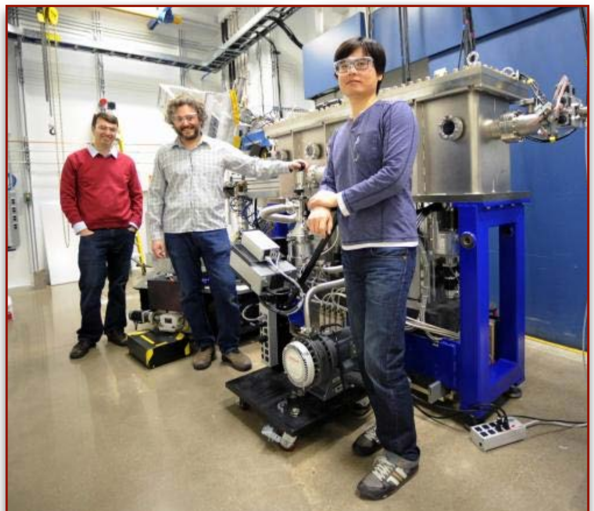
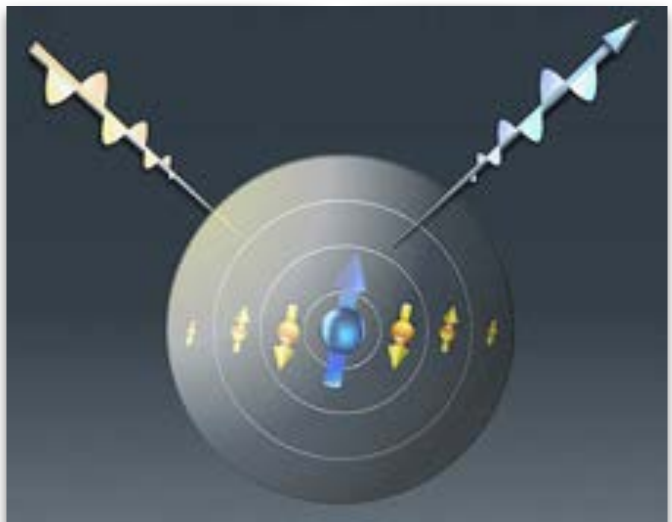
Resonant Inelastic X-Ray Scattering & Electron Dynamics

Jason N. Hancock
University of Connecticut
jason.hancock@uconn.edu


Neutron and X-ray Scattering School 2019
June 24, 2019, Argonne National Laboratory, Argonne, IL

UConn Condensed Matter Physics

Alexander Balatsky
Theory

Gayanath Fernando
Theory

Boris Sinkovic
Thin films synthesis
Electron spectroscopy

Elena Dormidontova
Soft Matter Theory

Jason Hancock
THz, Infrared, X-ray
Applied physics

Ilya Sochnikov
Transport
Scanning SQUID

Niloy Dutta
Photonics
Applied physics

Menka Jain
Thin film synthesis

Barrett Wells
PLD films, Muons,
Neutrons, ARPES

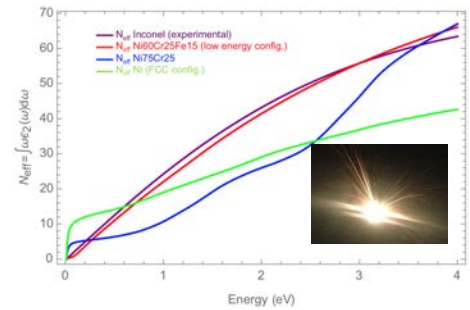
Plus strong connections with: AMO group, UConn Institute for Materials Science, New UConn Tech Park

Photon Science at UConn

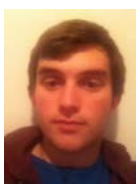
- Additive manufacturing

Erin Curry
PhD student

Kaitlin Lyszak
PhD student

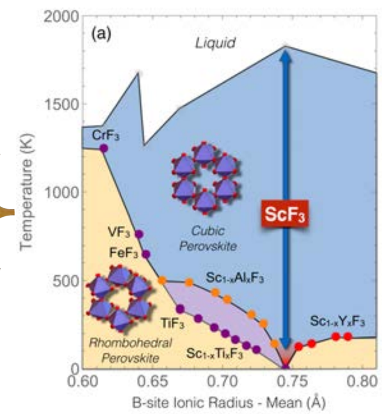


- Negative thermal expansion near structural quantum phase transitions



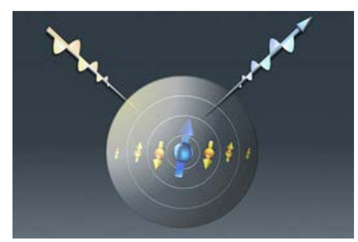
Connor Occhialini BS ’18
(PhD @ MIT Aug 2018)

Sahan Handunkanda (PhD ’18)



- *f*-electron physics via RIXS

Donal Sheets
PhD student



My PhD research does/will likely use…

A

X-rays

B

Neutrons

C

Both X-rays and Neutrons

D

Neither

E

I am a theorist

My PhD research does/will likely regard…

A
Mostly structural studies

B
Spectroscopy and electronic structure

C
Advanced imaging

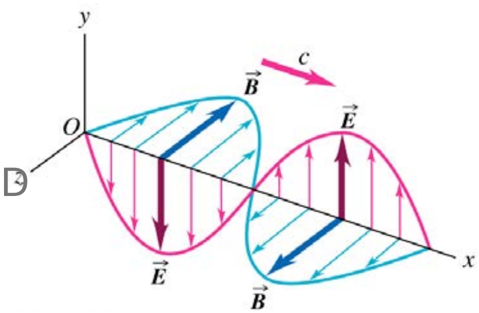
D
Still figuring it out

E
None of these

Spectroscopy in a nutshell

The Electromagnetic Field

- Photons are bosons, independent, luminal
- Described by Maxwell's equations at low energy, QED at high energy

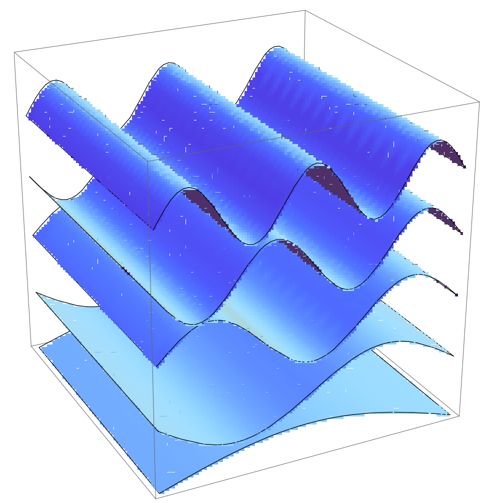


- Fully understood, quantized, modes are described as

$$|v\rangle = |n_0, ...n_{\mathbf{k}}...\rangle$$

Vector potential:

$$\mathbf{A}(\mathbf{r},t) = \sum_{\mathbf{k}} \sum_{\mu=-1,1} \left(\mathbf{e}^{(\mu)}(\mathbf{k}) a^{(\mu)}_{\mathbf{k}}(t)\, e^{i\mathbf{k}\cdot\mathbf{r}} + \bar{\mathbf{e}}^{(\mu)}(\mathbf{k}) \bar{a}^{(\mu)}_{\mathbf{k}}(t)\, e^{-i\mathbf{k}\cdot\mathbf{r}} \right)$$

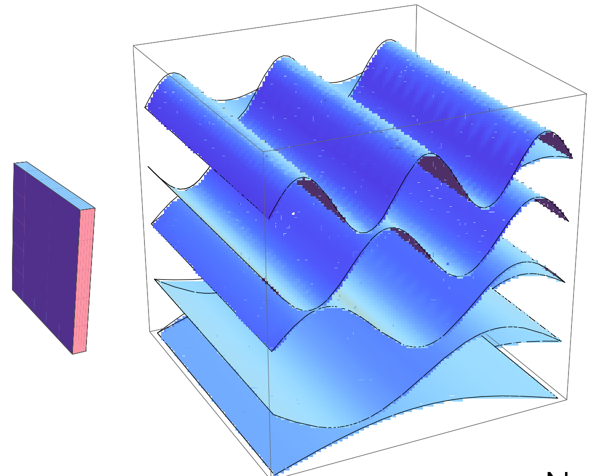


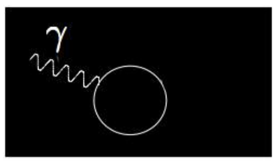
Spectroscopy, general remarks

- Sample can exchange energy with EM field

$$|\psi_g\rangle \otimes |v\rangle \rightarrow |\psi_e\rangle \otimes |v'\rangle$$

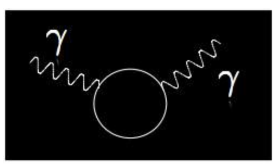
(sample) (vacuum)





One photon
Optical spectroscopy
X-ray absorption

$$|n_0, ...n_{\mathbf{k}}...\rangle \;\rightarrow\; |n_0, ...n_{\mathbf{k}} - 1...\rangle$$

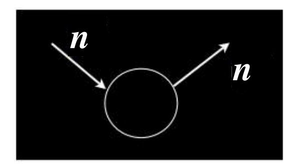


Two photon
Raman
Inelastic X-ray Scattering

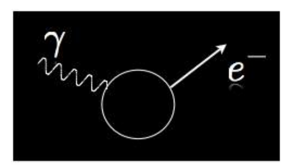
$$|n_0, ...n_{\mathbf{k}}...\rangle \;\rightarrow\; |n_0, ...n_{\mathbf{k}} - 1...n_{\mathbf{k}'} + 1...\rangle$$

Related spectroscopies:

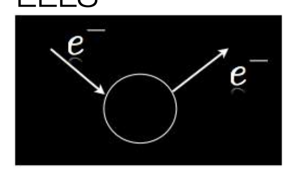
Neutron



ARPES



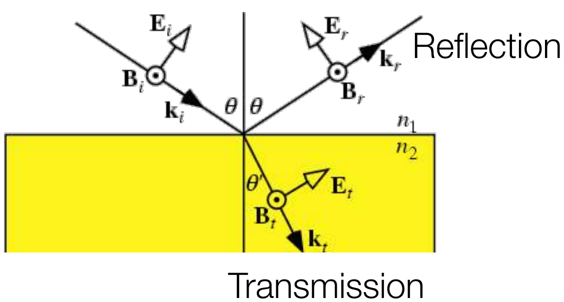
EELS

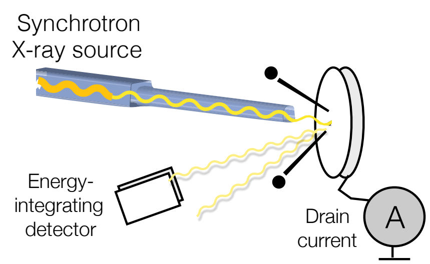


Photon spectroscopies

One-photon

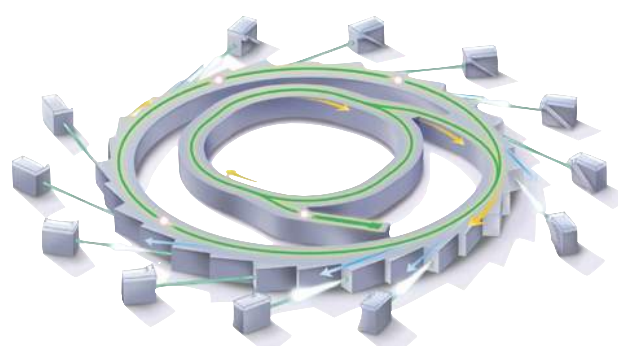
- Can measure from reflection or transmission in time or frequency domain
- Use Fresnel's equations to determine $n + ik$, . $\sigma_1 - i\sigma_2, \epsilon_1 + i\epsilon_2$ and relate to fundamental behavior
- X-ray absorption collected differently, through total electron or total fluorescence yield





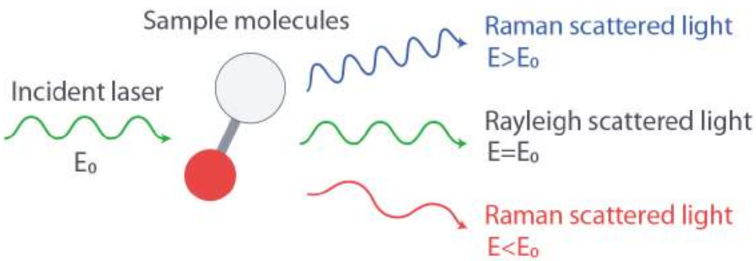
Two-photon

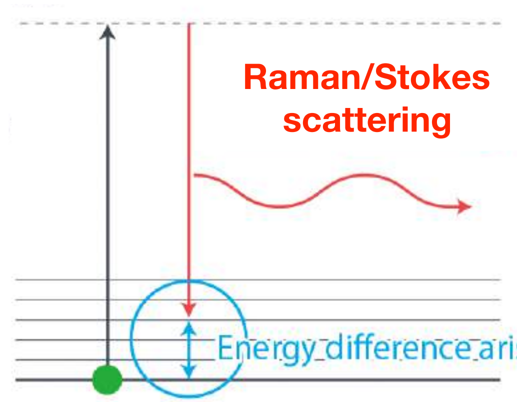
- IXS and RIXS (also REXS, Raman)
- Probes electronic excitations in a momentum-resolved way
- Technical advances making rapid progress

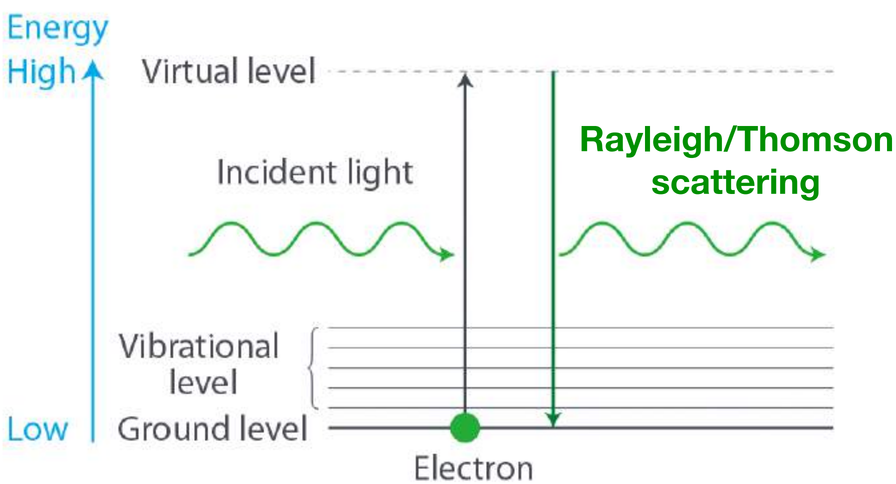


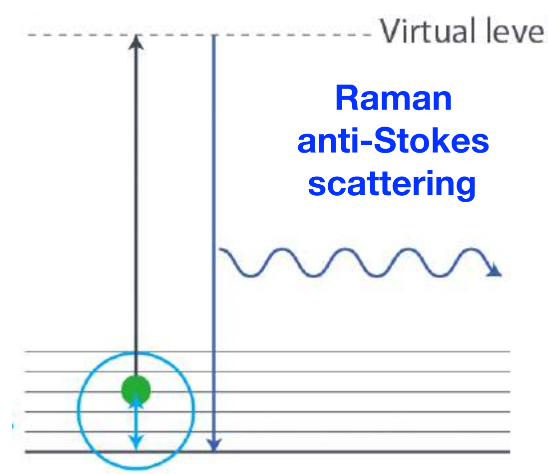
Two-photon scattering examples

Raman=inelastic light scattering









https://www.nanophoton.net/

Modern Raman scattering

HEAVY FERMIONS

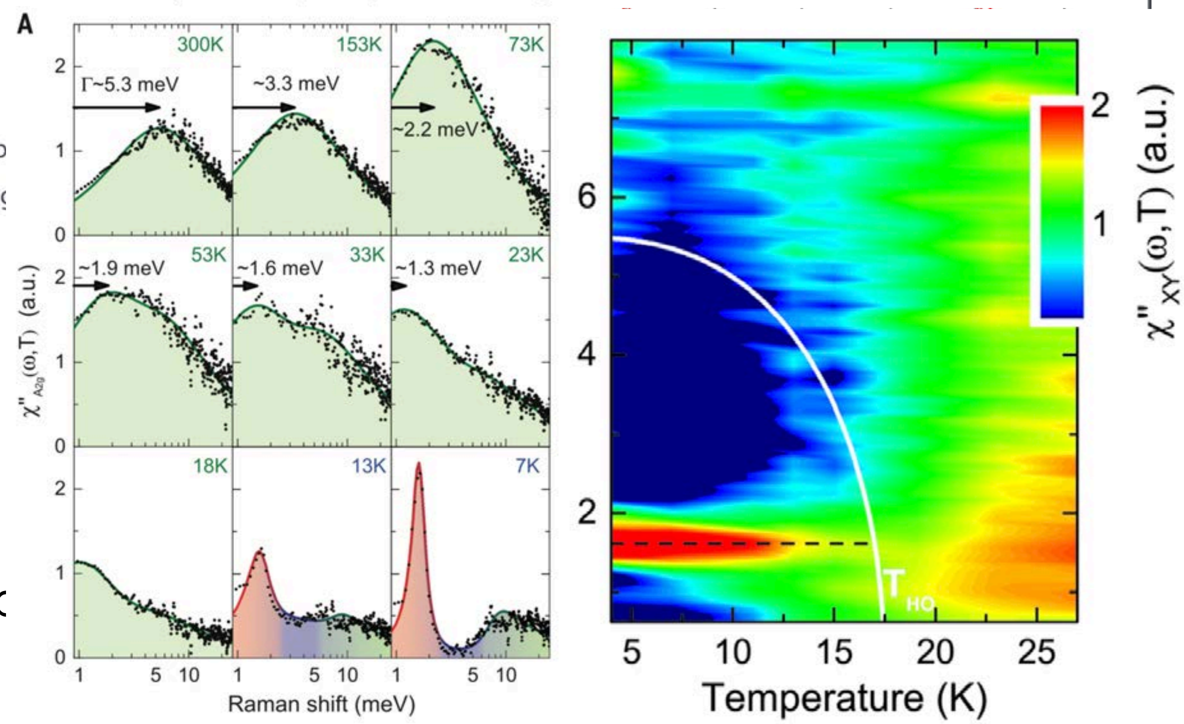
Kung, et al Science 347, 1339 (2015)

Chirality density wave of the "hidden order" phase in URu_2Si_2

H.-H. Kung,[1*] R. E. Baumbach,[2†] E. D. Bauer,[2] V. K. Thorsmølle,[1‡] W.-L. Zhang,[1] K. Haule,[1*] J. A. Mydosh,[3] G. Blumberg[1,4*]

