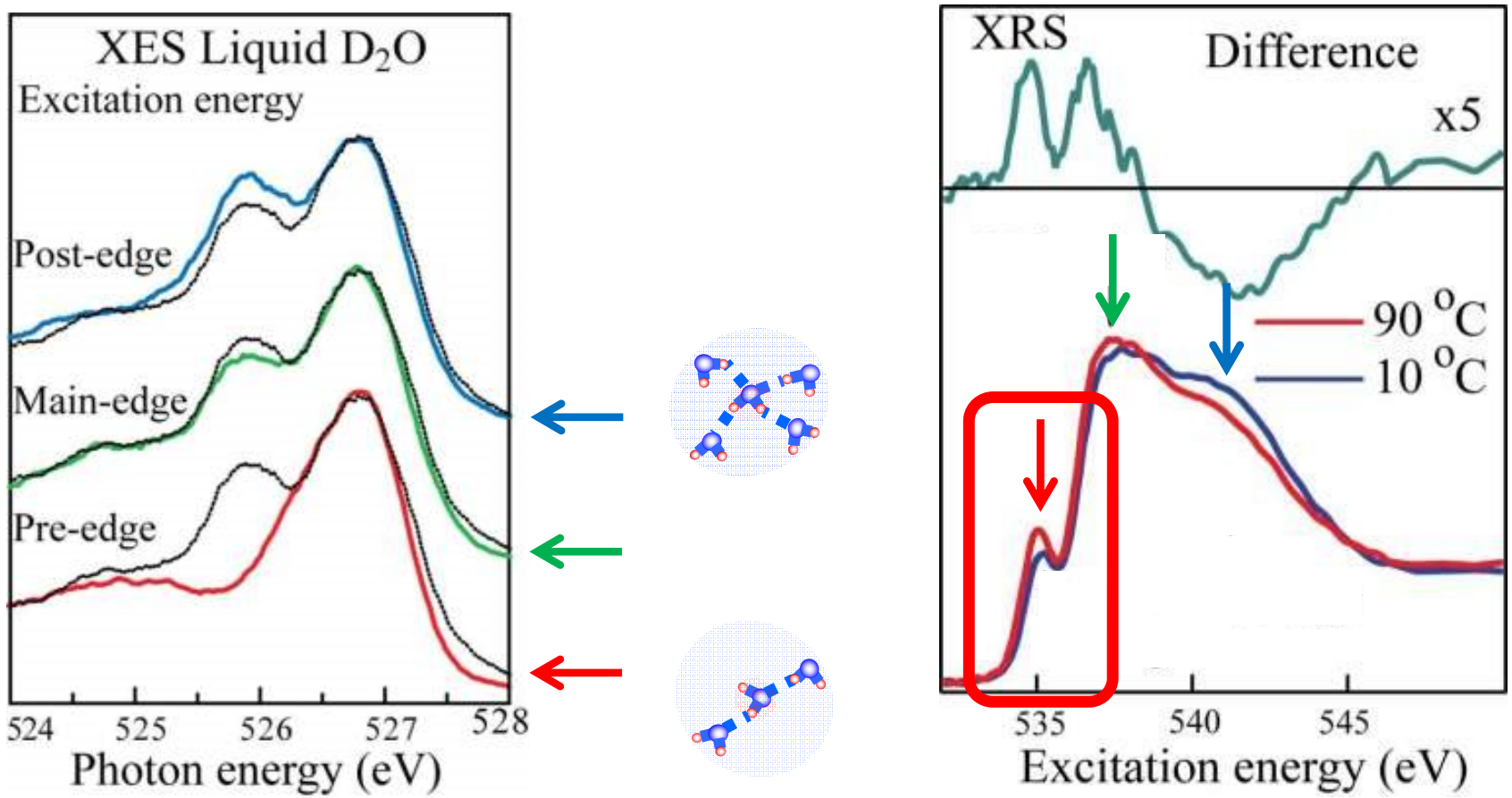


2:1 sum of H_2O and D_2O spectra well reproduces HDO spectrum.

