Measuring Charge-Transfer Processes in RIXS

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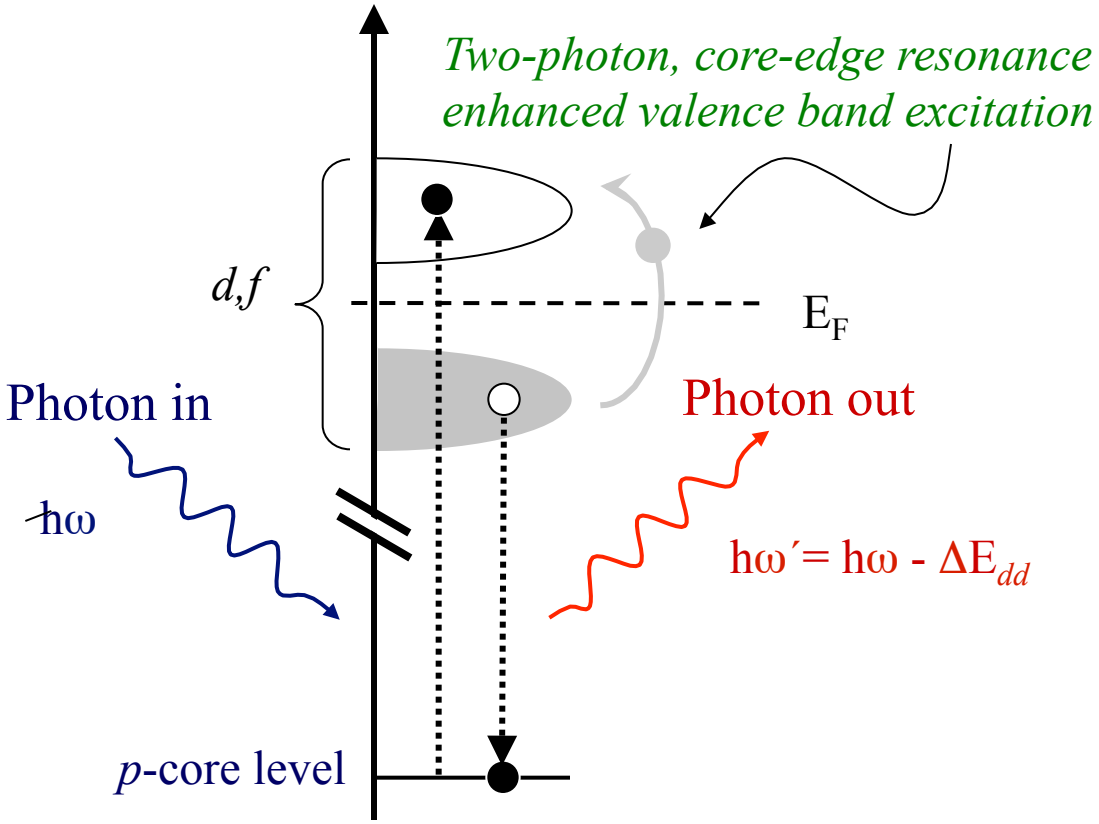
BERKELEY LAB

U.S. DEPARTMENT OF ENERGY | Office of Science

ALS-U ADVANCED LIGHT SOURCE

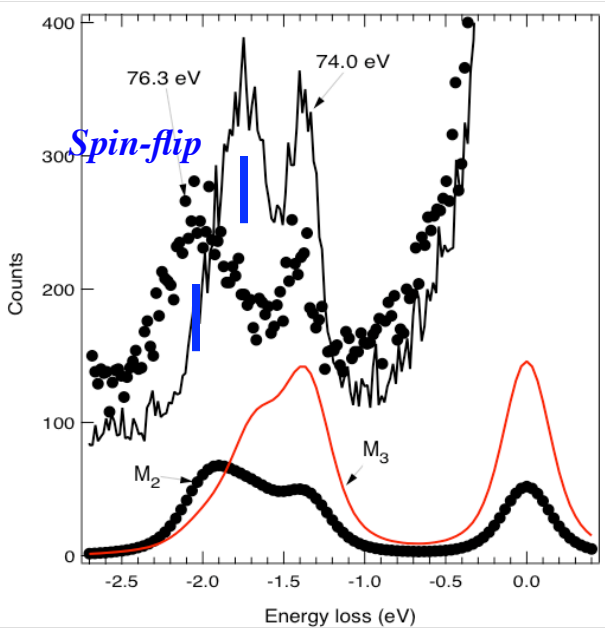
Resonant Inelastic Soft X-Ray Scattering

Appl. to *d* and *f* systems, see e.g.:
S. Butorin *et al.*, PRL **77**, 574 (1996)
Kuiper *et al.*, PRL **80**, 5204 (1998)



RIXS Basics:

- ✓ Element selectivity
- ✓ Energy conservation
- ✓ Symmetry selection (parity conservation)
- ✓ Dynamics
- ✓ Chemical bond probing



Kramers-Heisenberg formula:

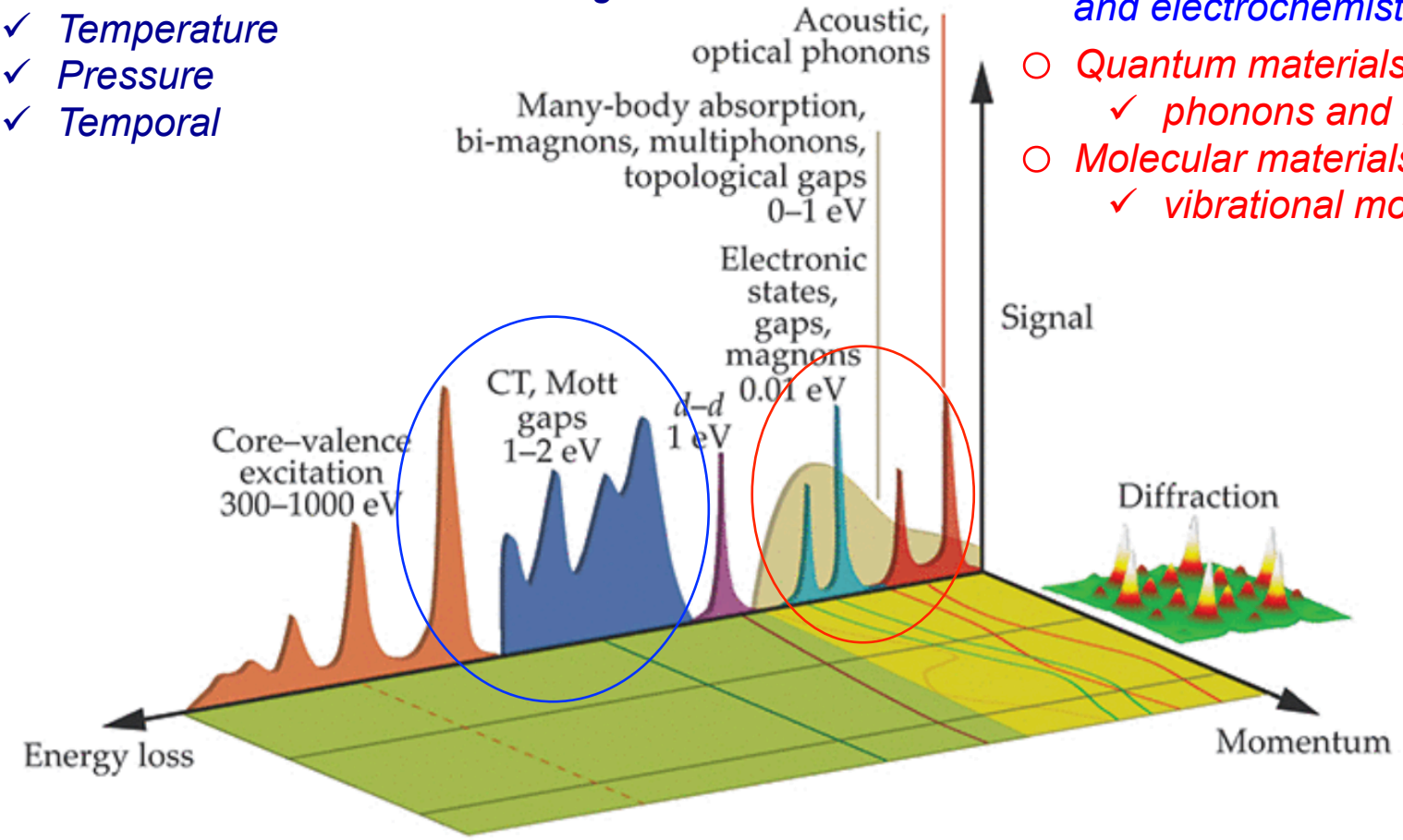
$$F(\omega,\omega') = \sum_f \left| \sum_m \frac{\langle f|D|m\rangle\langle m|D|g\rangle}{E_g + \omega - E_m - i\Gamma_m} \right|^2 \delta(E_g + \omega - E_f - \omega')$$