Wavenumb

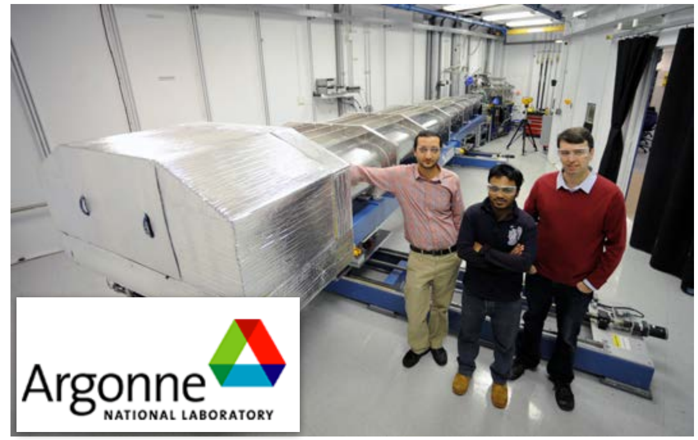
Waveleng

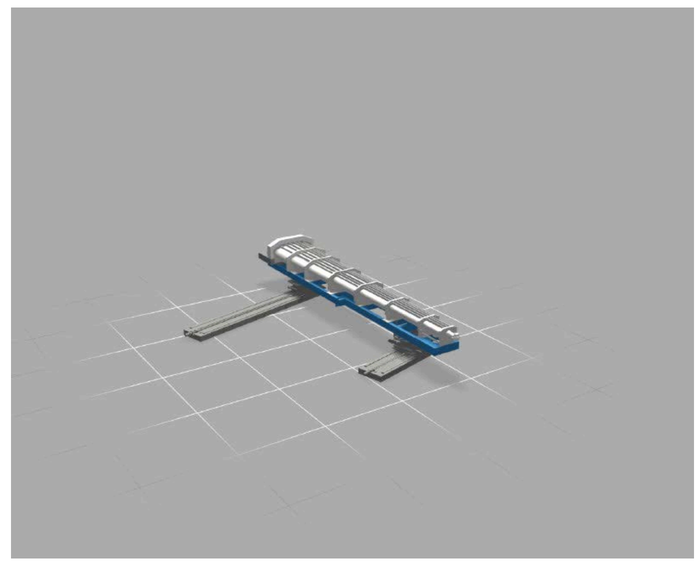


- Laser source=high resolution
- Lattice excitations easy to see
- Electronic and magnetic excitations p

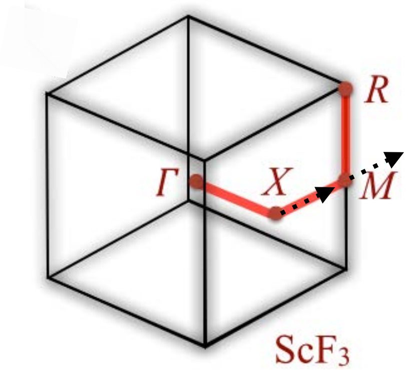
High **E**nergy **R**esolution **I**nelastic **X**-ray Scattering

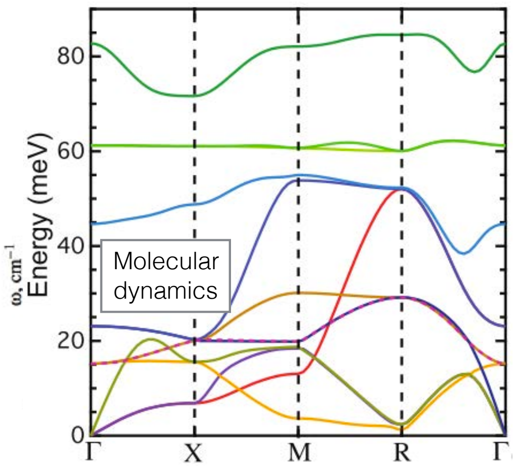
- Sector 30, Advanced Photon Source, Argonne National Lab
- 23,724 eV incident energy
- <1 meV incident bandwidth
- Resolving power $E_i/\Delta E_i = 2\times10^7$
- 9 analyzers sample, 9 momenta transfers simultaneously, 9m arm
- 1.5 meV energy resolution
- 20μm x 5μm spot size
- Measures energy and momentum distribution of lattice vibrations $S(\vec{q},\omega)$





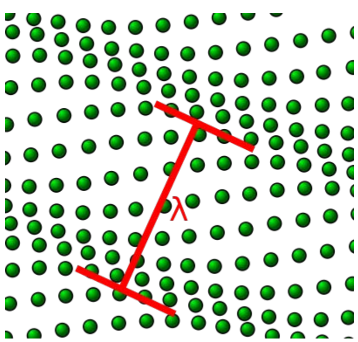
IXS from phonons





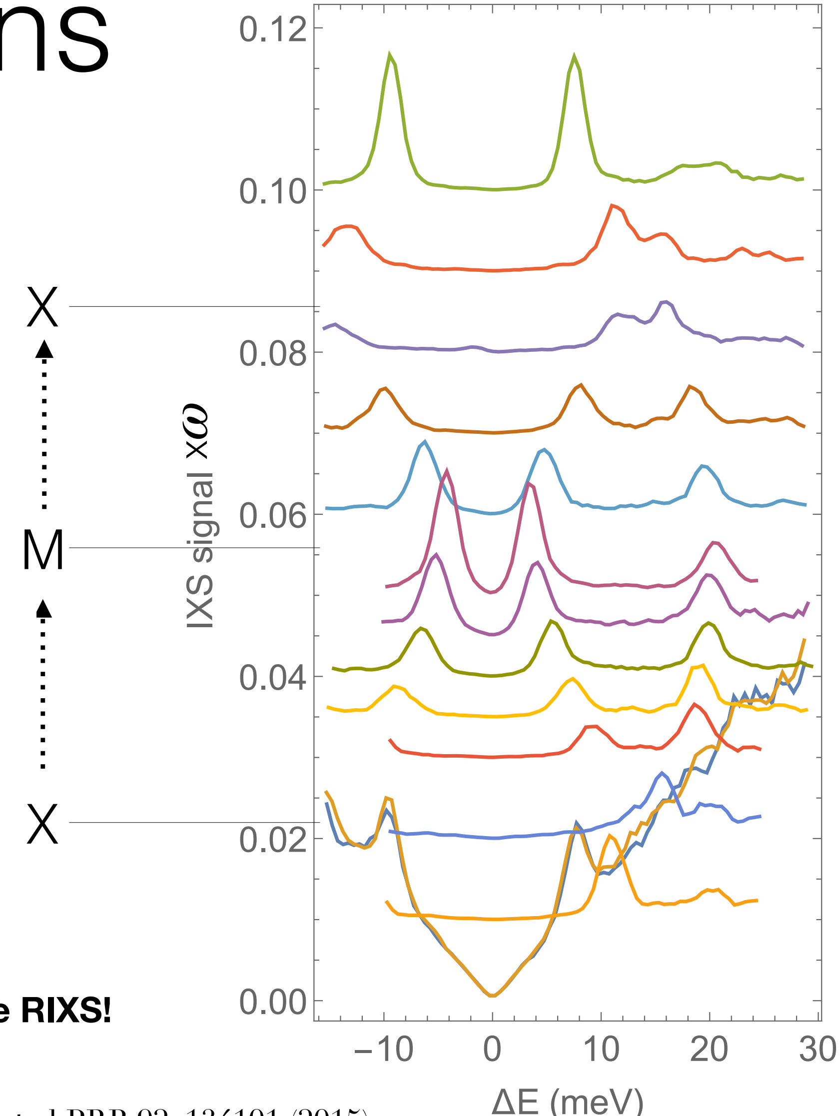
Li *et al, PRL* **107** 195504 (2011)

- IXS measures collective modes of lattice system: phonons



Energy of each mode at wavevector k

What about electronic or magnetic collective modes? Use RIXS!



S. U. Handunkanda, et al PRB 92, 134101 (2015)

What is this?

A The emission spectrum of a star at z=0 redshift

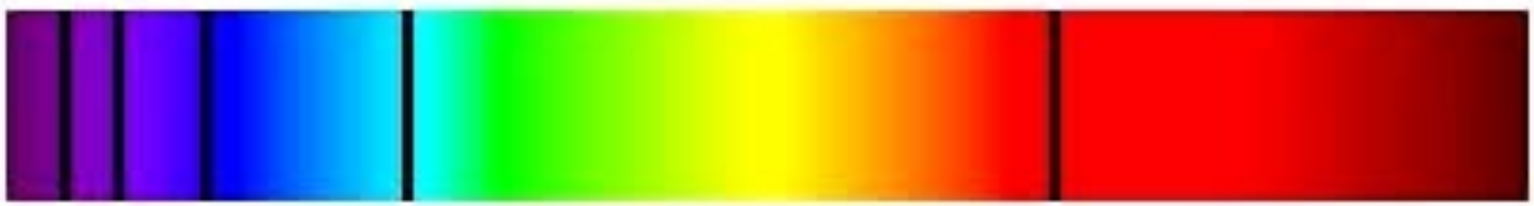
B A flat rainbow snake

C A fashionable belt

D Balmer series of emission by hydrogen

E There is more than one correct answer

What is this?



A — The absorption spectrum of a star at z=0 redshift

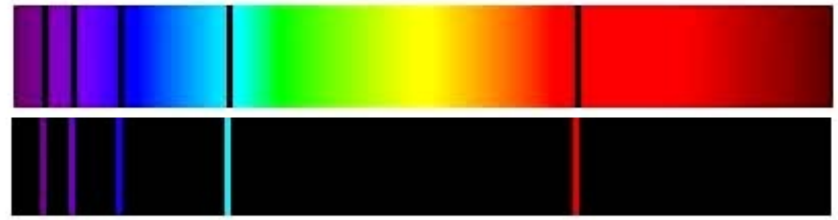
B — A flat rainbow snake

C — A fashionable belt

D — Balmer series of absorption by hydrogen

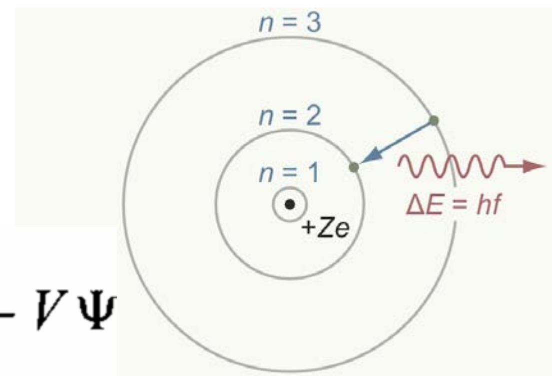
E — There is more than one correct answer

Balmer series



- Describes transitions between quantized energy levels in hydrogen (one proton, one electron)

$$\frac{1}{\lambda} = R_{\mathrm{H}} \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

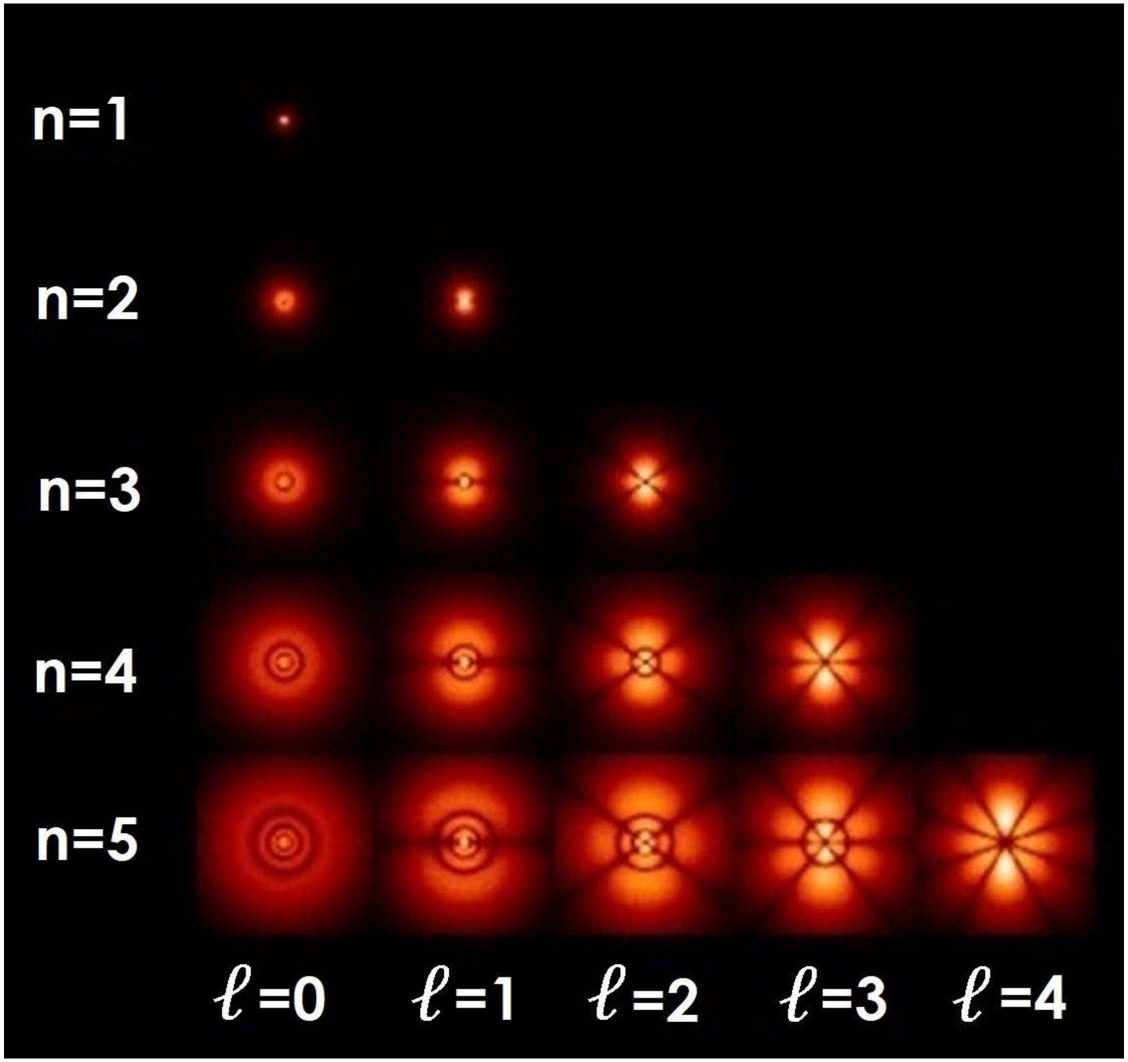


Schrodinger equation for 1/r potential: $$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi$$

Hydrogen wavefunctions: $$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) Y_l^m(\theta, \phi)$$

Energy levels: $$E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2}$$

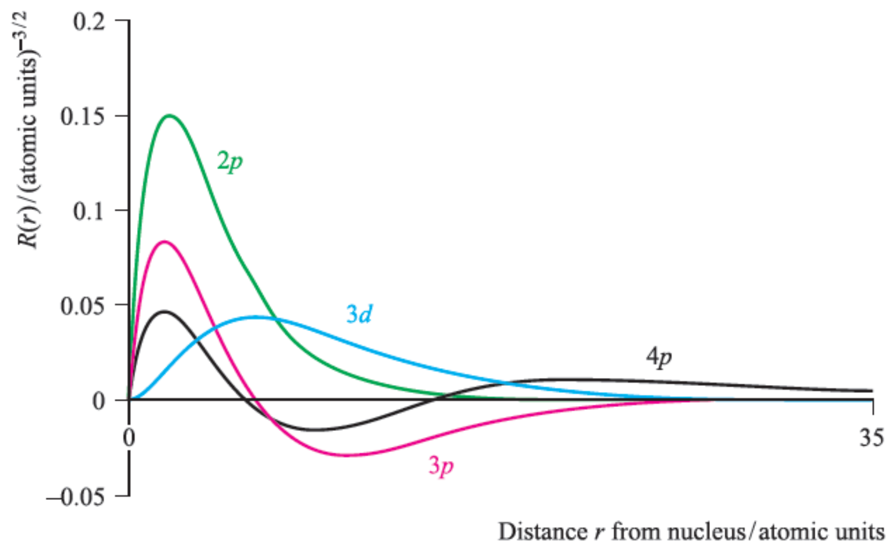
Bohr radius: $$a \equiv \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = 0.529 \times 10^{-10}\ \mathrm{m}$$



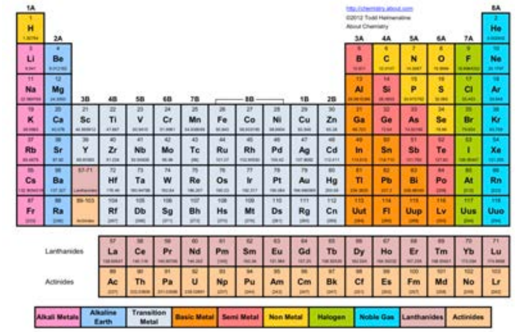
Quantum numbers: n, l, m

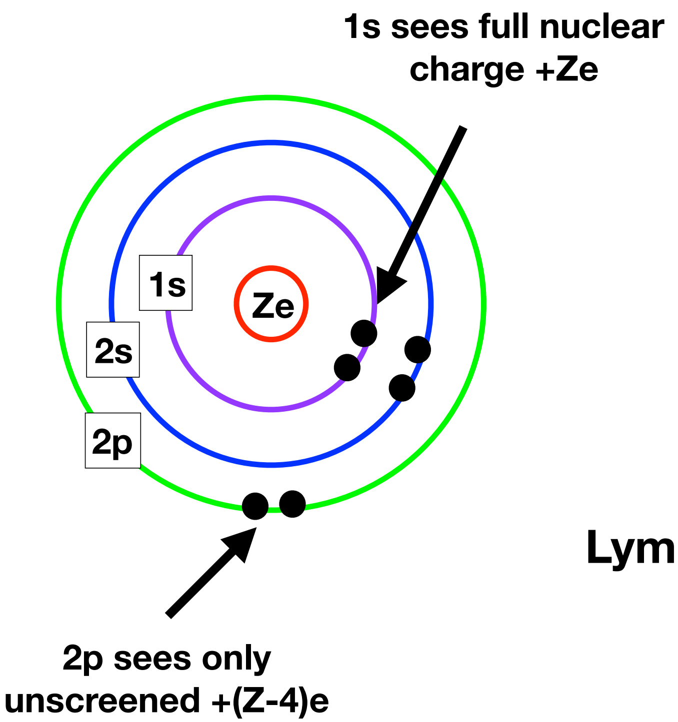
Generalize for nuclear charge +Ze:

$$E_{z,n} = -\frac{Z^2 R_H}{n^2} \qquad a_{Z,n} = \frac{n a_0}{Z}$$



How does Balmer series change multi-electron atoms like C?

