

RIXS-hXES @ XFELs

MARTINA DELL'ANGELA

CNR-IOM, TRIESTE

Outline

RIXS-hXES@ XFELs

I. Techniques

1. X-ray absorption (XAS)
2. X-ray emission (XES) / High resolution X-ray Emission (hXES)
3. Resonant Inelastic X-ray Scattering (RIXS)

II. Instruments

III. Selected RIXS-hXES applications @ XFELs

- I. RIXS @FLASH: Phase Transitions
- II. RIXS@LCLS: Femtochemistry
- III. RIXS@LCLS: Liquids
- IV. RIXS@SACLA: Magnetism
- V. RIXS@FERMI: dd excitations

I. Exp. Techniques

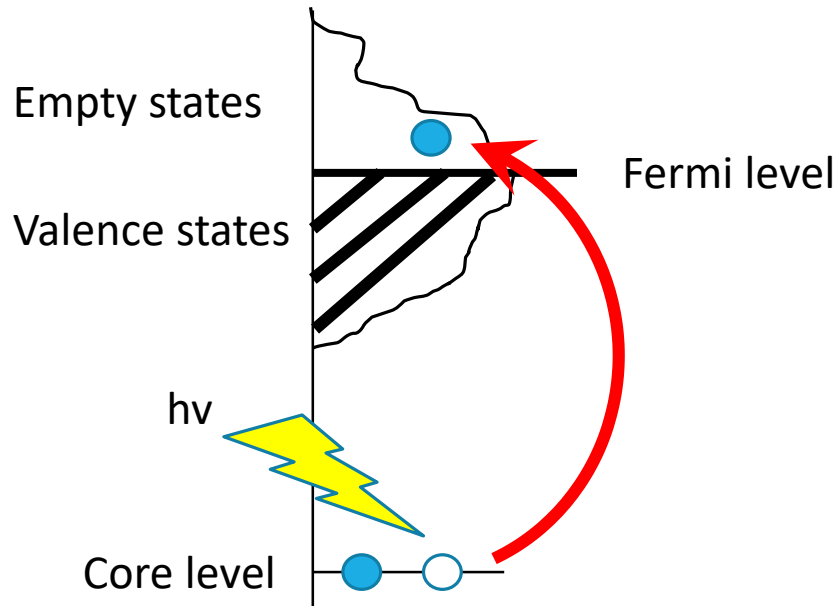
hXES

Core level spectroscopies

RIXS

Photon-in/Photon-out

X-ray absorption spectroscopy (XAS)



A photon is absorbed and a core electron is excited to an unoccupied state

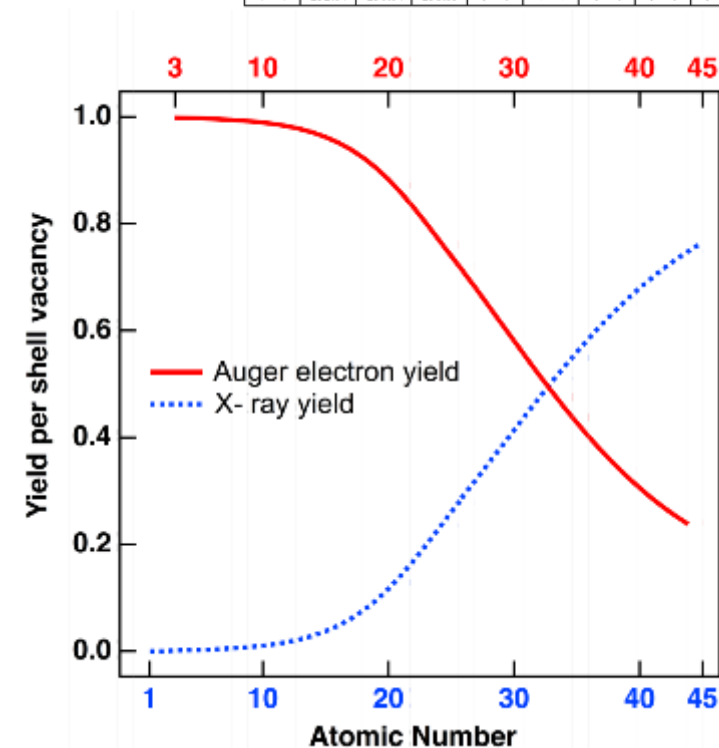
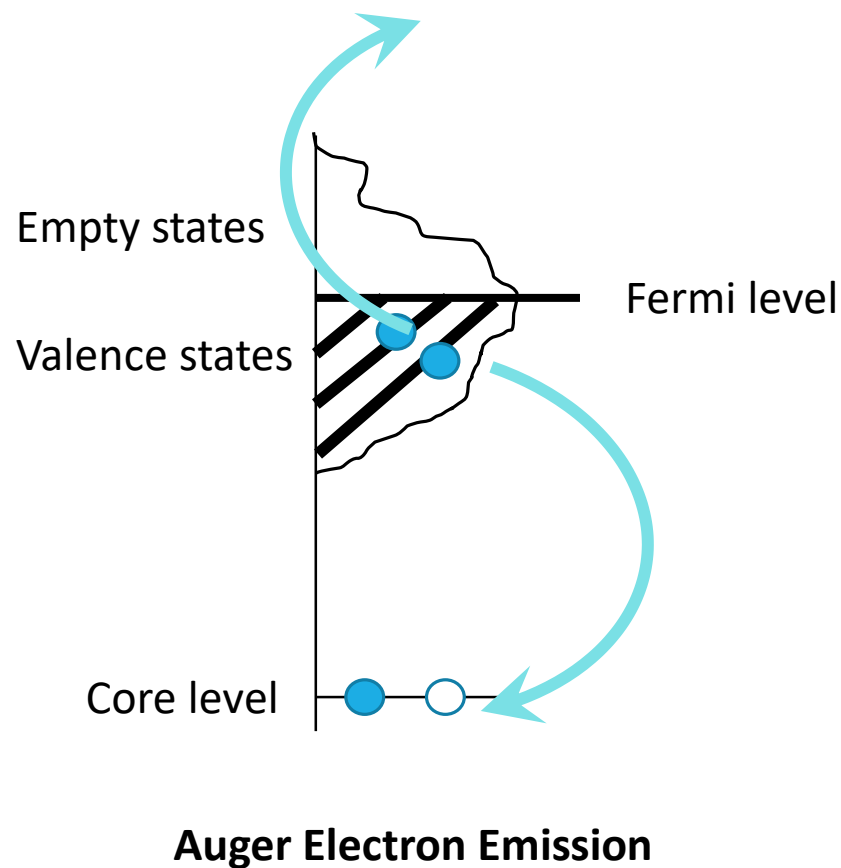
$$P_{i \rightarrow f} \propto |\langle f | H' | i \rangle|^2 \rho_f$$

$$H' = \mathbf{p} \cdot \mathbf{e} \exp(i\mathbf{k}\mathbf{r}) \quad \text{dipole approximation}$$

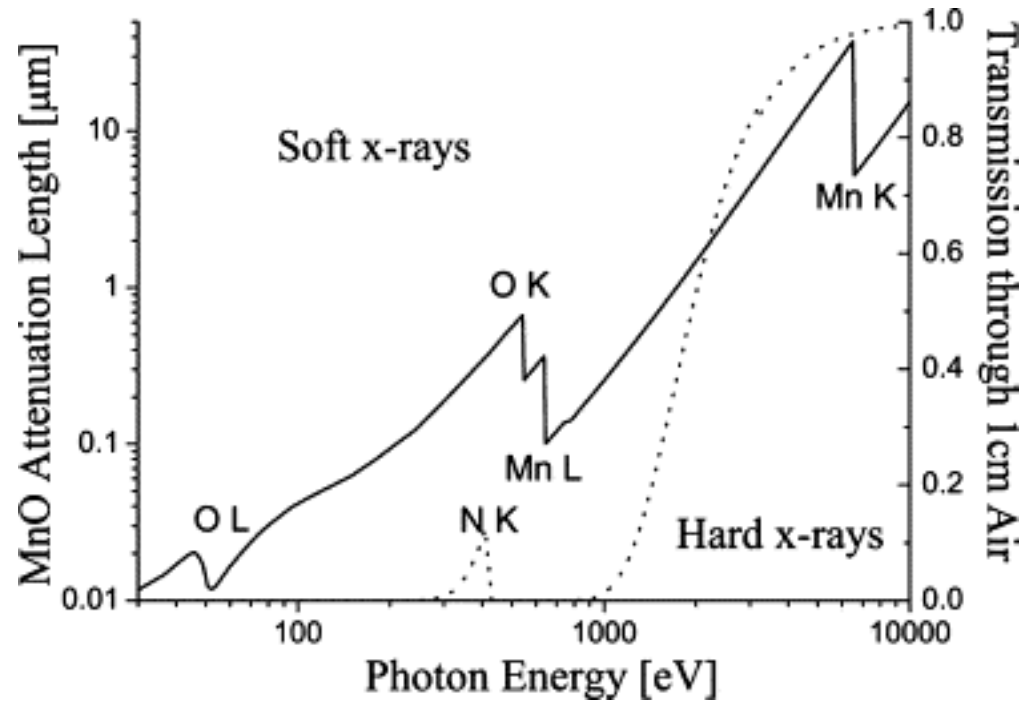
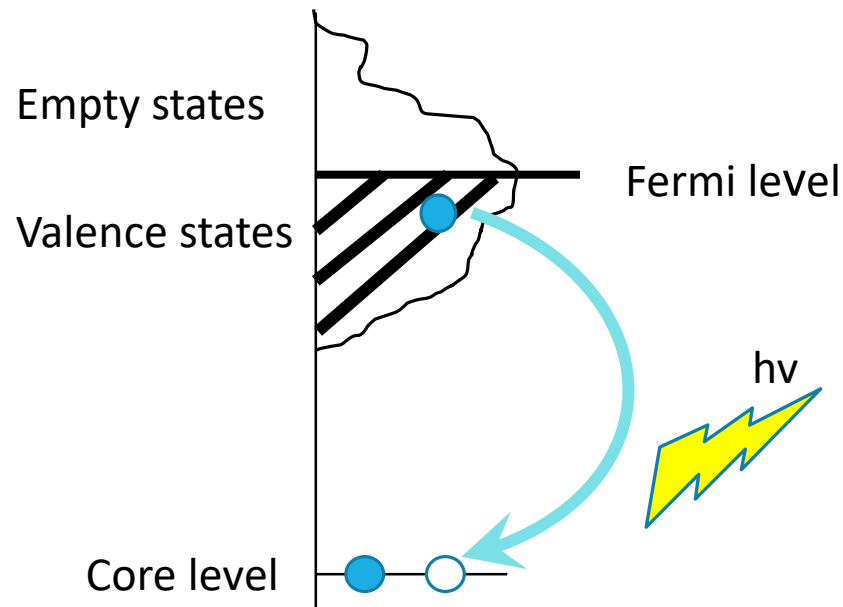
XAS is element-specific

Decay of core holes

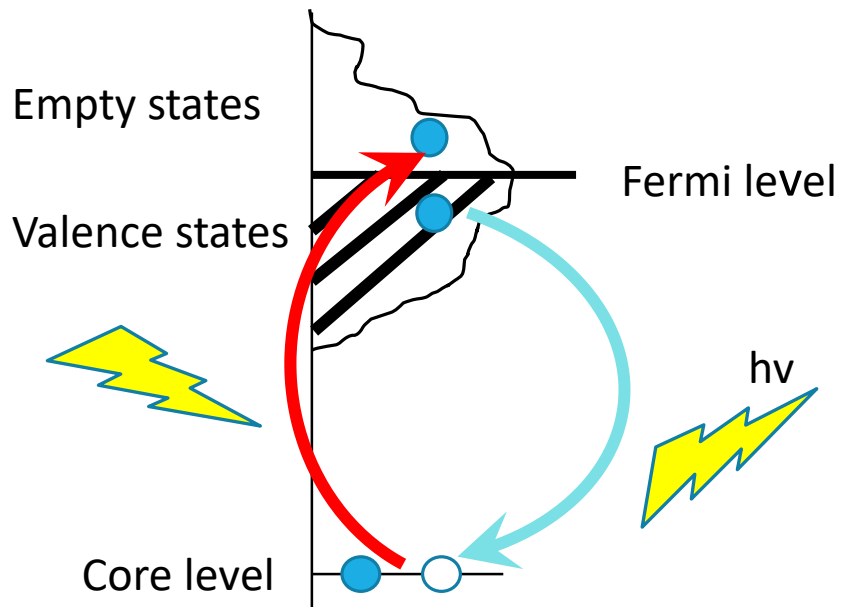
1																	2															
1 H 1.008																	2 He 4.0026															
3 Li 6.94	4 Be 9.0122											13 B 10.81	14 C 12.011	15 N 14.007	16 O 15.999	17 F 18.998	18 Ne 20.180															
11 Na 22.990	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948															
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.630	33 As 74.922	34 Se 78.97	35 Br 79.904	36 Kr 83.798															
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.95	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29															
55 Cs 132.91	56 Ba 137.33	57-71 *	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)															
87 Fr (223)	88 Ra (226)	89-103 #	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (289)	116 Lv (293)	117 Ts (294)	118 Og (294)															
* Lanthanide series																																
<table><tr><td>57 La 138.91</td><td>58 Ce 140.12</td><td>59 Pr 140.91</td><td>60 Nd 144.24</td><td>61 Pm (145)</td><td>62 Sm 150.36</td><td>63 Eu 151.96</td><td>64 Gd 157.25</td><td>65 Tb 158.93</td><td>66 Dy 162.50</td><td>67 Ho 164.93</td><td>68 Er 167.26</td><td>69 Tm 168.93</td><td>70 Yb 173.05</td><td>71 Lu 174.97</td></tr></table>																		57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97																		
# Actinide series																																
<table><tr><td>89 Ac (227)</td><td>90 Th 232.04</td><td>91 Pa 231.04</td><td>92 U 238.03</td><td>93 Np (237)</td><td>94 Pu (244)</td><td>95 Am (243)</td><td>96 Cm (247)</td><td>97 Bk (247)</td><td>98 Cf (251)</td><td>99 Es (252)</td><td>100 Fm (257)</td><td>101 Md (258)</td><td>102 No (259)</td><td>103 Lr (262)</td></tr></table>																		89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)
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X-ray emission spectroscopy (XES)



Resonant Inelastic X-ray Scattering (RIXS)



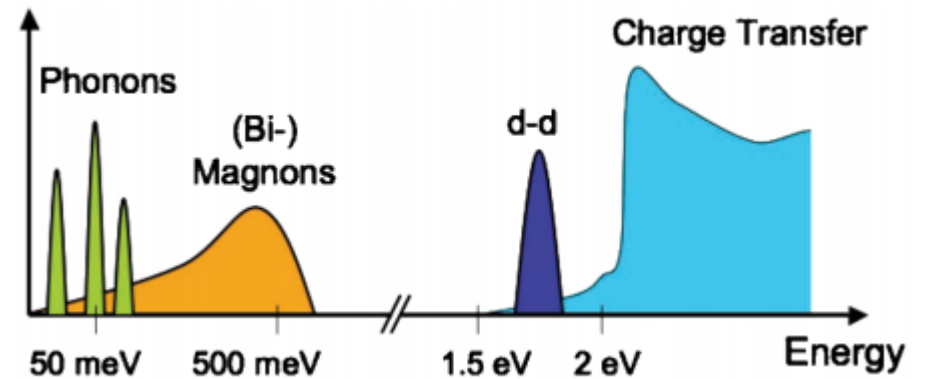
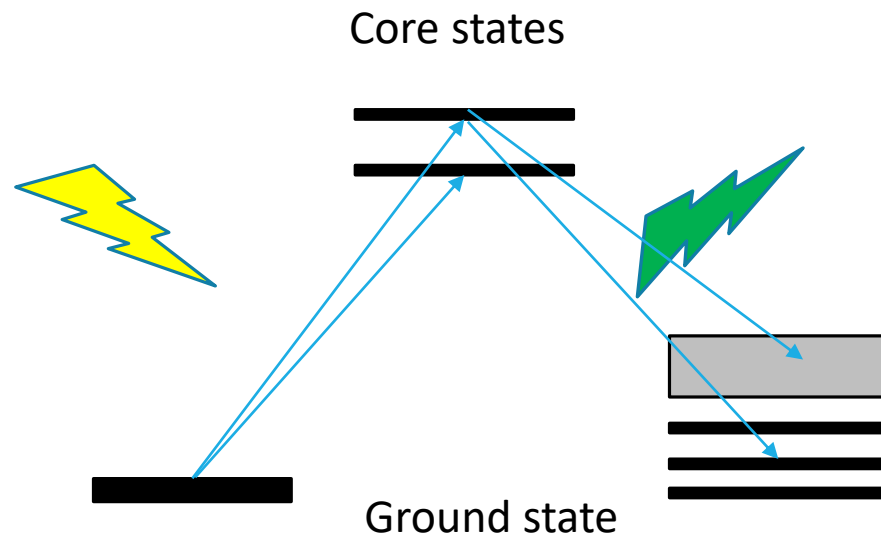
Inelastic scattering cross section (Kramers-Heisenberg formula):