OH side has more hydrogen bond broken species than OD side.

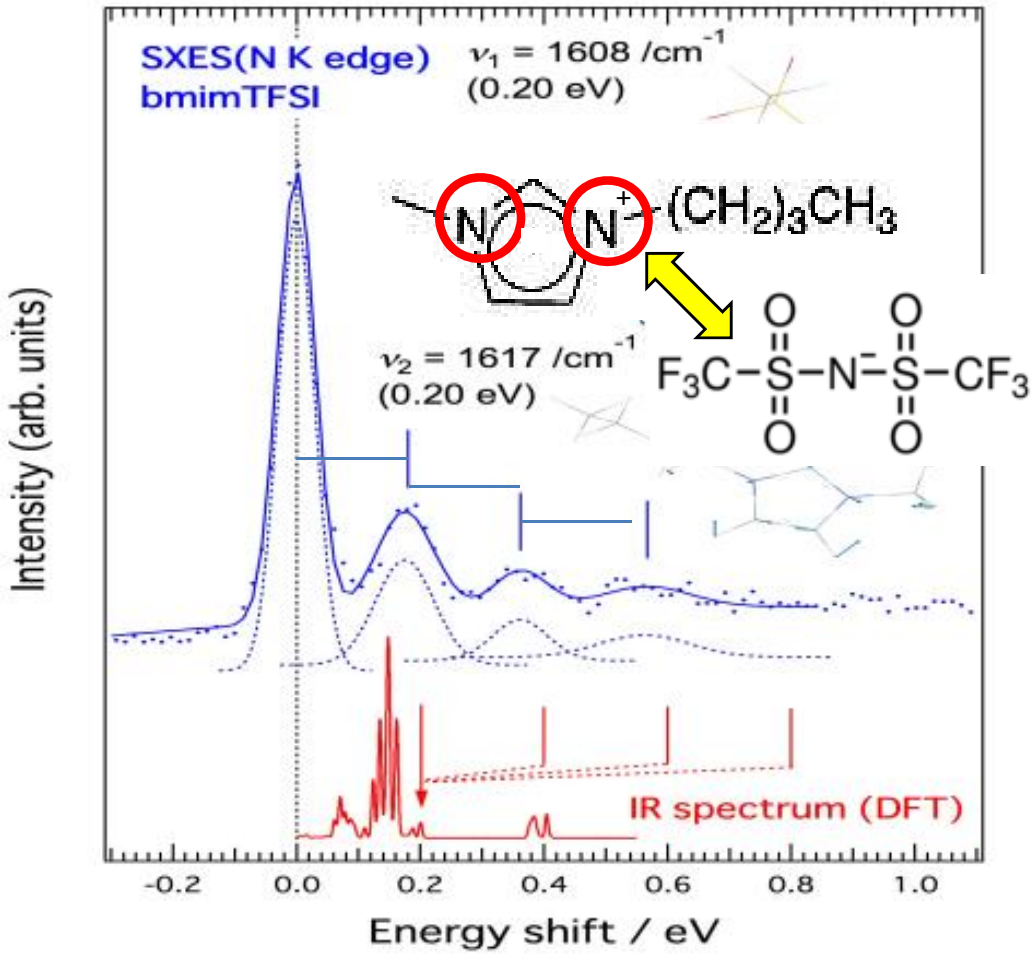
→consistent with the well known fact that D_2O has stronger hydrogen bond than H_2O.