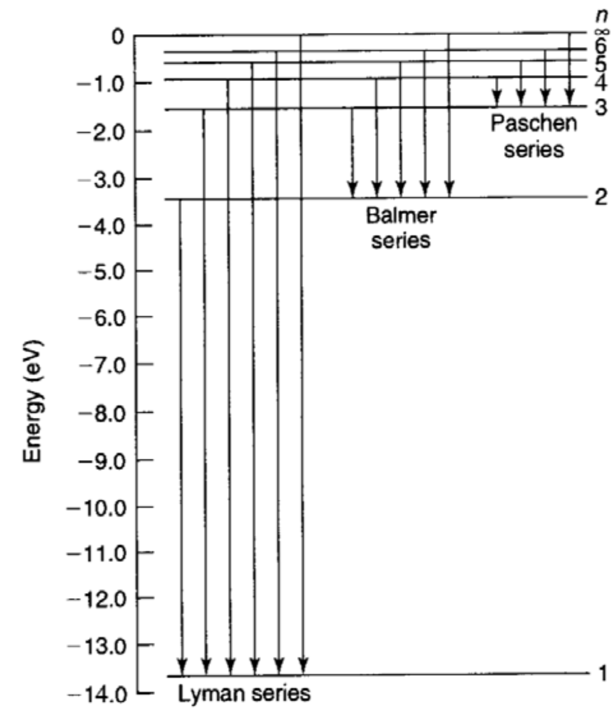




Inner “core” electrons are much smaller than outer and can effectively screen nucleus for other electrons

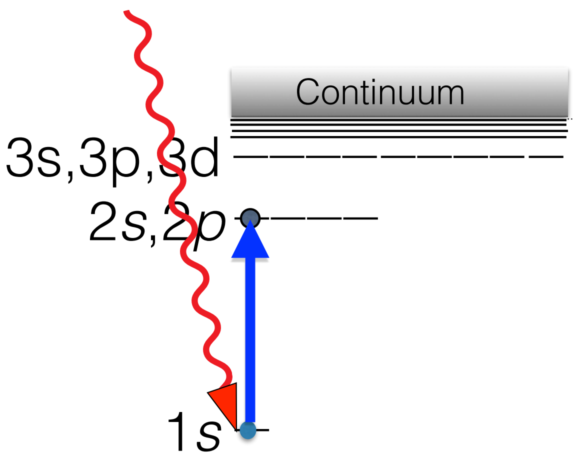
Core electrons much more tightly bound than outer ones

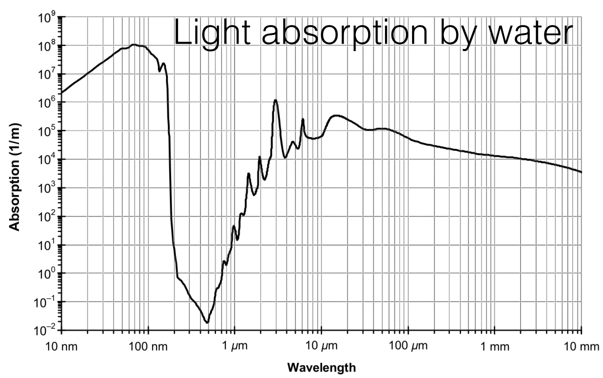
Lyman (1->n) series for multi-electro atoms form “K” X-ray edges



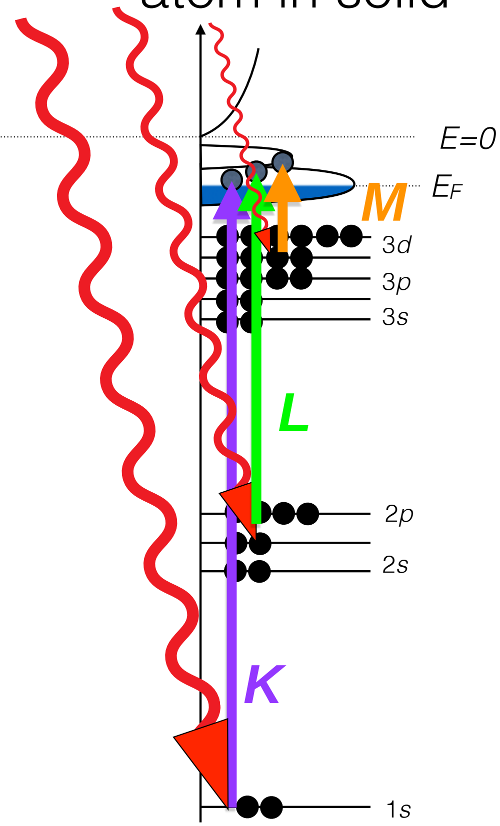
Atomic transitions in solids

Hydrogen atom

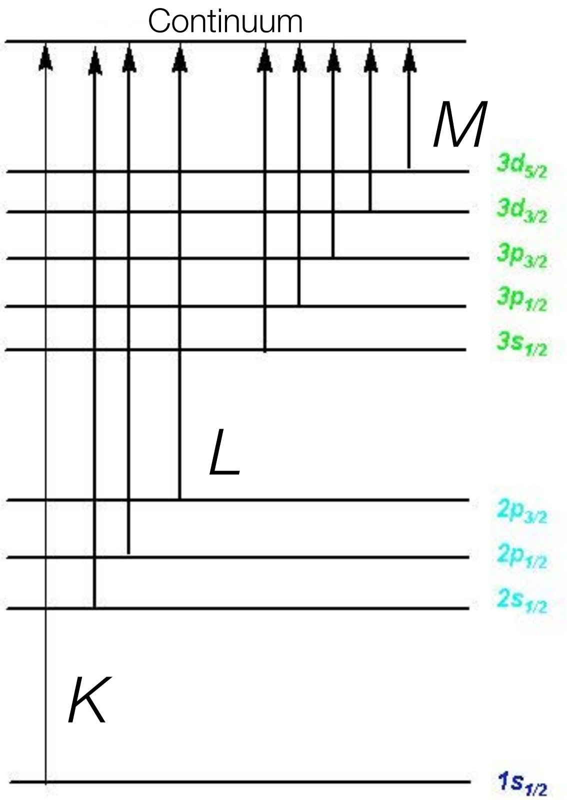




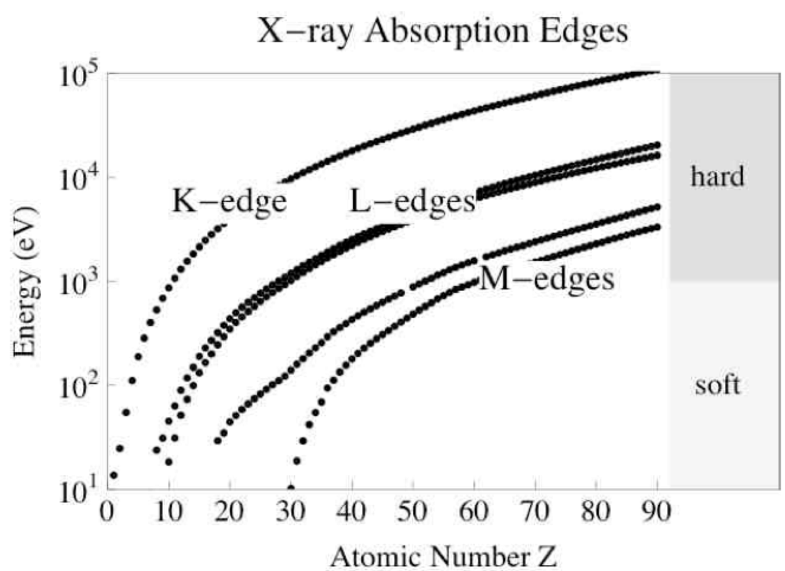
Multi-electron atom in solid



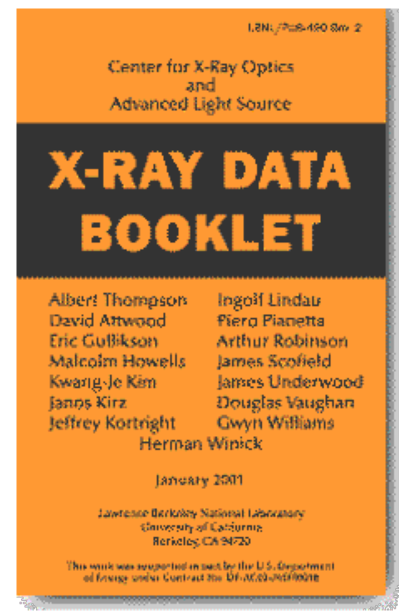
X-ray transition lines



Absorption

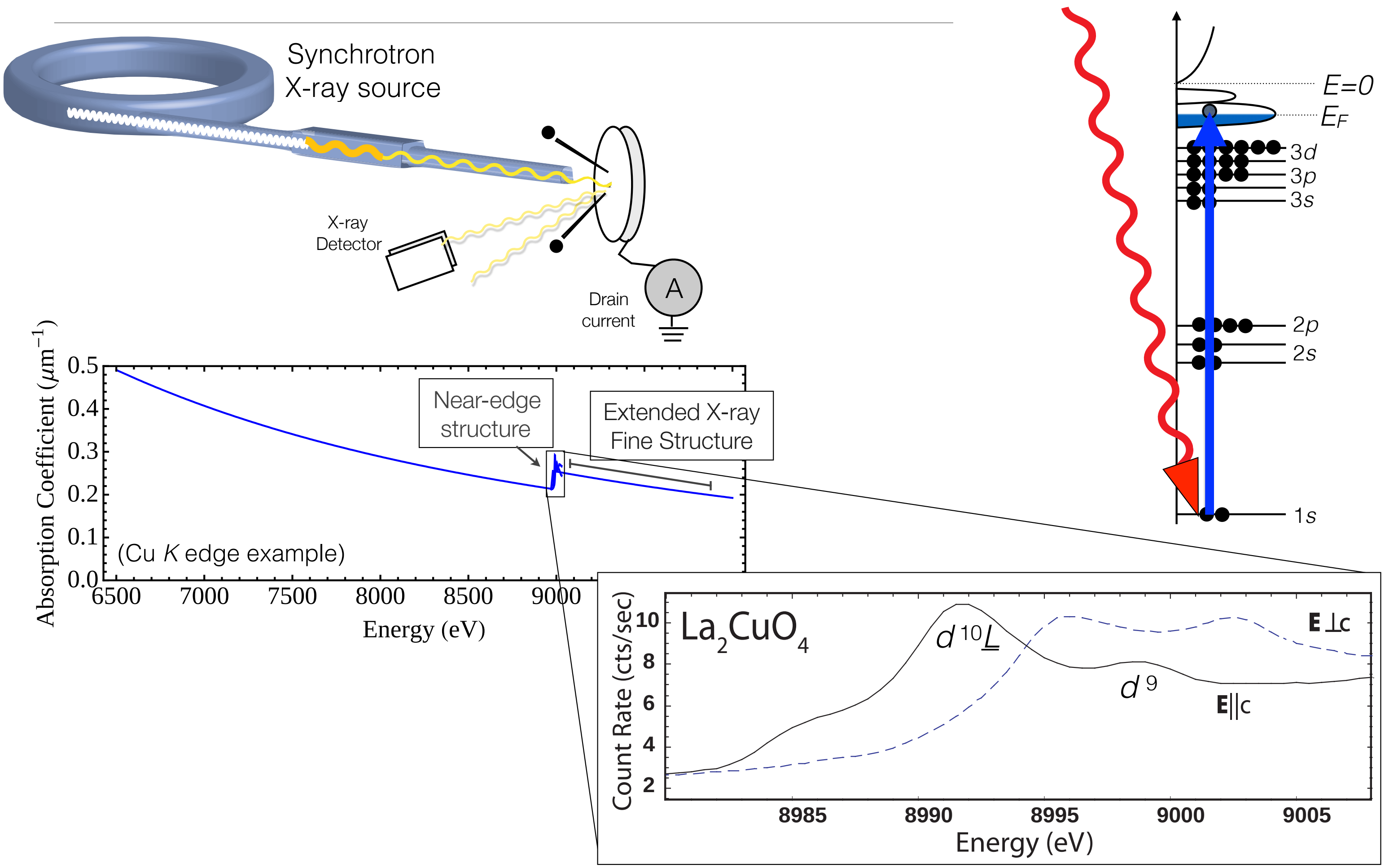


- Absorptive transitions of higher Z atoms lie in X-ray region

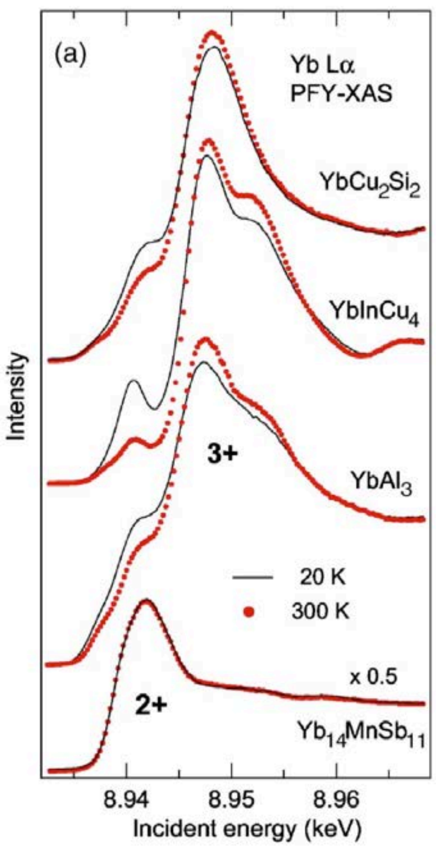


http://xdb.lbl.gov

X-ray absorption spectroscopy (XAS)



X-ray absorption spectroscopy, uses to determine valence state



Example: Yb

Has two stable valence states

Yb^{+2}, has f^{14} full shell - nonmagnetic ion

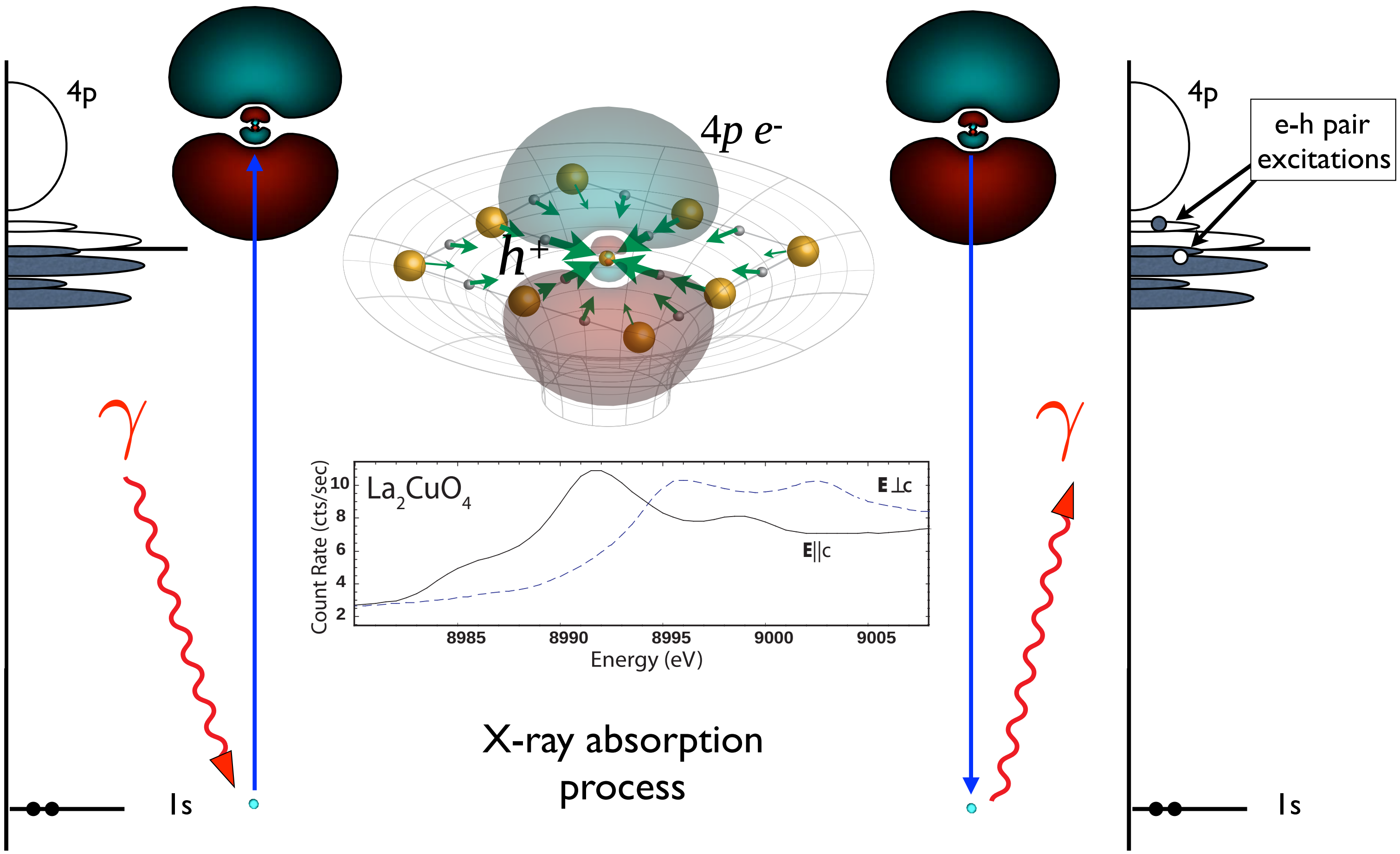
Yb^{+3} has f^{13} one hole in f shell - long j=7/2 mag moment

Real materials can have things in between, depends on interactions

Yb14MnSb11 - no magnetic moment coming from Yb

YbAl3 - long moment paramagnet from Yb^{+3} in f^{13} state

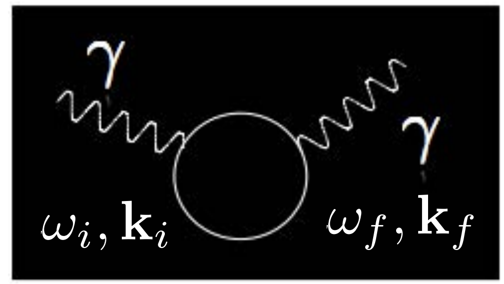
X-ray edge absorption… and RIXS



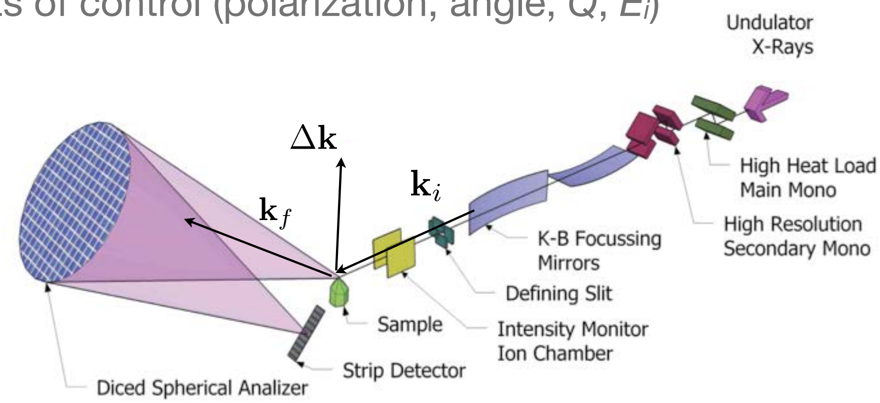
Copper *K* (example)

Resonant Inelastic X-ray Scattering (RIXS)

- Resonant Raman spectroscopy, with resonance at an X-ray edge
- Described by Kramers-Heisenberg formula
- Large momentum transfer
- Atomic-species and valence-specific information
- Lots of control (polarization, angle, *Q*, E_i)