RIXS: Resonant Inelastic X-ray Scattering

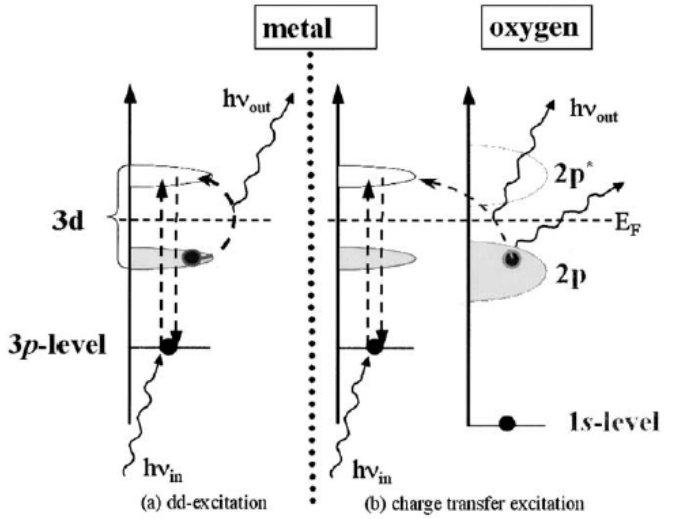
RIXS to Explore Chemical Transformation

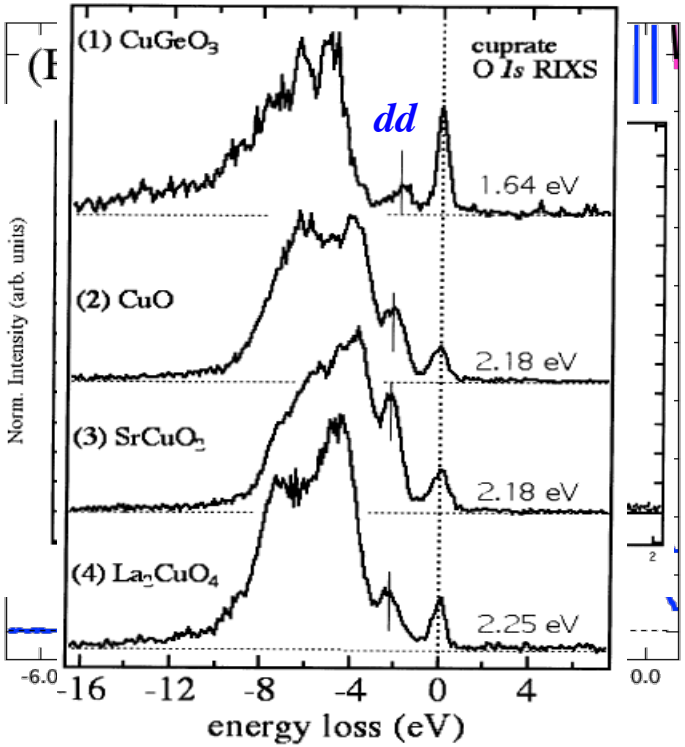
- ***In-situ/operando @ real-world conditions***
  - ✓ *Surface and interface (interphase)*
  - ✓ *Gas/solid and liquid/solid*
  - ✓ *External fields: electric and magnetic*
  - ✓ *Temperature*
  - ✓ *Pressure*
  - ✓ *Temporal*

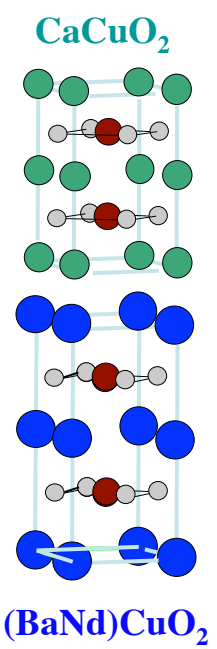
- ○ *Chemical bonding, charge transfer, catalytic reaction and electrochemistry*
- ○ *Quantum materials:*
  - ✓ *phonons and magnons*
- ○ *Molecular materials:*
  - ✓ *vibrational modes*

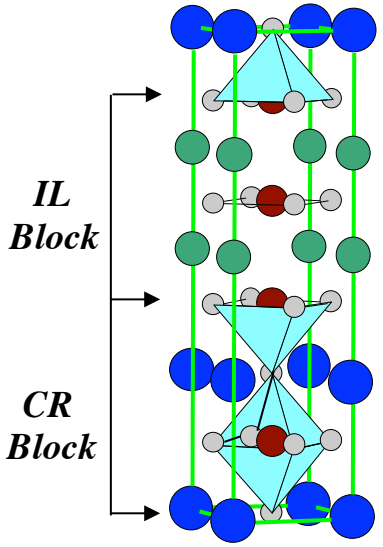


dd & CT excitations at O K-edges

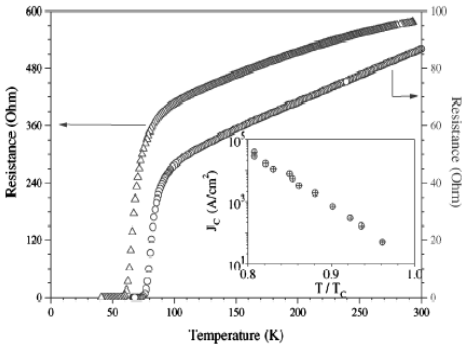


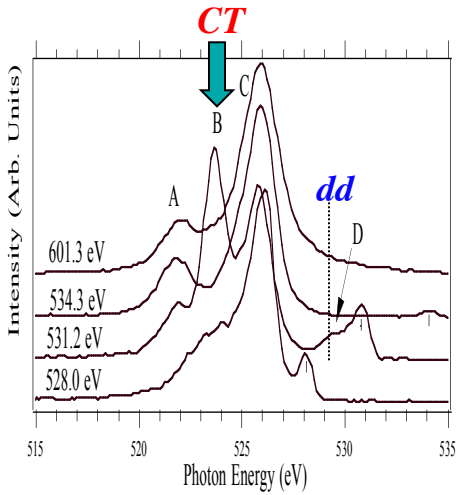


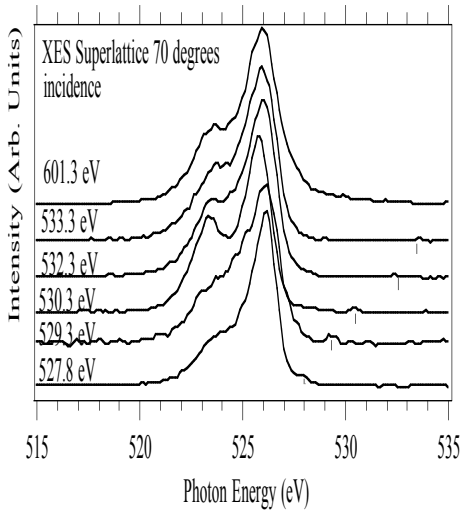




G. Balestrino, P.G. Medaglia, PRL 89, 156402 (2002)

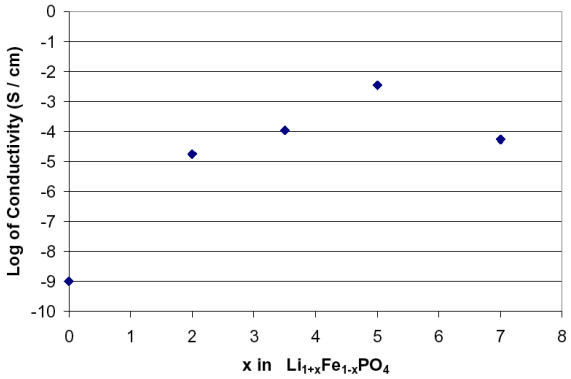




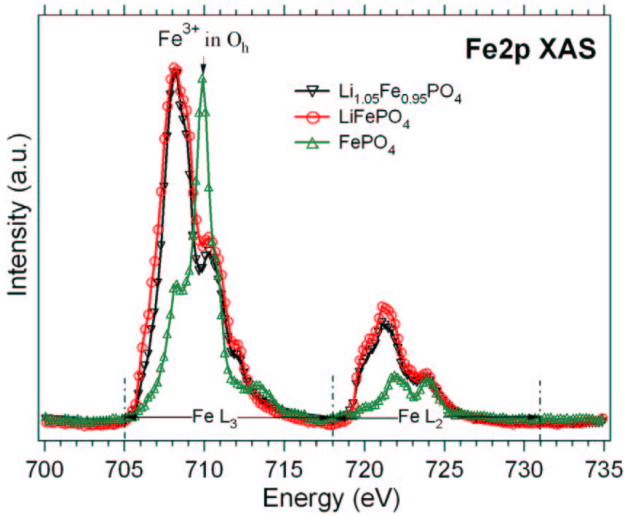


Freelon et al., PRL96, 017004 (2006)

$LiFePO_4$ and $Li_{1.05}Fe_{0.95}PO_4$



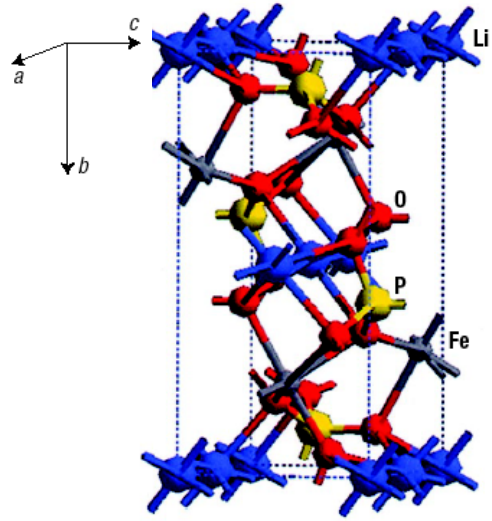
The increased conductivity upon Li doping

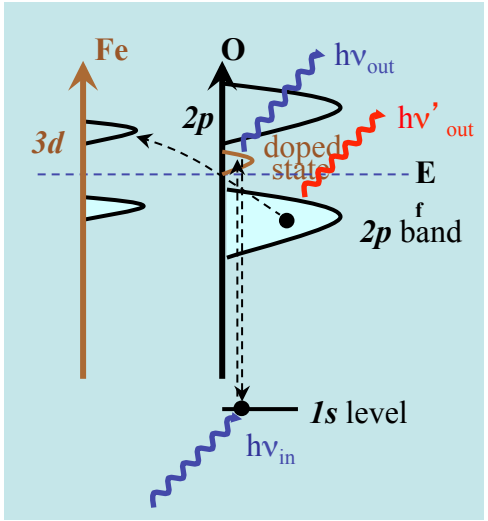


No Fe^{3+} observed upon doing!