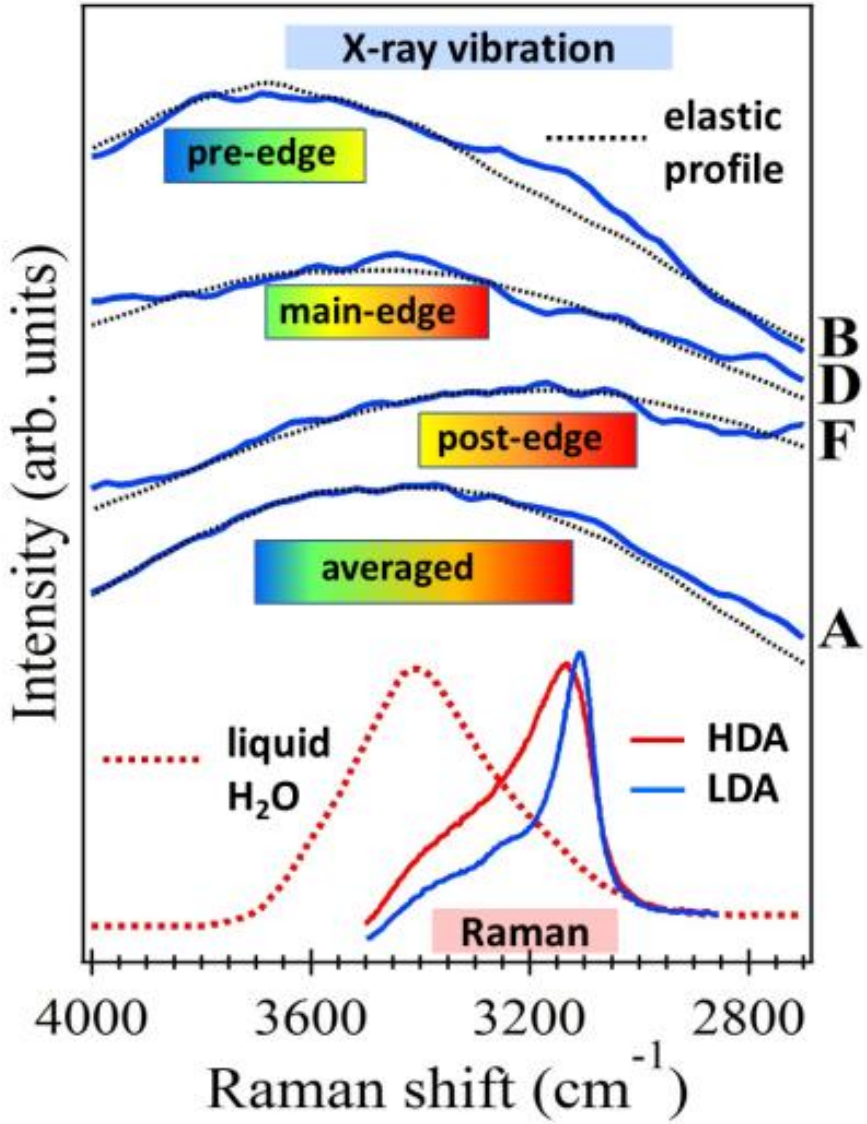
Interpretation of liquid water O 1s XAS



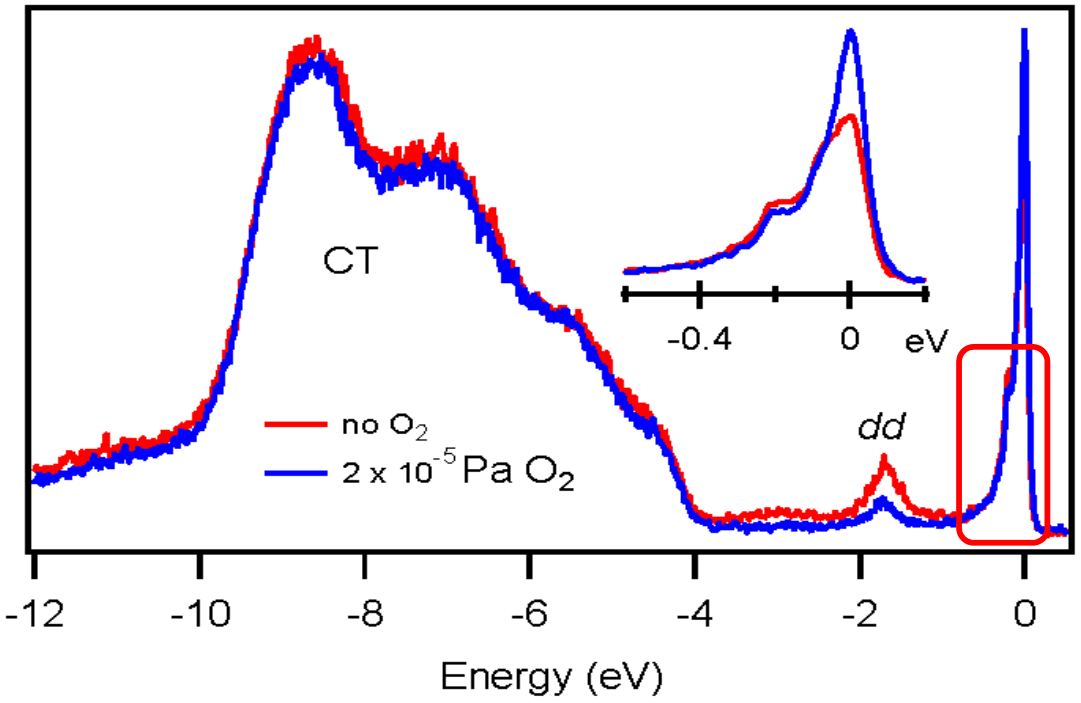
Two state model of liquid water is based on the broken-hydrogen-bond picture of the XAS pre-edge