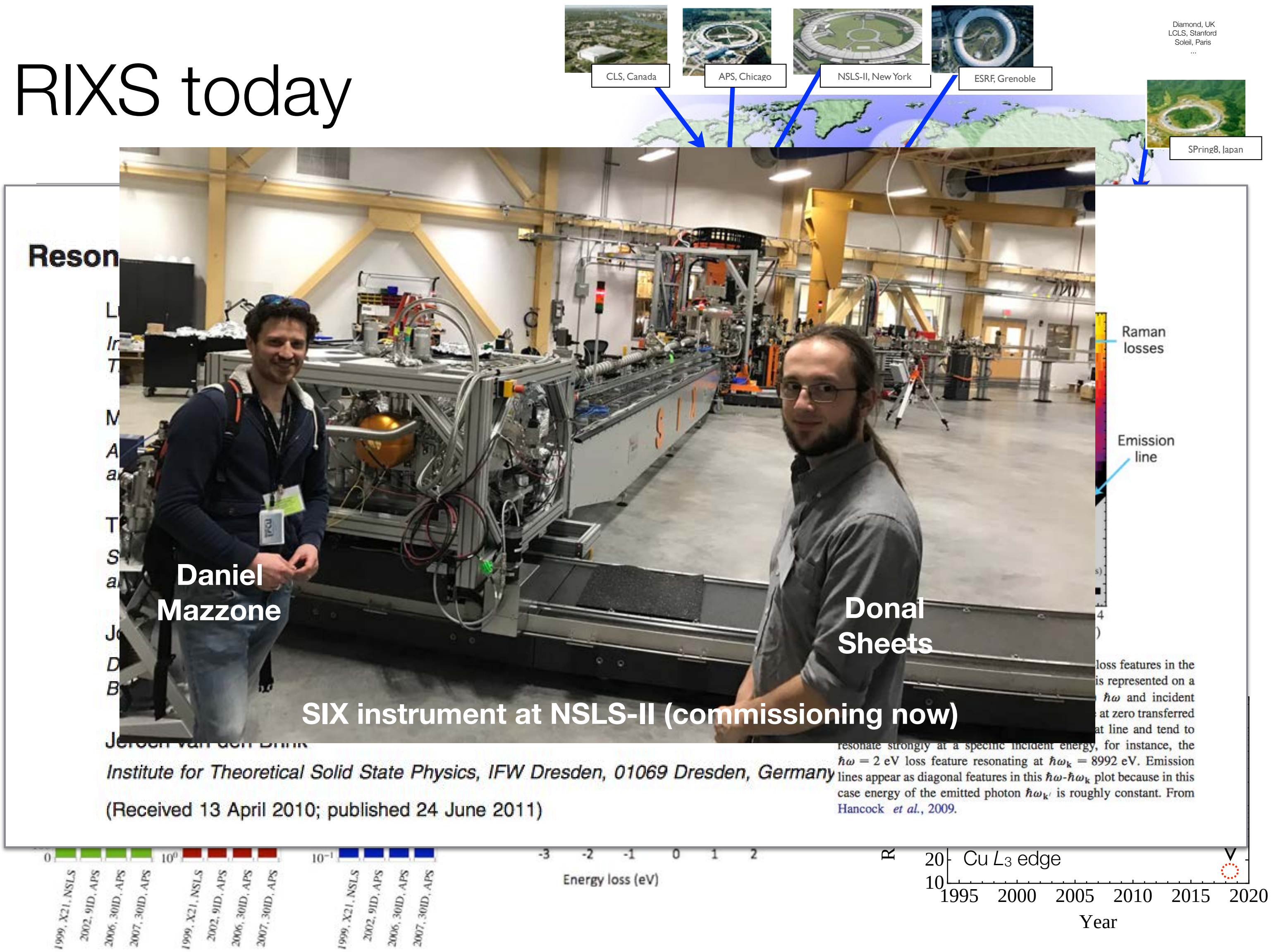


$$\Delta\omega = \omega_i - \omega_f$$
$$\Delta\mathbf{k} = \mathbf{k}_i - \mathbf{k}_f$$



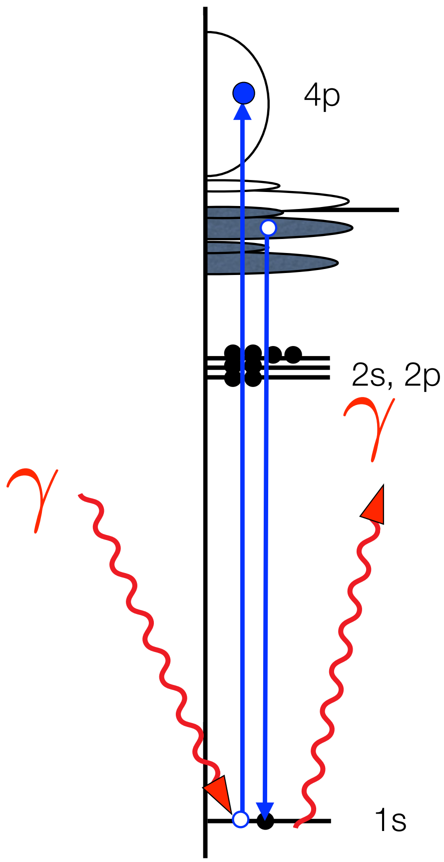
Kramers-Heisenberg:
$$\frac{d^2\sigma}{d\Omega_{k'} d(\hbar\omega'_k)} = \frac{\omega'_k}{\omega_k} \sum_{|f\rangle} \left| \sum_{|n\rangle} \frac{\langle f|T^\dagger|n\rangle\langle n|T|i\rangle}{E_i - E_n + \hbar\omega_k + i\frac{\Gamma_n}{2}} \right|^2 \delta(E_i - E_f + \hbar\omega_k - \hbar\omega'_k)$$

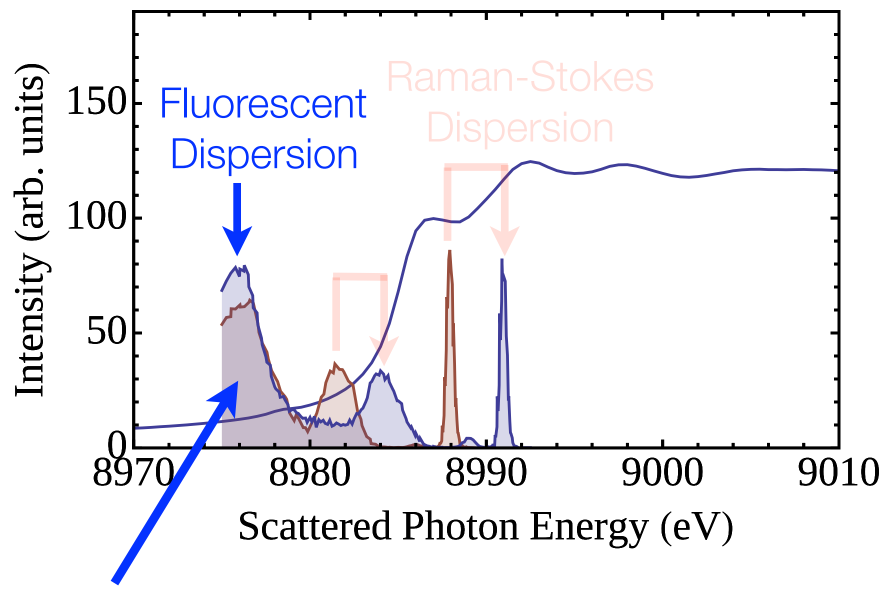
RIXS today



CLS, Canada
APS, Chicago
NSLS-II, New York
ESRF, Grenoble
Diamond, UK
LCLS, Stanford
Soleil, Paris
SPring8, Japan
Reson
Institute for Theoretical Solid State Physics, IFW Dresden, 01069 Dresden, Germany
(Received 13 April 2010; published 24 June 2011)
Raman losses
Emission line
Daniel Mazzone
Donal Sheets
SIX instrument at NSLS-II (commissioning now)
Energy loss (eV)
Cu L_3 edge
Year
1995
2000
2005
2010
2015
2020
1999, X21, NSLS
2002, 9ID, APS
2006, 30ID, APS
2007, 30ID, APS

Energy dispersion in RIXS

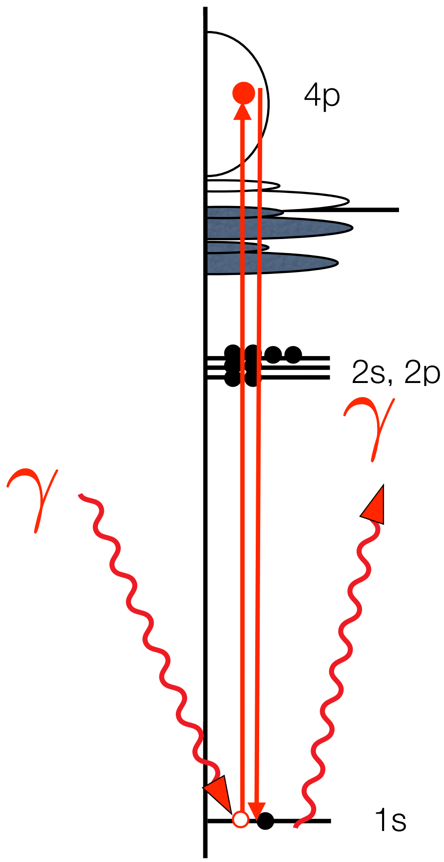


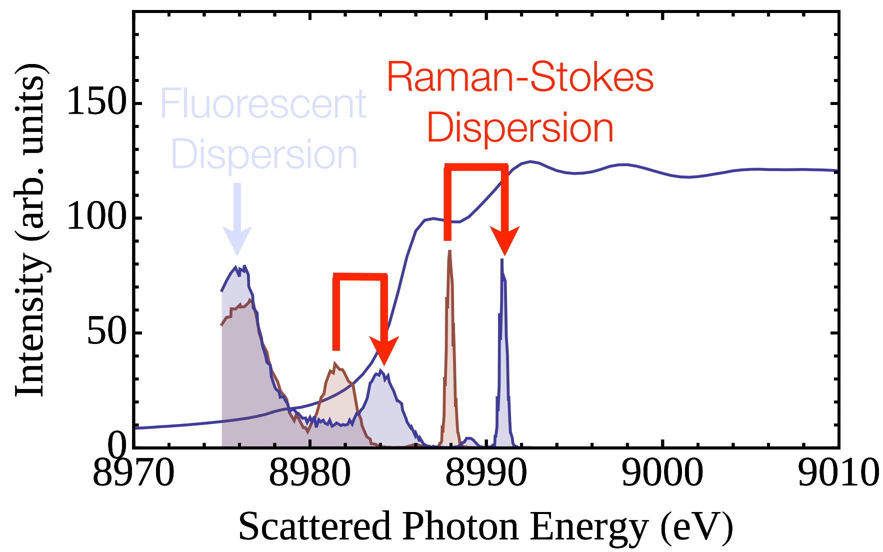


Emission line

- Fluorescent-type energy dispersions are independent of E_i

Energy dispersion



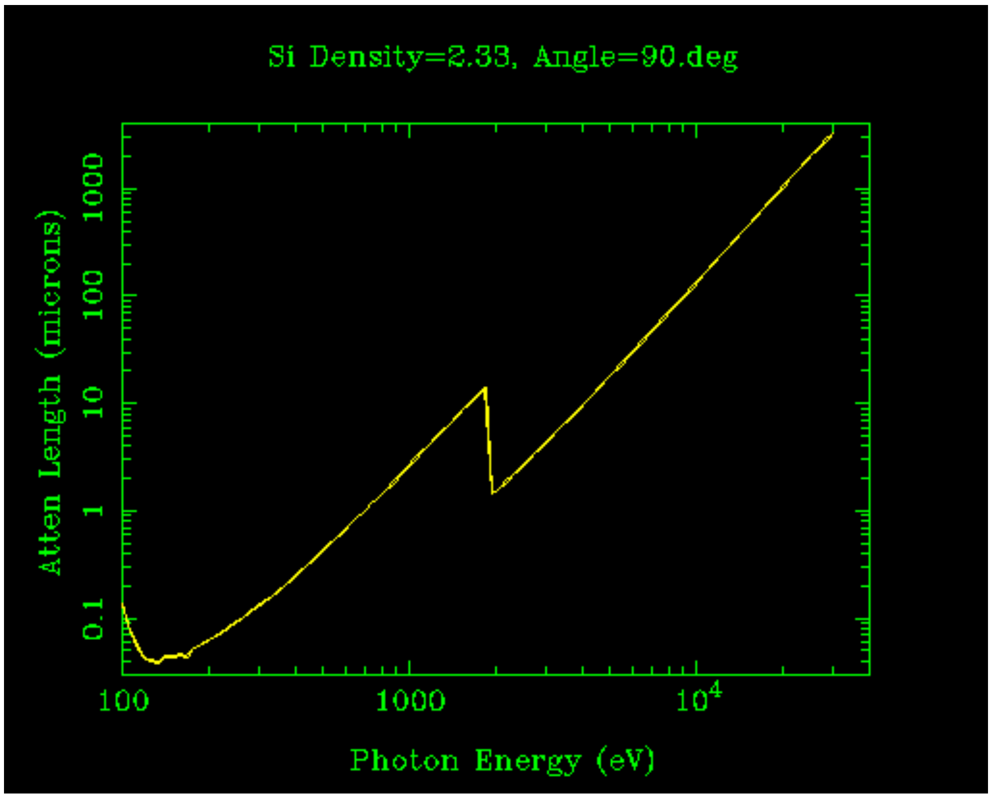


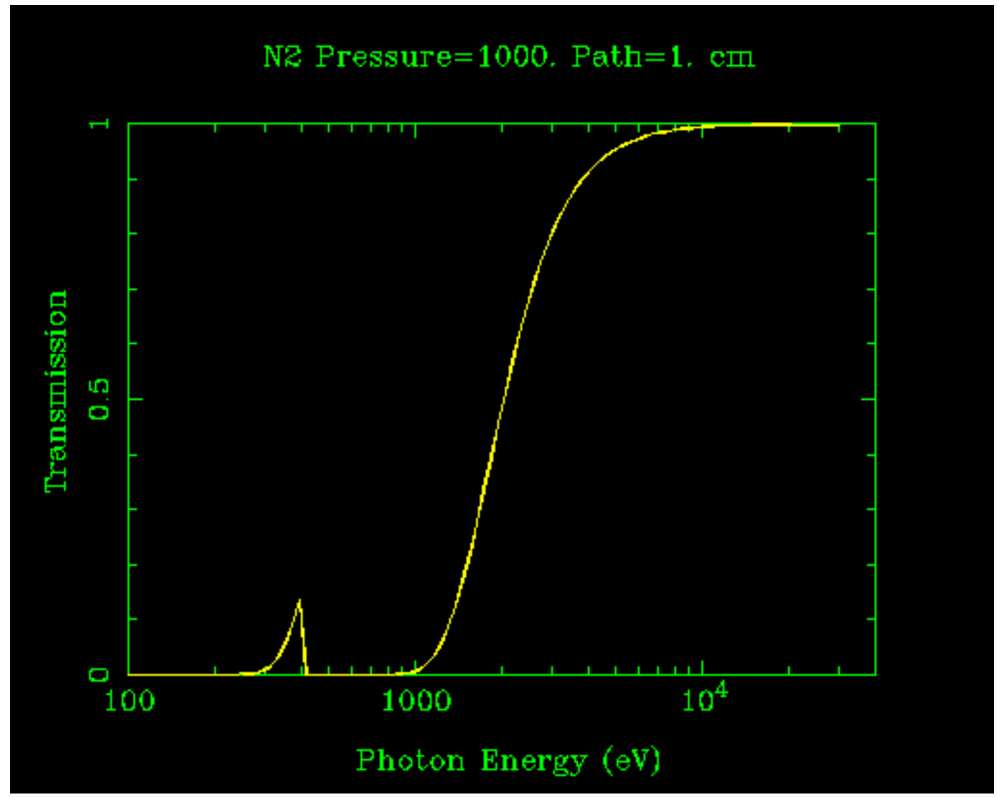
- Features following E_i represent Raman (RIXS) processes, connected to lower energy (valence) physics

Practical difference: Soft vs Hard RIXS

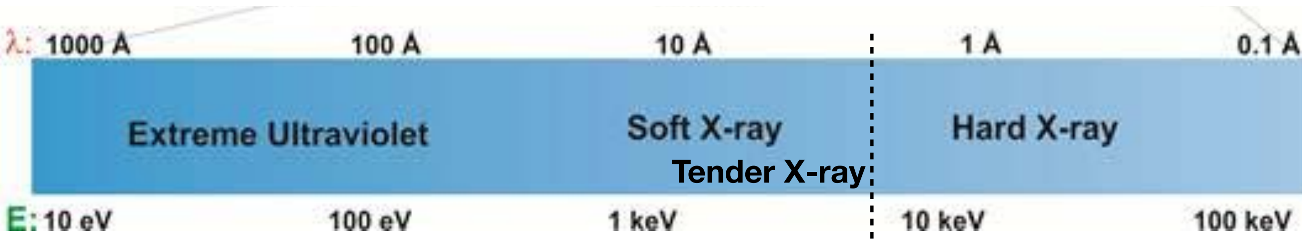
THE CENTER FOR X-RAY OPTICS

http://henke.lbl.gov/optical_constants/





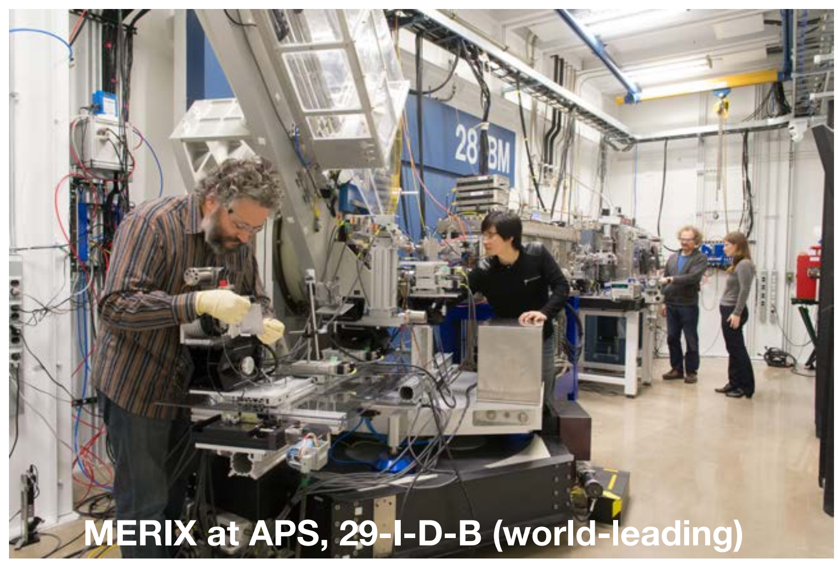
Practical difference: Soft vs Hard RIXS



X-rays must be in vacuum ← | → **X-rays can be in helium, air atmosphere**

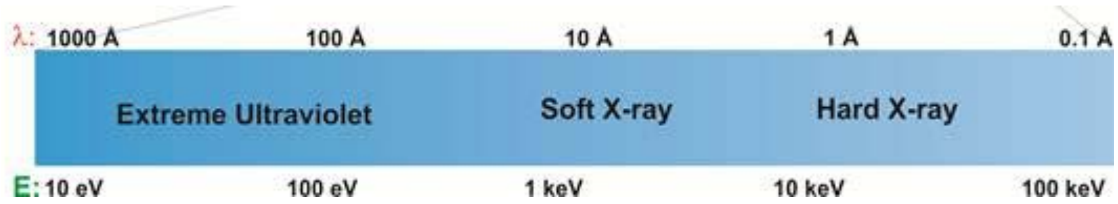
More scattering, lower penetration | **Less scattering, more bulk information**

SIX instrument at NSLS-II (commissioning now)



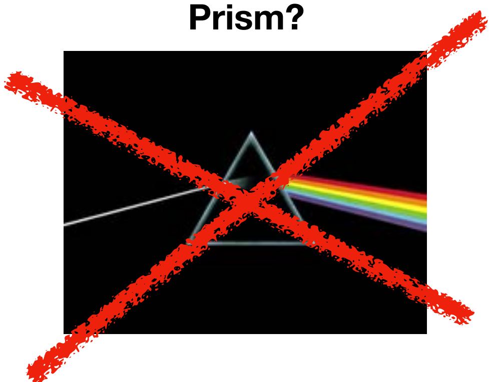
MERIX at APS, 29-I-D-B (world-leading)

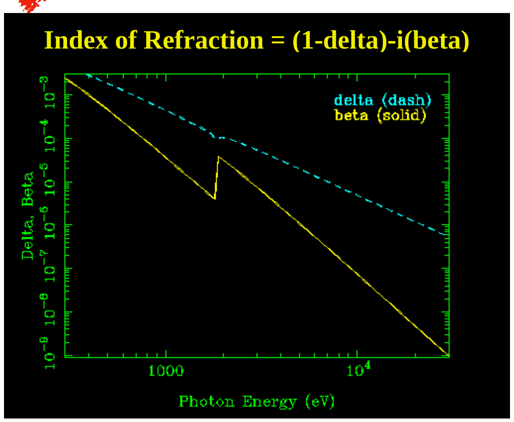
Technical difference: Soft vs Hard RIXS



How to disperse the X-rays?