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

- i. Site selectivity
- ii. Symmetry selectivity
- iii. Probe low energy excitations
- iv. Sub-natural width spectra
- v. Ultrafast dynamics
- vi. Bulk and buried structures
- vii. Band dispersion

J. Nordgren et al., in Handbook of Solid State Spectroscopy, Springer 2006, Ed. W.R. Wij

Low energy excitations in materials



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Requirements

1. Photon Detection System (energy resolution)
2. Tunable and brilliant photon source (VUV and X-ray)

Monochromatic synchrotron beamlines

Photon hungry

X-ray Spectrometers ...history



VG Scienta, XES 350 Grace

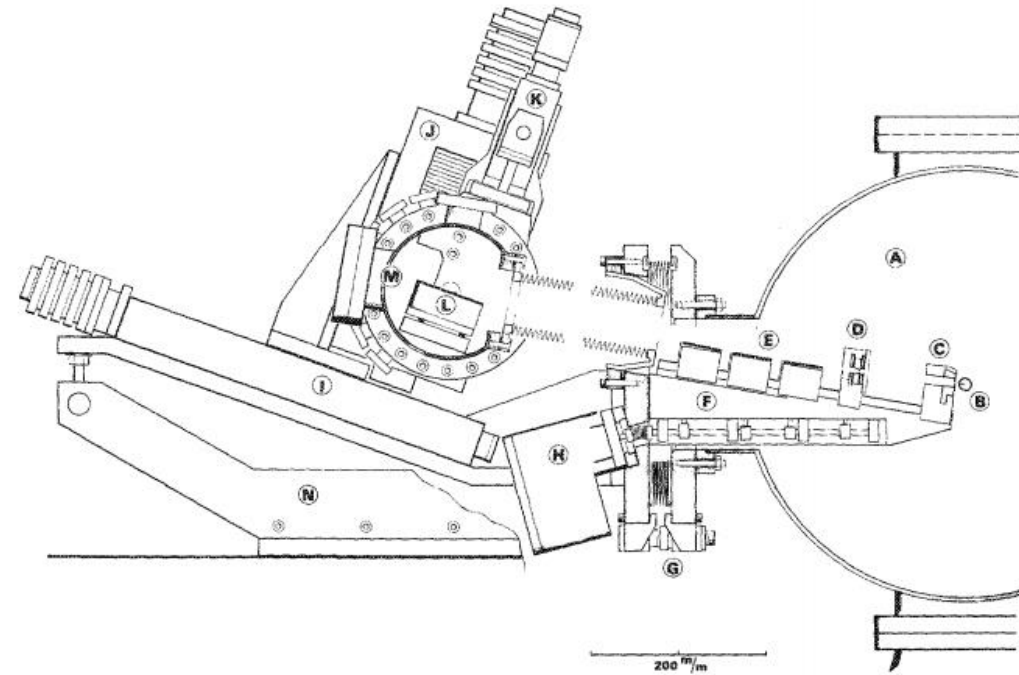
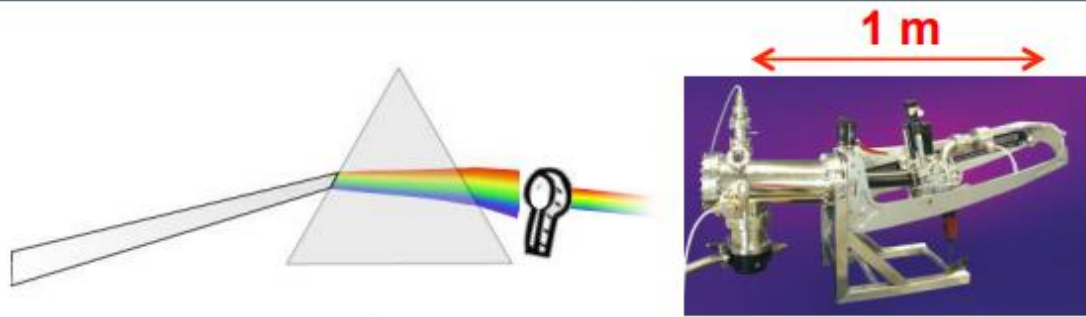


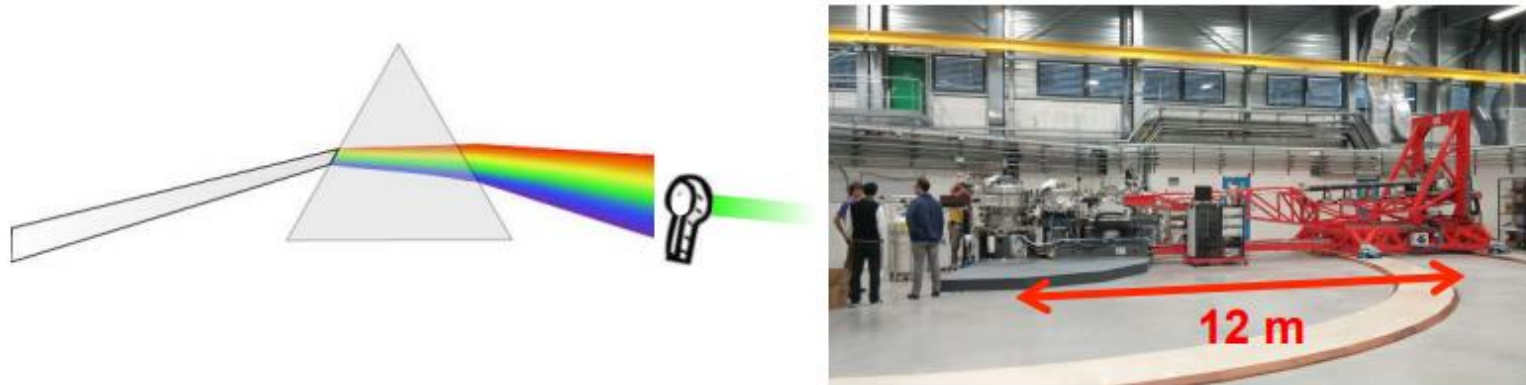
FIG. 1. Outline of the fixed-grating grazing incidence instrument. A; experiment chamber, B; sample, C; entrance slit, D; grating selector aperture, E; gratings, F; reference slab, G; optical axis adjustment, H; mechanical feedthroughs, I, J, K; coordinate tables, L; detector, M; detector house, and N; support structure.

Nordgren, J., Bray, G., Cramm, S., Nyholm, R., Rubensson, J.-E. & Wassdahl, N. (1989). *Rev. Sci. Instrum.* **60**, 1690–1696.

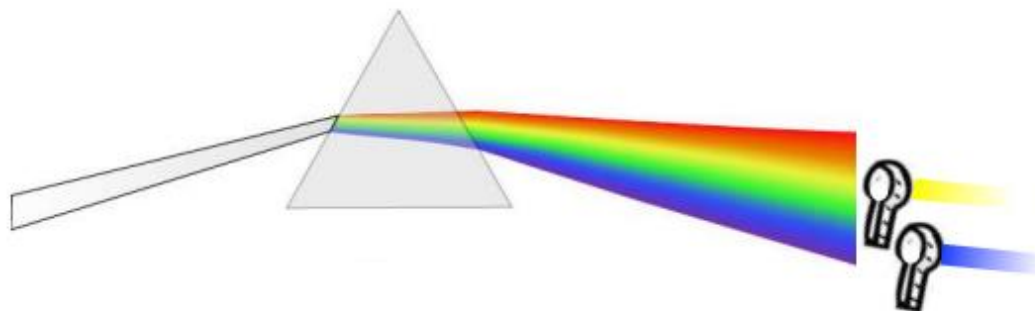


Commercial
Spectrometer

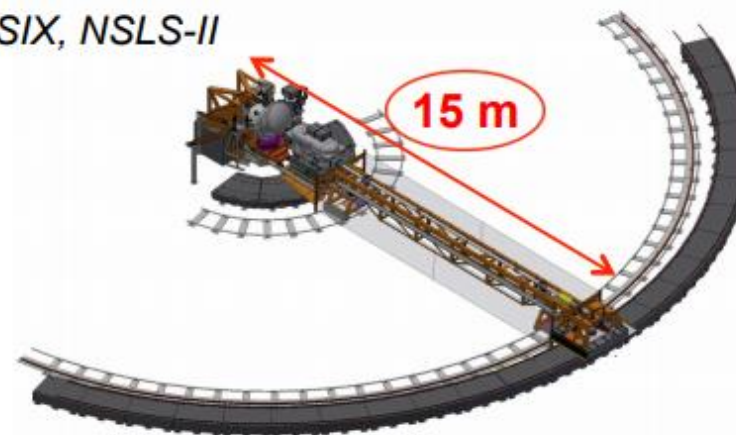
I. Jarrige, BNL



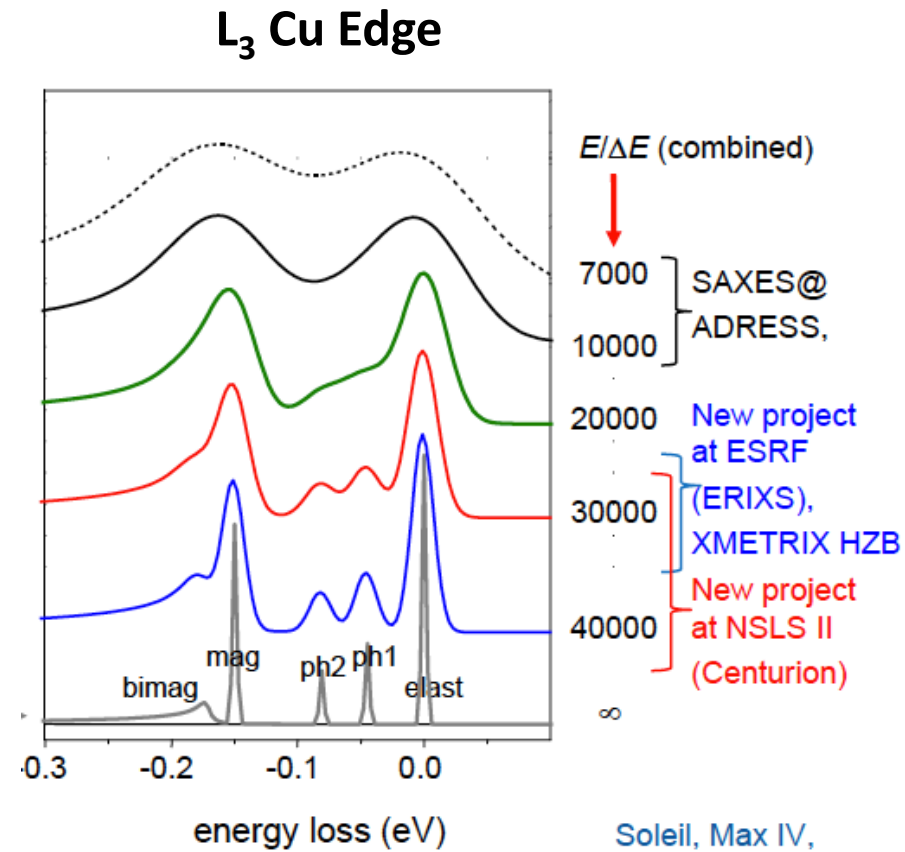
ID32
ESRF (France)



SIX, NSLS-II



RIXS resolution

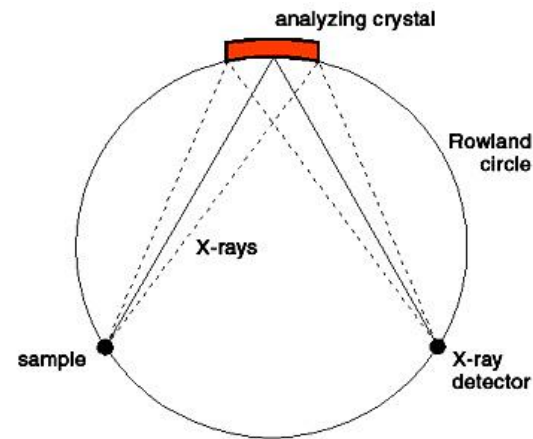


Soleil, Max IV,
NSRRC, Spring-8

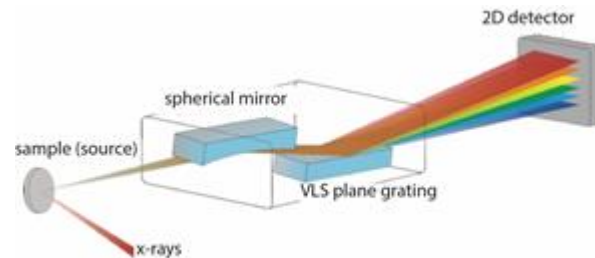
A. Fohlisch, XFEL hRIXS

Examples of X-ray spectrometers

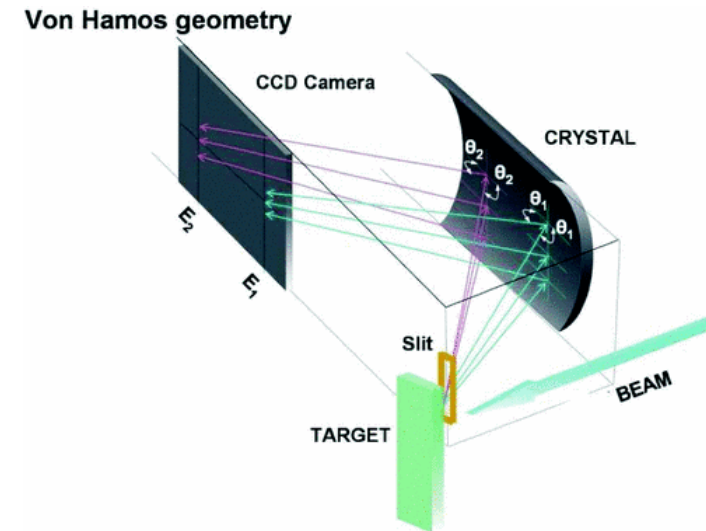
**Rowland geometry
(Monochromatic;
spherical mirror)**



**Hettrick-Underwood
(qRIXS, MERLIN(ALS))**



von Hamos (Dispersive)



M. Czarnota et al., Phys. Rev. A 88, 052505 (2013)

Lab based RIXS/XESfuture developments

PHYSICAL REVIEW X **6**, 031047 (2016)

Ultrafast Time-Resolved Hard X-Ray Emission Spectroscopy on a Tabletop

Luis Miaja-Avila,^{1,*} Galen C. O'Neil,¹ Young I. Joe,¹ Bradley K. Alpert,¹ Niels H. Damrauer,² William B. Doriese,¹ Steven M. Fatur,² Joseph W. Fowler,¹ Gene C. Hilton,¹ Ralph Jimenez,^{2,3} Carl D. Reintsema,¹ Daniel R. Schmidt,¹ Kevin L. Silverman,¹ Daniel S. Swetz,¹ Hideyuki Tatsuno,¹ and Joel N. Ullom^{1,4,†}

¹National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305, USA

²Department of Chemistry and Biochemistry, University of Colorado Boulder, Boulder, Colorado 80309, USA

³JILA, National Institute of Standards and Technology and University of Colorado Boulder, 440 UCB, Boulder, Colorado 80309, USA

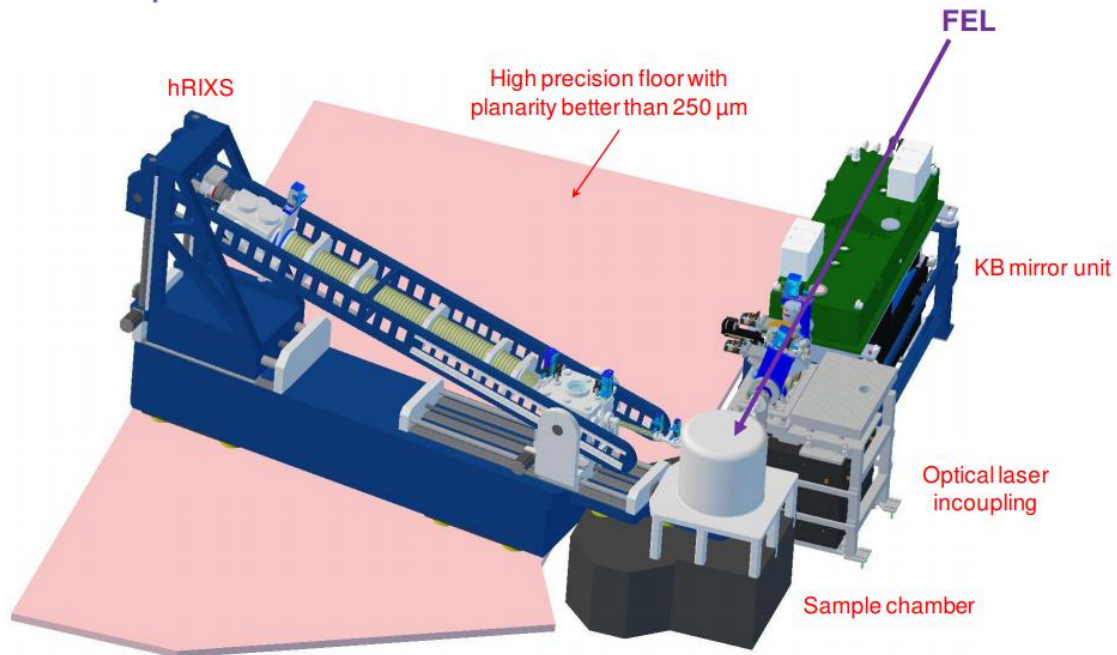
⁴Department of Physics, University of Colorado Boulder, Boulder, Colorado 80309, USA

(Received 28 March 2016; revised manuscript received 20 June 2016; published 27 September 2016)

Experimental tools capable of monitoring both atomic and electronic structure on ultrafast (femtosecond to picosecond) time scales are needed for investigating photophysical processes fundamental to light harvesting, photocatalysis, energy and data storage, and optical display technologies. Time-resolved hard x-ray (>3 keV) spectroscopies have proven valuable for these measurements due to their elemental specificity and sensitivity to geometric and electronic structures. Here, we present the first tabletop apparatus capable of performing time-resolved x-ray emission spectroscopy. The time resolution of the apparatus is better than 6 ps. By combining a compact laser-driven plasma source with a highly efficient array of microcalorimeter x-ray detectors, we are able to observe photoinduced spin changes in an archetypal polypyridyl iron complex $[\text{Fe}(\text{2,2'-'bipyridine})_3]^{2+}$ and accurately measure the lifetime of the quintet spin state. Our results demonstrate that ultrafast hard x-ray emission spectroscopy is no longer confined to large facilities and now can be performed in conventional laboratories with 10 times better time resolution than at synchrotrons. Our results are enabled, in part, by a 100- to 1000-fold increase in x-ray collection efficiency compared to current techniques.

