Ultrafast X-ray tools to look deep into materials

Jens Uhlig
Chemical Physics Lund University

NIST
National Institute of Standards and Technology Quantum Devices Group

DTU

LINXS

NanoLund
AT THE FOREFRONT OF NANOSCIENCE

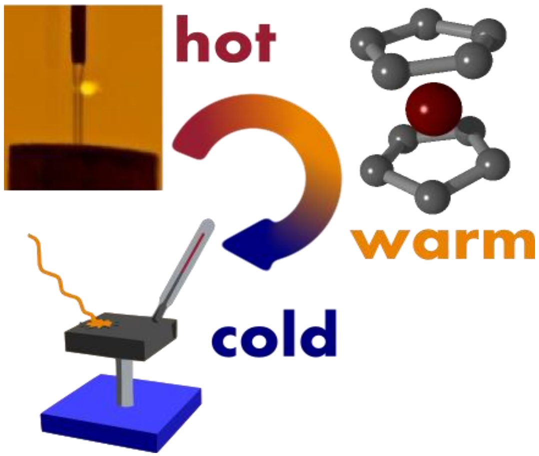
Lund Laser Centre

LCLS
SLAC NATIONAL ACCELERATOR LABORATORY
Argonne NATIONAL LABORATORY
MAX IV
eli beamlines
ESRF

The flow

1. The science of molecules, answering the simple, but important questions
    1. Charge transfer states and why they matter
    2. Our work on Iron
2. X-ray spectroscopy introduction
3. X-ray interactions overview
4. XPS
5. Scattering, Crystal and diffuse
6. X-ray absorption, general approach and information
    1. How to measure XAS at Facilities
    2. What information is in XANES?
    3. What information is in EXAFS?
7. X-ray emission spectroscopy
    1. What information is in XES?
    2. How to Measure XES in general.
    3. Detection technology.
8. The journey into ultrafast.

My background



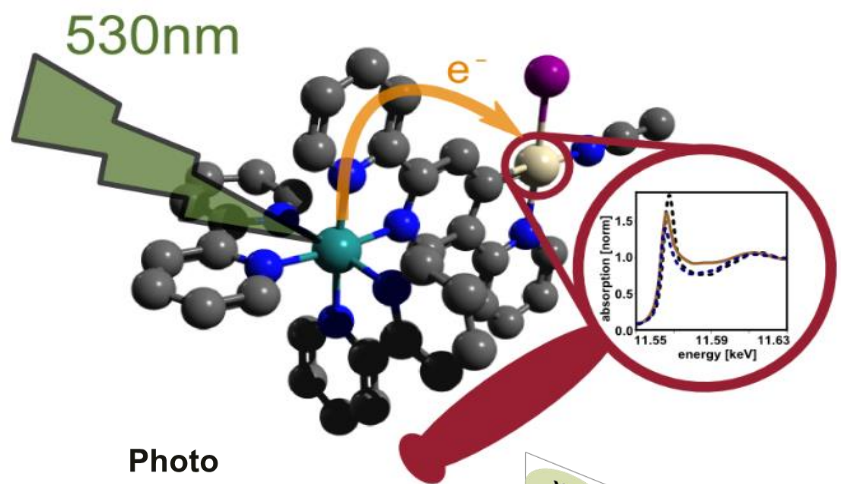
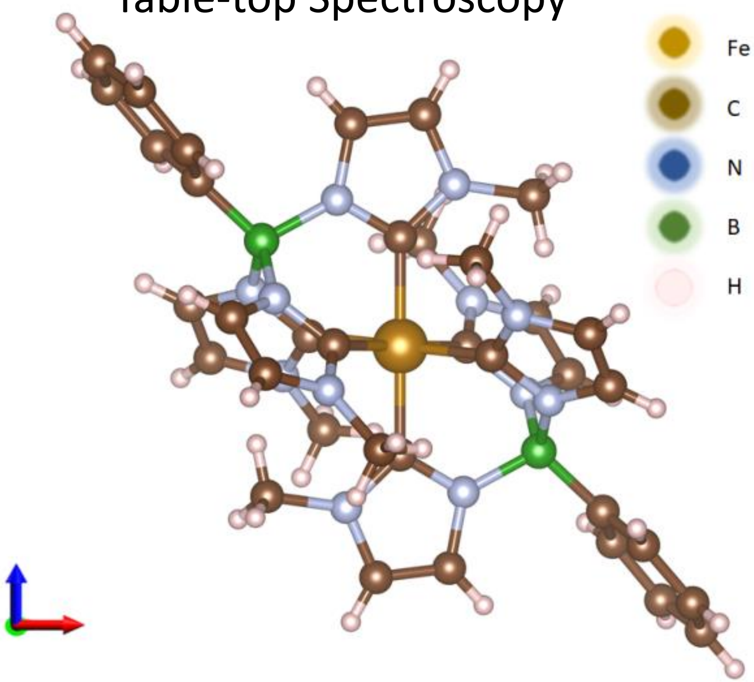
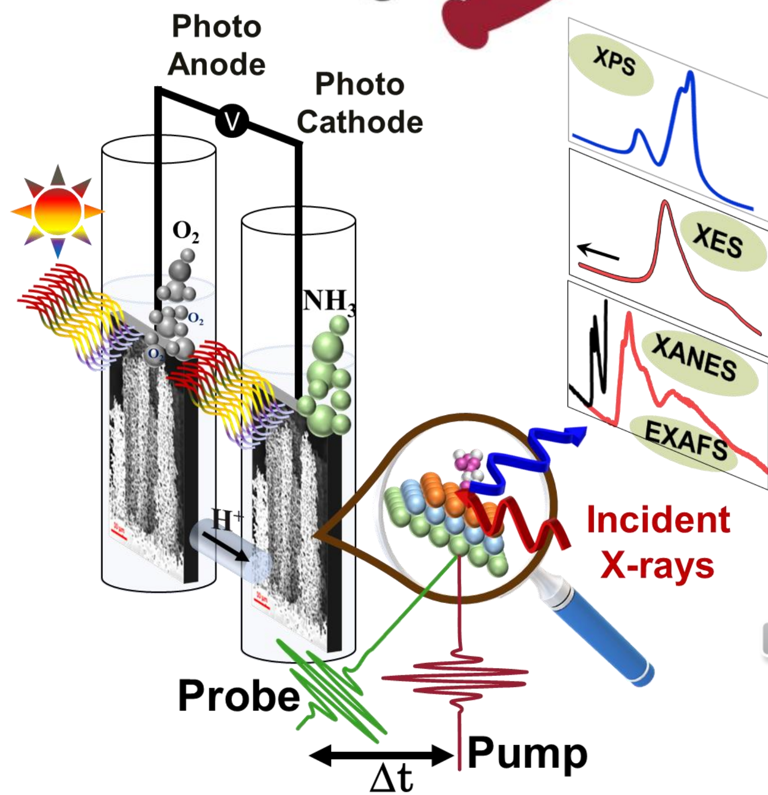


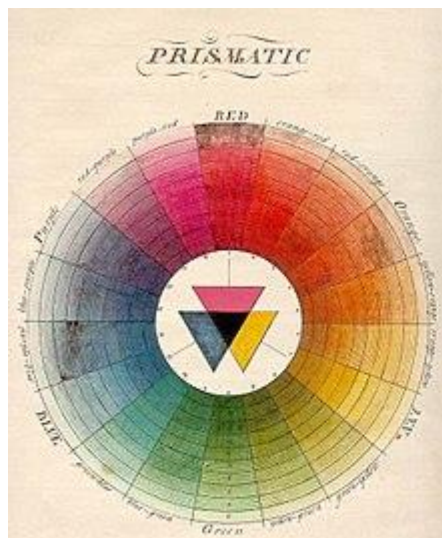
Table-top Spectroscopy





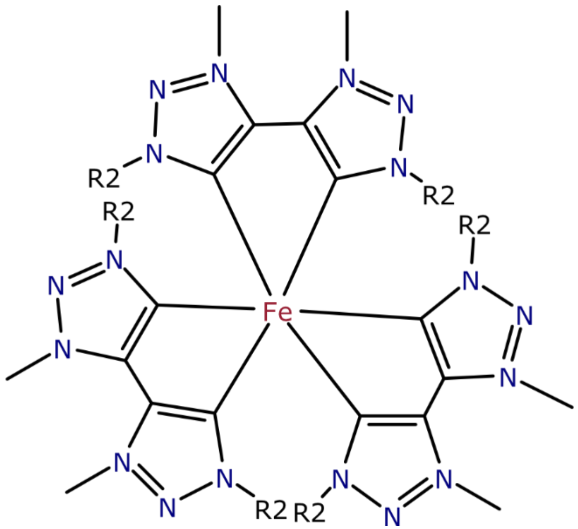
Transition metals Absorption

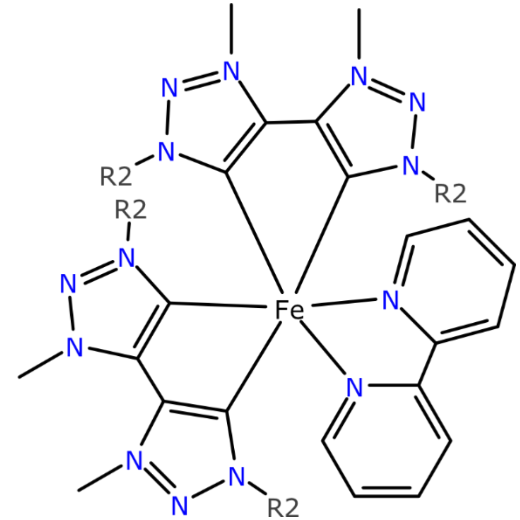
https://staff.buffalostate.edu
/nazareay/che112/ex9.htm

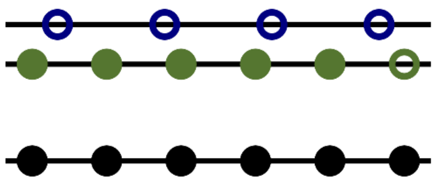


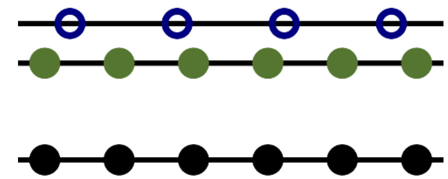
Moses Harris 1776

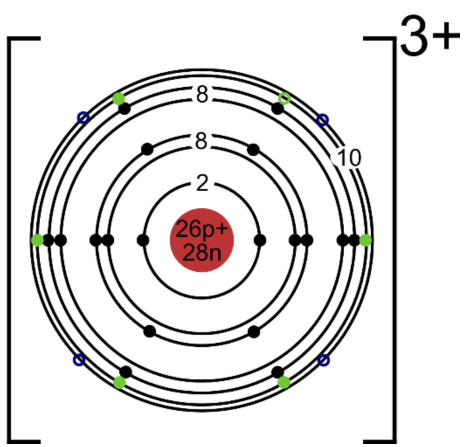
Made complexes

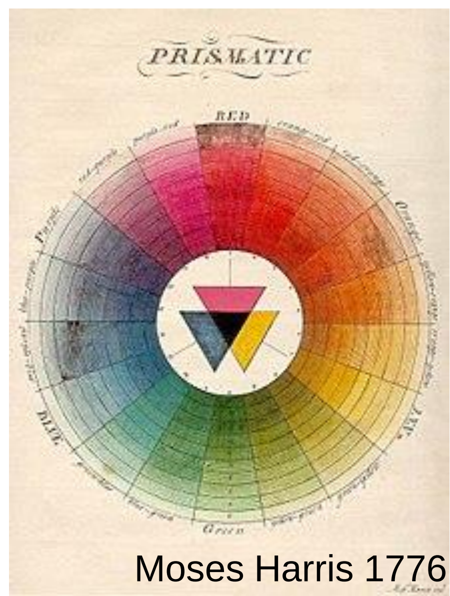


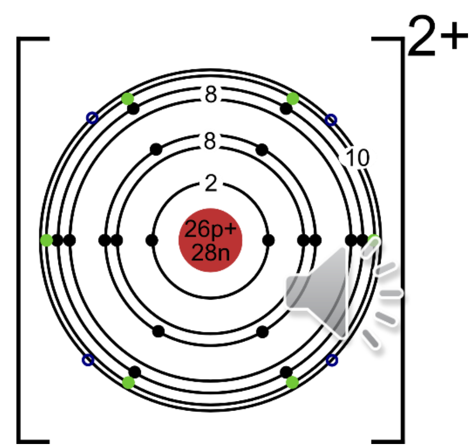




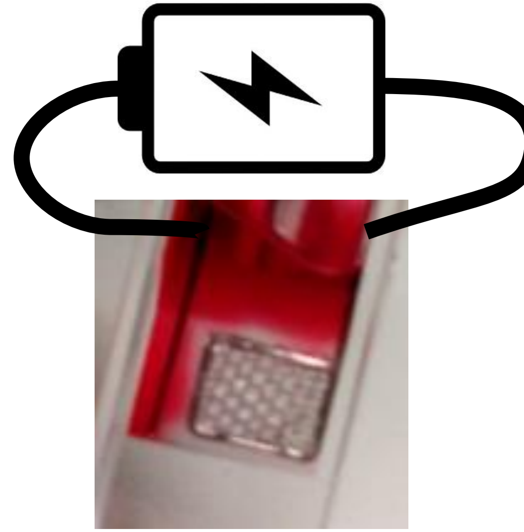


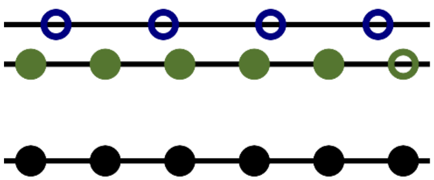


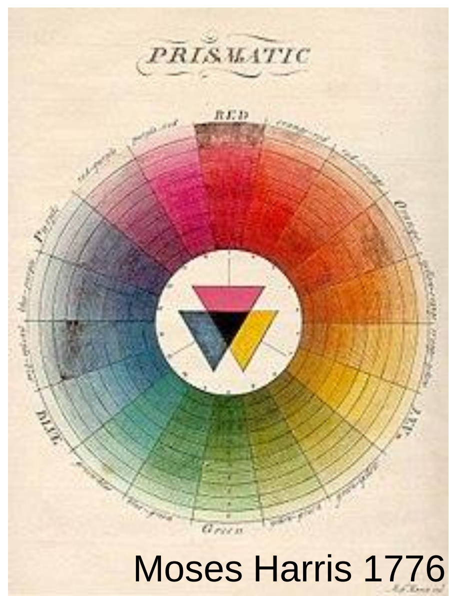


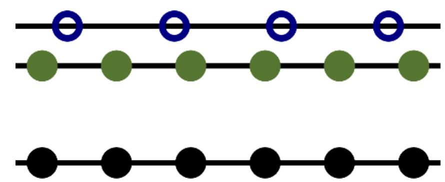


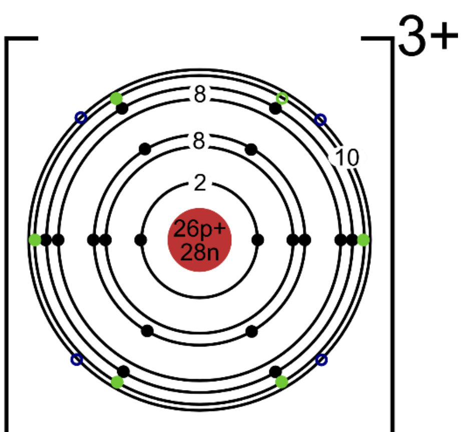
Absorption in iron

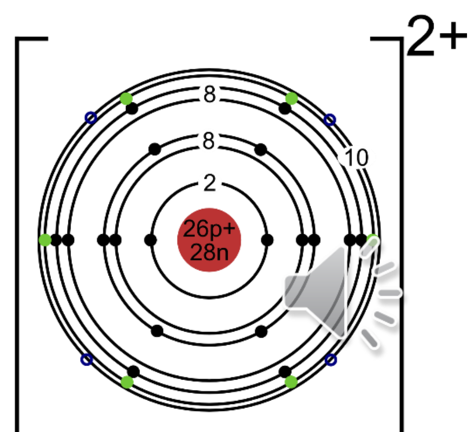




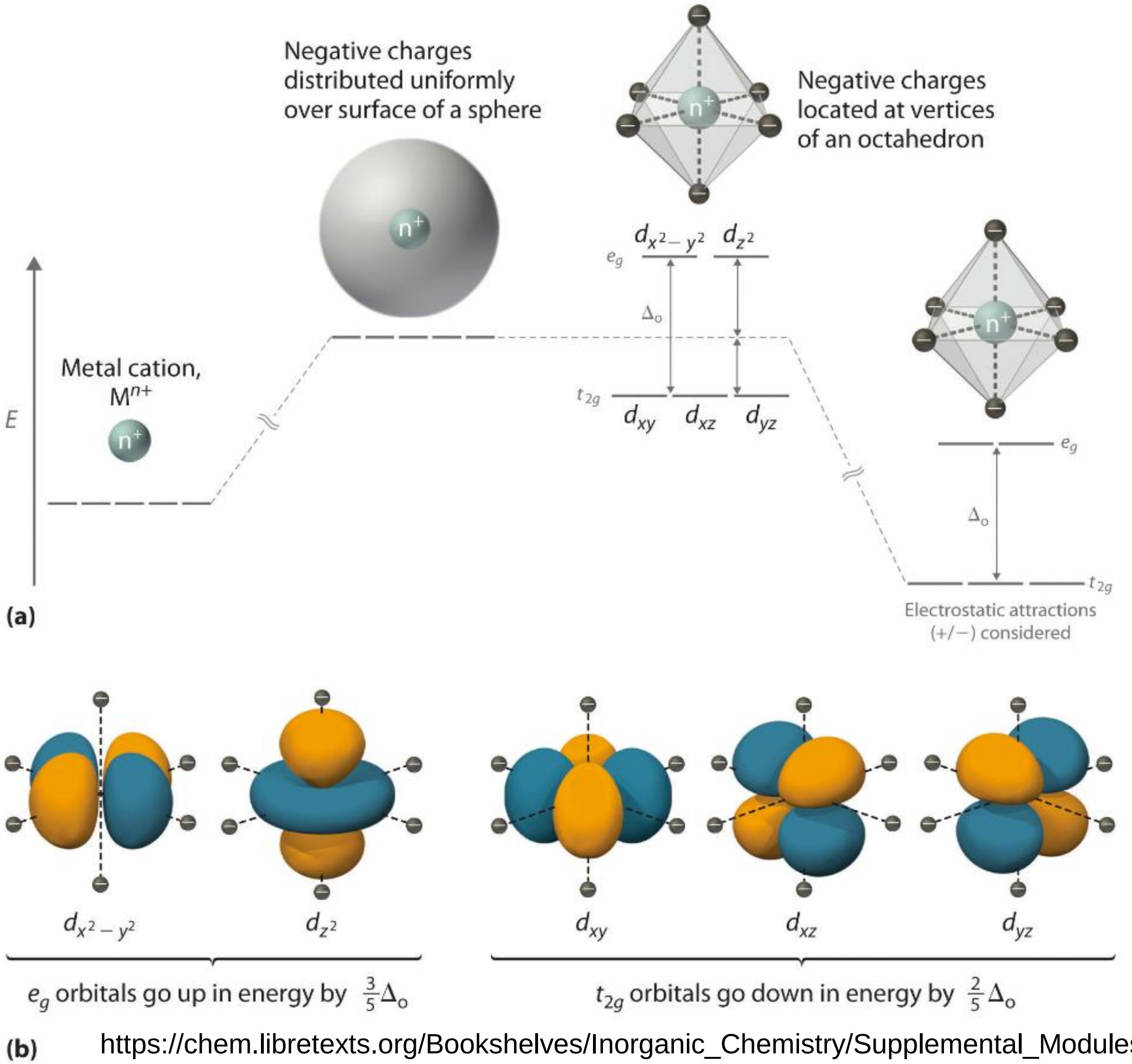


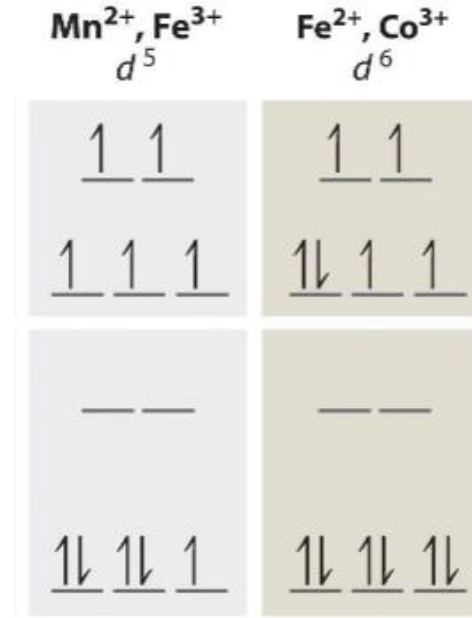






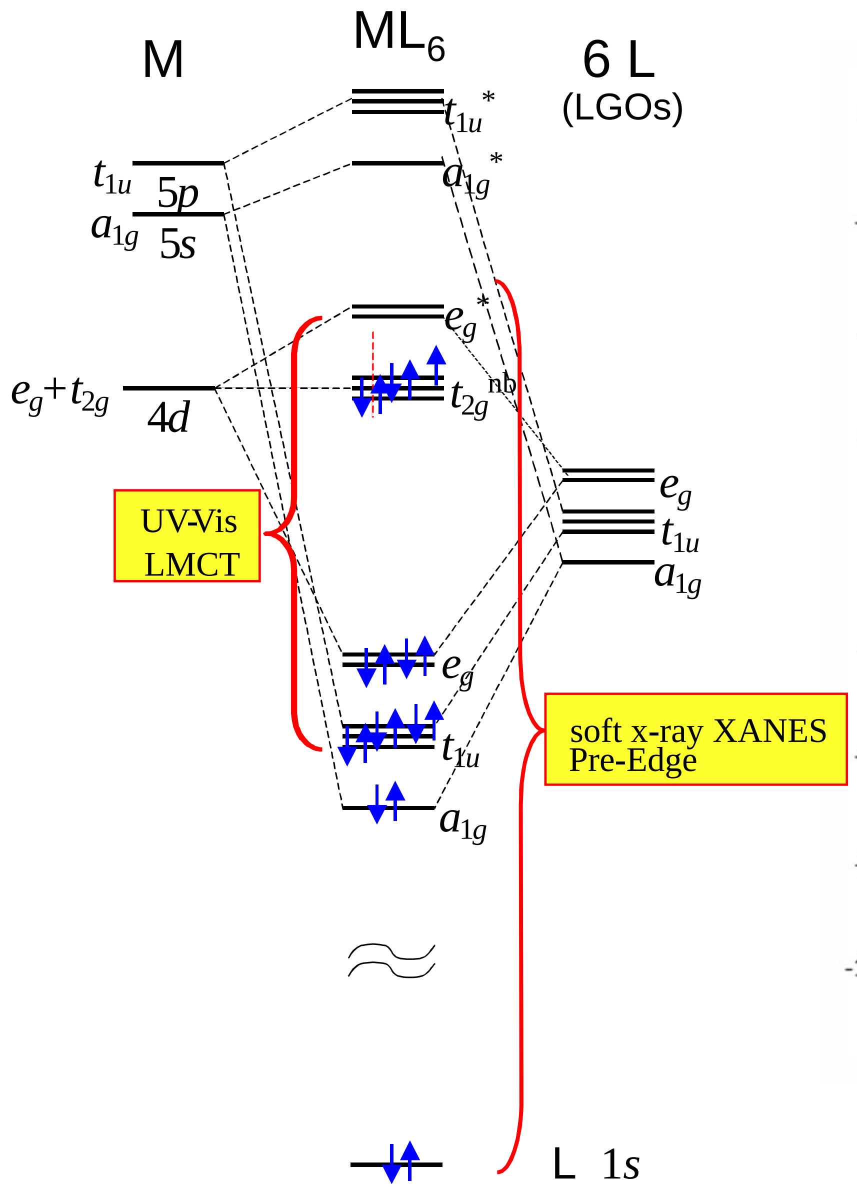
Ligand field

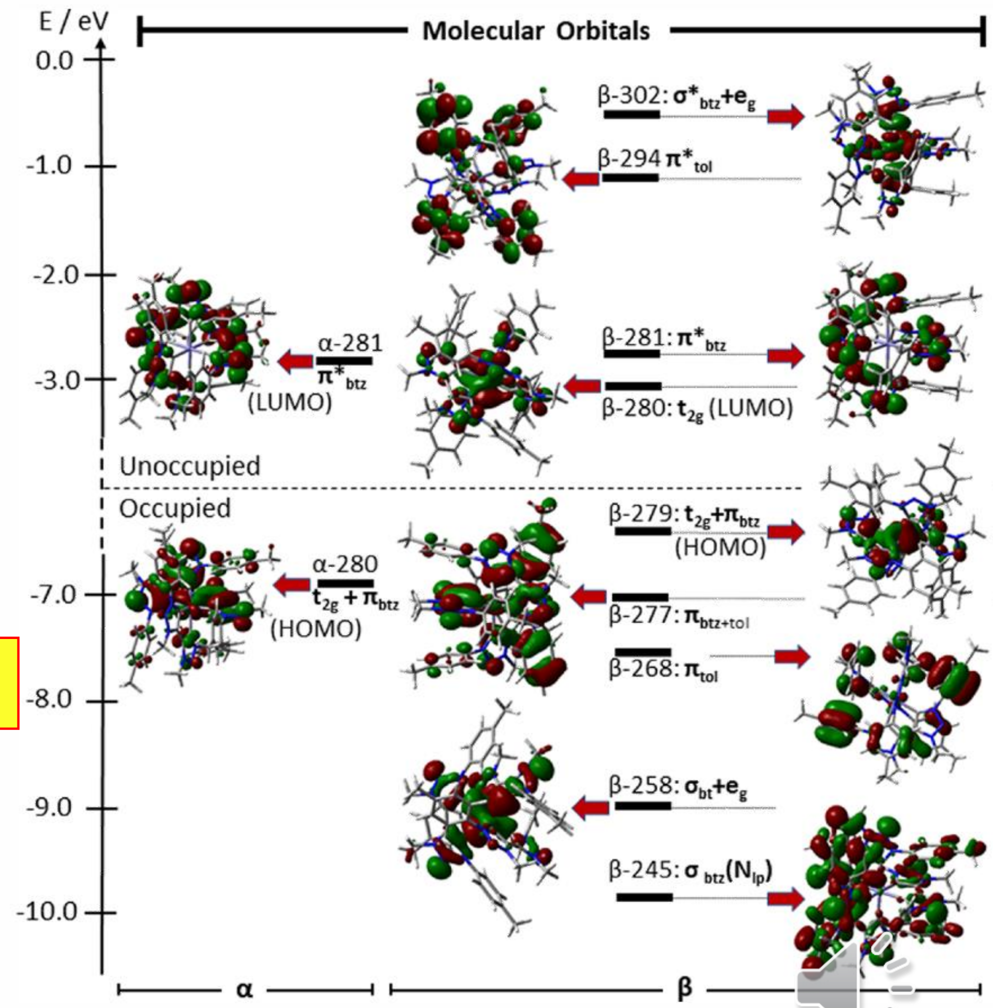




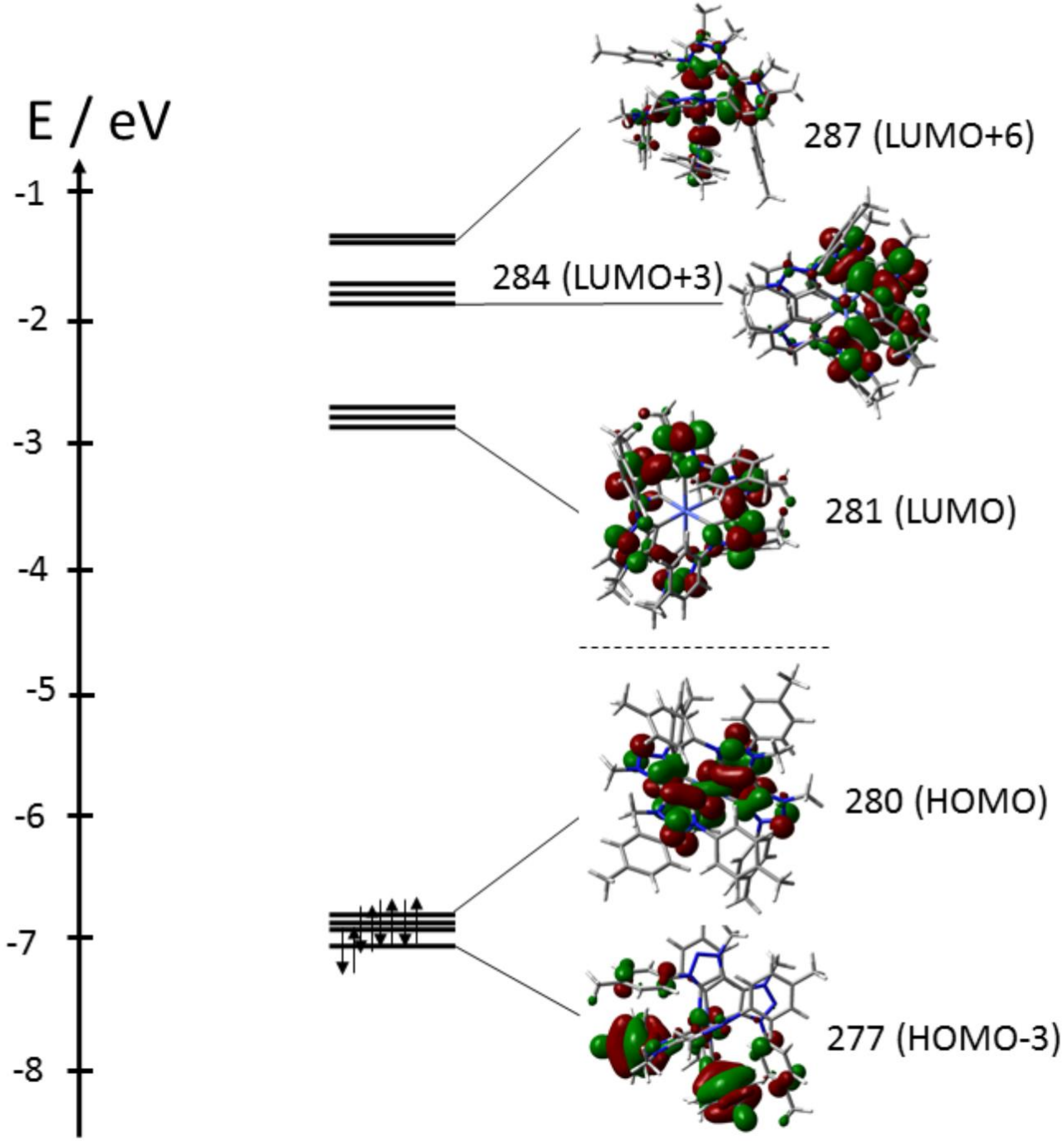
https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_(Inorganic_Chemistry)/Crystal_Field_Theory/Introduction_to_Crystal_Field_Theory

Position of states

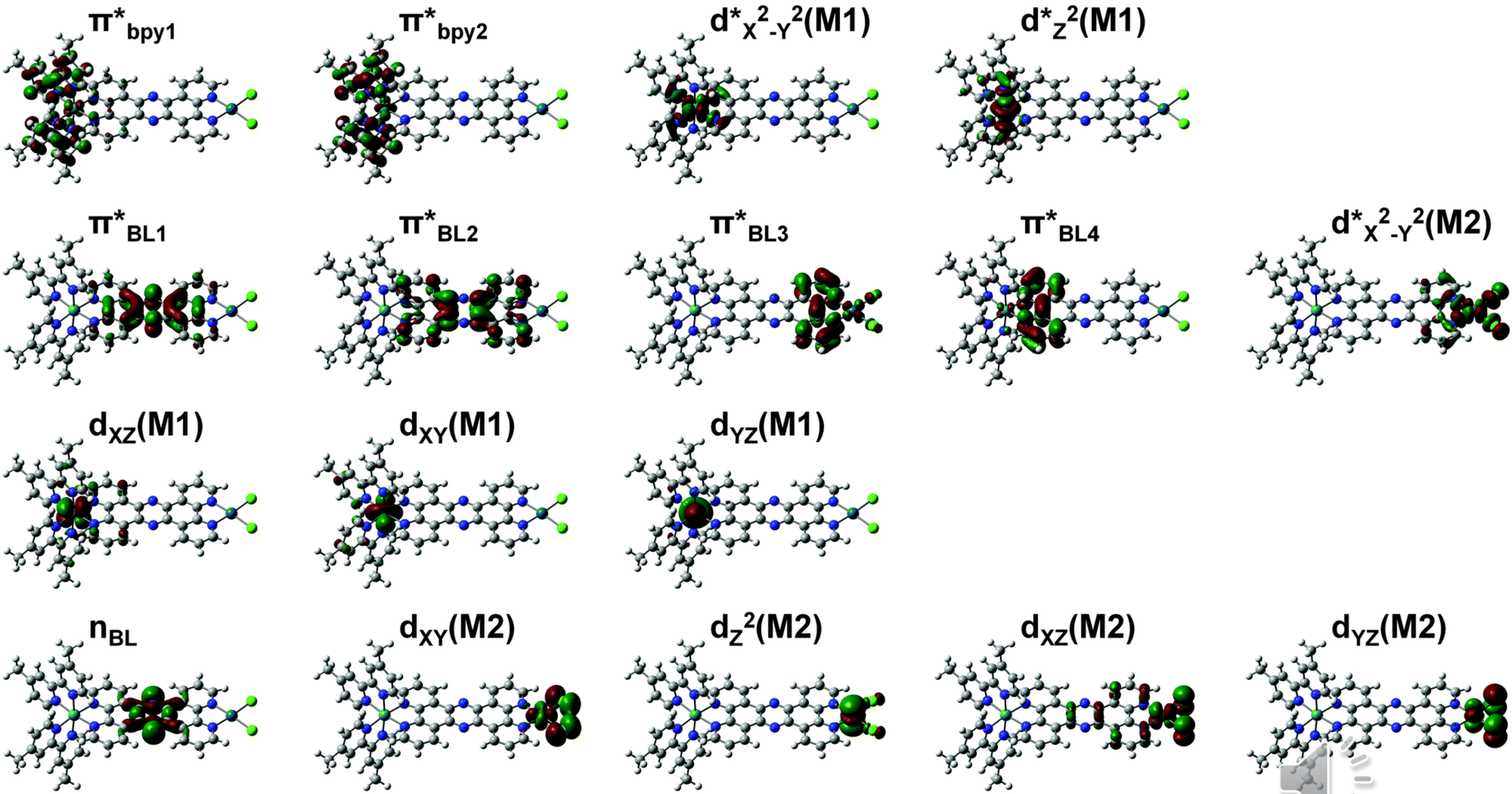




Orbitals in detail, Location definition

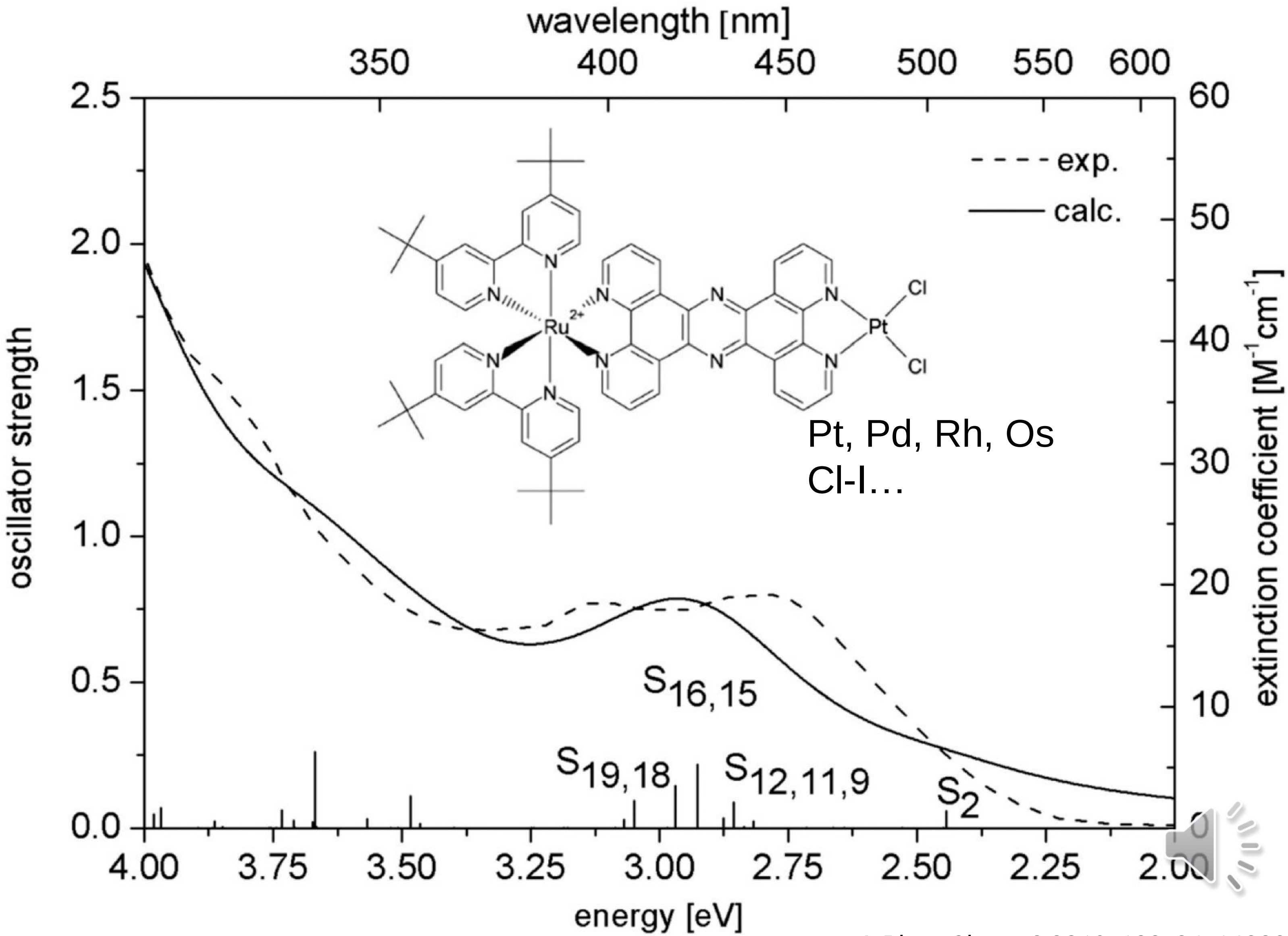


DFT and position



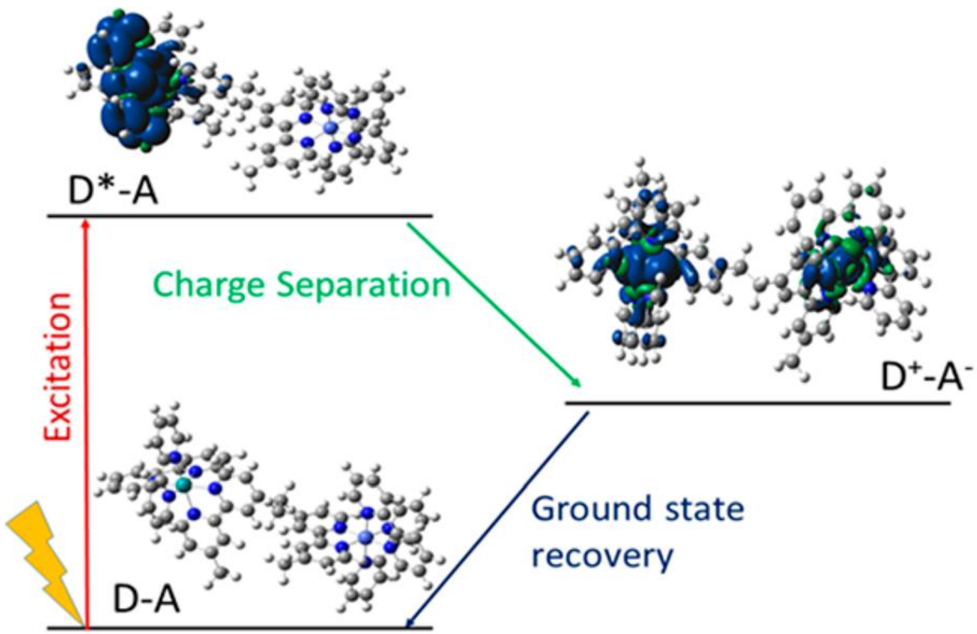
Phys. Chem. Chem. Phys., 2019,21, 9052-9060

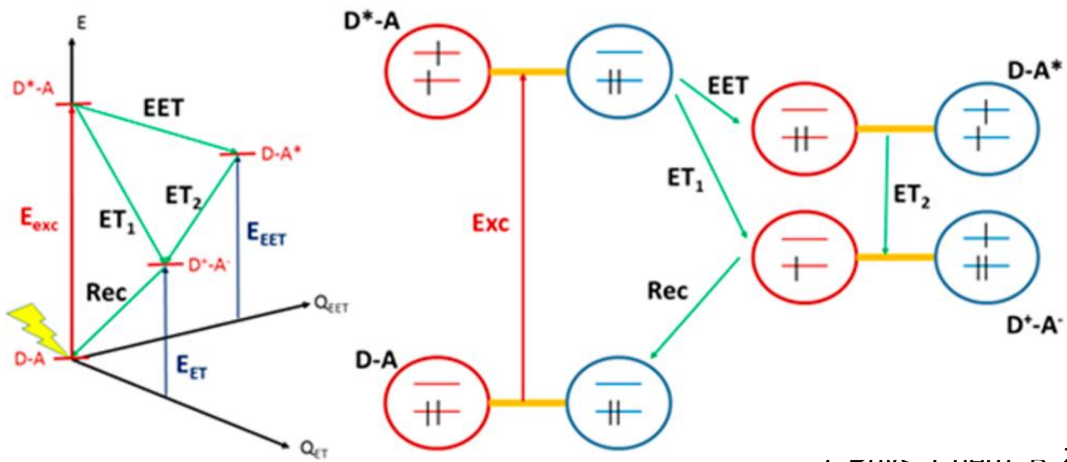
Ru-Pt example, Design your transitions, driving forces…



J. Phys. Chem. C 2019, 123, 26, 16003−16013

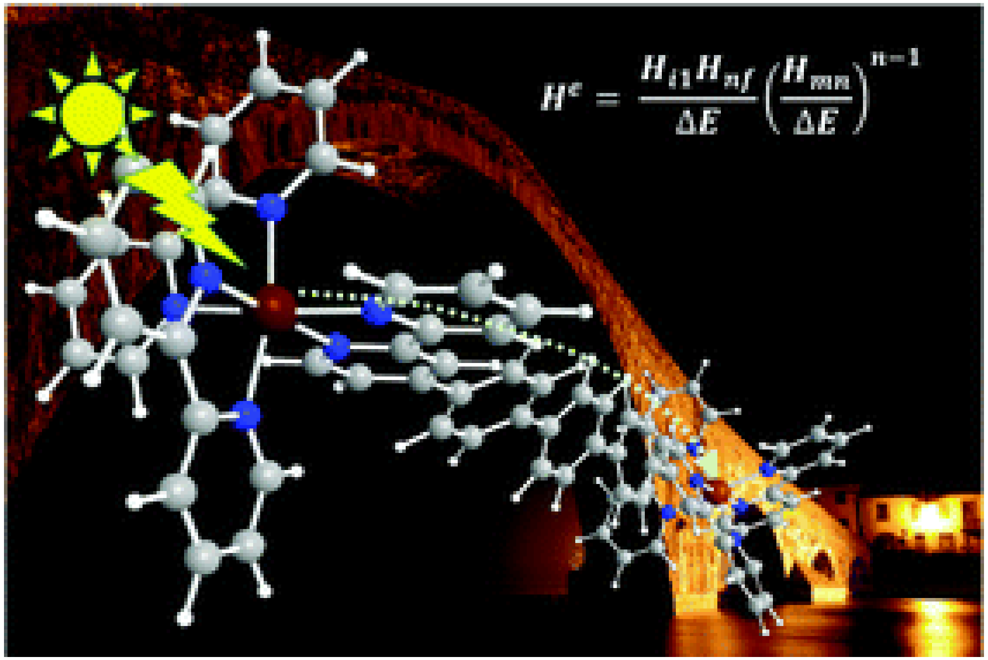
A playfield for Charge transfer studies and speeds





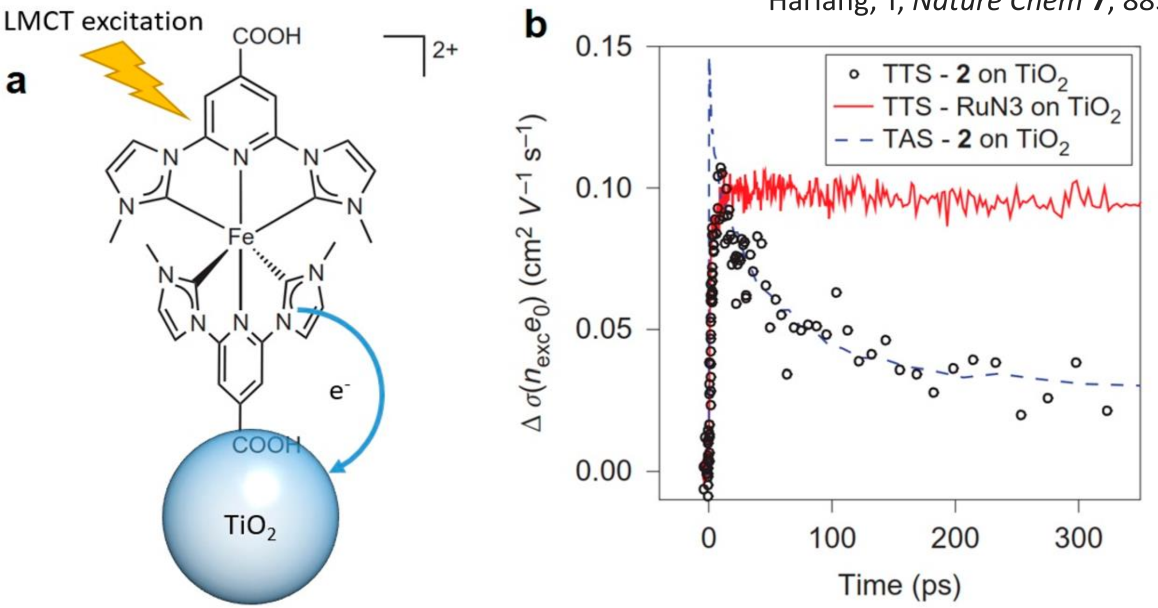
J. Phys. Chem. B 2015, 119, 7378−7392

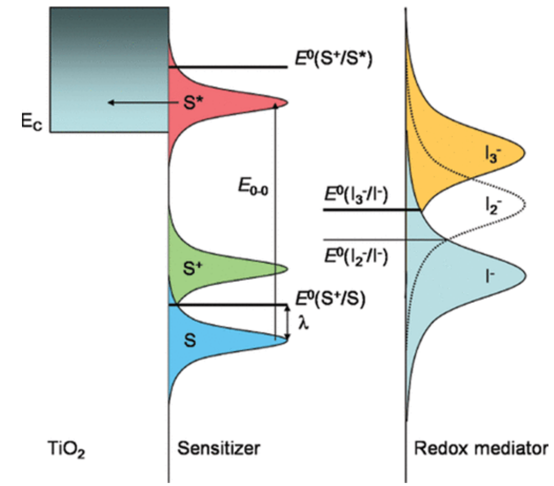
Tutorial Review
Photoinduced electron transfer across molecular bridges: electron- and hole-transfer superexchange pathways
Mirco Natali, Sebastiano Campagna and Franco Scandola
Chem. Soc. Rev., 2014,**43**, 4005-4018



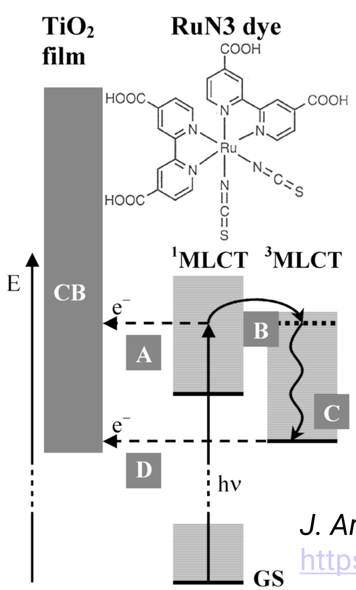
Grätzel cell

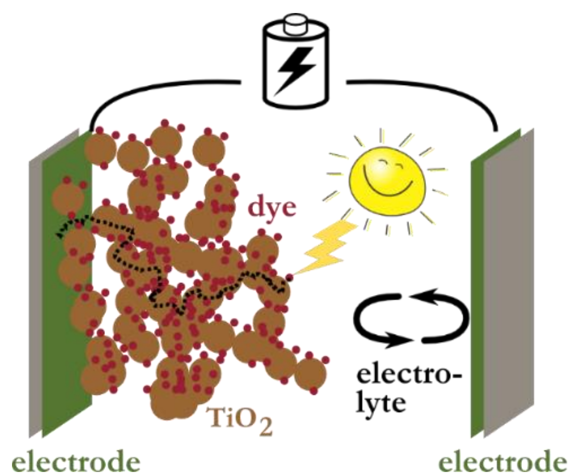
Harlang, T, *Nature Chem* **7**, 883–889 (2015). https://doi.org/10.1038/nchem.2365





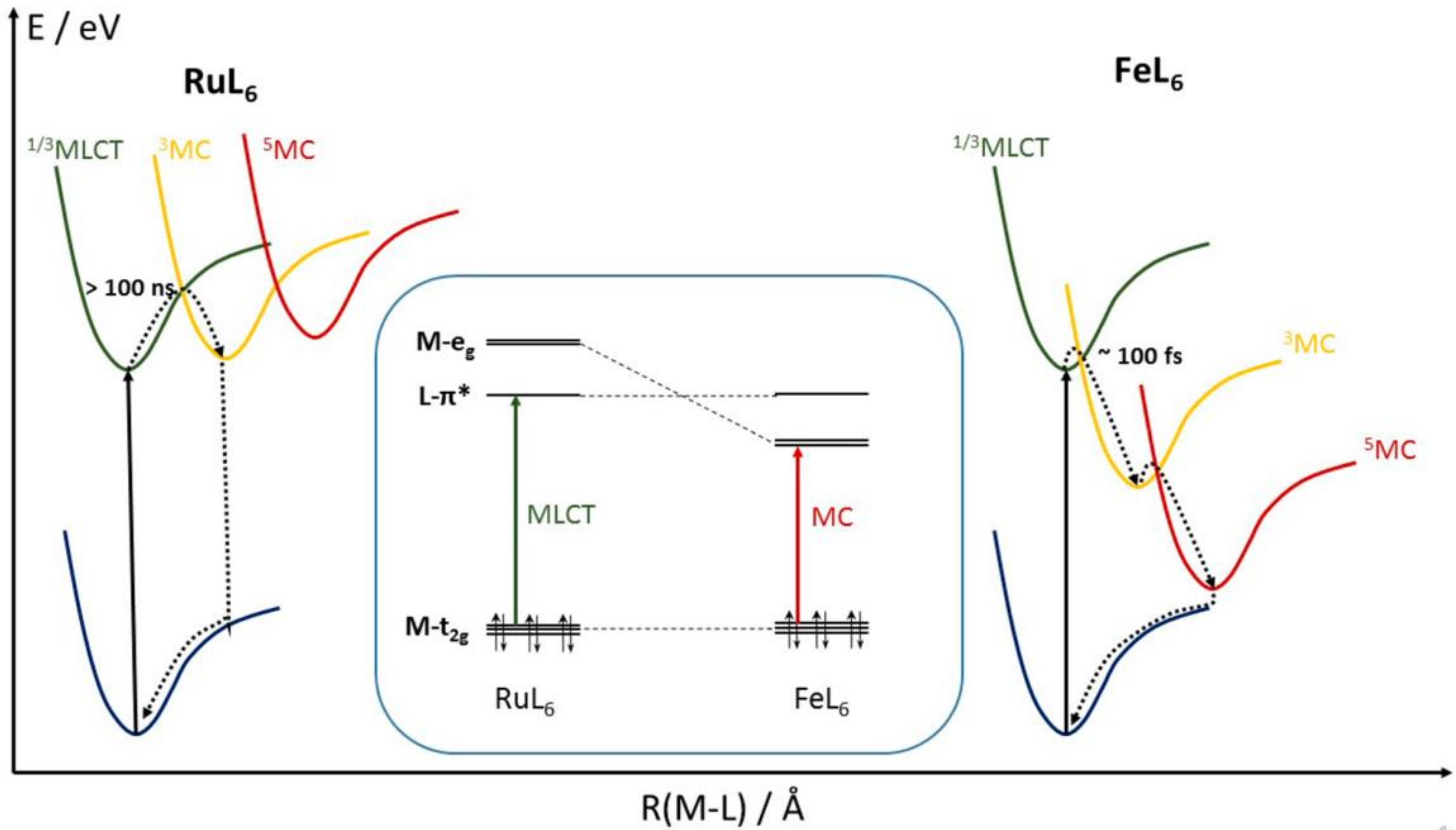
Chem. Rev. 2010, 110, 11, 6595−6663
https://doi.org/10.1021/cr900356p



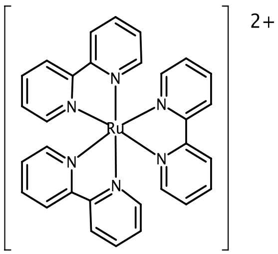


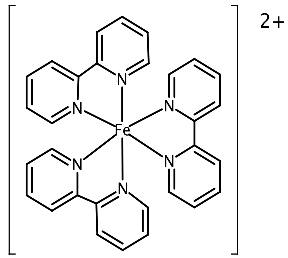
J. Am. Chem. Soc. 2002, 124, 3, 489−493
https://doi.org/10.1021/ja016561n

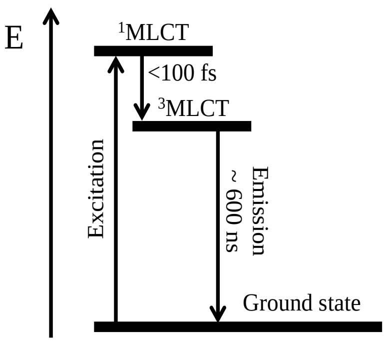
Octahedral Iron vs Ruthenium

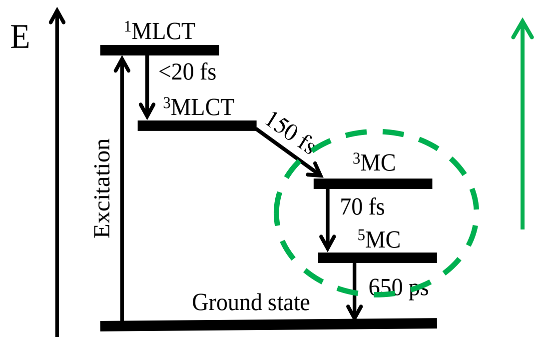


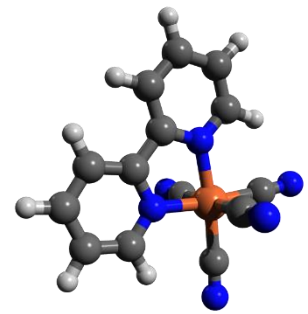
How carbene ligands change the MLCT lifetime