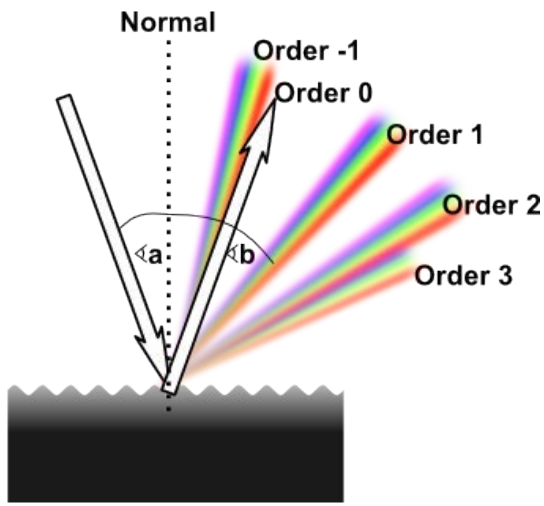
Prism?





Inefficient
Index changes too small to be effective

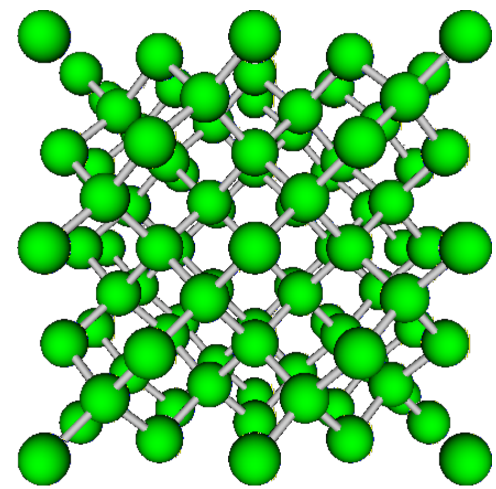
Grating?



If feature sizes can be on order wavelength

Soft X-ray ~ 1 nm

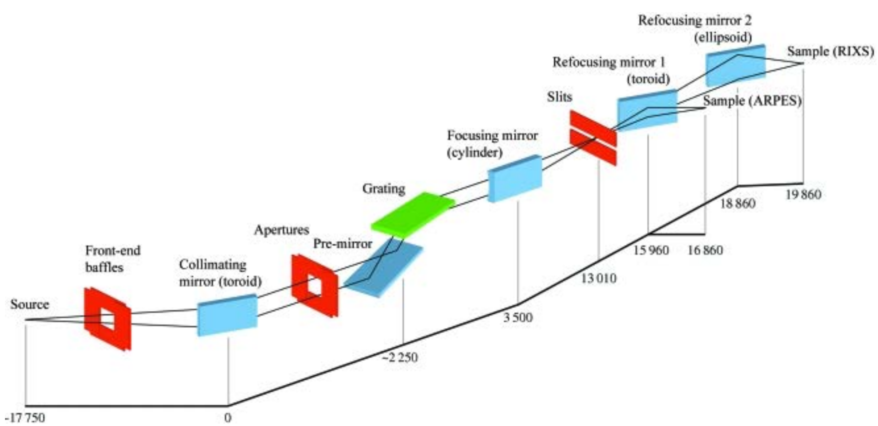
Crystal?



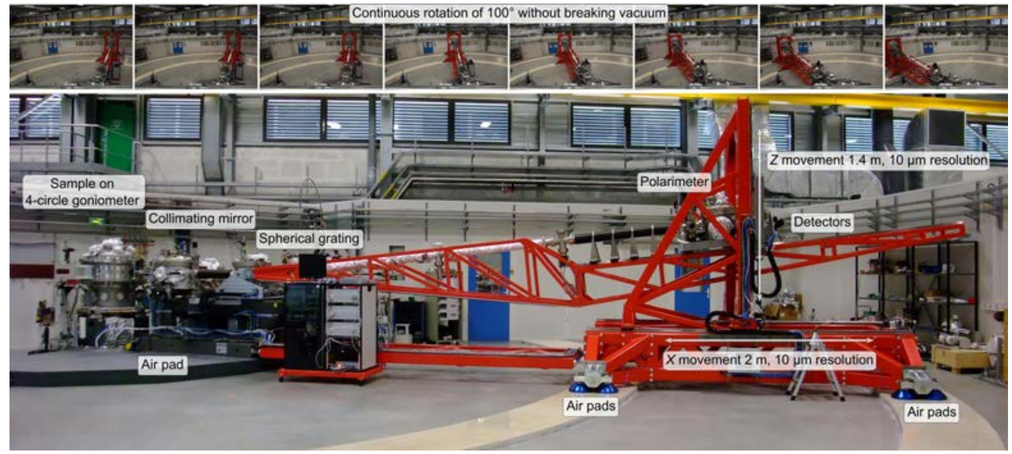
Feature size (atoms) of order X-ray wavelength

Hard X-ray << 1nm

Technical difference: Soft vs Hard RIXS

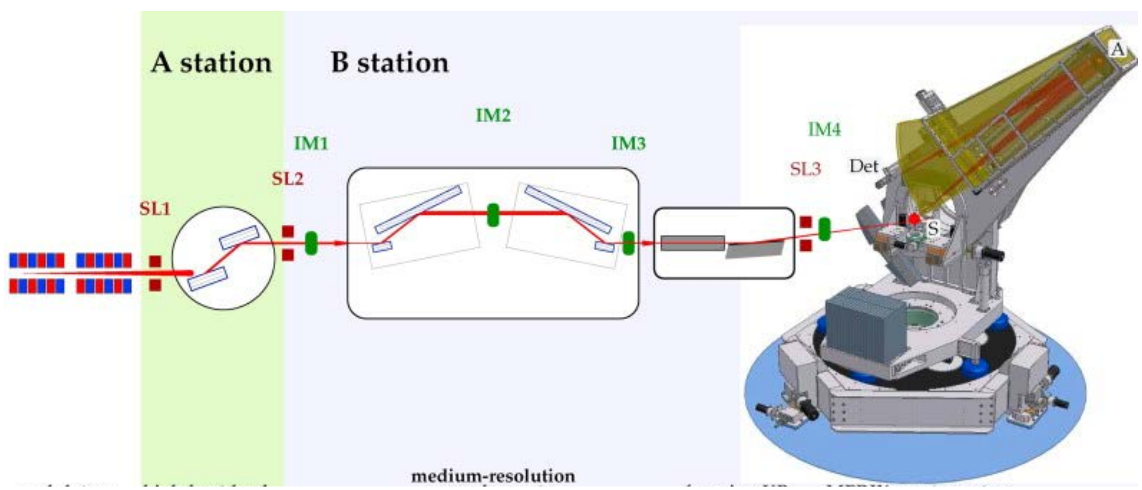


ADRESS beamline at PSI (no spectrometer)

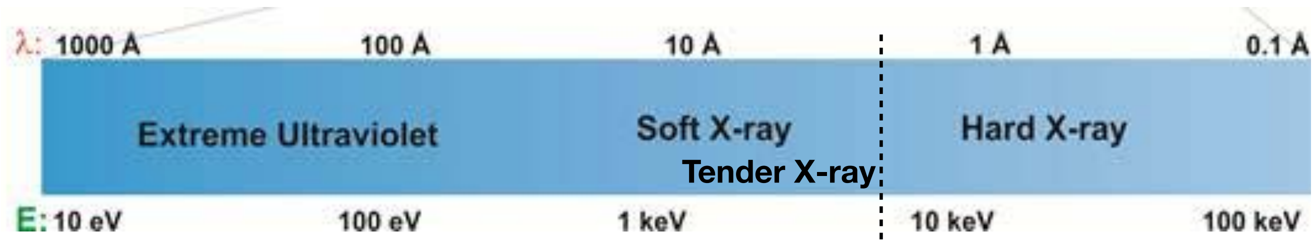


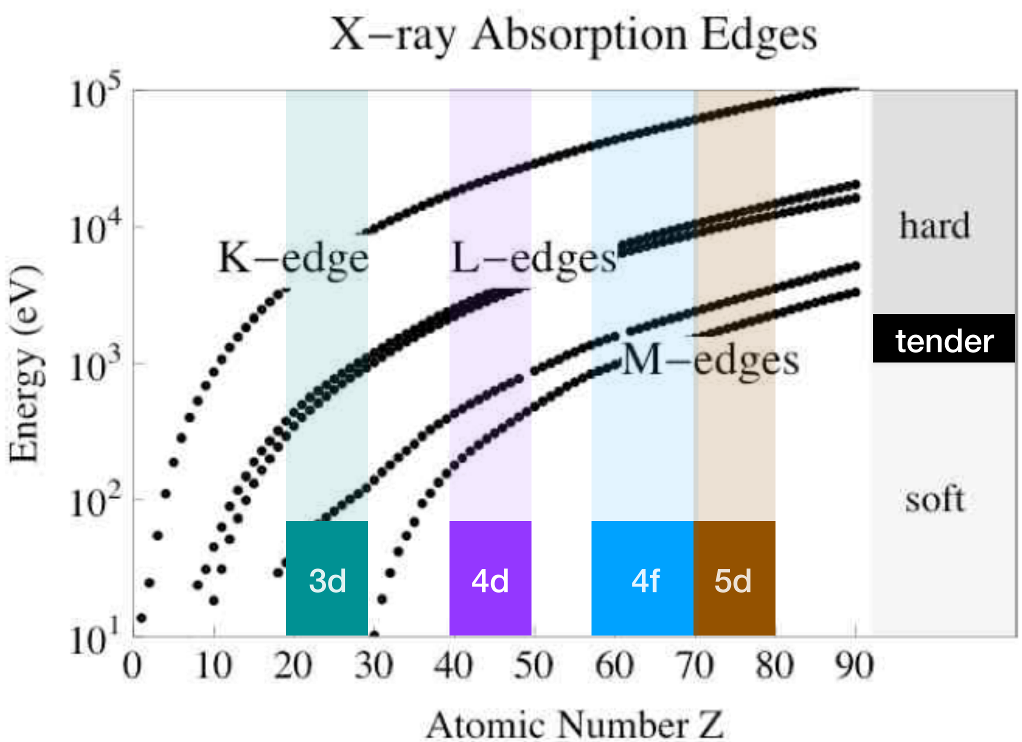
ERIXS endstation at ESRF (no beamline shown)

MERIX spectrometer, sector 27-ID-B, APS



Scientific difference: Soft vs Hard RIXS



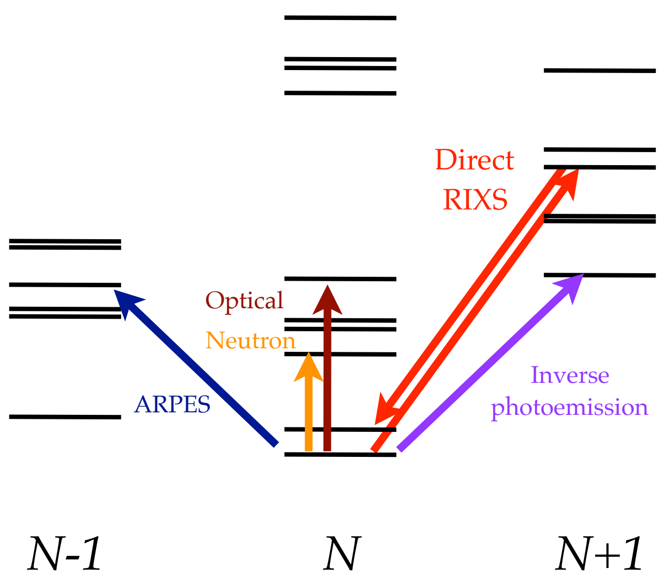


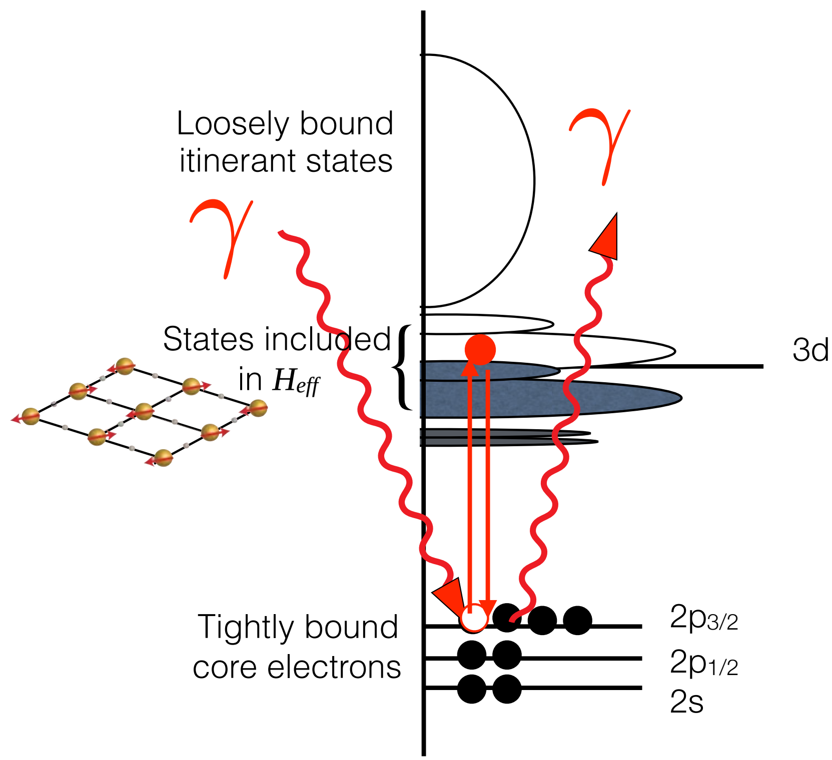
3d transition metal L edges
Rare-earth/4f M edges

3d transition metal K edges
Rare-earth/4f L edges
5d transition metal L edges

Edge and energy are determined by elements present and scientific question

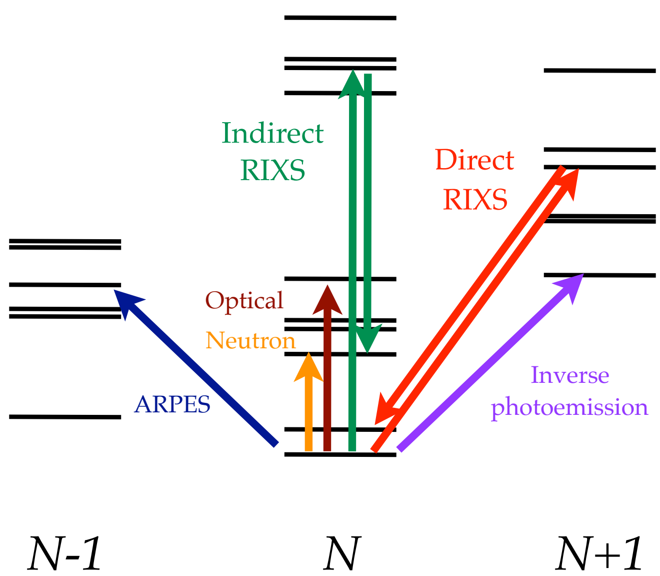
N-particle spectroscopy

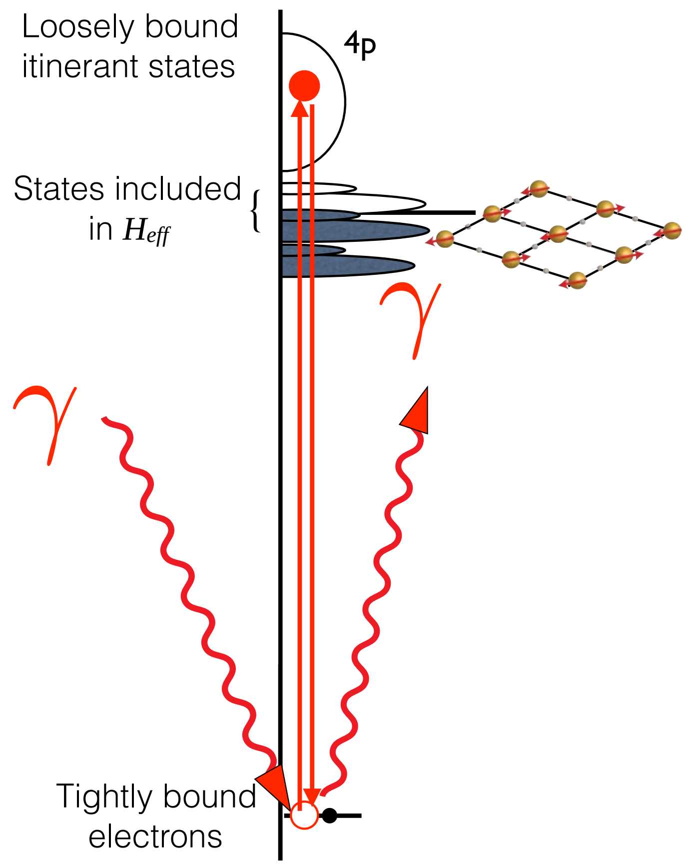




“Direct” RIXS at transition metal *L* edges

N-particle spectroscopy

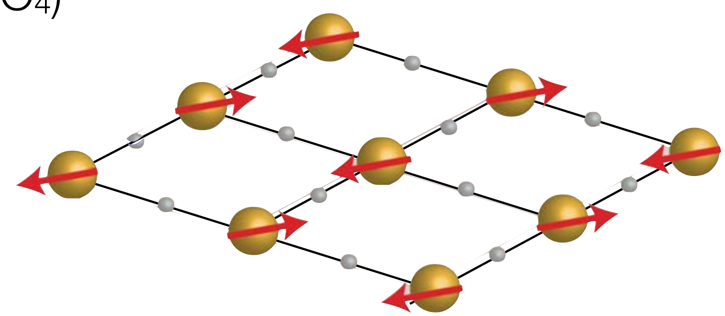




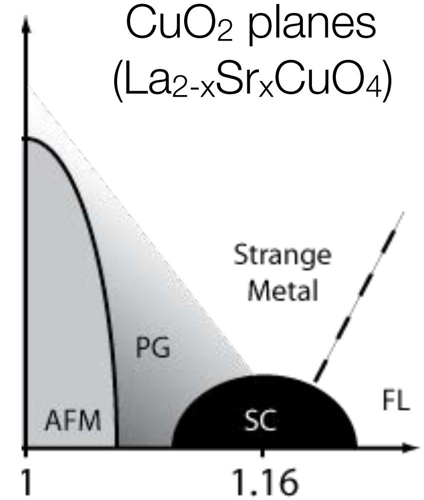
"Indirect" RIXS at transition metal *K* edges

High-*Tc* cuprate superconductors

1/2-filled
CuO_2 planes
(La_2CuO_4)



Hole-doped
CuO_2 planes
($La_{2-x}Sr_xCuO_4$)

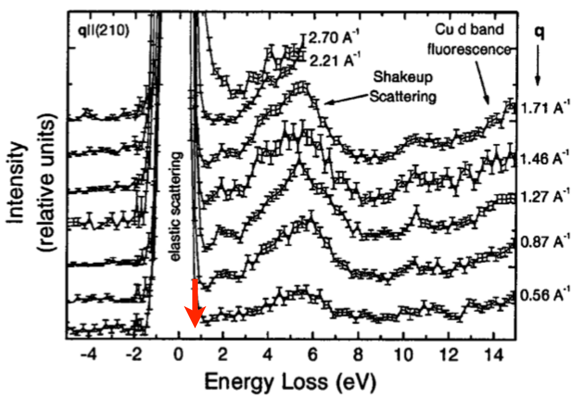


- Strong repulsion favors antiferromagnetic state
- Hubbard model describes AFM

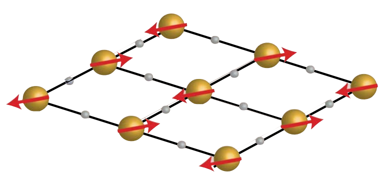
Hole doping a 2D Mott insulator induces high-temperature superconductivity