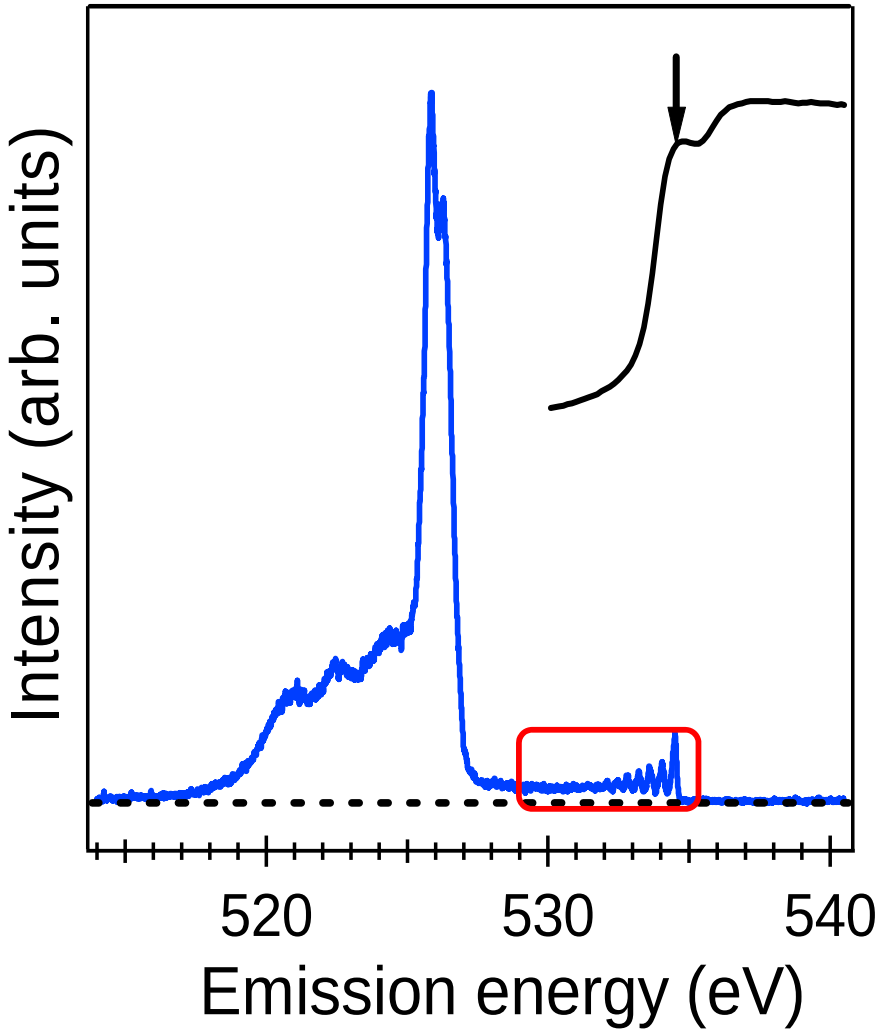
ΔE (振動RIXS) > ΔE (IR/Raman) * 100



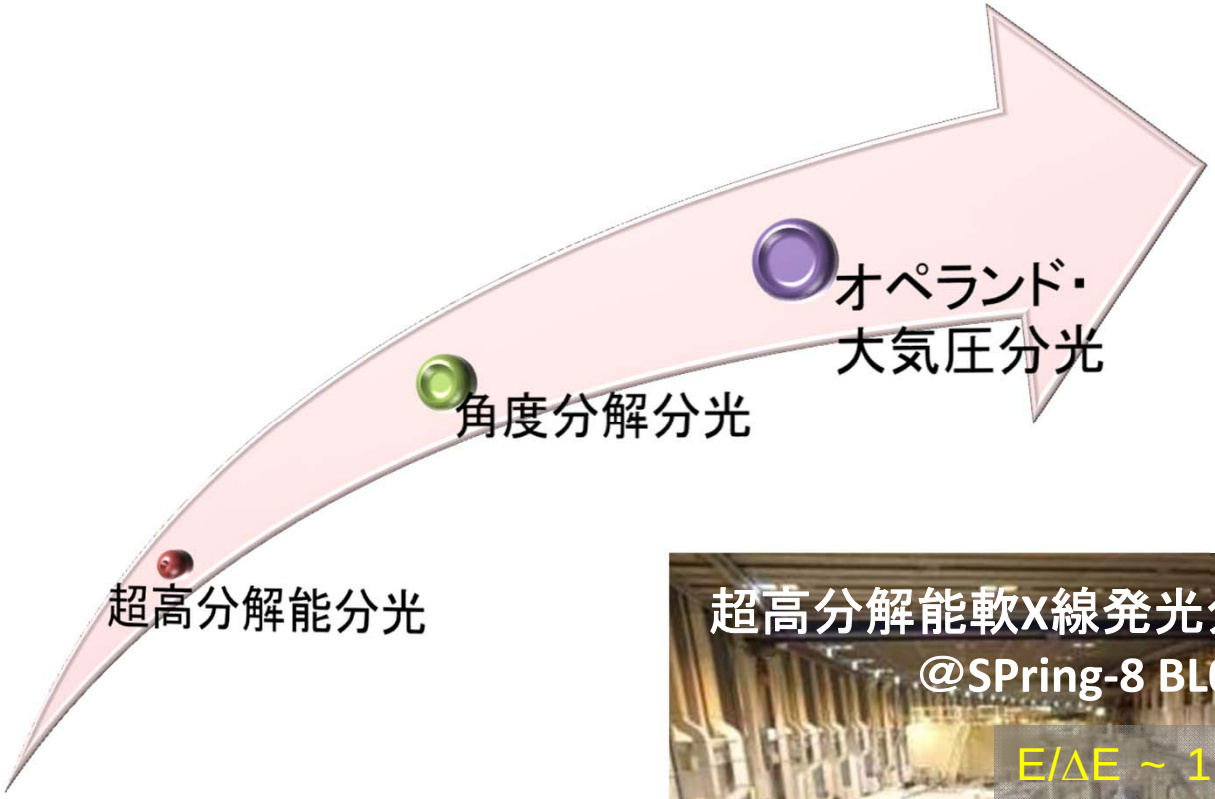