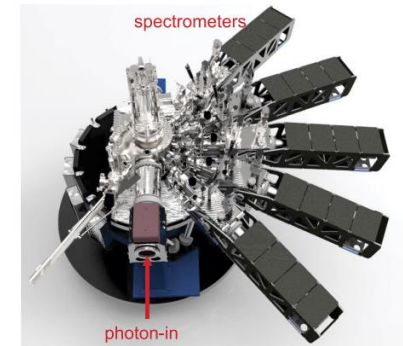
RIXS projects @FELs ...(soft X-rays)

XFEL Heisenberg RIXS (A. Fohlisch)



https://www.xfel.eu/sites/sites_custom/site_xfel/content/e51499/e60513/e63567/e63600/9_XFUM2017-SASE3_Satellite_Nepl_hRIXS_eng.pdf

LCLS qRIXS



Yi de Chuang et al. Review of Scientific Instruments **88**, 013110 (2017); <https://doi.org/10.1063/1.4974356>

PAL-XFEL,

Outline

RIXS-hXES@ XFELs

I. Techniques

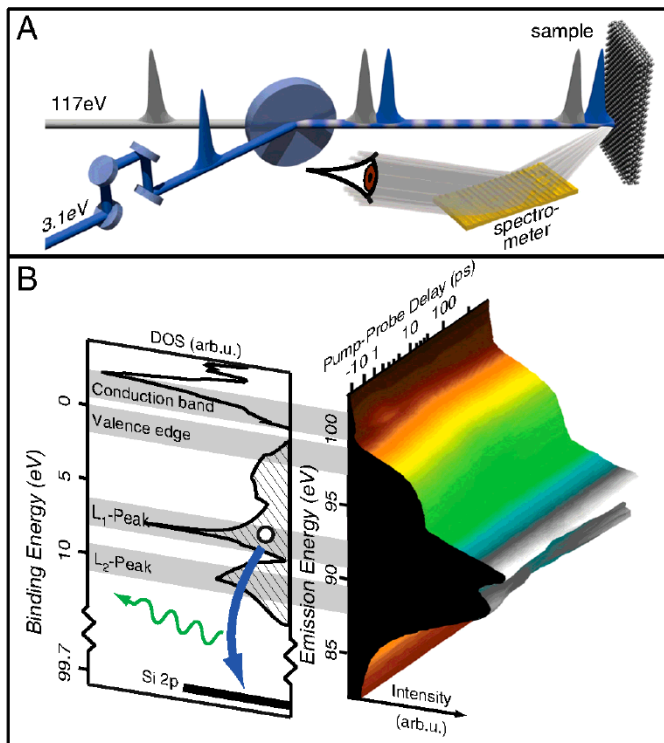
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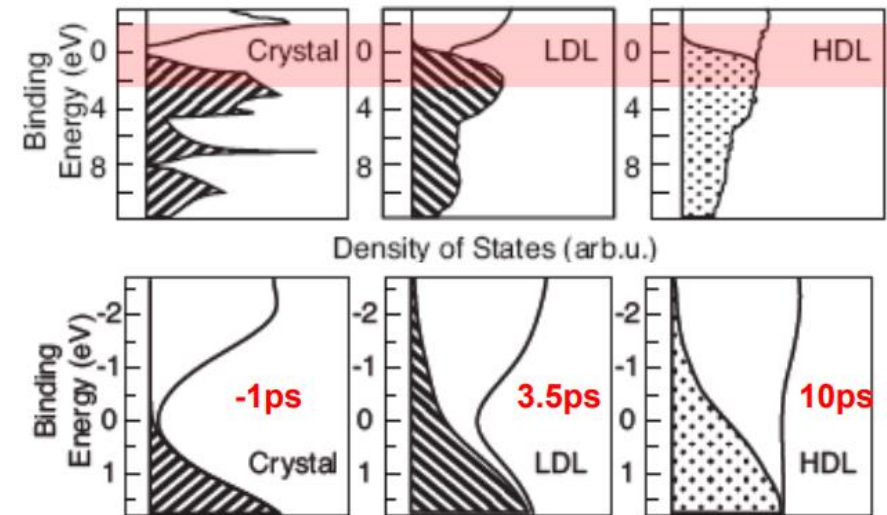
- I. **RIXS@FLASH: Phase Transitions**
- II. RIXS@LCLS: Femtochemistry
- III. RIXS@LCLS: Liquids
- IV. RIXS@SACLA: Magnetism
- V. RIXS@FERMI: dd excitations

Tr-XES on Silicon



M. Beye *et al.*, **PNAS** 107, 16772 (2010)

Liquid-liquid transition in silicon



Transient “low density” state accessible
at short timescales

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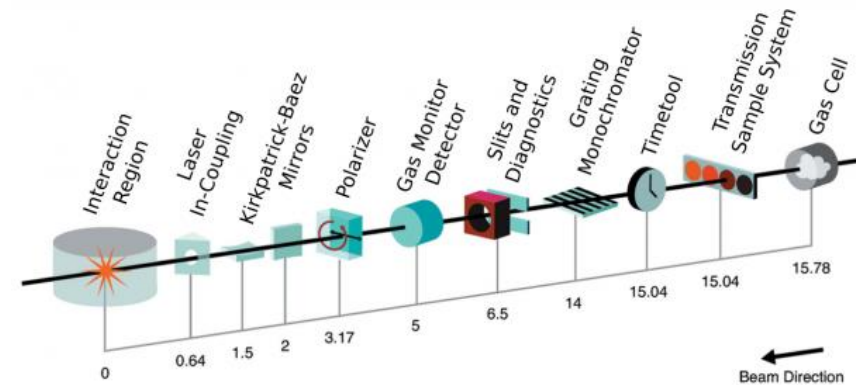
II. RIXS@LCLS: Femtochemistry

LCLS (Stanford)



<https://lcls.slac.stanford.edu/overview>

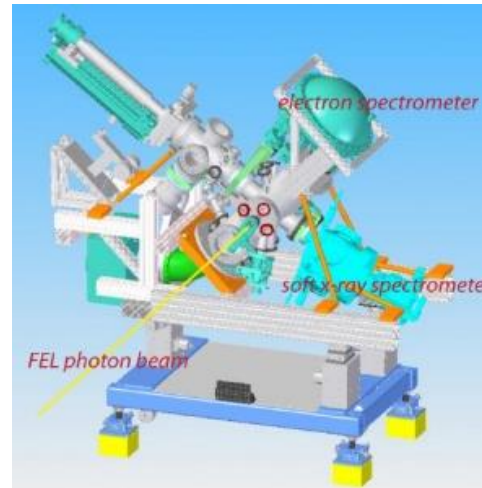
SXR Instrument



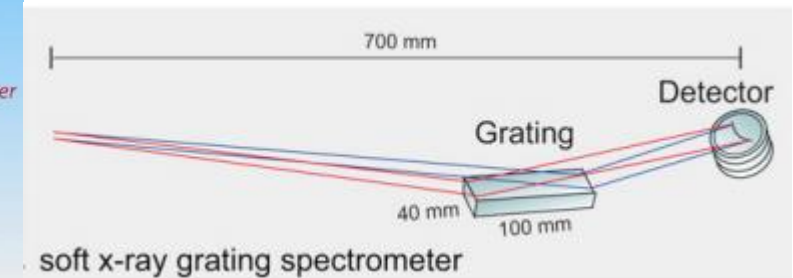
X-ray Spectrometer

Photon Beam Properties

Sample Configurations	Pre-Mono Transmission Sample Chamber, white beam	Endstation, white beam	Endstation, mono
Focusing Capability (Kirkpatrick-Baez)	1 x 1 mm (unfocused at sample)	= 2 x 2 μ m	= 2 x 2 μ m
Energy Range	280-2000 eV		grating 1 (100 lines/mm): 500-1500 eV
			grating 2 (200 lines/mm): 800-2000 eV
Energy Resolution	~0.1 eV (500 eV)	~0.5 eV (500 eV)	~0.1 eV (500 eV)
	~0.2 eV (1000 eV)	~1.0 eV (1000 eV)	~0.5 eV (1000 eV)
	~0.6 eV (2000 eV)	~2.0 eV (2000 eV)	~0.6 eV (2000 eV)
Flux (ph/pulse) @ resolution limit	1 x 10 ¹² (500 eV)	1 x 10 ¹¹ (500 eV)	1 x 10 ¹⁰ (500 eV)
	1 x 10 ¹³ (1000 eV)	1 x 10 ¹² (1000 eV)	3 x 10 ¹² (1000 eV)
	1 x 10 ¹³ (2000 eV)	1 x 10 ¹² (2000 eV)	2 x 10 ¹² (2000 eV)



Surface Science Endstation (prof. A. Nilsson)



T. Katayama, et al. J. Elect. Spec. Rel Phen 187 (2013) 9

Spectrometer (Rowland type):

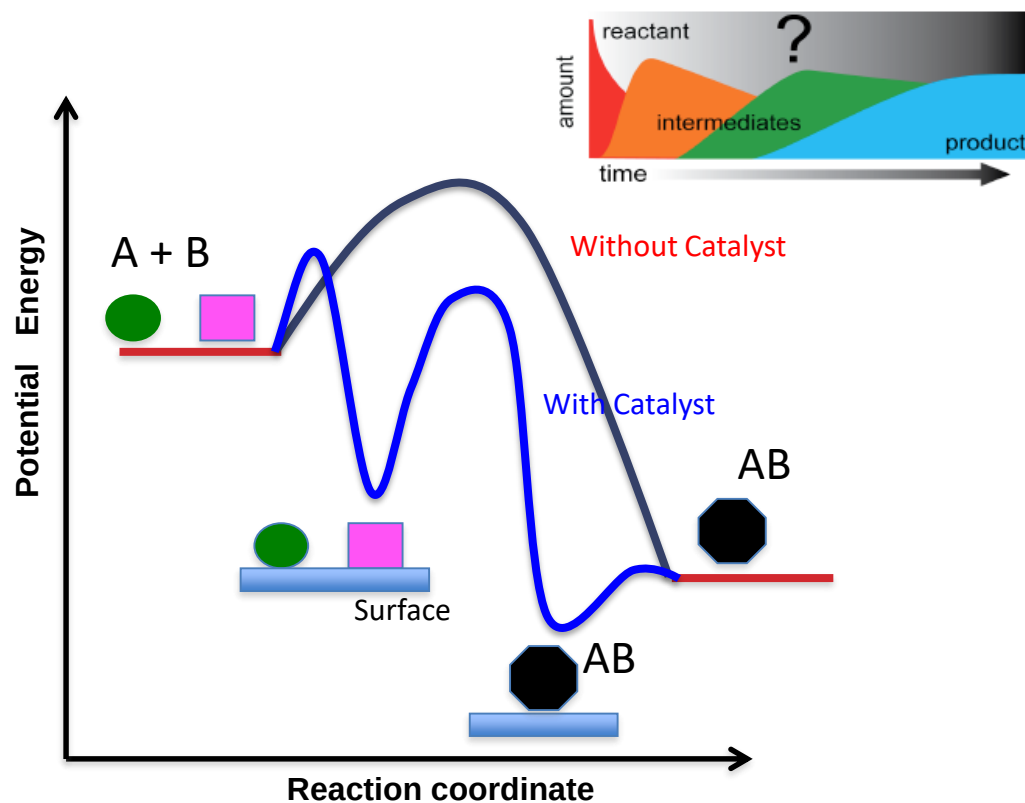
Elliptical grating (Ni coated)

Negative Diffraction Order

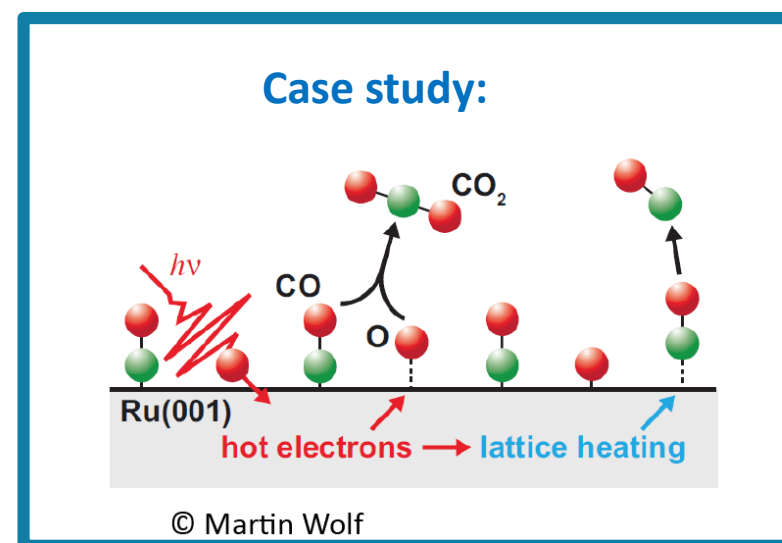
No entrance slit

<https://lcls.slac.stanford.edu/instruments/sxr/specifications>

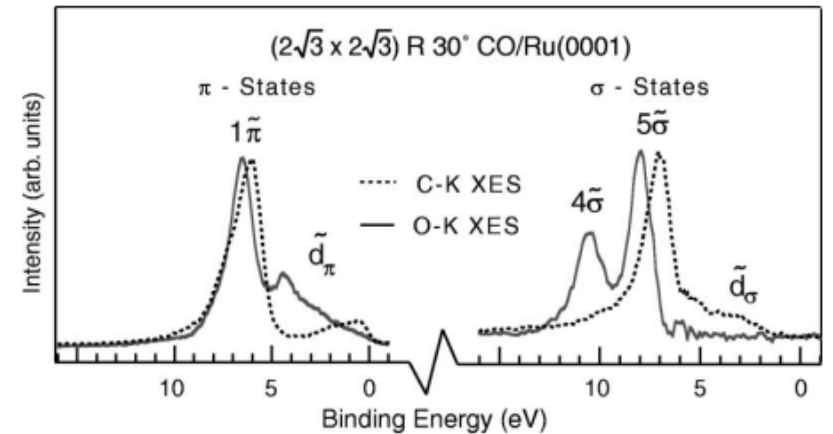
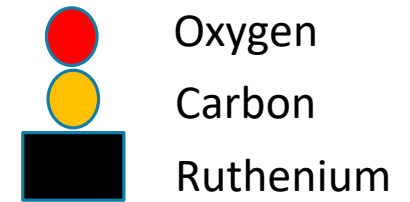
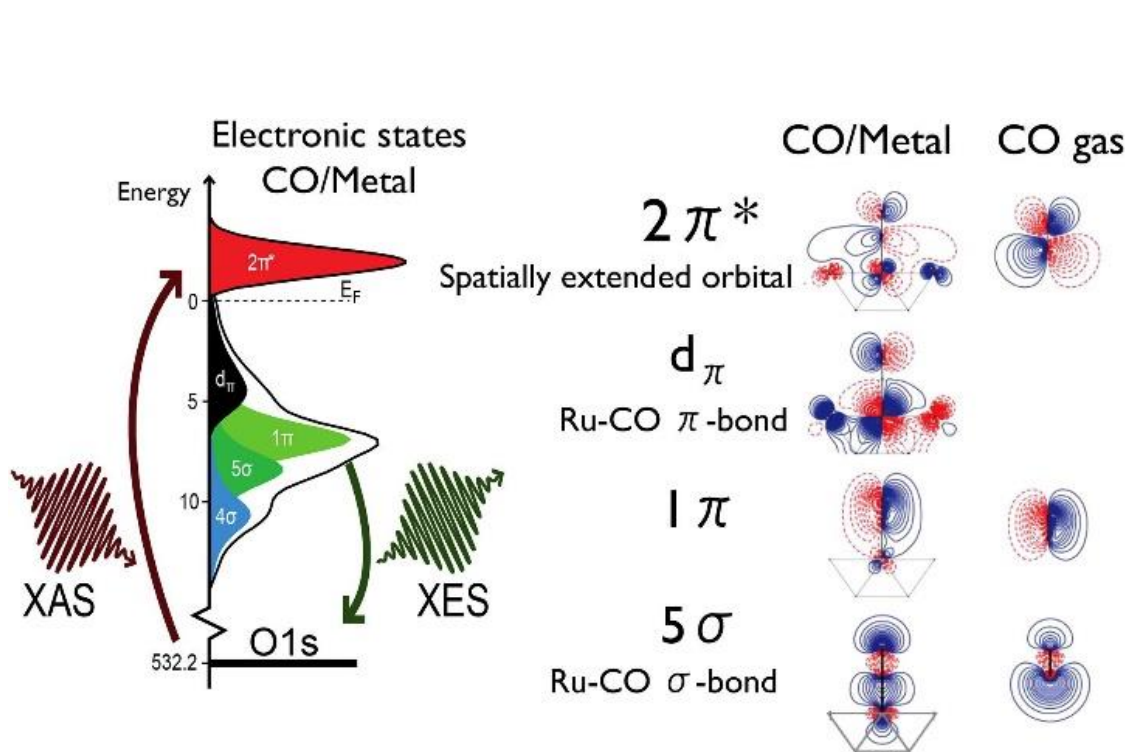
Femtochemistry