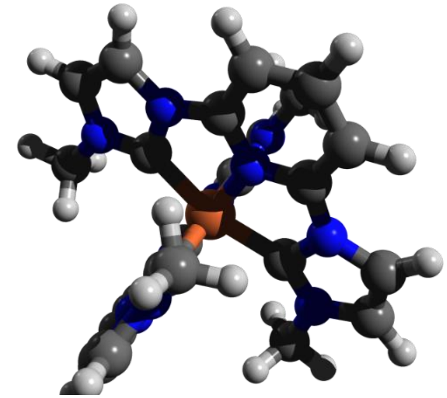


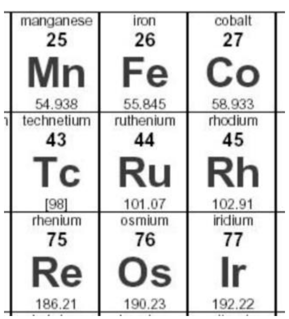


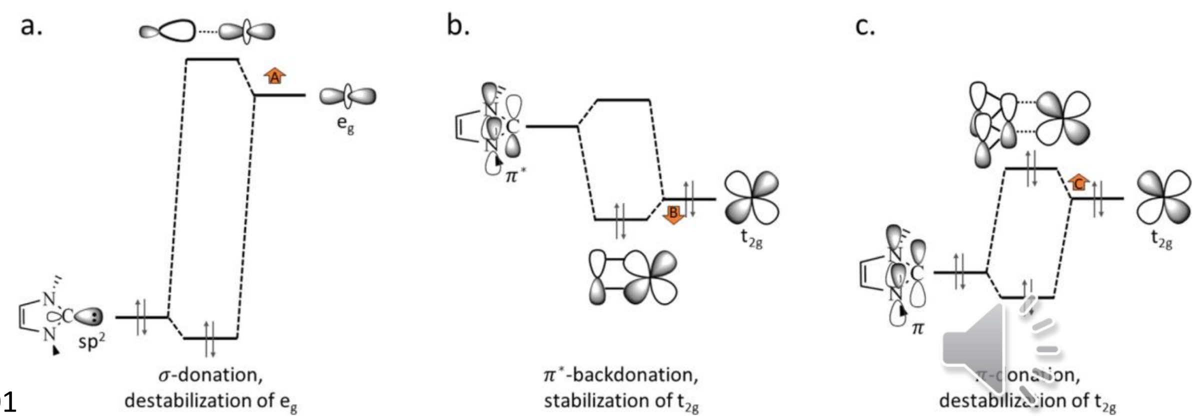








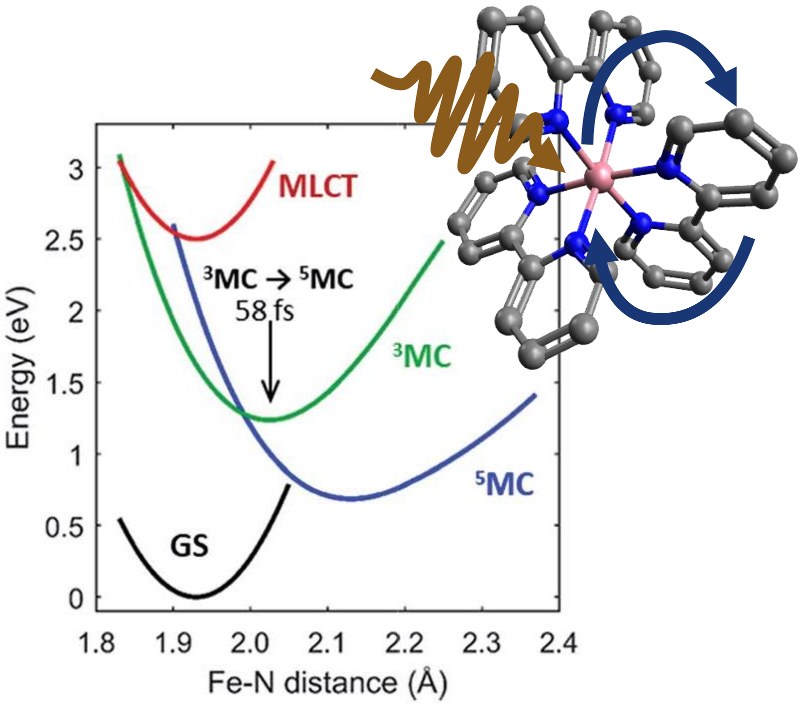


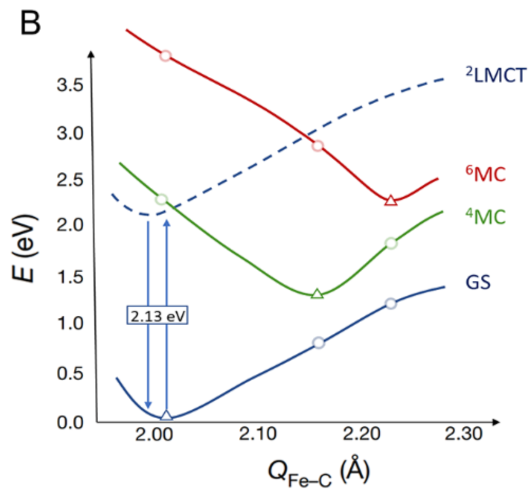


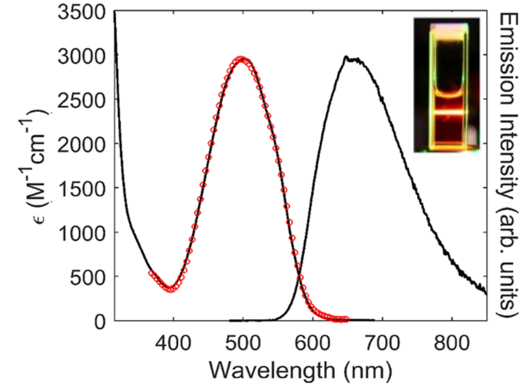
Y. Liu, et al. Chem. Commun. 49, 6412-6414, 201

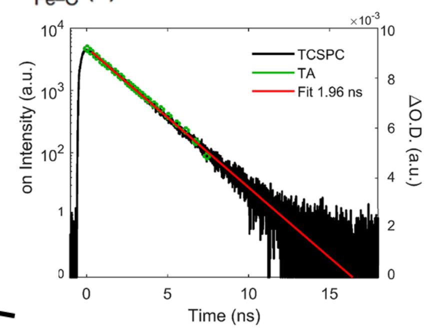
P. Chábera Coord. Chem. Rev., vol. 426, p. 213517, Jan. 2021, doi: 10.1016/j.ccr.2020.213517

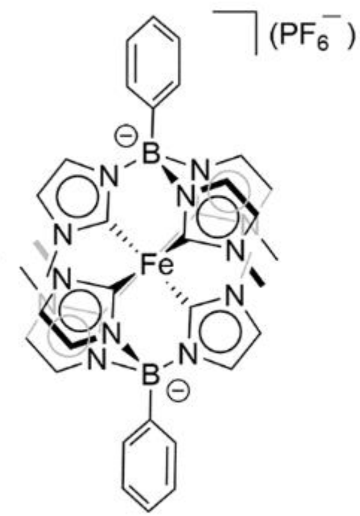
The Iron case



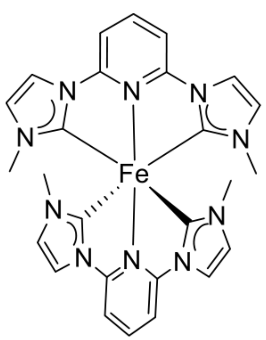


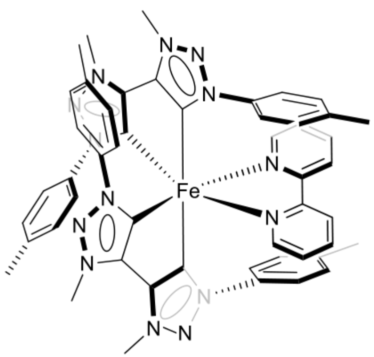


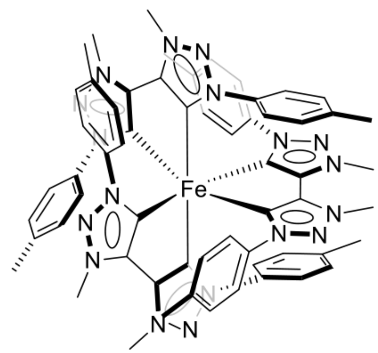




2ns Kjær et al.
Science, ,2018 , 363 , 249-253
https://doi.org/10.1126/science.aau7160



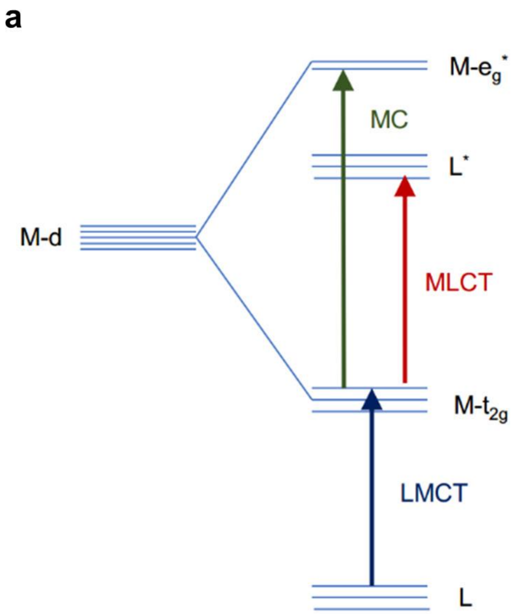


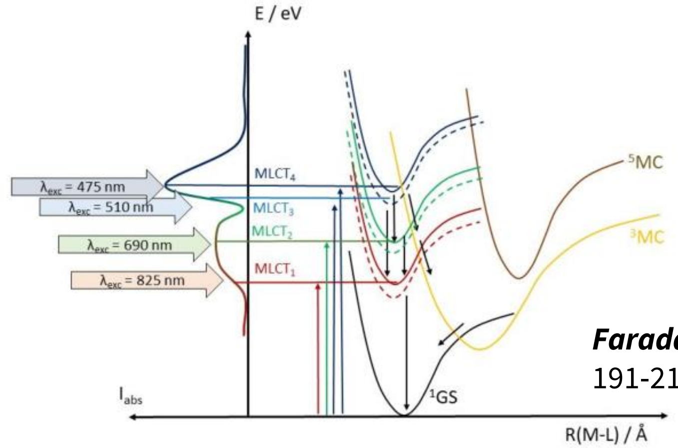


16ps Liu et al.
Chemistry, 2014 , 21 , 3628-3639
https://doi.org/10.1002/chem.201405184

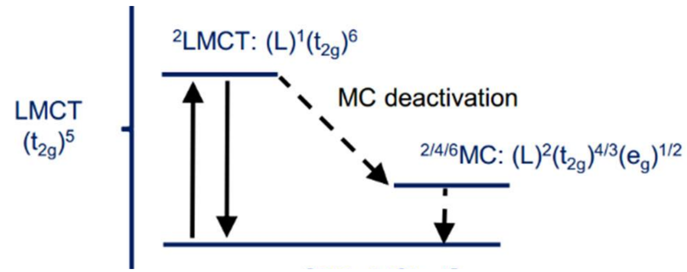
550ps Chábera et al.
Nature, 2017 , 543 , 695-699
https://doi.org/10.1038/nature21430

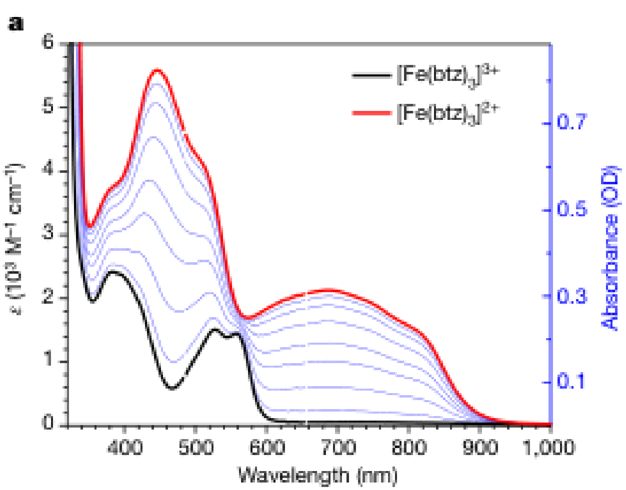
Carbene state Identification

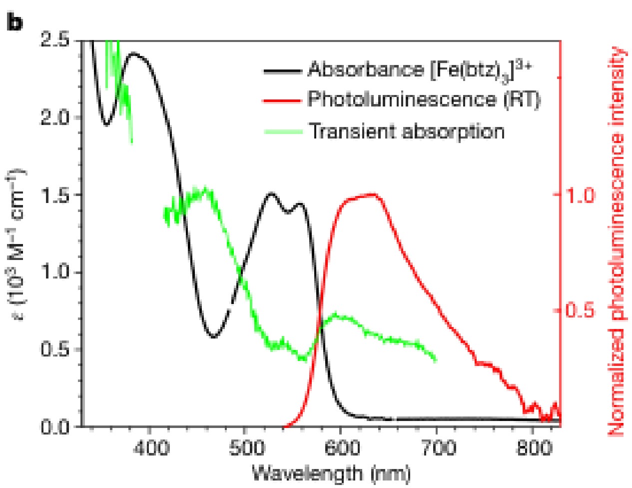




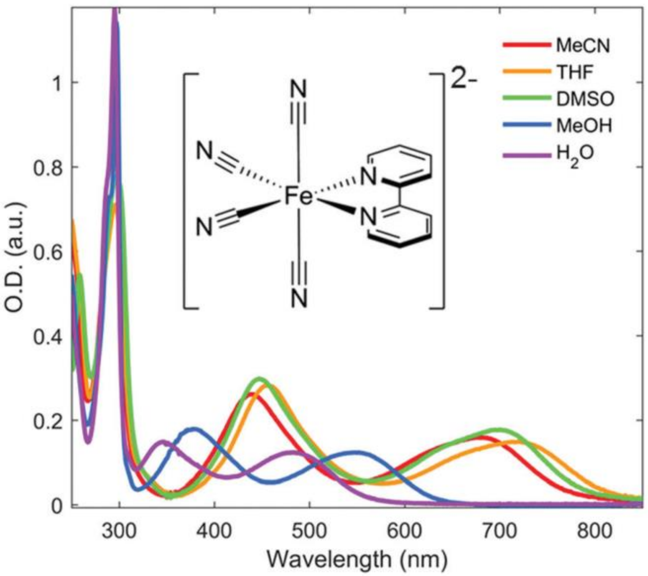
Faraday Discuss., 2019,**216**, 191-210

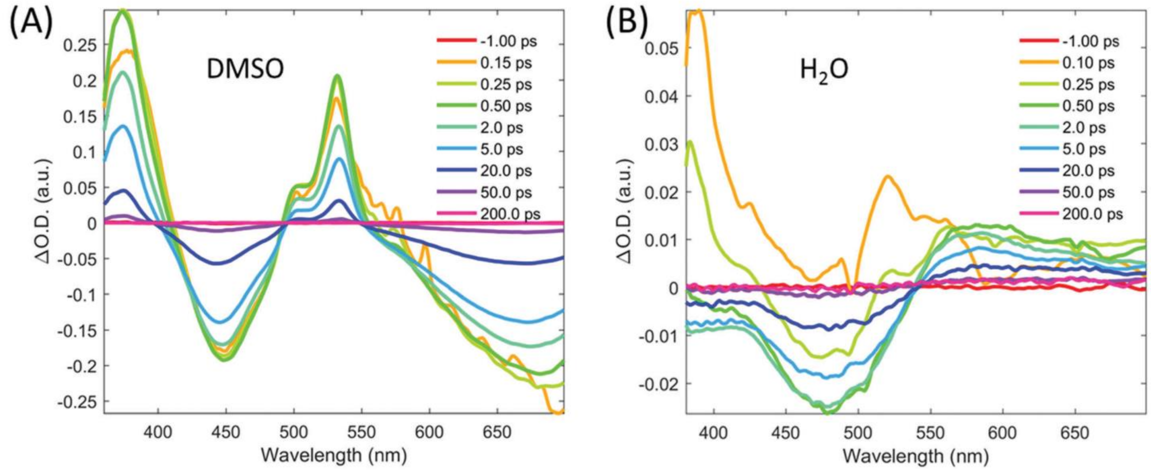


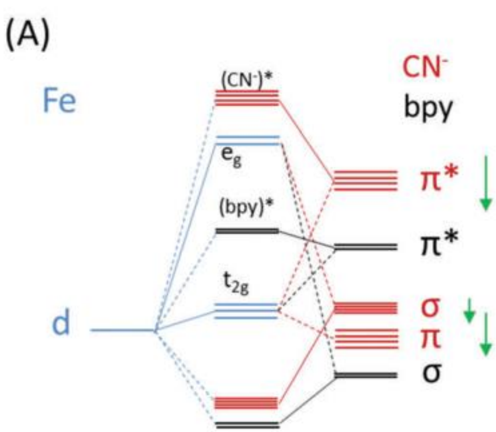


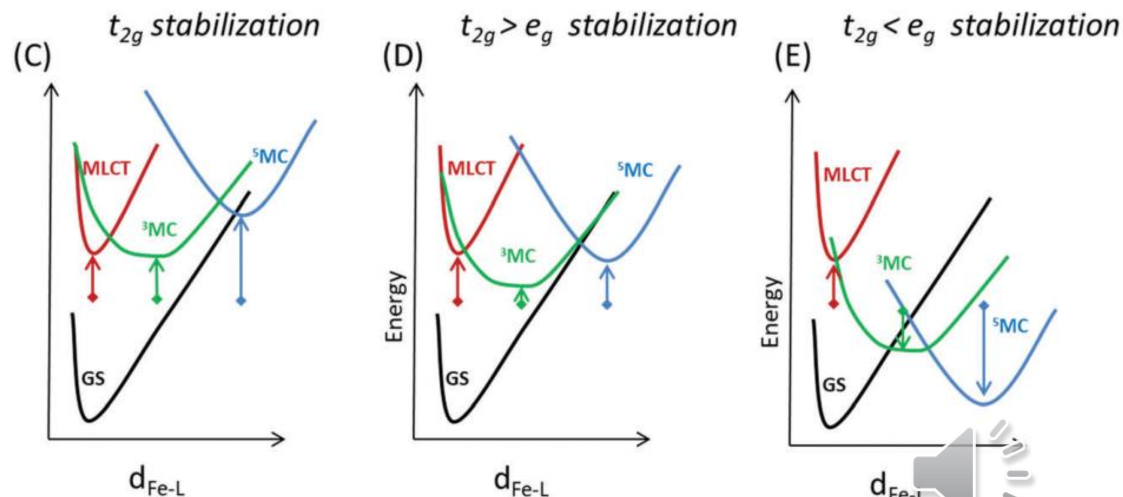


Fe(bpy)(CN)4 Lewies interaction



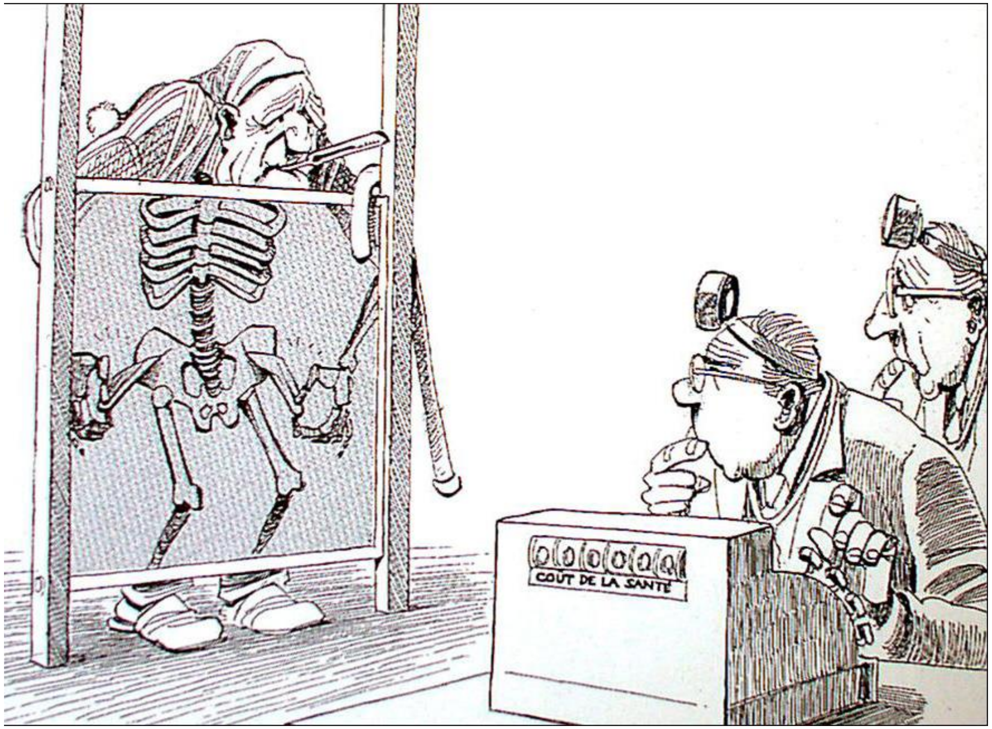


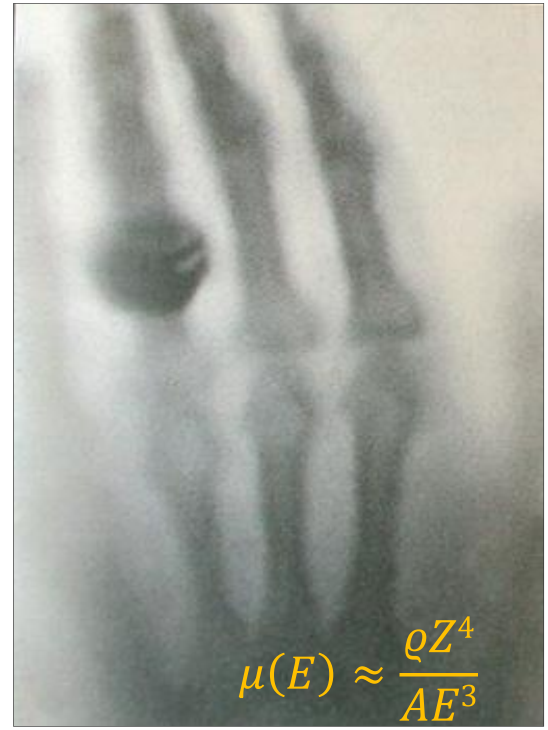




Phys. Chem. Chem. Phys., 2018,**20**, 4238-4249

X-rays shadow

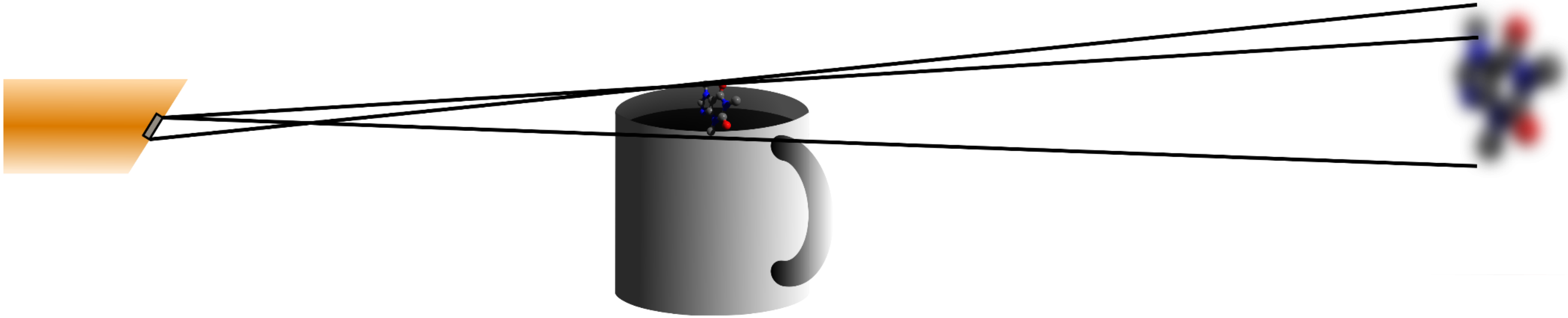


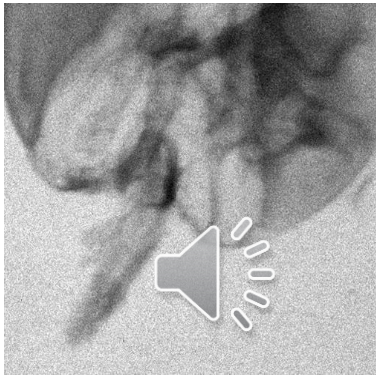


Why can’t we see molecules directly?

(Not the correlated scattering!)

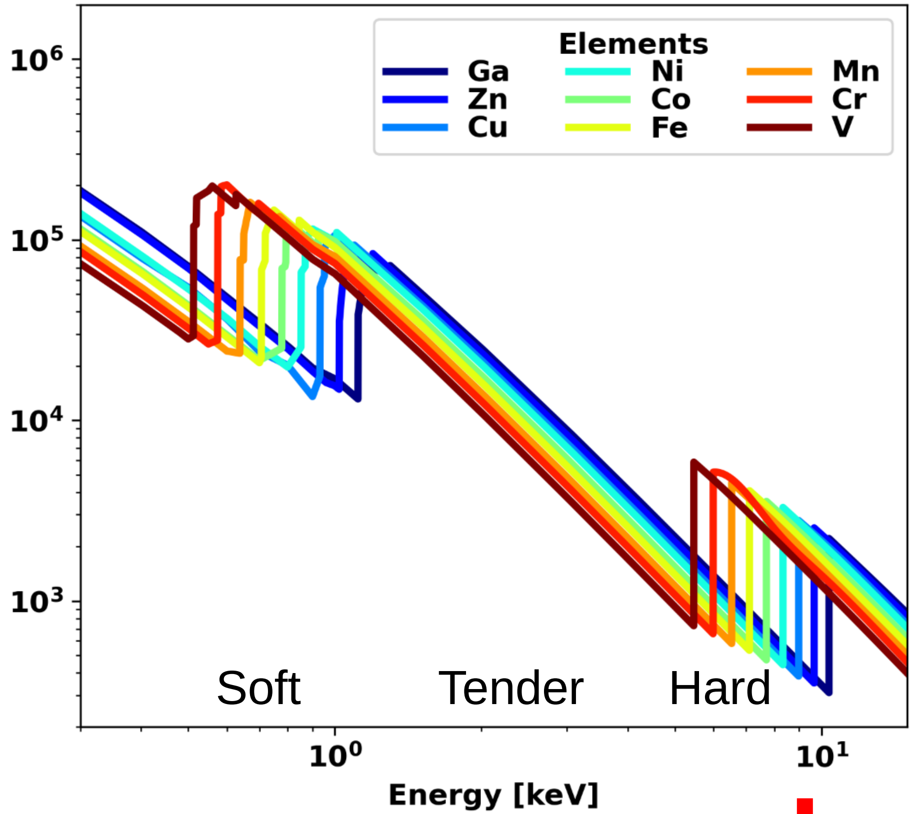
Spatial resolution for shadow techniques

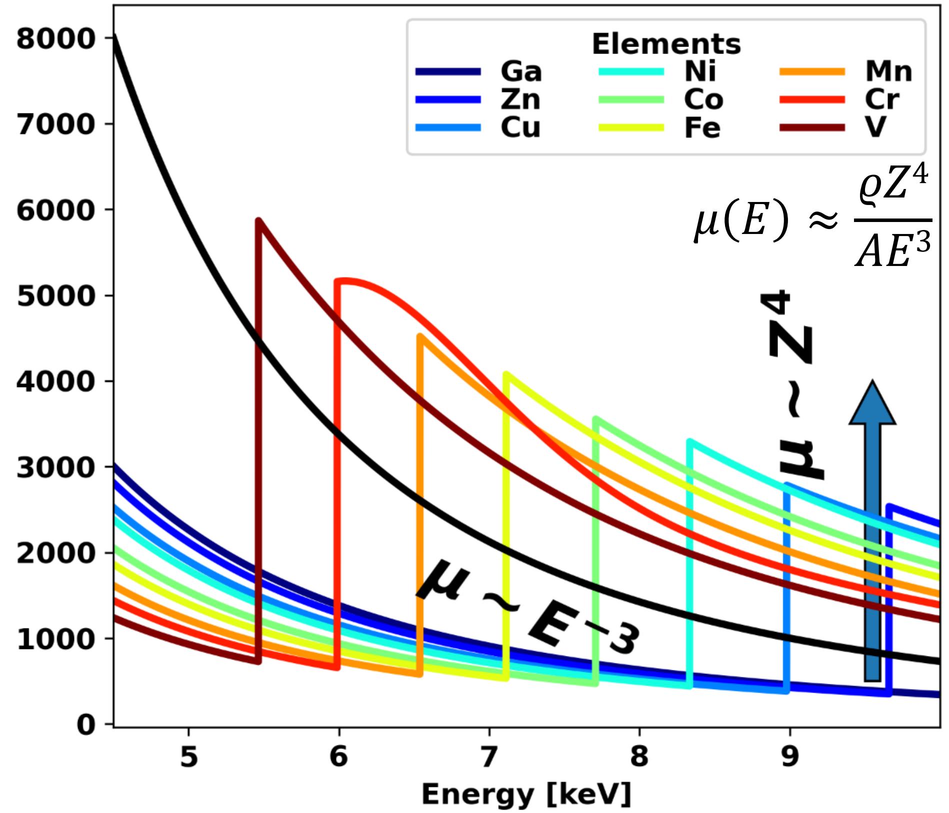


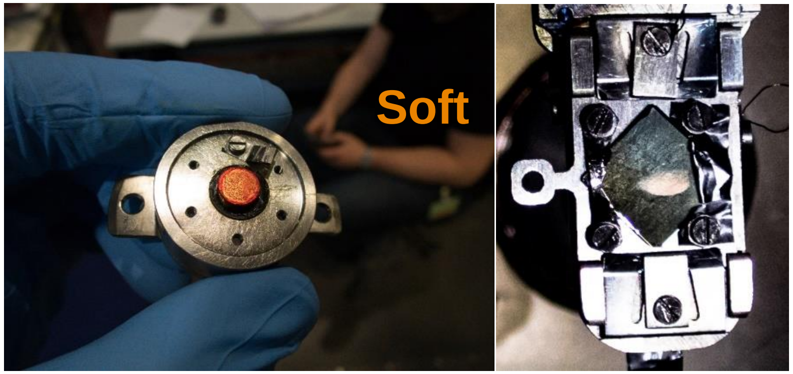


How can we beat this?

So why do XAS/XES - Elemental energy separation







Excursion, Z^4? E^{-3}?

Why?

$$\Gamma = \frac{2\pi}{\hbar^2} \sum_{i,f} \left| \langle \Psi_f \,|\, \overrightarrow{\mu} \,|\, \Psi_i \rangle \right|^2 \delta(h\nu - E_f - E_i)$$

$$\mu(E) \approx \frac{\varrho Z^4}{AE^3}$$

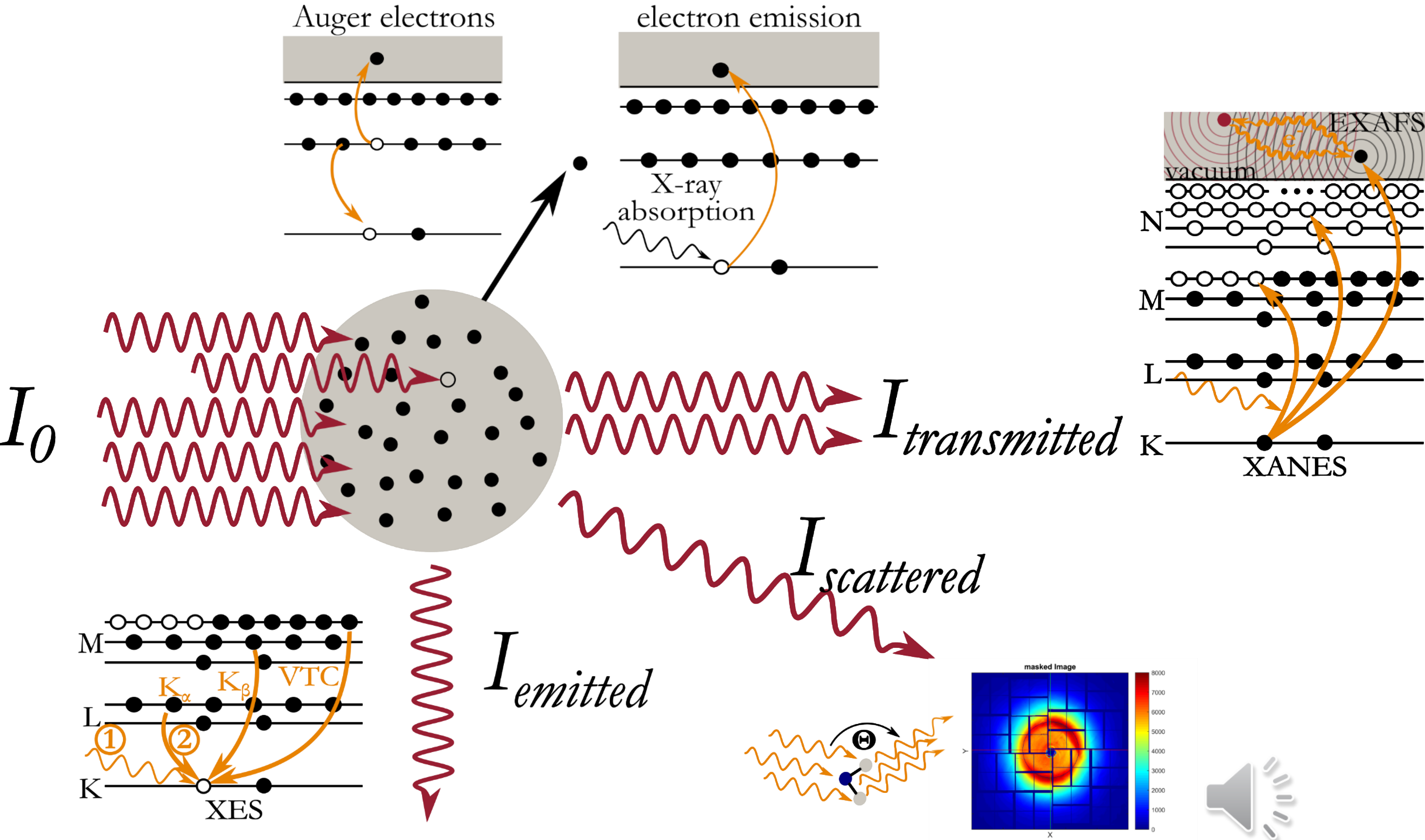
electron wavelength

$$\lambda = \frac{h}{p} \quad \text{with} \quad \hbar = \frac{h}{2\pi} \quad p = \hbar k$$

$$E_{kin} = \frac{p^2}{2m_e} \quad k = \frac{1}{\hbar}\sqrt{2m_e(E - E_0)}$$

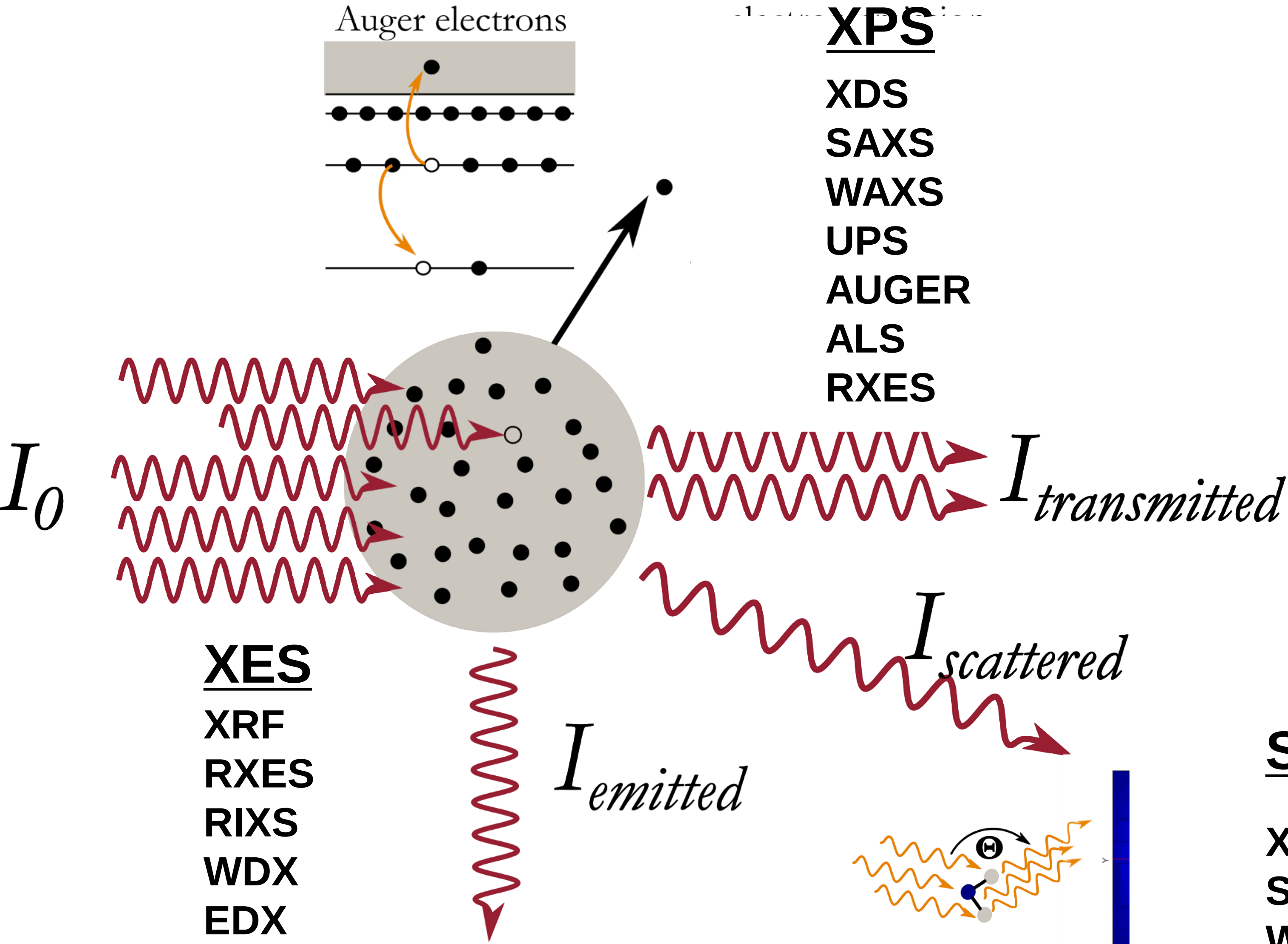
Excursion - Dipol

Interactions with light, most of them



$$I_0 = I_{transmitted} + I_{absorbed} + I_{scattered}$$

Interactions with light, most of them, and confusing names



XPS

XDS
SAXS
WAXS
UPS
AUGER
ALS
RXES

XAS

XAFS
XANES
EXAFS
HEROS
HERFD

XES

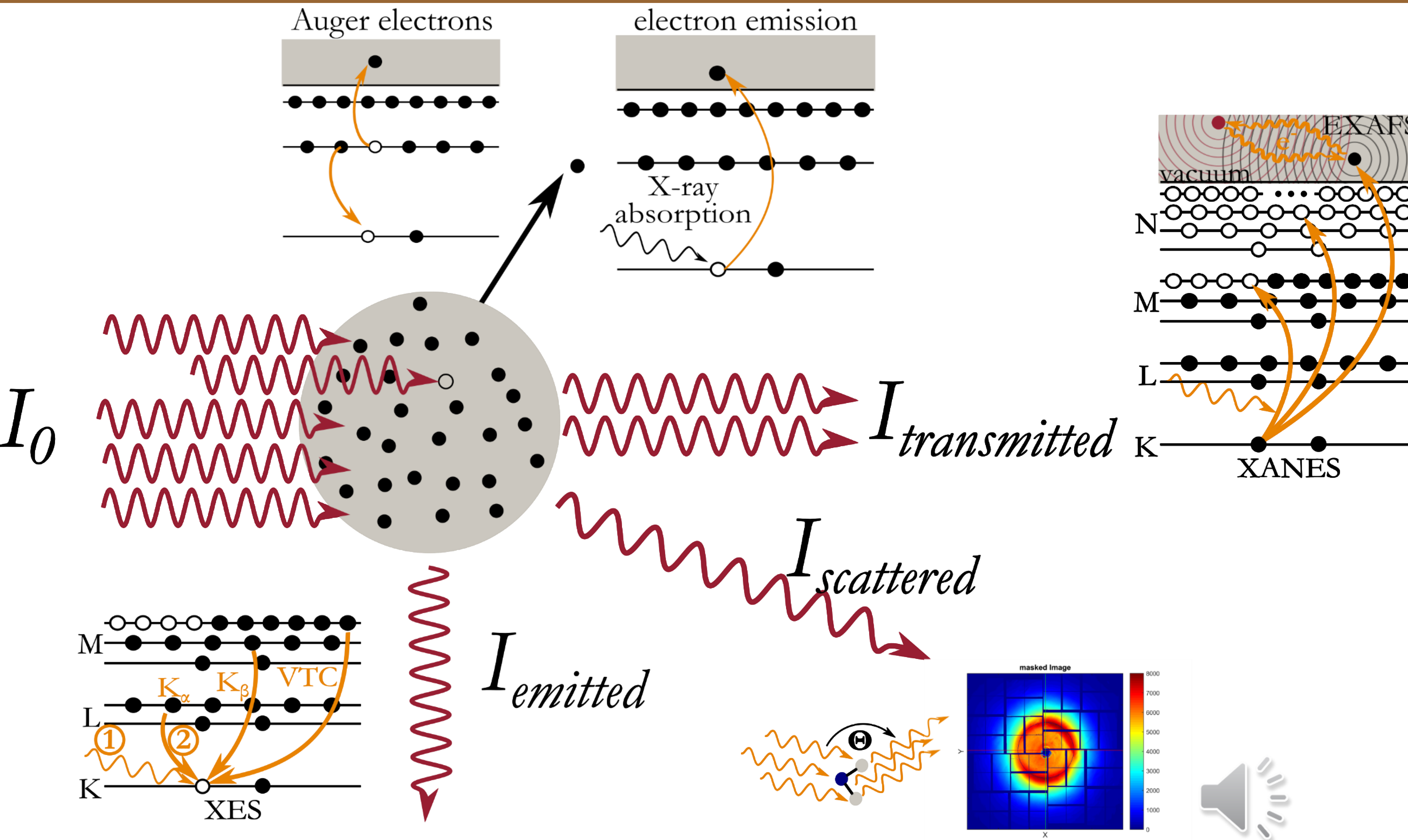
XRF
RXES
RIXS
WDX
EDX

Scattering

XDS
SAXS
WAXS

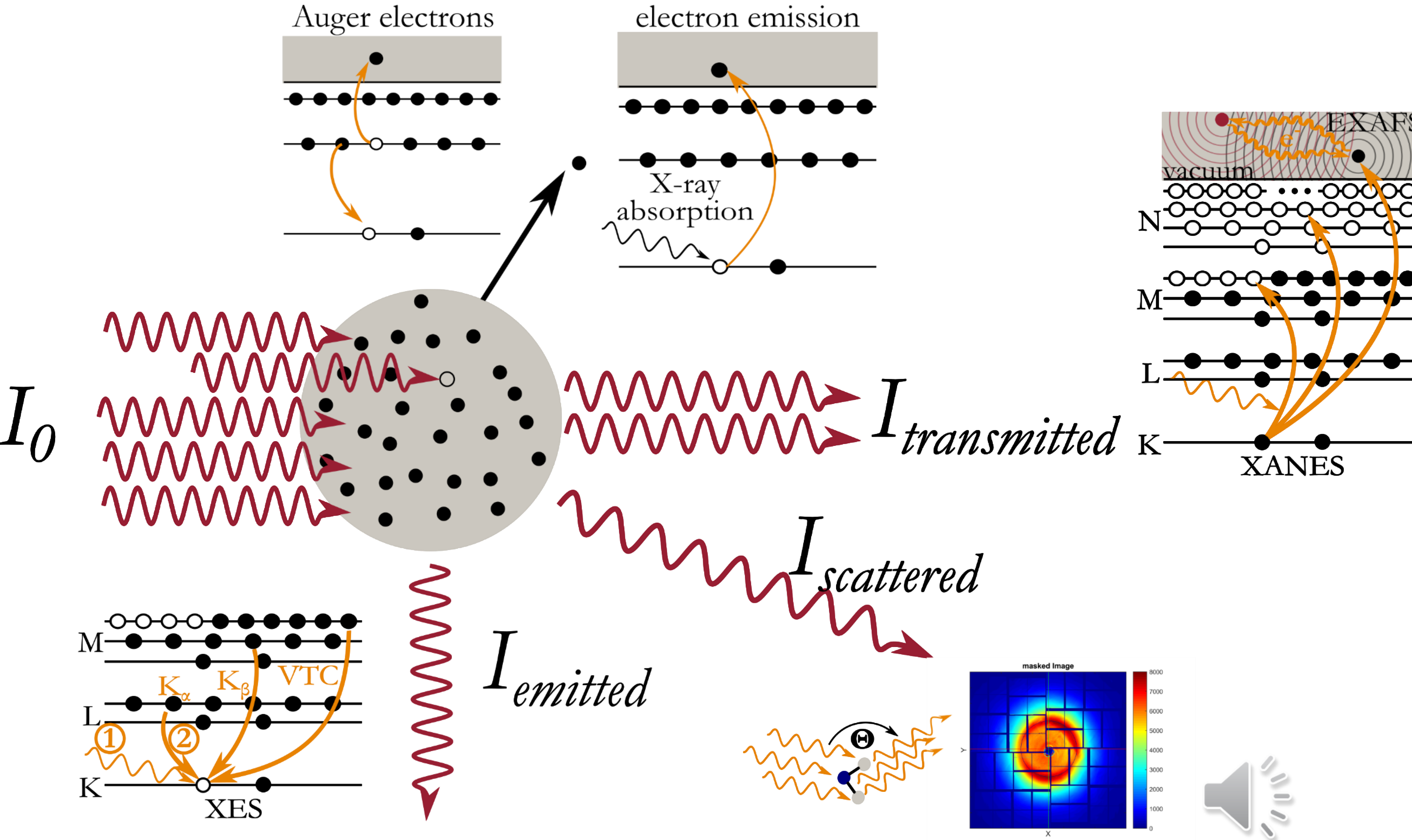
$$I_0 = I_{transmitted} + I_{absorbed} + I_{scattered}$$

Interactions with light, most of them



$$I_0 = I_{transmitted} + I_{absorbed} + I_{scattered}$$

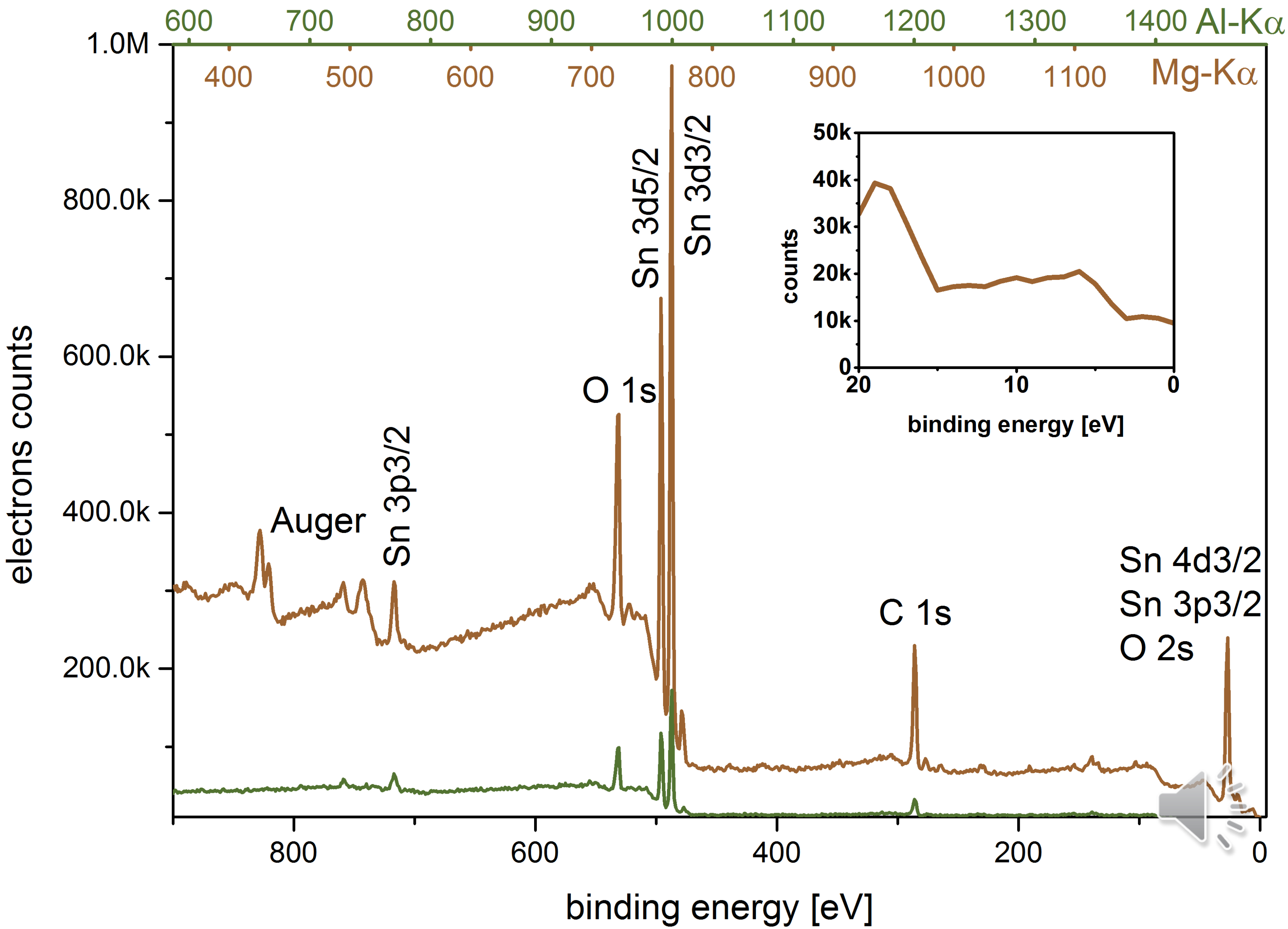
Interactions with light, most of them



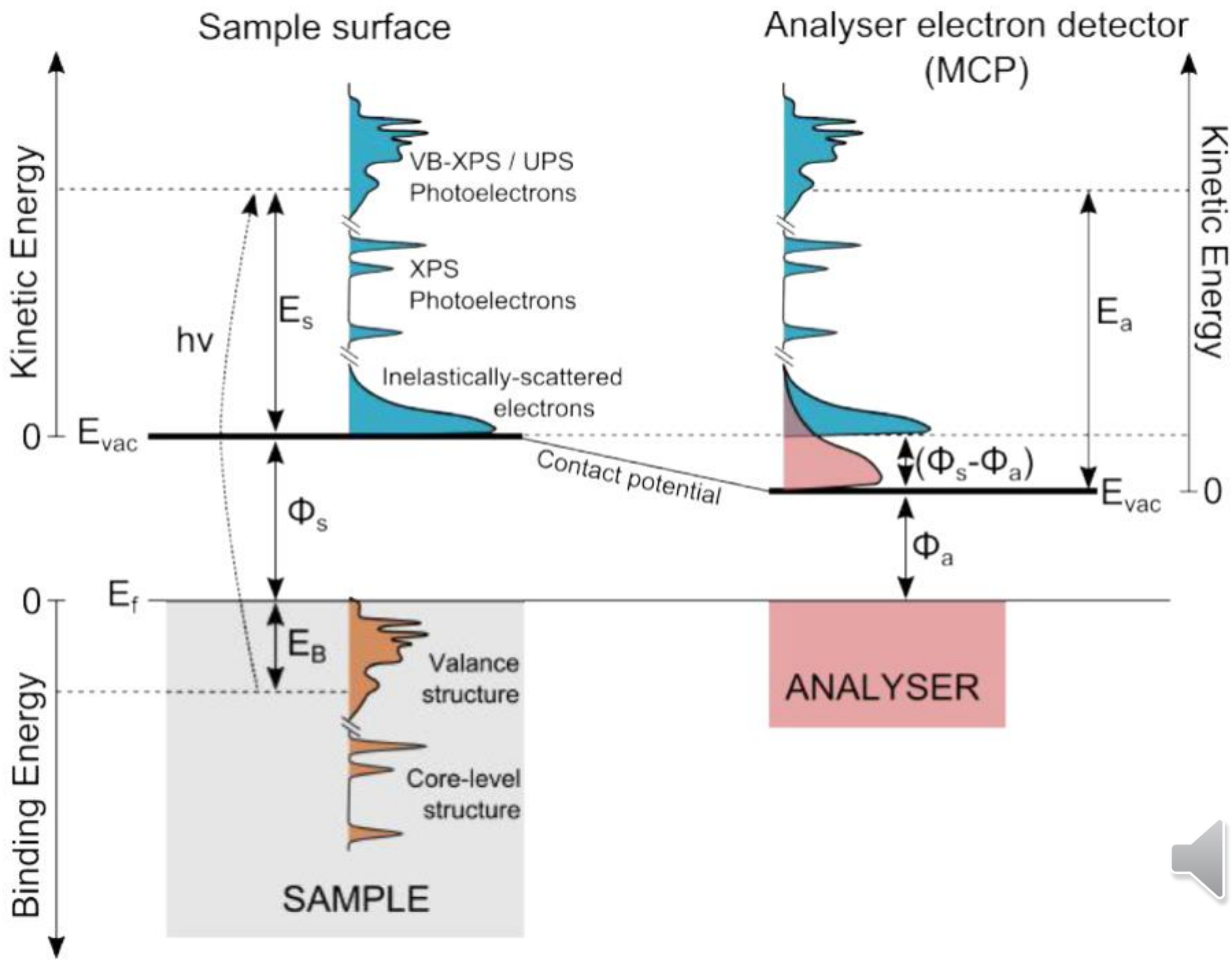
$$I_0 = I_{transmitted} + I_{absorbed} + I_{scattered}$$