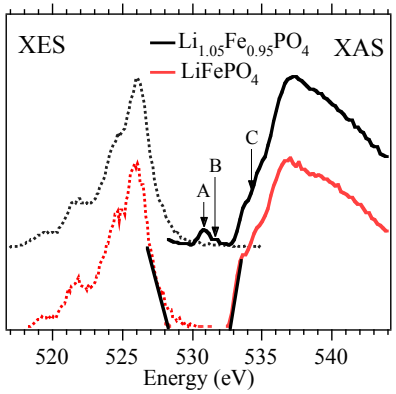
Vera Zhuang & Phil Ross (MSD);

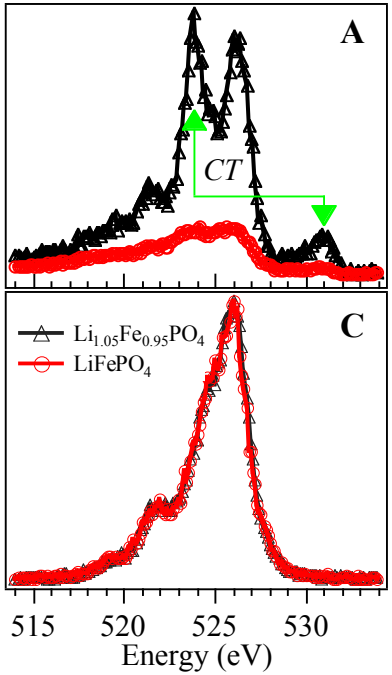
Jinghua Guo (ALS); J. L. Allen (US ARL)





Strong correlation between Fe 3d and O 2p induced by Li doping

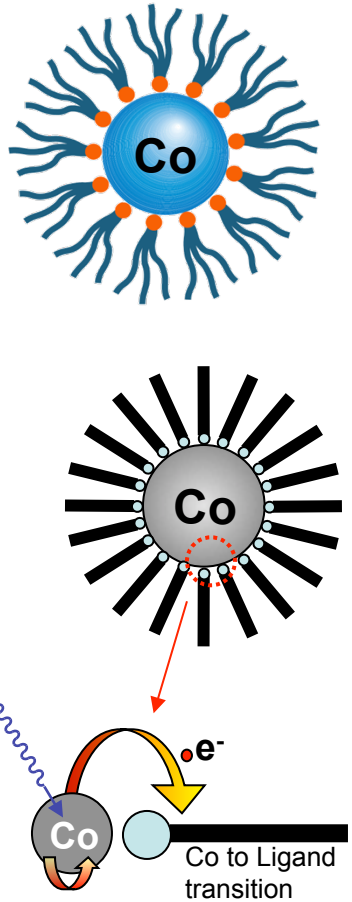


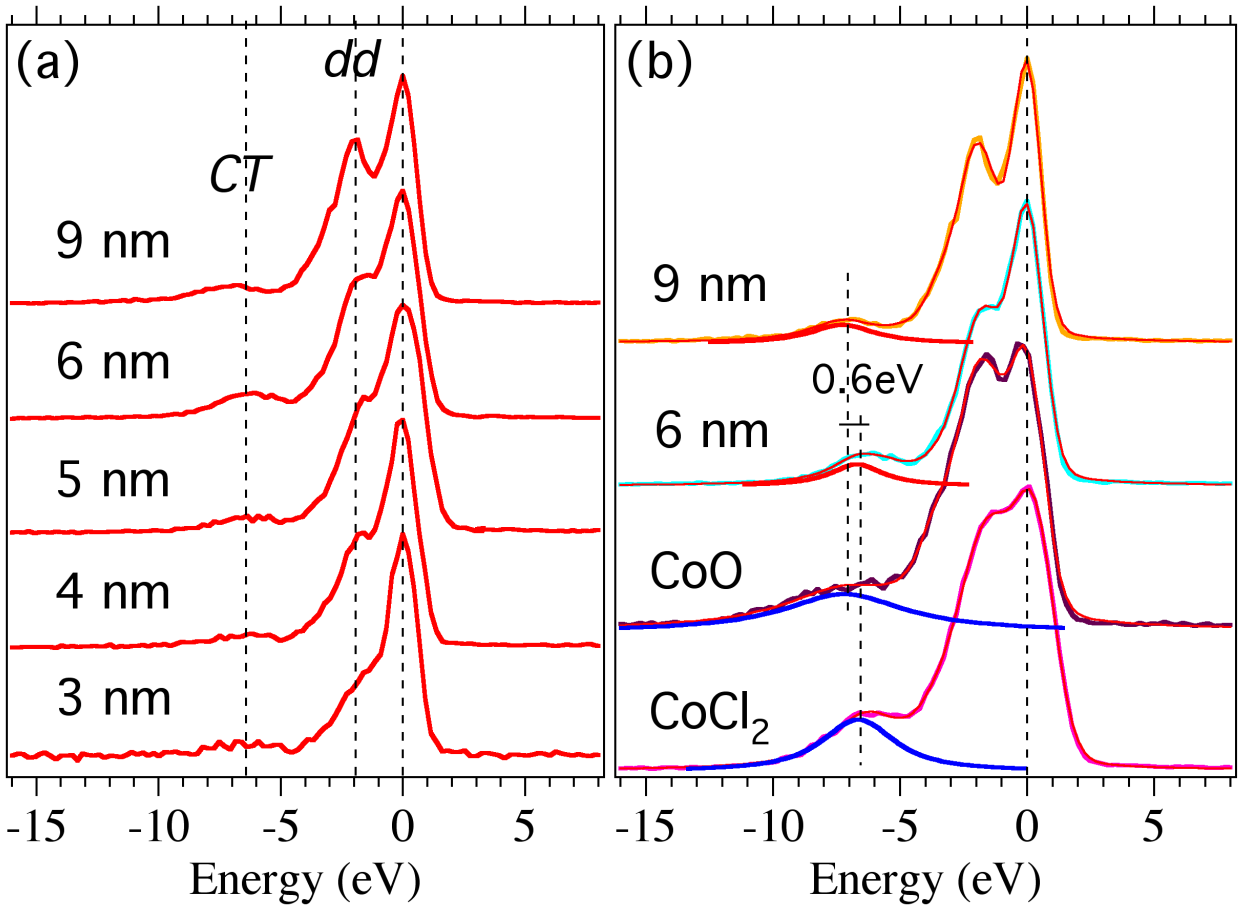


J. Chem. Phys. **123**, 184717 (2005)

ECS Transactions **1**, 69 (2006)

RIXS of Co Nanoparticles

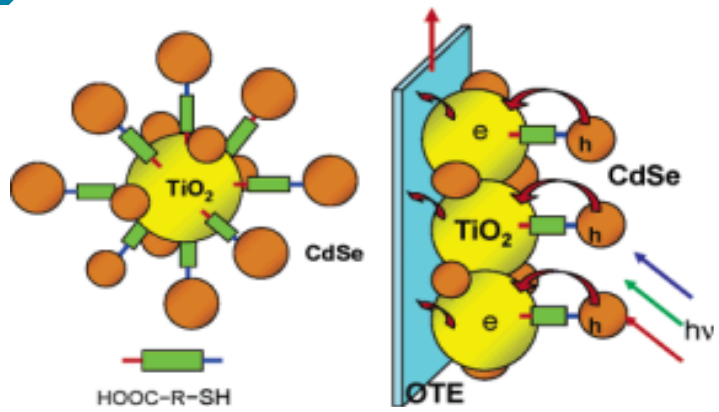




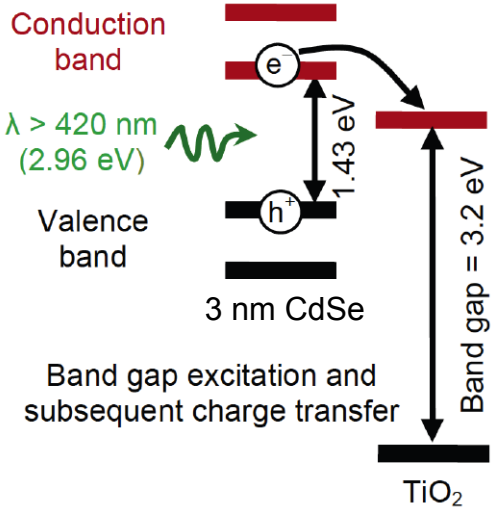
- **Surfactant:** *Oleic Acid, $C_{18}H_{34}O_2$ [$CH_3(CH_2)_7CH{:}CH(CH_2)_7CO_2H$]*
- **Solvent:** *Dichlorobenzene, $C_6H_4Cl_2$*

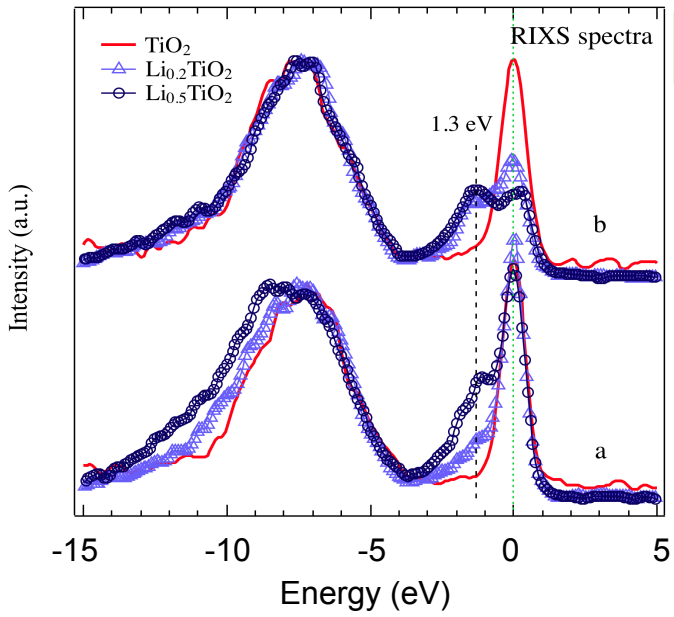
H. Liu et al., Nano Letters 7, 1919 (2007)