Challenge:
Understand reaction mechanism
and dynamics



CO RIXS @synchrotron

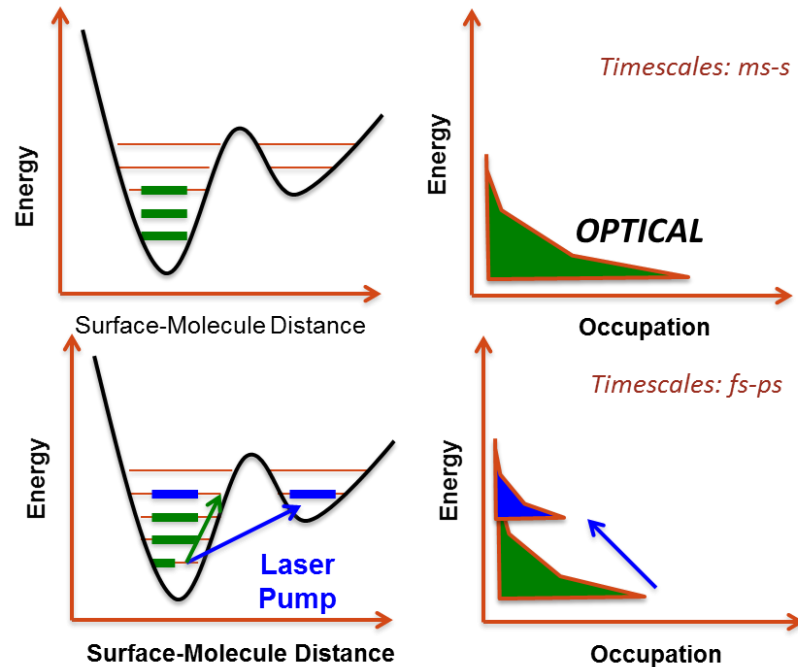


A. Nilsson et al., Chem Phys Lett, 675 (2017) 145

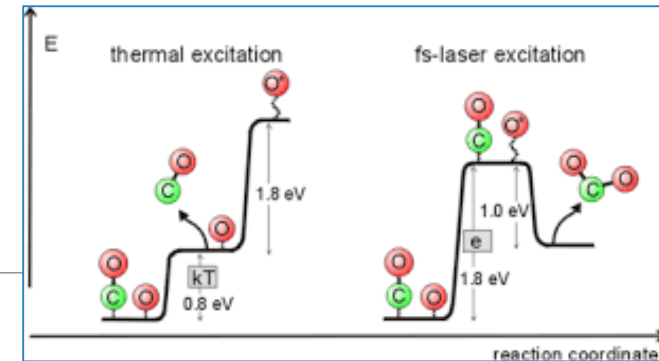
A. Föhlisch et al., J. Chem Phys, 121 (2004) 4848

Tr-RIXS in catalysis

Create HOT ELECTRONS that trigger reactions



THERMAL vs ULTRAFAST
laser induced heating

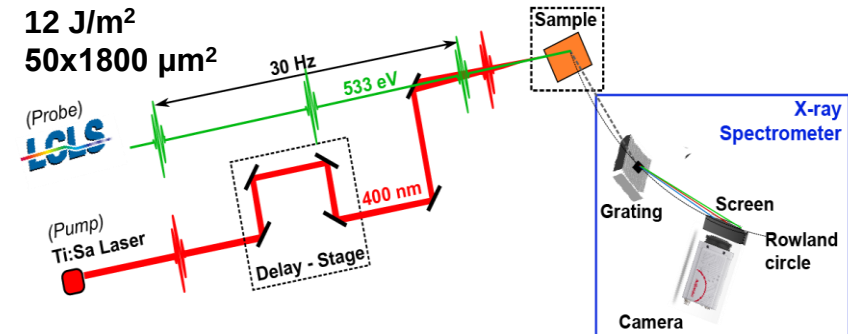


M. Bonn et al, Science 285, 1042 (1999)

LCLS set up

60 Hz
533eV
(100 l/mm grating)
100fs
12 J/m²
50x1800 μm²

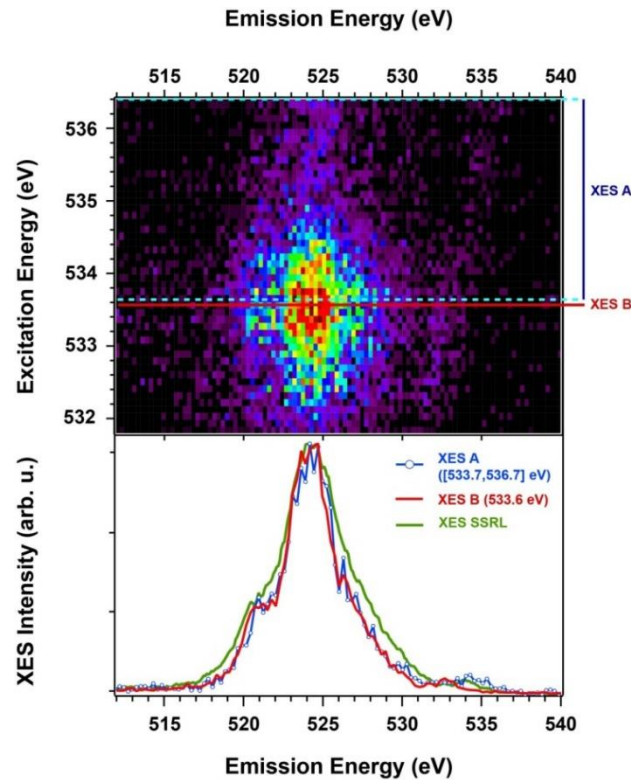
Scienta R3000
Electron Spectrometer



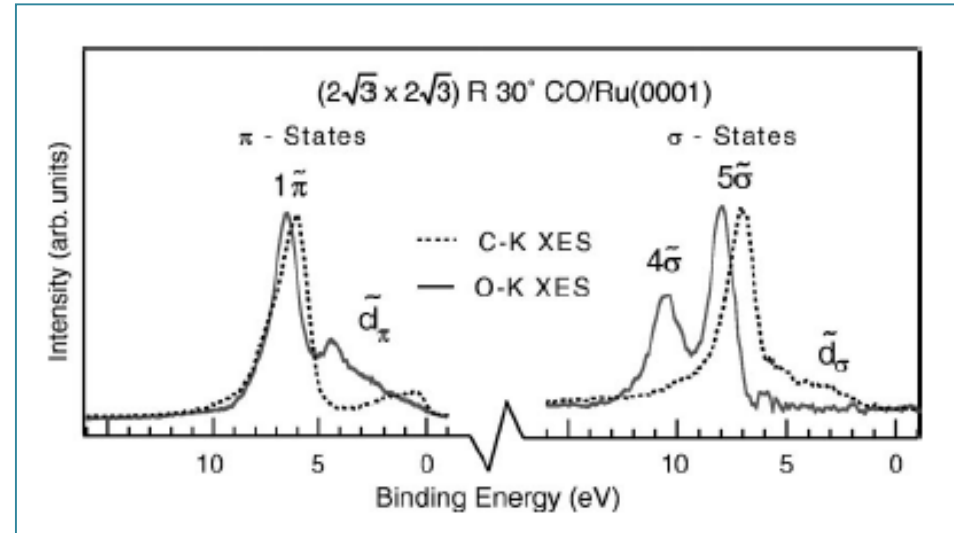
FEL vs Synchrotron “static” data

RIXS MAP

FEL Bandwidth

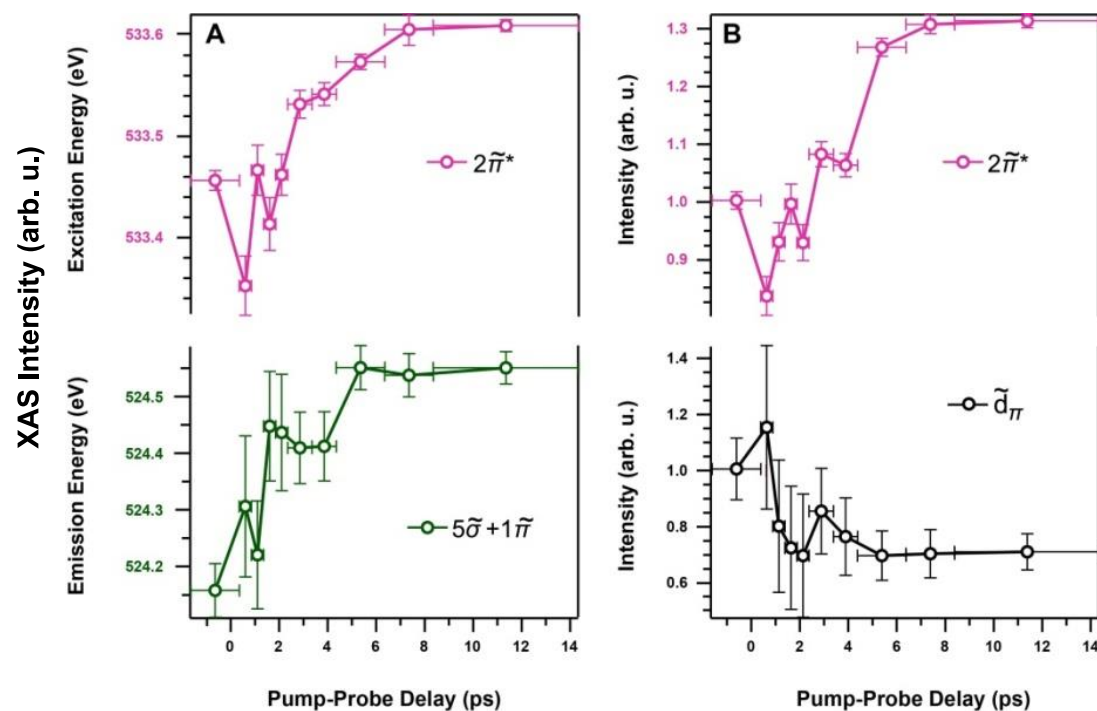
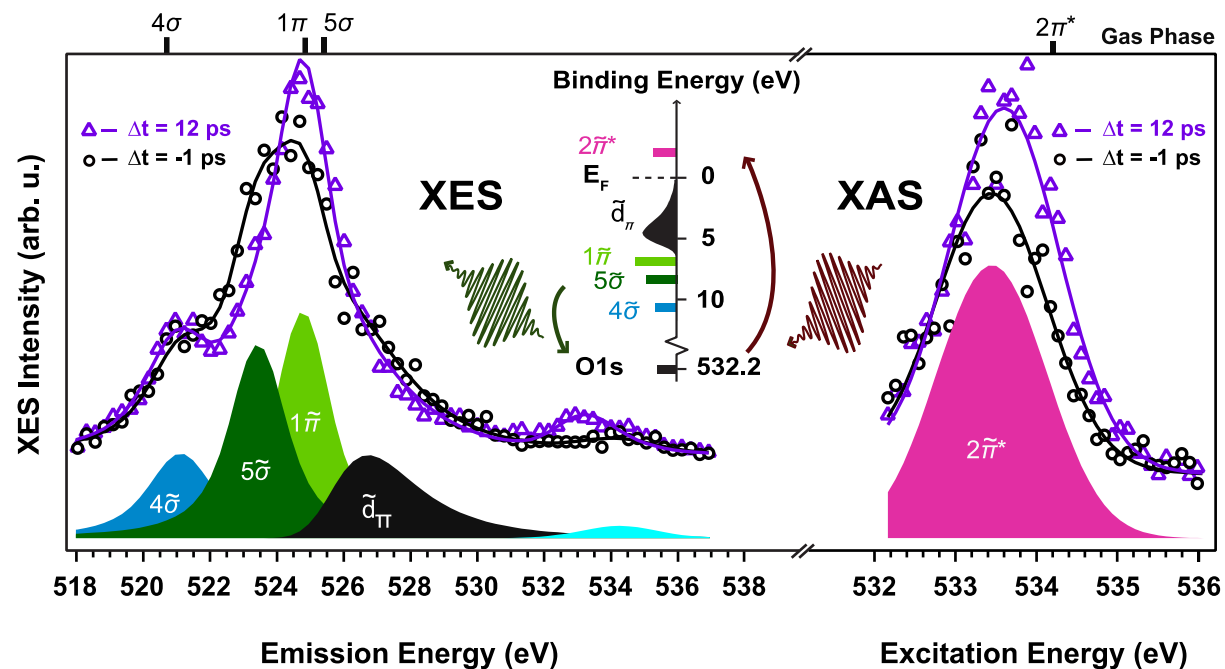


CO/Ru(0001)



A. Fohlisch et al., J. Chem Phys 121 (2004) 4848

Co desorption from Ru(0001)

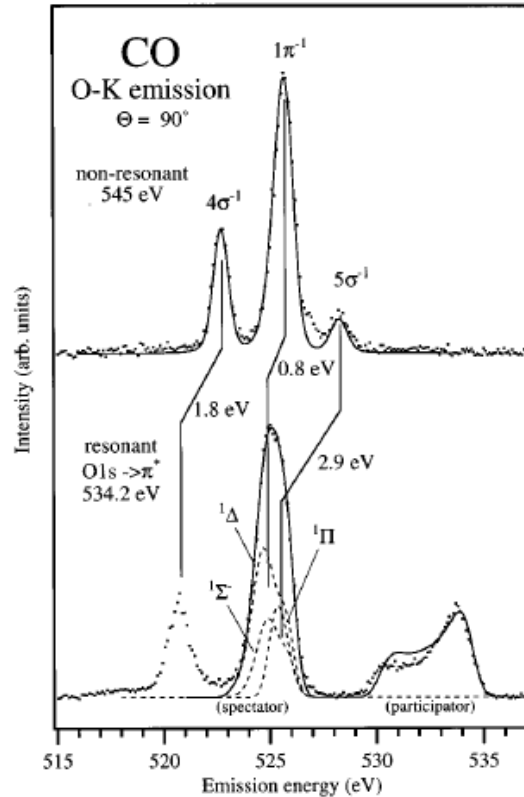


M. Dell'Angela, et al. Science 339, 1302 (2013)

Bond Weakening towards gas phase

Are the molecules in the gas phase?