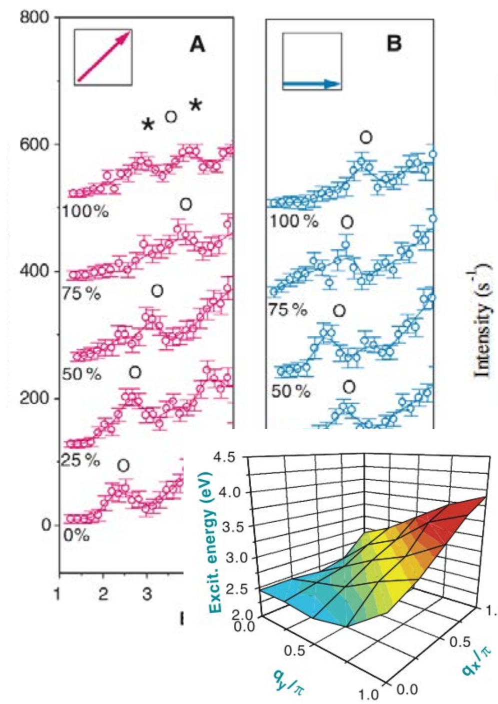
$$H = -t \sum_{<i,j>,\sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c.) + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow}$$

Mott gap dispersion in high-Tc superconductors (Cu *K* edge)

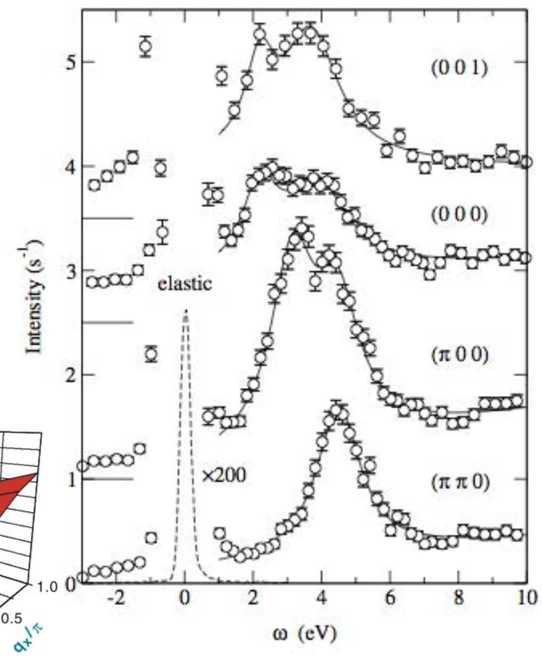


Abbamonte *et al. PRL* **83**, 860 (1999)



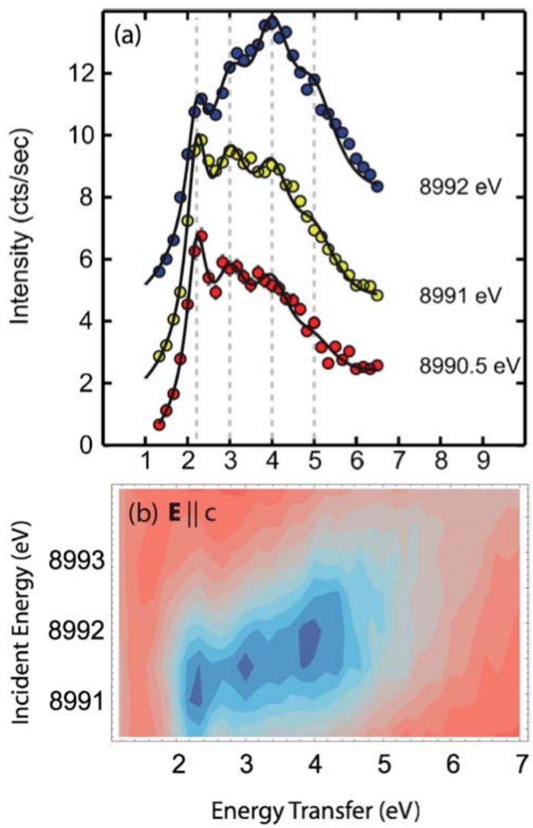


Hasan *et al. Science* **288**, 1811 (2000)



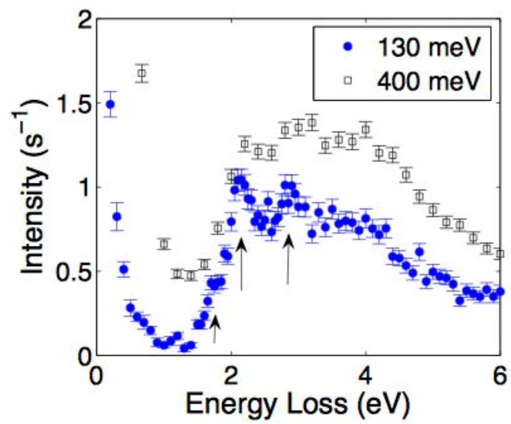
Kim *et al. PRL* **89**, 177003 (2002)

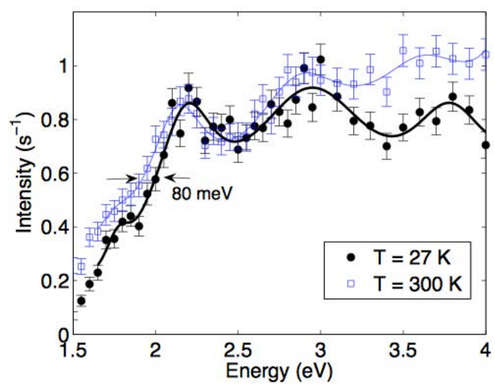
Incident energy and temperature dependence



Lu, JNH, *et al. PRL* **95**, 217003 (2005)

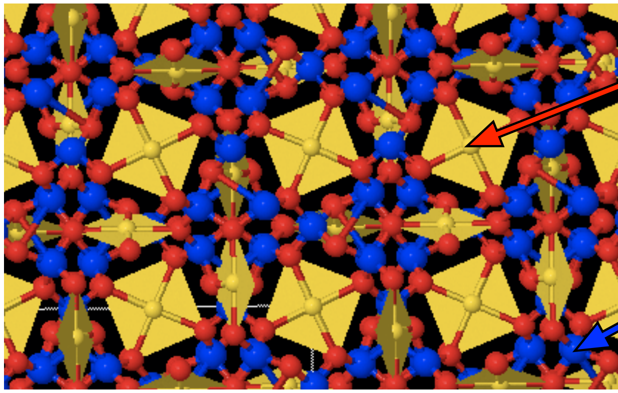
Lu, JNH, *et al. PRB* **74**, 224509 (2006)





Ellis, *et al. PRB* **77**, 060501 (2008)

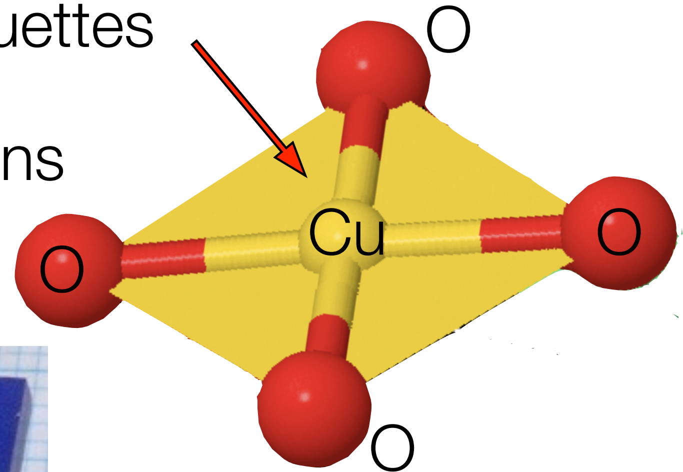
Experimental realization of 0-D HTSC



CuO_4 plaquettes

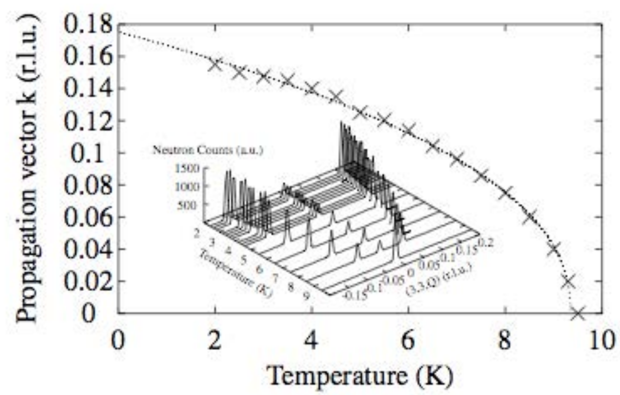
B^{3+} ions

CuB_2O_4, <001> view



- Low-*Z* nonresonant species
- Tractable electronic structure
- Ideal system for exploring RIXS phenomenology

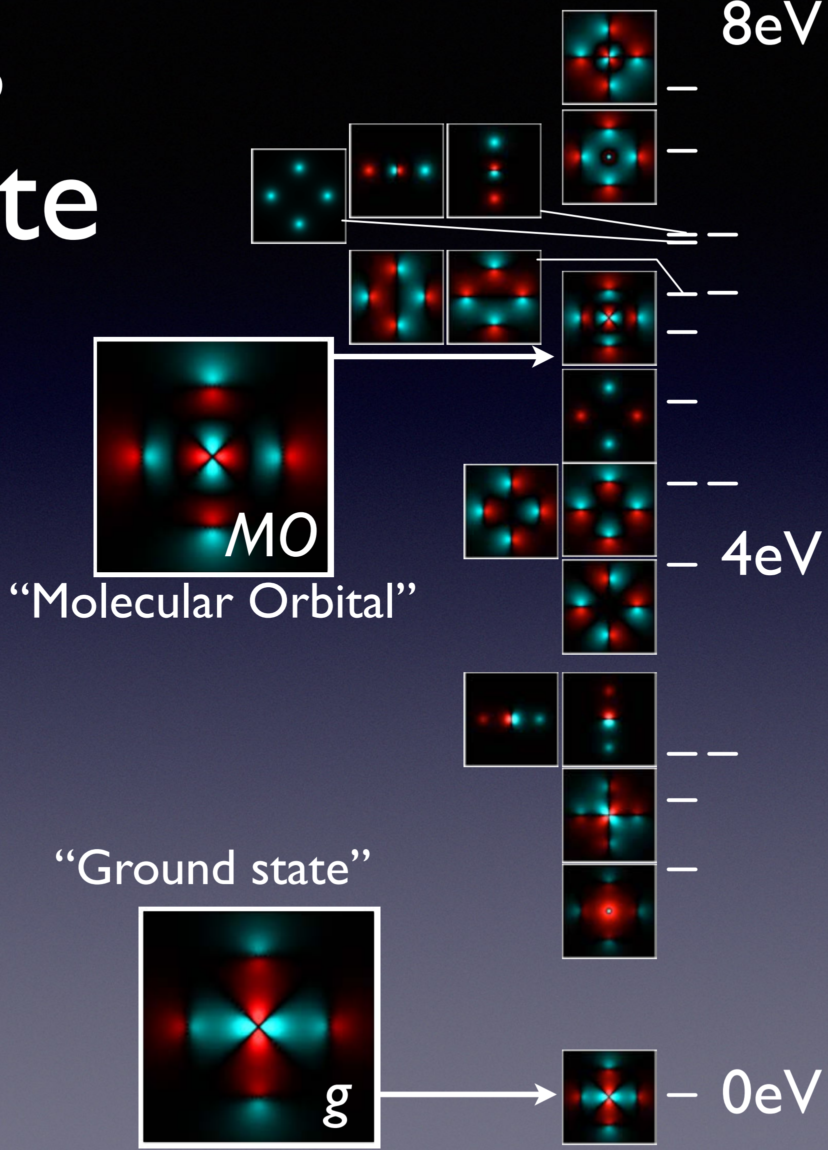
Hancock *et al. PRB* **80**, 092509 (2009)
Hancock *et al. NJP* **12**, 033001 (2010)

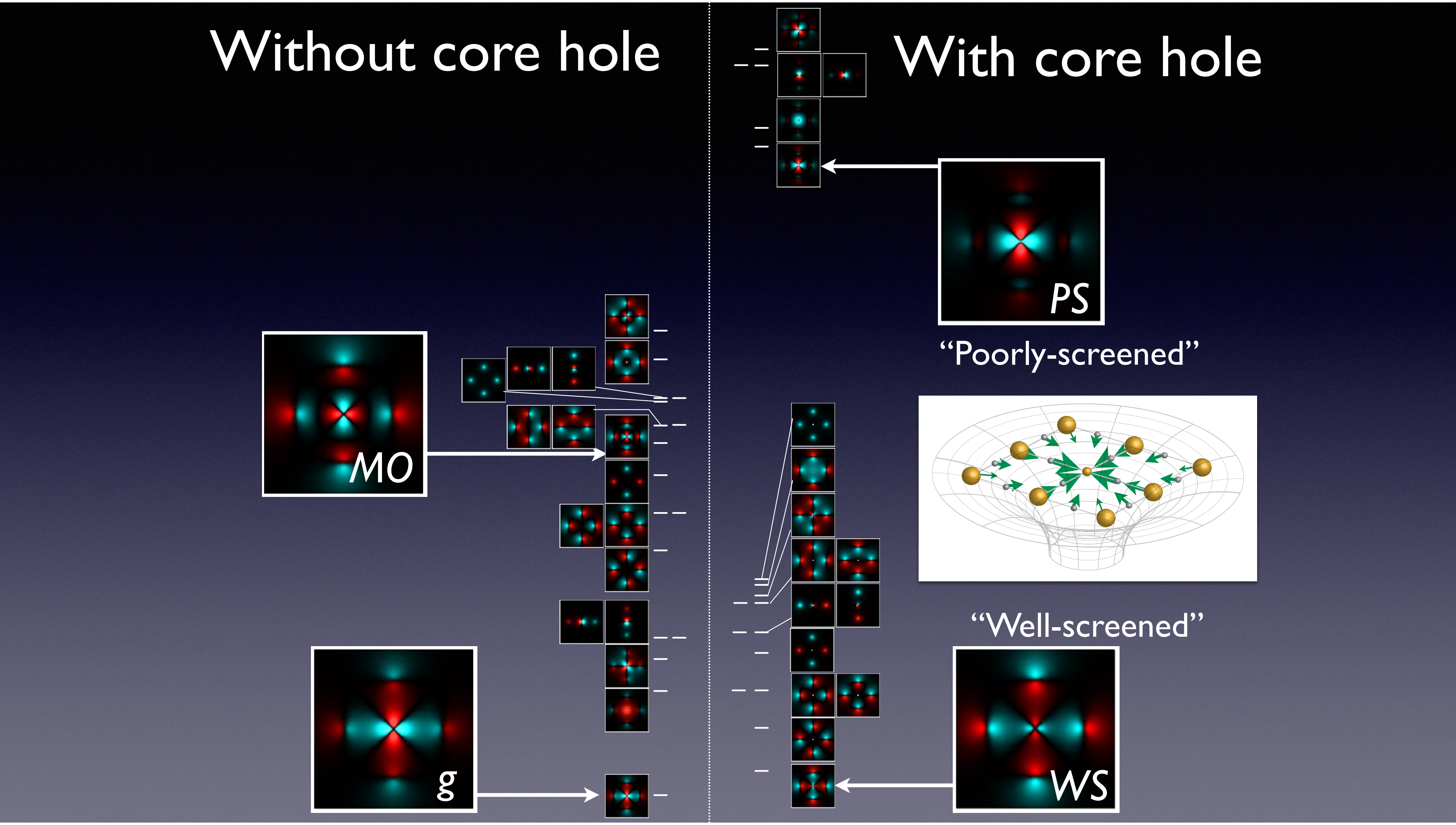


B. Roessli et al, PRL 86, 1885 (2001)

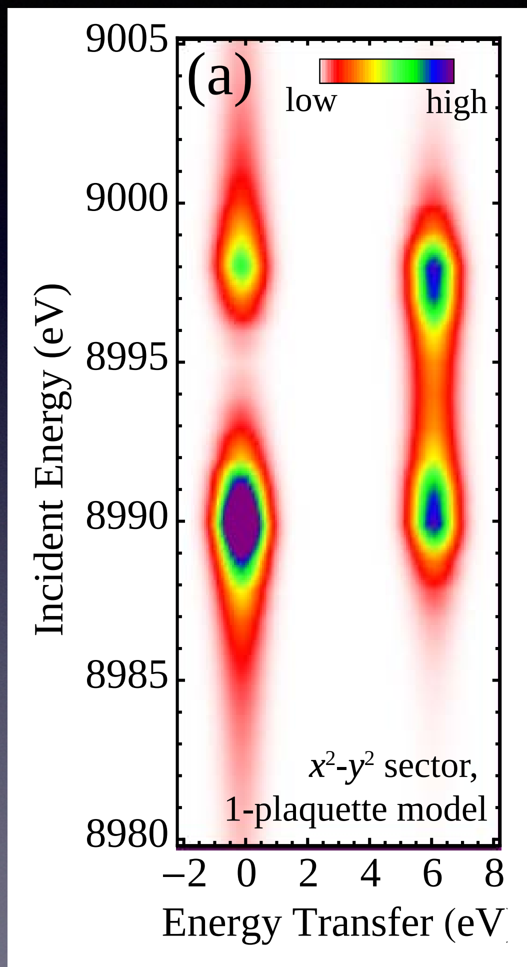
One hole, one plaquette

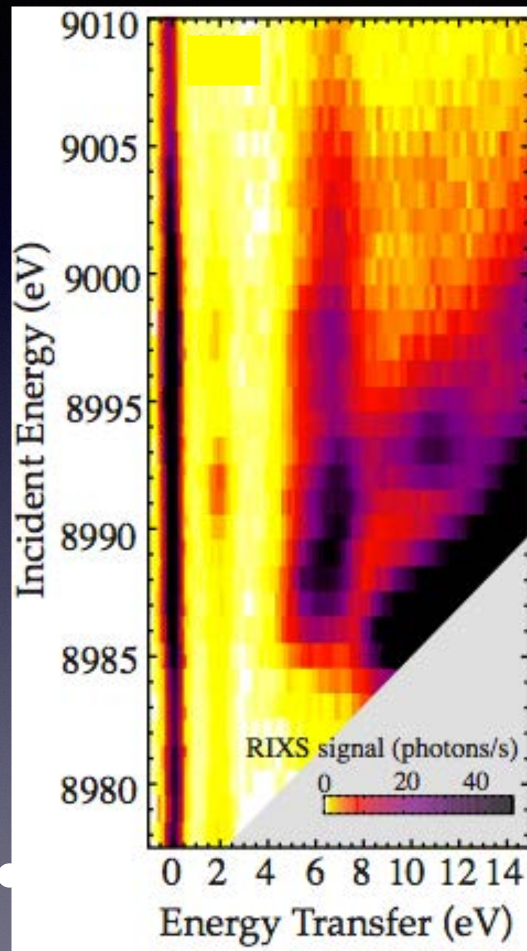
- Many wavefunctions of varied angular symmetry
- Ground and molecular orbital states are the only ones of x^2-y^2 symmetry
- Simple RIXS selection rule (for indirect, *K* edge transitions): symmetry=constant