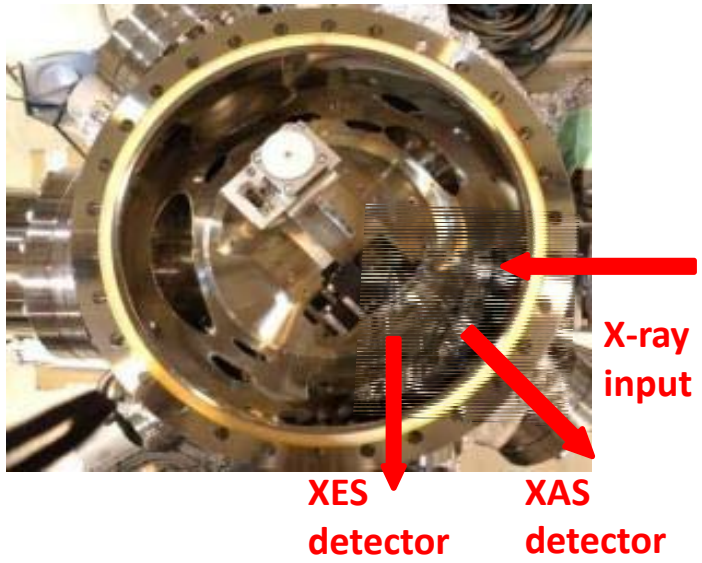
I(振動RIXS) < I(valence RIXS)/100



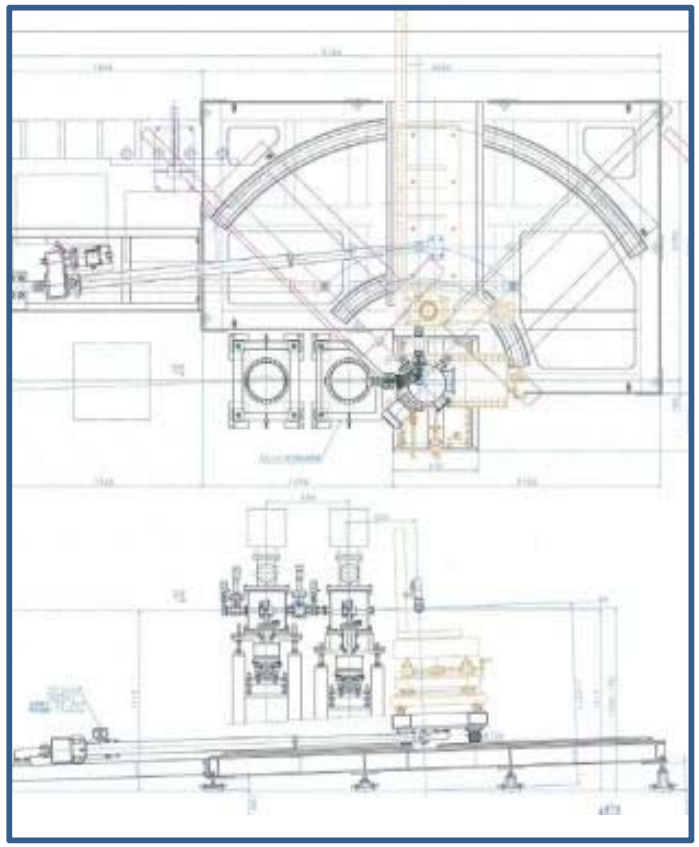