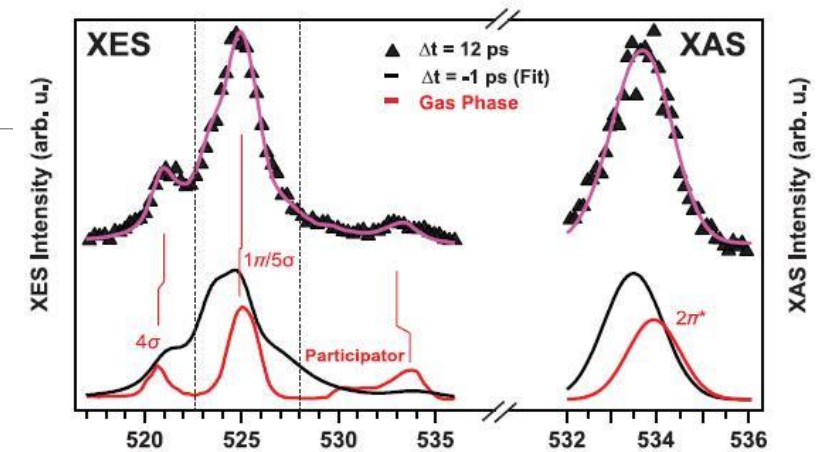
Literature



P. Skytt et al, PRA 55 (1997) 134

**Spectator shifts
due to $2\pi^*$**

Our data



**FIT = Chemisorbed + Gas Phase Resonant
70% Unpumped + 30 % “Gas phase”**

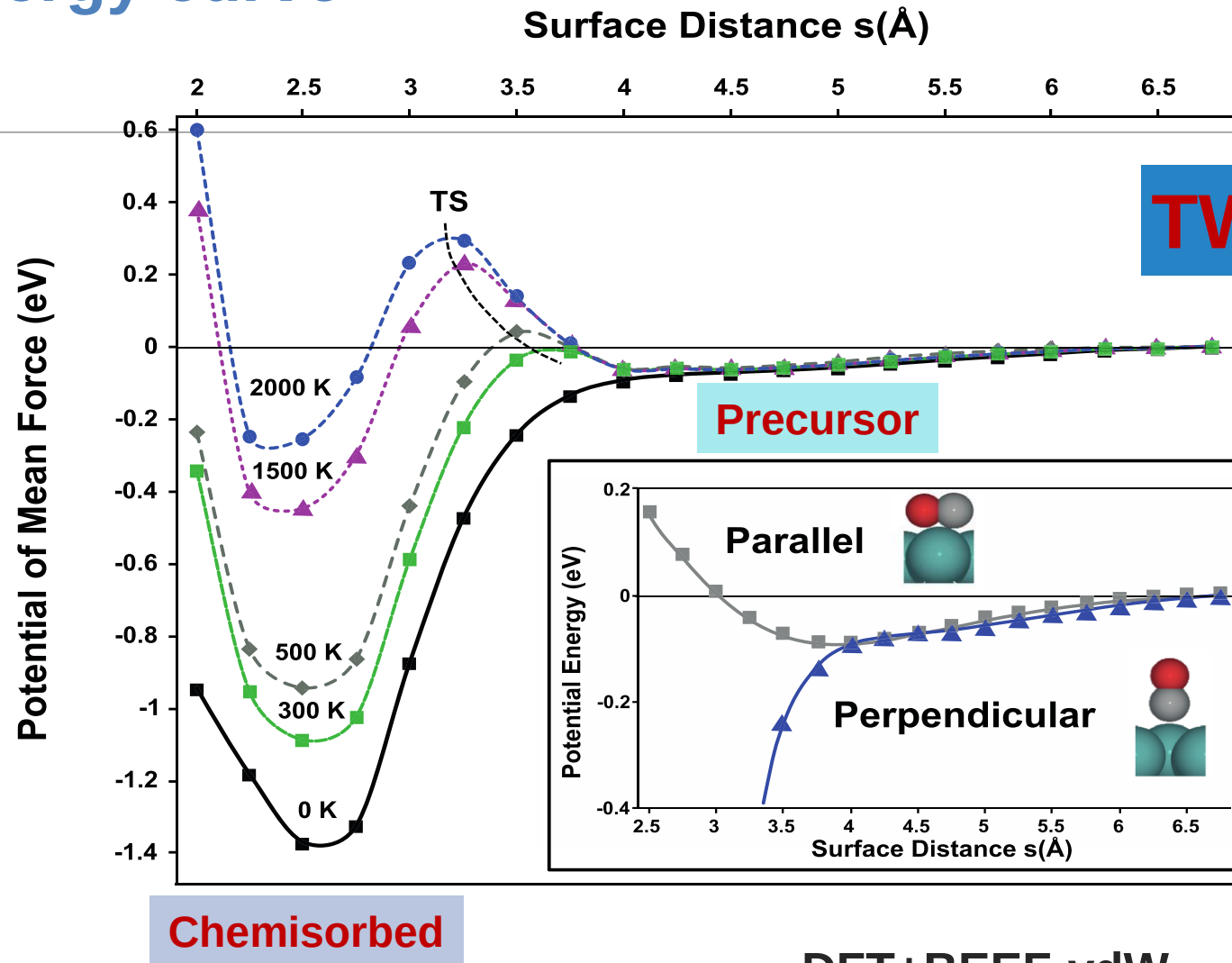
Spectator shifts: 1π 0.1eV less

4σ 0.3eV less

Participator: -0.5eV and x0.5

Not really! ...PRECURSOR?

Free-energy curve



DFT+BEEF-vdW Wellendorff L. et al PRB 85, 235149 (2012)

Conclusion II

We have been able to measure for the first time molecules in the precursor state upon desorption.

Review of FEL femtochemistry experiments:

Chemical Physics Letters 675 (2017) 145–173

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Frontiers article

Catalysis in real time using X-ray lasers



A. Nilsson^{a,*}, J. LaRue^b, H. Öberg^{a,1}, H. Ogasawara^c, M. Dell'Angela^d, M. Beye^e, H. Öström^a, J. Gladh^a, J.K. Nørskov^{f,g}, W. Wurth^{e,h}, F. Abild-Pedersen^f, L.G.M. Pettersson^a

^a Department of Physics, AlbaNova University Center, Stockholm University, SE-106 91 Stockholm, Sweden
^b Schmid College of Science and Technology, Chapman University, One University Drive, Orange, CA 92866, USA
^c SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA
^d CNR-IOM, Strada Statale 14 - km 163.5, 34149 Trieste, Italy
^e DESY Photon Science, Notkestr. 85, 22607 Hamburg, Germany
^f SUNCAT Center of Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, United States
^g SUNCAT Center of Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, 443 Via Ortega, Stanford, CA 94305, United States
^h University of Hamburg and Center for Free Electron Laser Science, Luruper Chaussee 149, D-22761 Hamburg, Germany

Ultrafast Surface Chemistry and Catalysis Collaboration

Toyli Anniyev (1)
Martin Beye (1,4)
Ryan Coffee (1)
Martina Dell'Angela (2)
Alexander Foehlich (4)
Jorgen Gladh (3)
Florian Hieke (2)
Markus Hantschmann (5)
Tetsuo Katayama (1)
Sarp Kaya (1)
Oleg Krupin (1)
Jerry LaRue (1)
Giuseppe Mercurio (2)
Ankush Mitra (1)
Stefan Moeller (1)
Andreas Moegelhoef (1)
Anders R. Nilsson (1)
May Ling Ng (1)
Dennis Nordlund (1)

Jens Norskov (1)
Henrik Oberg (3)
Hirohito Ogasawara (1)
Henrik Ostrom (3)
Frank Abild-Pedersen (1)
Lars Pettersson (3)
Mats Persson (6)
William F. Schlottter(1)
Jonas A. Sellberg (1)
Florian Sorgenfrei (2)
Joshua J. Turner (1)
Hongliang Xin (1)
Martin Wolf (5)
Wilfried Wurth (2)

(1) SLAC National Accelerator Laboratory, USA;
(2) Institut für Experimentalphysik, Universität Hamburg
and Center for Free Electron Laser, Hamburg, Germany;
(3) Department of Physics, Stockholm University,
Sweden;
(4) Methods and Instrumentation in Synchrotron
Radiation, Helmholtz-Zentrum Berlin, Berlin, Germany;
(5) Department of Physical Chemistry, Fritz-Haber-Institut,
Berlin, Germany.
(6) Surface Science Research Centre, Department of
Chemistry, University of Liverpool, United Kingdom



Outline

RIXS-hXES@ XFELs

I. Techniques

1. X-ray absorption (XAS)
2. X-ray emission (XES) / High resolution X-ray Emission (hXES)
3. Resonant Inelastic X-ray Scattering (RIXS)

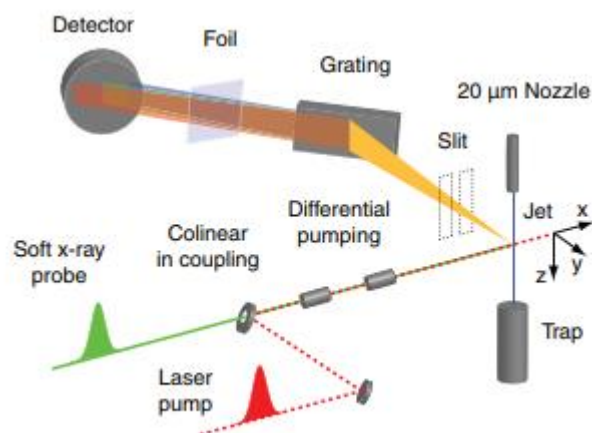
II. Instruments

III. Selected RIXS-hXES applications @ XFELs

- I. RIXS@FLASH: Phase Transitions
- II. RIXS@LCLS: Femtochemistry
- III. RIXS@LCLS: Liquids**
- IV. RIXS@SACLA: Magnetism
- V. RIXS@FERMI: dd excitations

III. RIXS@LCLS: Liquids

(next lecture by Ph. Wernet)



REVIEW OF SCIENTIFIC INSTRUMENTS **83**, 123109 (2012)



A setup for resonant inelastic soft x-ray scattering on liquids at free electron laser light sources

Kristjan Kunnus,^{1,2,a)} Ivan Rajkovic,³ Simon Schreck,^{1,2} Wilson Quevedo,^{3,b)} Sebastian Eckert,¹ Martin Beye,¹ Edlira Suljoti,¹ Christian Weniger,¹ Christian Kalus,⁴ Sebastian Grübel,^{3,c)} Mirko Scholz,³ Dennis Nordlund,⁵ Wenkai Zhang,⁶ Robert W. Hartsock,⁶ Kelly J. Gaffney,⁶ William F. Schlotter,⁷ Joshua J. Turner,⁷ Brian Kennedy,⁸ Franz Hennies,⁸ Simone Techert,^{3,9,d)} Philippe Wernet,^{1,e)} and Alexander Föhlisch^{1,2,f)}

¹Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin GmbH, Albert-Einstein-Straße 15, 12489 Berlin, Germany
²Institut für Physik und Astronomie, Universität Potsdam, Karl-Liebknecht-Straße 24/25, 14476 Potsdam, Germany
³IFG Structural Dynamics of (Bio)chemical Systems, Max Planck Institute for Biophysical Chemistry, Am Fassberg 11, 37070 Göttingen, Germany
⁴Abteilung Betrieb Beschleuniger BESSYII, Helmholtz-Zentrum Berlin GmbH, Albert-Einstein-Straße 15, 12489 Berlin, Germany
⁵Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA
⁶PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA
⁷Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA
⁸MAX-lab, PO Box 118, 221 00 Lund, Sweden
⁹Advanced Study Group of the MPG, CFEL, Notkestraße 85, 22603 Hamburg, Germany

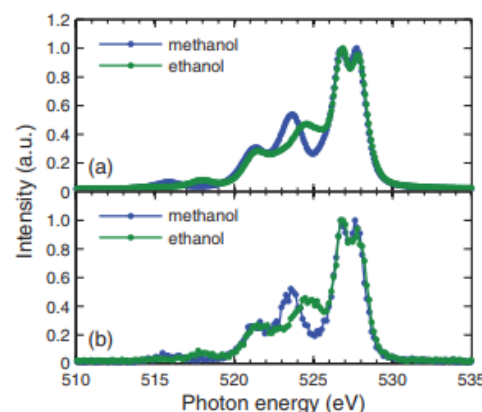


FIG. 6. Comparison of liquid methanol and ethanol RIXS spectra taken at an incident photon energy of 540 eV and measured (a) at the BESSYII U41-PGM beamline and (b) at the LCLS SXR beamline. For details on the experimental parameters see Table II.

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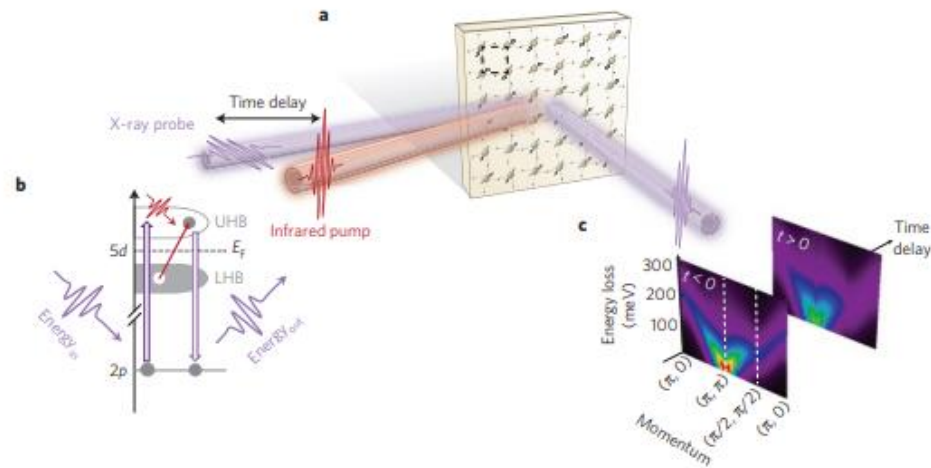
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- II. RIXS@LCLS: Femtochemistry
- III. RIXS@LCLS: Liquids
- IV. RIXS@SACLA: Magnetism**
- V. RIXS@FERMI: dd excitations

Tr-RIXS on Sr_2IrO_4

Strongly correlated system



nature
materials

LETTERS

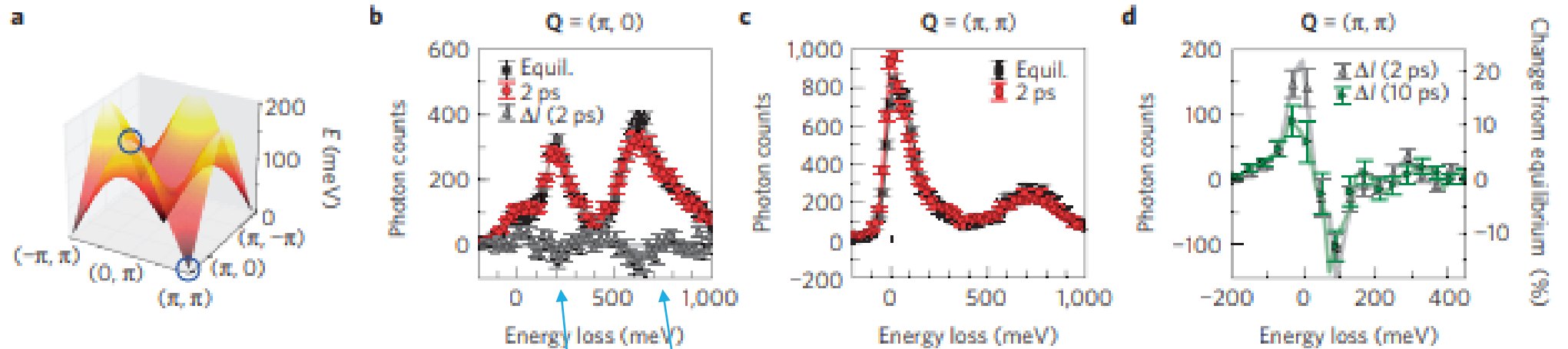
PUBLISHED ONLINE: 9 MAY 2016 | DOI: 10.1038/NMAT4641

Ultrafast energy- and momentum-resolved dynamics of magnetic correlations in the photo-doped Mott insulator Sr_2IrO_4

M. P. M. Dean^{1*}, Y. Cao^{1*}, X. Liu^{2,3*}, S. Wall⁴, D. Zhu⁵, R. Mankowsky^{6,7}, V. Thampy¹, X. M. Chen¹, J. G. Vale⁸, D. Casa⁹, Jungho Kim⁹, A. H. Said⁹, P. Juhas¹, R. Alonso-Mori⁵, J. M. Glownia⁵, A. Robert⁵, J. Robinson⁵, M. Sikorski⁵, S. Song⁵, M. Kozina⁵, H. Lemke⁵, L. Patthey¹⁰, S. Owada¹¹, T. Katayama¹², M. Yabashi¹¹, Yoshikazu Tanaka¹¹, T. Togashi¹², J. Liu¹³, C. Rayan Serrao¹⁴, B. J. Kim¹⁵, L. Huber¹⁶, C.-L. Chang¹⁷, D. F. McMorrow⁸, M. Först^{6,7} and J. P. Hill¹

$$h\nu = 11.22 \text{ keV (L}_3 \text{ Ir)}$$

Tr-RIXS on Sr_2IO_4

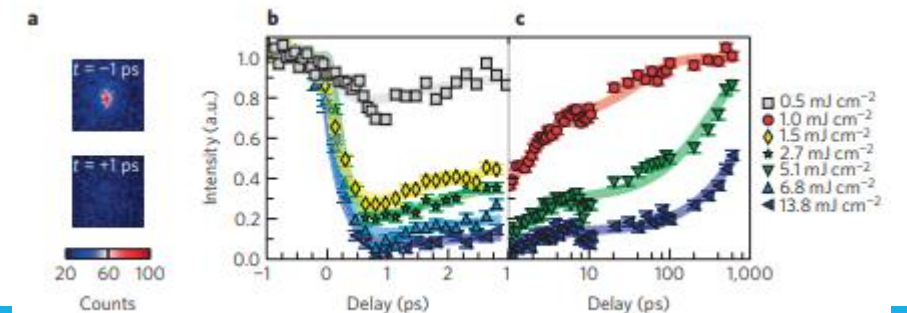


Magnons or spin waves

magnetic

orbital

Bragg peak



Outline

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- III. RIXS@LCLS: Liquids
- IV. RIXS@SACLA: Magnetism
- V. RIXS@FERMI: dd excitations