XPS

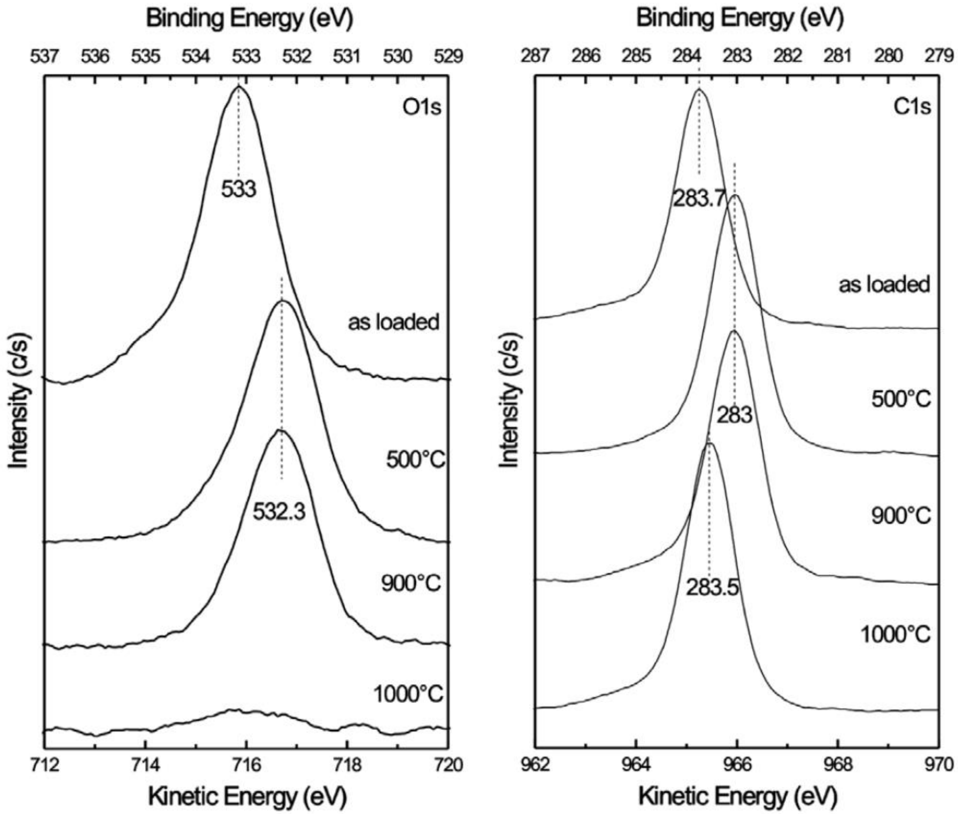
interactions

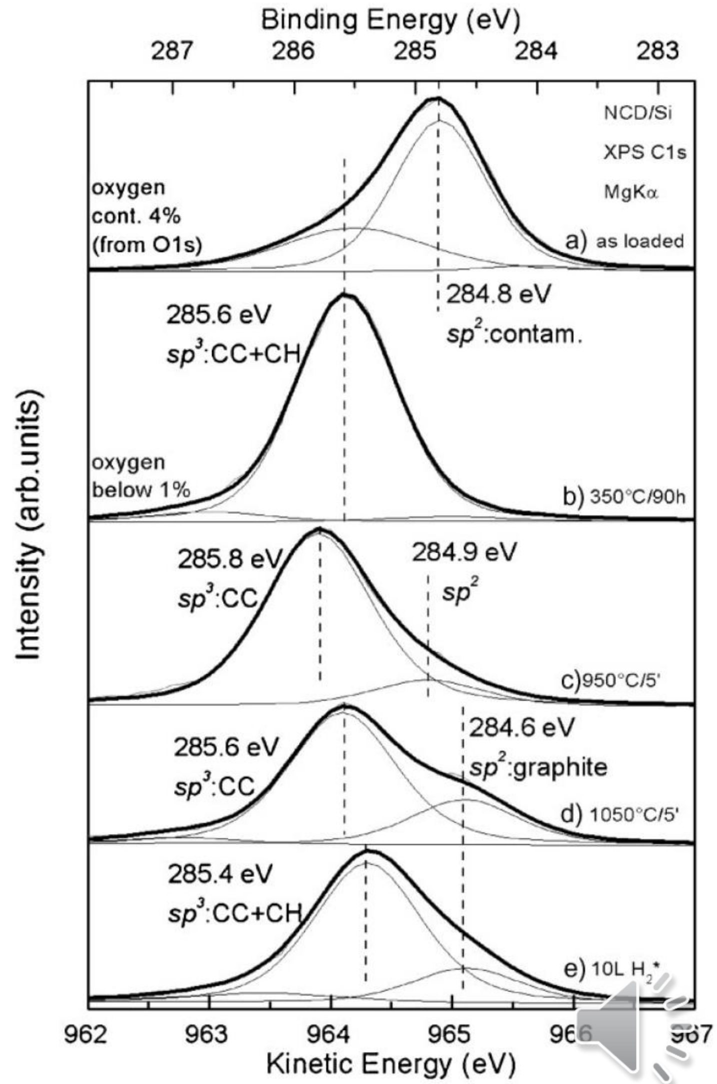


XPS – mapping of the filled electron density



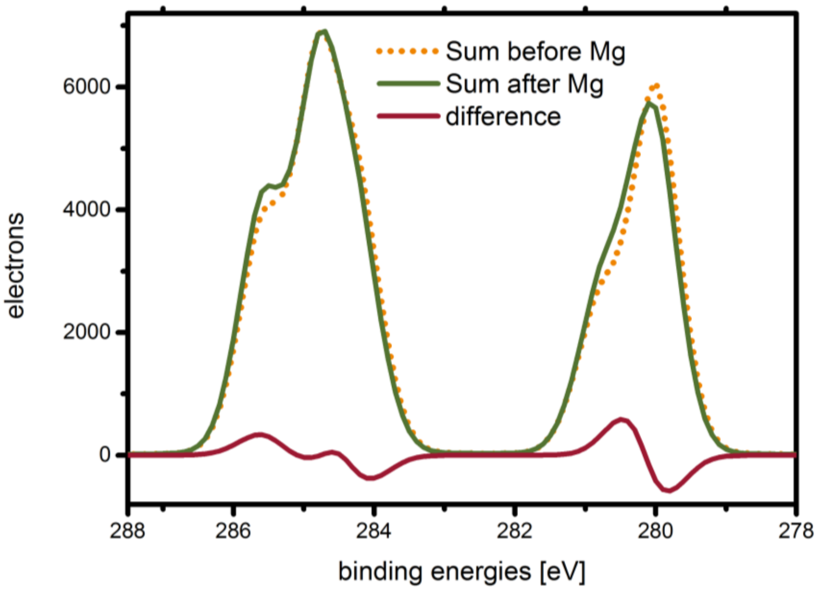
XPS

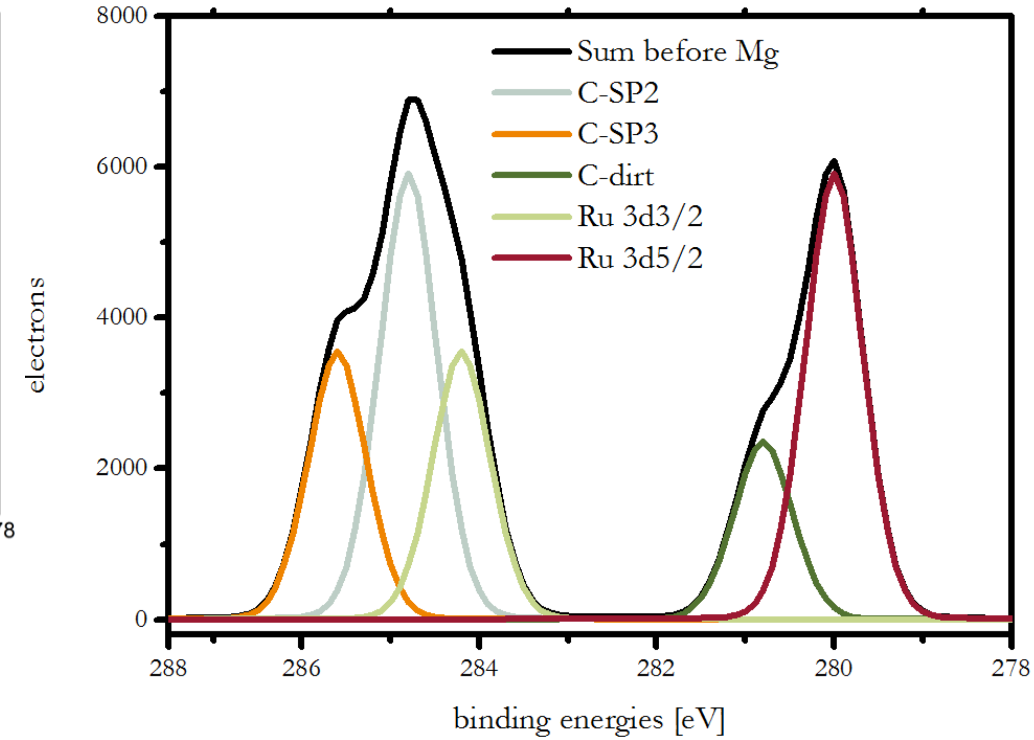


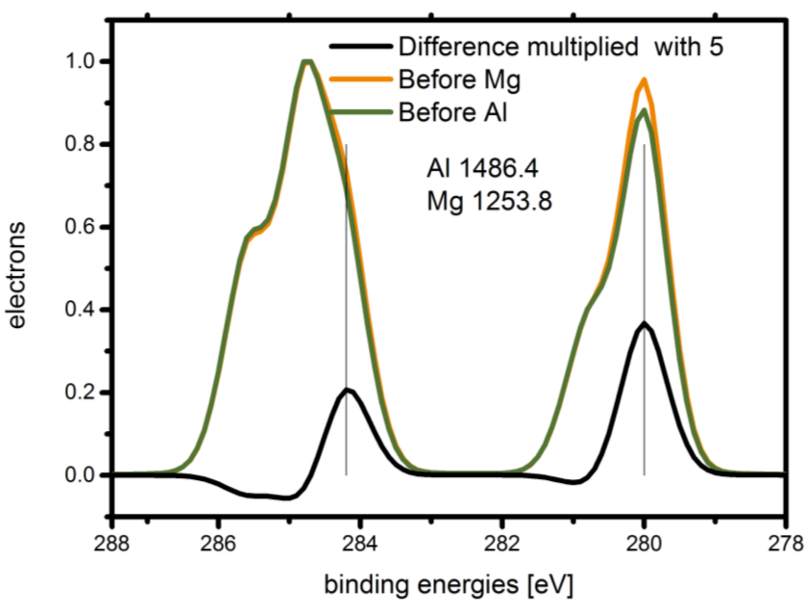


Haensel, T. et al.
physica status solidi A, **2009**, *206*, 2022-2027

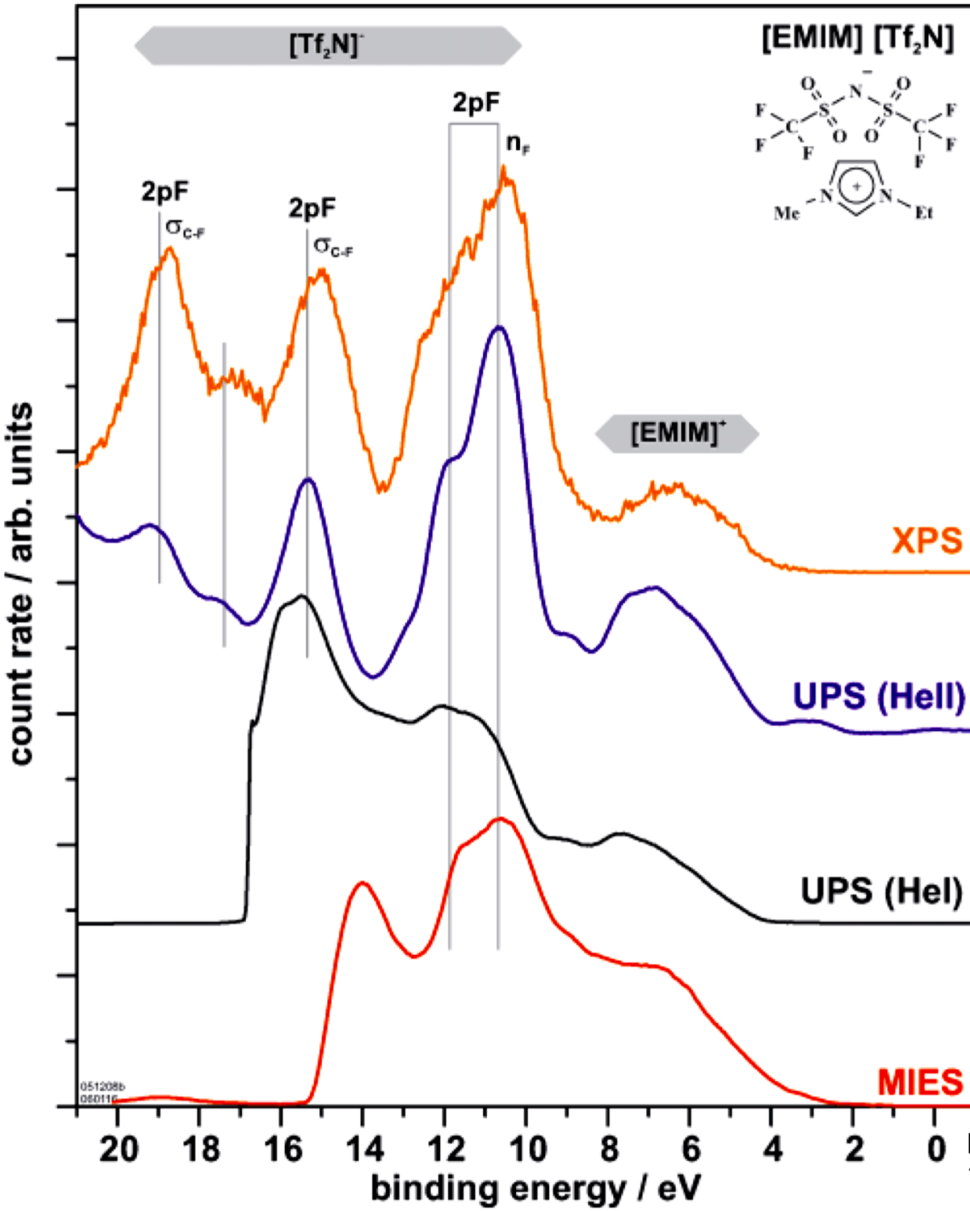
How to analyze XPS



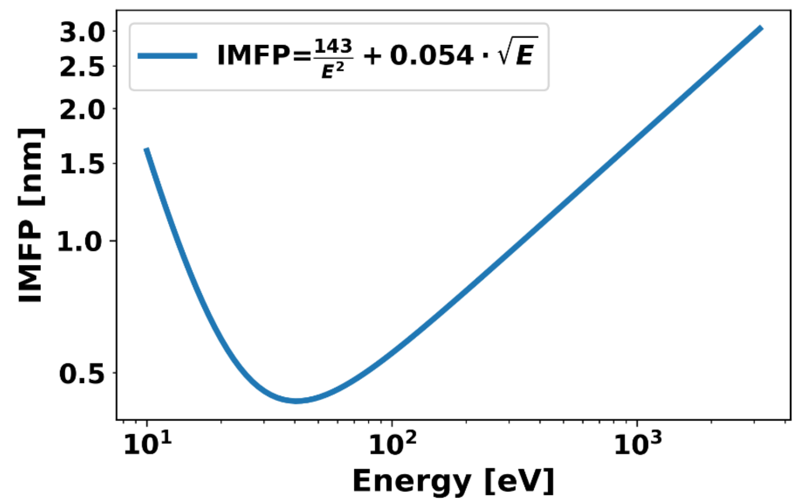




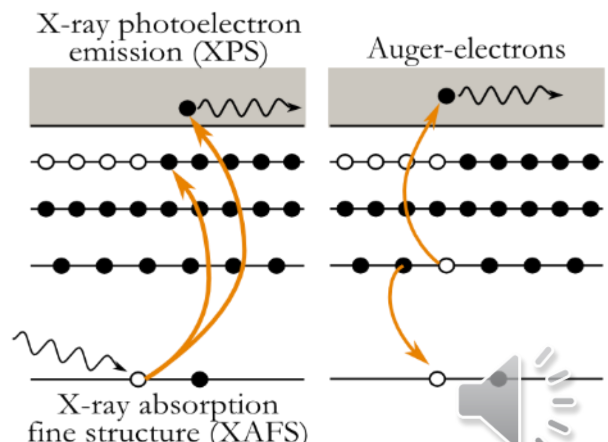
XPS/UPS surface sensitivity on Ionic liquids

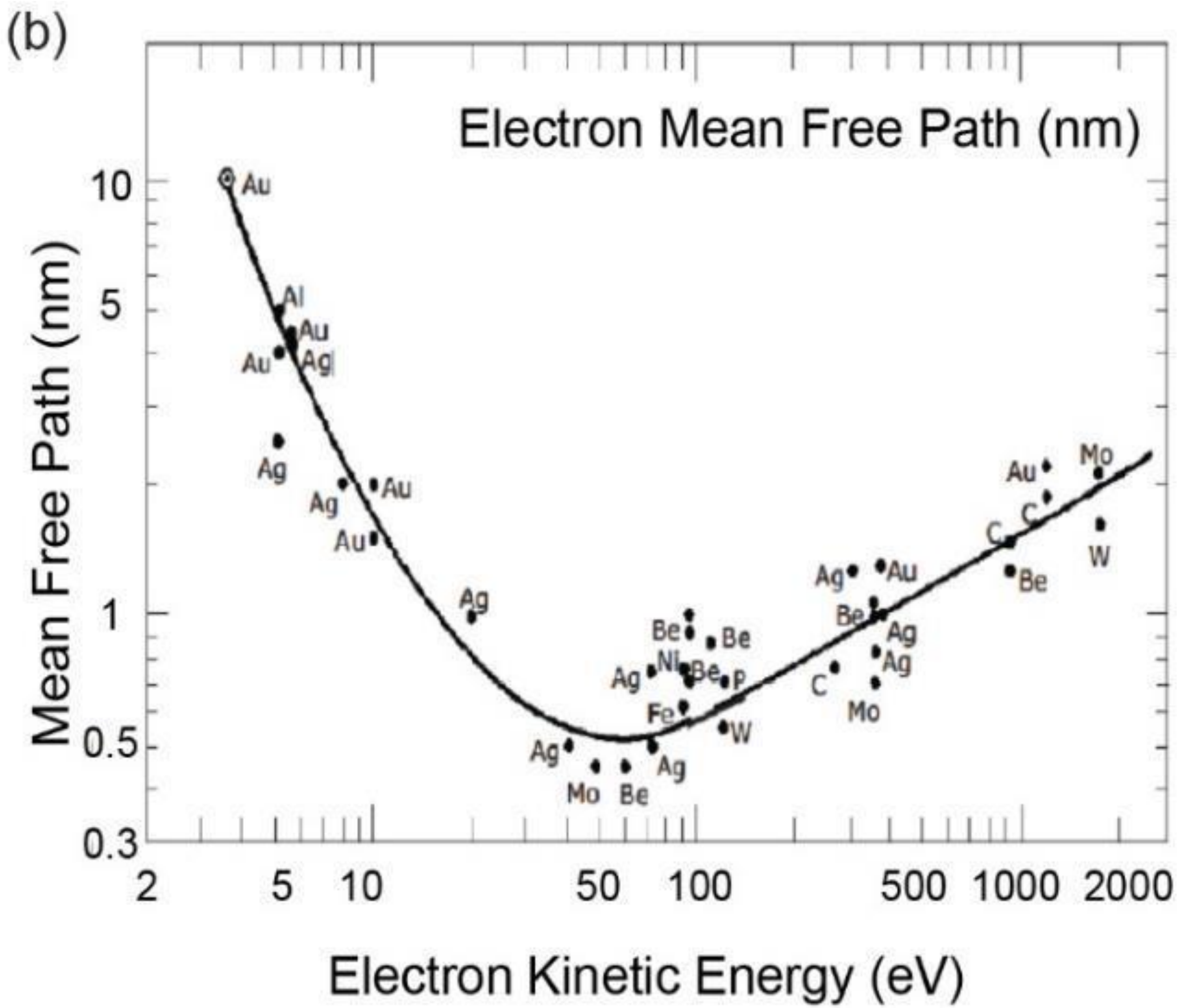


Krischok, S. et al.
The Journal of Physical Chemistry B, **2007**, *111*, 4801-6

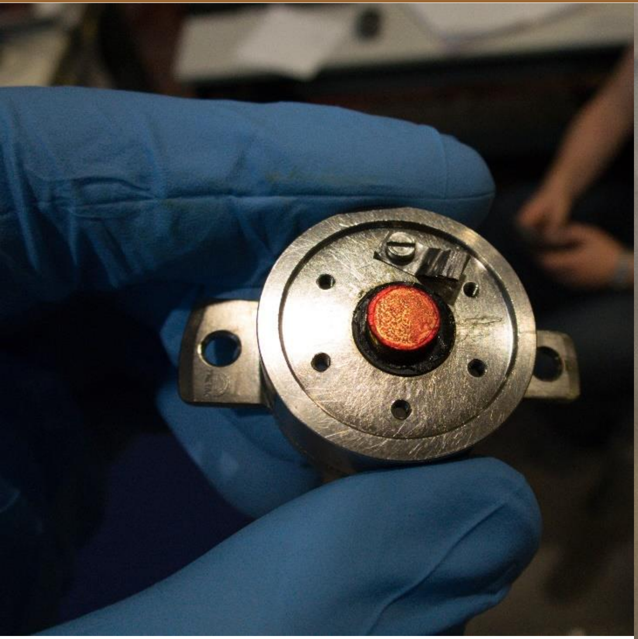


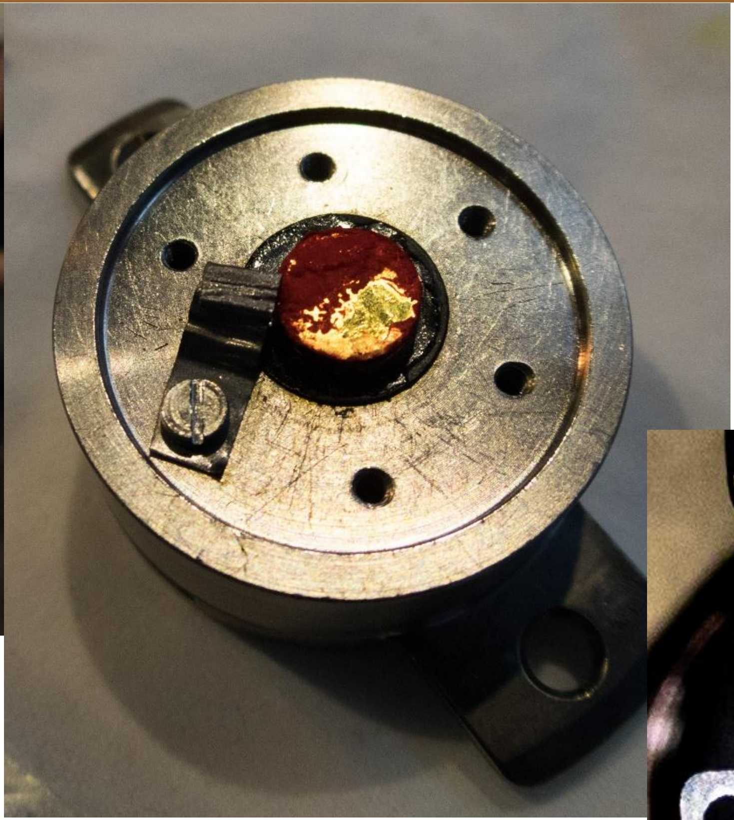
Formula (for all materials) after Seah & Dench
Surface and Interface Analysis, Wiley, 1979, 1, 2-11

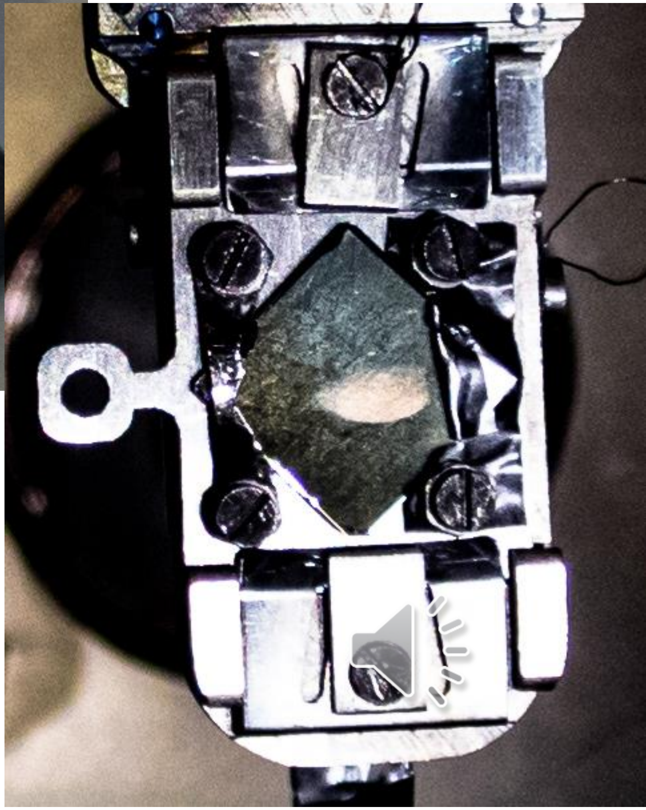



(b)
Electron Mean Free Path (nm)
Mean Free Path (nm)
Electron Kinetic Energy (eV)
10
5
1
0.5
0.3
2
5
10
50
100
500
1000
2000
Au
Al
Au
Au
Ag
Ag
Ag
Au
Au
Ag
Ag
Mo
Be
Ag
Be
Be
Ni
Be
P
Fe
W
Ag
C
Mo
Ag
Au
Be
Ag
Ag
C
Be
C
Au
Mo
W

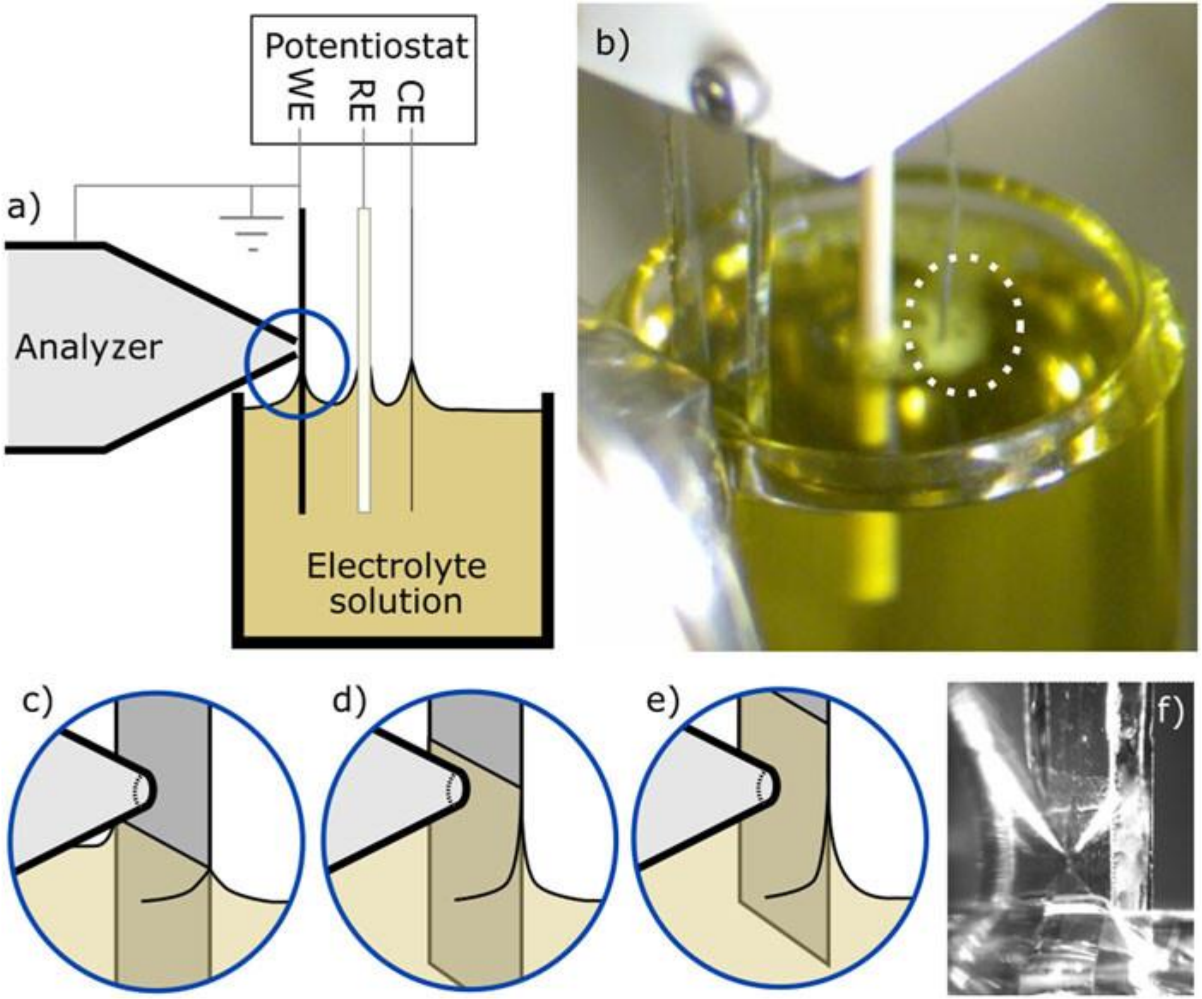
XPS/UPS/MIES



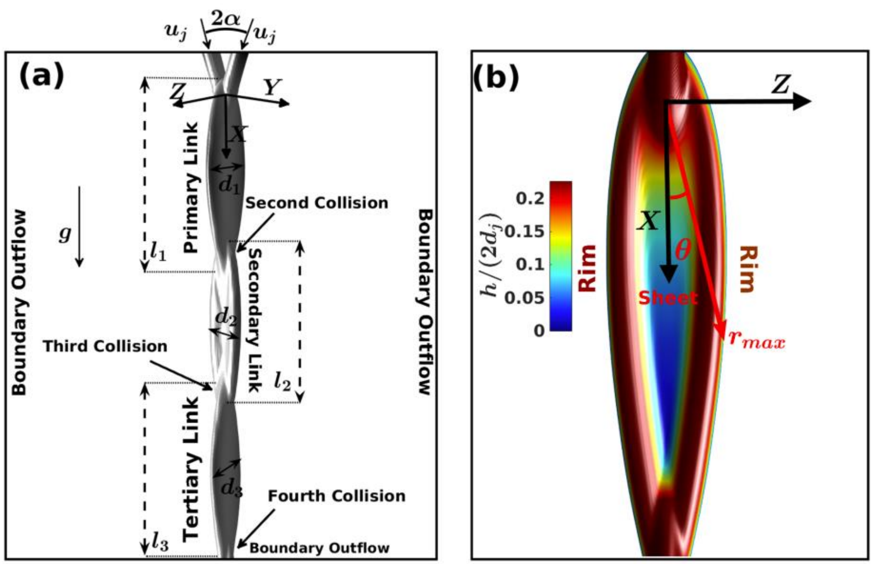




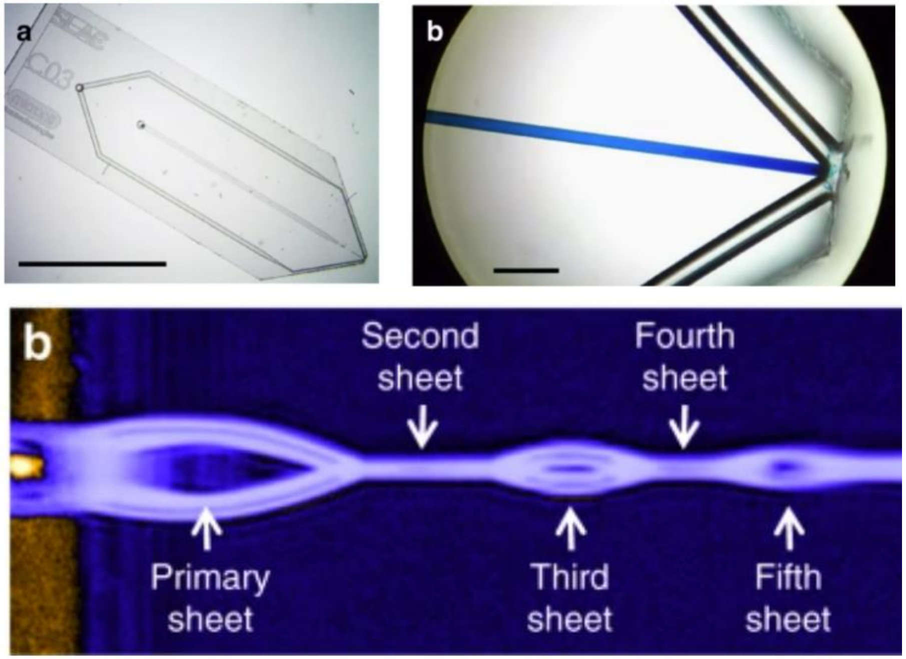
XPS/UPS/MIES



a)
Potentiostat
WE
RE
CE
Analyzer
Electrolyte
solution
b)
c)
d)
e)
f)

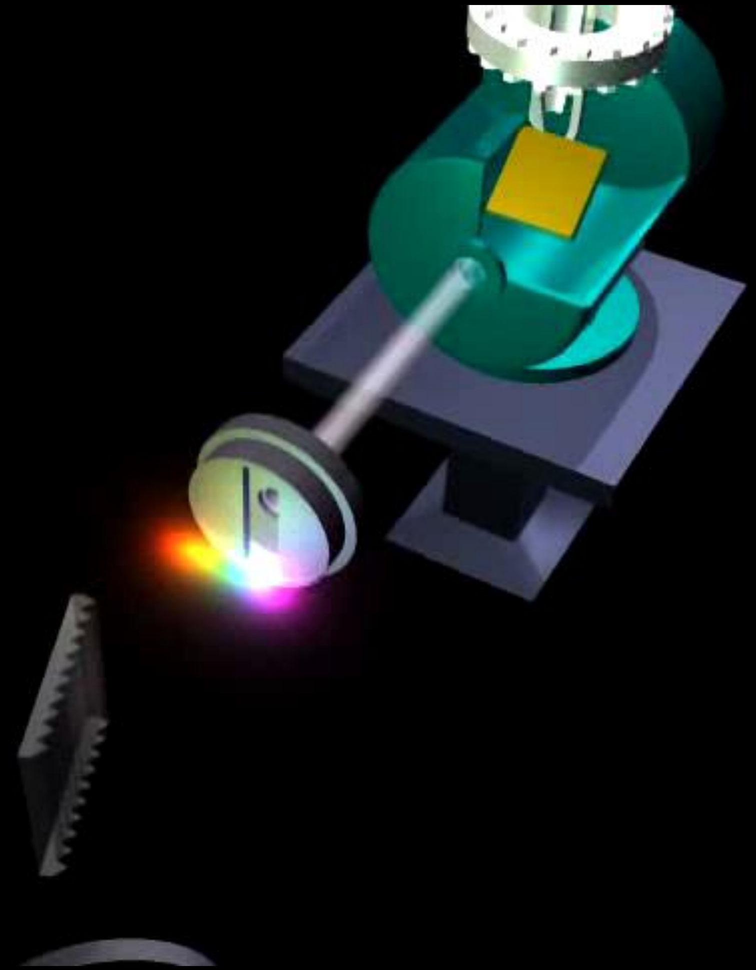


Physics of Fluids 29, 112101 (2017)
https://doi.org/10.1063/1.4998288



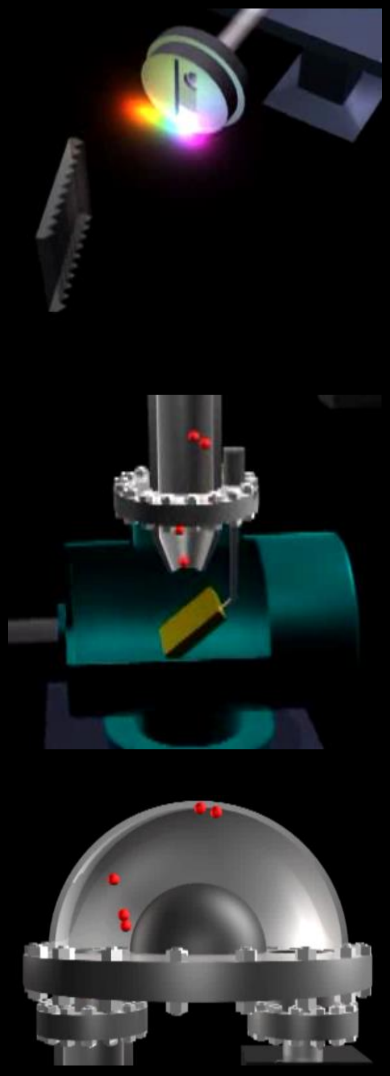
Nat Commun **9**, 1353 (2018).
https://doi.org/10.1038/s41467-018-03696-w

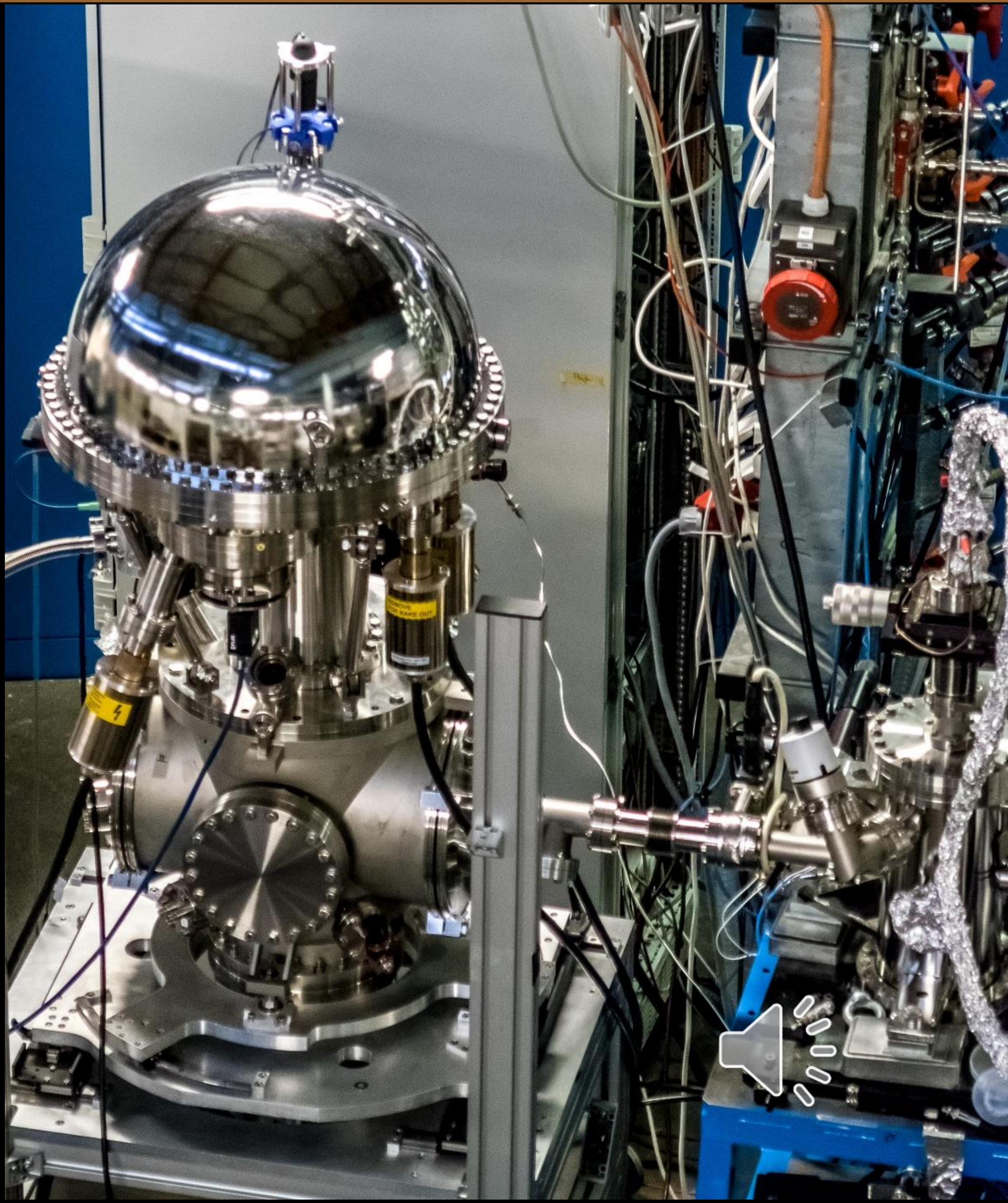
Video XPS



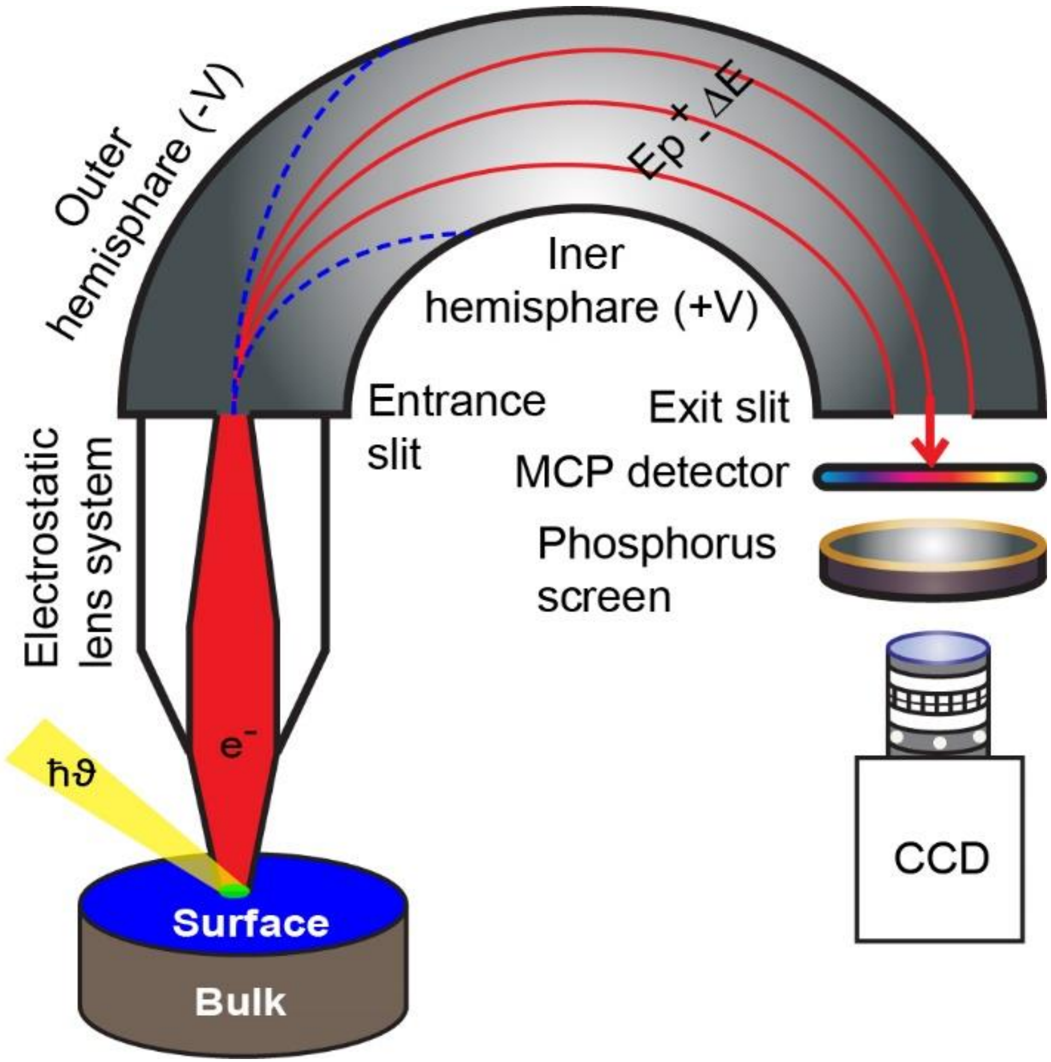
ISA, Centre for Storage Ring Facilities, Aarhus
https://www.isa.au.dk/animations/animations.asp
Accessed May 11 2020

XPS electron energy Analyser



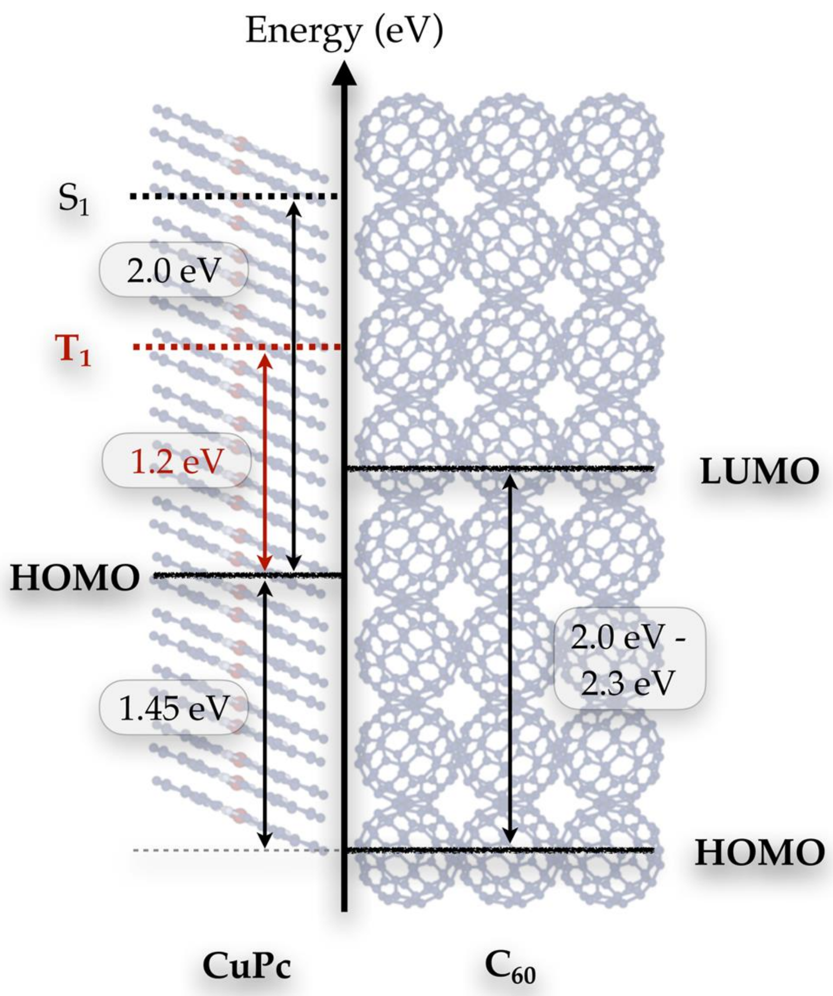


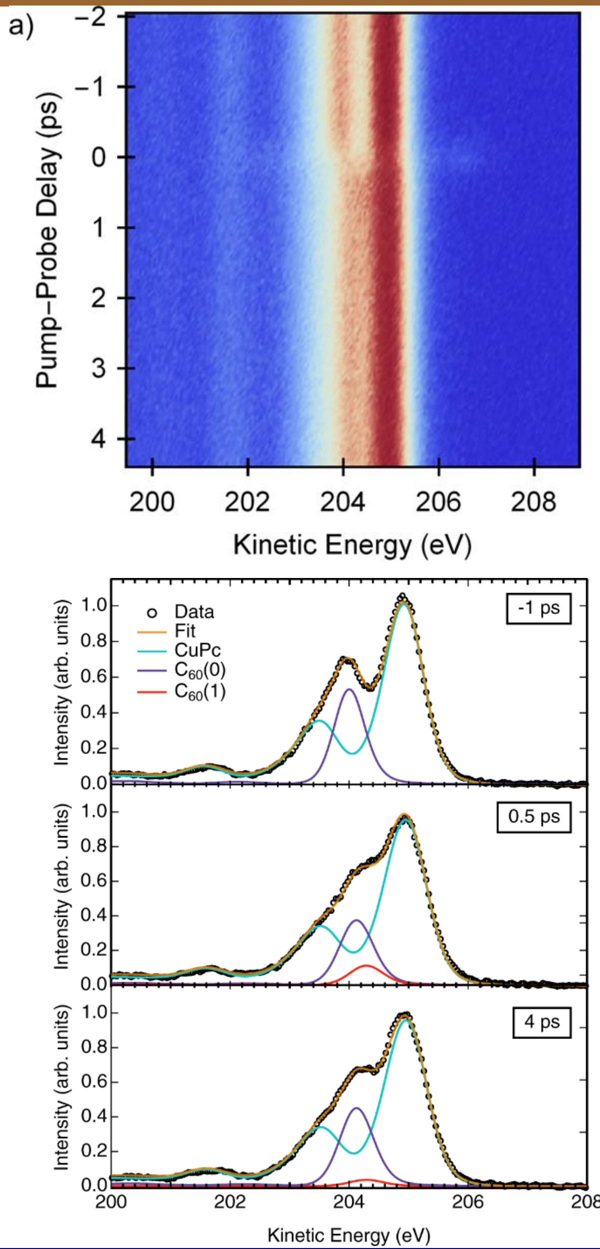
XPS/UPS/MIES



Outer hemisphare (-V)
Ep + - ΔE
Iner hemisphare (+V)
Entrance slit
Exit slit
MCP detector
Phosphorus screen
Electrostatic lens system
e⁻
ħϑ
Surface
Bulk
CCD

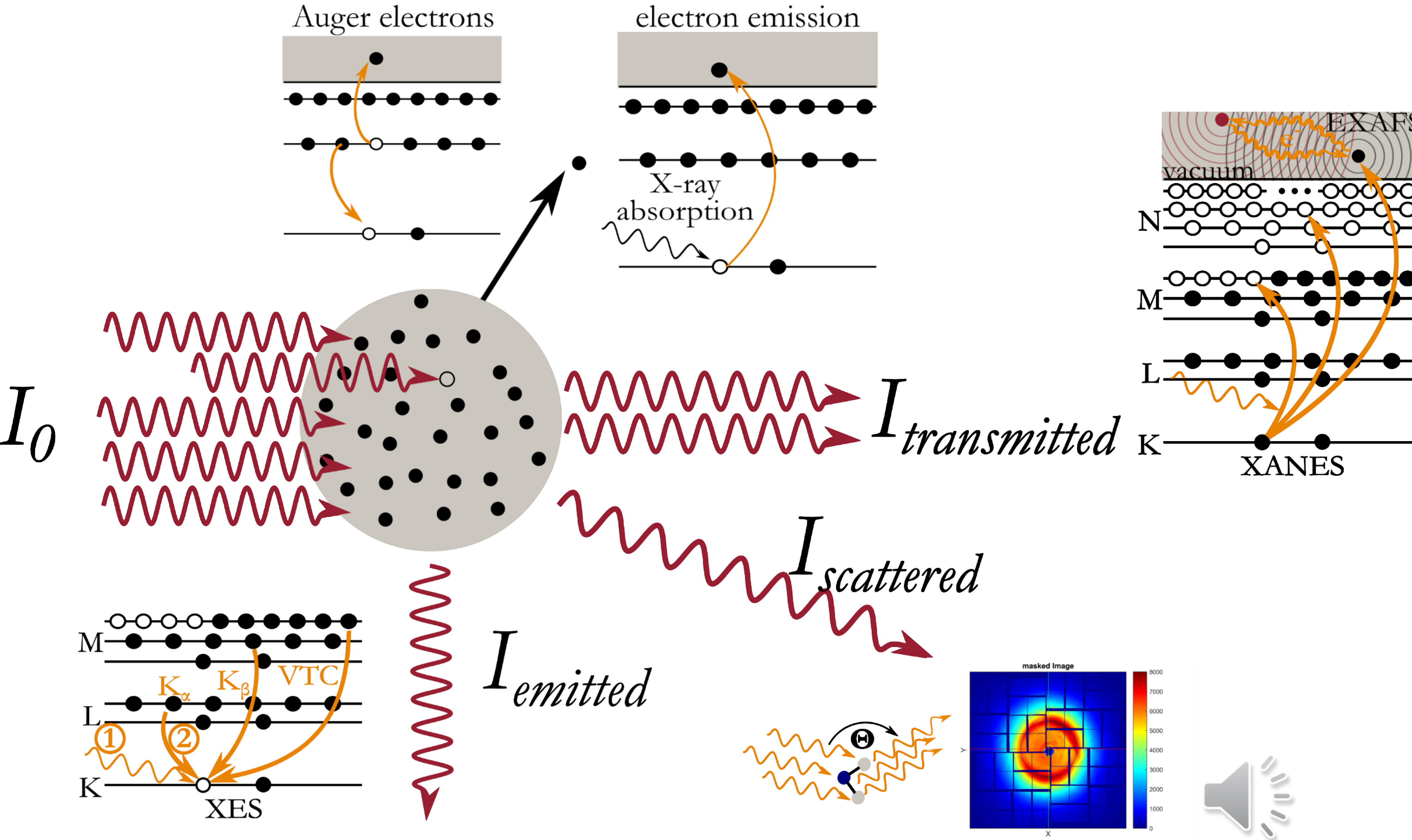
XPS at FLASH (fs)





Nat Commun **12**, 1196 (2021).
https://doi.org/10.1038/s41467-021-21454-3

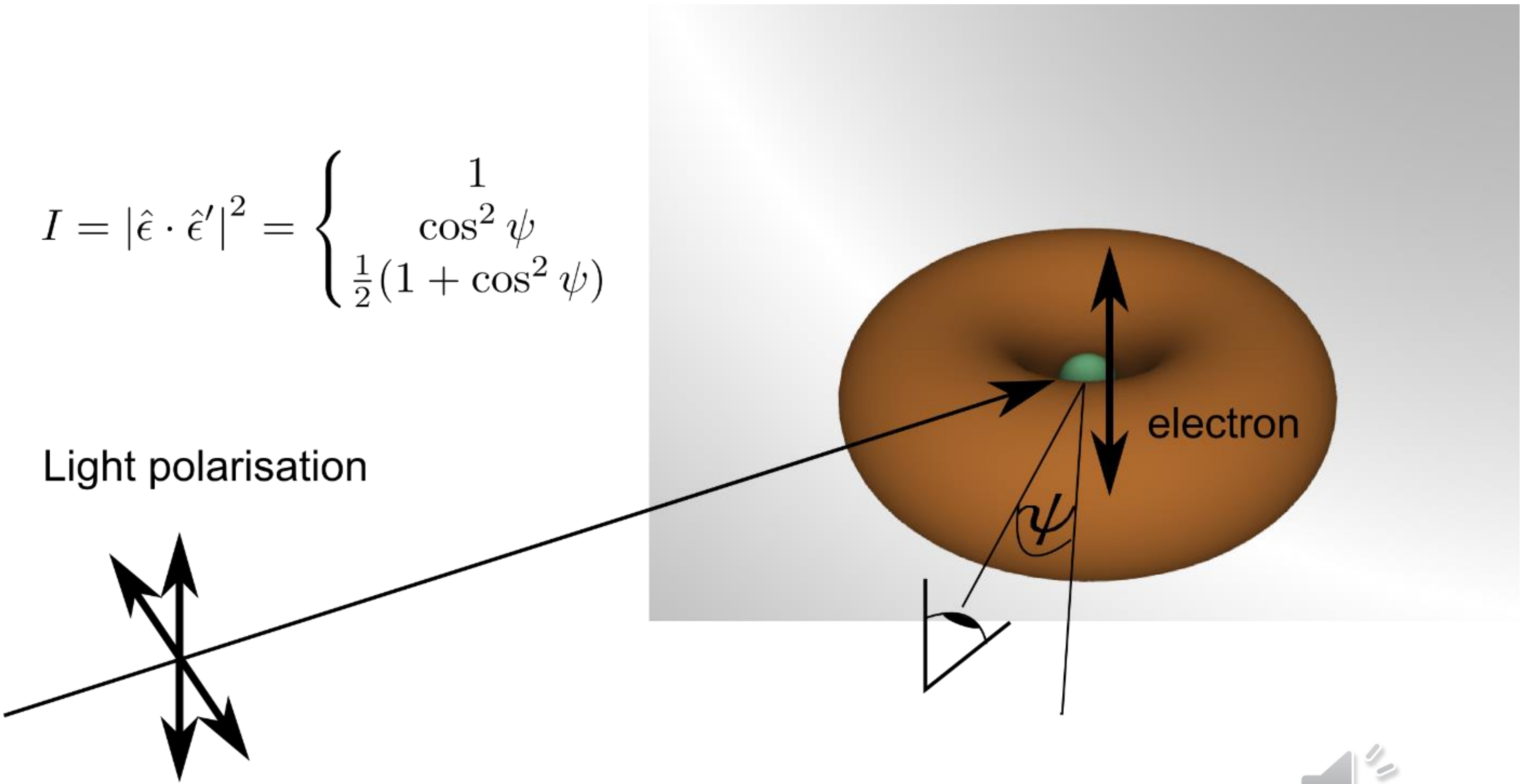
Interactions with light, most of them

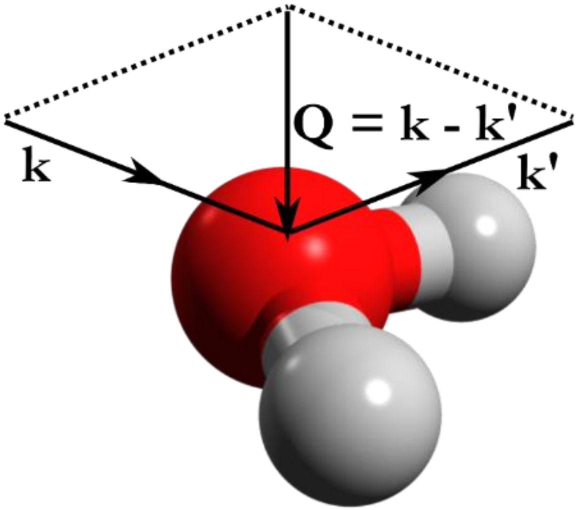


$$I_0 = I_{transmitted} + I_{absorbed} + I_{scattered}$$

Electron scattering factor

$$I = |\hat{\epsilon} \cdot \hat{\epsilon}'|^2 = \begin{cases} 1 \\ \cos^2 \psi \\ \frac{1}{2}(1 + \cos^2 \psi) \end{cases}$$

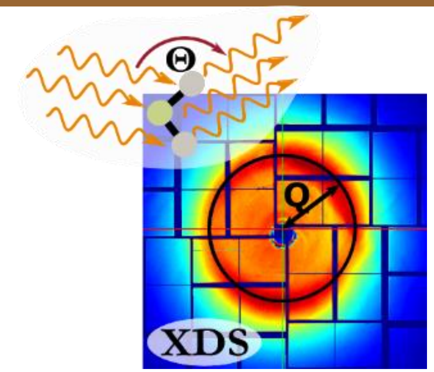


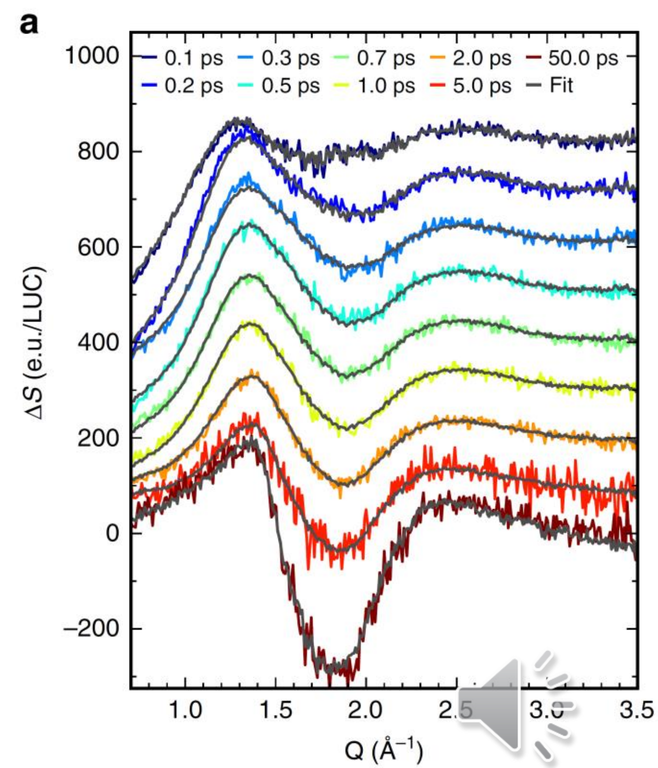


electron density as function of r

Single atom $f^0(\mathbf{Q}) = \int \rho(\mathbf{r}) e^{i\mathbf{Q}\mathbf{r}} d\mathbf{r}$

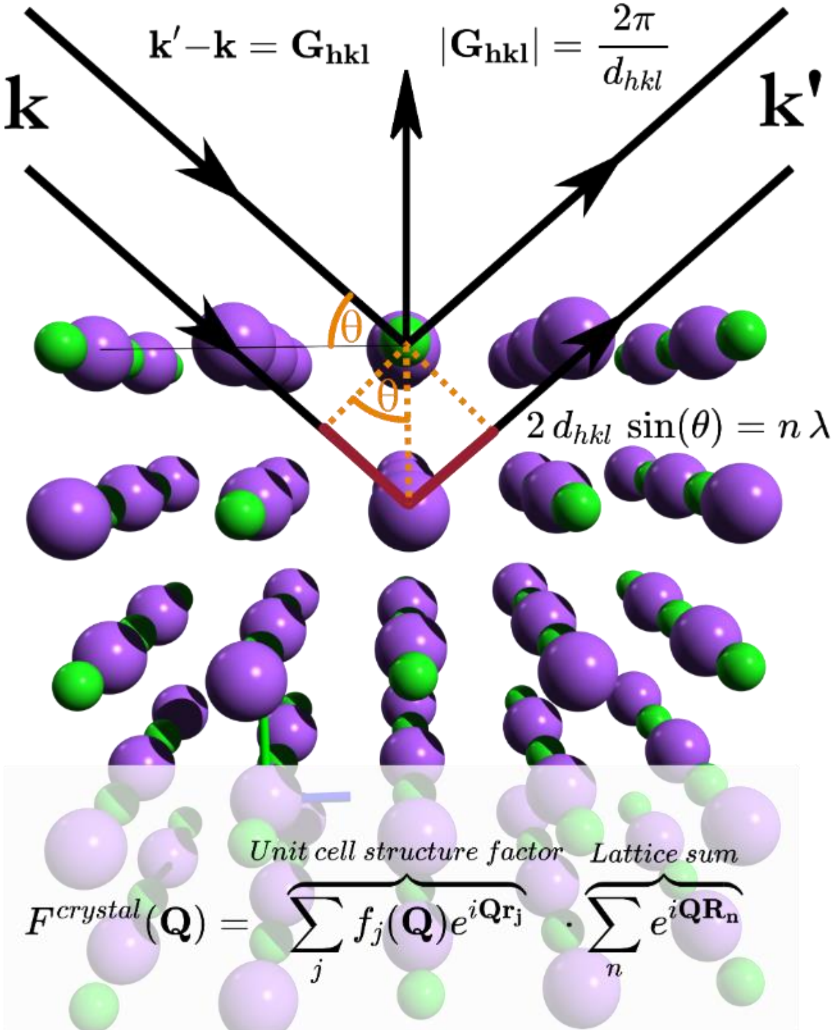
phase difference between different volume elements

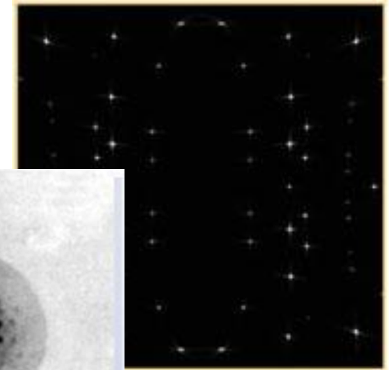




Kunnus et al. *Nature Communications* **11**, 634 (2020).