d-d Excitations: e⁻ Injection at Nanointerface

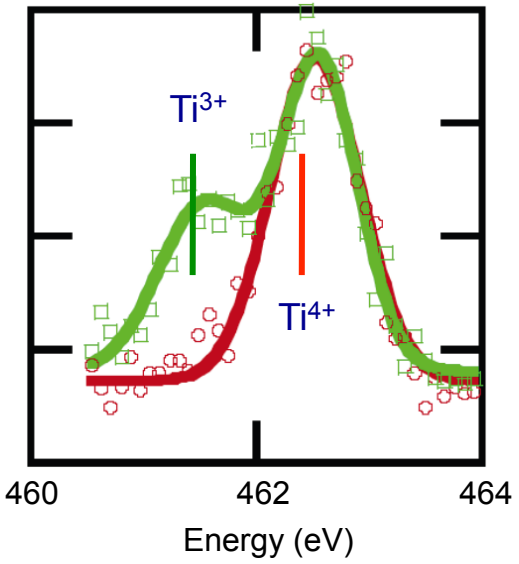


Robel et al., *J. Am. Chem. Soc.*, 2006





Ti L-edge RIXS



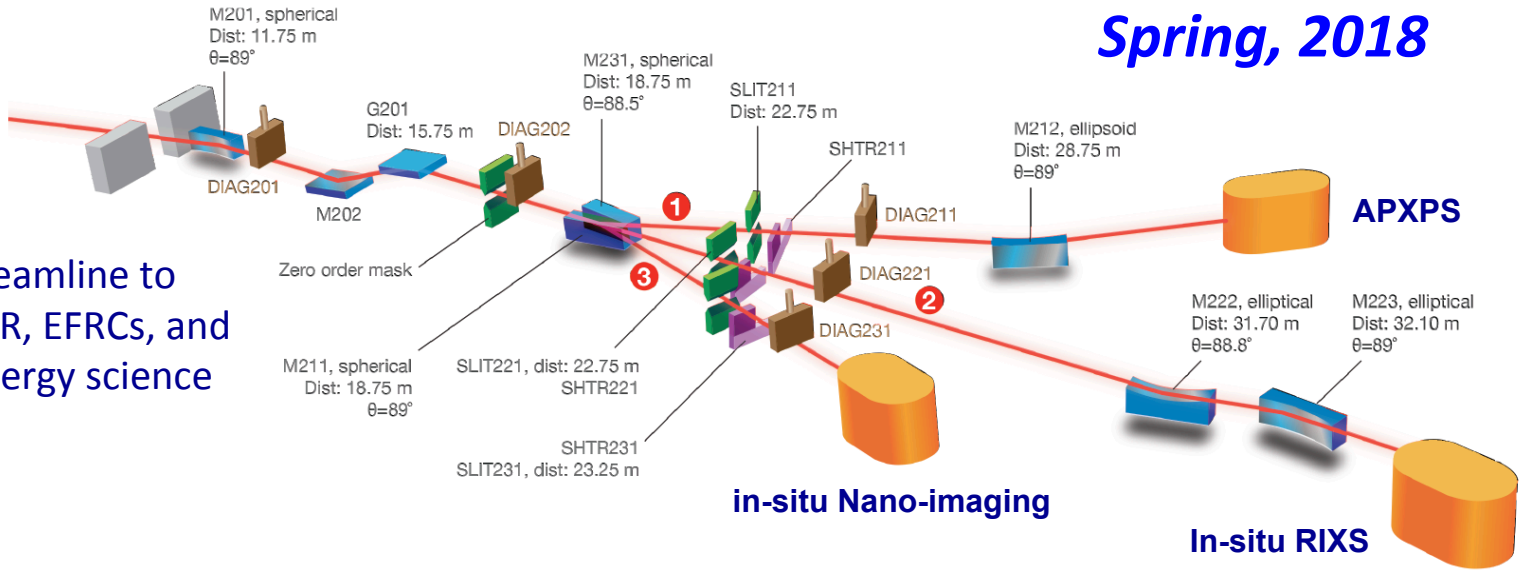
C. Wang, X. Deng, C. Matranga (NETL); J.-H. Guo (ALS)

Augustsson, J. Chem. Phys. 119, 3983 (2003)
Guo, Int. J. Quant. Chem. 109, 2714 (2009)

Y.-S. Liu et al., J. Electr. Spectr. Rel. Phenom. ***200****, 282 (2015)*

Advanced Materials Beamline for Energy Research

Spring, 2018

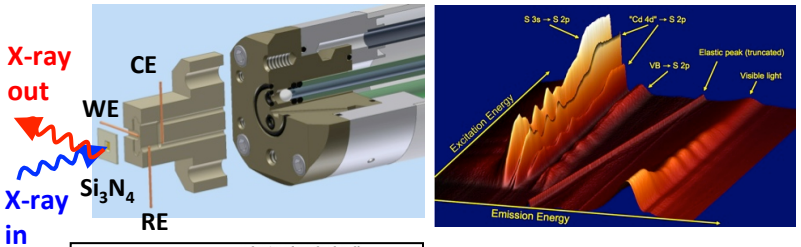


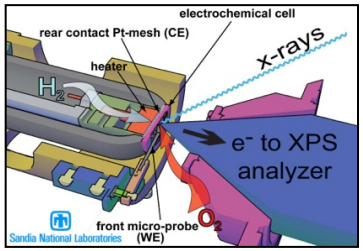
AMBER - A new beamline to support JCAP, JCESR, EFRCs, and general users in energy science research

50 -2500 eV
- RP = 10,000
- in-situ RIXS/APXPS/Nano-imaging

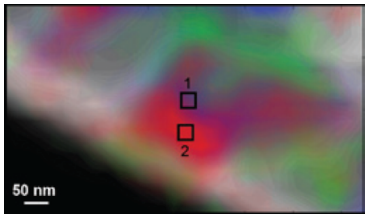
Science

In-situ/operando Spectroscopy (RIXS)