V. RIXS@FERMI: dd excitations

Photon Beam Parameters	FEL-1 *	FEL-2 *
Photon Energy (eV)	12.4-65	65-310
Average pulse energy [μ J]	200-25 **	100-10 **
Pulse duration [fs] (FWHM)	100-50	60-20
Peak power [GW]	3-0.4	2.5-0.4
Repetition rate [Hz]	10-50	10-50
FEL mode	SEEDED, TEM_00	SEEDED, TEM_00
Photon energy fluctuations [meV][rms]	1-2	4-15
FEL bandwidth $\Delta E/E$ [rms]	2.5-5 ($\times 10^{\text{sup-4}}$)	2-7 ($\times 10^{\text{sup-4}}$)
FEL bandwidth fluctuations [%][rms]	3-5	3-40
Polarization	Linear Horizontal Linear Vertical Circular Left Circular Right	Linear Horizontal Linear Vertical Circular Left Circular Right

FERMI (Elettra Sincrotrone Trieste)

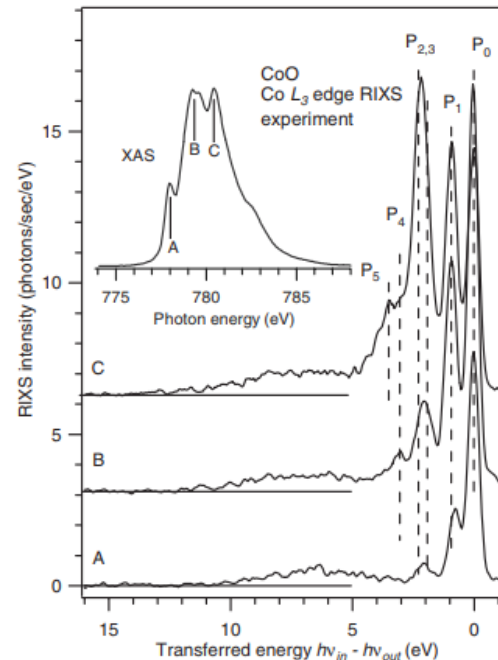
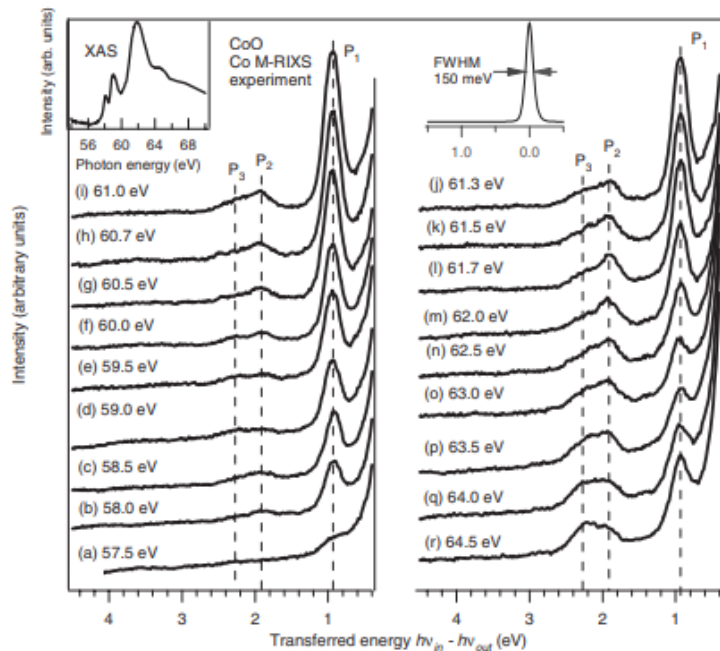


FERMI = $M_{2,3}$ Edges of Cu, Ni, Co

M-edge vs L-edge

Energy
Resolving Power

50 eV -100 eV	500 eV -1 keV
100 eV/10 meV = 10^4	1 keV/ 10 meV = 10^5



PHYSICAL REVIEW B 78, 245102 (2008)

Combining *M*- and *L*-edge resonant inelastic x-ray scattering for studies of 3d transition metal compounds

S. G. Chiuzbăian,^{1,*} T. Schmitt,² M. Matsubara,³ A. Kotani,^{4,5} G. Ghiringhelli,⁶ C. Dallera,⁷ A. Tagliaferri,⁸ L. Braicovich,⁸ V. Scagnoli,⁹ N. B. Brookes,⁹ U. Staub,² and L. Patthey²

¹Laboratoire de Chimie Physique-Matière et Rayonnement, UPMC Université Paris 06, CNRS UMR 7614, 75005 Paris, France

²Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

³Laboratoire des Colloïdes, Verres et Nanomatériaux (UMR 5587), Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

⁴RIKEN/Spring8, 1-1-1 Kouto, Sayo, Hyogo 679-5148, Japan

⁵Photon Factory, IMSS, High Energy Accelerator Research Organization, 1-1 Oho Tsukuba, Ibaragi 305-0801, Japan

⁶Dipartimento di Fisica, CNR/INFN Coherentia and SOFT, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

⁷Dipartimento di Fisica, CNR/INFN ULTRAS, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

⁸Dipartimento di Fisica, CNR/INFN SOFT, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

⁹European Synchrotron Radiation Facility, BP 220, 38043 Grenoble Cedex, France

(Received 15 July 2008; revised manuscript received 16 October 2008; published 2 December 2008)

Small machine
Larger throughput
but
Strong elastic peak
More branching

M-edge RIXS

Nordgren Spectrometer @ SLS

meV Resolution Soft X-Ray Inelastic Scattering Beamline (MERLIN)

Specifications:

- > Resolving power: $E/\Delta E = 100,000$ with $5\mu\text{m}$ slits
I.e. better than 1 meV when photon energy is below 100eV
- > Photon energy range: 15eV to 100eV, fully optimized
maximum achievable photon energy ~140eV
- > Elliptically Polarized Undulator (EPU): full polarization selection (linear and/or circular)
- > Photon Flux: $\sim 5 \times 10^{11}$ photons/s/meV

Optical Layout (SGM)

✓ Ultra High Resolution & High Resolution Modes
✓ Asymmetric Undulator to suppress higher orders

LAWRENCE BERKELEY NATIONAL LABORATORY

Z. Hussain, CORPES 07

PRL 95, 197402 (2005)

PHYSICAL REVIEW LETTERS

week ending
4 NOVEMBER 2005

Localized Electronic Excitations in NiO Studied with Resonant Inelastic X-Ray Scattering at the Ni M Threshold: Evidence of Spin Flip

S. G. Chiuzbăian,^{1,*} G. Ghiringhelli,² C. Dallera,² M. Grioni,³ P. Amann,^{1,†} X. Wang,³ L. Braicovich,² and L. Patthey¹

¹Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

²INFN-Dipartimento di Fisica, Politecnico di Milano, p. Leonardo da Vinci 32, 20133 Milano, Italy

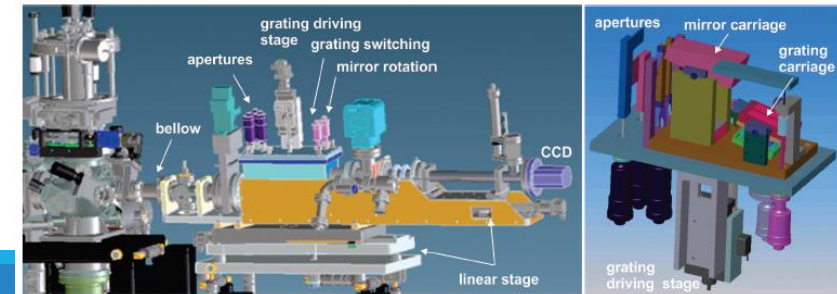
³IPN, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

(Received 24 February 2005; published 31 October 2005)

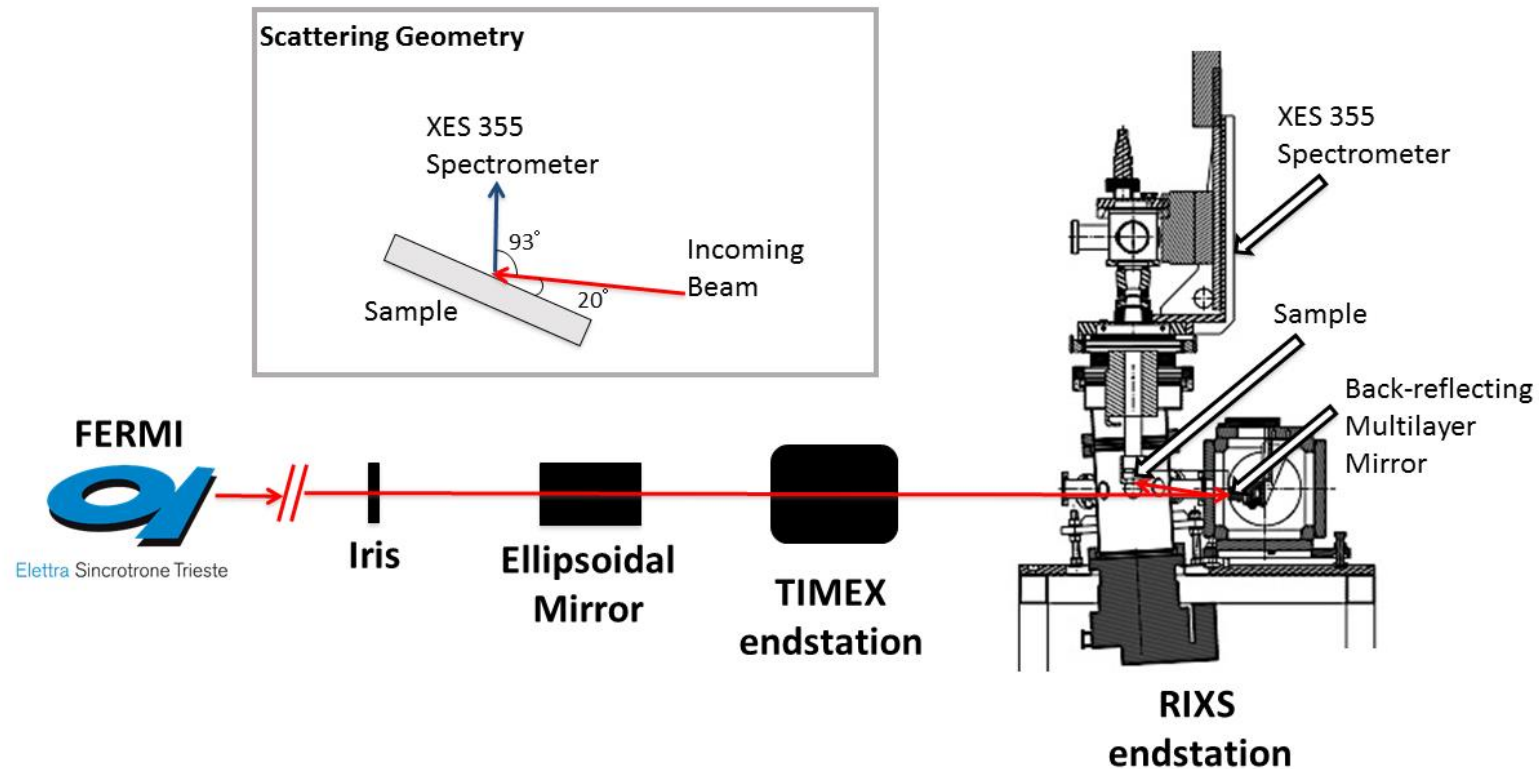
We studied the neutral electronic excitations of NiO localized at the Ni sites by measuring the resonant inelastic x-ray scattering (RIXS) spectra at the Ni $M_{2,3}$ edges. The good energy resolution allows an unambiguous identification of several spectral features due to dd excitations. The dependence of the RIXS spectra on the excitation energy gives evidence of local spin flip and yields a value of 125 ± 15 meV for the antiferromagnetic exchange interaction. Accurate crystal field parameters are also obtained.

MERIXS/MERLIN @ ALS (Worldwide Record)

Y.D. Chuang, *Synchrotron Radiation News*, 25 (4), 22 (2012)



Set-up for RIXS @FERMI



First experiment: KCoF_3

MERIXS Beamline @ALS

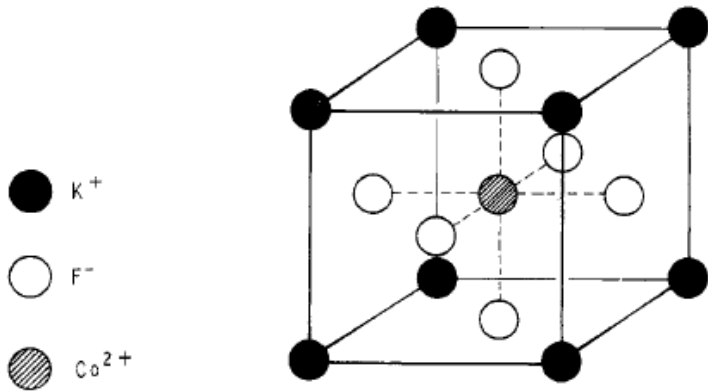
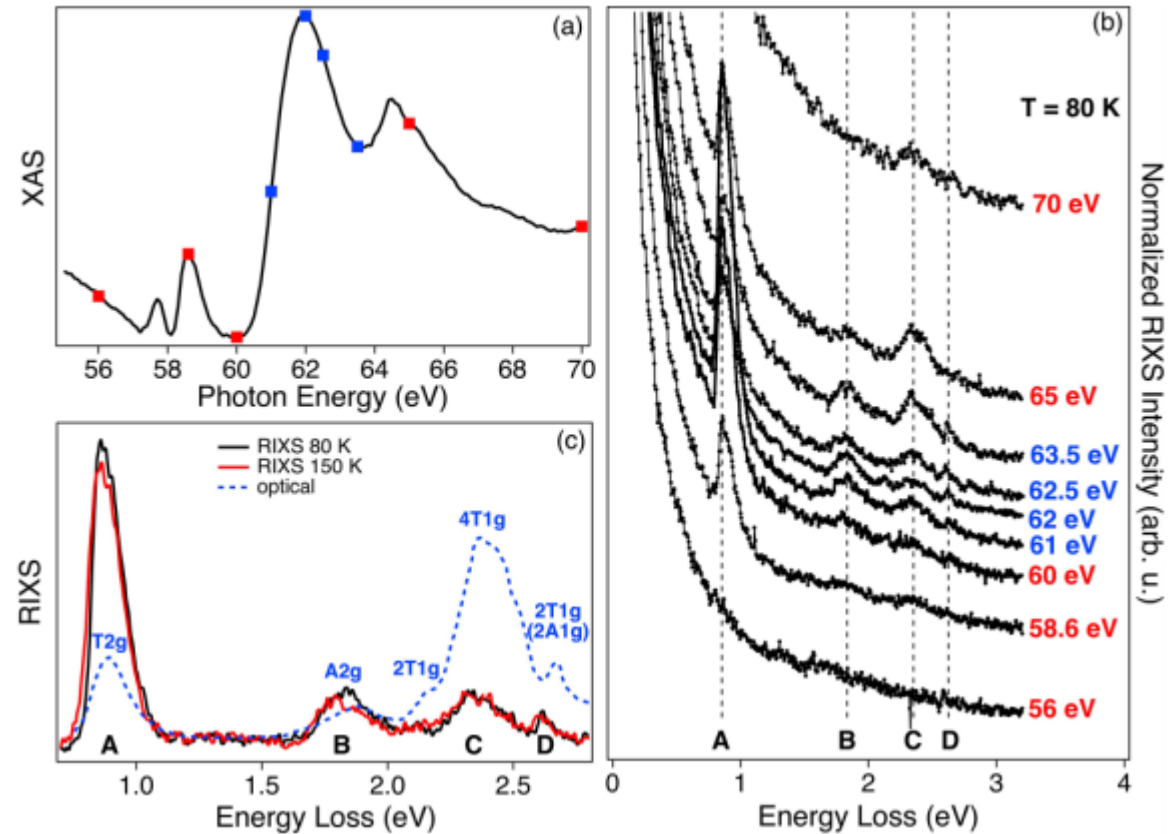


Figure 1. The crystal structure of KCoF_3 .