Crystal scattering

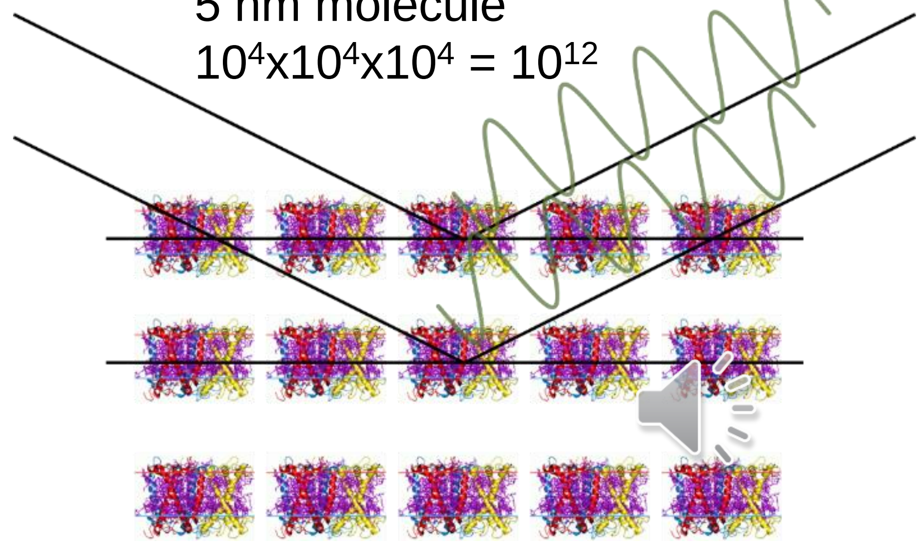




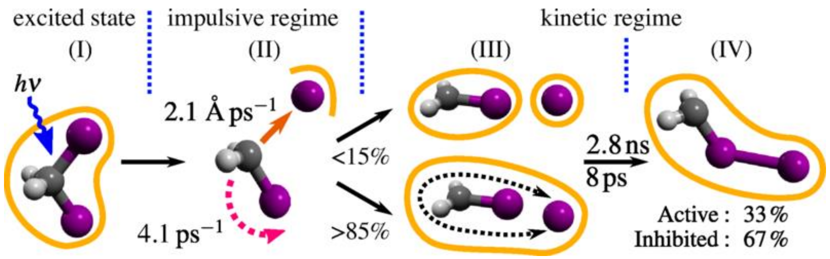
First X-ray diagramme by Laue in 1912.

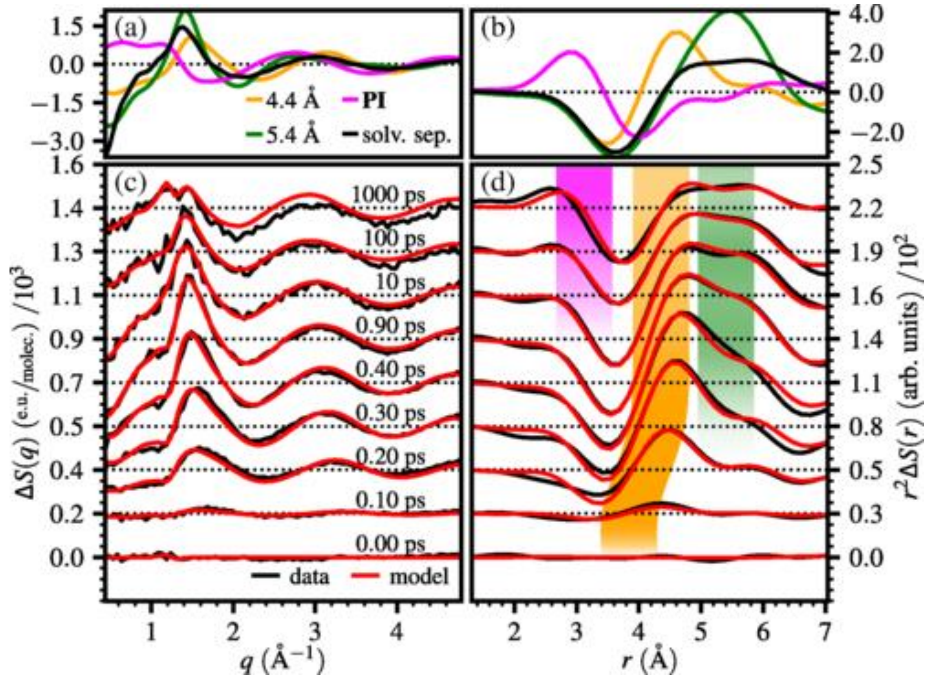
$V(H_2PO_4)_3$

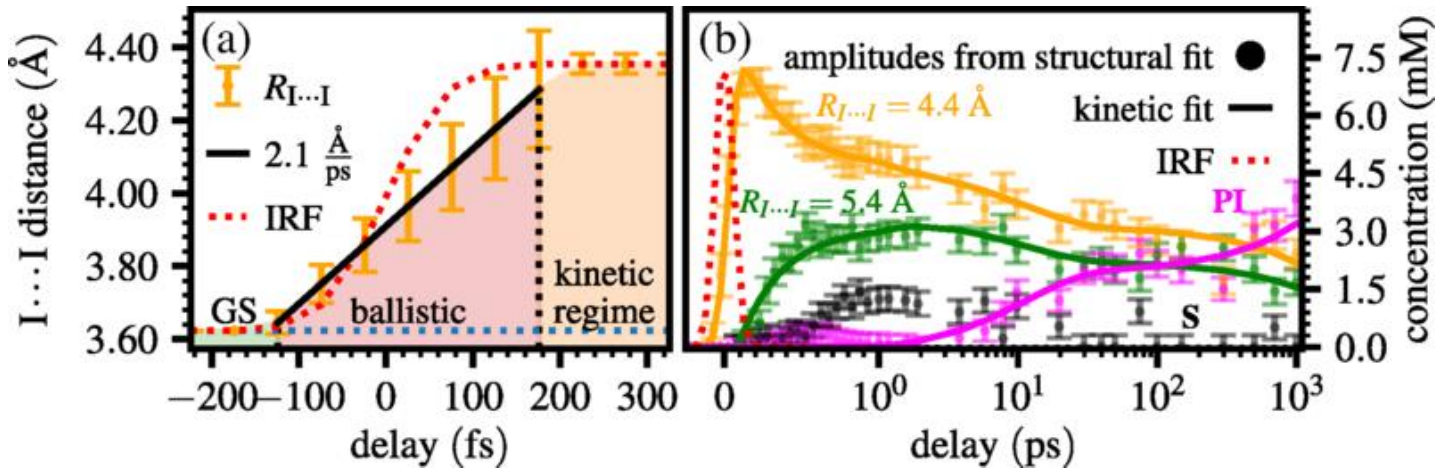
50 µm crystal
5 nm molecule
$10^4 x 10^4 x 10^4 = 10^{12}$



XDS – Diiodomethane

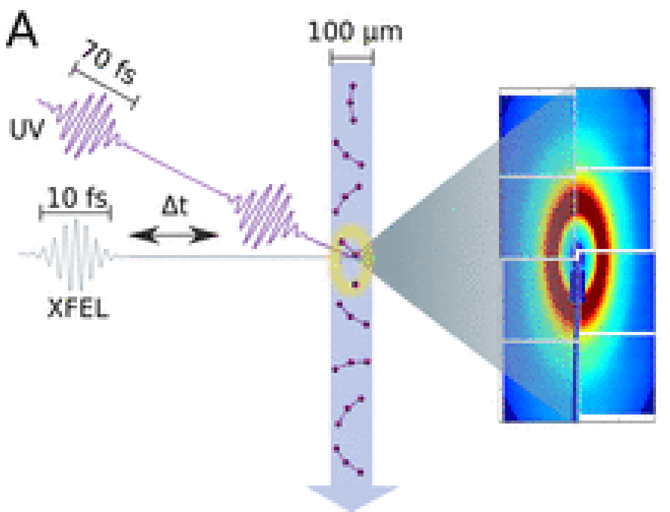


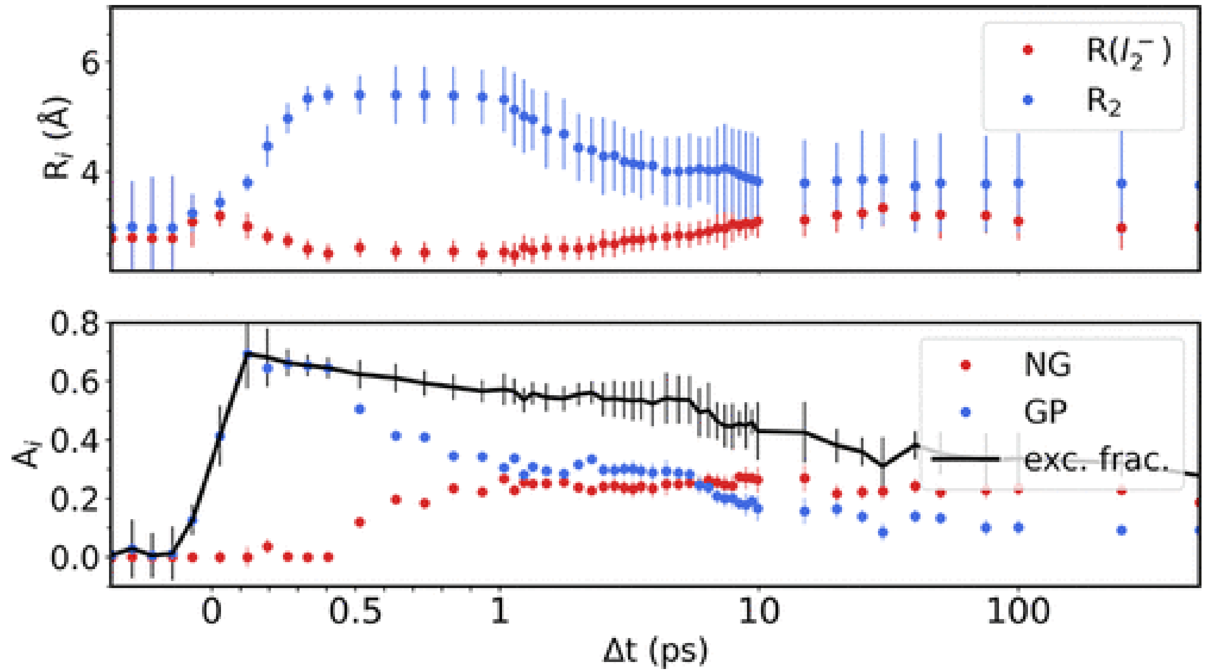


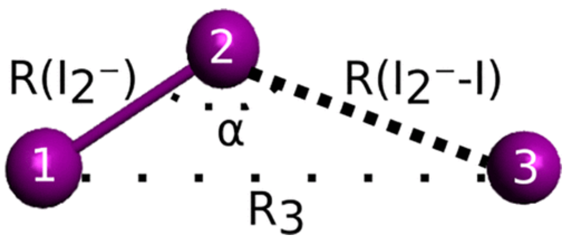


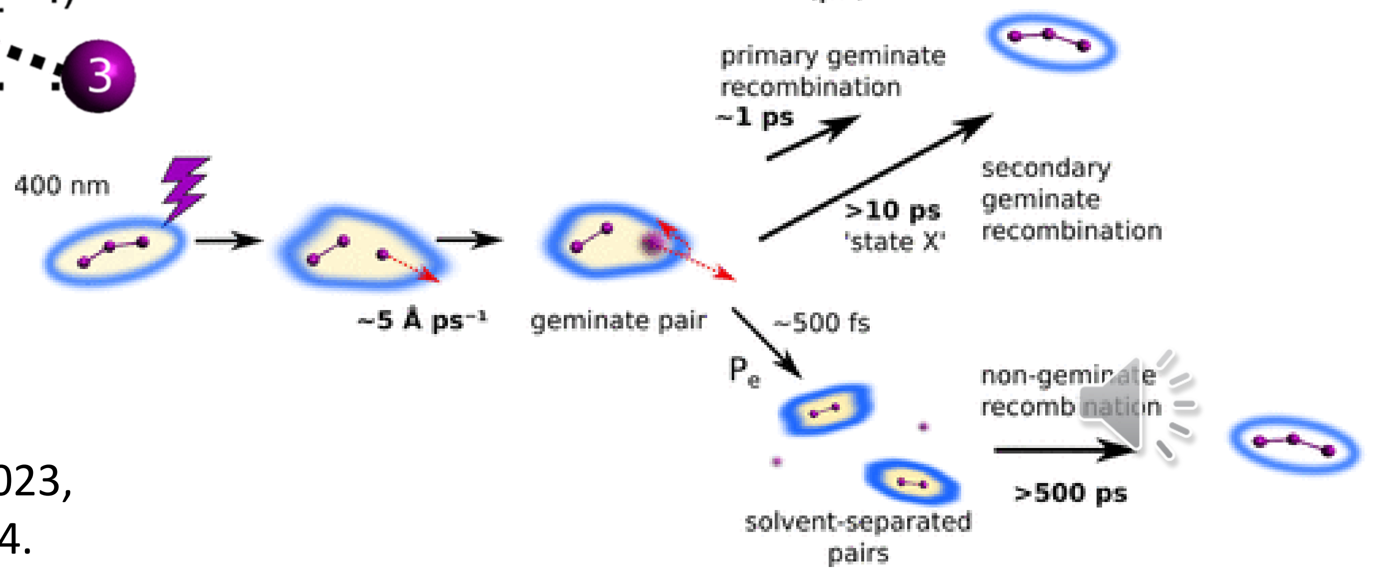
Phys. Rev. Lett. **125**, 226001(2020) https://doi.org/10.1103/PhysRevLett.125.226001

I3 solvent dependent geminate recombination 1



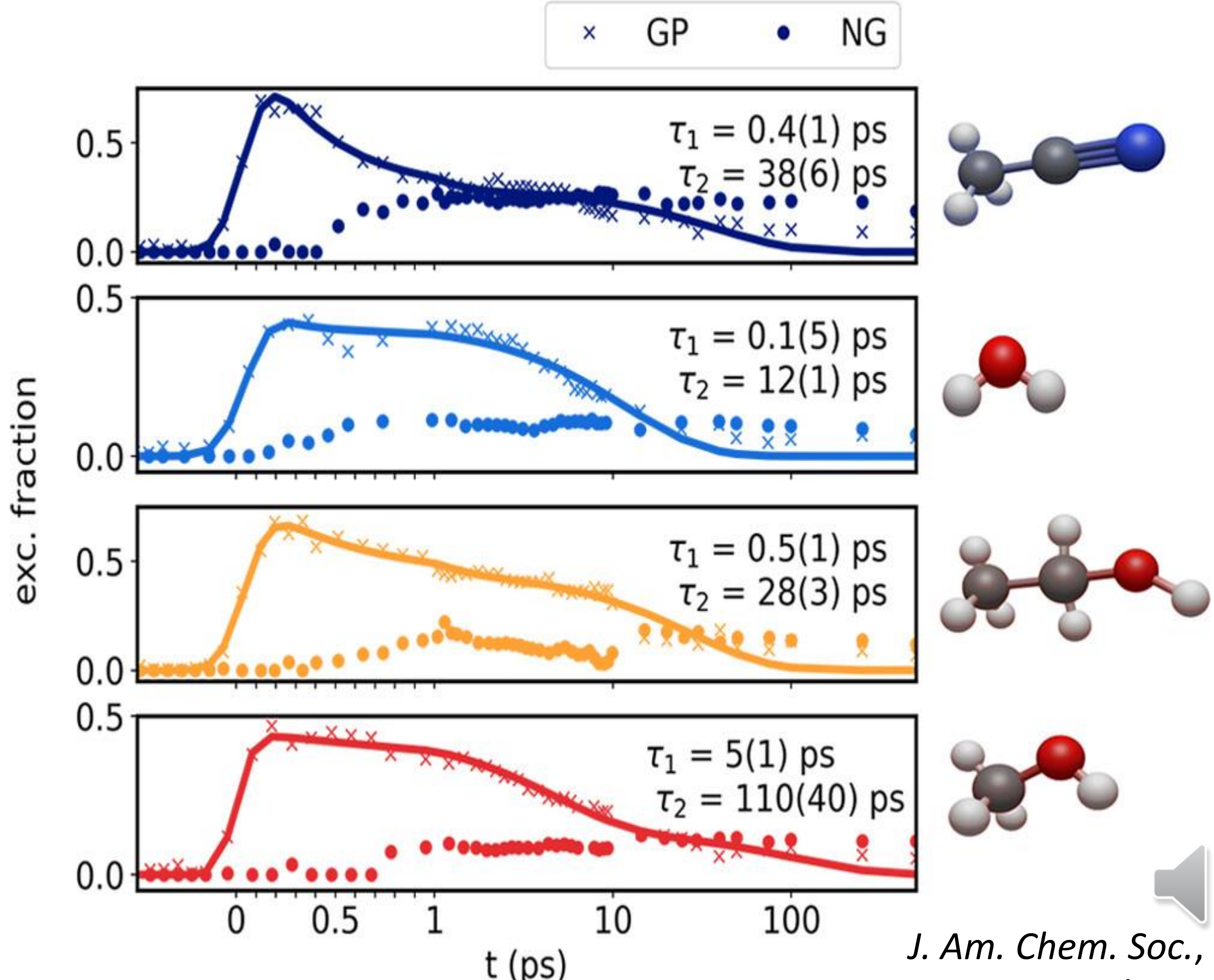






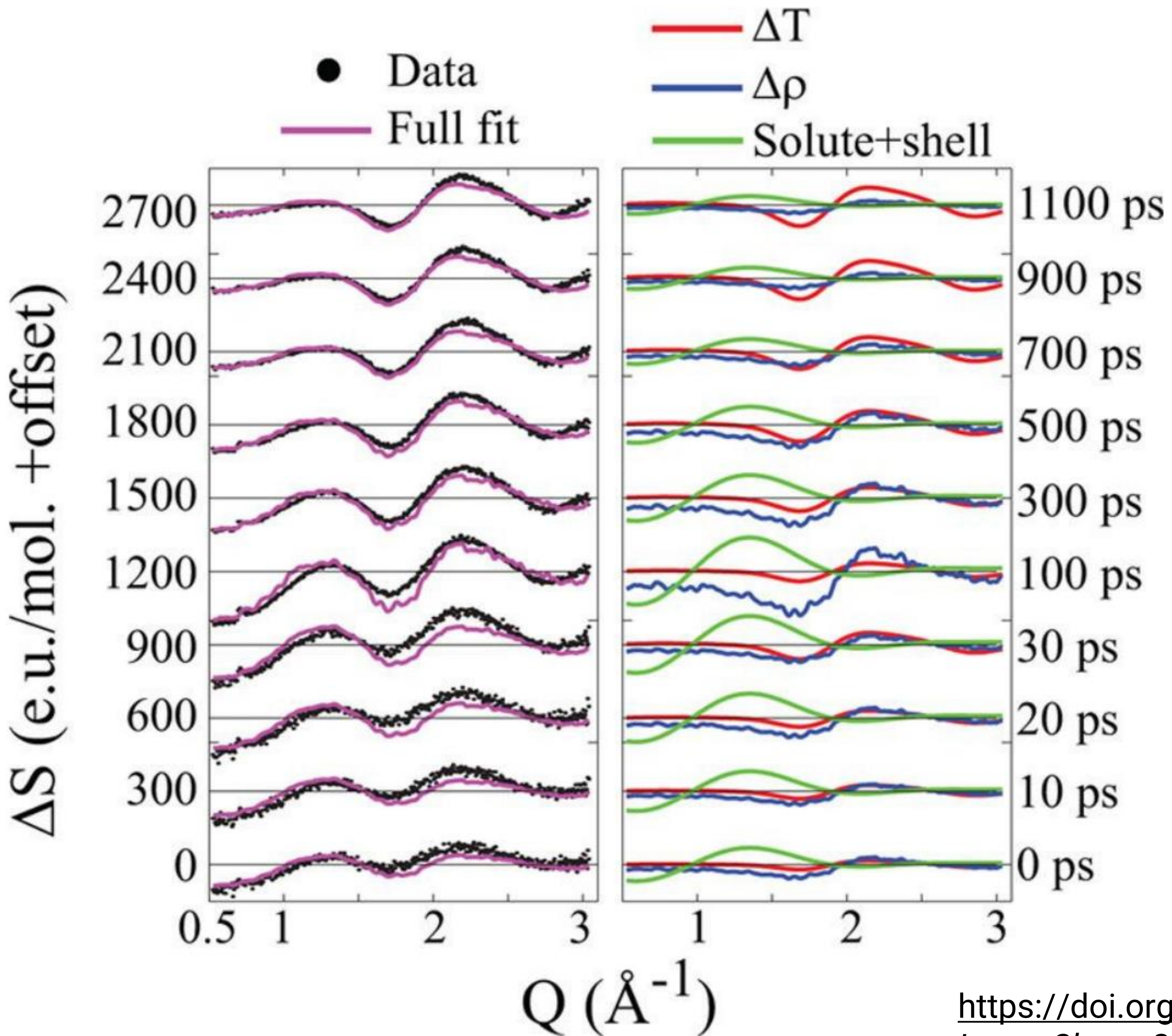
J. Am. Chem. Soc., May 2023,
doi: 10.1021/jacs.3c00484.

I3 solvent dependent geminate recombination 2



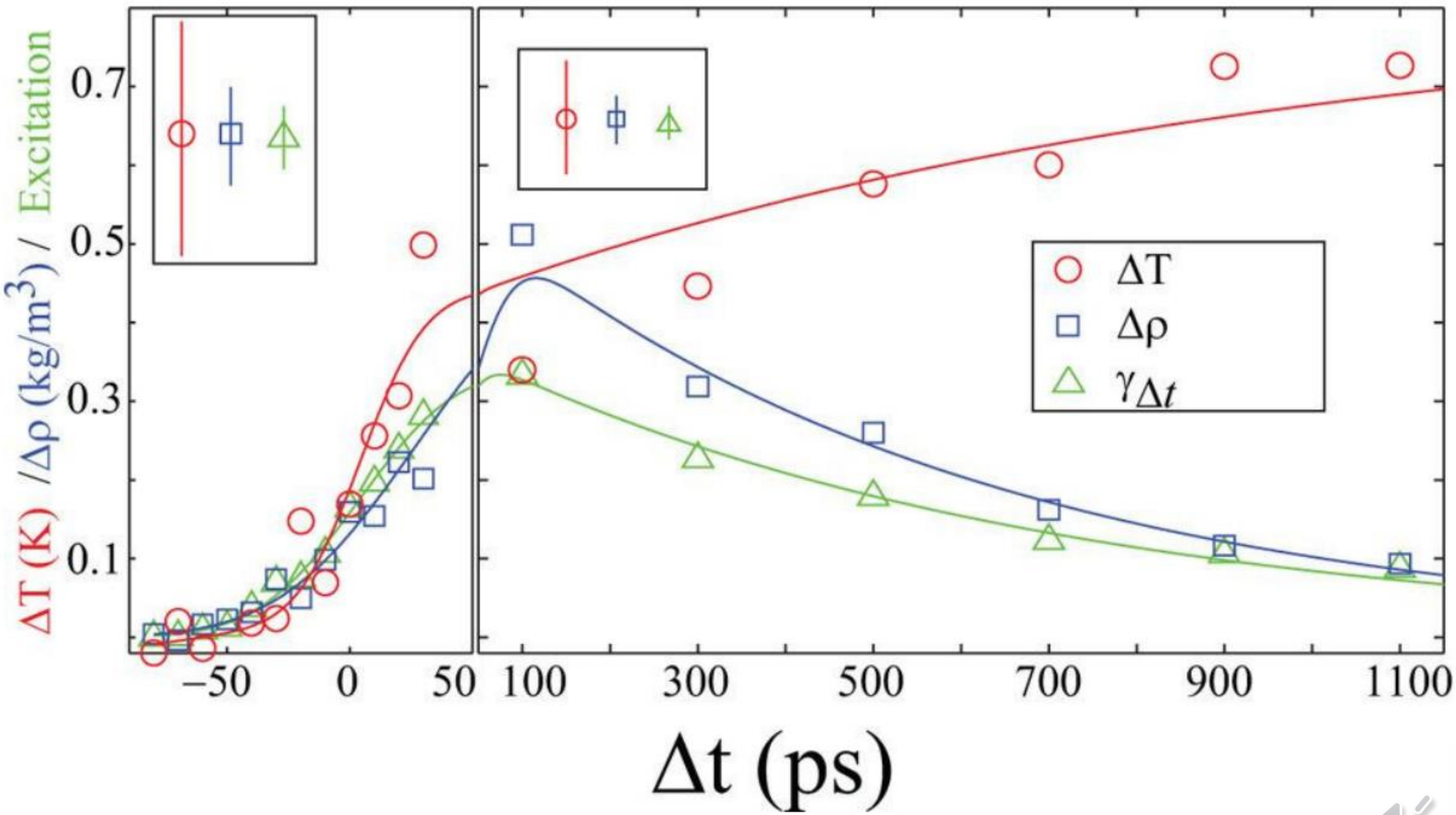
J. Am. Chem. Soc., May 2023, doi: 10.1021/jacs.3c00484.

Di-iridium vs solvent scattering



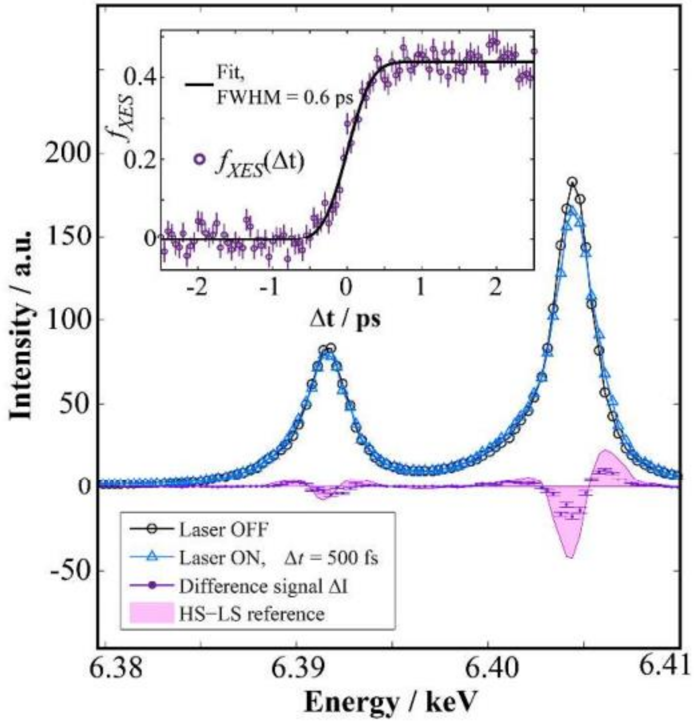
https://doi.org/10.1021/ic2006875
Inorg. Chem. 2011, 50, 19, 9329−9336

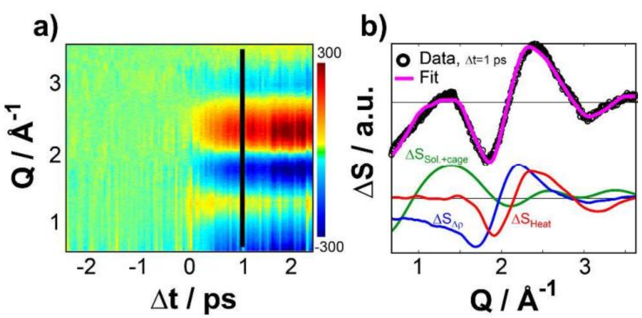
Di-iridium

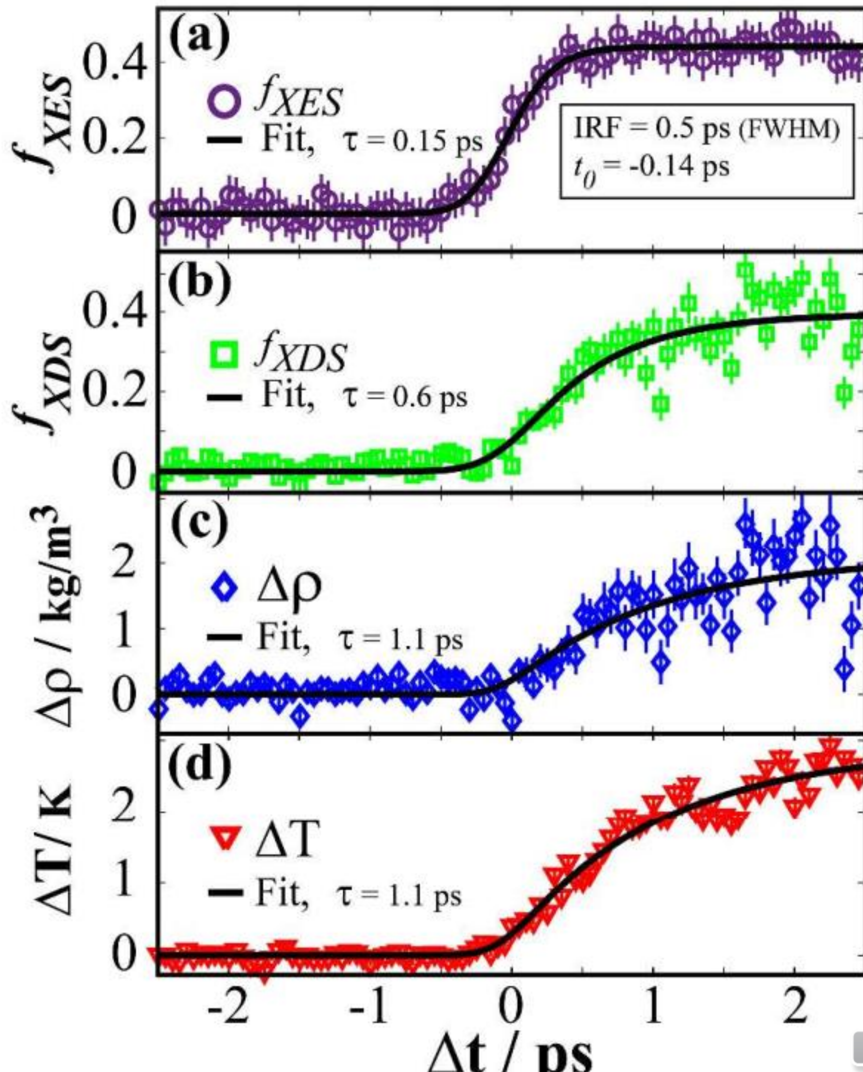


https://doi.org/10.1021/ic2006875
Inorg. Chem. 2011, 50, 19, 9329−9336

Iron Tris, Fe-N bond stretch

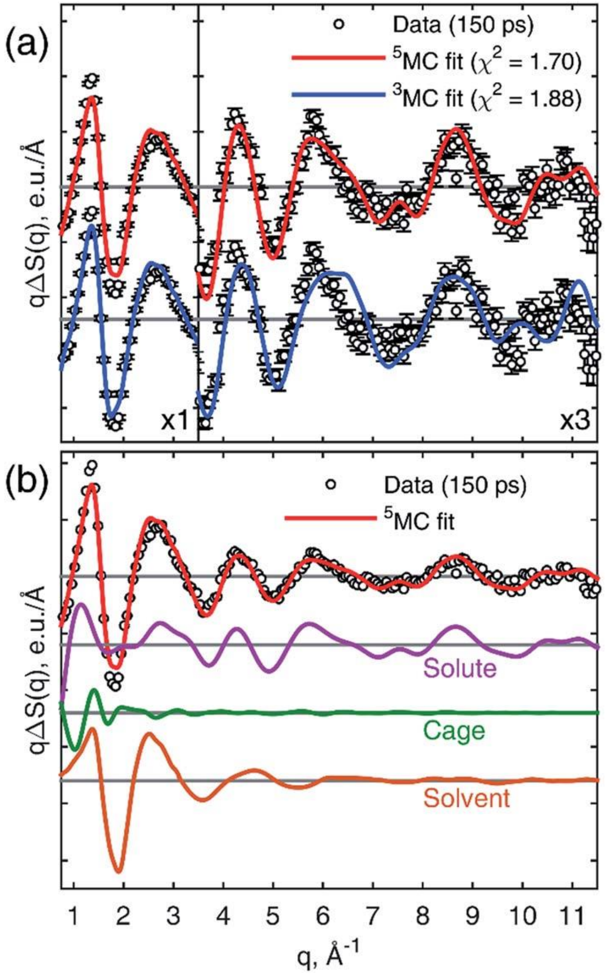


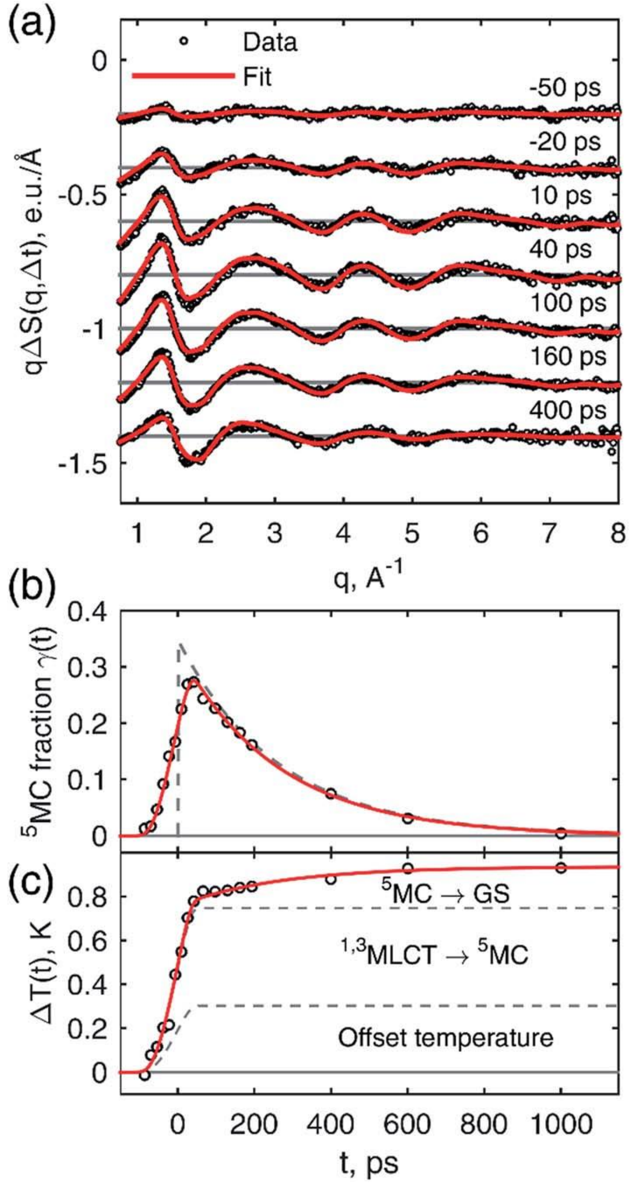


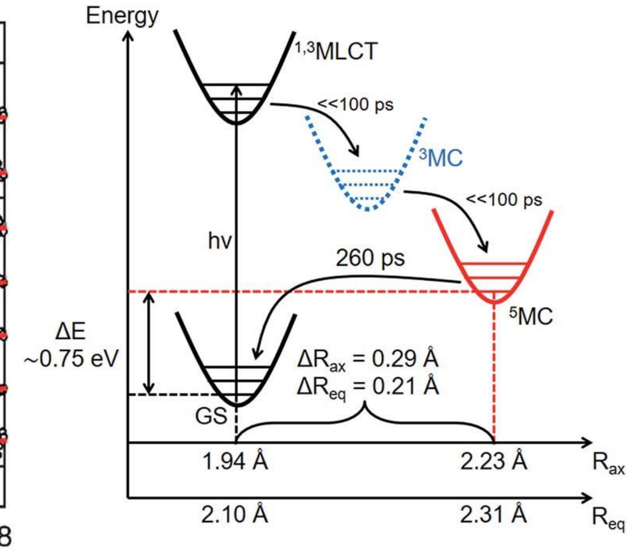


K. Haldrup et al., J. Phys. Chem. B, vol. 120, no. 6, pp. 1158–1168, Jan. 2016, doi: 10.1021/acs.jpcb.5b12471.

Iron CAB2 quintet energy, An expensive thermometer

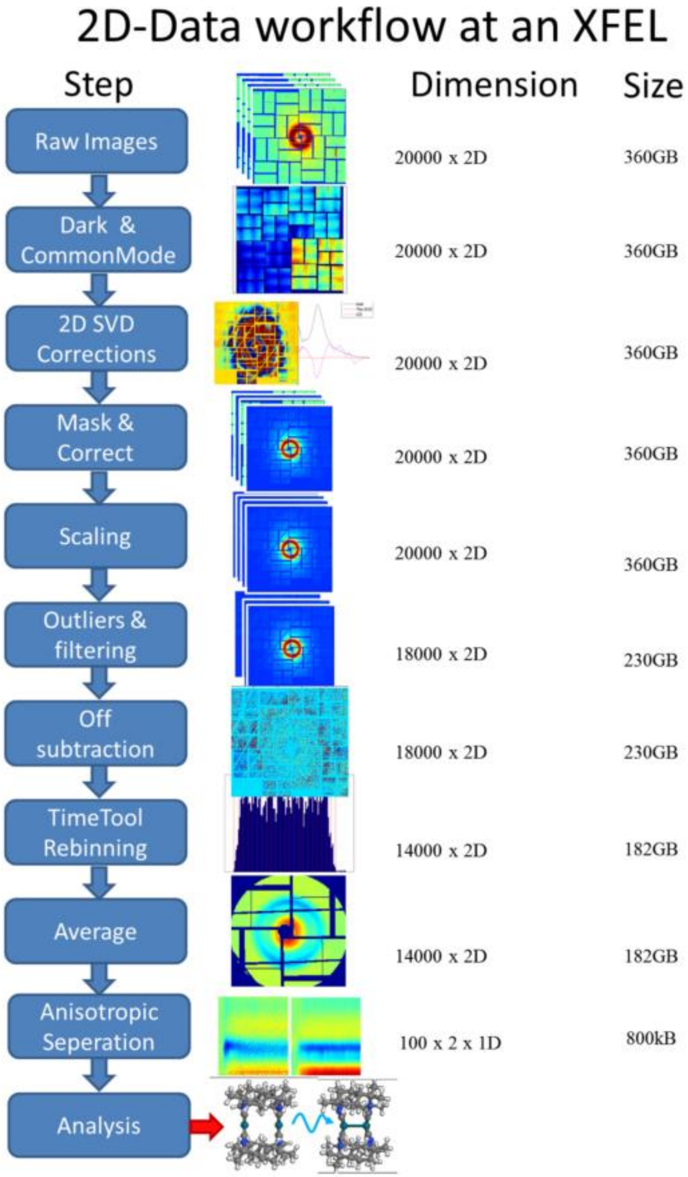


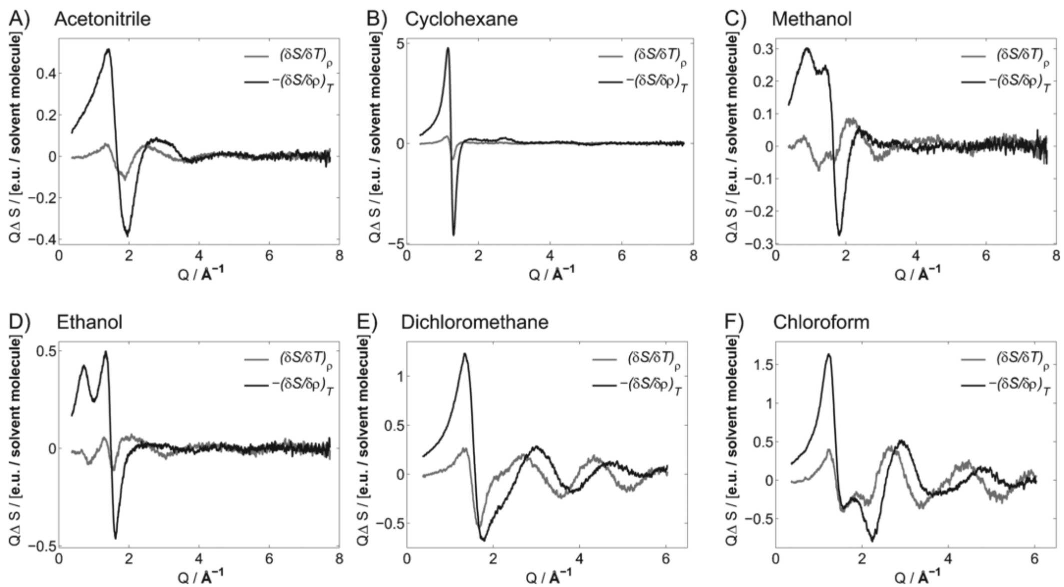




D. Leshchev et al. Chem. Sci., vol. 9, no. 2, pp. 405–414, 2018, doi: 10.1039/c7sc02815f.

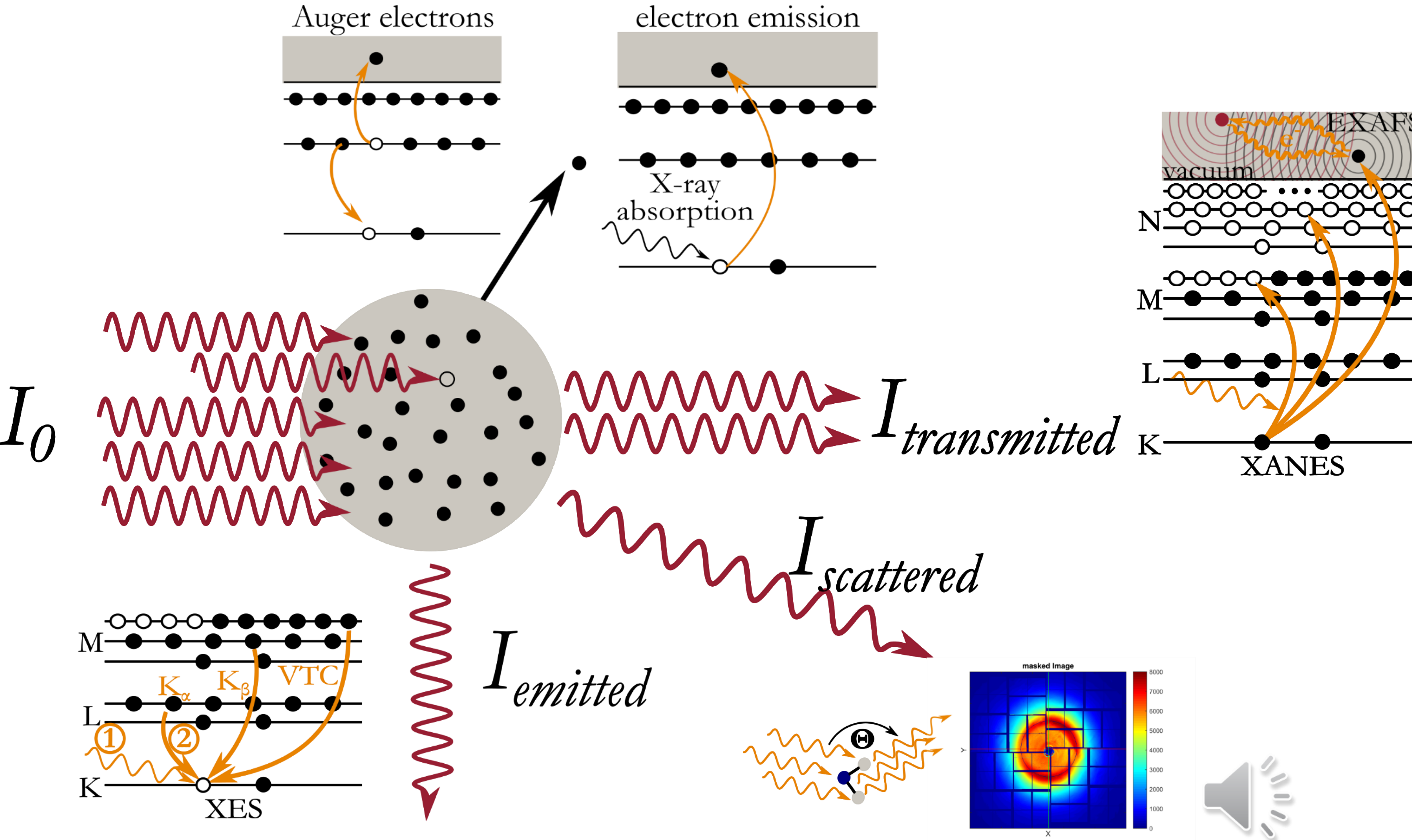
Data-extraction



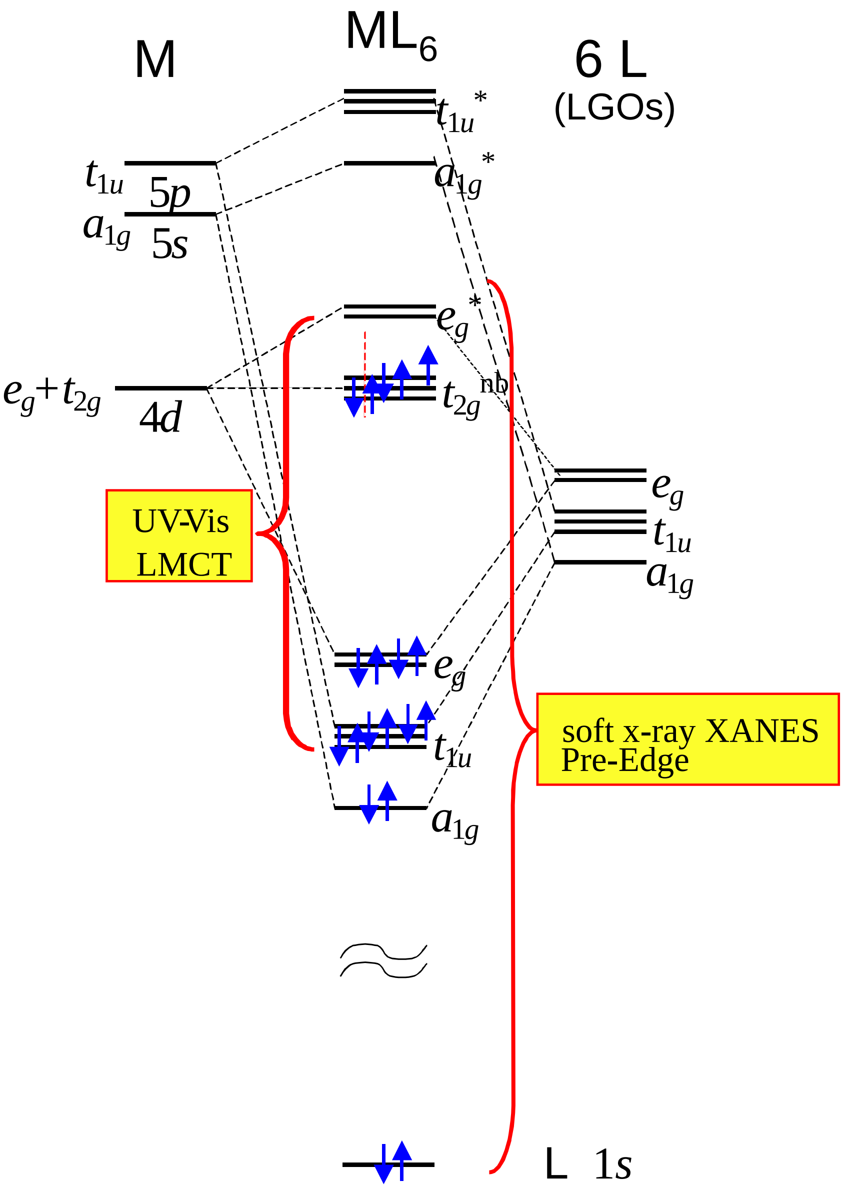


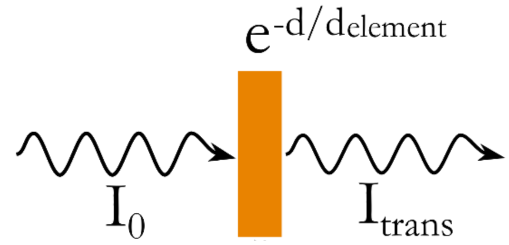
Tim Brandt van Driel
PhD Thesis 2014

Interactions with light, most of them



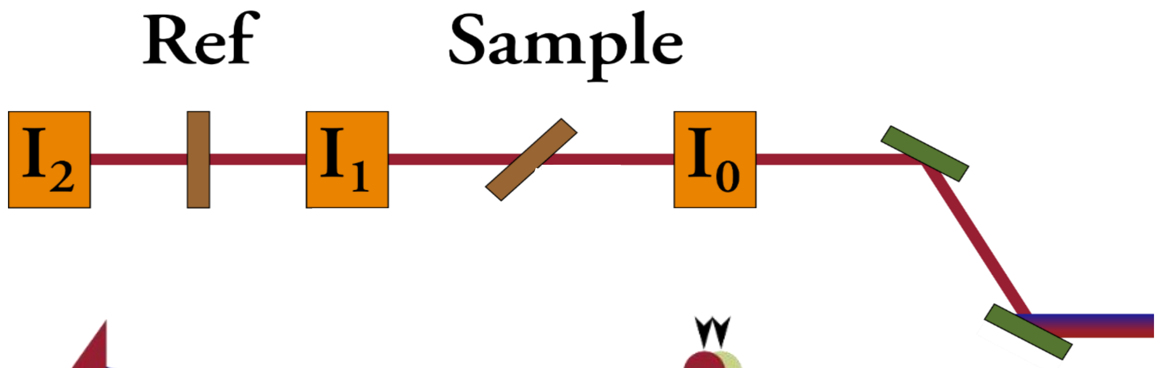
$$I_0 = I_{transmitted} + I_{absorbed} + I_{scattered}$$

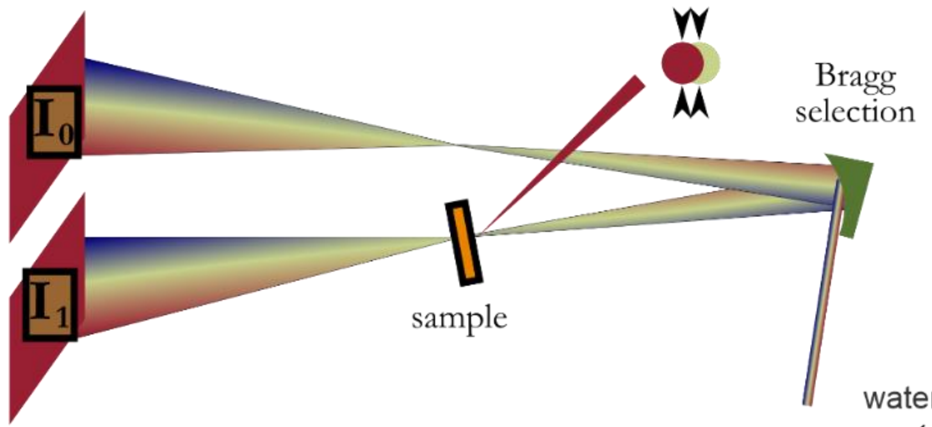




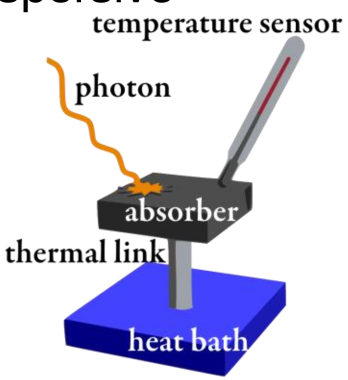
$$\Gamma = \frac{2\pi}{\hbar^2} \sum_{i,f} \left| \langle \Psi_f \,|\, \overrightarrow{\mu} \,|\, \Psi_i \rangle \right|^2 \delta(h\nu - E_f - E_i)$$