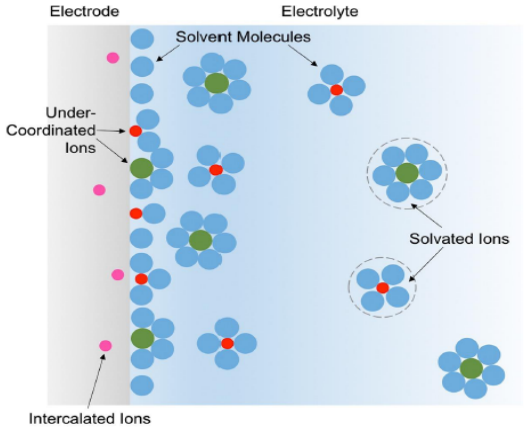


APXPS: Spectroscopy



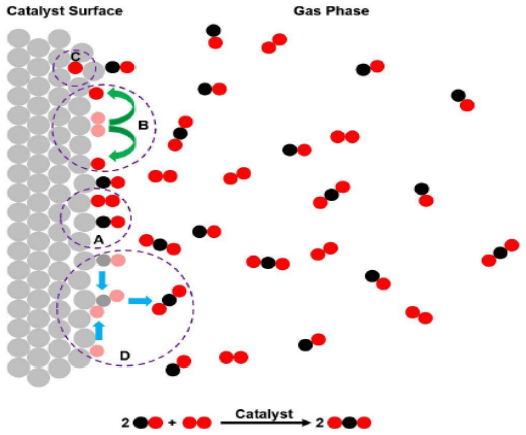
Nanospectroscopy

JCESR:
Beyond Li-ion batteries



Electrochemistry, Ion Solvation

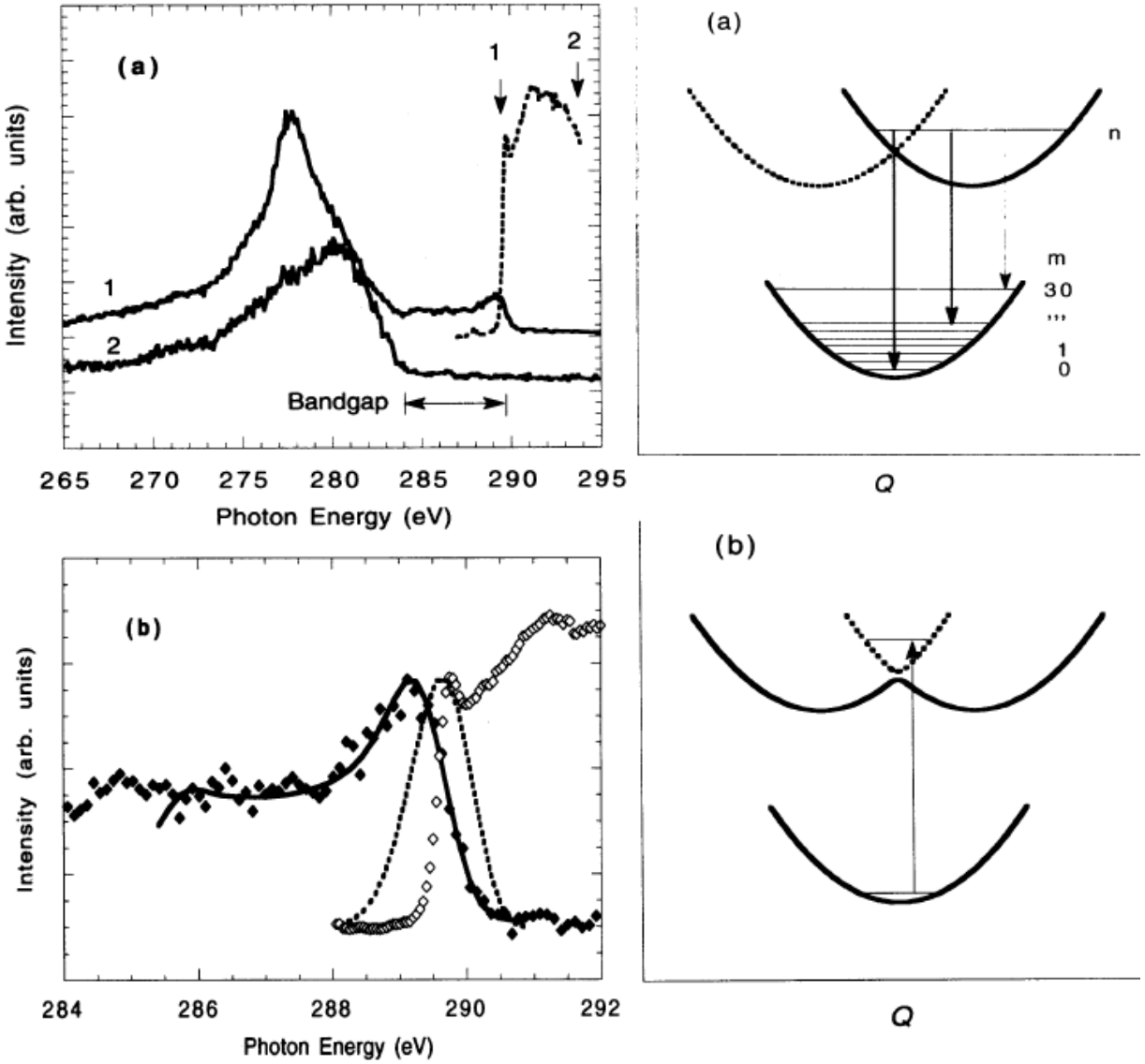
JCAP:
CO_2 Reduction



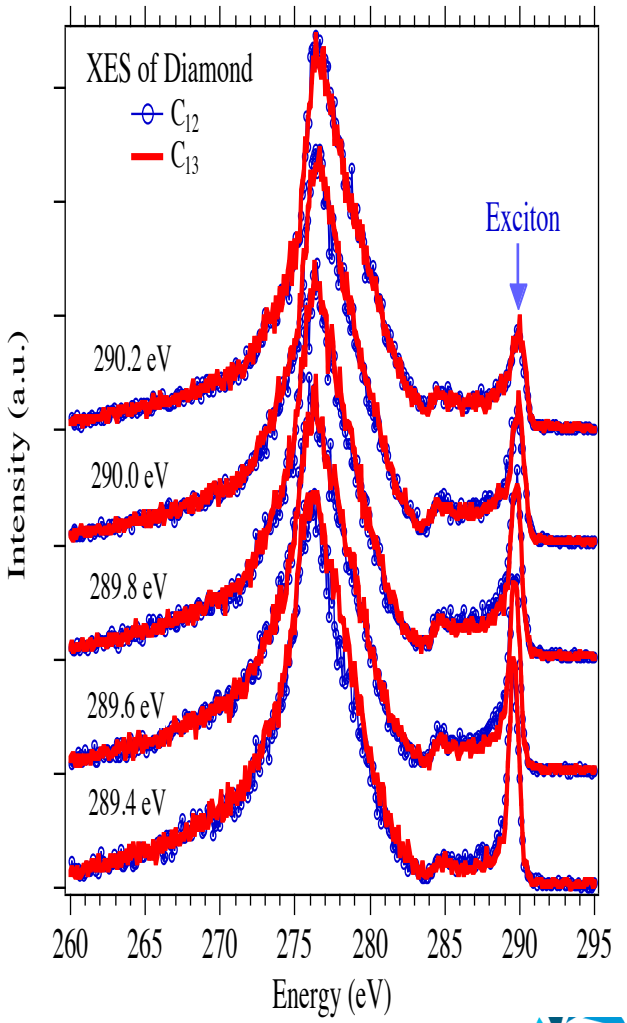
Heterogeneous Catalysis

RIXS of Diamond: from different light sources

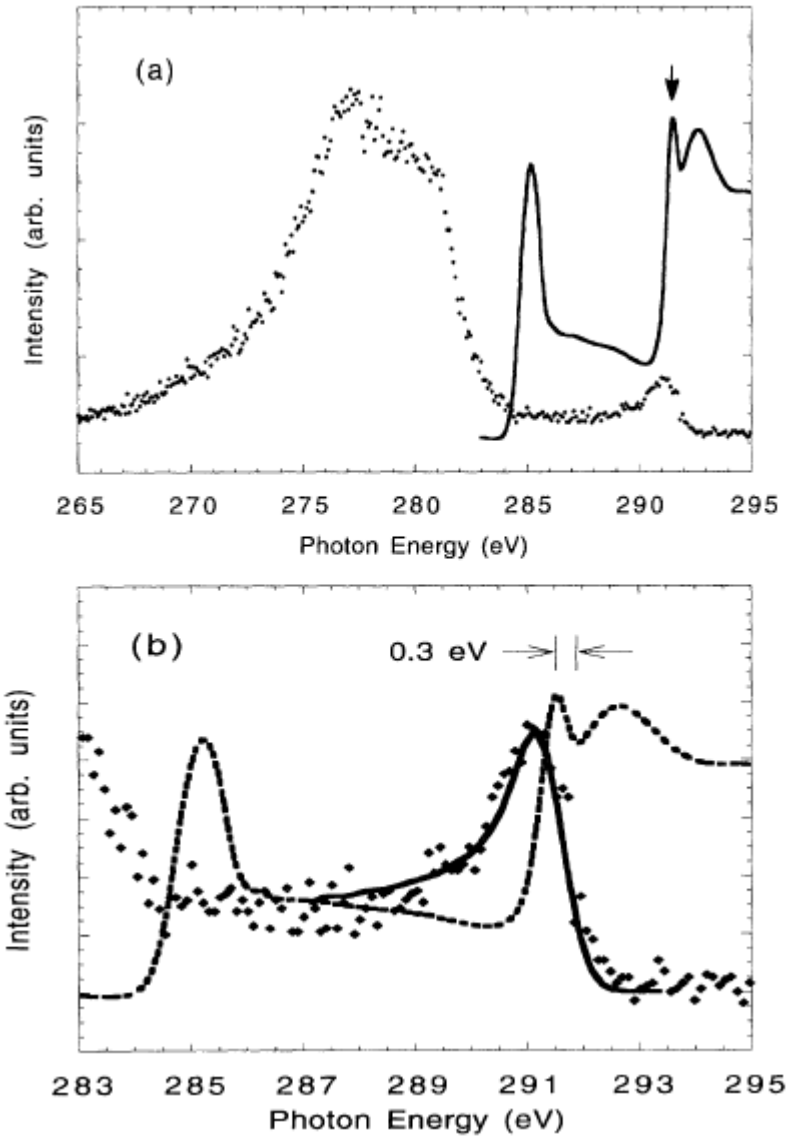
Y. Ma et al., @NSLS, PRL (1992), PRL (1993)



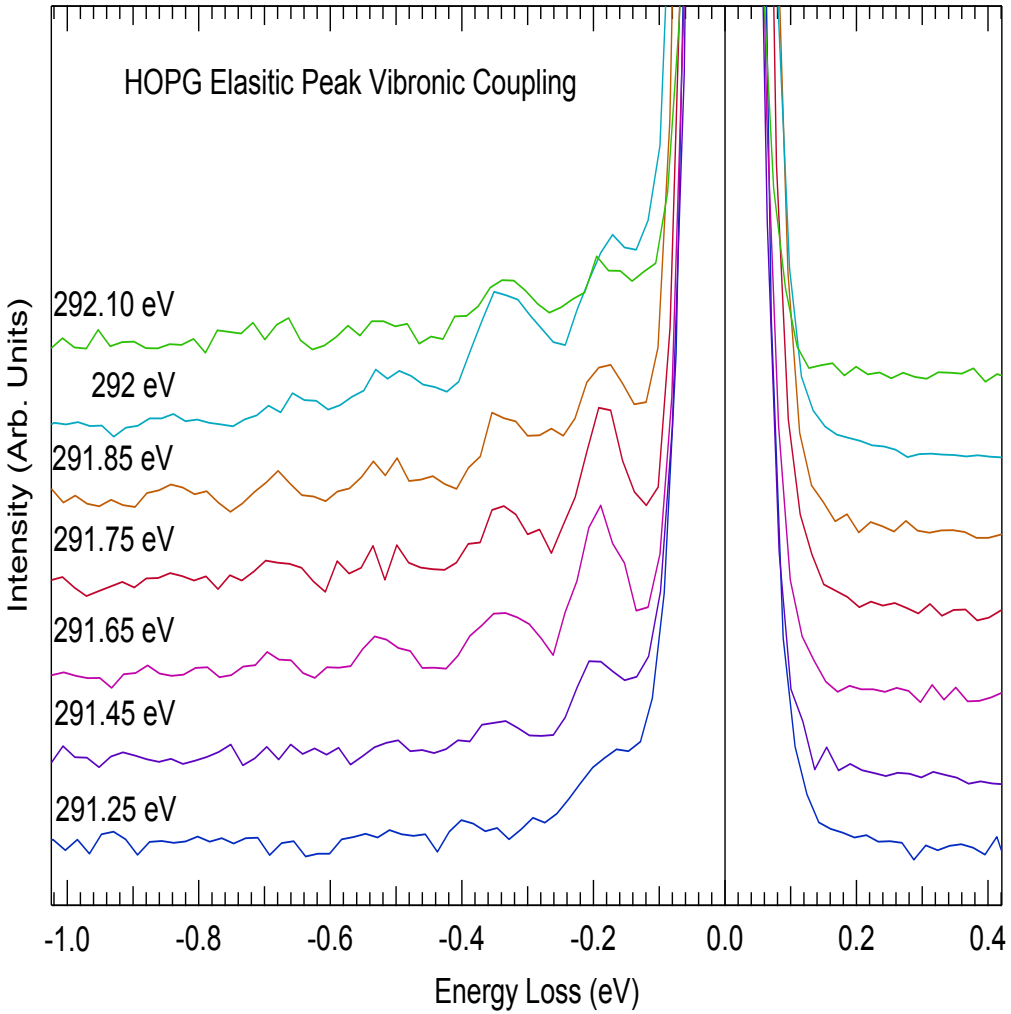
J.-H. Guo et al., AXIS@BL7.0.1 (1995)