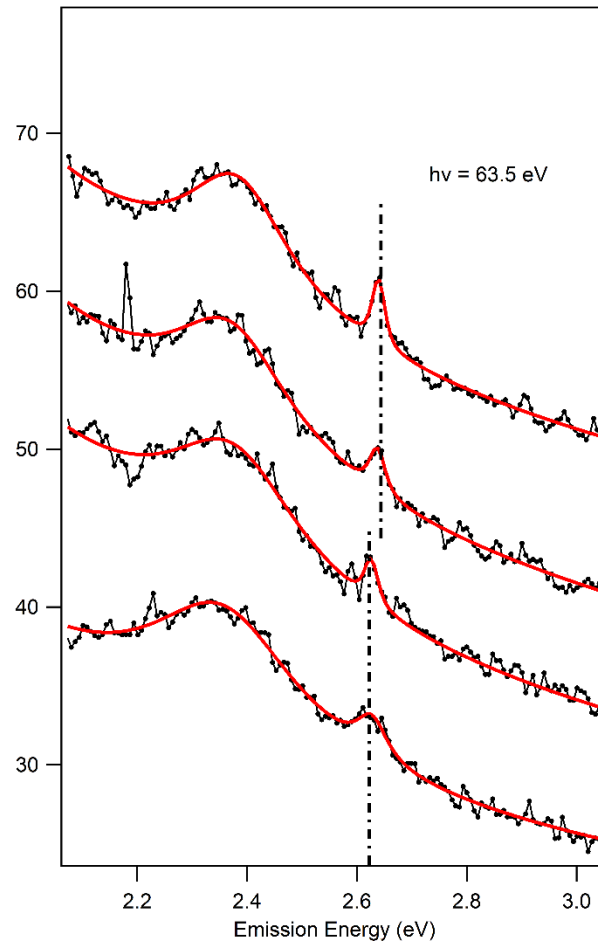
-Perovskite

-114K Neel Temperature
(small tetragonal distortion)



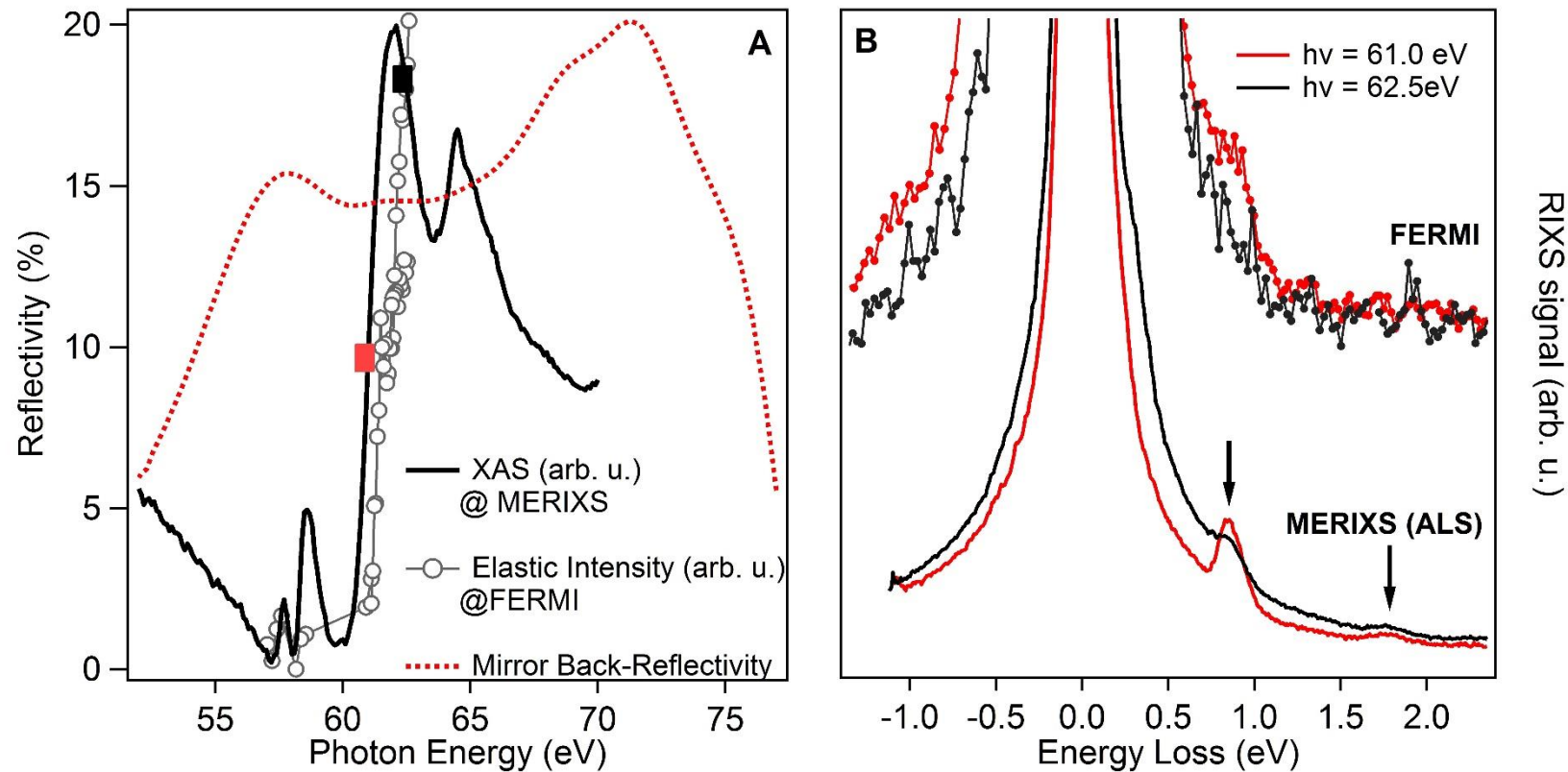
A. Caretta et al., PRB 96, 184420 (2017)

KCoF₃ M-edge RIXS



The onset of magnetic ordering, which quenches the spin-flip excitation channel, affects the overall energy of dd excitations.

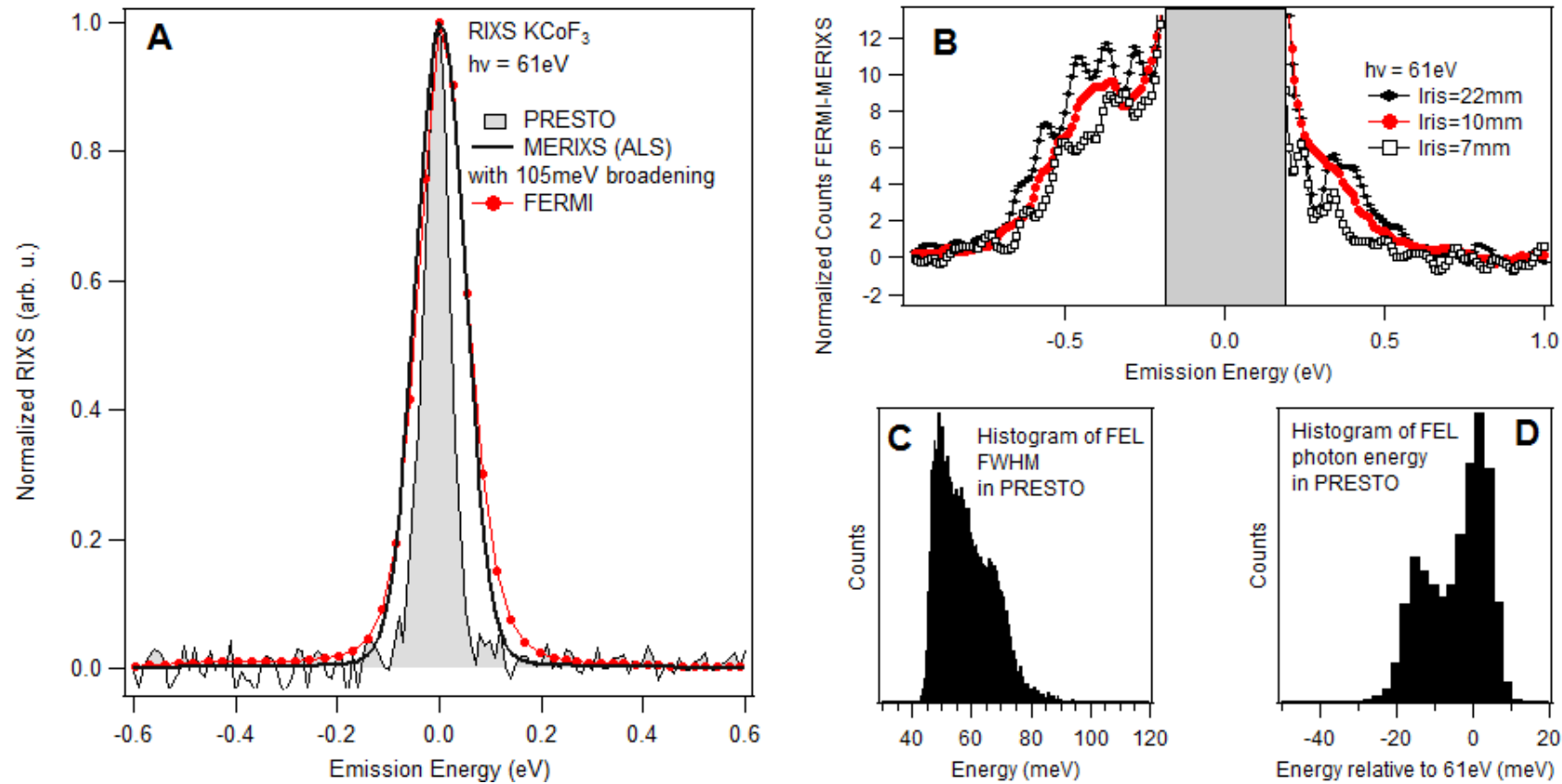
High resolution RIXS at FERMI: KCoF_3



NEXAFS is feasible

RIXS is also feasible

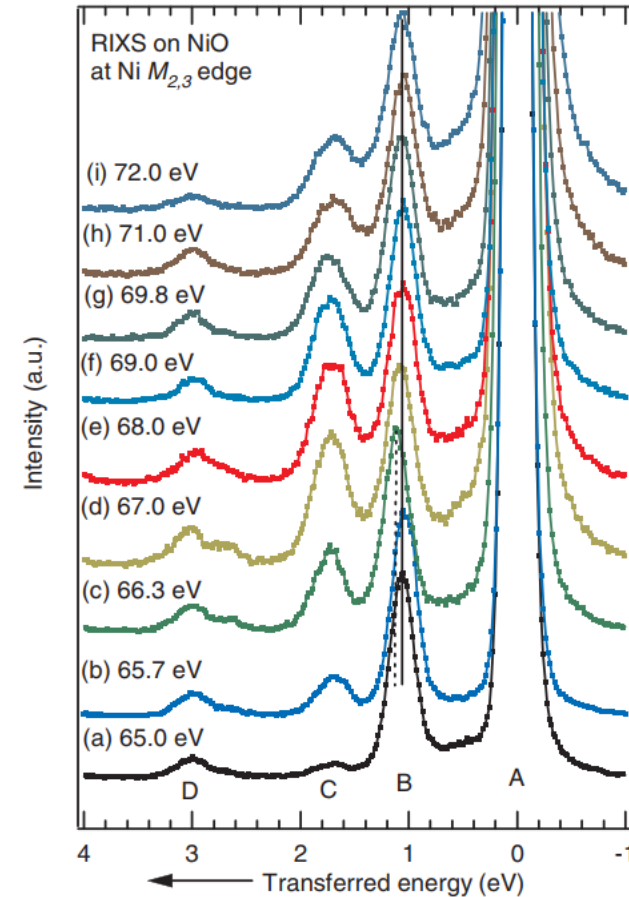
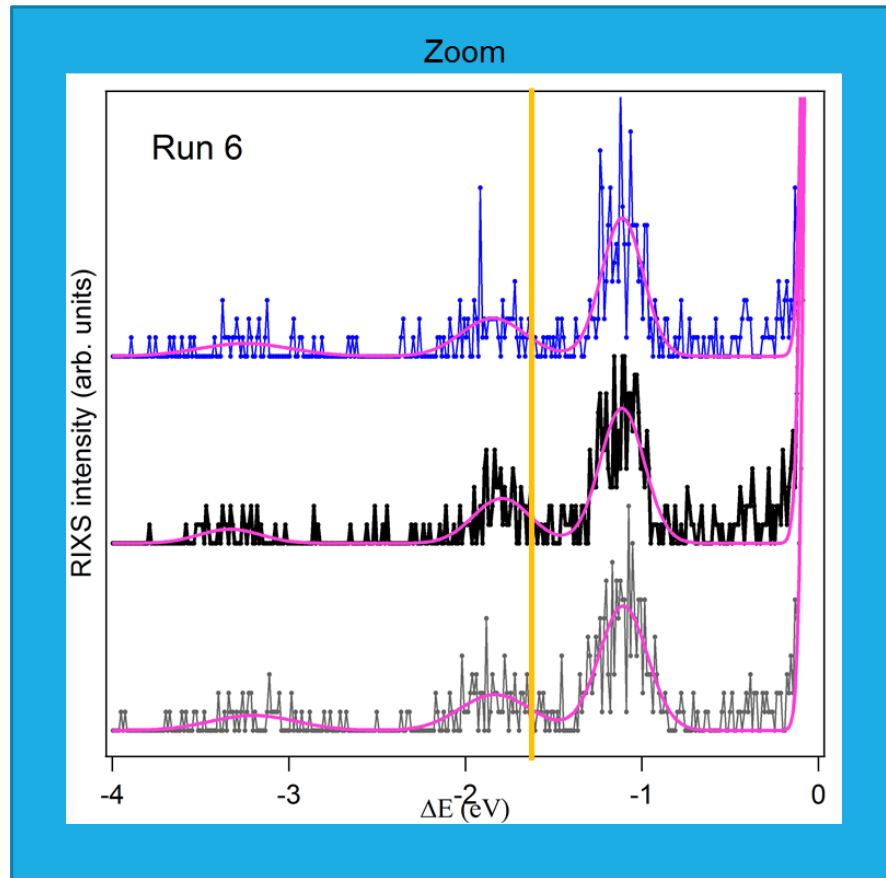
High resolution RIXS at FERMI: KCoF_3



Resolution is
not limited by FERMI

NiO: FEL vs Synchrotron

S. G. Chiuzaian et al. PRL 95, 197402 (2005)

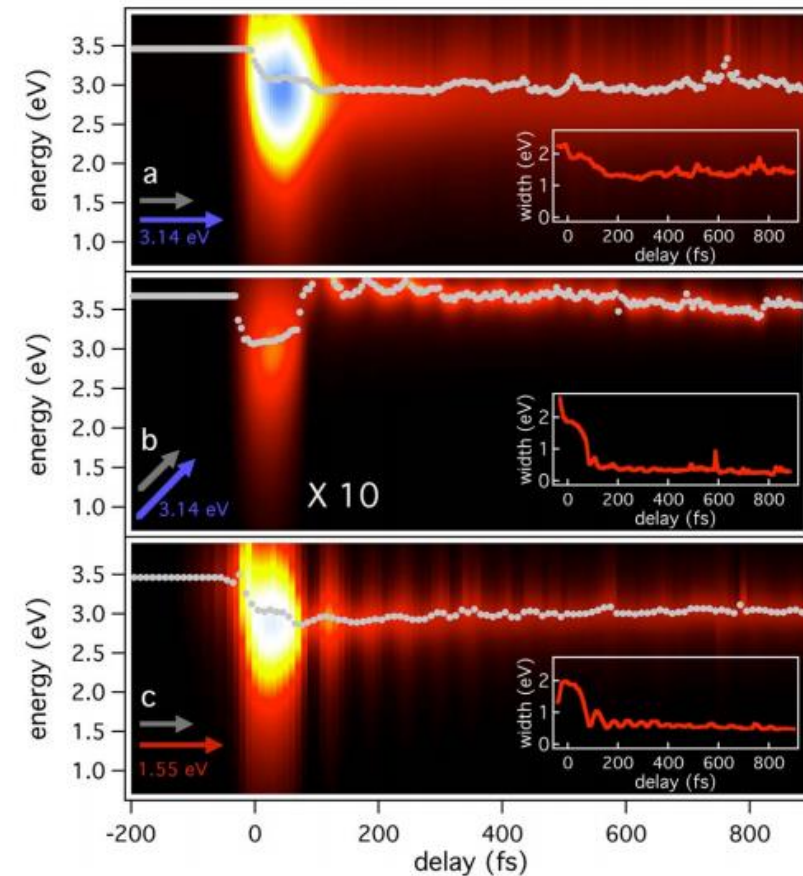
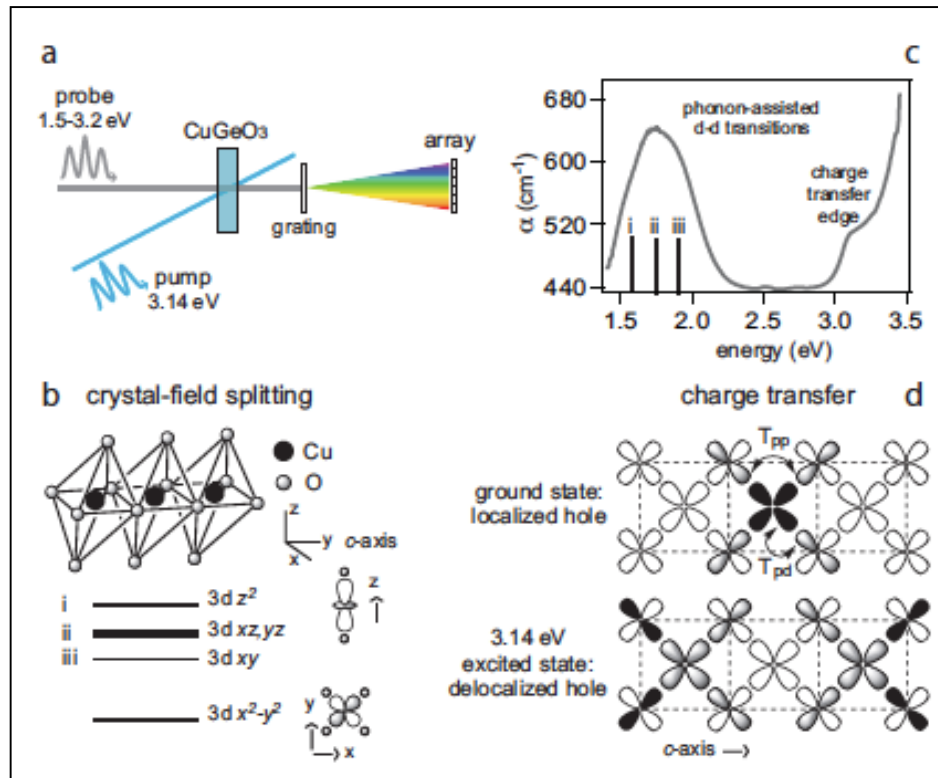