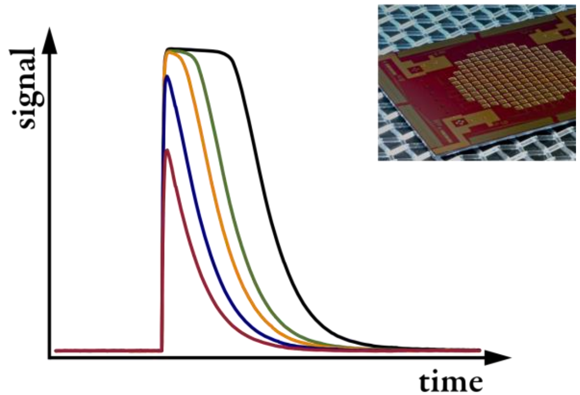
XAFS measurement process

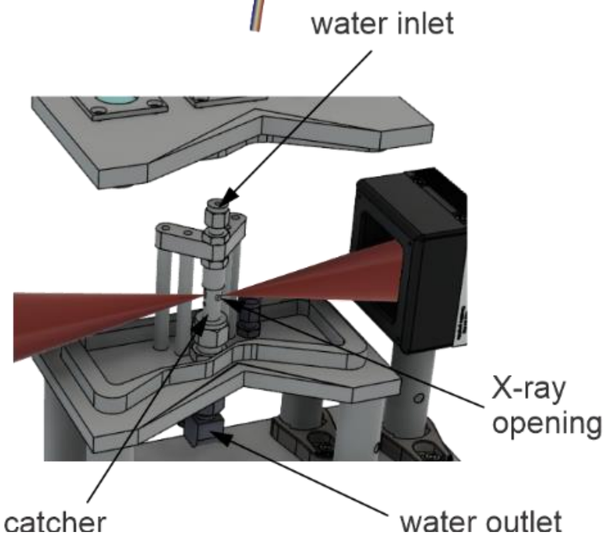


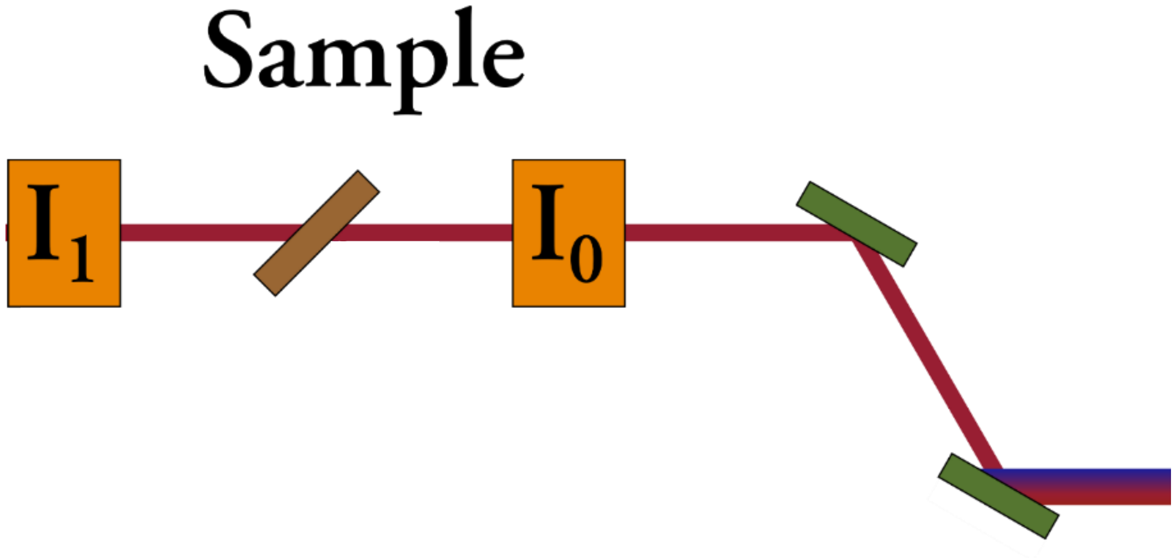


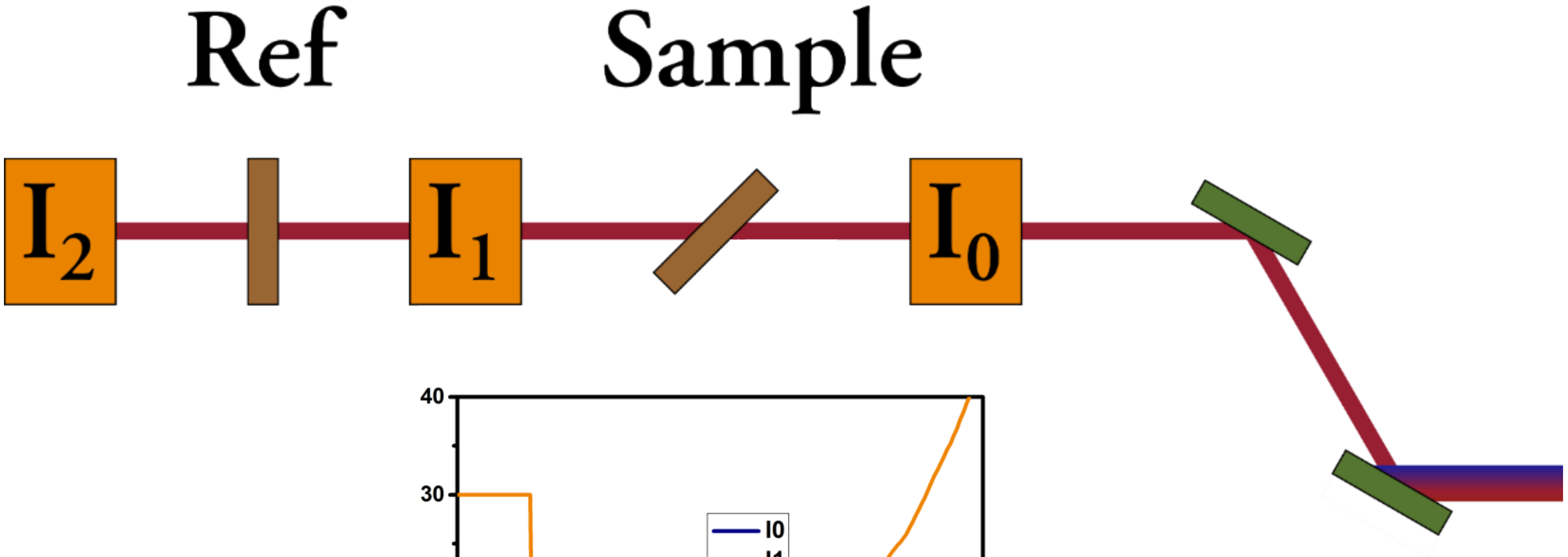
Cryogenic
Energy
dispersive

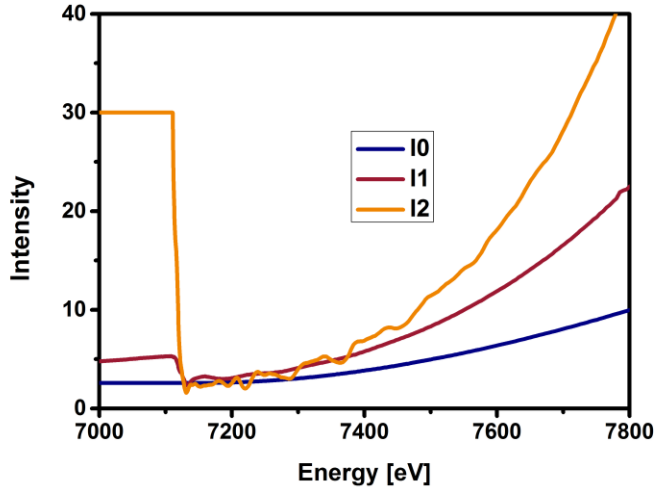




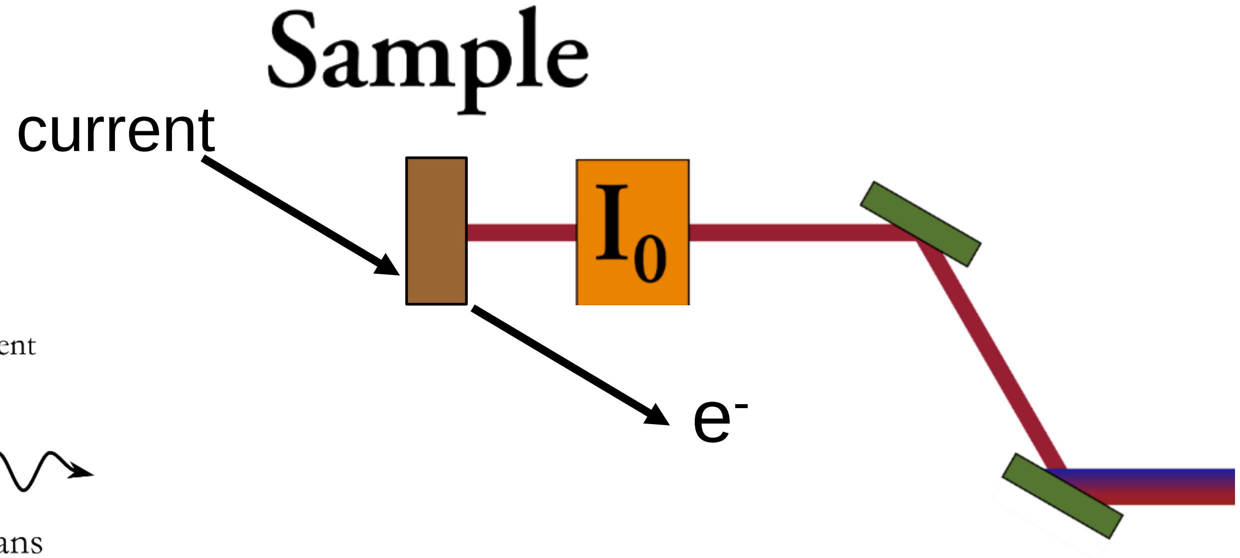


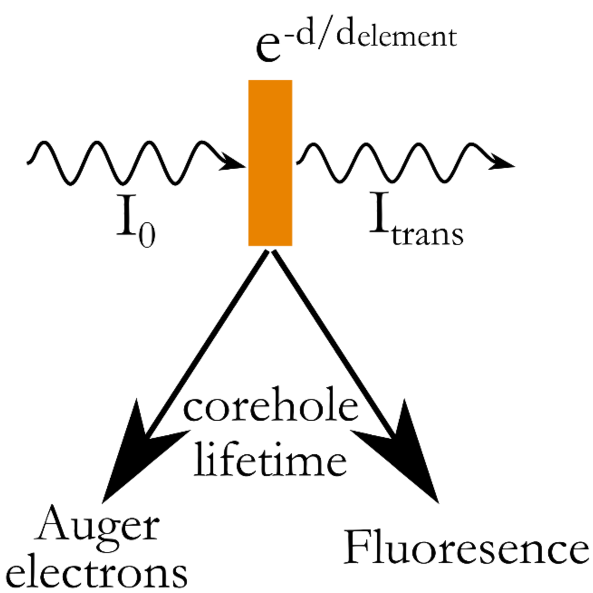

Sample
I_1
I_0


Ref
Sample
I2
I1
I0


40
30
20
10
0
7000
7200
7400
7600
7800
Energy [eV]
Intensity
I0
I1
I2

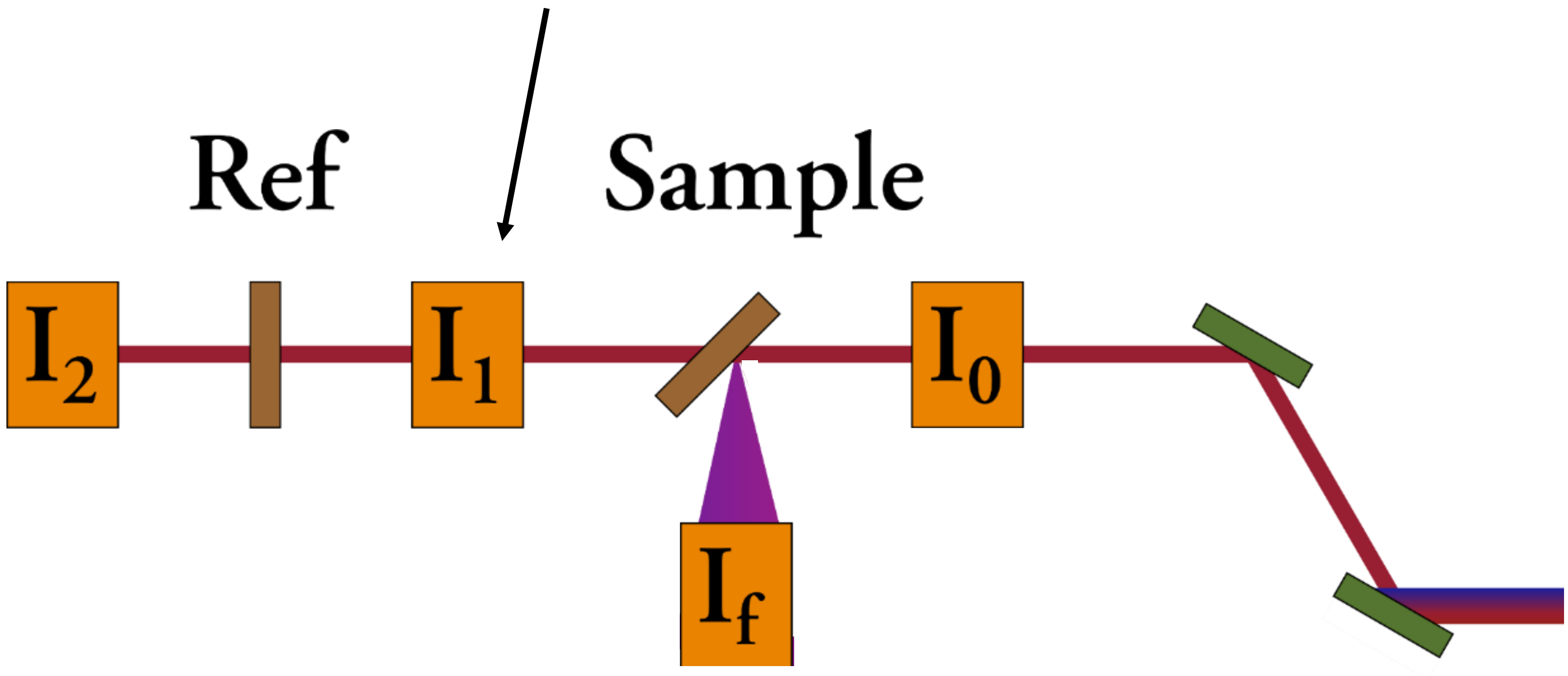
XAFS measurement – electron yield





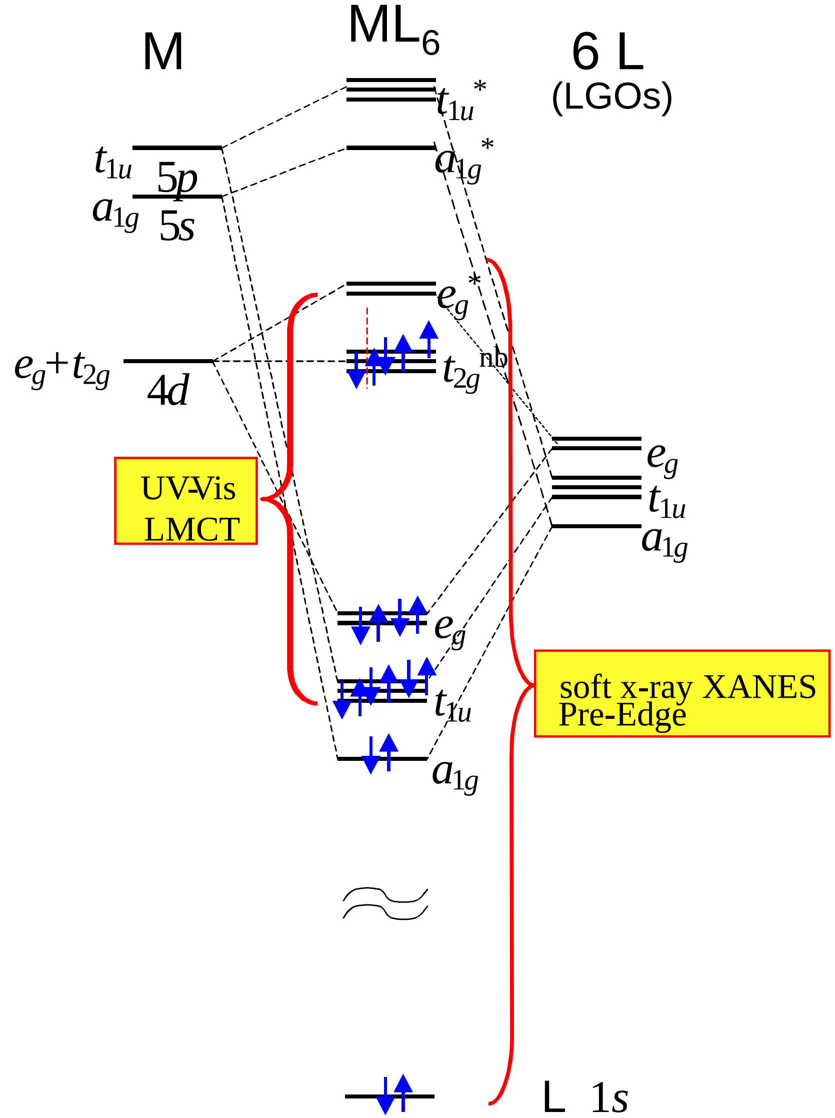
XAFS measurement – Fluorescence detected mode

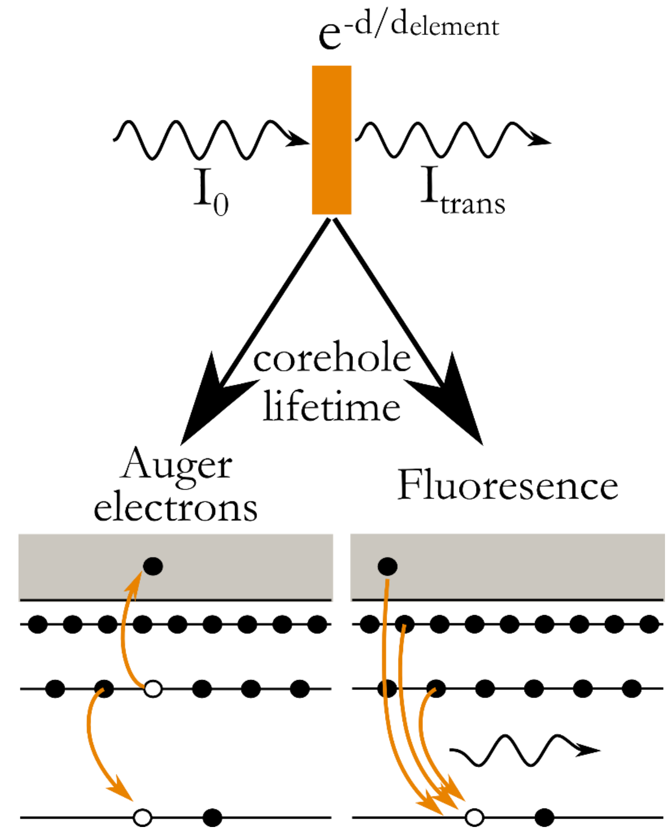
Transmission mode XAFS
("thick" but not to thick samples)



Emission mode XAFS
("thin" samples or samples without transmission)

XAS with complications (lifetime broadening)





$$\Delta x \Delta p \geq \hbar/2$$

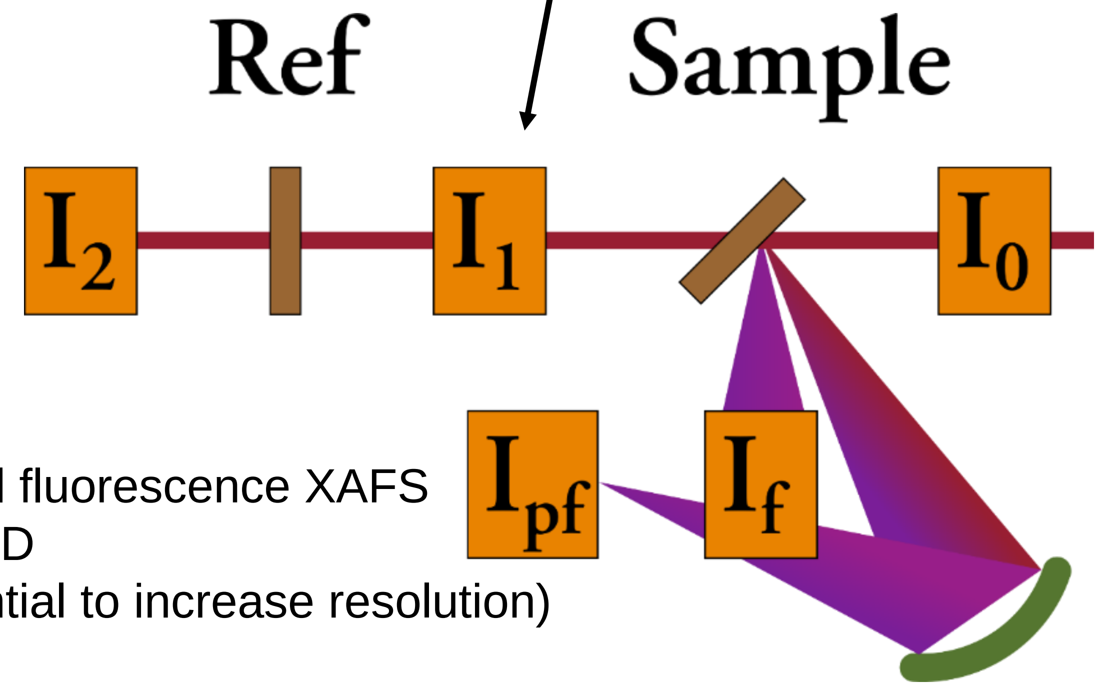
If we assume $\Delta E \Delta t \geq \hbar/2$

$$\frac{\hbar/2}{\sim 0.5 fs} \approx 10^{-19} J \approx 1eV$$

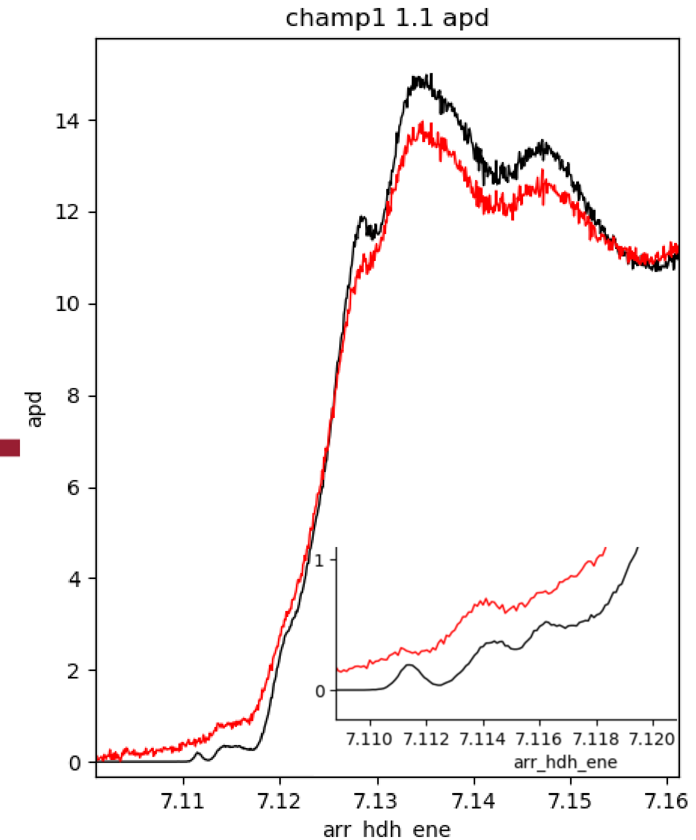
$$\Gamma = \frac{2\pi}{\hbar^2} \sum_{i,f} |\langle \Psi_f | \overrightarrow{\mu} | \Psi_i \rangle|^2 \delta(h\nu - E_f - E_i)$$

HERFD measurement

Transmission mode XAFS
(“thick” but not to thick samples)



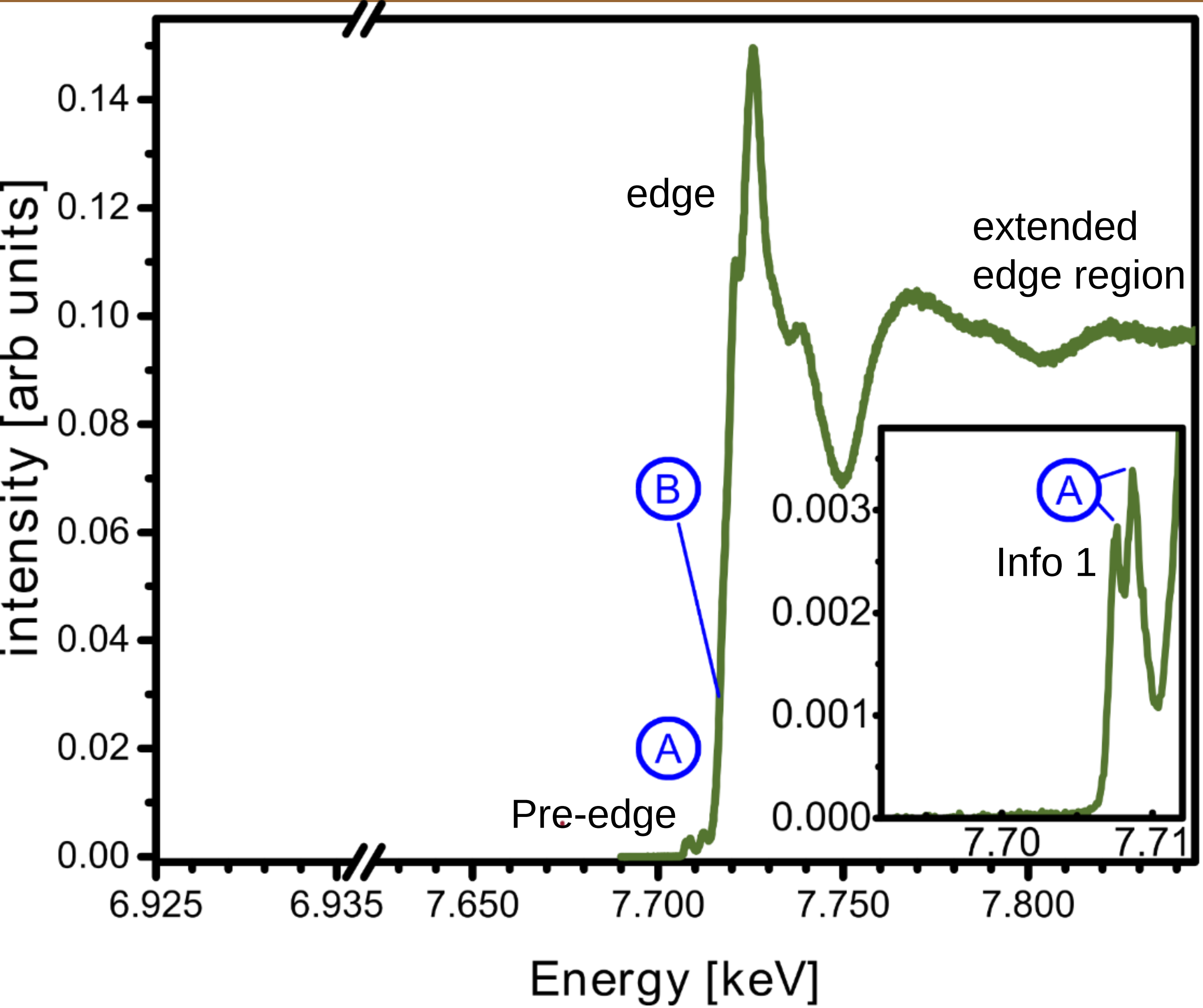
Partial fluorescence XAFS
HERFD
(potential to increase resolution)

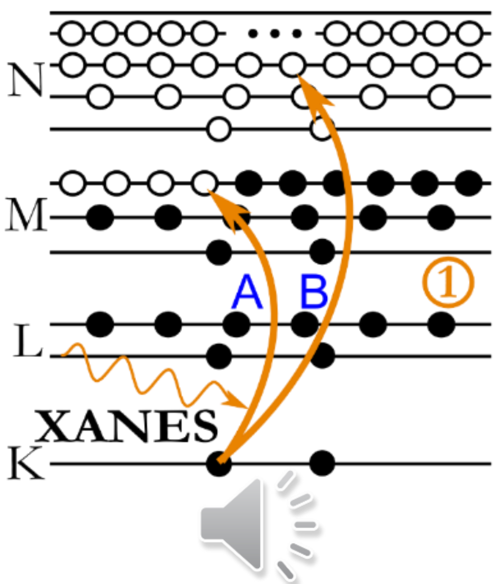


HERFD ≠ XAS

Emission mode XAFS
(“thin” samples or samples without transmission)
(Need to consider self absorption → later more)

Lecture in a slide XANES 4 - regions of information

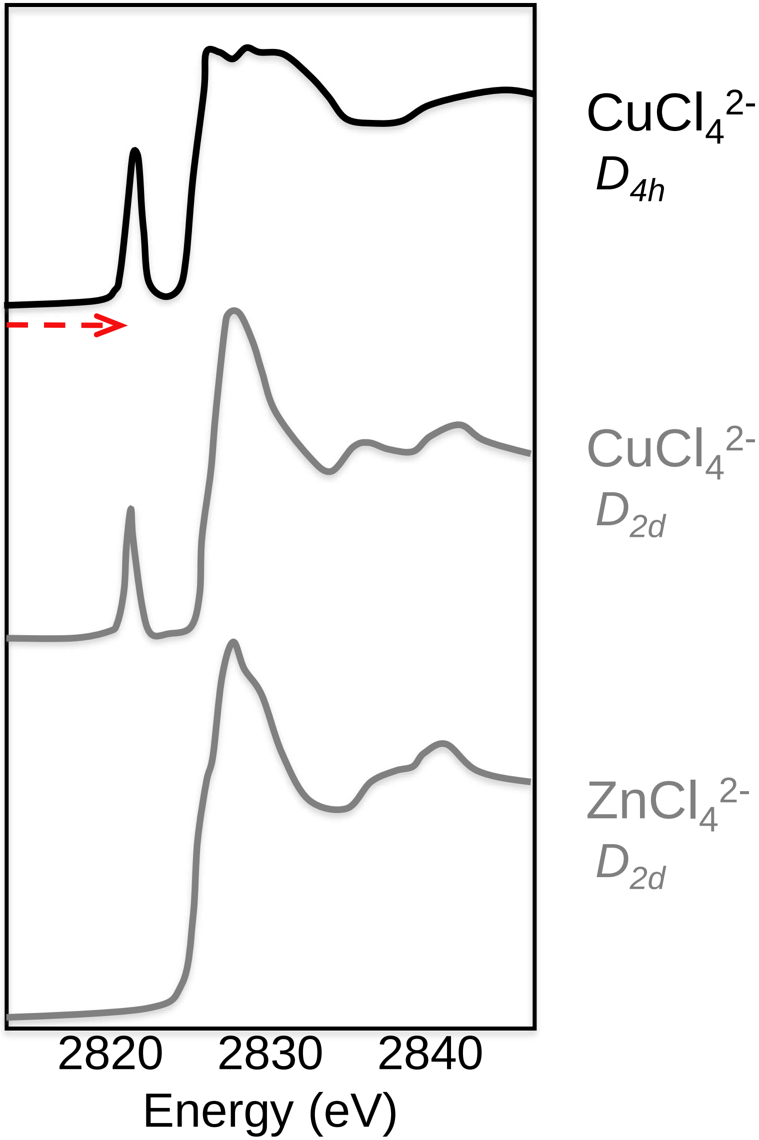


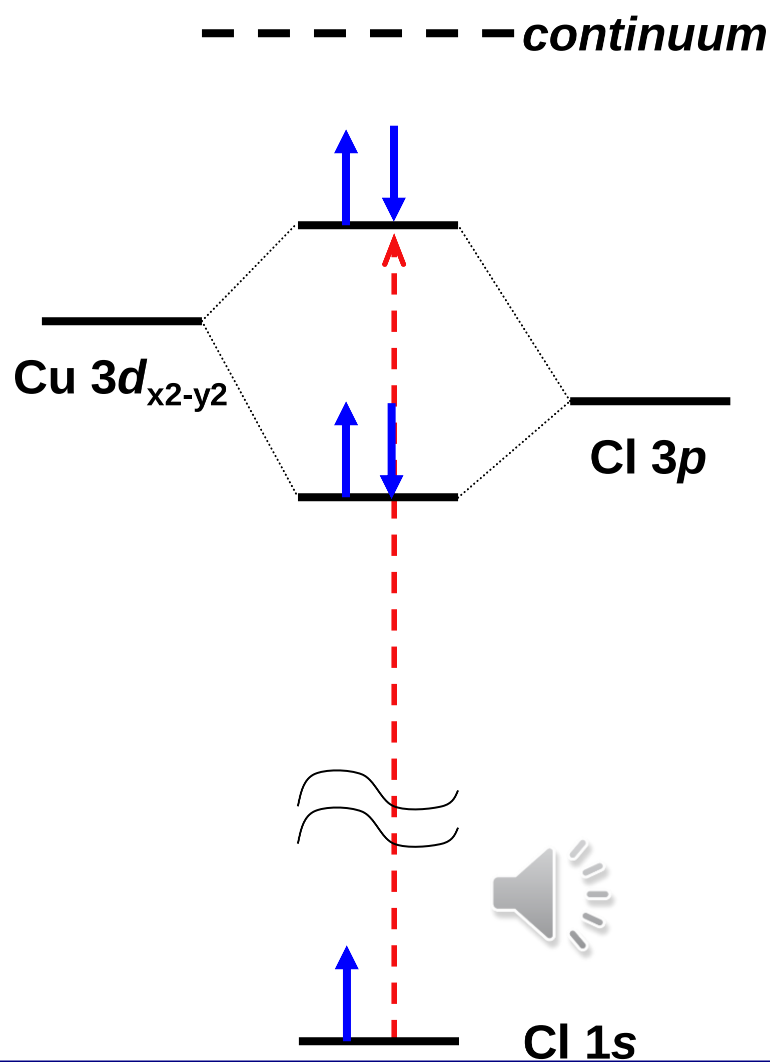


modified from Ponseca, C. S. et al.
Chemical Reviews **2017**, *117*, 10940-11024

Existence of pre-K-edge Chlorine XANES in MCl_4^{2-}

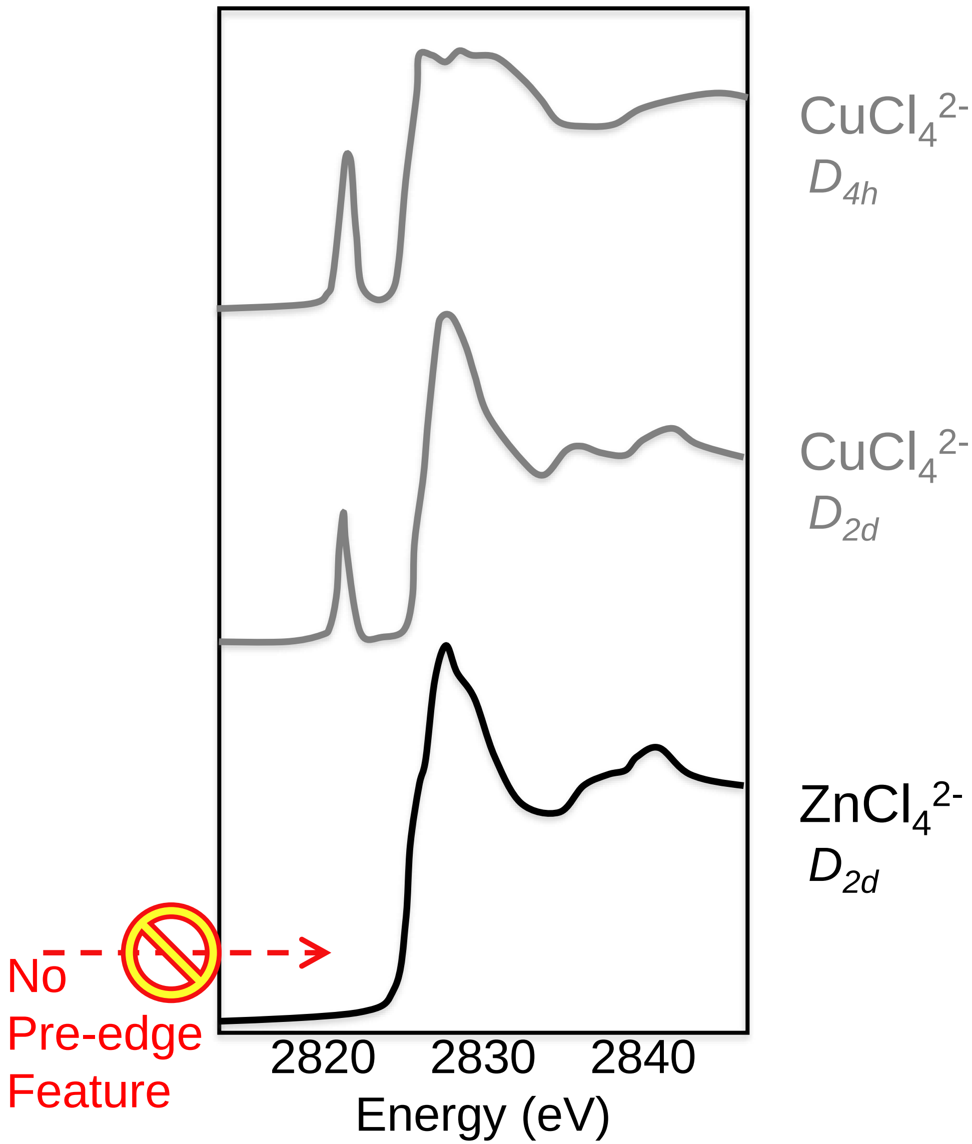
Curtesy Pieter Glatzel

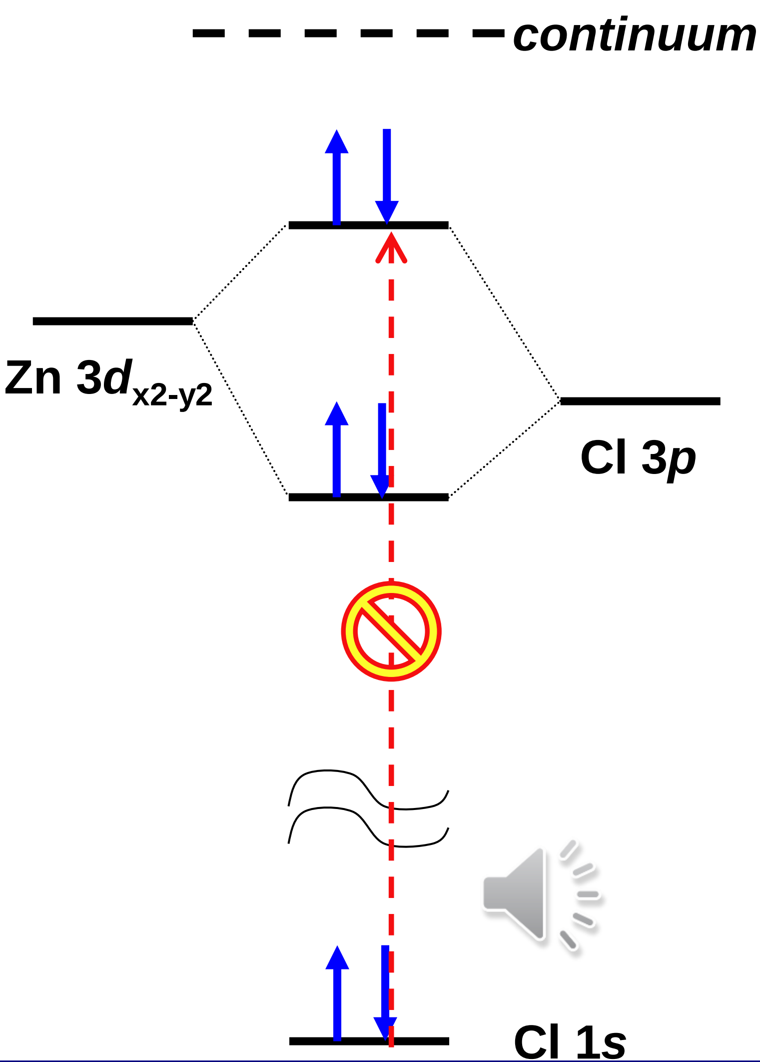




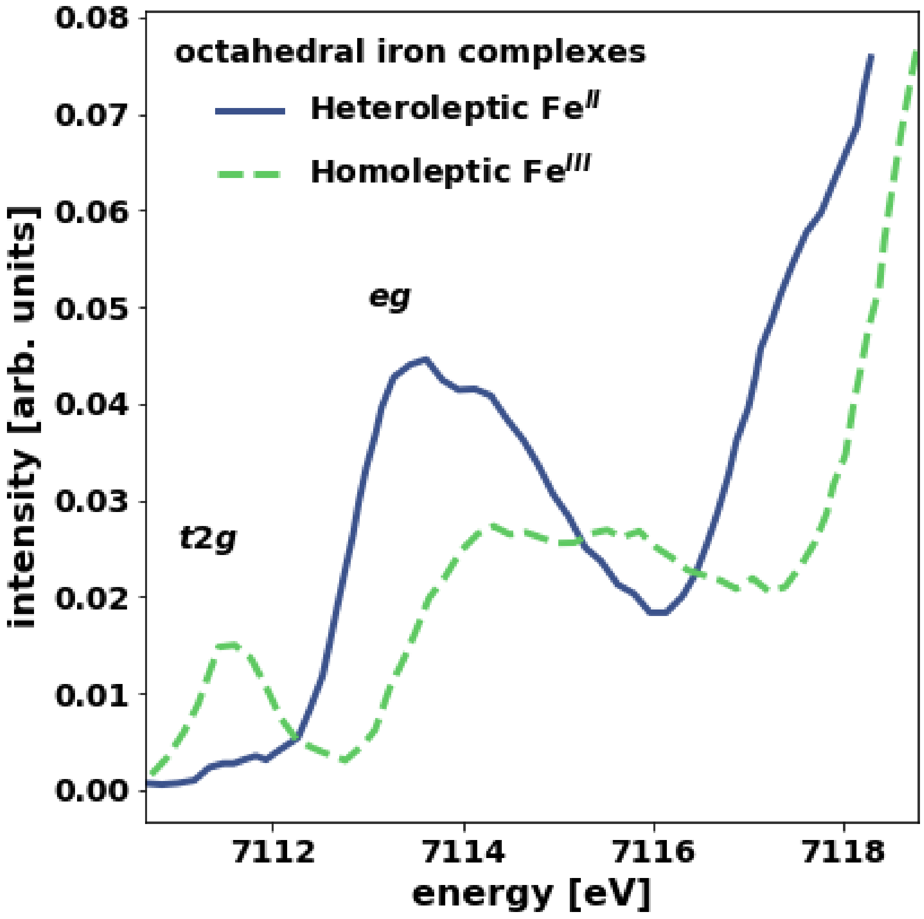
Existence of pre-K-edge Chlorine XANES in MCl_4^{2-}

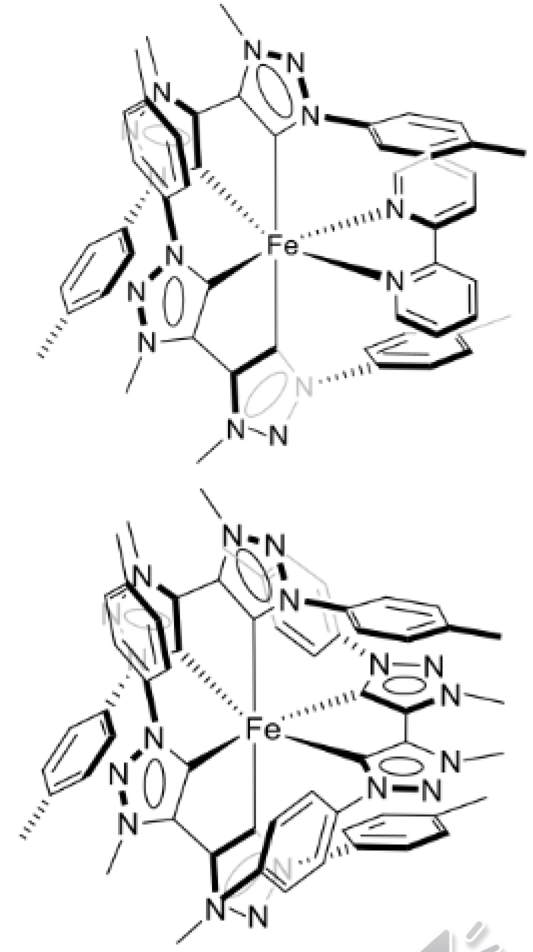
Curtesy Pieter Glatzel





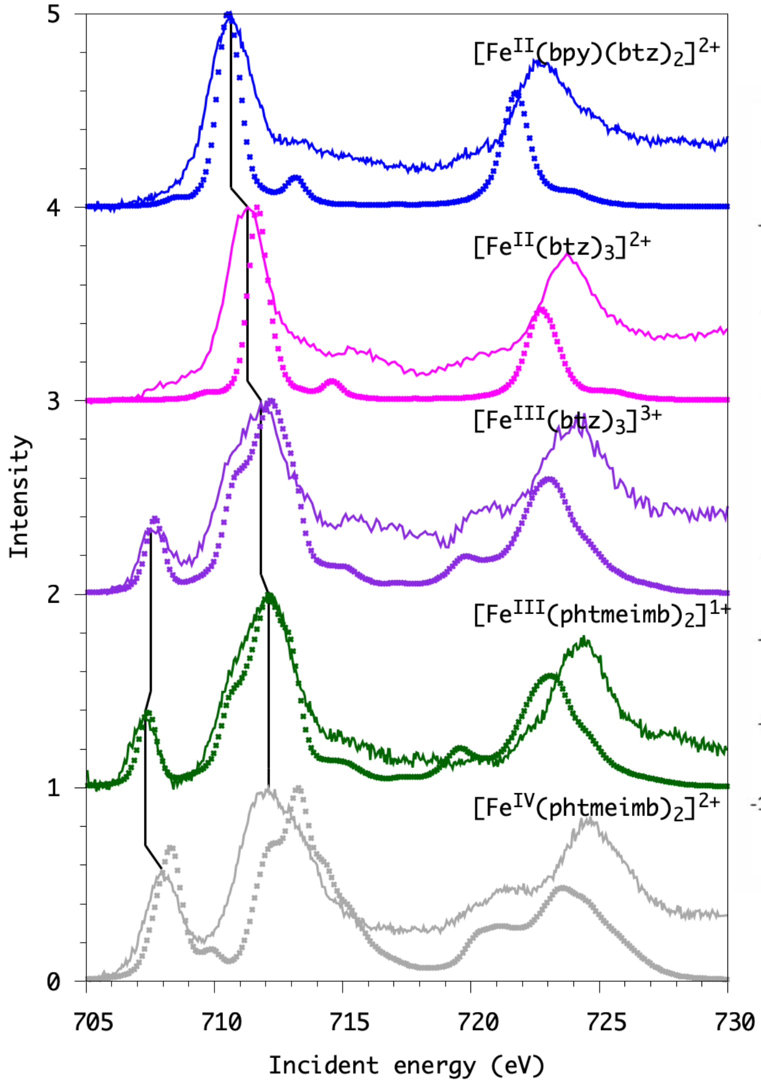
XANES – t2g ($Fe^{II/III}$) in Carbene Pre-edge

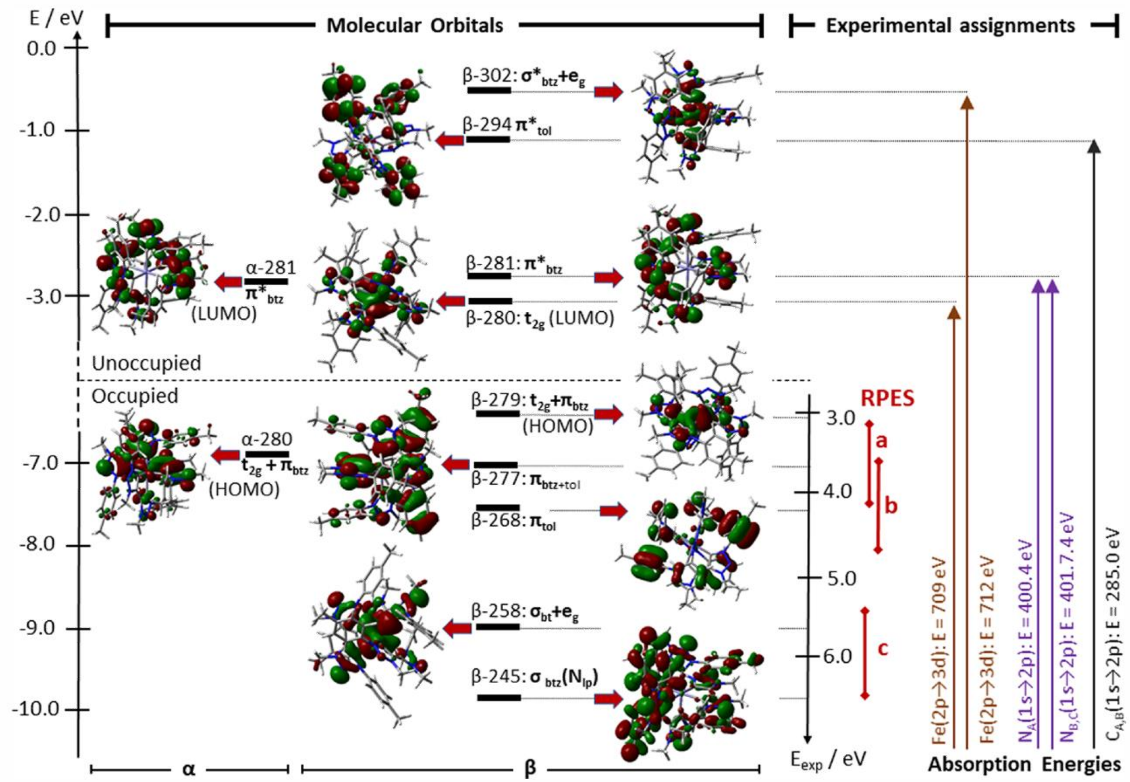




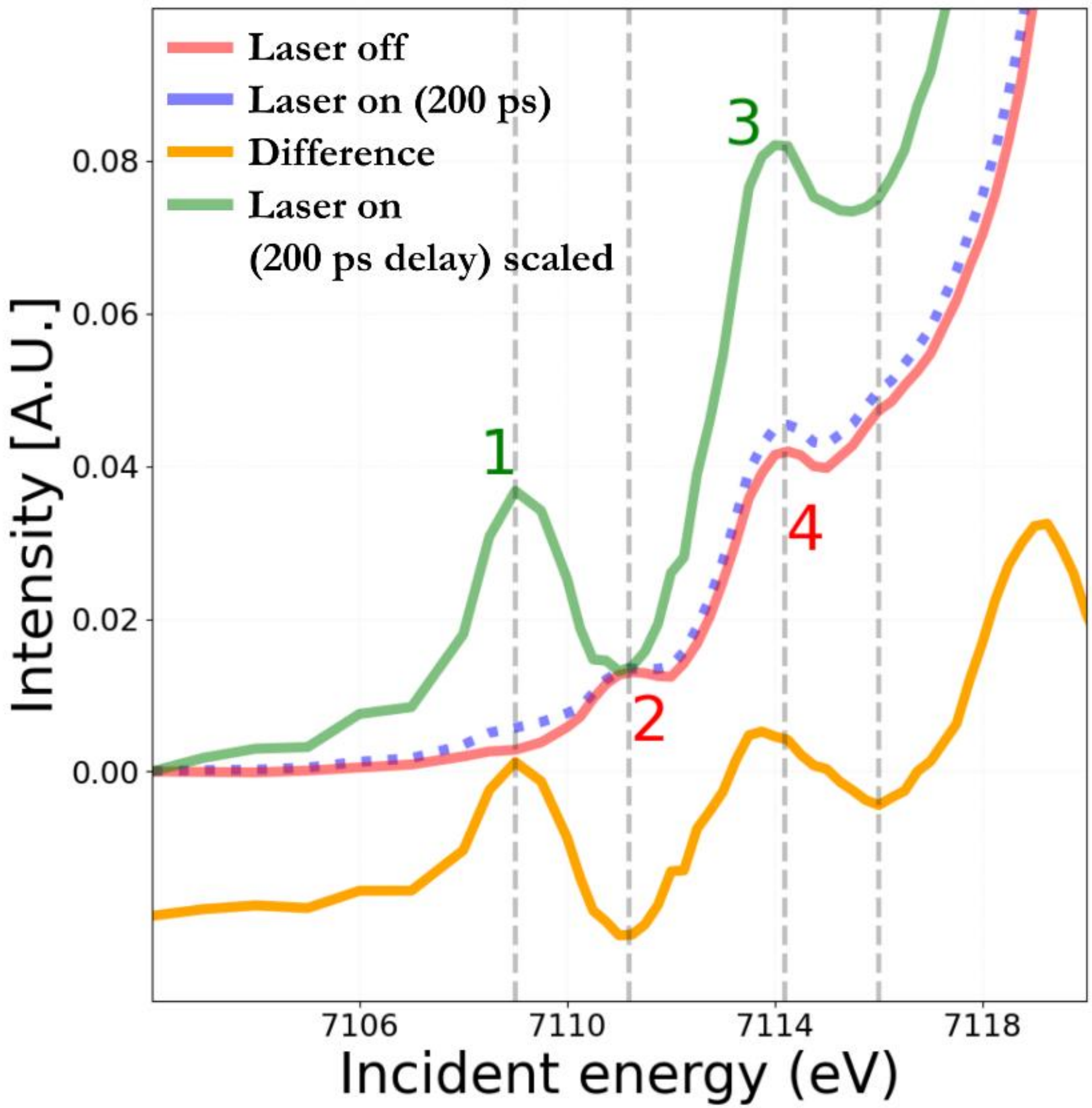
M. Guo et al. *PCCP* **2020**, *22*, 9067-9073 2020.
DOI: 10.1039/c9cp06309a.

Fe – XAS in Soft x-rays t2g and energy shift





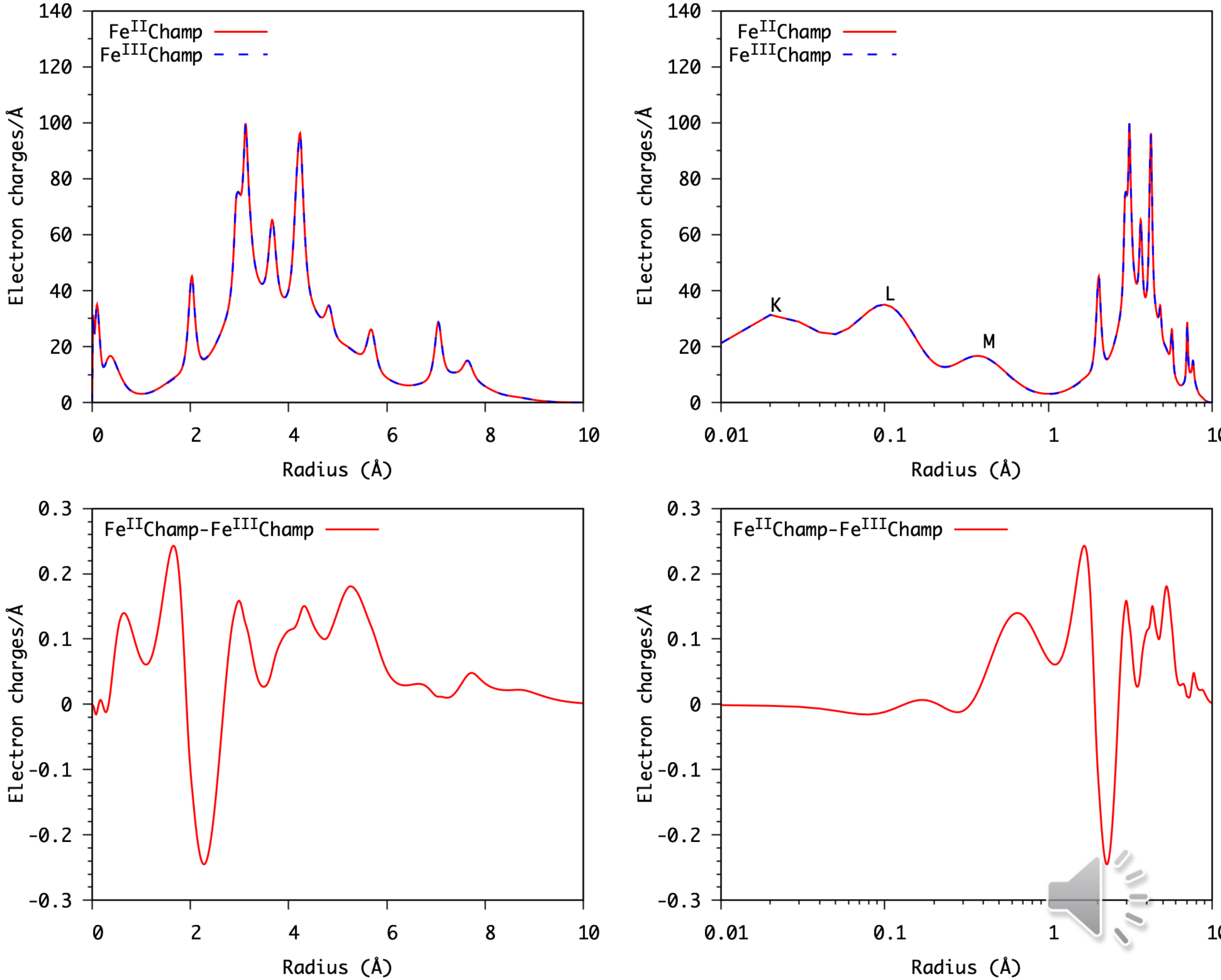
Time-resolved XANES = Oxidation state + Covalency



Position of charges

Where are the charges?