RIXS of HOPG: from different light sources



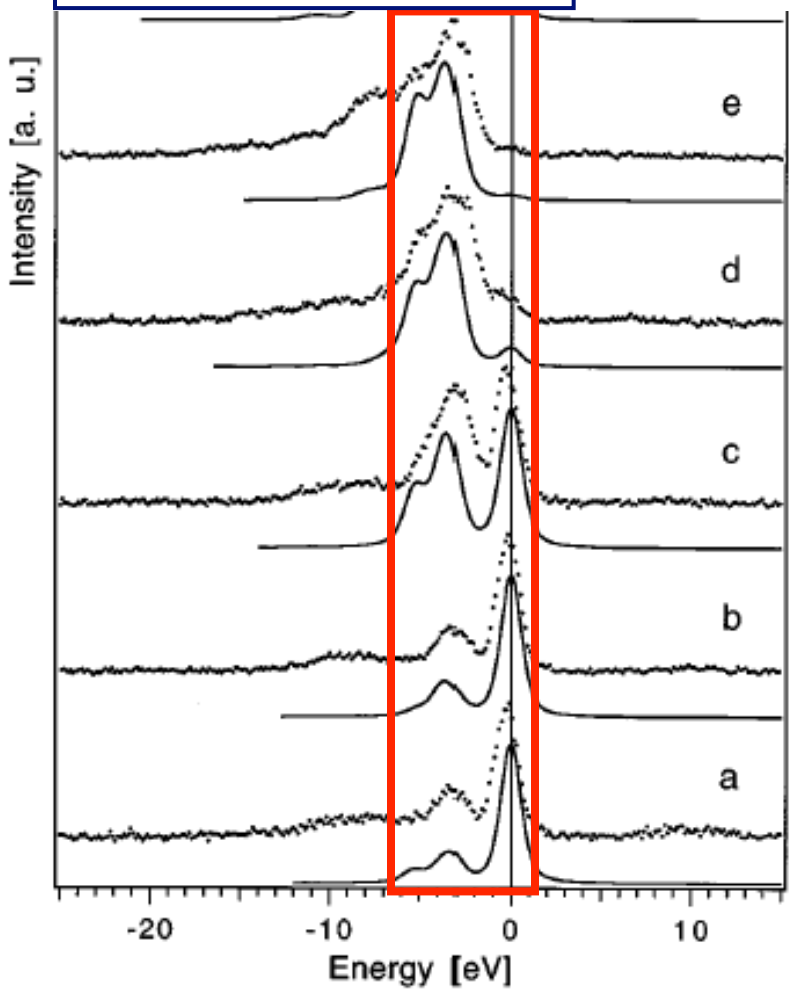
W. Yang et al., iRIXS@BL8.0.1 (2016)

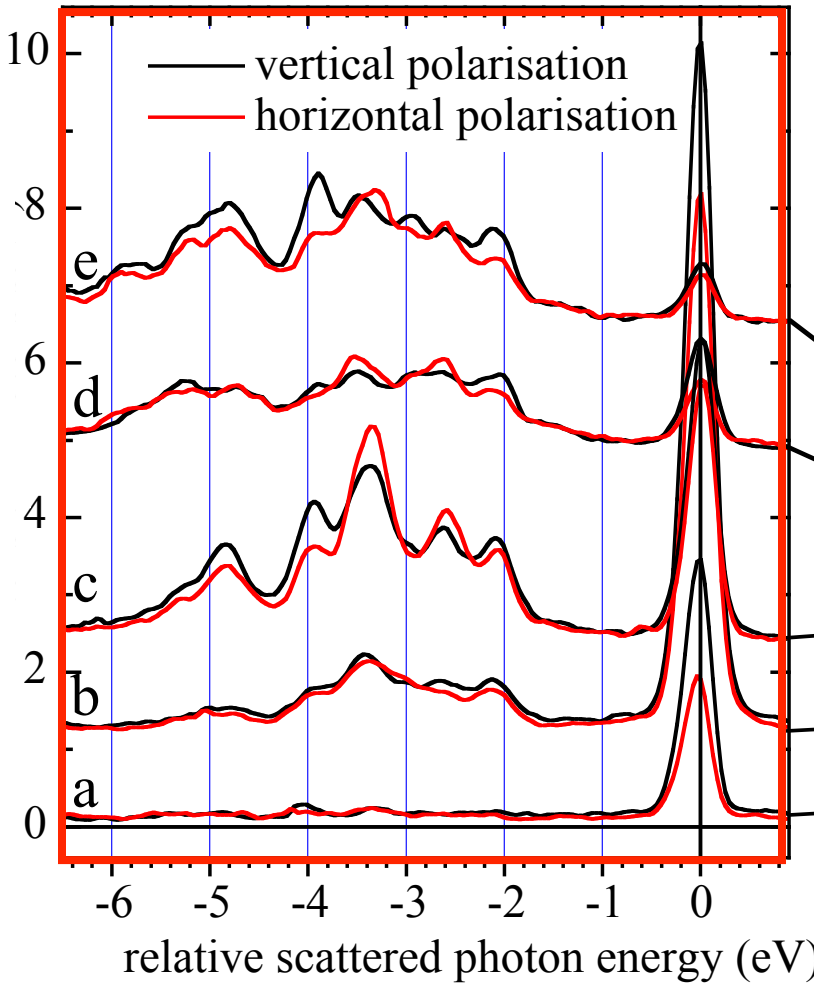


*Y. Ma et al., PRL **71**, 3725 (1993)*

Spectral Resolution

MnO, L_3 RIXS (640 eV)

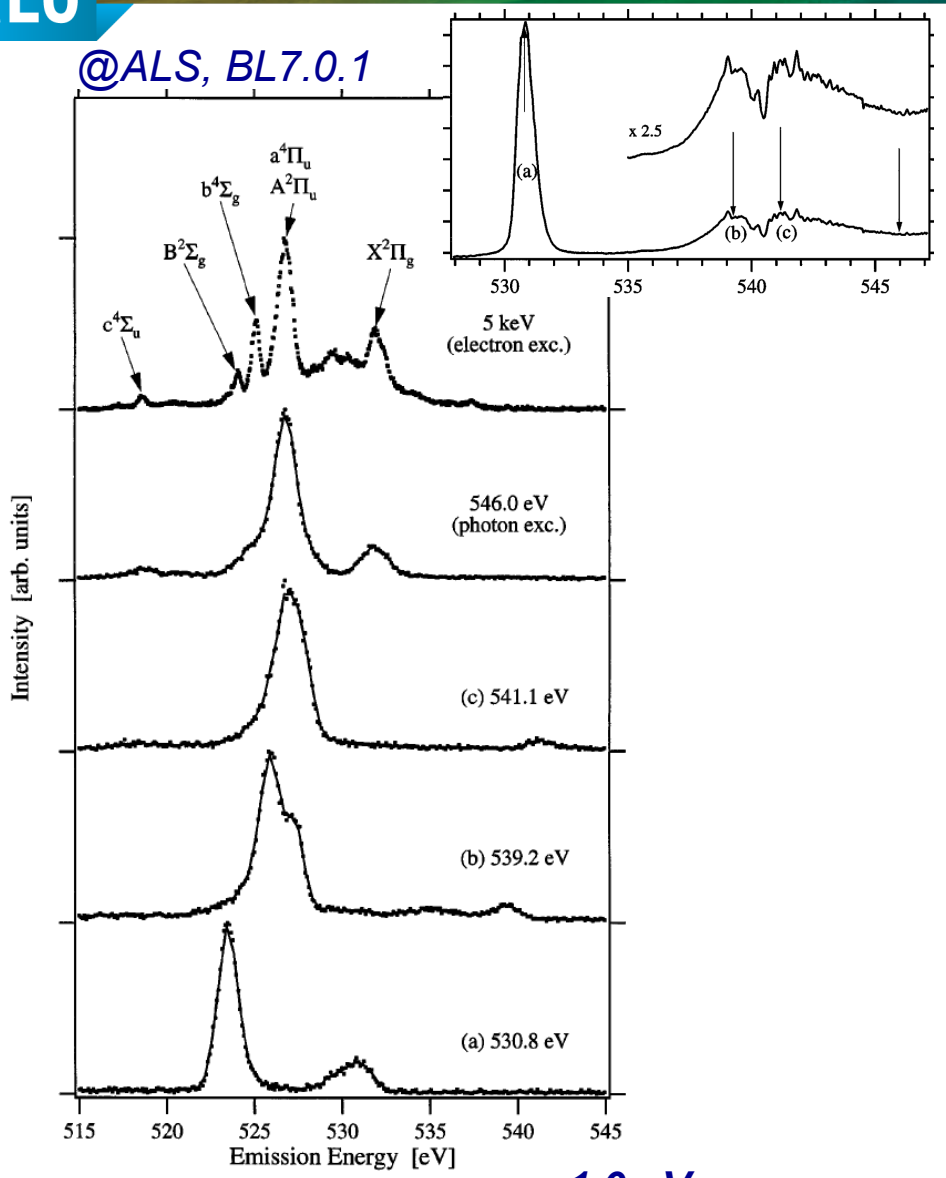




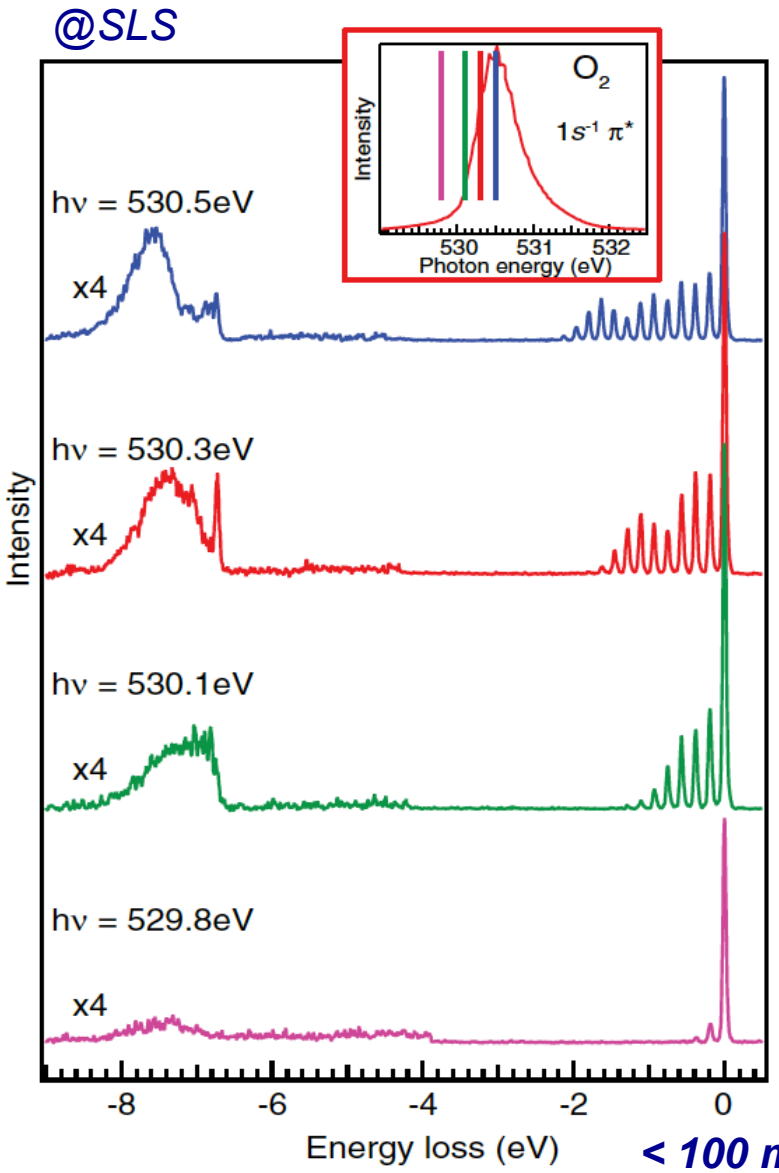
S. M. Butorin *et al* Phys. Rev. B **54**, 4405 (1996)
ΔE = 1.5 eV, Data and atomic calculations