Collaboration with

G. Ghiringhelli
A. Scherz
J. Schlappa

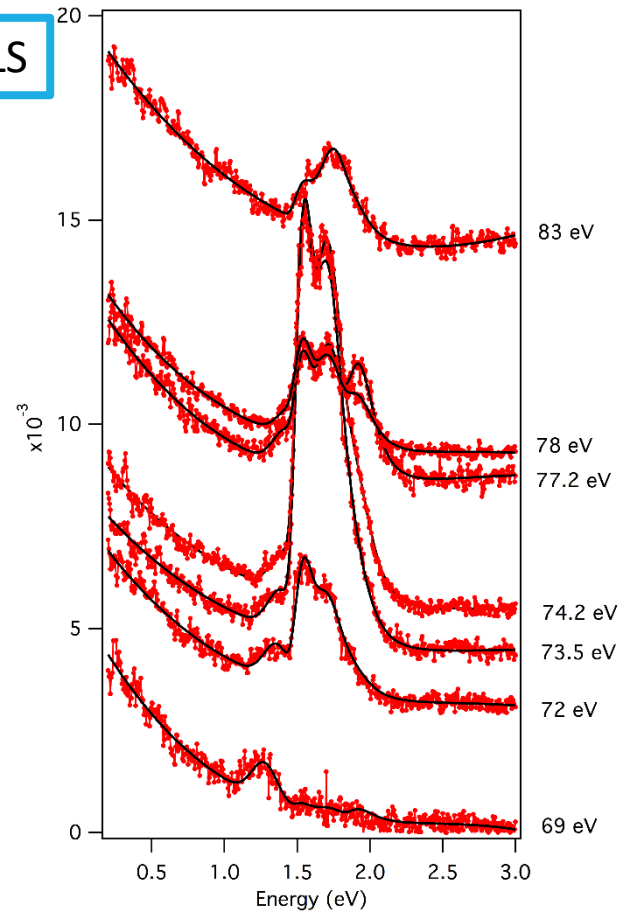
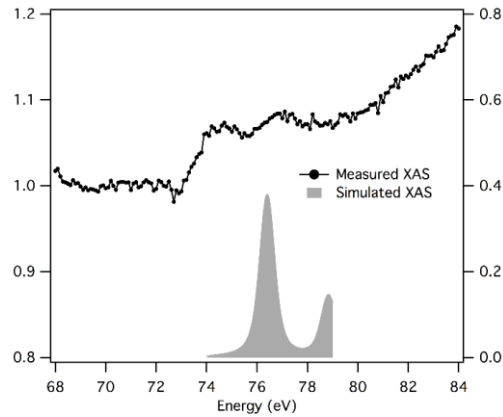
Time resolved reflectivity of CuGeO_3

Giannetti et al. PRB 80 (2009) 235129

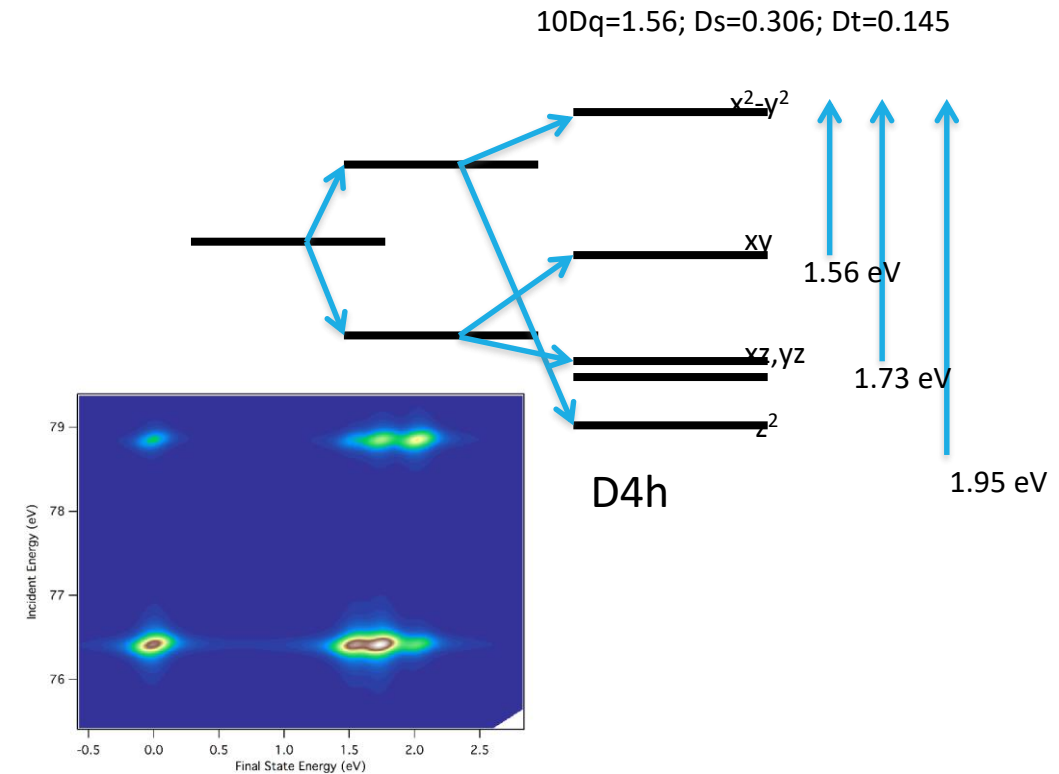


High resolution RIXS on CuGeO_3

MERIXS Beamline @ALS



CTM4XAS, CTM4RIXS (only crystal field, no CT)



Unpublished data

High resolution RIXS on CuGeO₃

De Graaf, Broer PRB 62 (2000) 705

TABLE III. CASPT2 energies (in eV) of the $d-d$ transitions in a series of cuprates compared to available experimental data. The different $3d^9$ states are characterized by the character of the singly occupied orbital, i.e., the hole character.

	Hole character						
	x^2-y^2	z^2	xy	xz	yz	xy (expt)	xz, yz (expt)
CuO	0.00	0.00	1.02	1.02	1.02		
La ₂ CuO ₄	0.00	0.99	1.29	1.57	1.57	1.4, 1.7	1.6
CuGeO ₃	0.00	1.75	1.41	1.70	1.70	1.3, 2.9	1.7
Sr ₂ CuO ₂ Cl ₂	0.00	1.18	1.23	1.50	1.50	1.4	1.7
YBa ₂ Cu ₃ O ₆	0.00	1.69	1.21	1.61	1.61	1.5	
Ca ₂ CuO ₃	0.00	2.15	1.10	1.65	1.54		
Sr ₂ CuO ₃	0.00	2.11	1.08	1.67	1.53		

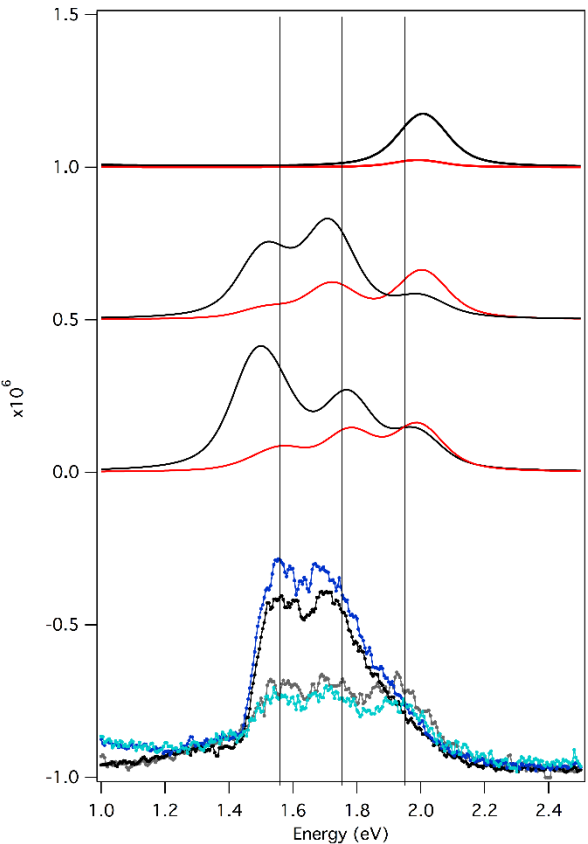
x^2-y^2
 xy
 xz,yz
 z^2

PHYSICAL REVIEW B 84, 235125 (2011)

TABLE II. CASSCF/MRCI $d-d$ excitation energies for edge-sharing chains of CuO₄ plaquettes (eV). The MRCI values include Davidson corrections.³⁵ The y axis is parallel to the CuO₂ chains, z is perpendicular onto the CuO₄ plaquettes, see text.

Hole orbital	LiVCuO ₄	CuGeO ₃	LiCu ₂ O ₂	Li ₂ CuO ₂
xy	0	0	0	0
x^2-y^2	1.08/1.28	1.19/1.41	1.13/1.43	1.20/1.52
xz	1.25/1.47	1.42/1.61	1.58/1.88	1.72/2.04
yz	1.29/1.52	1.45/1.64	1.64/1.94	1.72/2.04
z^2	0.98/1.18	1.50/1.71	1.67/1.98	1.93/2.30

xy
 x^2-y^2
 xz,yz
 z^2

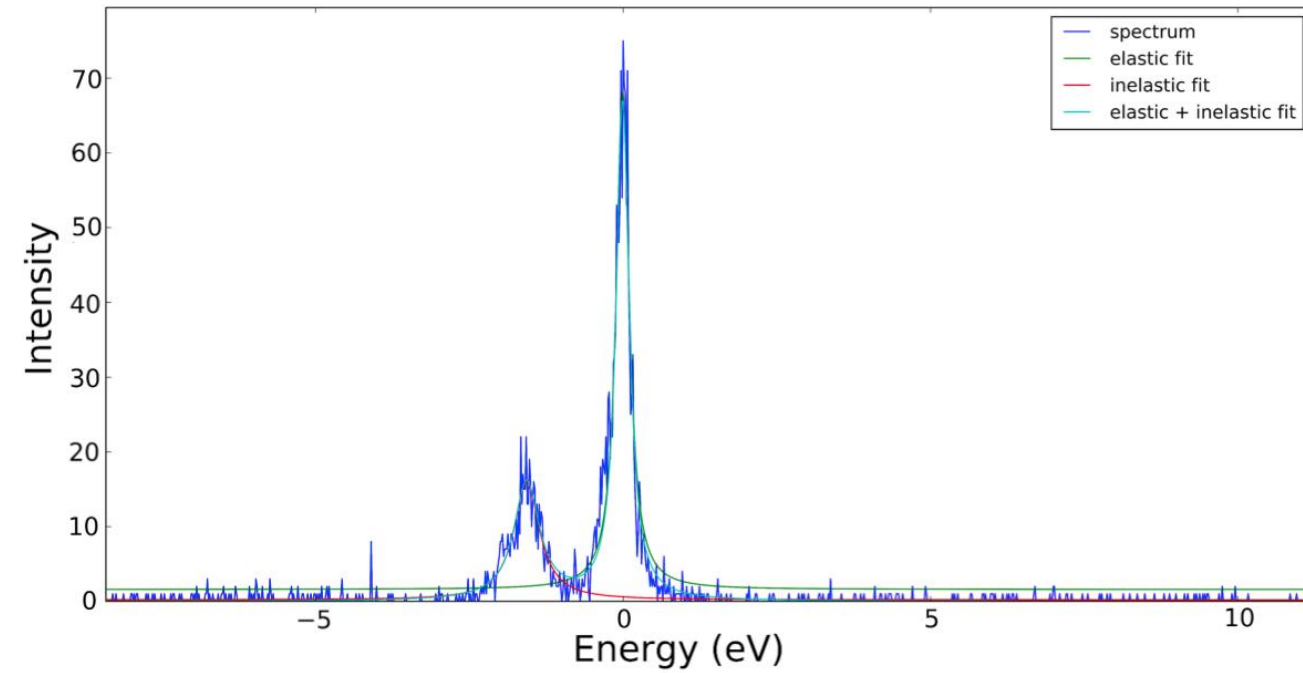


x^2-y^2
 xy
 z^2
 xz,yz

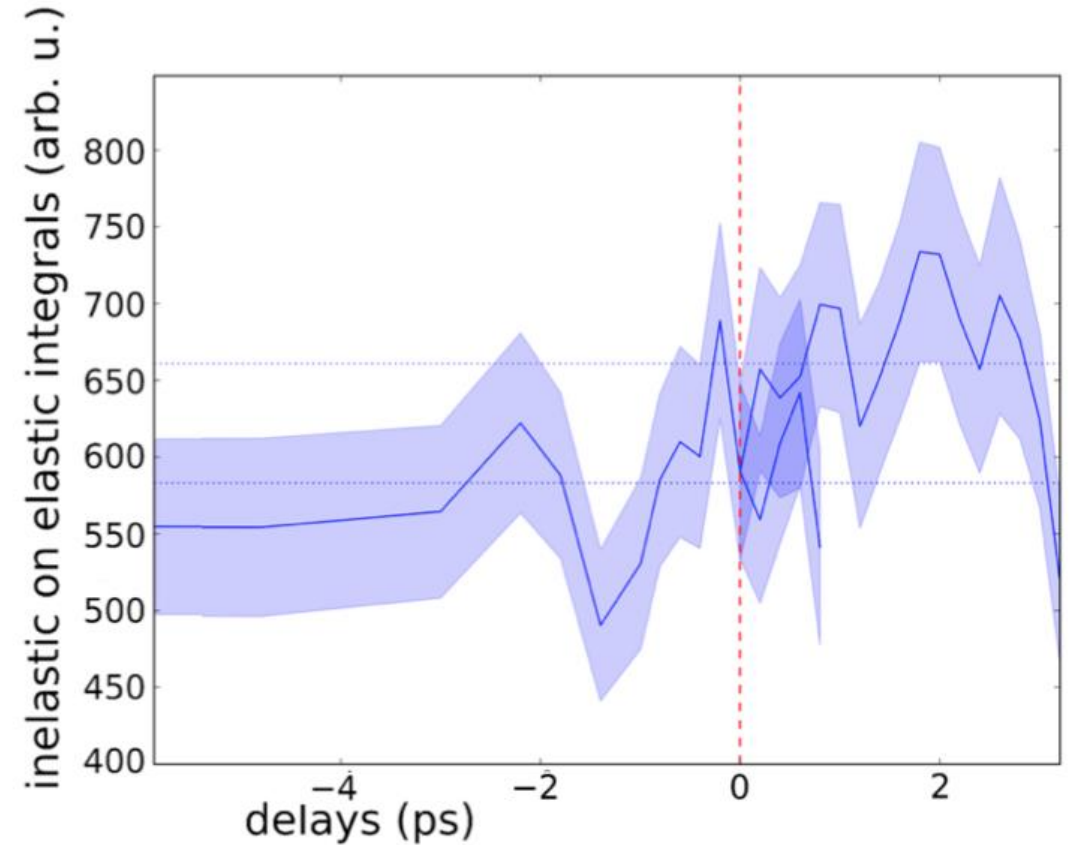
Giannetti et al. PRB 80 (2009) 235129

Unpublished data

Pump Probe M-edge RIXS of CuGeO_3



We observe dynamics in dd transitions !



Unpublished data

Conclusions IV

We measured high resolution M-edge RIXS spectra at FERMI

We measured a femtosecond dynamics in the dd-transitions in a pump-probe RIXS experiment

Acknowledgments RIXS@FERMI

RIXS@TIMEX:

Fulvio Parmigiani

Marco Malvestuto

Antonio Caretta

Luca Sturari

Wilfried Wurth (CFEL/DESY)

Florian Hieke

Sasa Bait

TIMEX staff:

Emiliano Principi

Riccardo Mincigrucci

Laura Foglia

Alberto Simoncig

Measurements @ ALS:

Yi De Chuang

Lewis A. Wray (NYU)

NiO measurements

Giacomo Ghiringhelli (PoliMi)

Andreas Scherz (XFEL)

Justine Schlappa