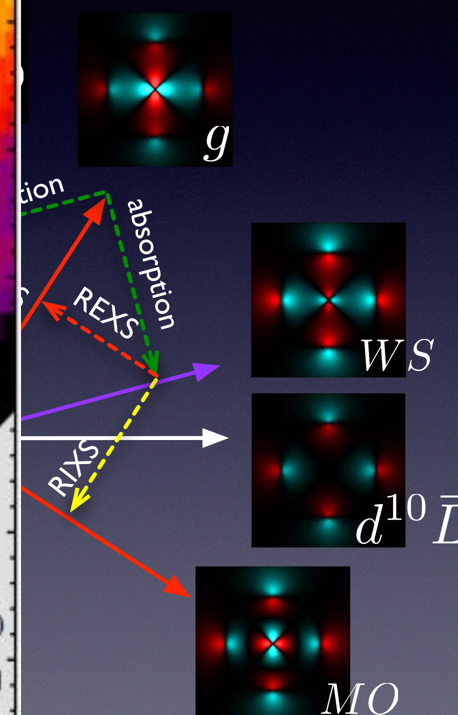



Without core hole
With core hole
PS
“Poorly-screened”
MO
“Well-screened”
g
WS

1-plaquette RIXS calculation



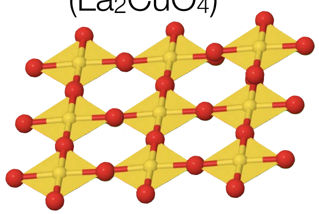




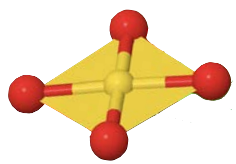
- capable of giving phase information

A simple cuprate, CuB_2O_4

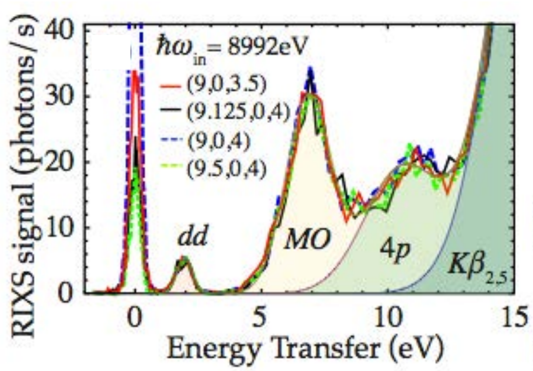
CuO_2 planes
(La_2CuO_4)

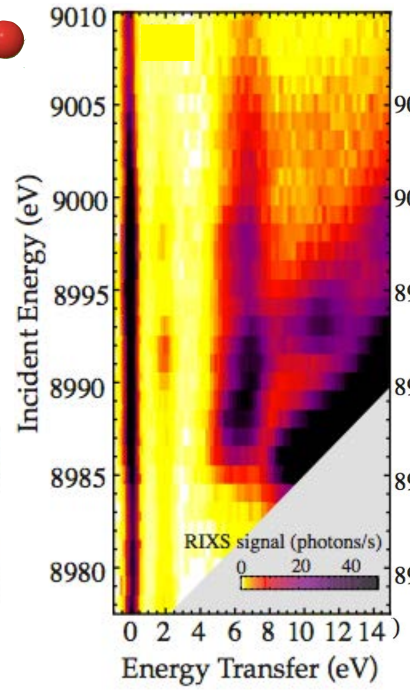


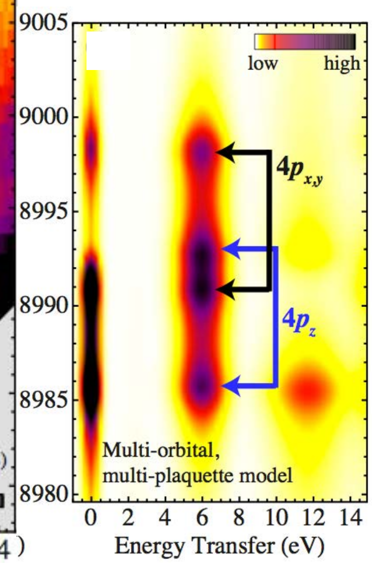
CuO_4 plaquette
(CuB_2O_4)

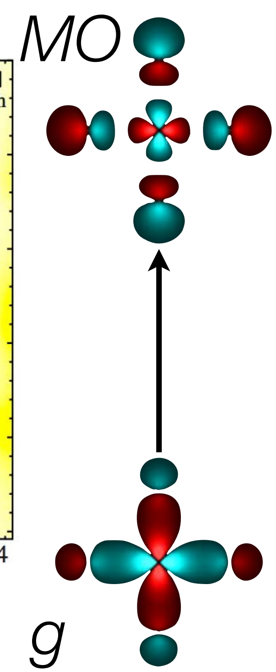


- Cluster modeling gave good, but imperfect agreement



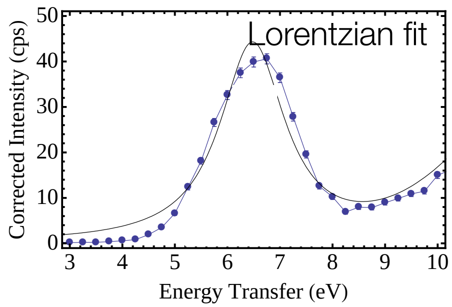


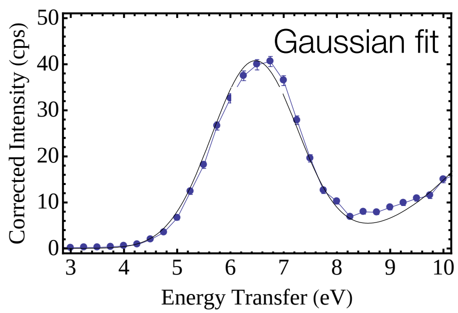




Hancock *et al. PRB* **80**, 092509 (2009)
Hancock *et al. NJP* **12**, 033001 (2010)

Elusive properties of MO excitation

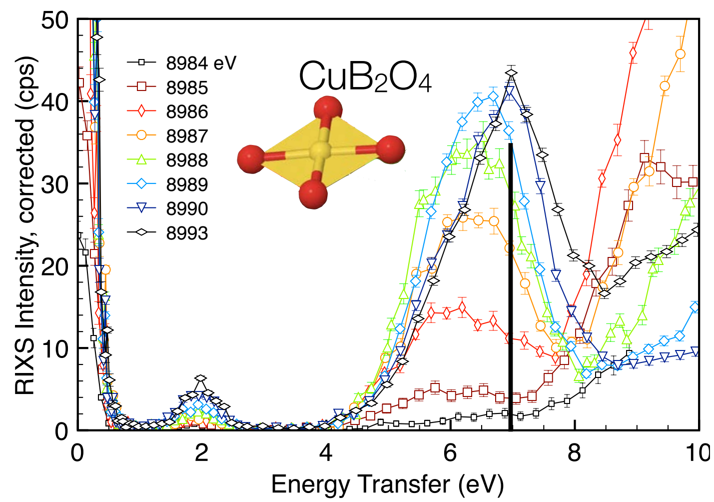


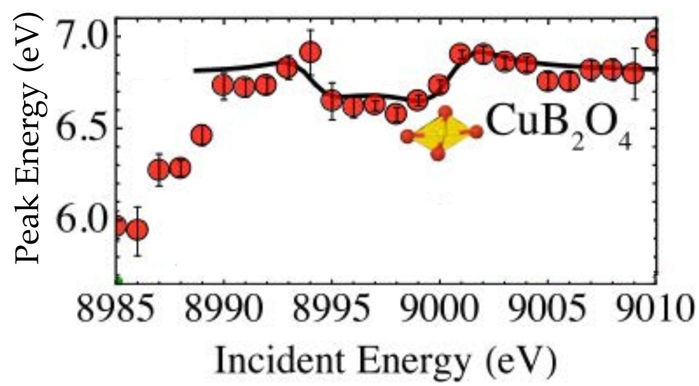


- Gaussian lineshape

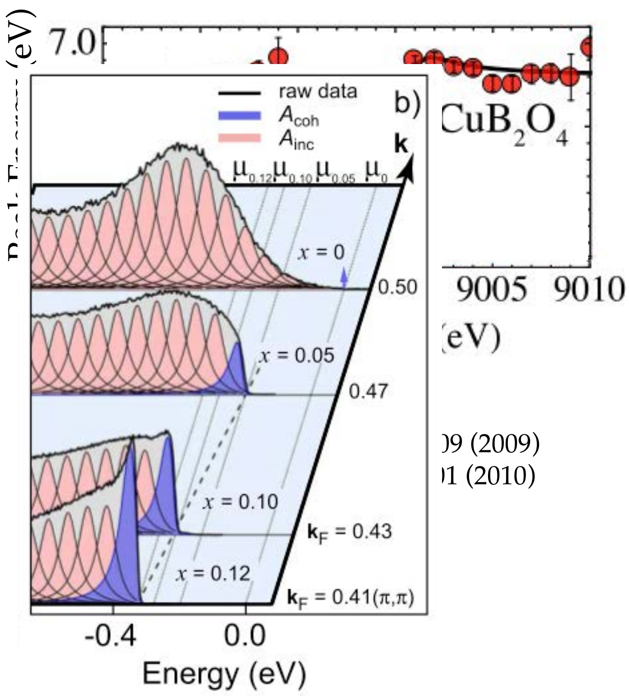
- Shifting resonance behavior

Hancock *et al. PRB* **80**, 092509 (2009)
Hancock *et al. NJP* **12**, 033001 (2010)

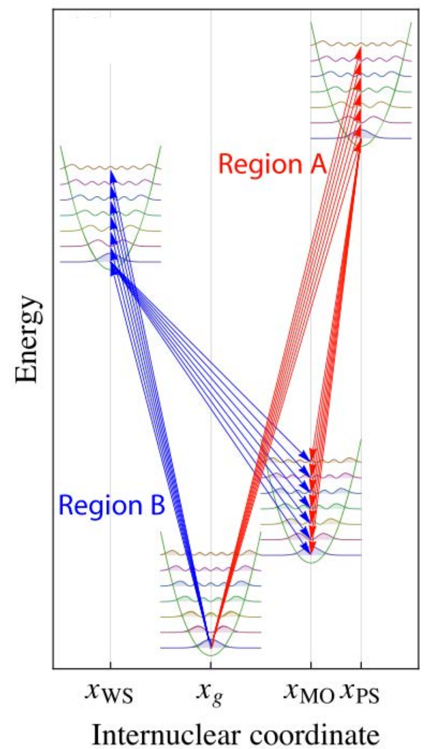


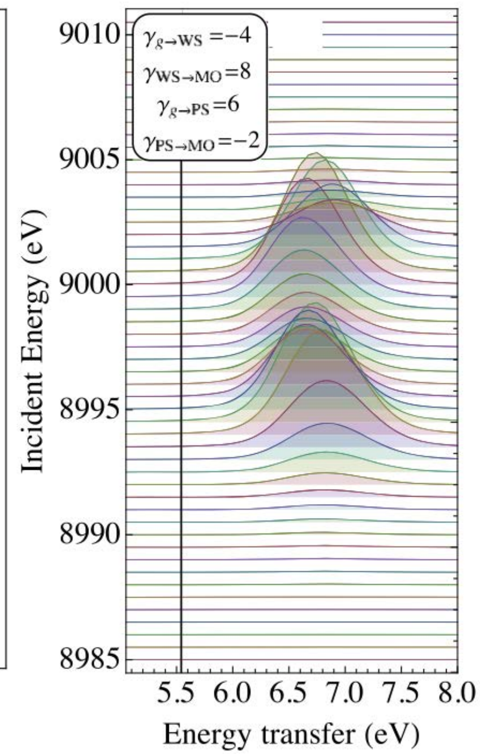


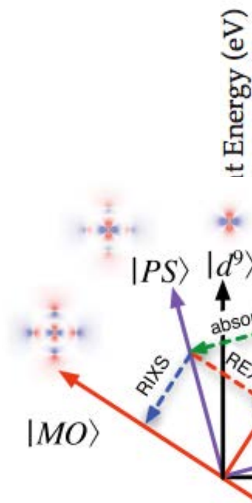
Electron-phonon coupling at the MO excitation



Shen, *et al*, *PRL* **93,** 267002 (2004)





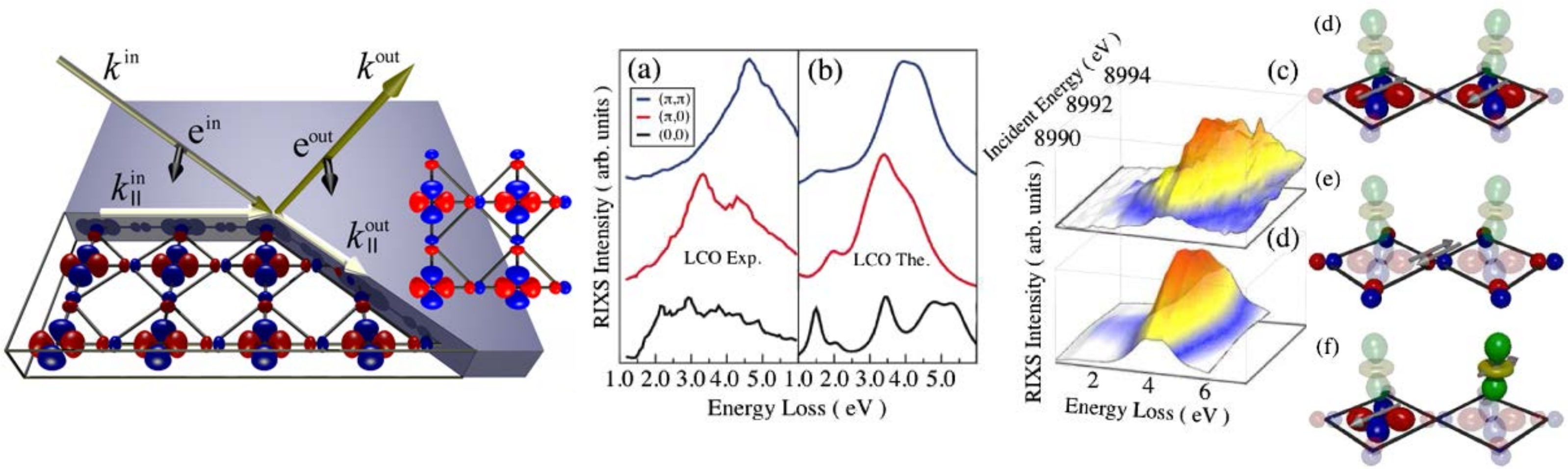


- Simple Franck-Condon model explains remaining features of the spectra
- Gives an estimate of the electron-phonon coupling parameter

Theory of RIXS in the cuprates

Kramers-Heisenberg Formula

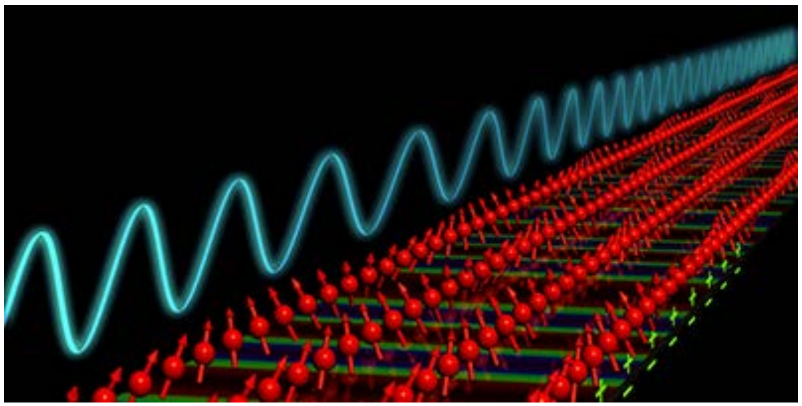
$$I(\omega, \mathbf{q}, \omega', \mathbf{q}') = \sum_f \left| \sum_n \frac{\langle f|T|n\rangle\langle n|T|g\rangle}{\hbar\omega - E_n + i\frac{\Gamma}{2}} \right|^2 \delta(\hbar\omega' + E_f - \hbar\omega - E_g),$$

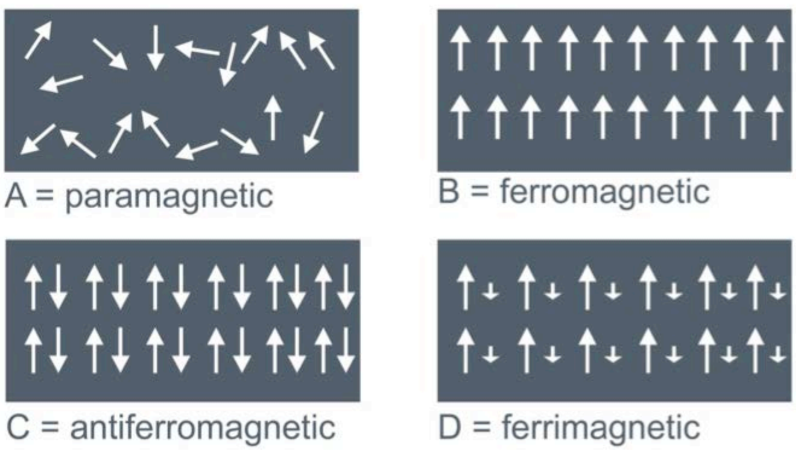


- Calculations model RIXS cross section to understand electronic structure of high-T_c superconductors

Chen, ... Hancock, ... *et al.* *PRL* **105**, 177401 (2010)

Magnetically-ordered states

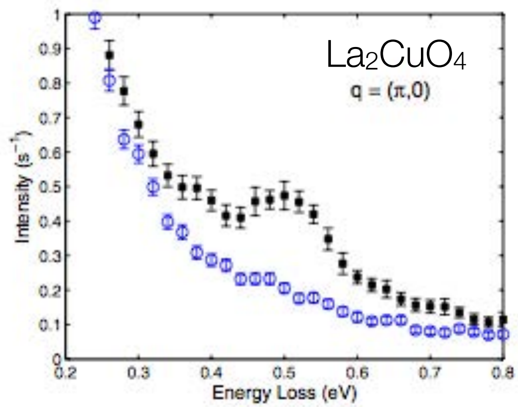


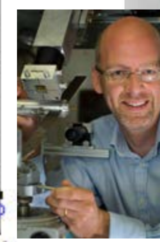


- Magnetic interactions between magnetic ions can lead to ordered states
- Disturbance in order forms “spin waves” or “magnons”
- Like sound, magnons carry momentum and energy
- Dispersion relation is important

Magnetic excitations via RIXS

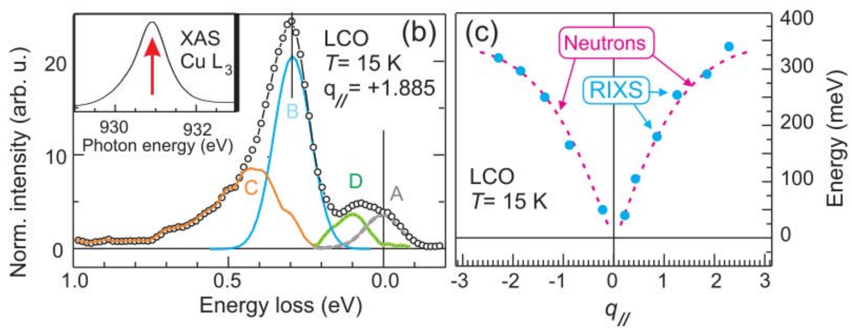
- 2008 Cu K edge RIXS showed bi-magnon feature, consistent with Raman q=0 result