G, Ghiringhelli *et al*. submitted to PRB
ΔE = 0.32 eV (from ESRF)

High-Resolution RIXS at SLS (O_2 molecule)



1.0 eV

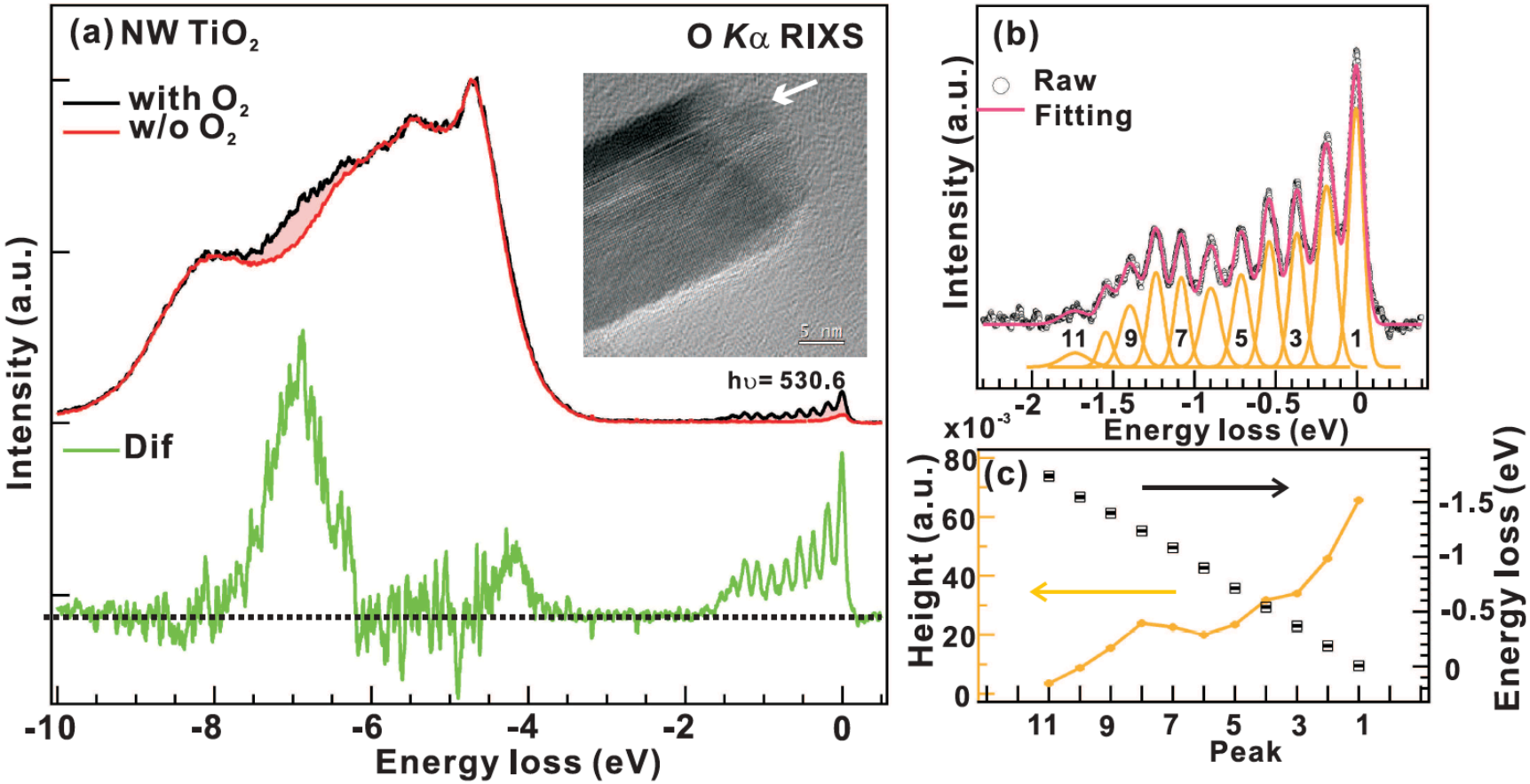


< 100 meV

P. Glans et al., PRL 76, 2448 (1996)

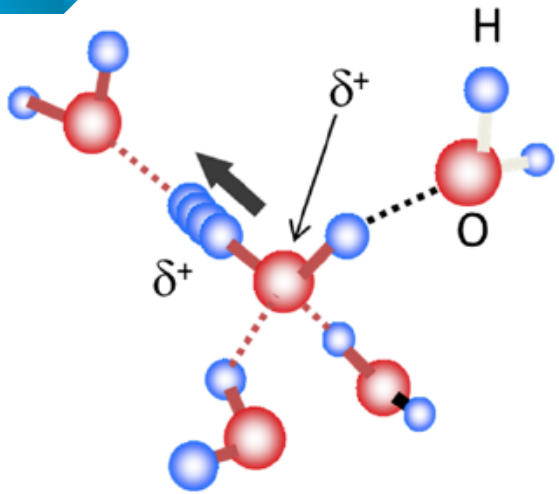
F. Hennies et al., PRL 104, 193002 (2010)

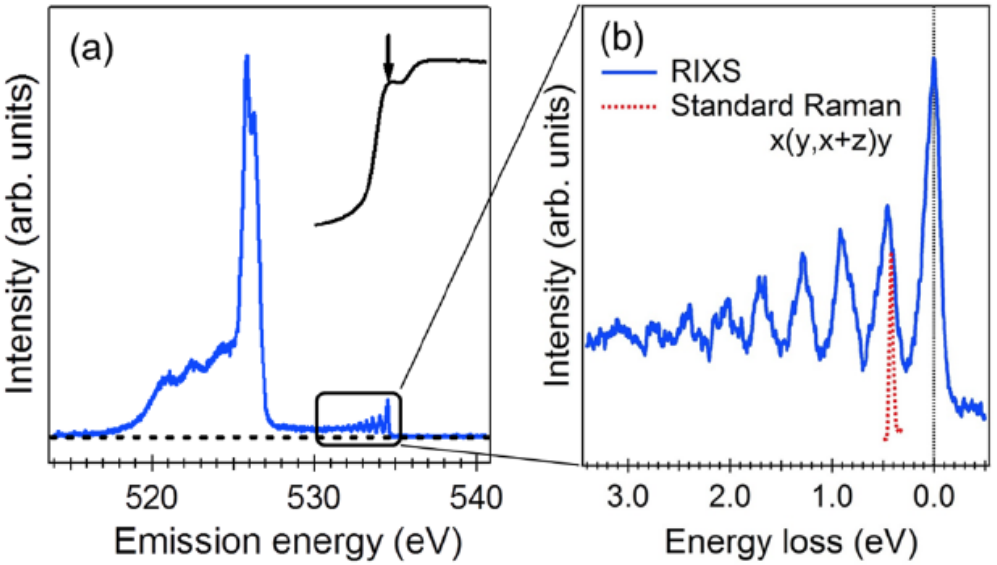
High-Resolution RIXS at SPring-8 (gas/solid)

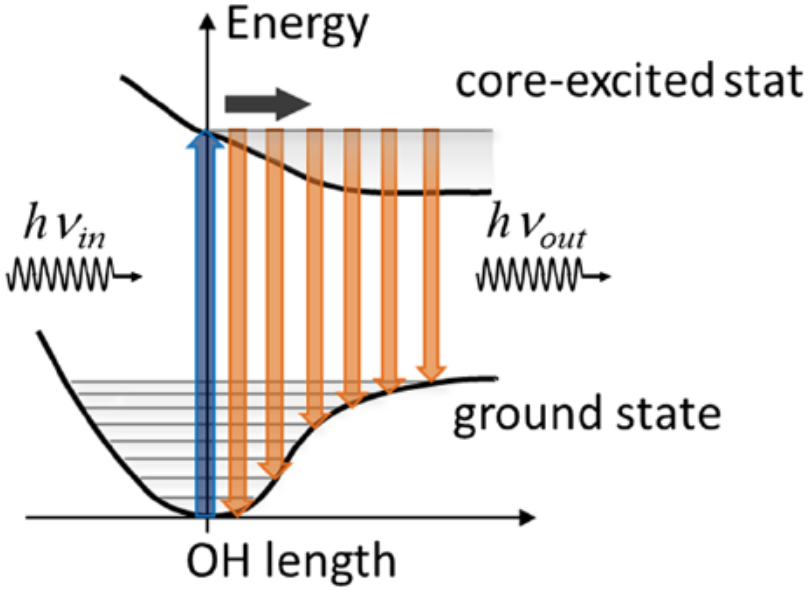


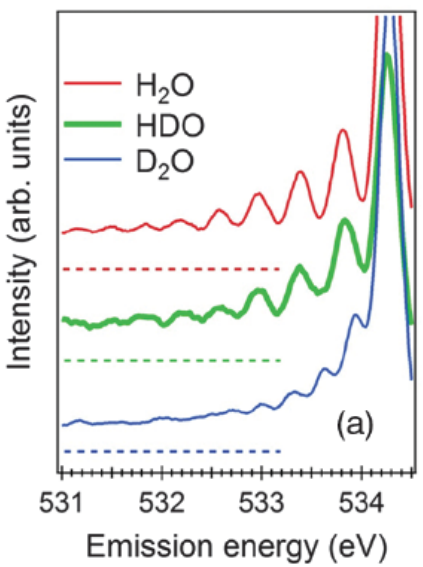
Cheng-Hao Chuang and Way-Faung Pong (Tamkang Univ.)
Jinghua Guo (ALS)
Yoshihisa Harada (Univ. of Tokyo)
Yat Li and Jin Zhang (UC Santa Cruz)