軟X線発光分光の段階的発展計画





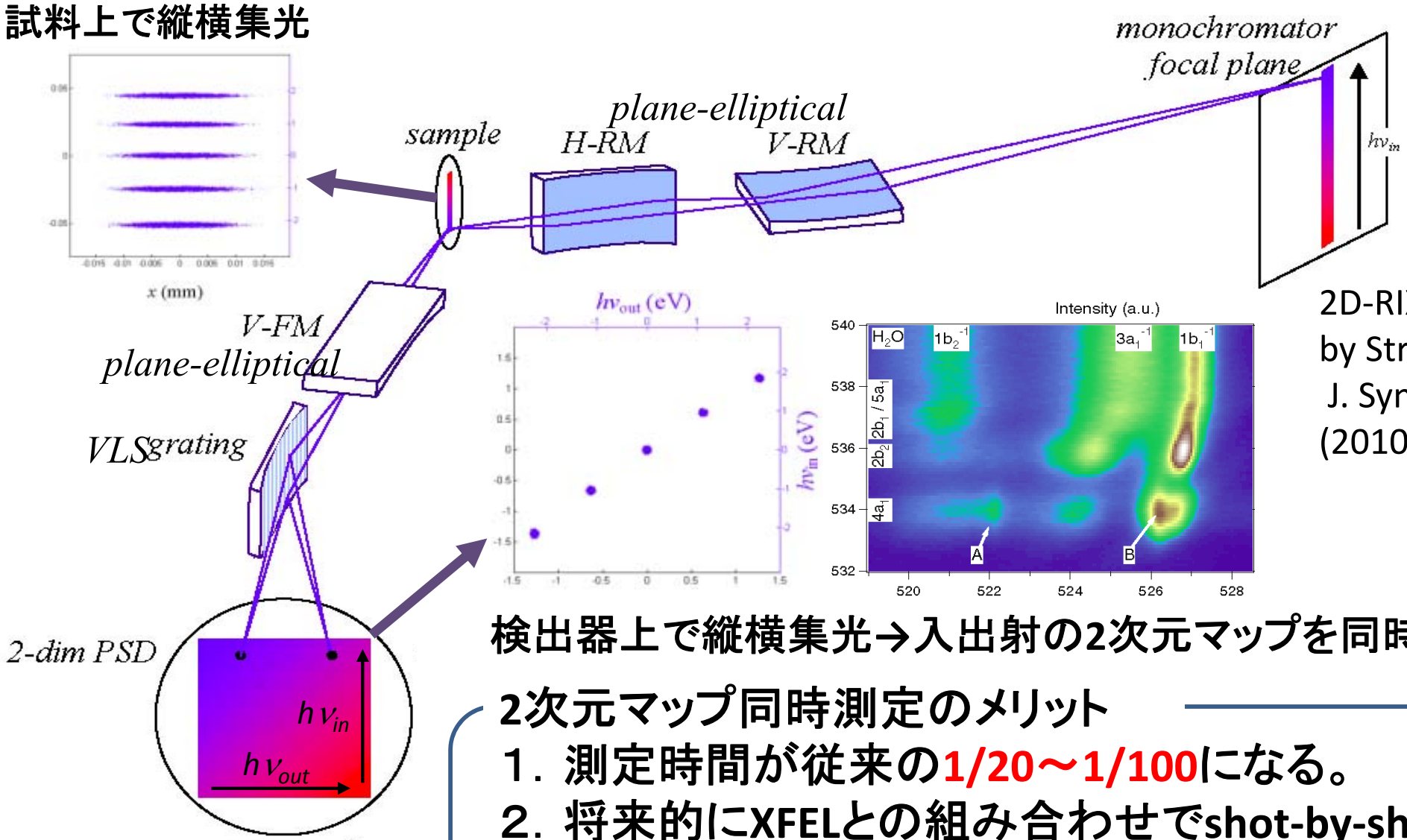
大気圧分光用差動排気システム



角度分解用分光器回転

軟X線発光分光の新たな展開：2D-RIXS

試料上で縦横集光



2D-RIXS concept by Strocov *et al.* J. Sync. Rad. **17** (2010) 103.