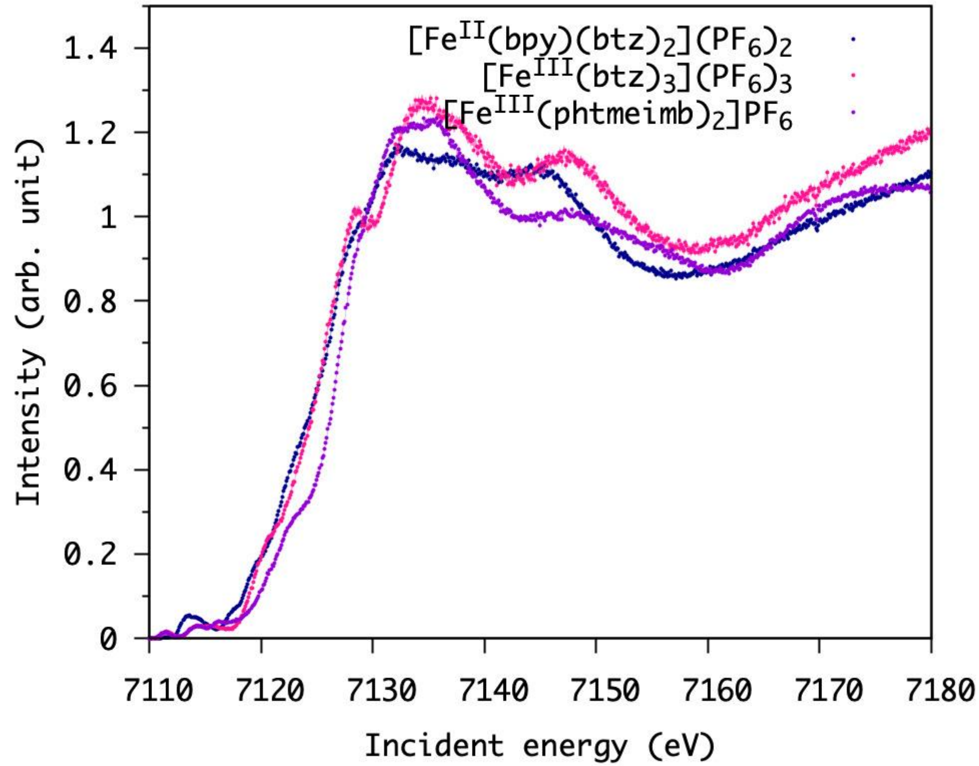
Where are the differences?



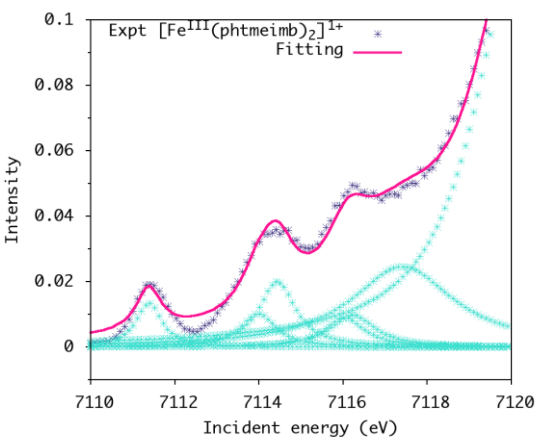
Calculating pre-edges

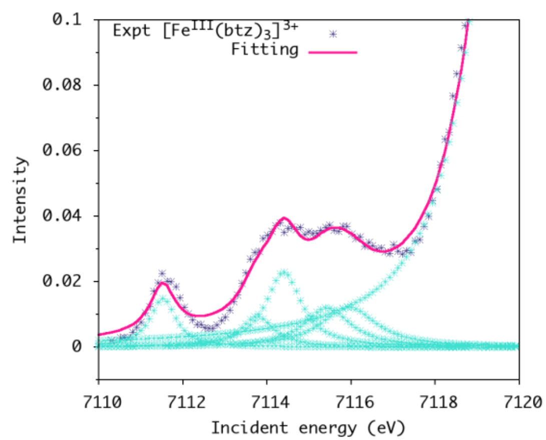
$$\mu(\omega) \sim \sum_f |\langle f\,|d|\,i\rangle|^2\,\delta(\hbar\omega + E_i - E_f))$$

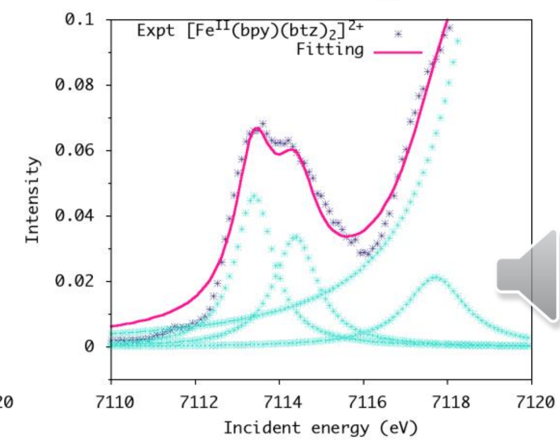
3d transition metals
1s → 3d forbidden
Multi-configurations



Serious calculations:
ORCA-ROCIS
Molcas-RAS
Crispy (fast)



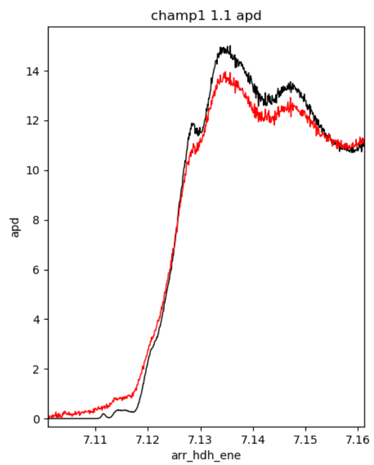


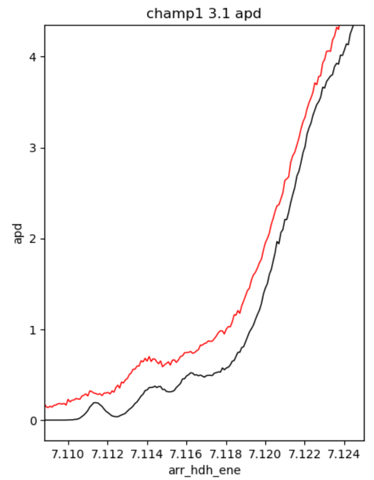


120 -180 states

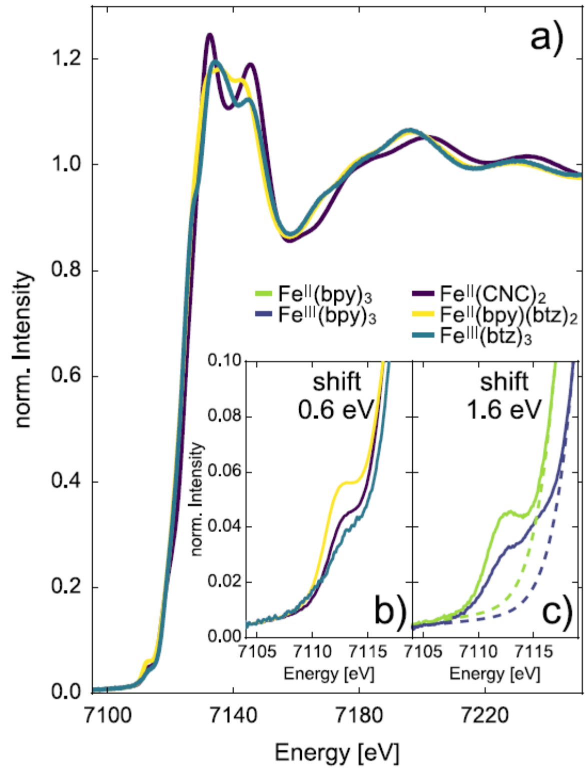
Measuring pre-edges

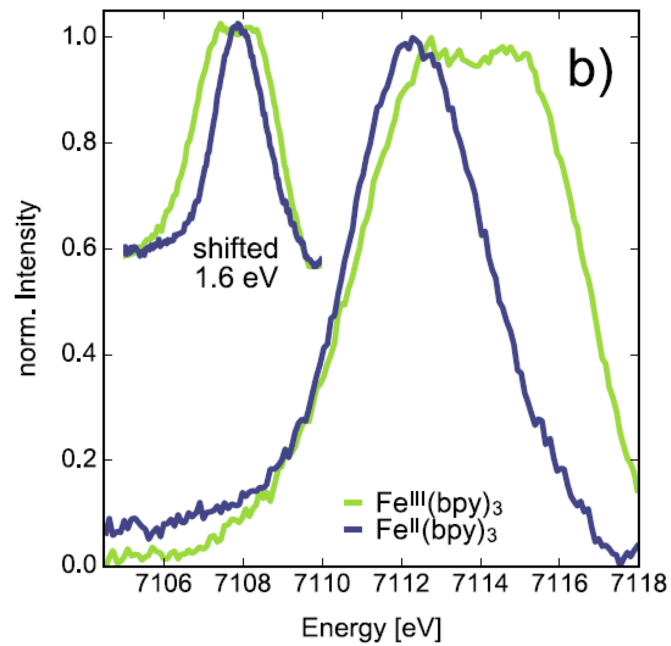
Challenge 1&2
resolution and signal



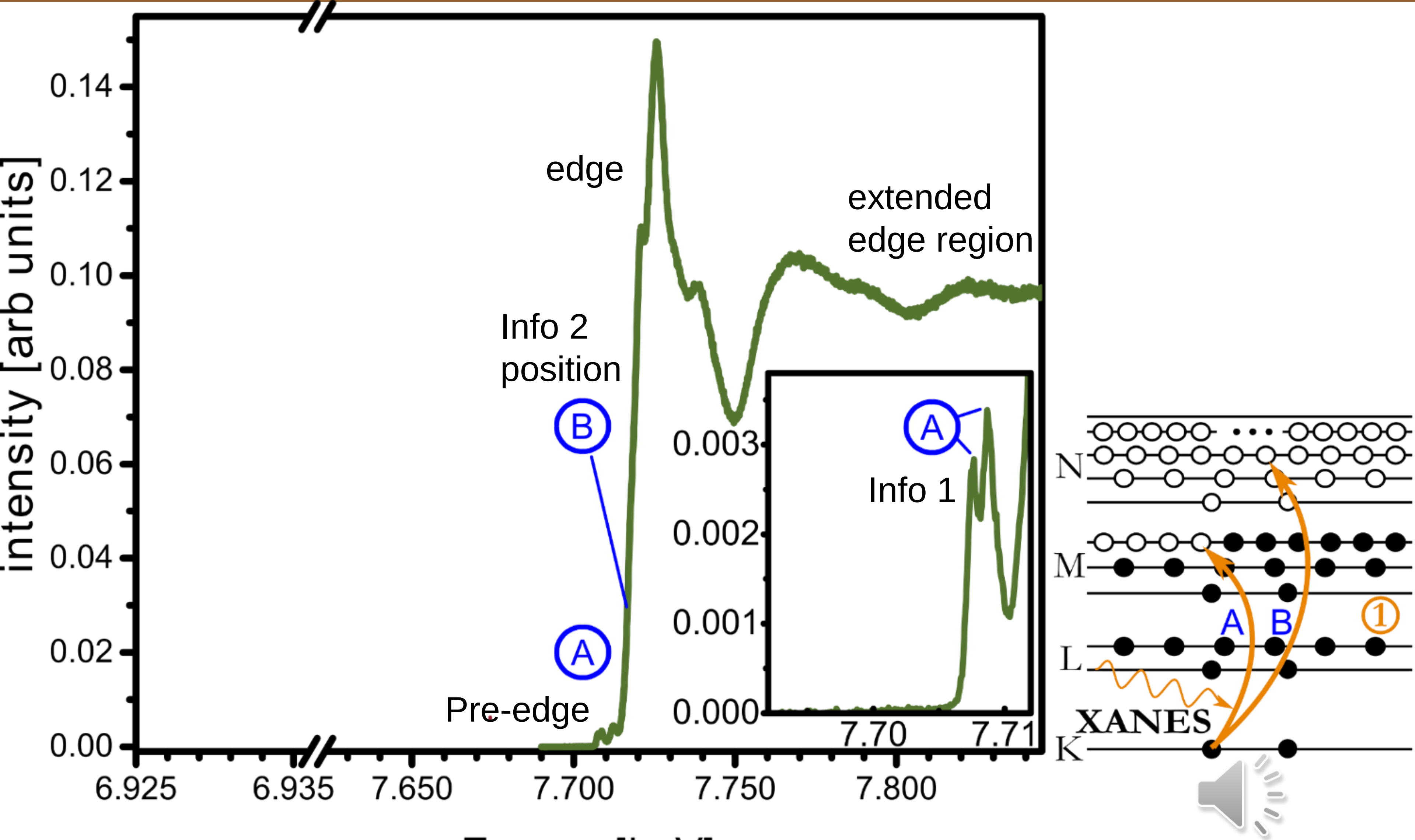


Challenge 2 chemical shift





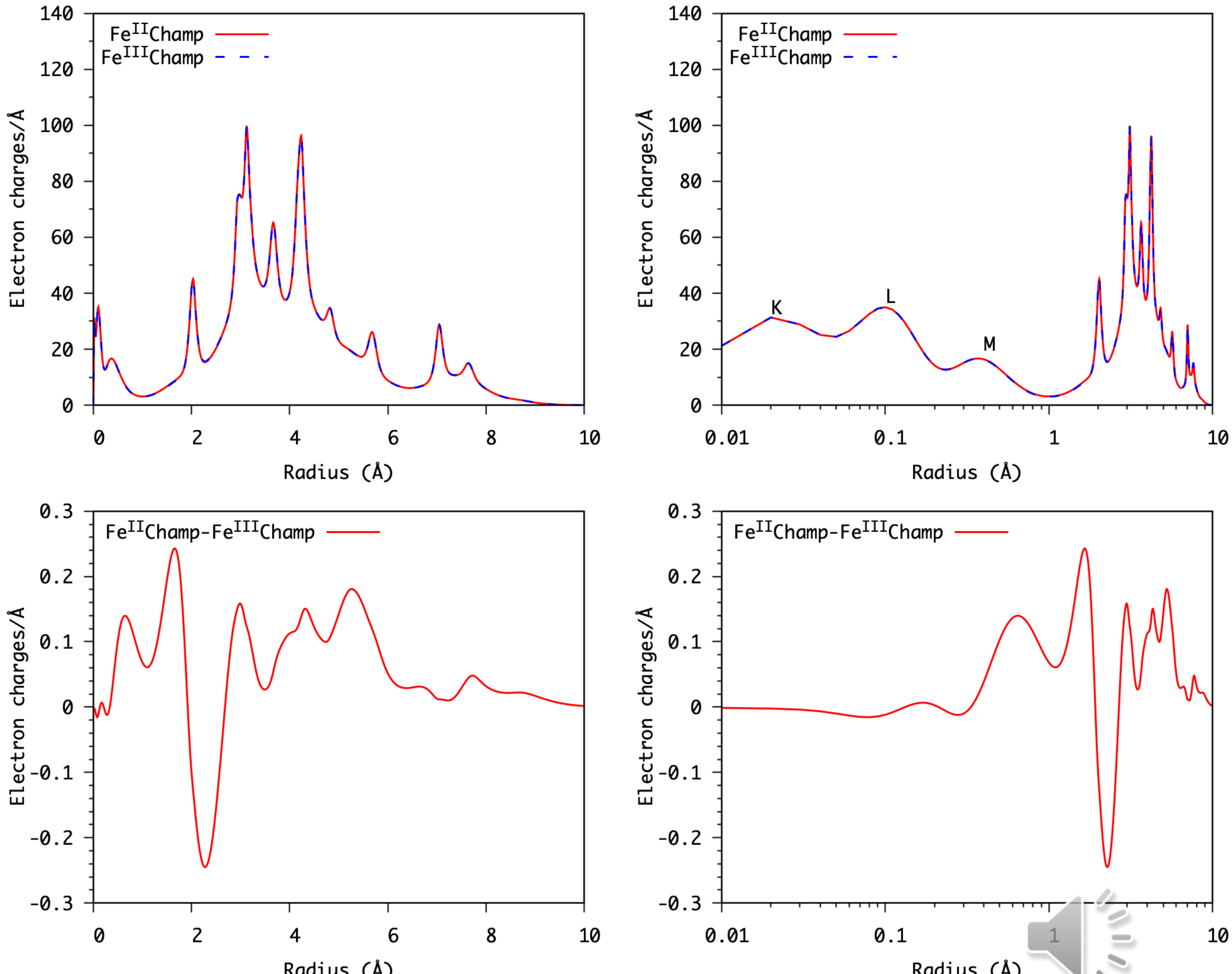
Lecture in a slide XANES Edge position



modified from Ponseca, C. S. et al.
Chemical Reviews **2017**, *117*, 10940-11024

Position of Charges

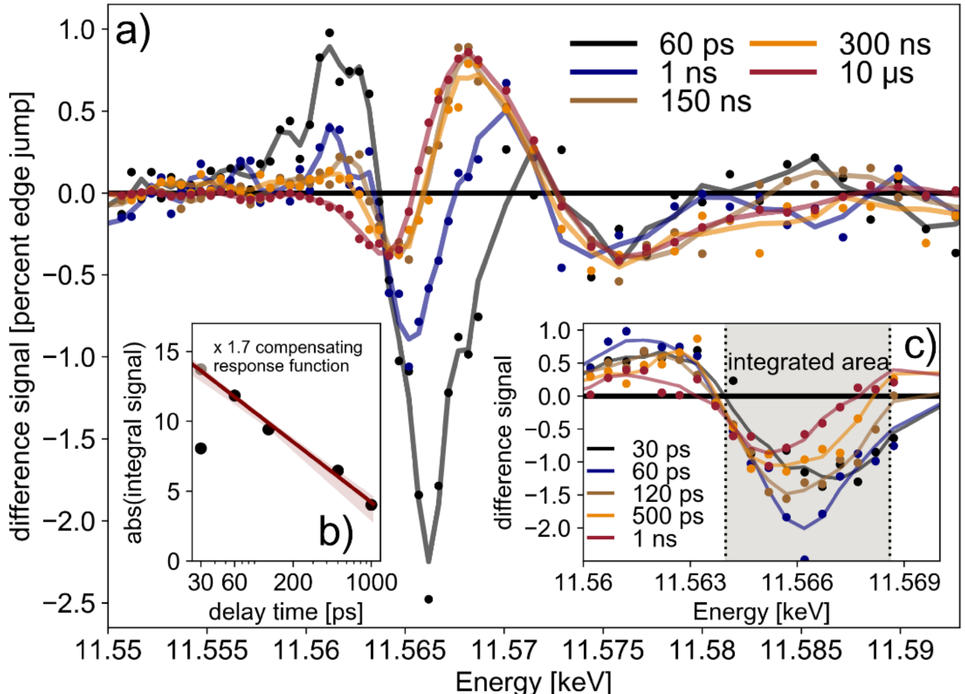
Where are the charges?



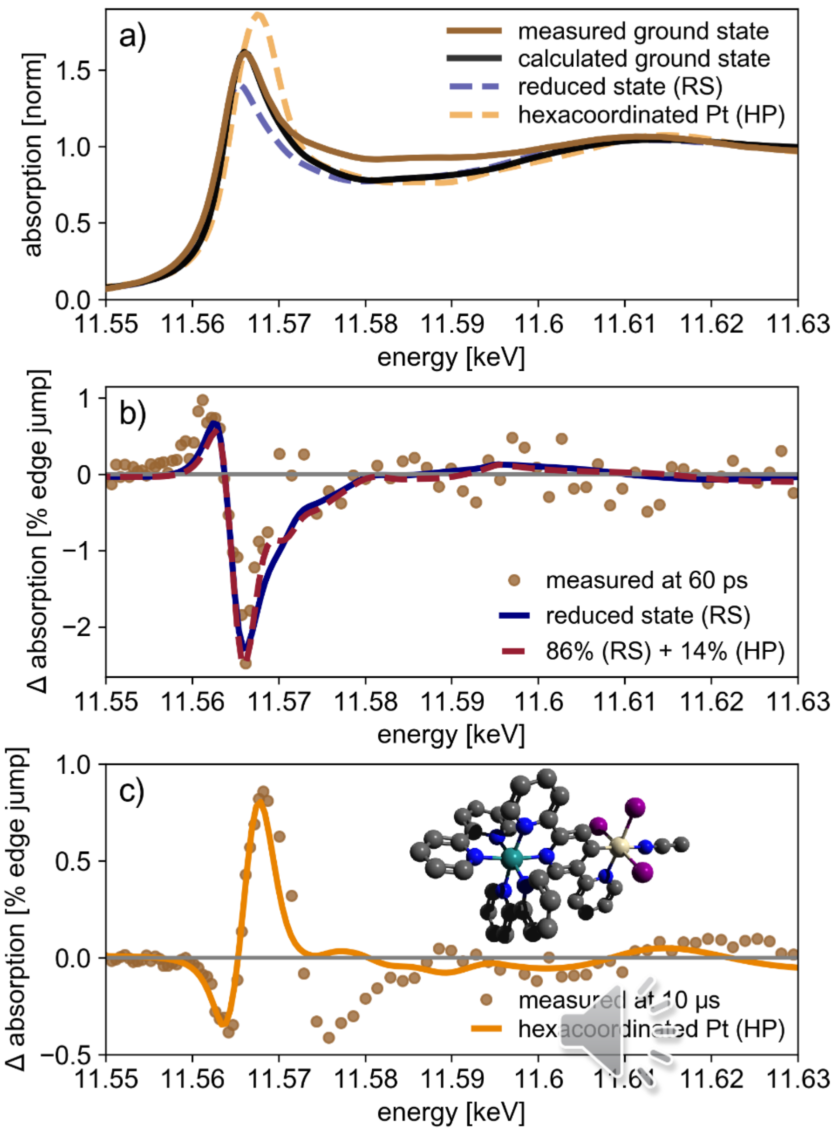
Where are the differences?

$$\Gamma = \frac{2\pi}{\hbar^2} \sum_{i,f} \left| \langle \Psi_f \left| \overrightarrow{\mu} \right| \Psi_i \rangle \right|^2 \delta(h\nu - E_f - E_i)$$

The advantage of synchrotrons

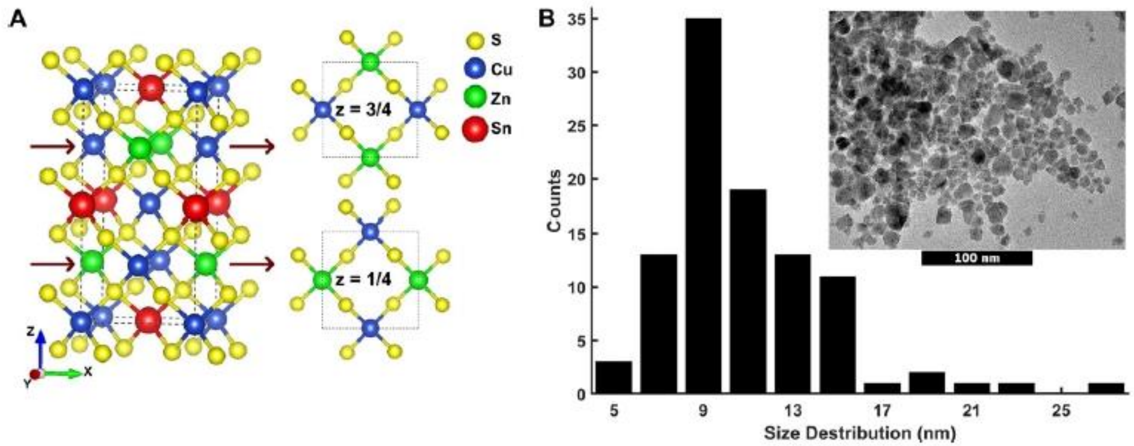


90% transfer



1. loses 1 Iodine in solution
2. absorbs one photon
3. transfers one electron (reduction)
4. goes in oxidized state
(2 electron process without accumulation)
5. eventually recovers

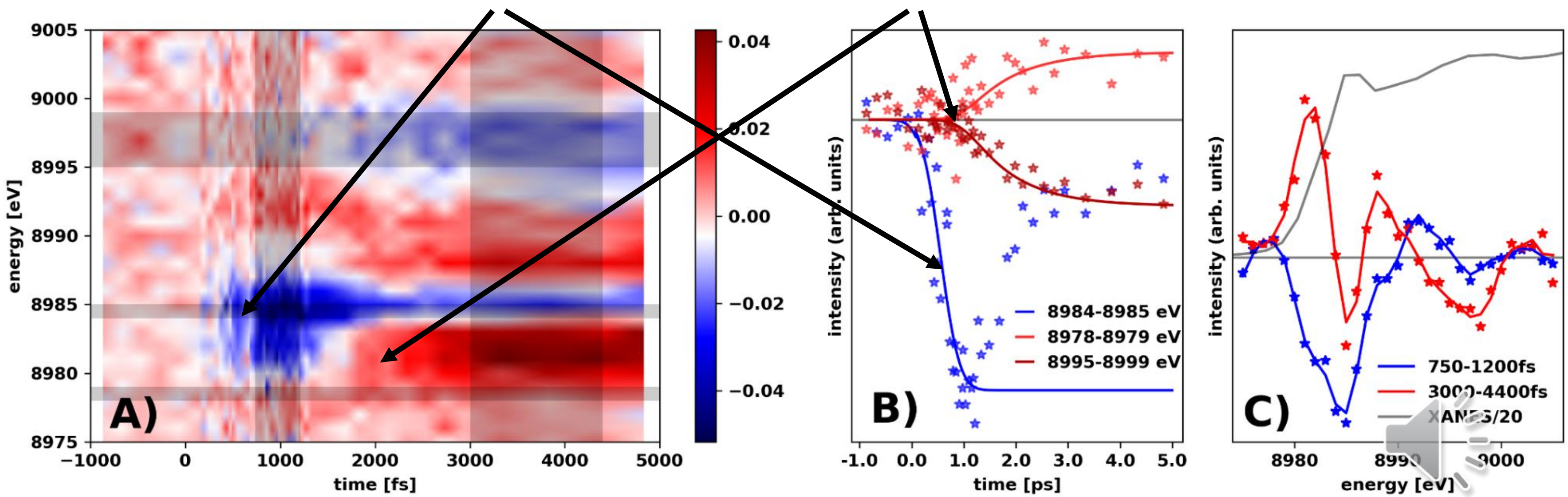
Ultrafast charge transfer dynamics induce structural response



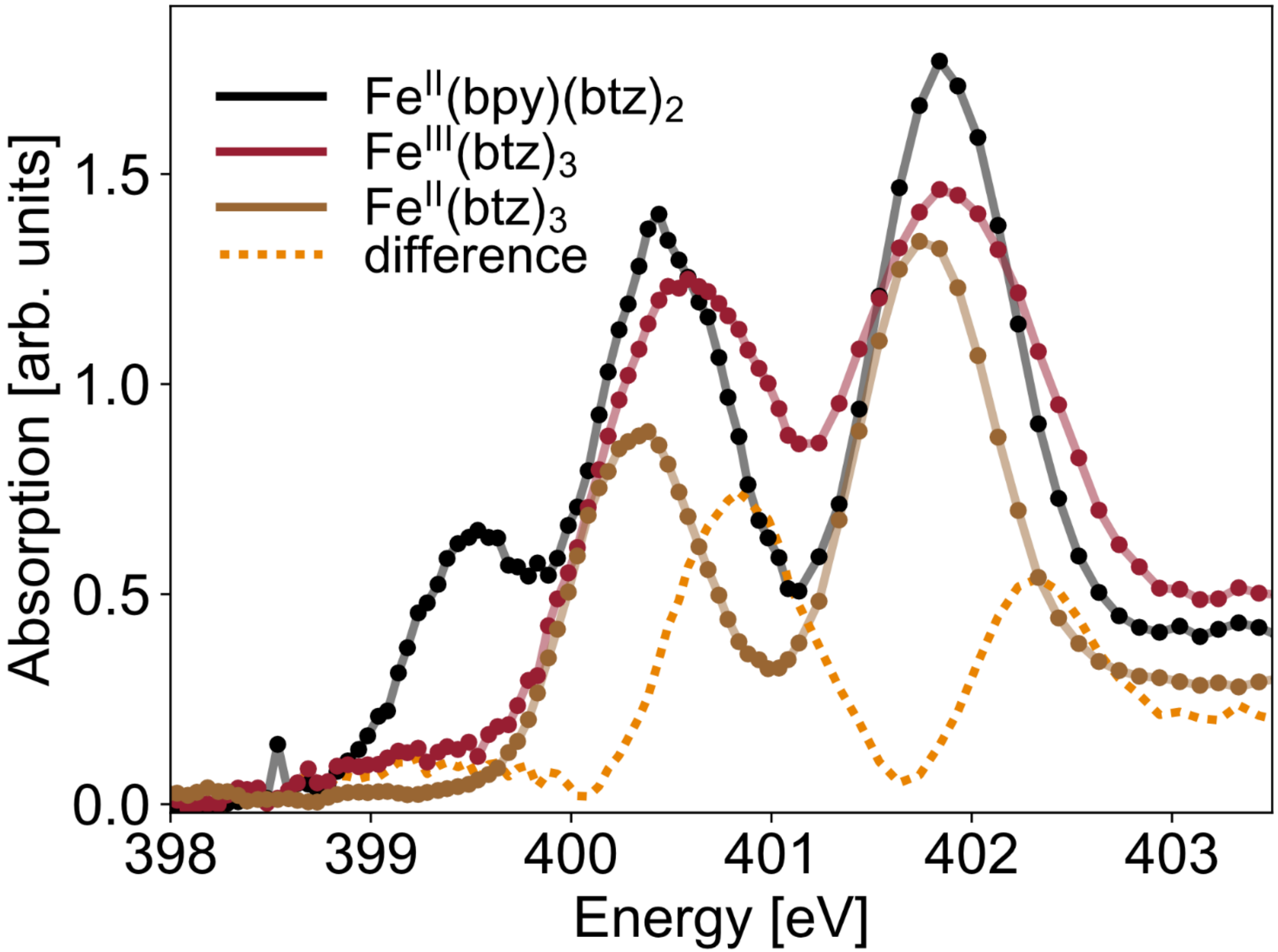
CZTS Kesterite
Charges move
and create structure

First transfer

Second structural response

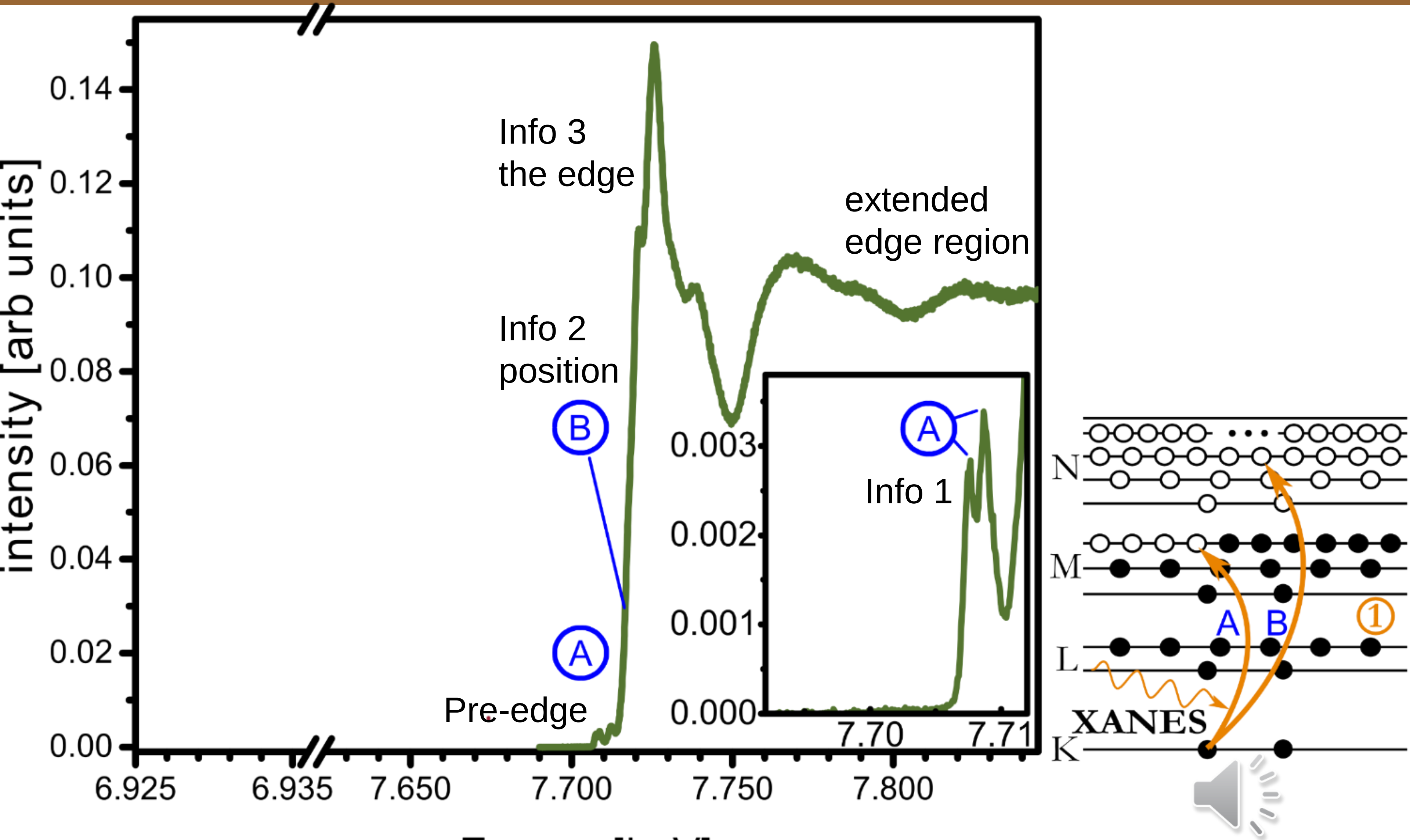


Rein et al. DOI: 10.1063/4.0000055.
Structural Dynamics. **2021**, *8* (2), 24501.



Fe^II(bpy)(btz)2
Fe^III(btz)3
Fe^II(btz)3
difference
Absorption [arb. units]
1.5
1.0
0.5
0.0
398
399
400
401
402
403
Energy [eV]

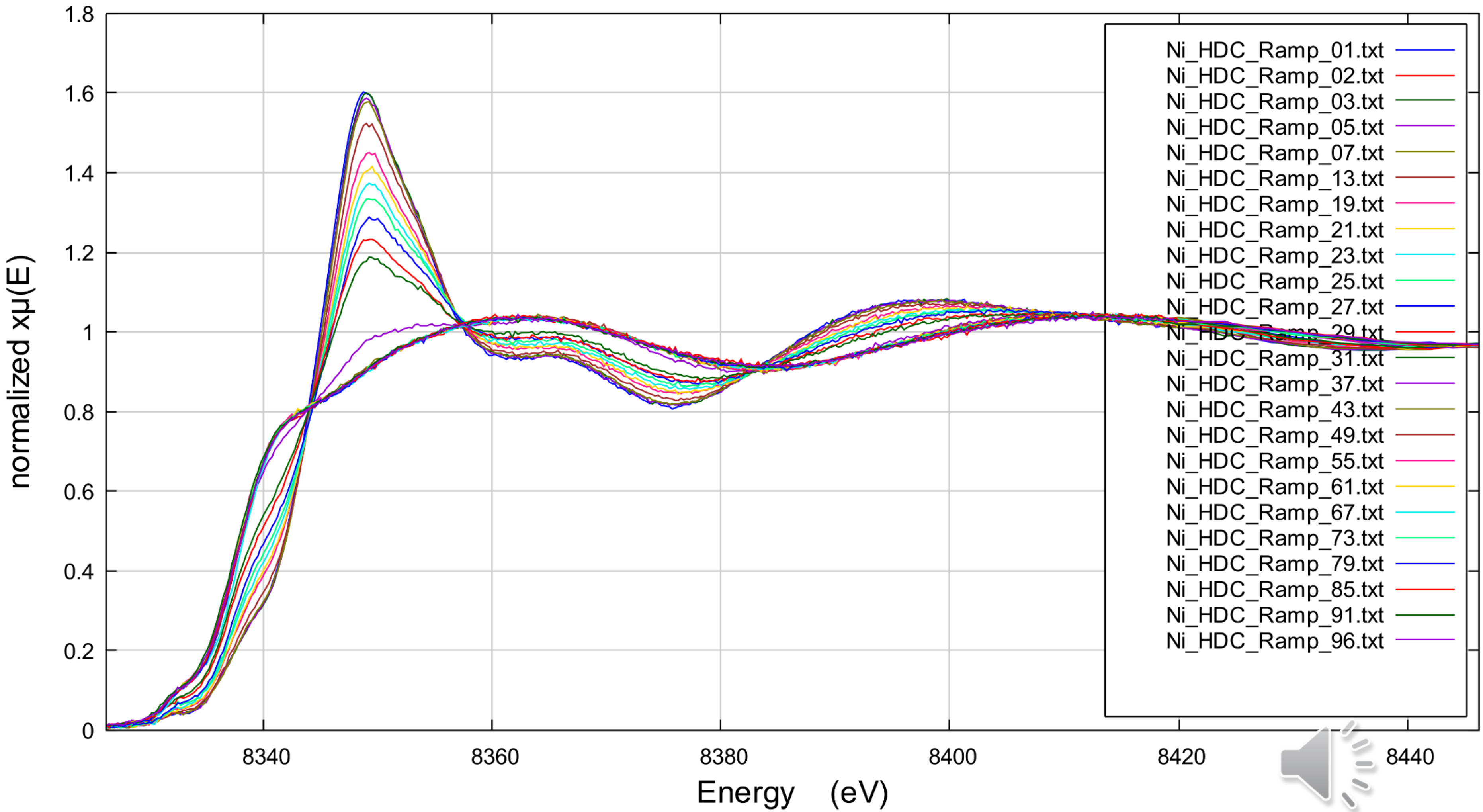
Lecture in a slide XANES Finger printing



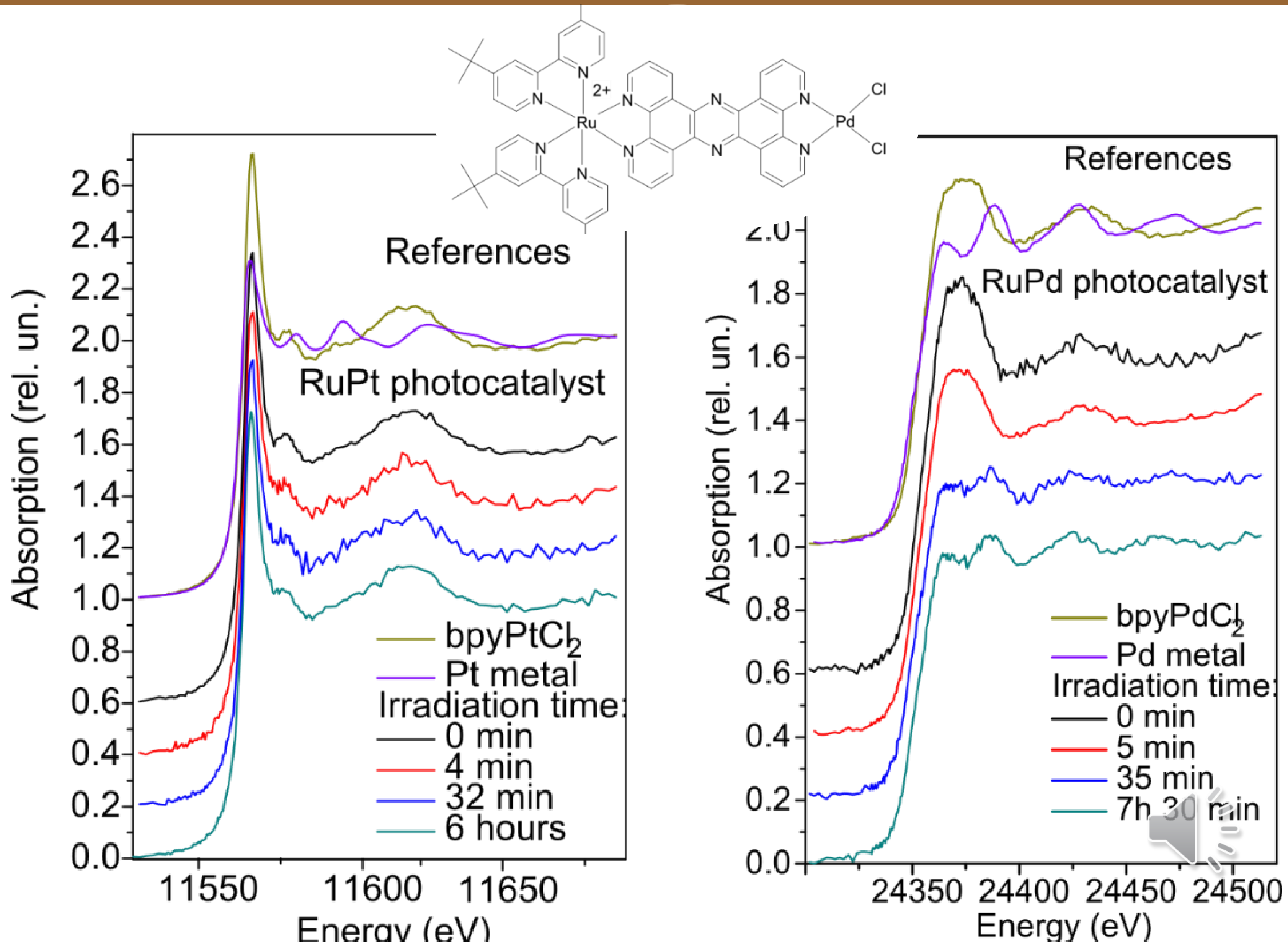
modified from Ponseca, C. S. et al.
Chemical Reviews **2017**, *117*, 10940-11024

Nickel sulfide catalyst ramp

Curtesy Lindsay Merten



Fingerprinting using the local "atomic" sensor



Sulfur K-edge XANES Spectra

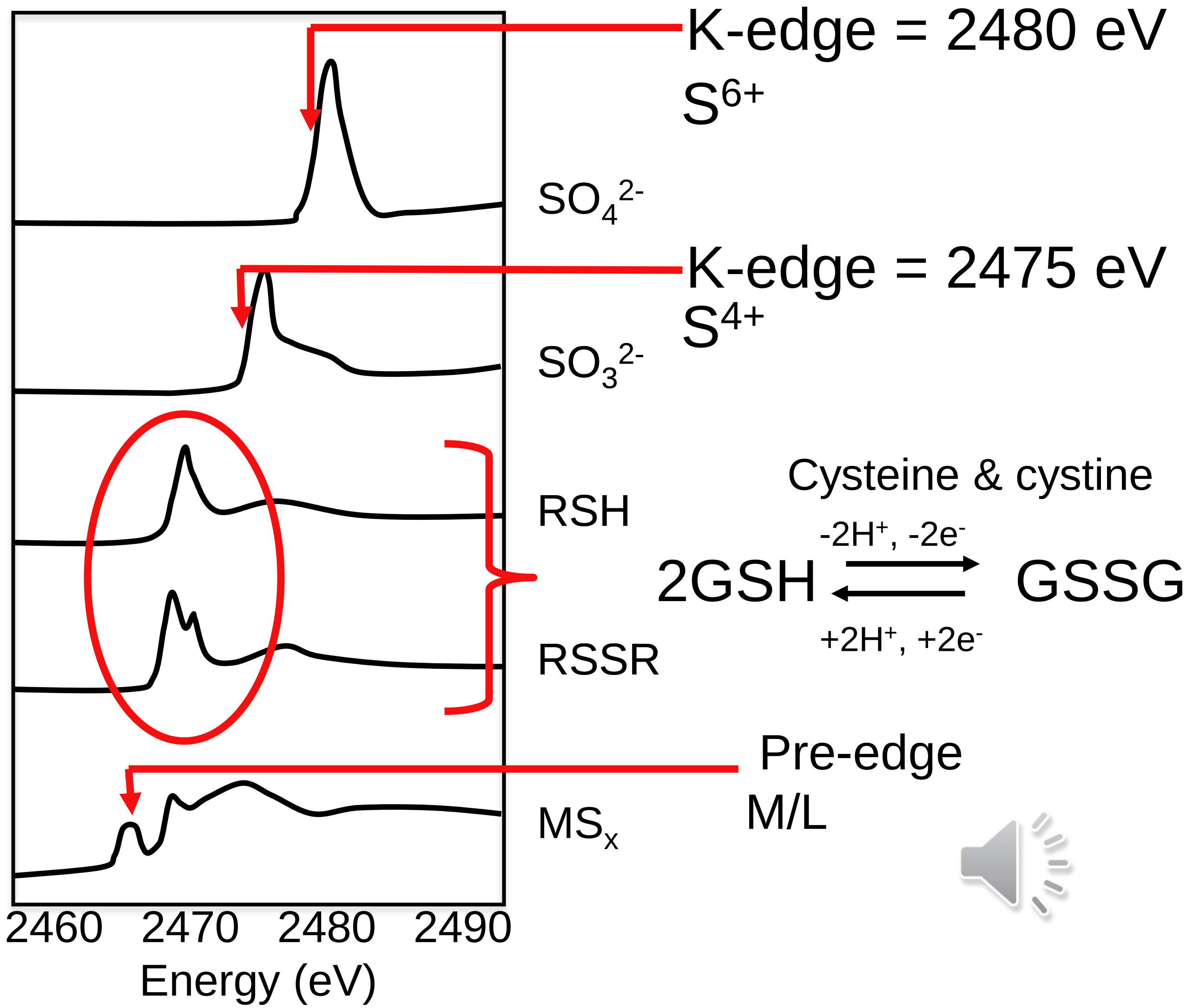
Adapted from I.J. Pickering, R.C. Prince, T. Divers, G.N. George, *FEBS Letters* **1998**, *441*, 11-14.

Linear Combination Analysis….
Of life science

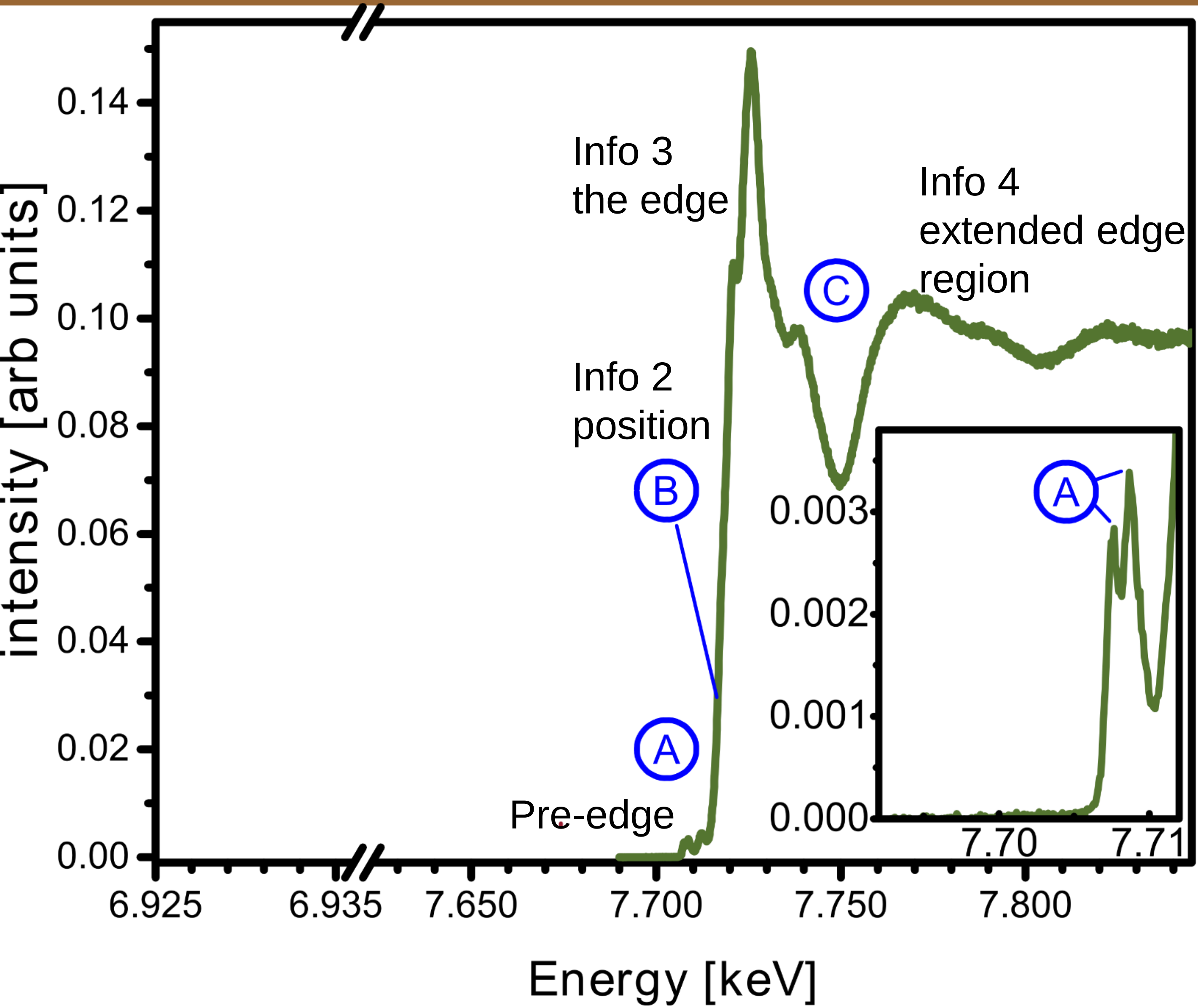
For calculation
kind of “local” DFT:

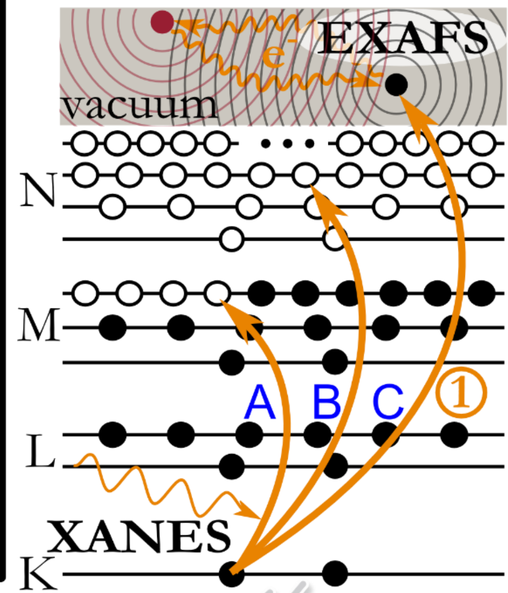
FDMNES
FEFF
Orca

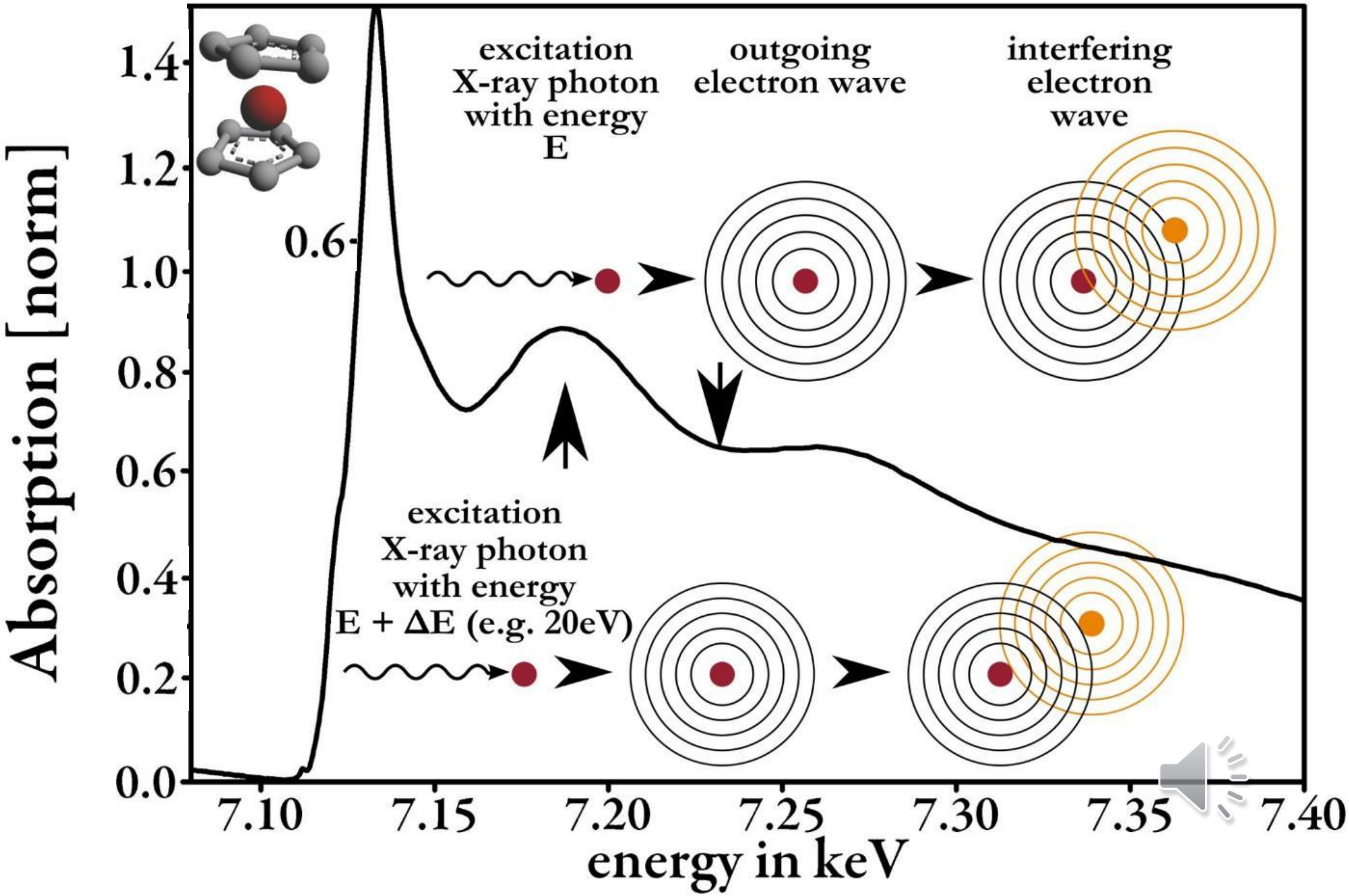
But references are better



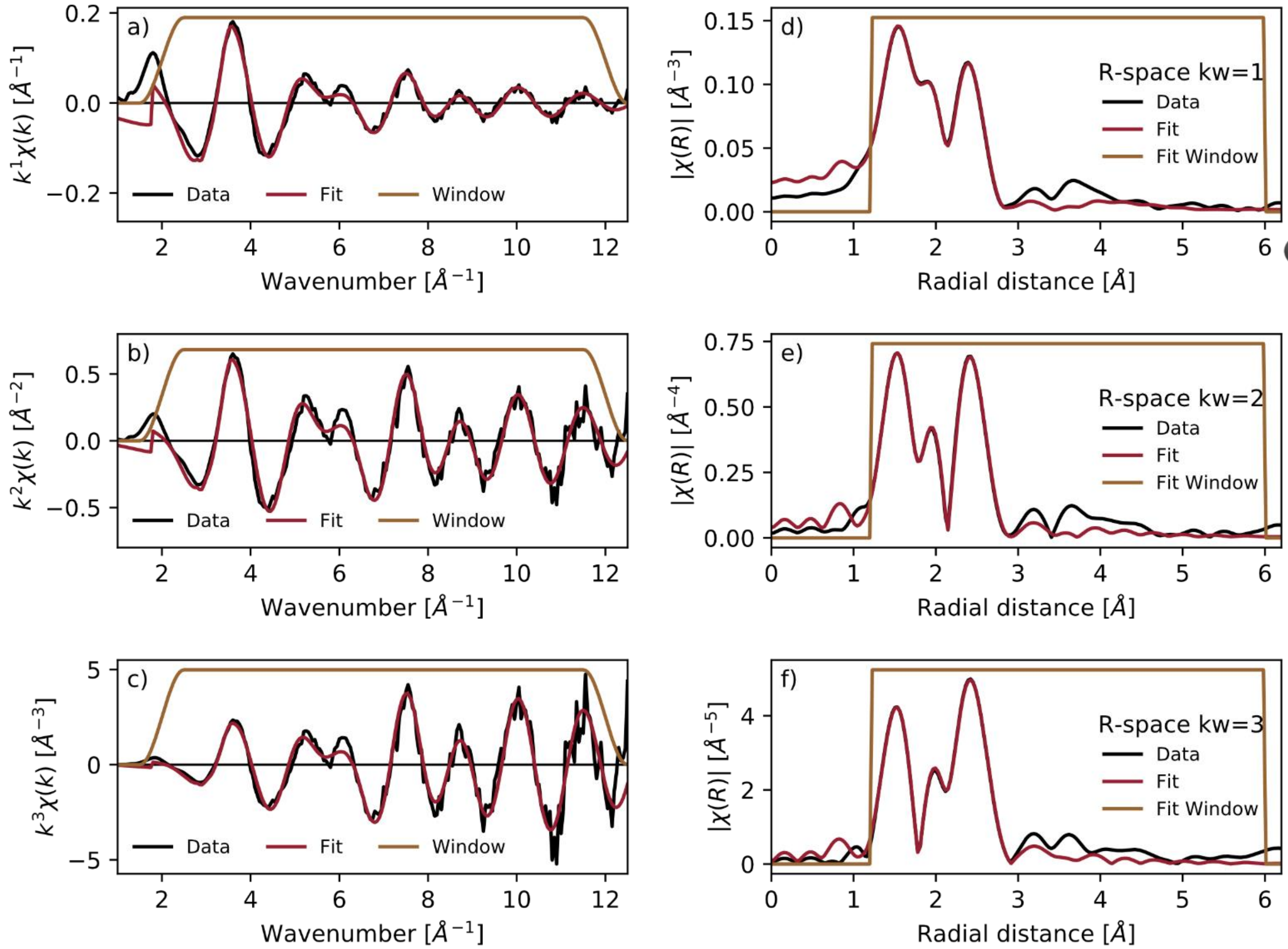
Lecture in a slide EXAFS

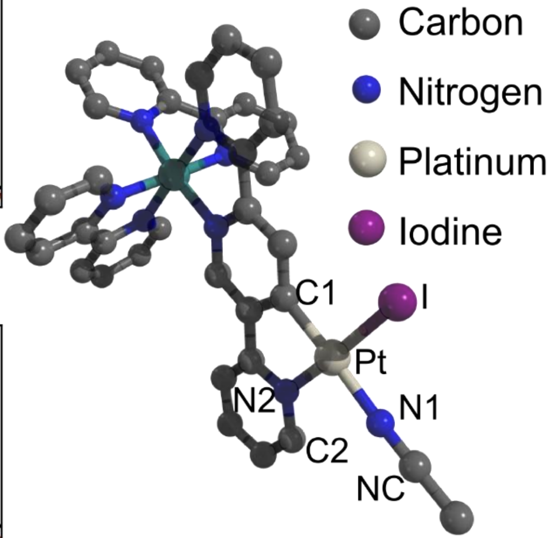





excitation
X-ray photon
with energy
E
outgoing
electron wave
interfering
electron
wave
excitation
X-ray photon
with energy
E + ΔE (e.g. 20eV)
0.6
Absorption [norm]
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
7.10
7.15
7.20
7.25
7.30
7.35
7.40
energy in keV