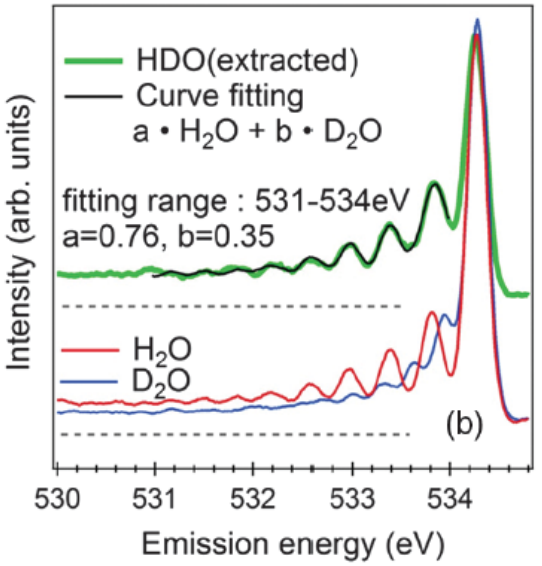
RIXS of Liquid Water (H_2O and D_2O)









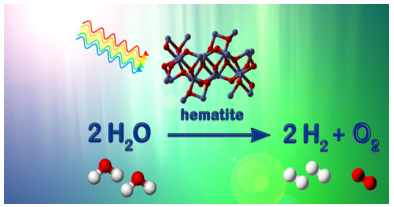


*Yoshihisa Harada et al., **111**, 193001 (2013)*

Soft X-Ray Probing Charge Transfer and Ion Transport at Catalytic and Electrochemical Interfaces

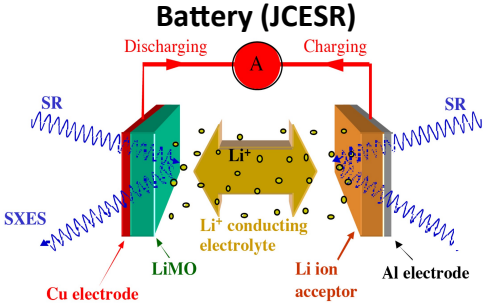
Energy Conversion and Energy Storage

Photosynthesis (JCAP)



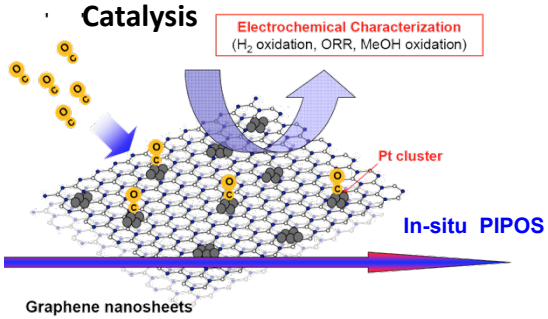
OER, CO_2RR

Battery (JCESR)



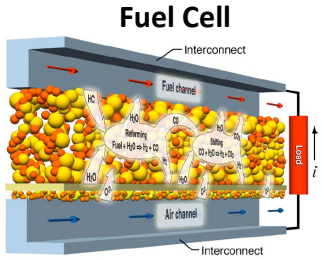
Beyond Li-ion: Li-S, Mg-ion

Catalysis

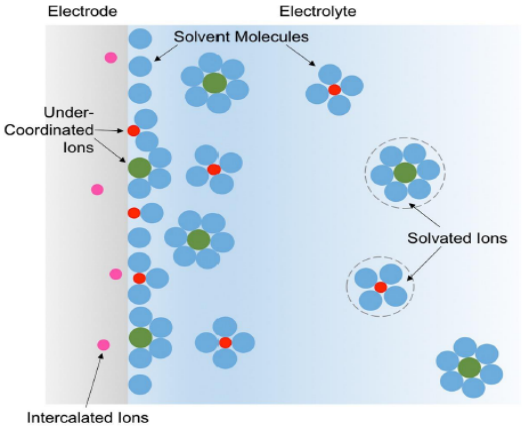


3d TM & alloy catalysts

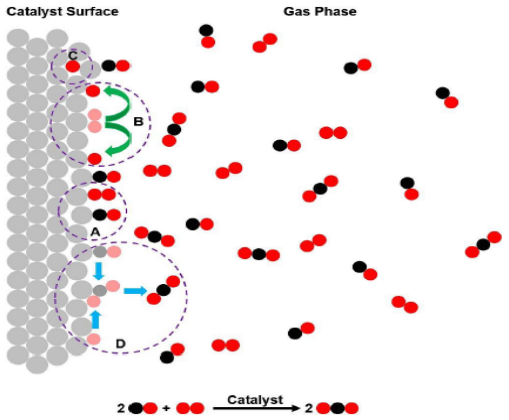
Fuel Cell



3d TM and RE catalsts



Electrochemistry, Ion Solvation



Heterogeneous Catalysis

Multi-Modal and Dimensional Soft X-ray:

Soft X-ray Spectroscopy

- APXPS: 1 - 20 nm probing depth
- XAS: 5 - 100 nm probing depth
- XES and RIXS: 100 nm probing depth
- STXM: transmission, spatial resolution (10 nm)

Key Electronic Structure

- Conduction and valence bands
- Ligand p-band and metal d-orbital levels

Chemical selective (Elemental selective)

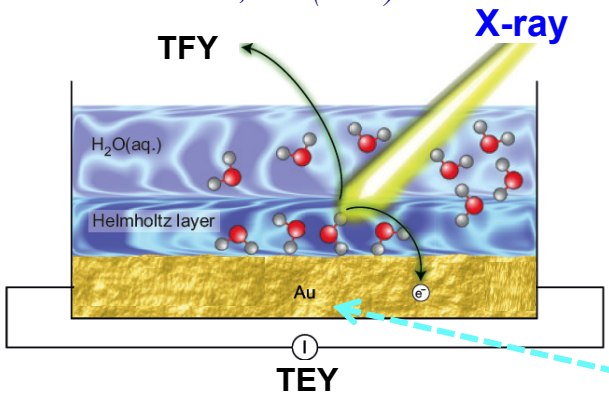
- Chemical bonding; oxidation states

Dynamics while alive:

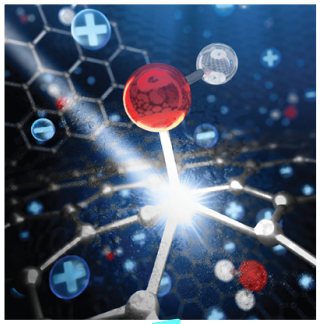
- In-situ/operando (intermediate/transient states)
- Charge transfer, ion transport, electron injection …
- Multi time domains (100 ps, ns, us, and ms, …)

In-Situ/Operando Soft X-ray Spectroscopy

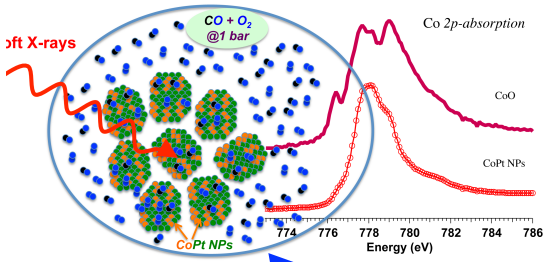
Water/Au EC-interface:
*Science **346**, 831 (2014)*



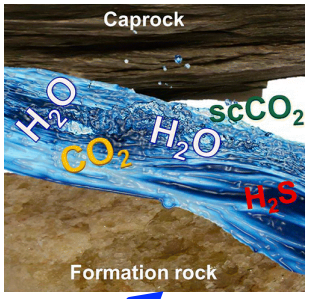
Energy Storage:
*Adv. Mater. **27**, 1512 (2015)*



Nanocatalysts:
*JACS **136**, 9898 (2014)*
*Nano Letters **12**, 3091 (2012)*
*Nano Letters **11**, 847 (2011)*



Subsurface Science:



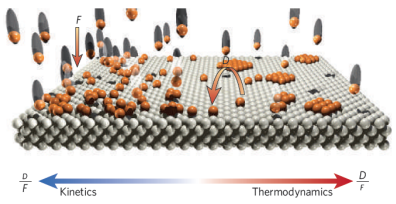
Pressure dependent Chemical Transformation

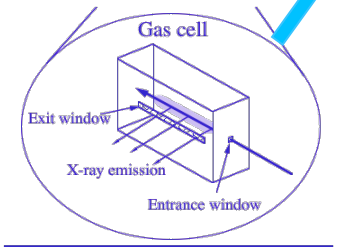
UHV
10^{-8}
Soft X-ray for Surface science

1 mbar
1 bar
10-100 bar

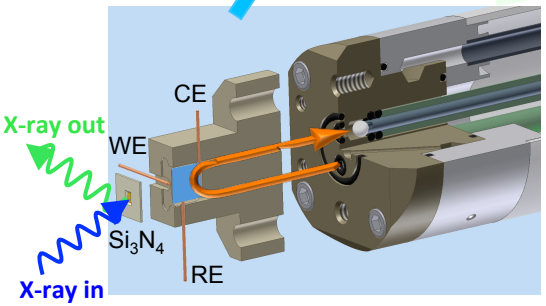
10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4} 10^{5} 10^{6} 10^{7} 10^{8} 10^{9} 10^{10} (Pa)

On-going LDRD project:
High-pressure (1-10 MPa) soft X-ray spectroscopy for H_2 storage and subsurface science

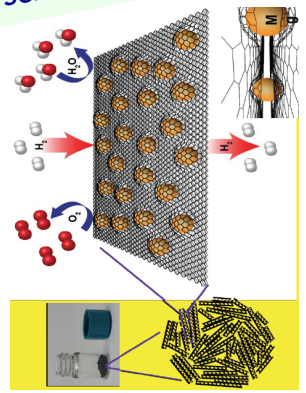




O_2: PRL **76**, 2448 (1996)
CO_2: PRL **77**, 5035 (1996)
CH_2, CH_4, CH_6: PRL **83**, 1315 (1999)



Water: PRL **89**, 137402 (2002)
Water+Methanol: PRL **91**, 157401 (2003)
Electrochem.: EC2010, EC2012



Solid-state hydrogen storage:
Nature Comm. **7**, 10804 (2016)