検出器上で縦横集光→入出射の2次元マップを同時測定

2次元マップ同時測定のメリット

1. 測定時間が従来の**1/20～1/100**になる。
2. 将来的にXFELとの組み合わせでshot-by-shotの**化学反応追跡実験**も可能になる。
3. 自動的に**100nmオーダーの顕微分光**へ移行可能。

HORNET users（since 2011）（敬称略）

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仙波泰徳 (JASRI/SPring-8)
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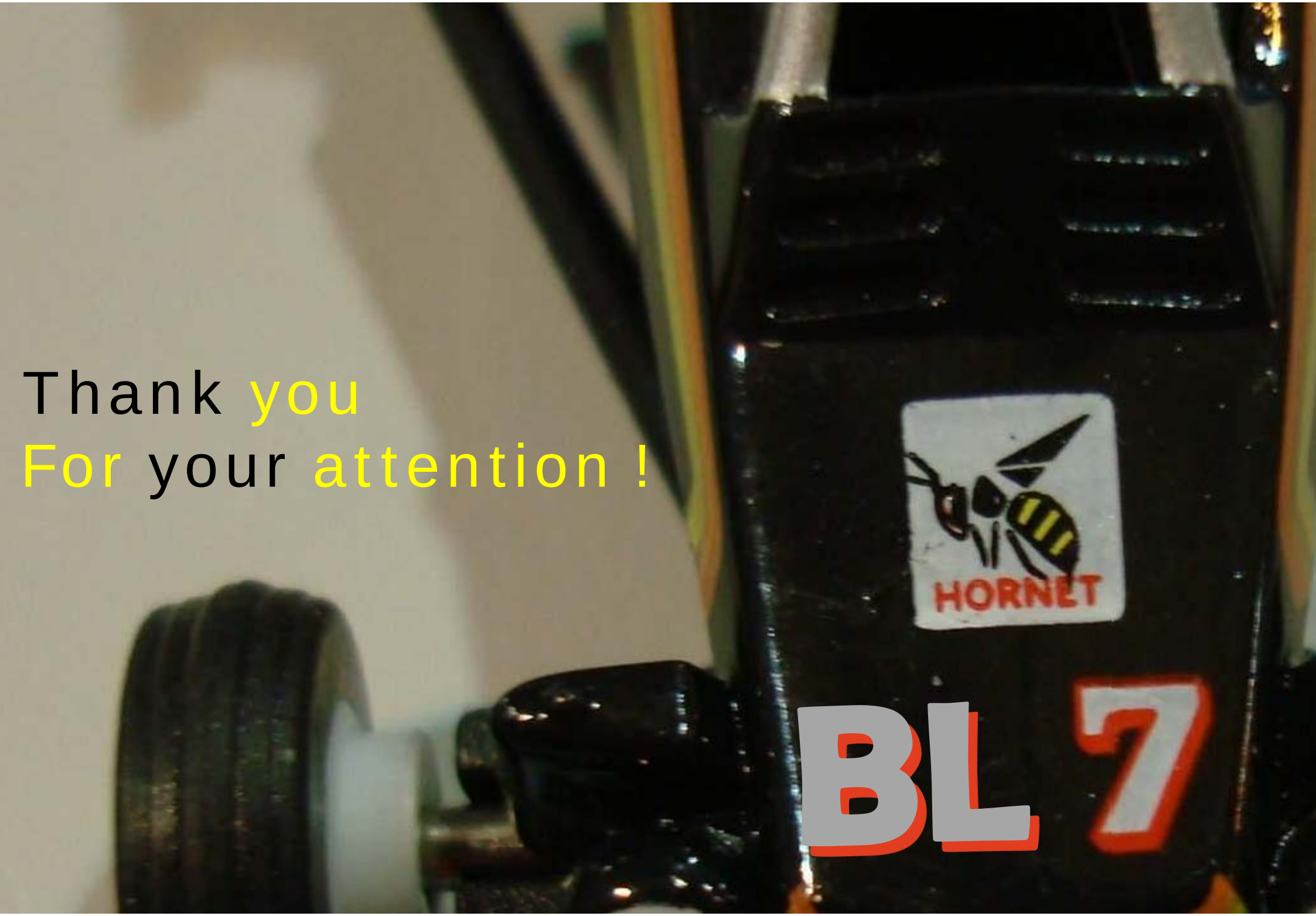

Thank you
For your attention !