EXAFS – Ru-Pt light activated catalyst

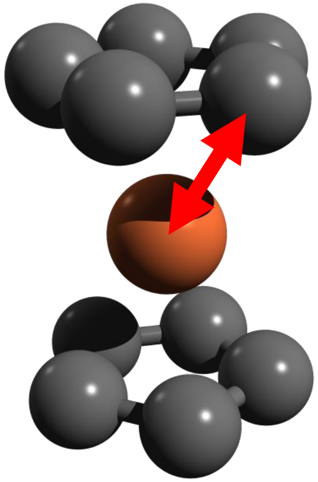




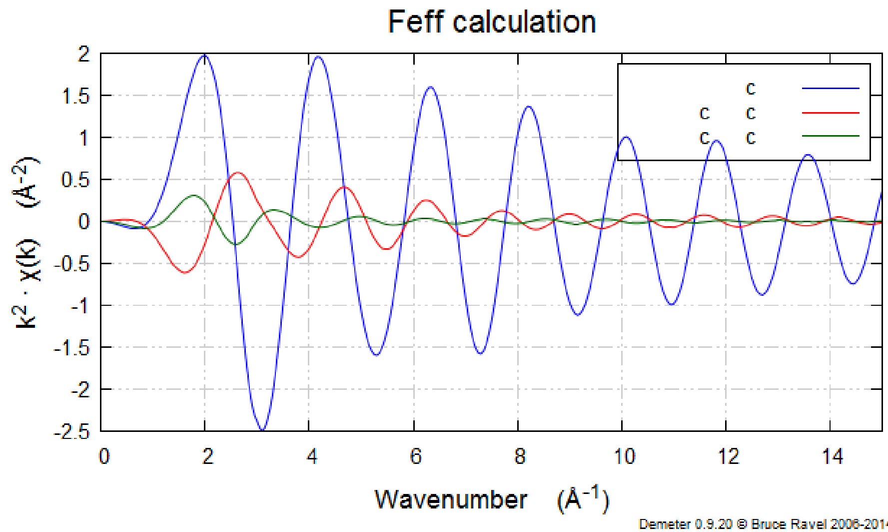
Fit in R-space with Kw=1,2,3:
R=0.023, X^2=35.4
Pt-N1:Reff=1.97±0.032
Pt-C1:Reff=1.98±0.016
Pt-N2:Reff=2.090±0.0037
Pt-I:Reff=2.648±0.0051
Pt-C2:Reff=3.07±0.018
Pt-NC:Reff=3.13±0.041

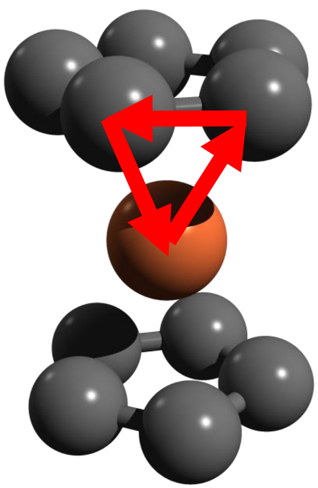
Huijser, A et al.
The Journal of Physical Chemistry A, **2018**, *122*, 6396-6406

What is a path

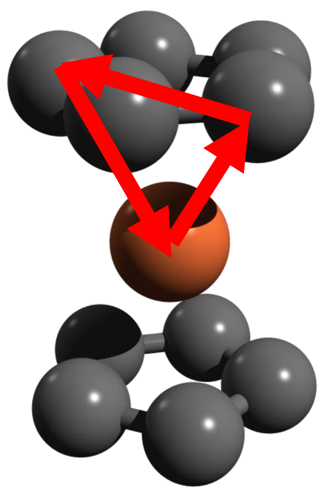


n = 10 D = 2.2

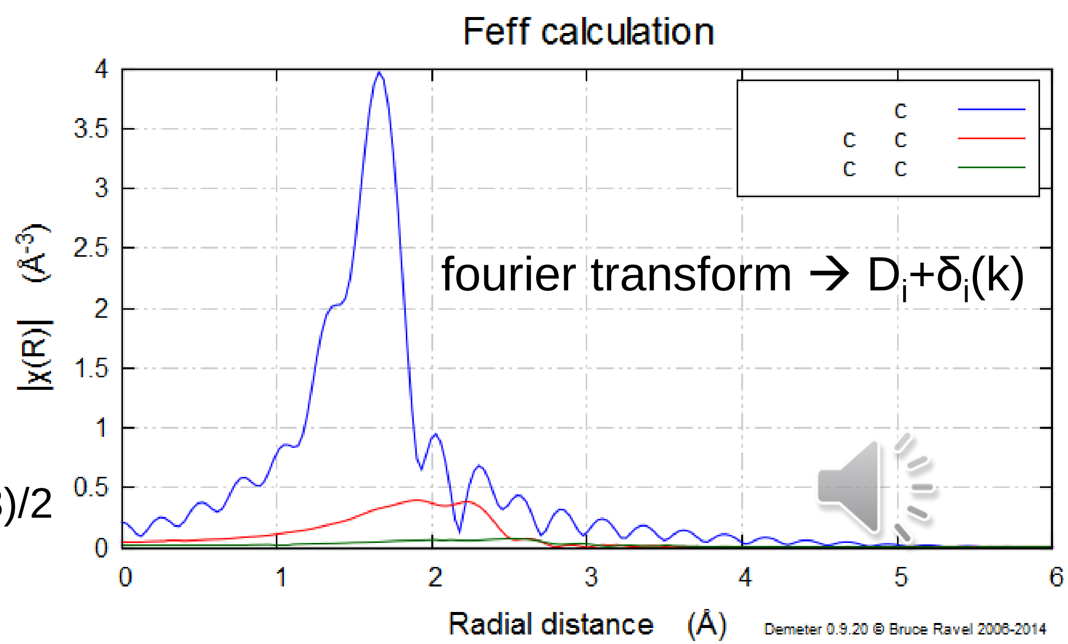




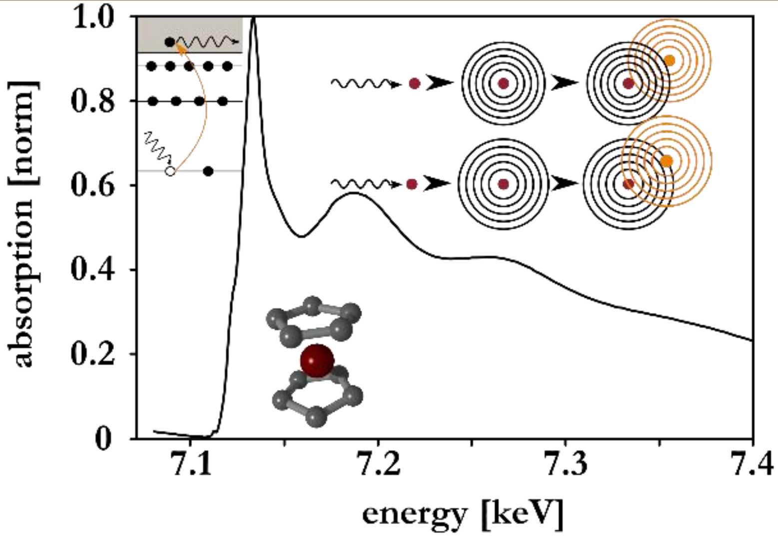
n = 20
D = (2.2+2.2+1.4)/2
= 2,9



n = 20
D = (2.2+2.2+2.3)/2
= 3,35



EXAFS Theory (only for the curious)



electron wavelength

$$\lambda = \frac{h}{p} \quad \text{with} \quad \hbar = \frac{h}{2\pi} \quad p = \hbar k$$

$$E_{kin} = \frac{p^2}{2m_e} \quad k = \frac{1}{\hbar}\sqrt{2m_e(E - E_0)}$$

$$\chi \sim sin\left(2\pi\frac{2D}{\lambda}\right)$$

$$\chi(k) = \tilde{f}(k) sin\,(2Dk) \quad \text{summing}$$

$$\chi(k) = \sum_i \tilde{f}_i(k) sin\,(2D_i k) \quad \text{multiplicity}$$

$$\chi(k) = \sum_i N_i \tilde{f}_i(k) sin\,(2D_i k)$$

$$f(\mathbf{Q}, \hbar\omega) = f^0((Q)) + f'(\hbar\omega) + i f''(\hbar\omega) \quad \text{scattering, absorption, phasejump}$$

$$\chi(k) = \sum_i N_i \tilde{f}_i(k) sin\,(2D_i k + \delta_i(k)) \quad \text{wavelength depending atomic scattering (renaming)}$$

$$\chi(k) = \sum_i N_i \frac{f_i(k)}{k} sin\,(2D_i k + \delta_i(k)) \quad \text{spherical wave}$$

$$\chi(k) = \sum_i \frac{1}{D_i^2} N_i \frac{f_i(k)}{k} sin\,(2D_i k + \delta_i(k)) \quad \text{scaling factor}$$

$$\chi(k) = S_0^2 \sum_i \frac{1}{D_i^2} N_i \frac{f_i(k)}{k} sin\,(2D_i k + \delta_i(k)) \quad \text{mean free path + core hole lifetime}$$

$$\chi(k) = S_0^2 \sum_i \frac{1}{D_i^2} N_i \frac{f_i(k)}{k} e^{-2D_i/\lambda_e} sin\,(2D_i k + \delta_i(k)) \quad \text{mean square displacement/Debye waller}$$

$$\chi(k) = S_0^2 \sum_i \frac{1}{D_i^2} N_i \frac{f_i(k)}{k} e^{-2D_i/\lambda_e} e^{-2k^2\sigma_i^2} sin\,(2D_i k + \delta_i(k))$$

Calculation with path extension

$$\chi(k) = S_0^2 \sum_i \frac{1}{D_i^2} N_i \frac{f_i(k)}{k} e^{-2D_i/\lambda_e} e^{-2k^2\sigma_i^2} sin\left(2D_i k + \delta_i(k)\right)$$

Path but not distance specific

$$\chi(k) = S_0^2 \sum_i \frac{1}{D_i^2} N_i \frac{f_i(k)}{k} e^{-2D_i/\lambda_e} e^{-2k^2\sigma_i^2} sin\left(2D_i k + \delta_i(k)\right)$$

Distance but not atom type specific

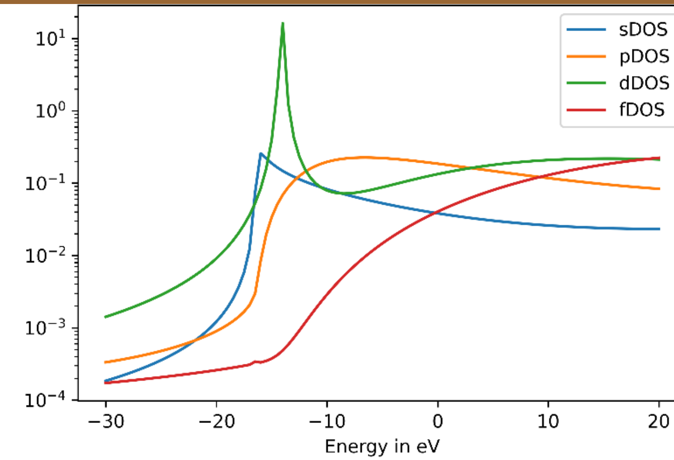
$$\chi(k) = S_0^2 \sum_i \frac{1}{D_i^2} N_i \frac{f_i(k)}{k} e^{-2D_i/\lambda_e} e^{-2k^2\sigma_i^2} sin\left(2D_i k + \delta_i(k)\right)$$

3 parameter per path, Ni is set (model),
2 per path are fitted

$$\chi(k) = S_0^2 \sum_i \frac{1}{D_i^2} N_i \frac{f_i(k)}{k} e^{-2D_i/\lambda_e} e^{-2k^2\sigma_i^2} sin\left(2D_i k + \delta_i(k)\right)$$

$$k = \frac{1}{\hbar}\sqrt{2m_e(E - E_0)}$$

2 for all paths are fitted



paths.dat

```
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 -----------------------------------------------------------------------
    1     2  12.000  index, nleg, degeneracy, r=  2.5527
      x            y            z      ipot  label       rleg      beta        eta
  -1.805000    -1.805000     0.000000    1 'Cu    '     2.5527  180.0000    0.0000
   0.000000     0.000000     0.000000    0 'Cu    '     2.5527  180.0000    0.0000
    2     2   6.000  index, nleg, degeneracy, r=  3.6100
      x            y            z      ipot  label       rleg      beta        eta
  -3.610000     0.000000     0.000000    1 'Cu    '     3.6100  180.0000    0.0000
```
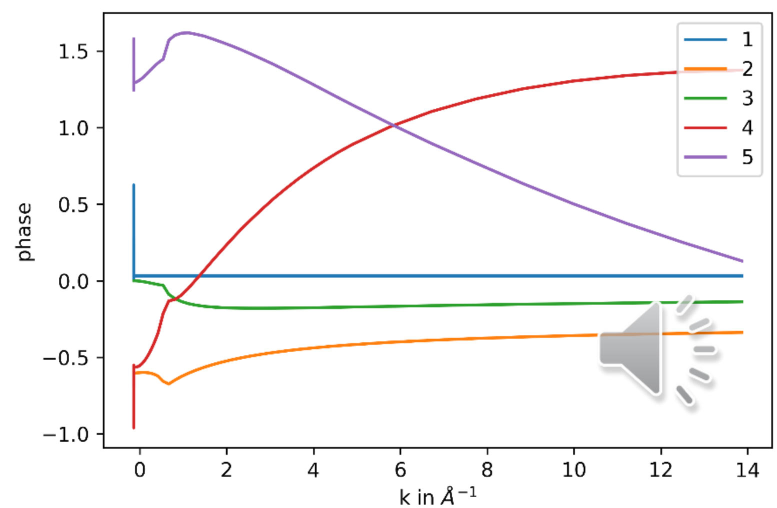
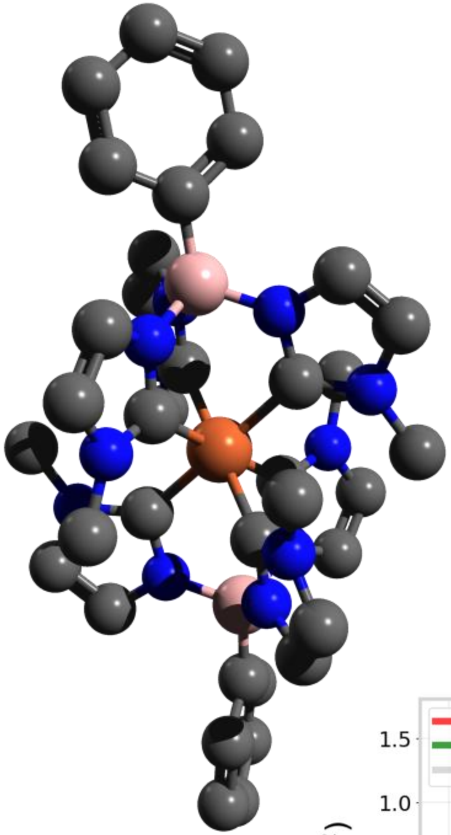
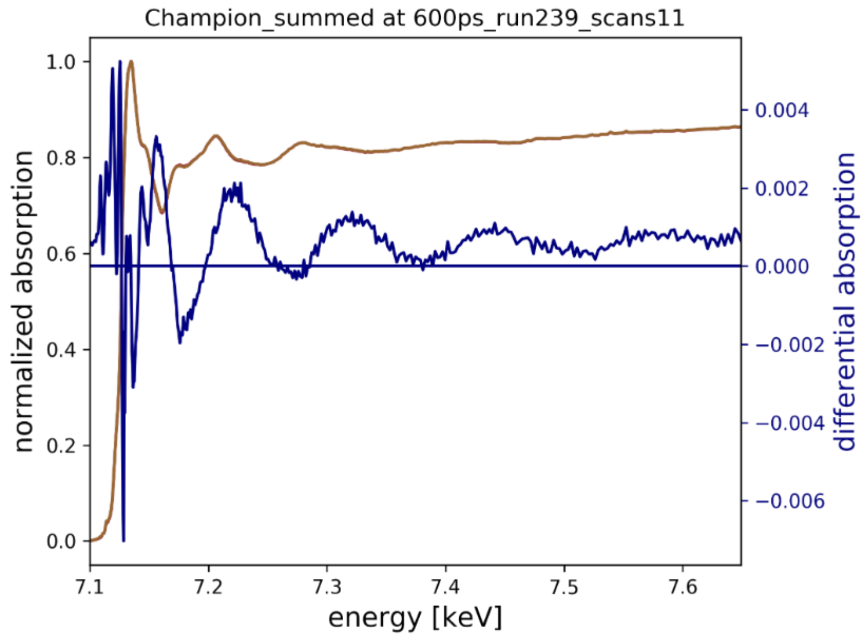
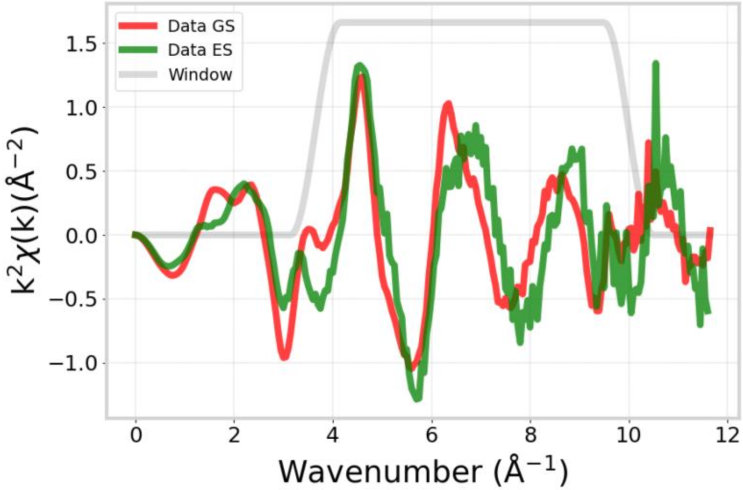
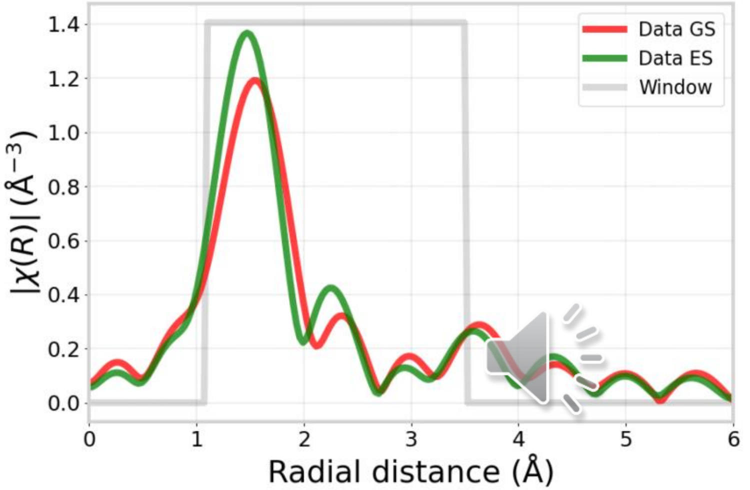



Transient EXAFS?

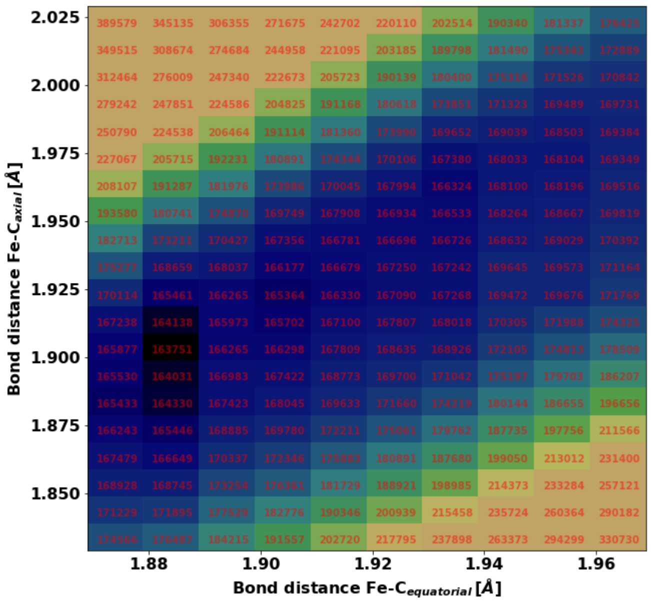


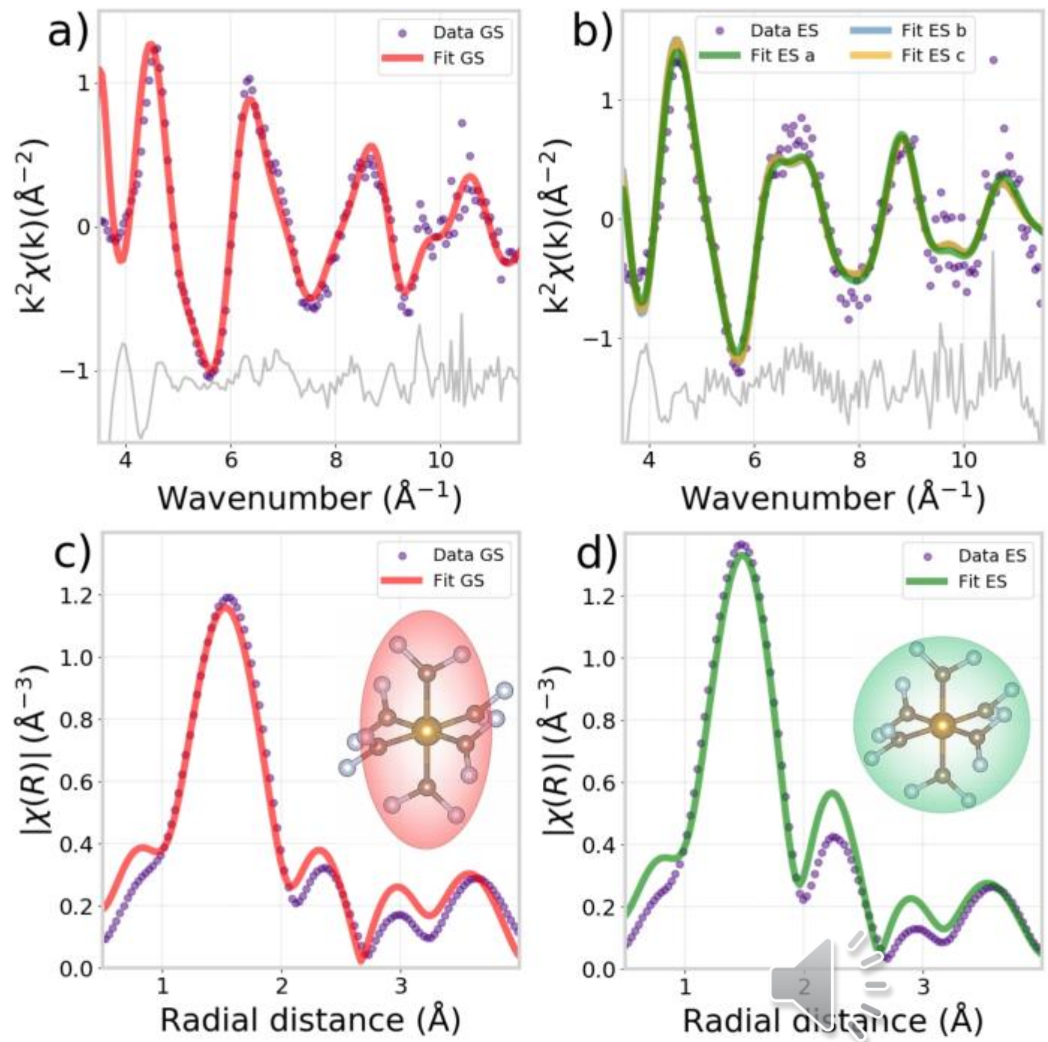




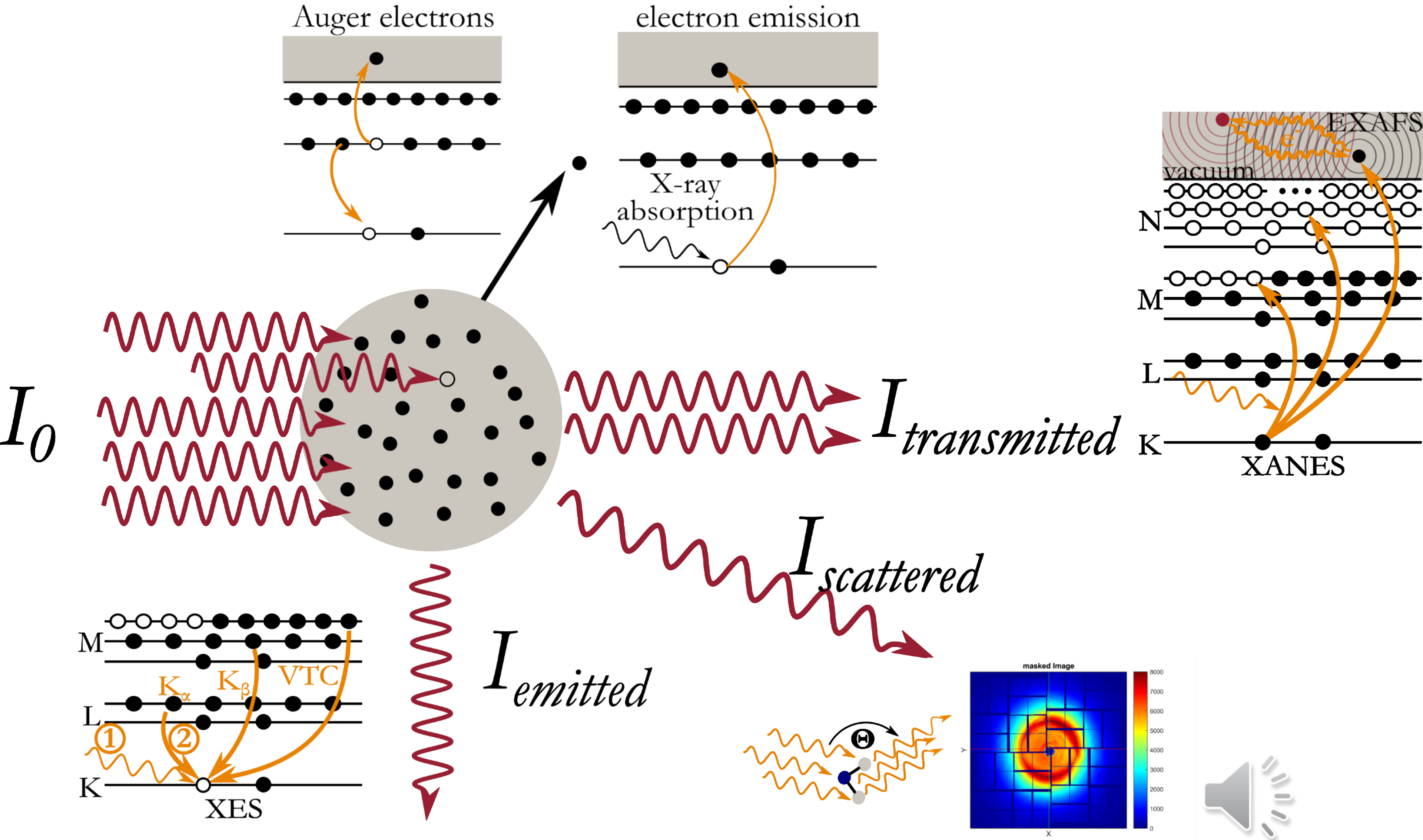


TR-EXAFS Analysis, restricted movements…



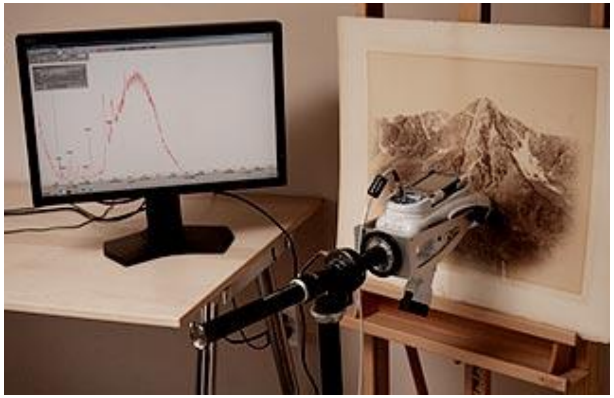


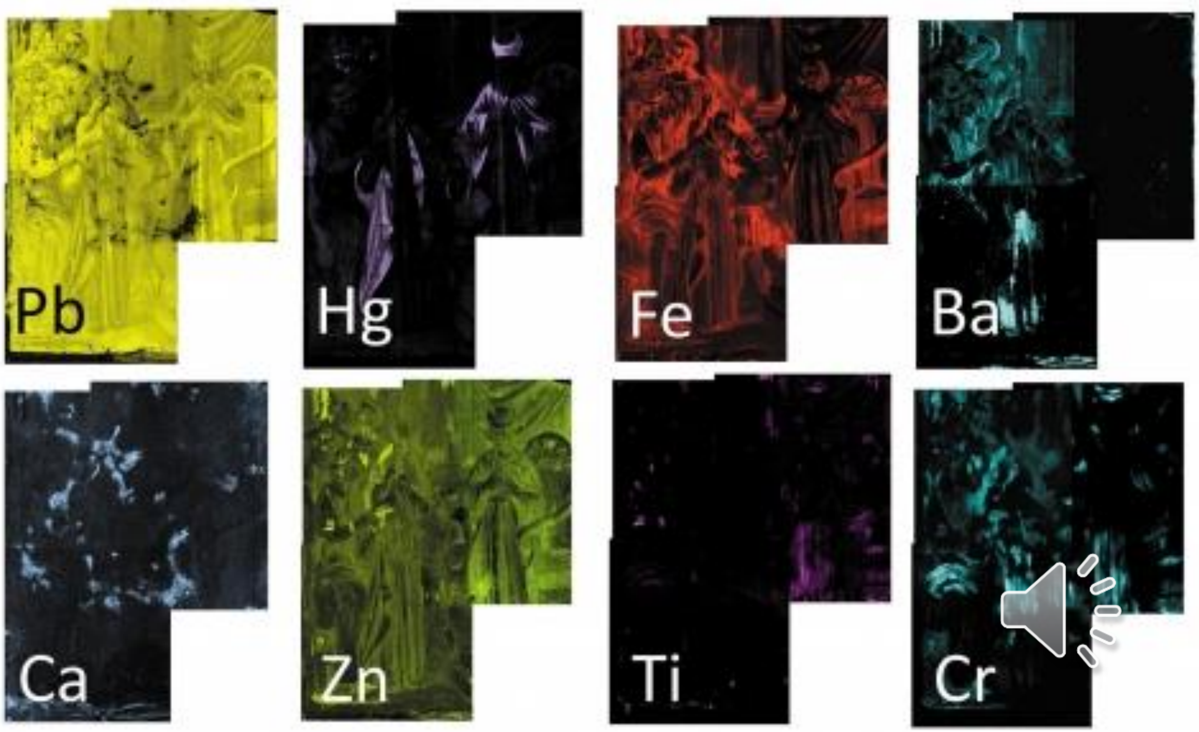
Interactions with light, most of them



$$I_0 = I_{transmitted} + I_{absorbed} + I_{scattered}$$

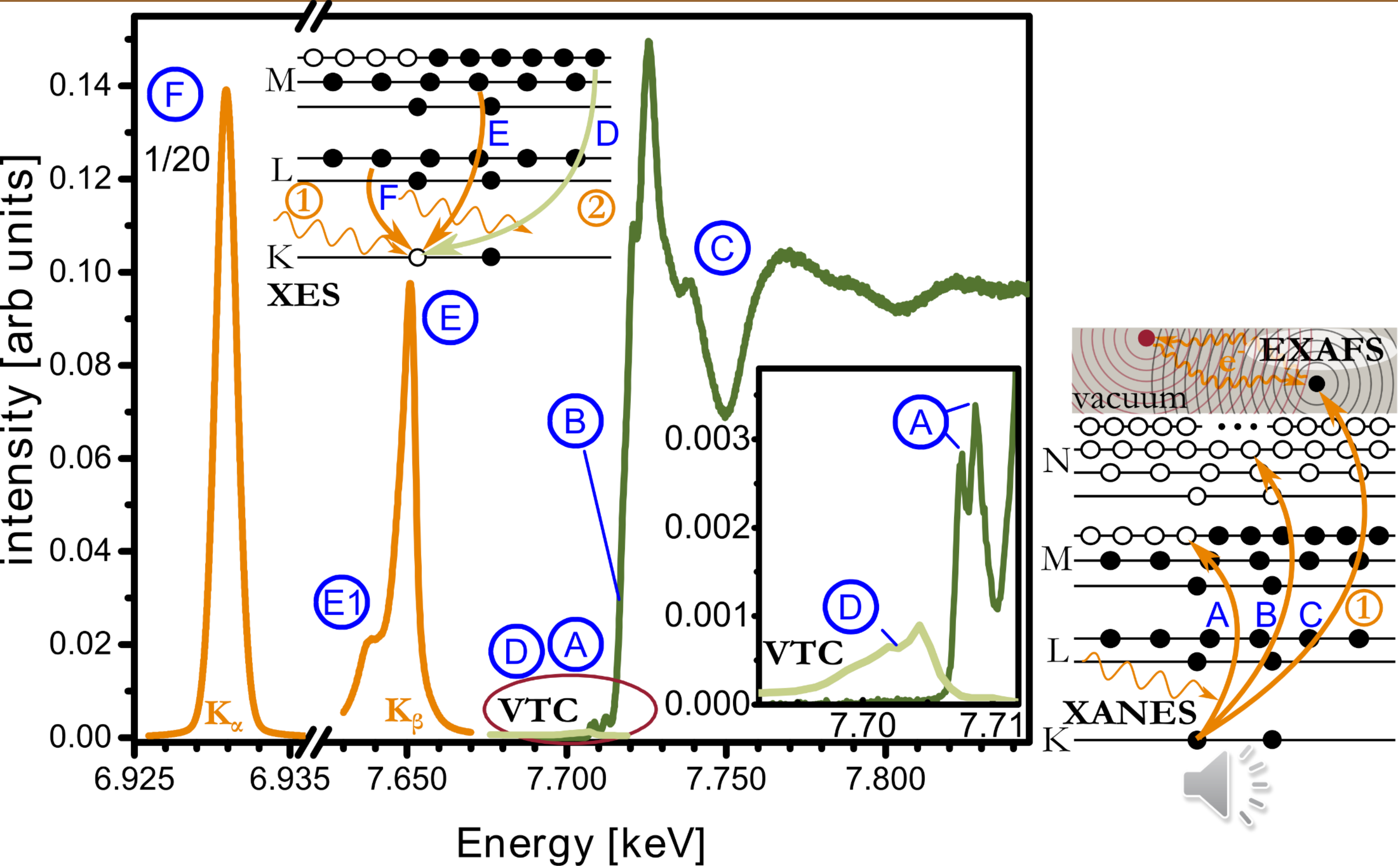
XRF/EDX



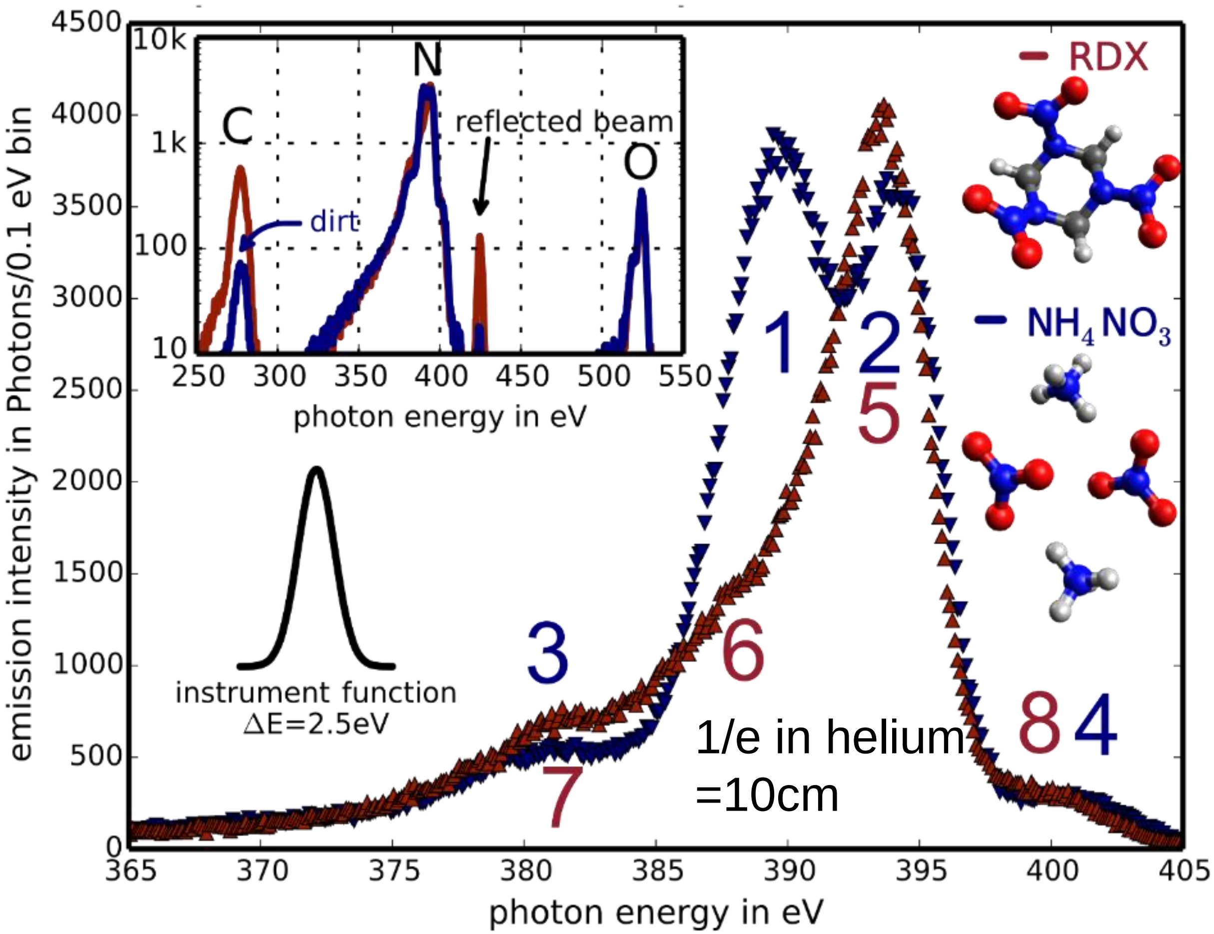


XRF
In air often hand held
(heavy elements > sulfur)
industry

Lecture in a slide XES – K_α and K_β



XES chemical-shift + dispersive detection



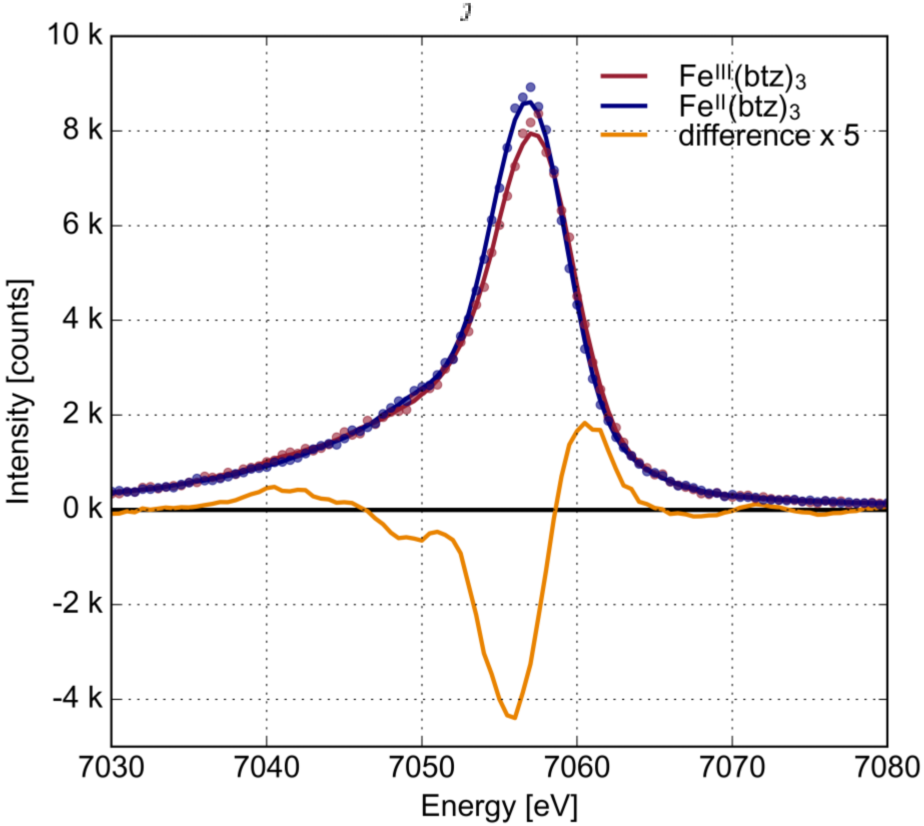
Uhlig, J. et al.
Journal of Synchrotron Radiation, **2015**, *22*, 766-775

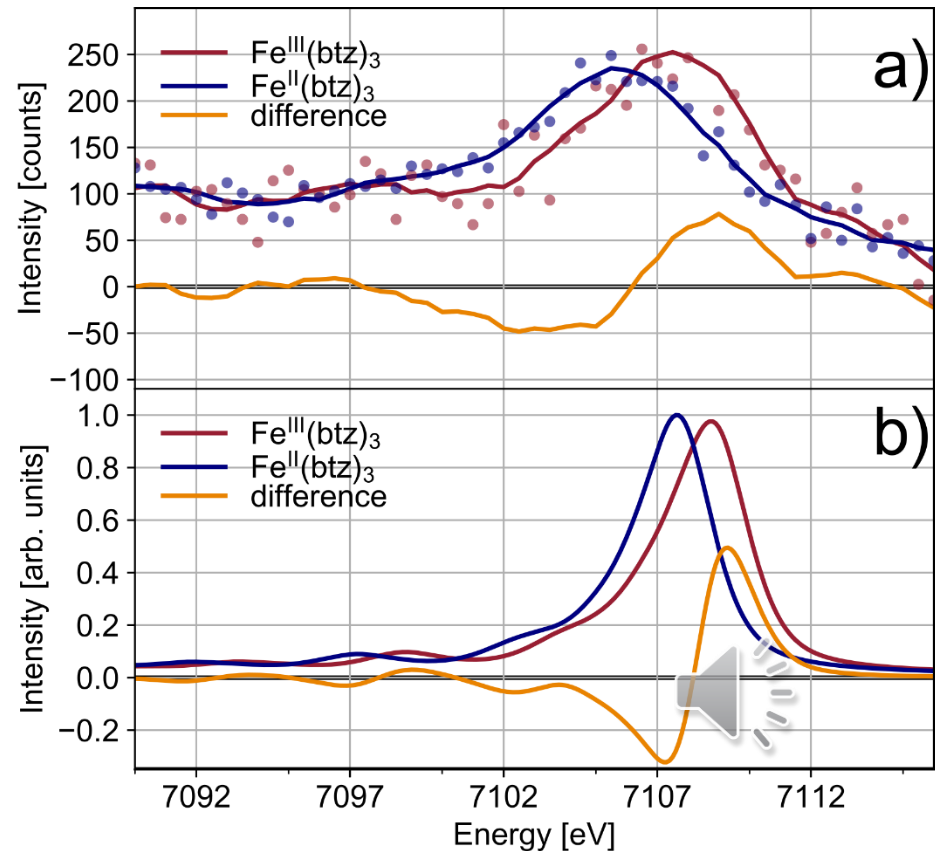
XES Iron K_β and VTC sensitive to oxidation state

$$F_{KH}(\omega_{in}, \omega_{out}) = \frac{\omega_{out}}{\omega_{in}} \sum_f \left| \sum_n \frac{\left\langle f \left| \hat{O}'^\dagger \right| n \right\rangle \left\langle n \left| \hat{O} \right| g \right\rangle}{E_n - E_g - \hbar\omega_{in} - i\Gamma_n} \right|^2 \frac{\frac{\Gamma_f}{\pi}}{(E_f - E_g - \hbar(\omega_{in} - \omega_{out}))^2 + \Gamma_f^2}$$

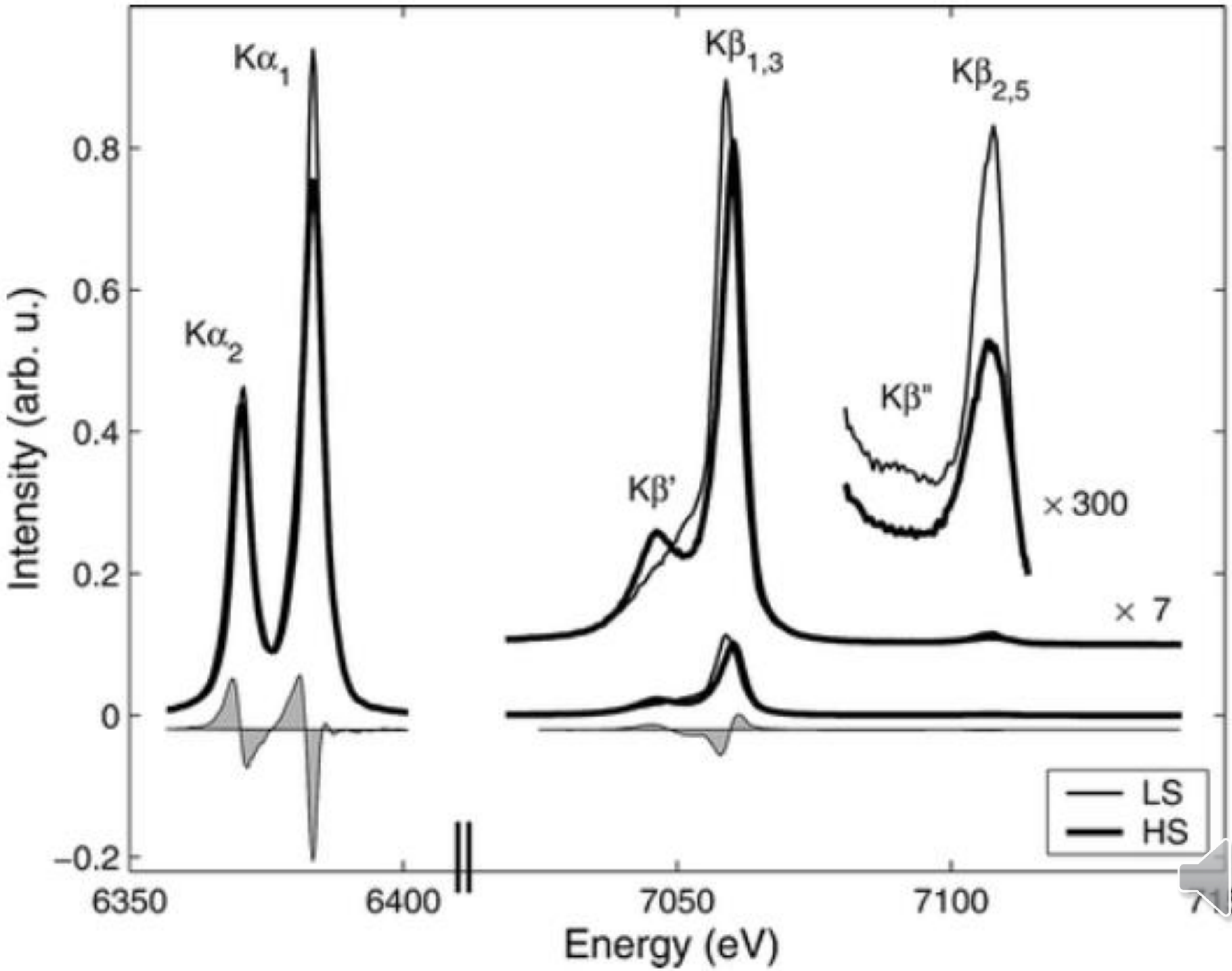
$$\text{with} \quad \hat{O}'^\dagger = \sum_{j'} (\epsilon^*_{out} \cdot p_{j'}) e^{-ik_{out} r_{j'}}$$

$$\text{with} \quad \hat{O}^\dagger = \sum_{j} (\epsilon^*_{in} \cdot p_{j}) e^{-ik_{in} r_{j}}$$



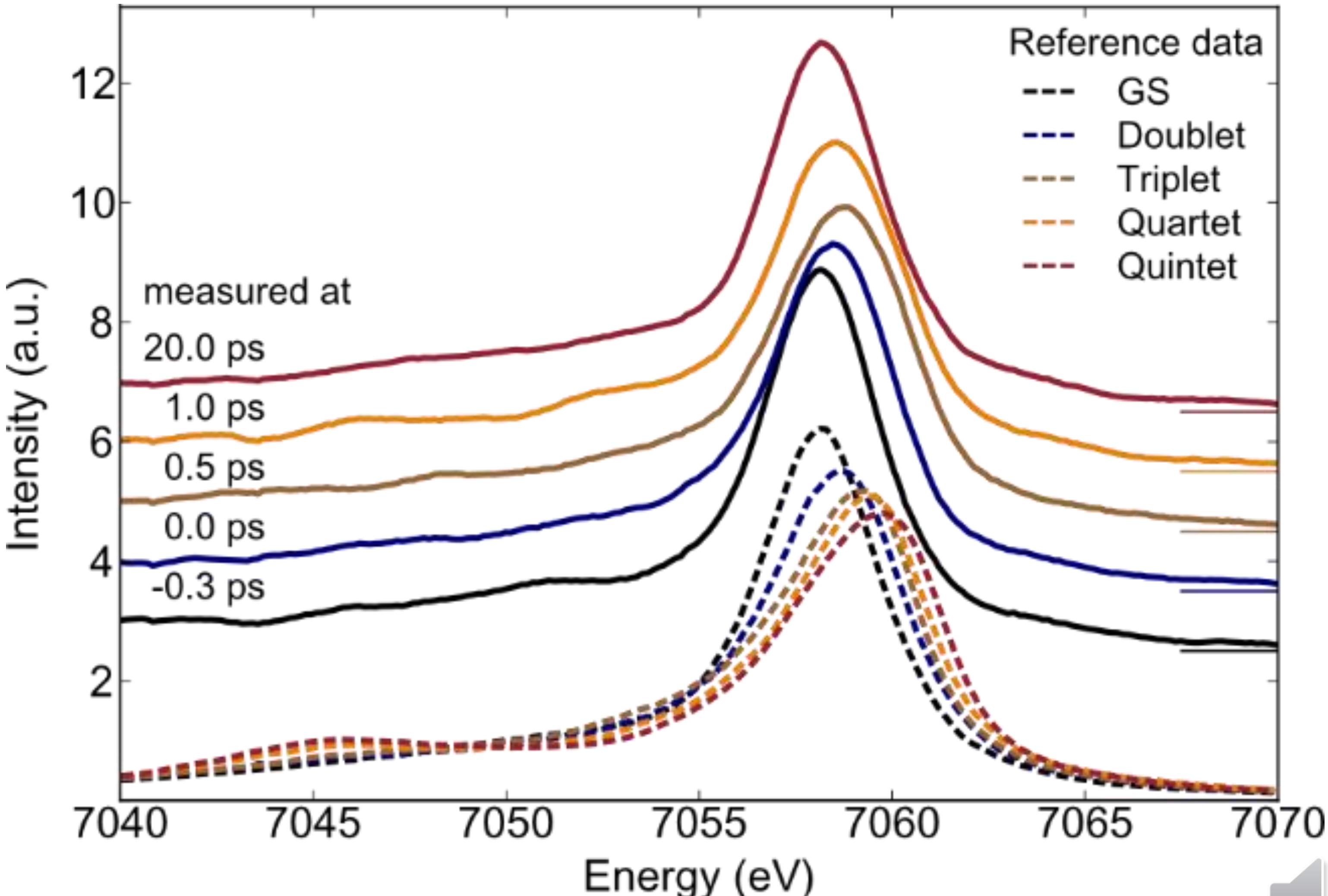


XES Iron K_β based state transition tracing



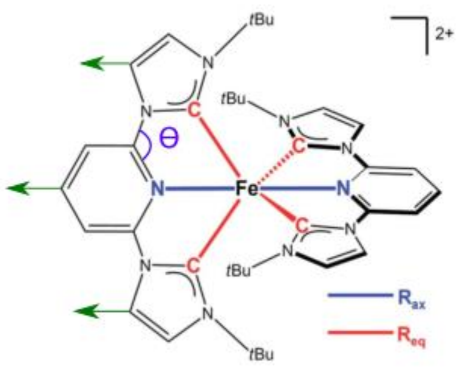
Vanko, J. Phys. Chem. B 2006, 110, 24, 11647–11653, https://doi.org/10.1021/jp0615961

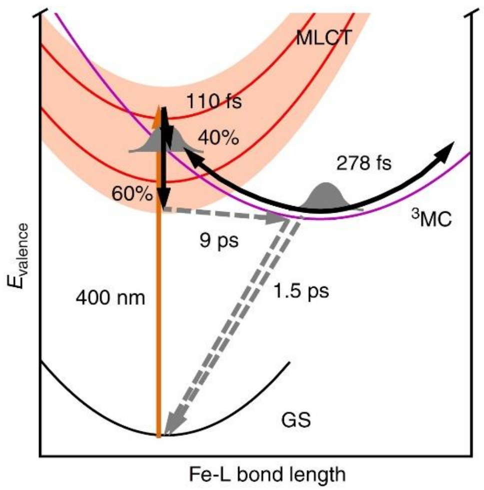
XES Iron K_β based state transition tracing

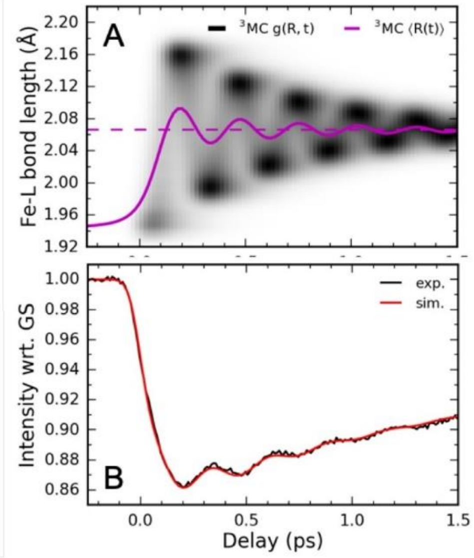


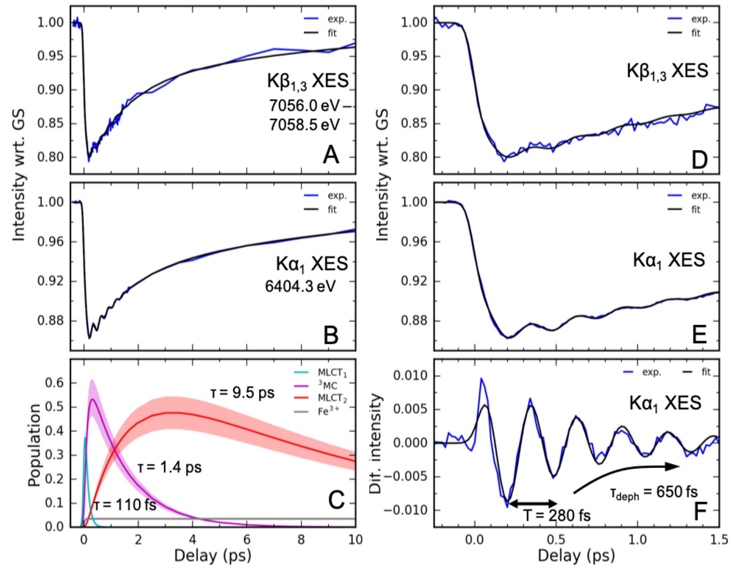
Tatsuno, H. et al.
Angewandte Chemistry, **2019**, *132*, 372-380