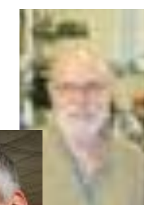




Hill, Blumberg, et al, PRL 100 097001 (2008)

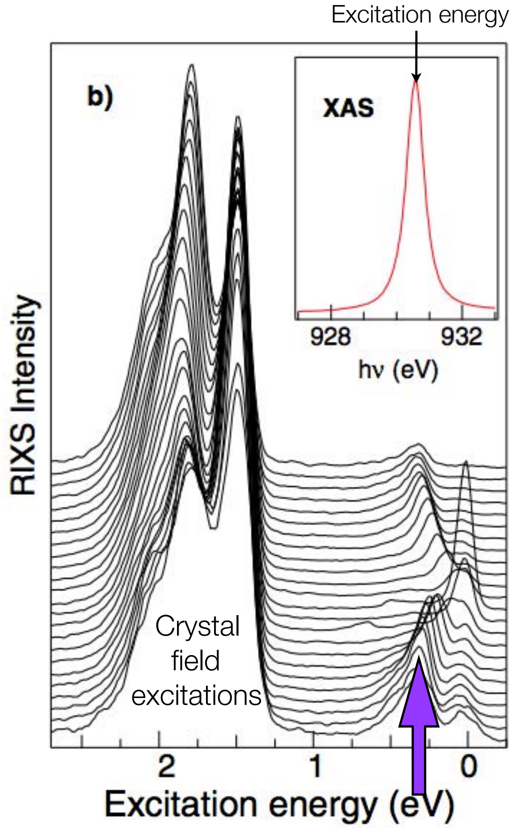
- 2009 Cu L edge (soft X-ray) RIXS showed a shoulder of elastic line consistent with *single*-magnon excitation



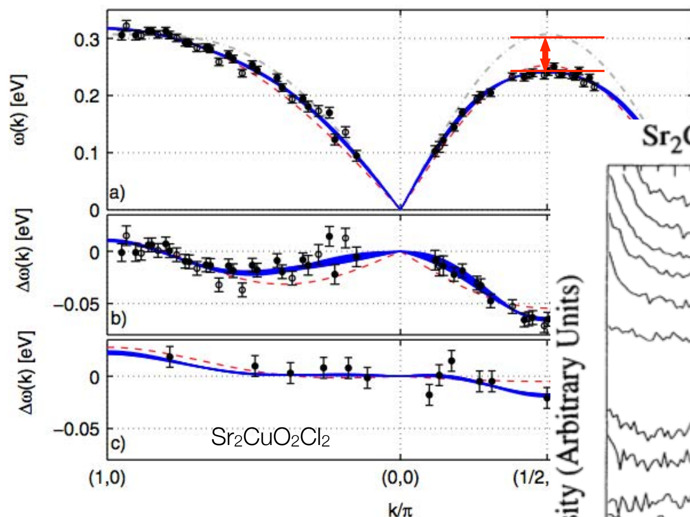


Braicovich, Ghiringhelli, et al, PRL 102 167401 (2009)

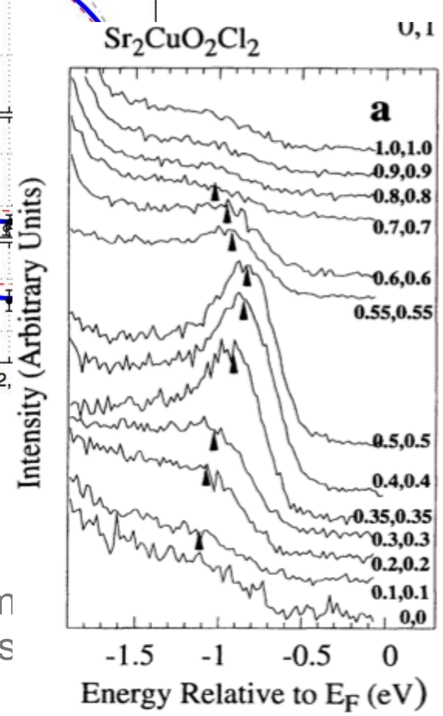
Extended interactions in a Mott insulator $Sr_2CuO_2Cl_2$



Guarise, ...JNH,... *et al. PRL* **12**, 033001 (2010)



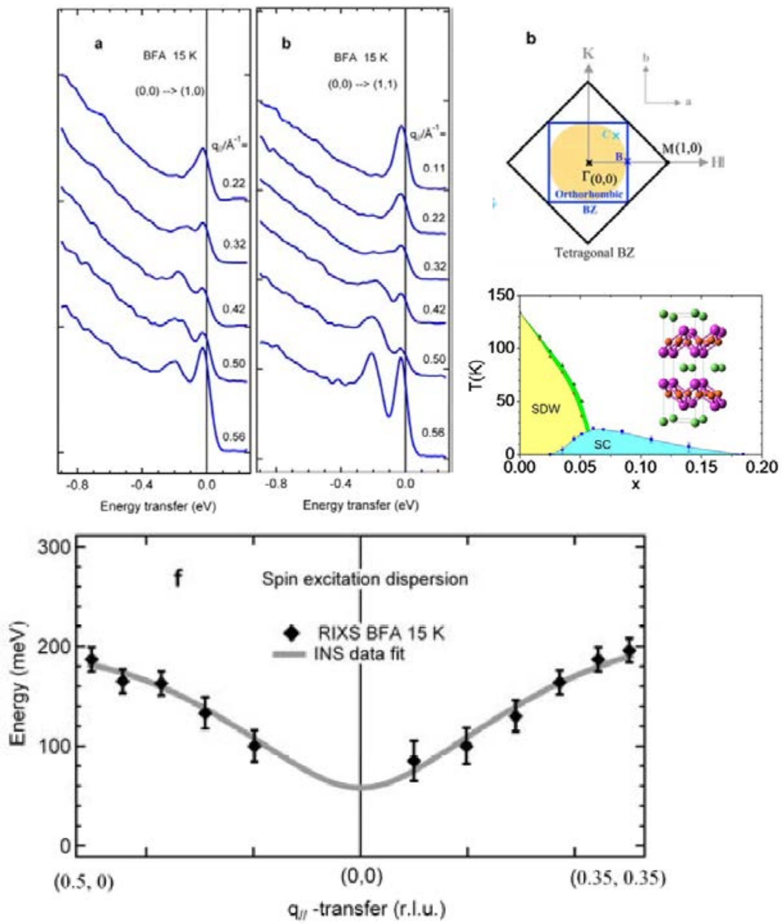
- Suggestive of extended m
  interactions in 2D Mott ins



Wells, *et al*, *PRL* **74,** 964 (1994)

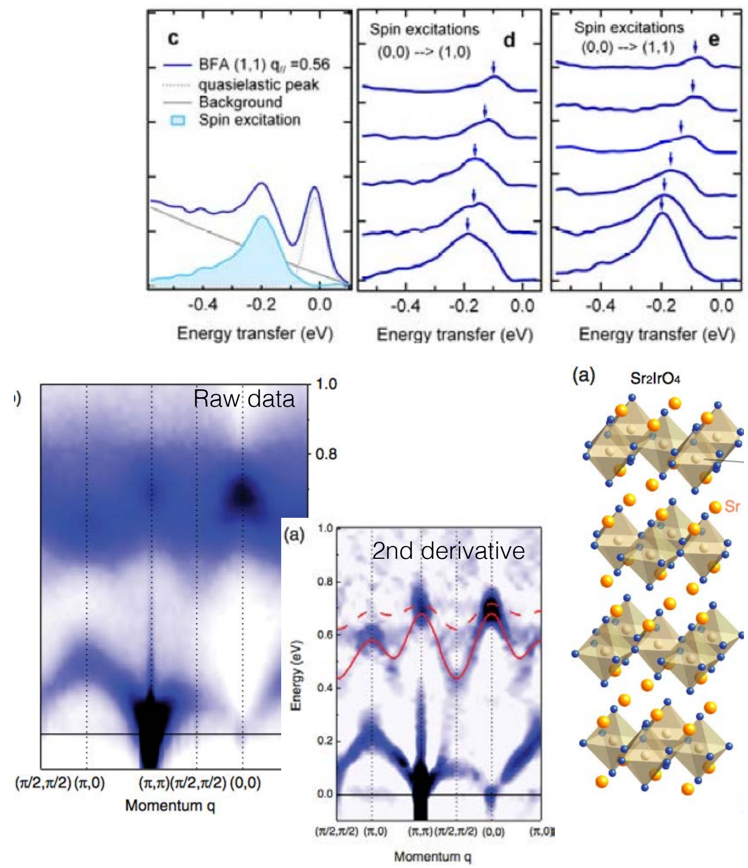
Iron pnictide superconductors and Correlated 5d systems

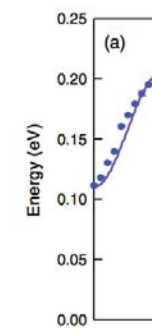
$BaFe_2As_2$



Zhou, et al, *Nature Comm.* **4**, 1470 (2013)

$SrIr_2O_4$

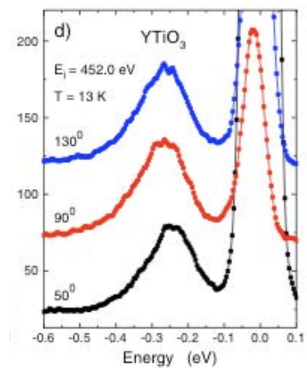




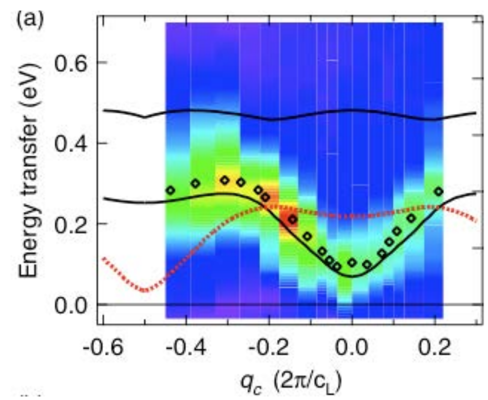
Kim, et al, Phys. Rev. Lett. **108**, 177003 (2012)

Other RIXS highlights

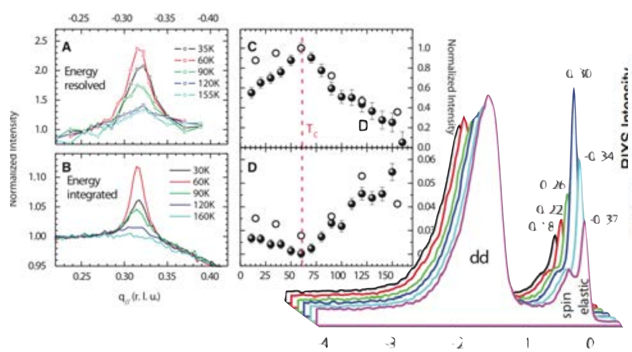
- **Orbiton** dispersion
- **Phonons** excited through core hole intermediates
- **Spin-2** (triplon) excitations
- **Incipient CDW** effect at Tc in YBCO
- **Paramagnon fluctuations** in doped cuprates



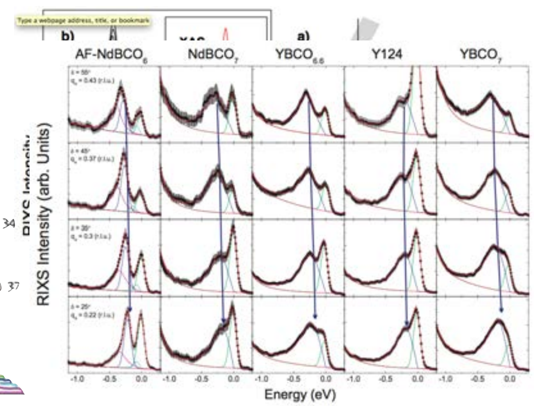
Ulrich, *et al PRL* **103**, 107205 (2009)



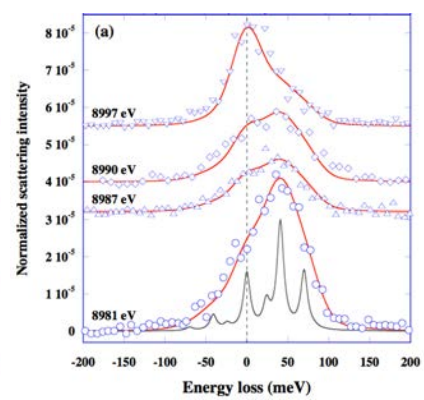
Schlappa, *et al PRL* **103**, 047401 (2009)



Ghiringhelli, et al Science 337, 821 (2012)



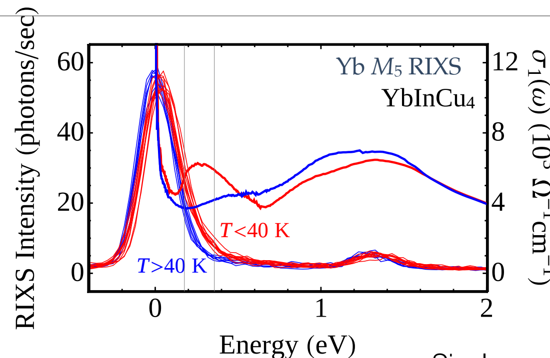
Le Tacon, et al, *Nat. Phys.* 2011

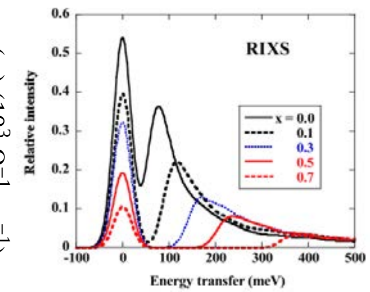


Yavas, et al JPCM **22**, 485601 (2010)

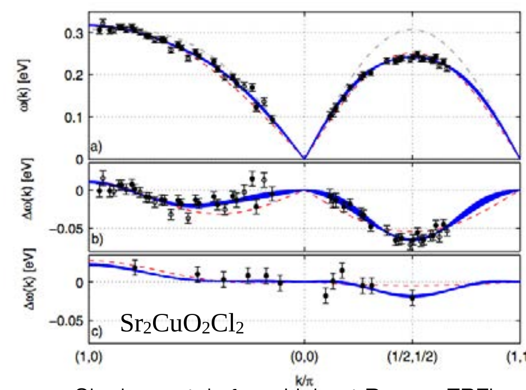
Soft X-ray RIXS work

- Rediscovery of the Kondo gap (now with X-rays)
- 1st mapping of magnon spectra in $Sr_2CuO_2Cl_2$ (non-local exchange)
- Connected RIXS to edge singularity physics



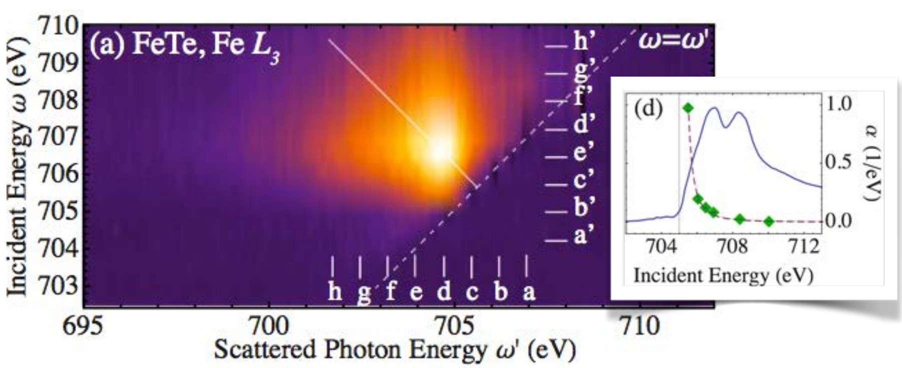


Single crystals from John Sarrao, LANL



Single crystals from Helmut Berger, EPFL

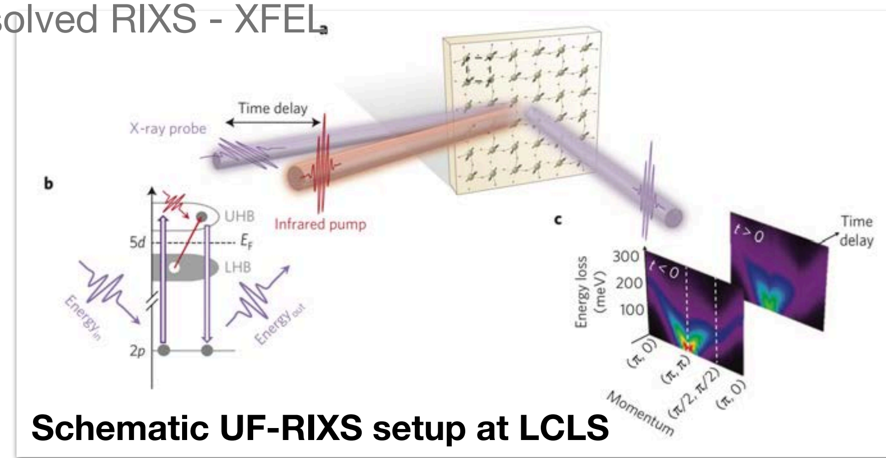
Hancock *et al.* (2011)
Kotani, in review (2011)
Guarise *et al.* *PRL* **12**, 033001 (2010)
Hancock *et al.* *PRB* **82**, 020513R (2010)



Single crystals from Enrico Giannini group, Geneva

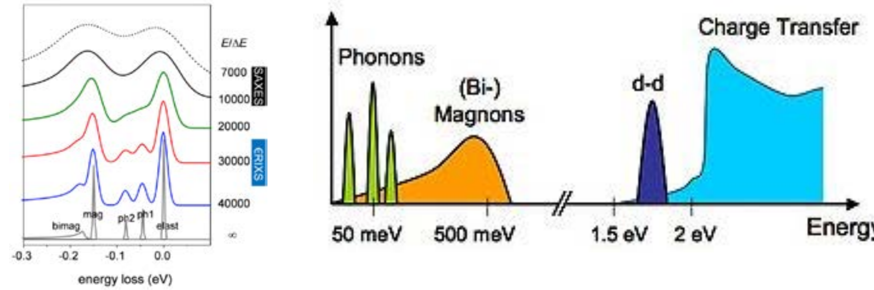
Future technique directions with RIXS

- Time-resolved RIXS - XFEL



Schematic UF-RIXS setup at LCLS

- Higher energy resolution

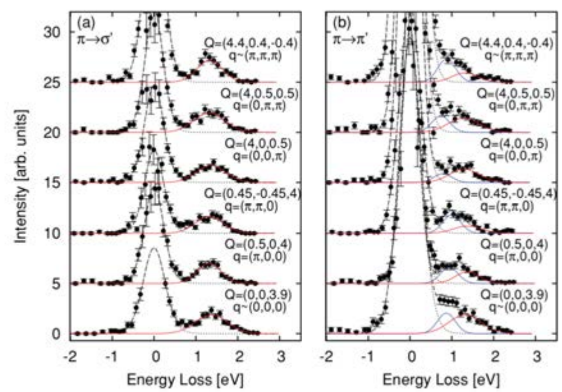


Energy scales in correlated electron systems

- Tender X-ray RIXS - new edges and opportunities

In-vacuum RIXS spectrometer at DESY

- Polarization analysis of scattered photon



High potential to resolve subtle changes, identify excitation channels

Summary/outlook

- RIXS is a 21st century technique, deep probe of exotic excitations
- Many opportunities on horizon for new generation of synchrotron scientists
- APS and NSLS-II have world-leading opportunities in hard and soft RIXS science

- New opportunities for science of correlated electron materials
  - Mixed-valent/Kondo lattice physics
  - High-temperature superconductivity
  - Search for exotic phases for quantum information science

Thank you!