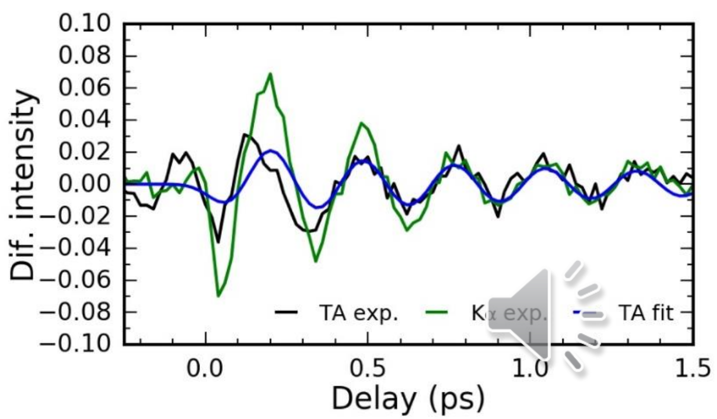
Hot dynamics and structural response





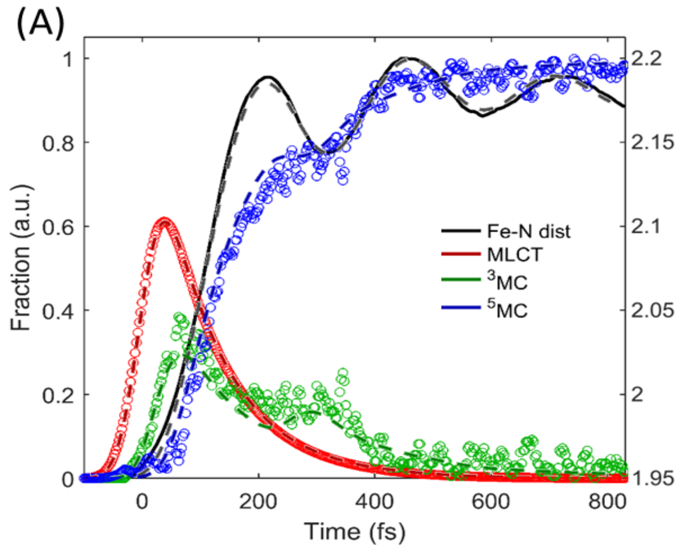


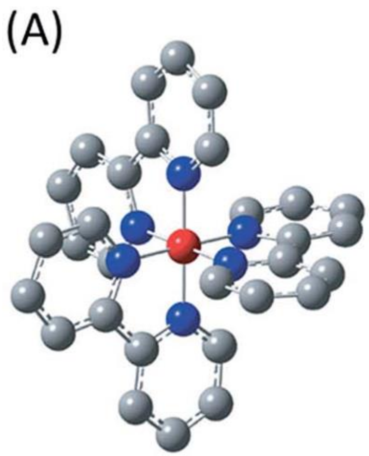


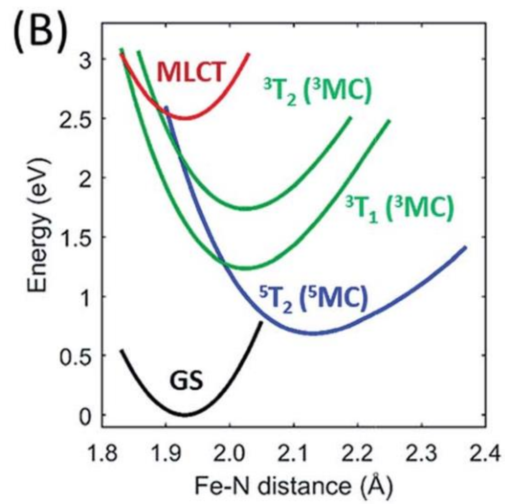


Nature Communications 10.1038/s41467-020-14468-w Kristjan Kunnus

Oscillations

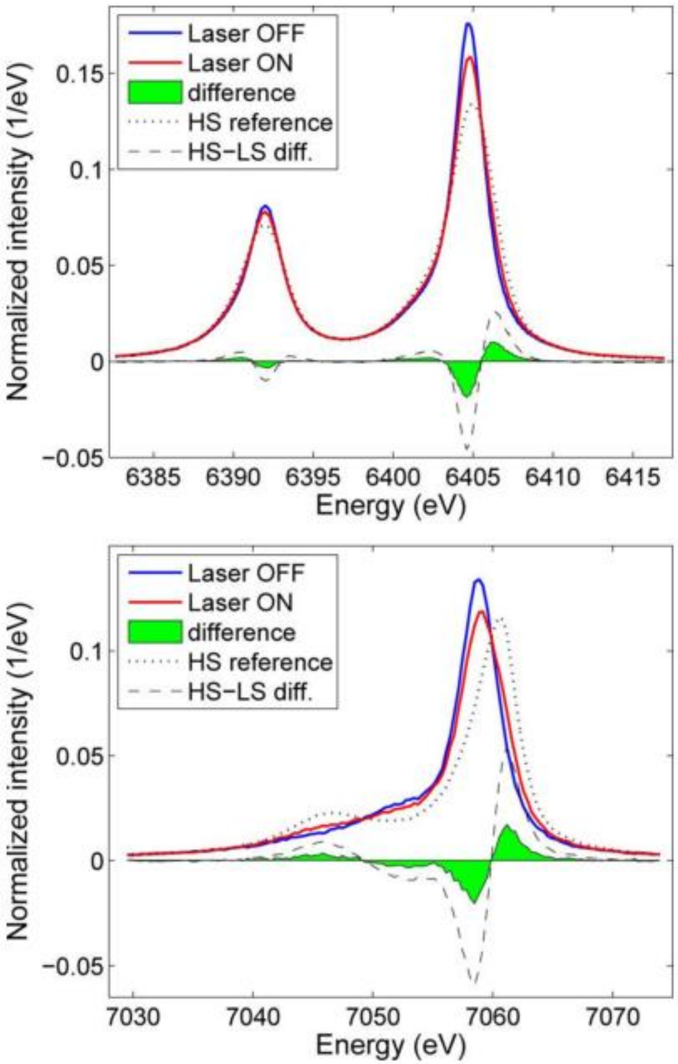


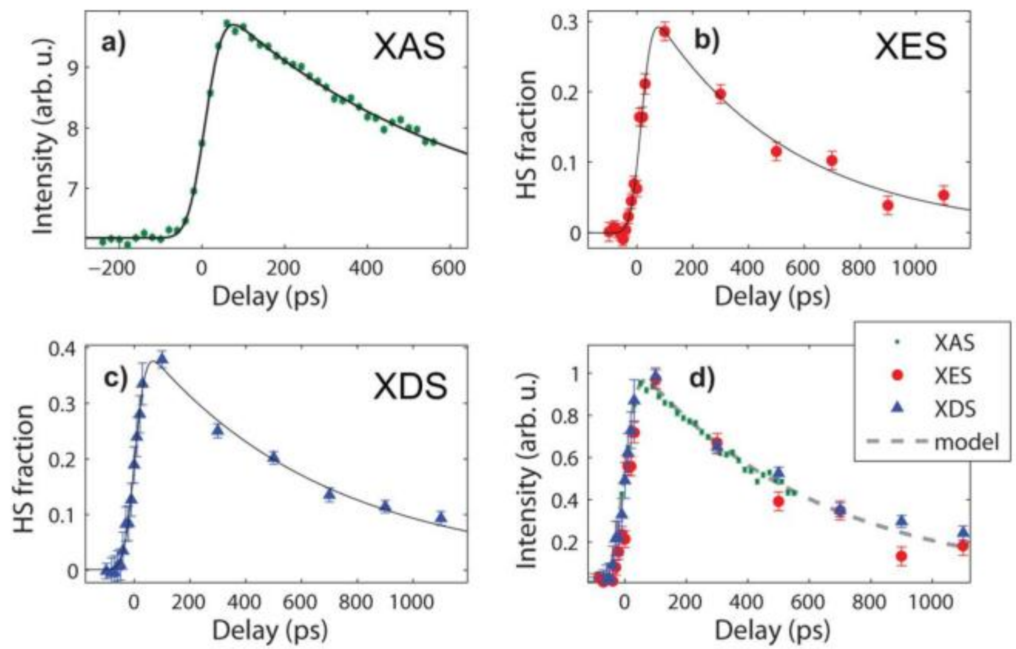




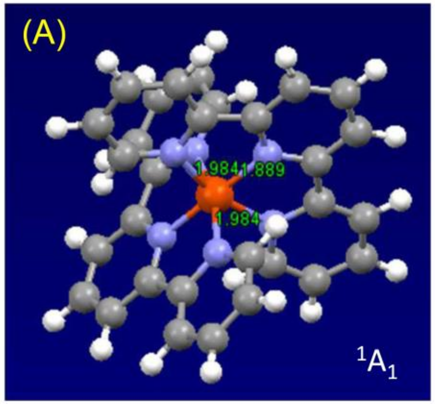
Kjær et al. Chemical Science, 2019, advance article
https://doi.org/10.1039/c8sc04023k

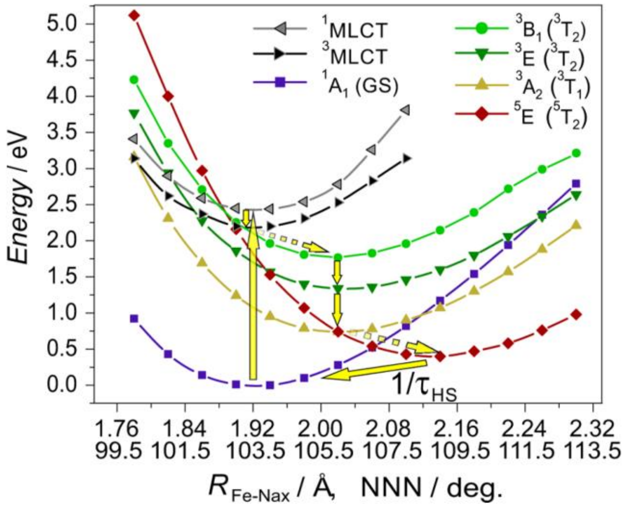
Static XES and XAS using pulsed source with ps length

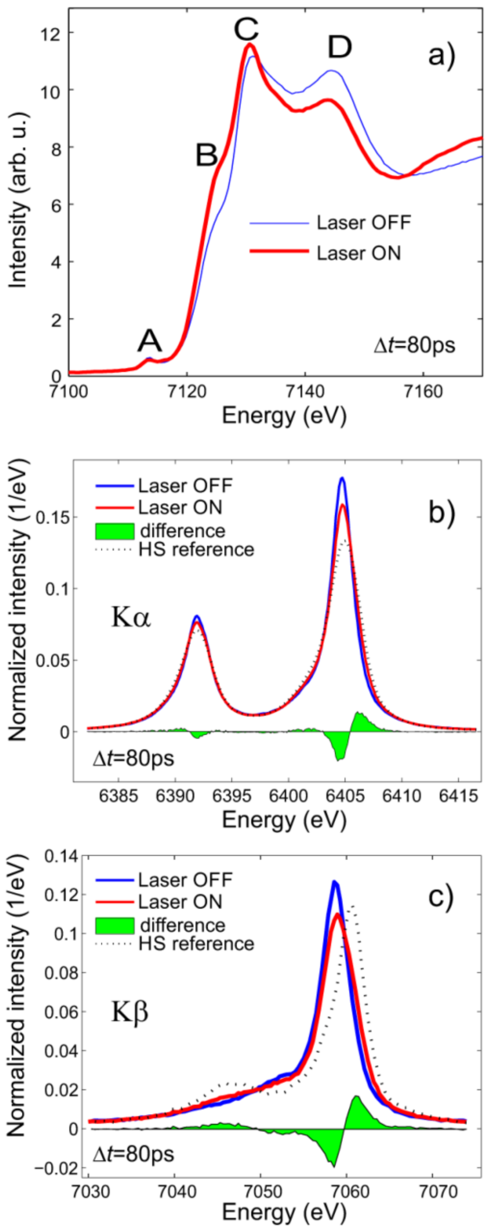




Combining techniques







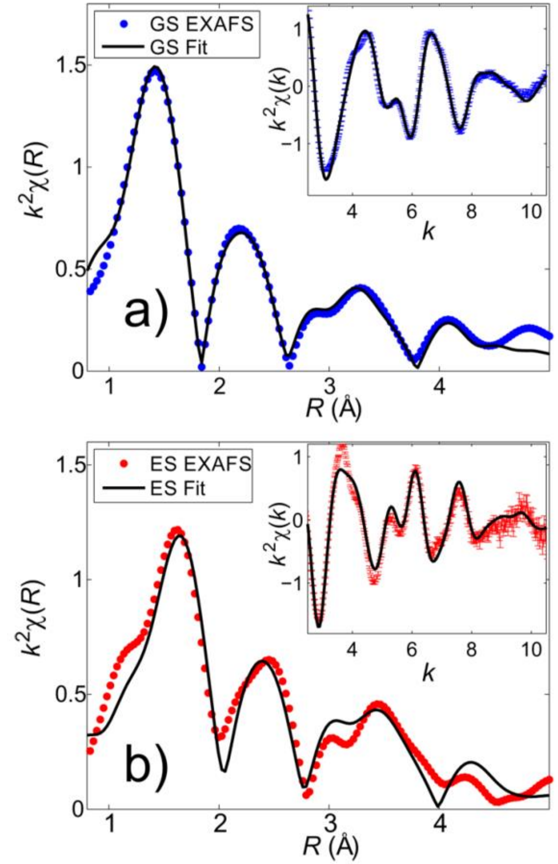
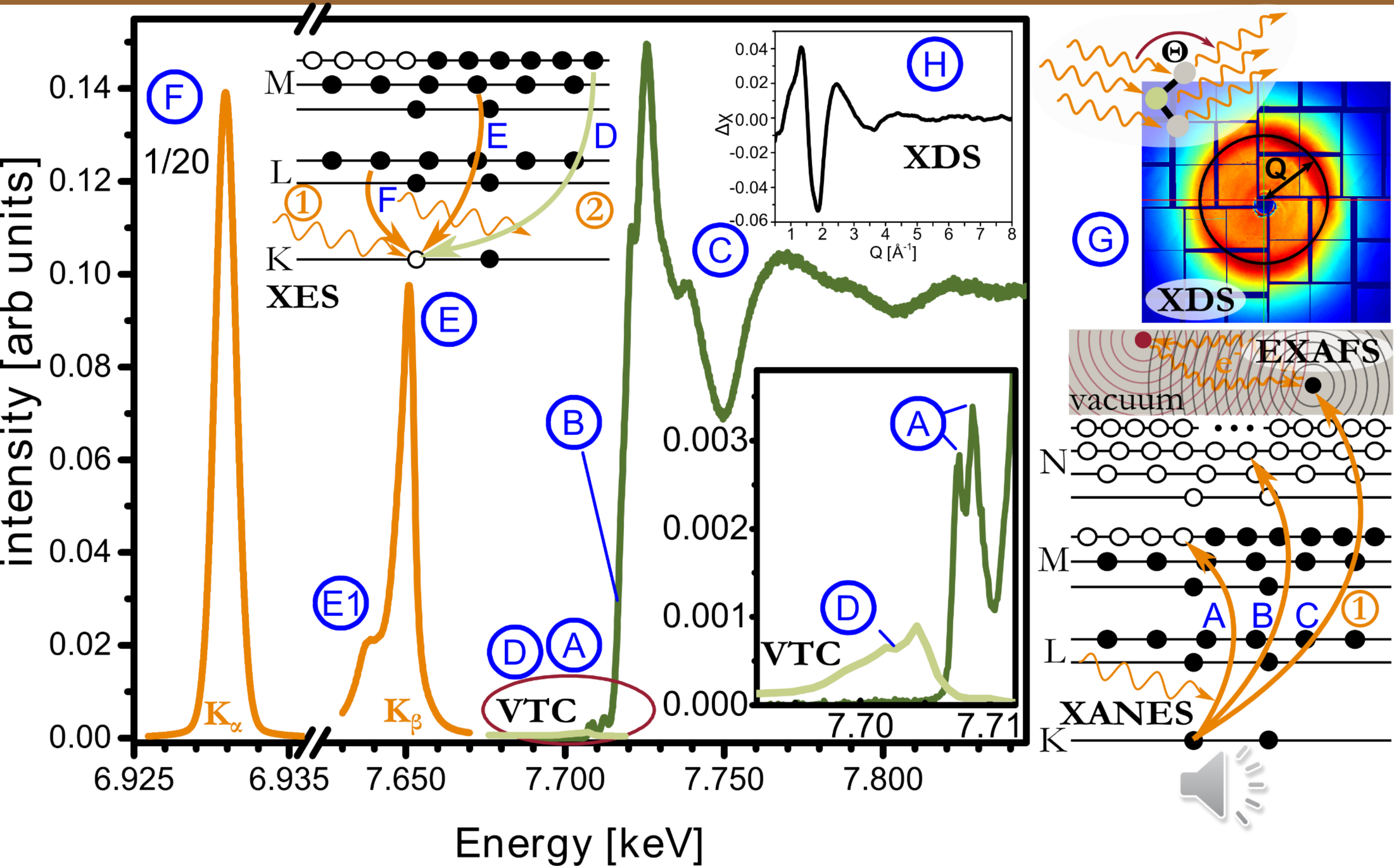
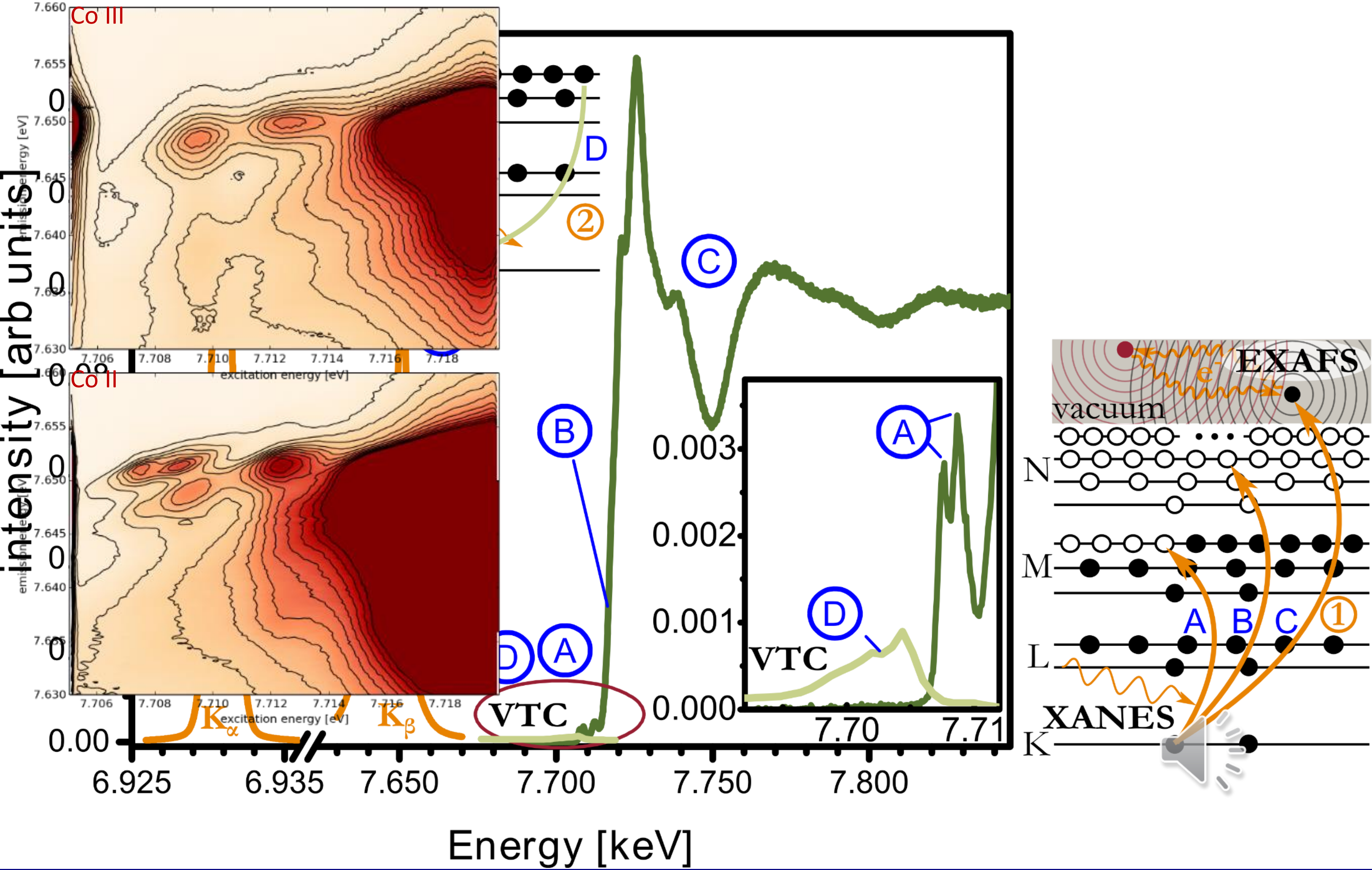


Figure 4. (a) EXAFS of $[Fe(terpy)_2]^{2+}$ in the ground state; the fitted bond lengths are $R(Fe{-}N_{ax})$ = 1.874 ± 0.004 Å and $R(Fe{-}N_{eq})$ = 1.969 ± 0.004 Å. (b) EXAFS spectrum of the photoexcited quintet state of $[Fe(terpy)_2]^{2+}$; the fitted bond lengths are $R(Fe{-}N_{ax})$ = 2.08 ± 0.02 Å and $R(Fe{-}N_{eq})$ = 2.20 ± 0.01 Å.

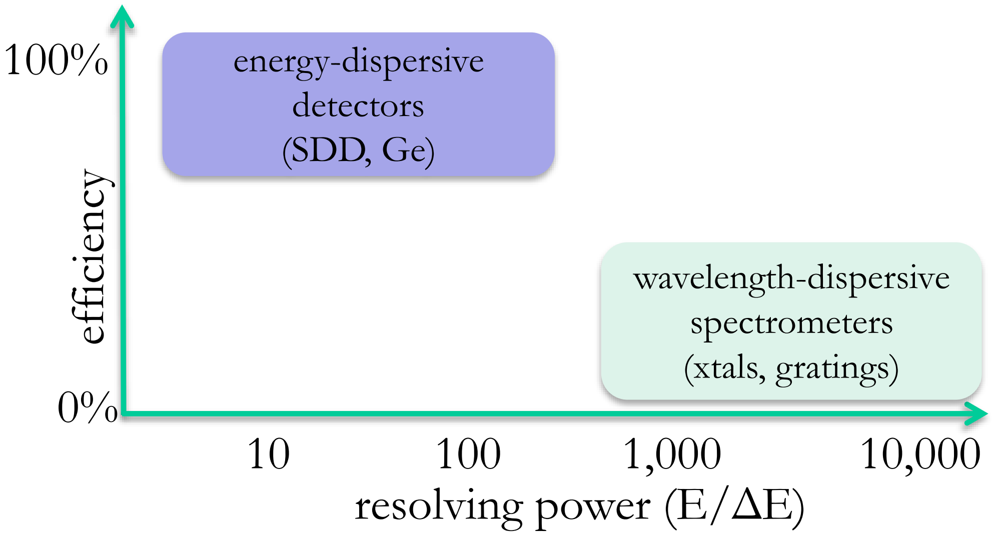
Lecture in a slide RIXS

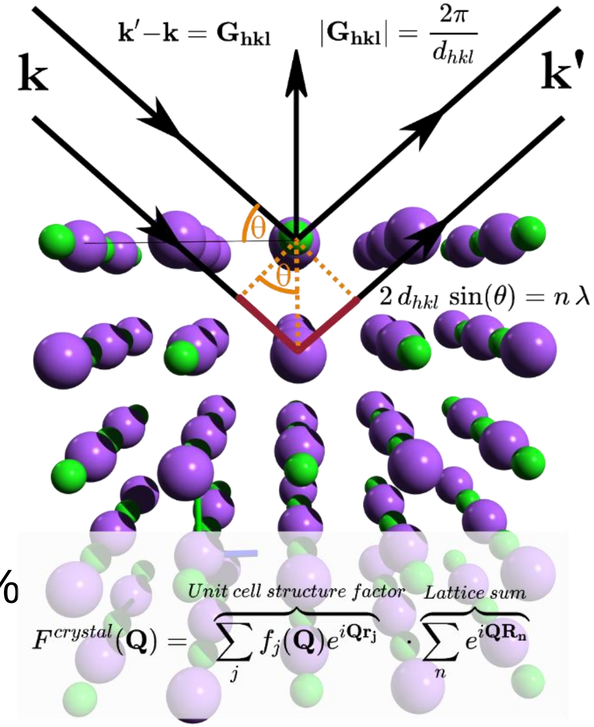


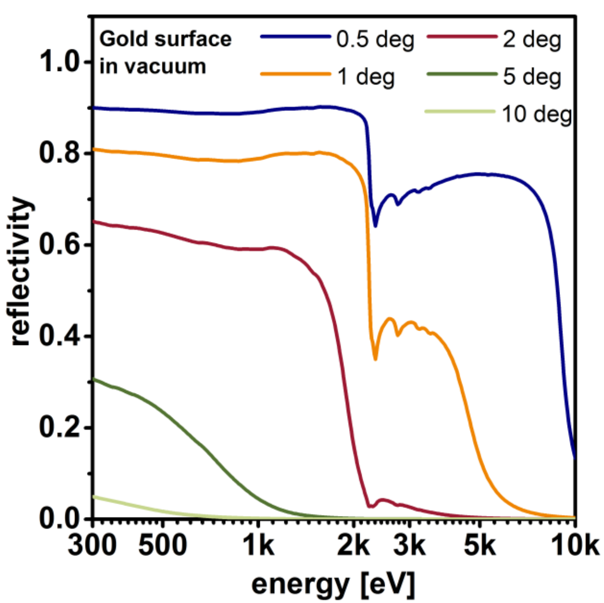
Lecture in a slide RIXS



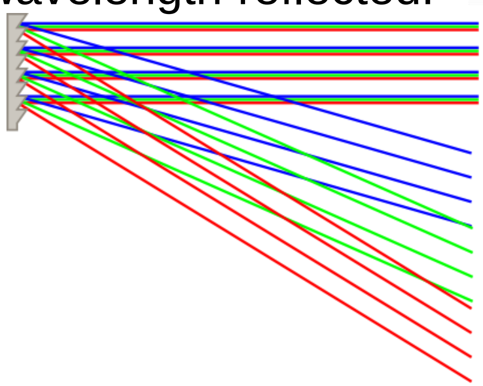
X-ray detection Crystal reflections

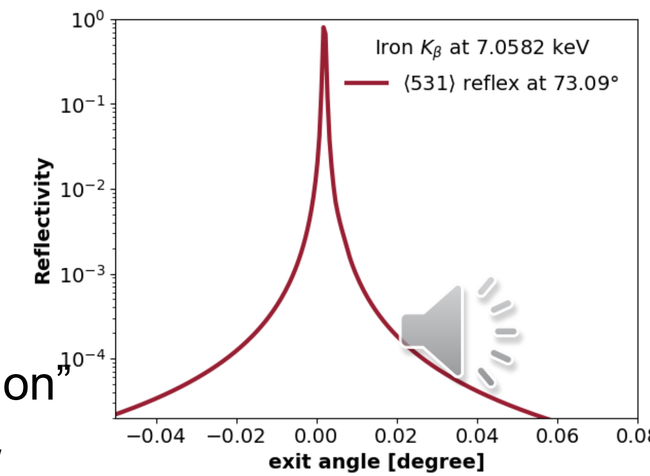






Classical grating >50% reflectivity and all wavelength reflected!





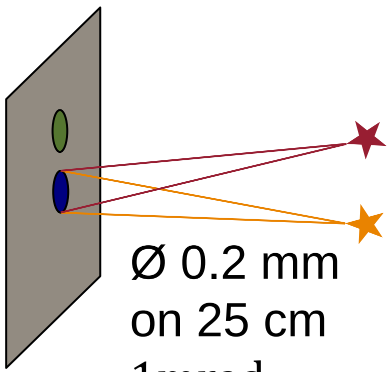
Classic Bragg ”-selection”

Sergey Stepanov X-ray server

https://x-server.gmca.aps.anl.gov/

Crystal geometries

Flat



Ø 0.2 mm
on 25 cm
1mrad
$\approx 1 \times 10^{-7}$

cylindrical bend
von-Hamos

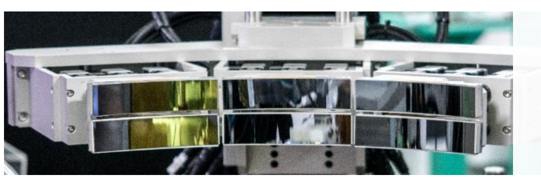
0.2 mm x 10 cm
on 25 cm
$\approx 3 \times 10^{-5}$

Spherical bend,
Johan/Johannson

motor
control

Ø 10 cm 1/3
on 50 cm
$\approx 8 \times 10^{-4}$

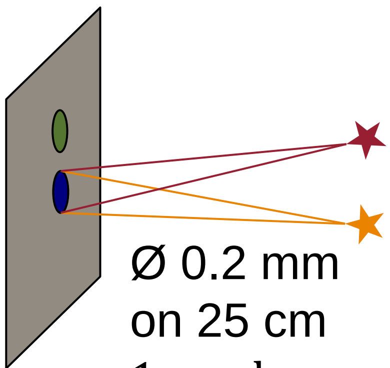
0.5 eV
scanning



https://www.youtube.com/watch?v=3lJ9uE7Xvcg&t=101s

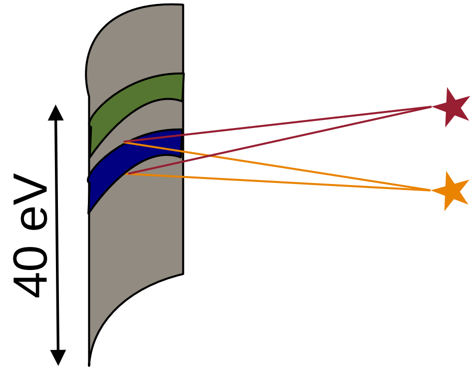
Crystal geometries

Flat



Ø 0.2 mm
on 25 cm
$1\text{mrad} \approx 1 \times 10^{-7}$

cylindrical bend
von-Hamos

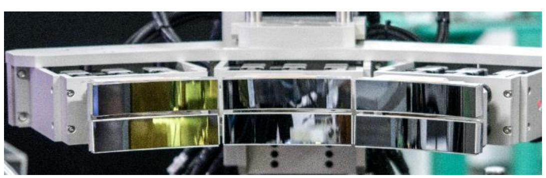


0.2 mm x 10 cm
on 25 cm
$\approx 3 \times 10^{-5}$

Spherical bend,
Johan/Johannson

Ø 10 cm 1/3
on 50 cm
$\approx 8 \times 10^{-4}$

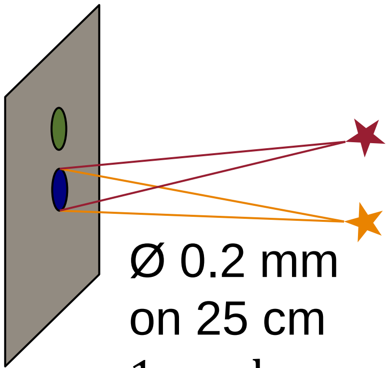
0.5 eV
scanning



https://www.youtube.com/watch?v=3lJ9uE7Xvcg&t=101s

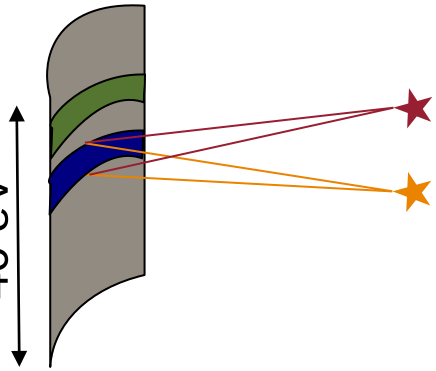
Crystal geometries

Flat



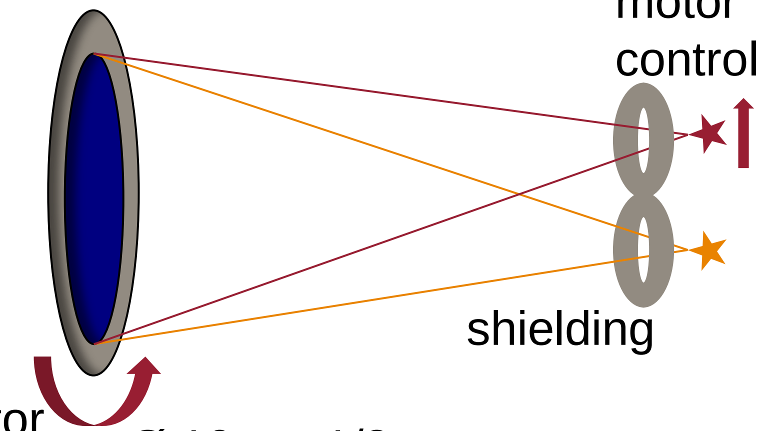
Ø 0.2 mm
on 25 cm
$\frac{1\text{mrad}}{} \approx 1 \times 10^{-7}$

cylindrical bend von-Hamos



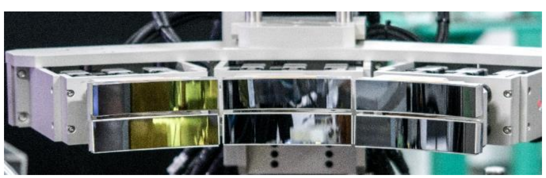
0.2 mm x 10 cm
on 25 cm
$\approx 3 \times 10^{-5}$

Spherical bend, Johan/Johannson



Ø 10 cm 1/3
on 50 cm
$\approx 8 \times 10^{-4}$

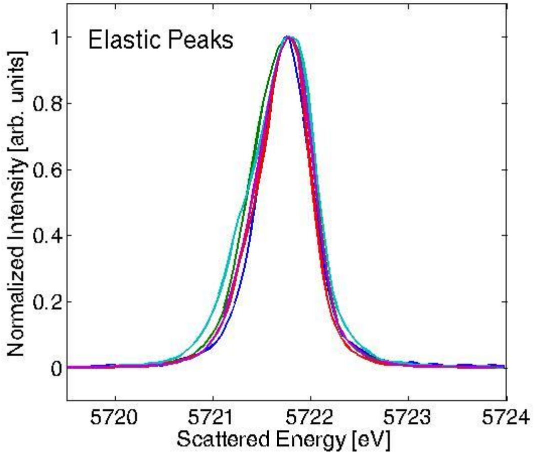
0.5 eV
scanning



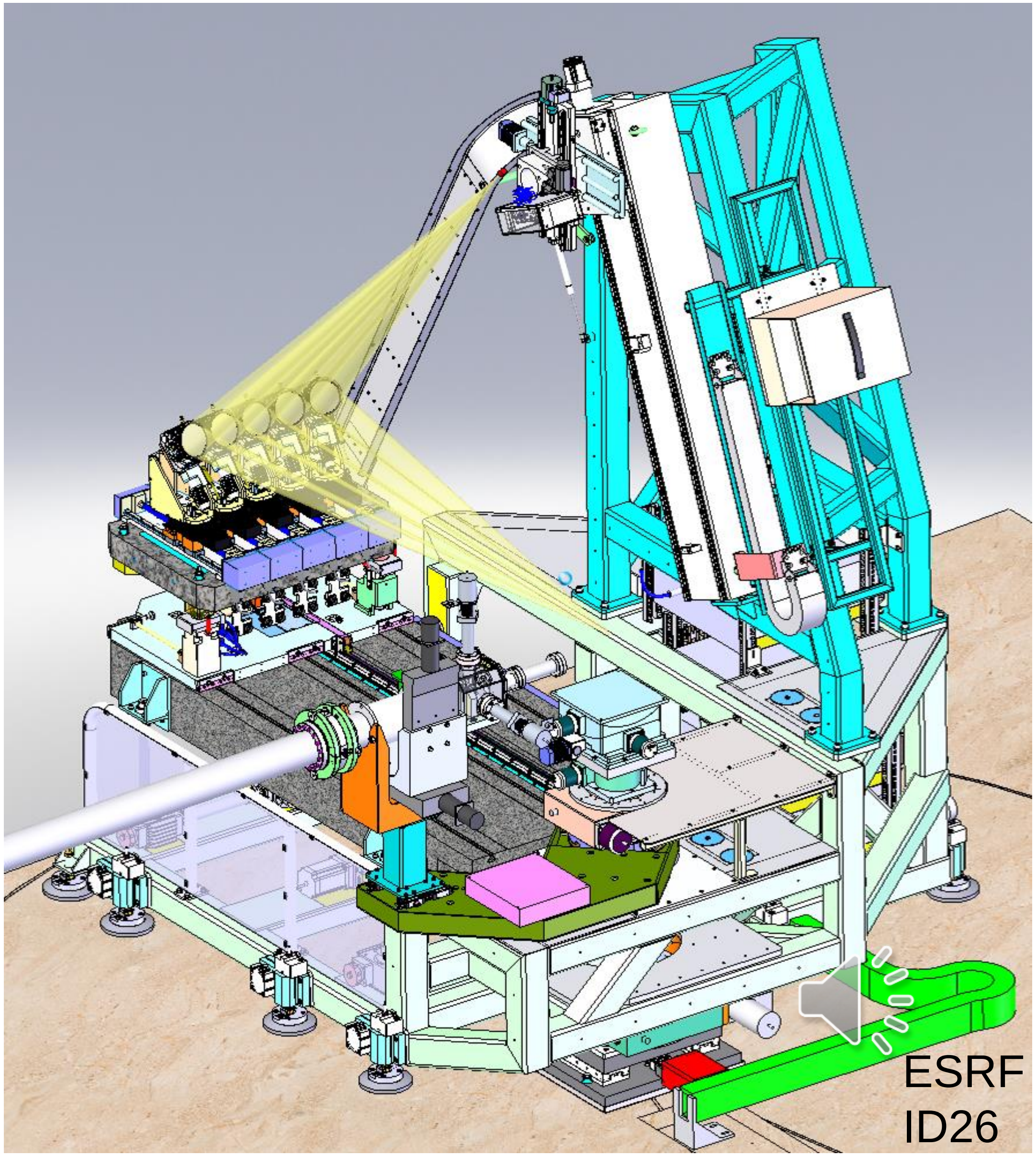
Gerry Seidler
https://www.youtube.com/watch?v=3lJ9uE7Xvcg&t=101s

Medium resolution large luminescence spectrometer

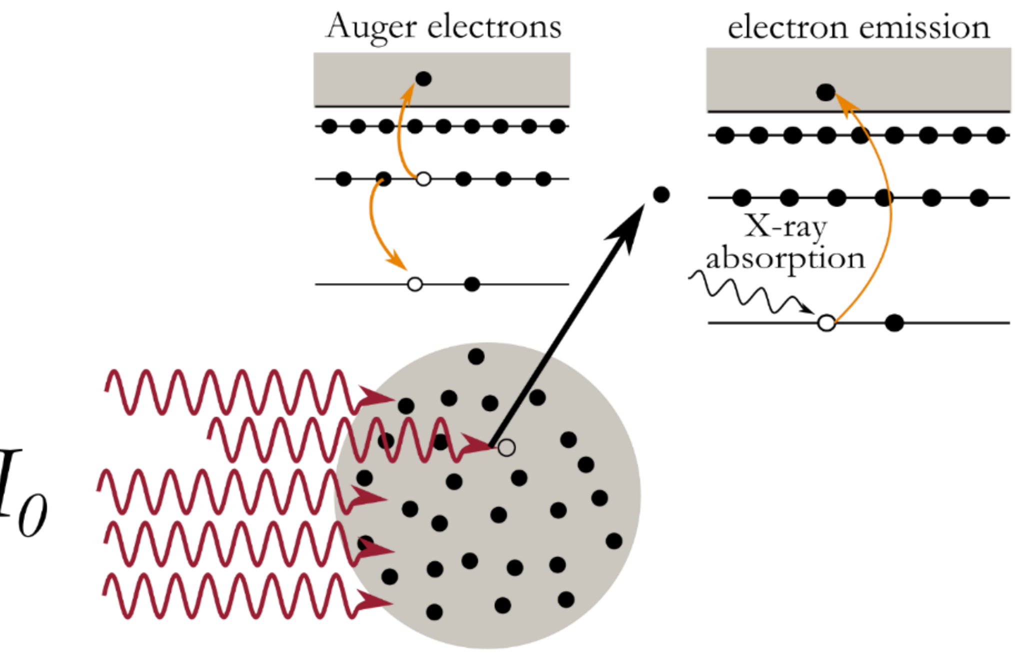
- 5 analyzer crystals
- Bending radius = 0.5 - 2 m
- Exact Rowland tracking
- Scattering angle 0 – 180 degrees
- No degradation of resolution in multi-analyzer spectrometer



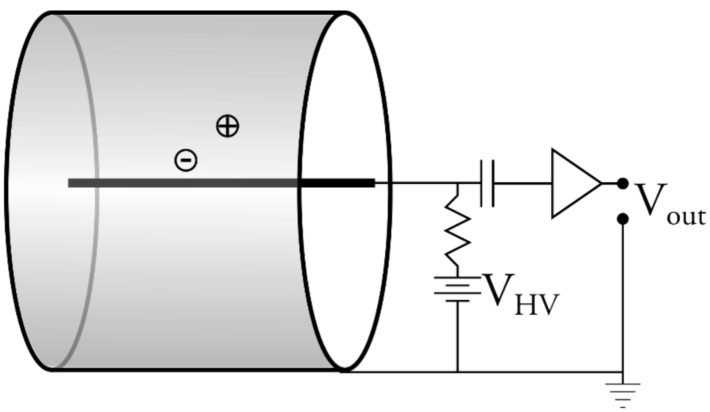
Standard: ~ 1 eV
Best: 0.43 eV



ESRF
ID26

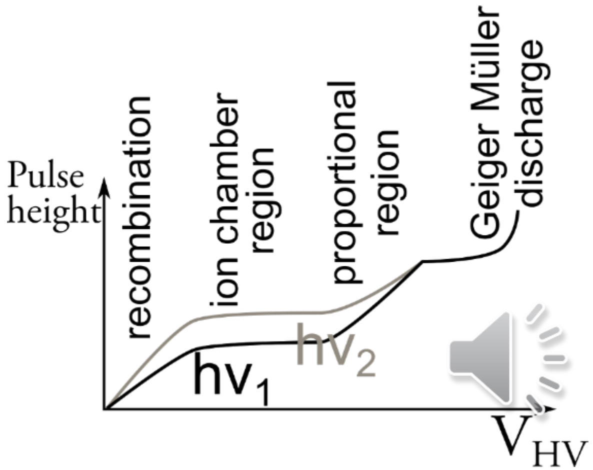


Auger electrons
electron emission
X-ray
absorption
I_0



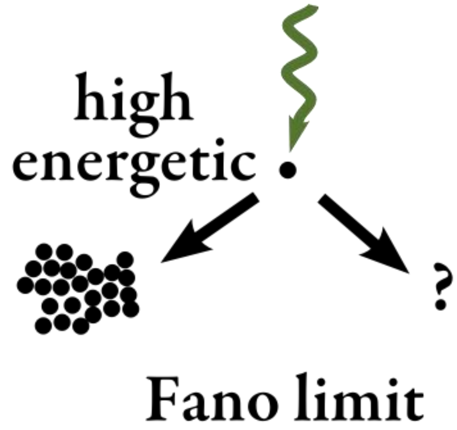
⊕
⊖
V_{out}
V_{HV}

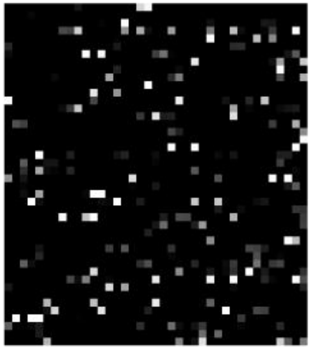
POLIMASTER
REC 10:23
DER 26%
0.14 µSv/h
START NEXT

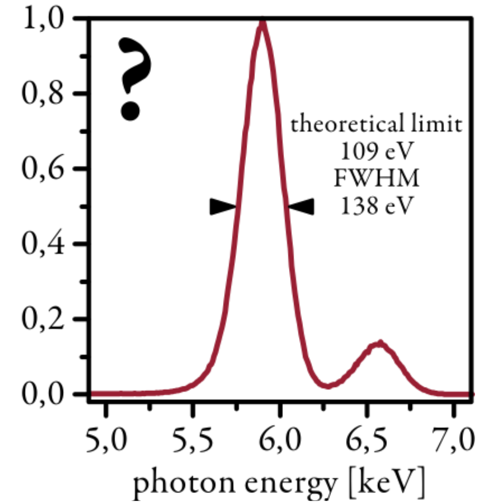


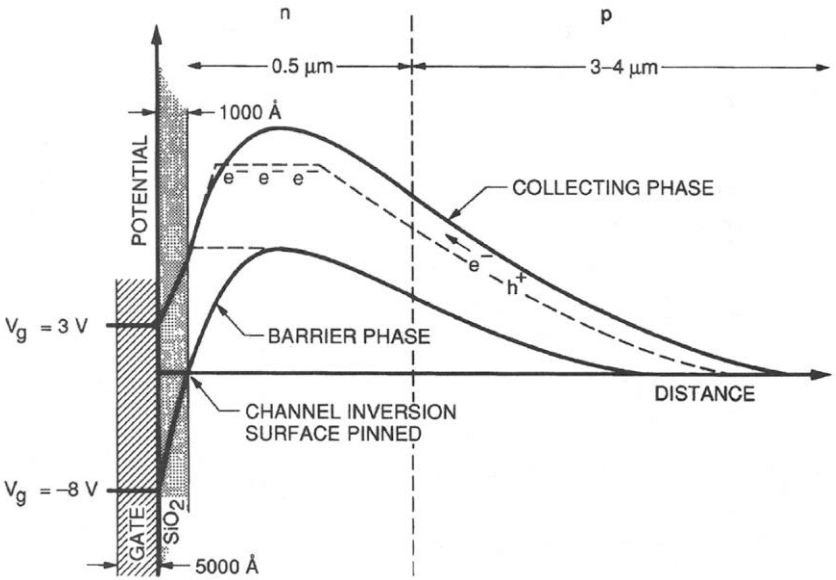
Pulse
height
recombination
ion chamber
region
proportional
region
Geiger Müller
discharge
$h\nu_1$
$h\nu_2$
V_{HV}

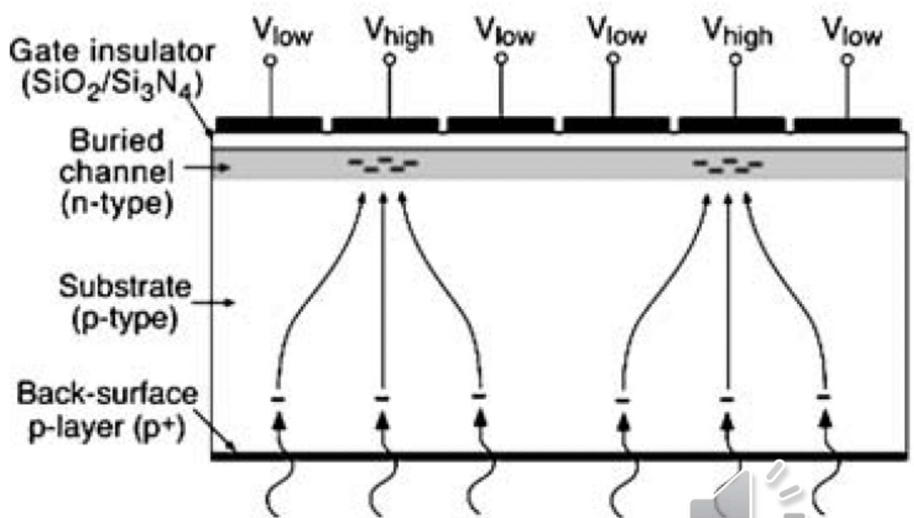
Direct detection



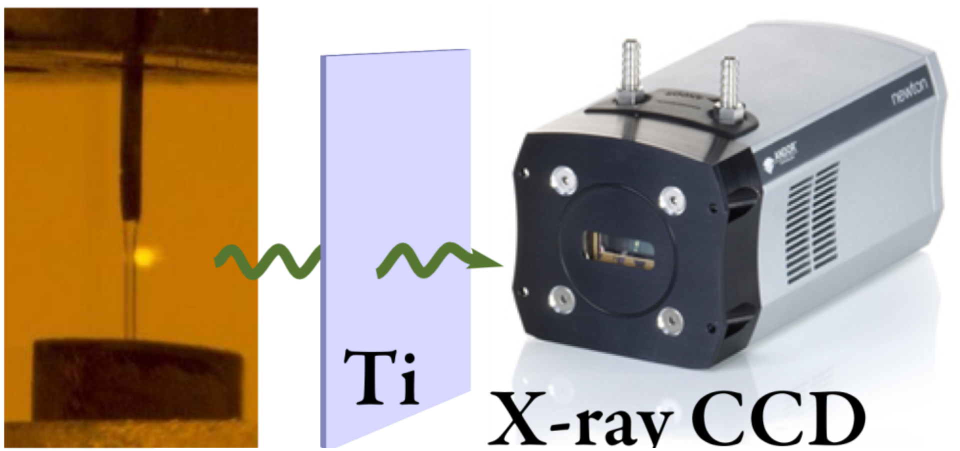


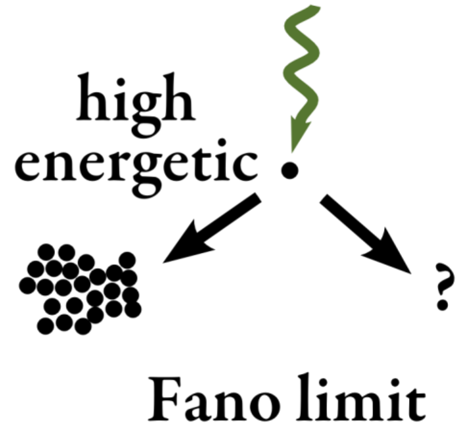


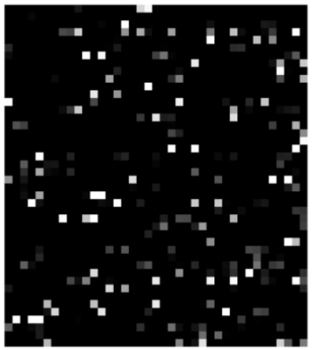




Janesick, J.
Scientific charge-coupled devices
SPIE Press, 2001

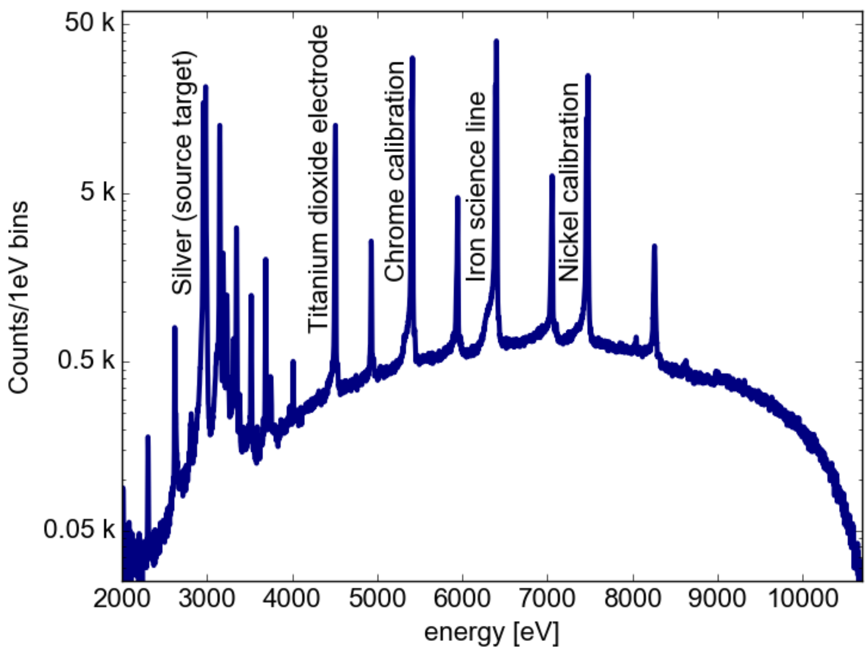




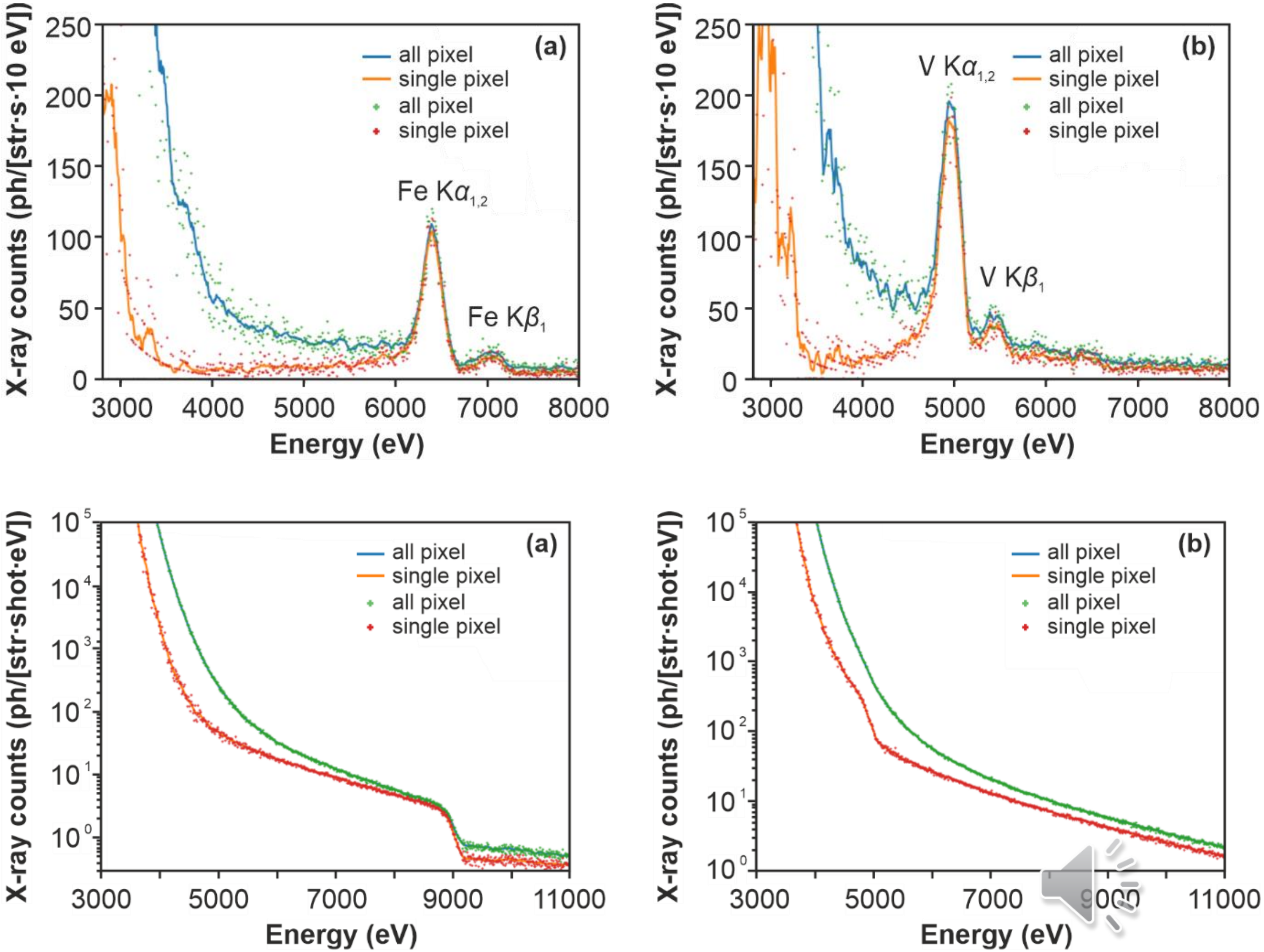


Rev. Sci.

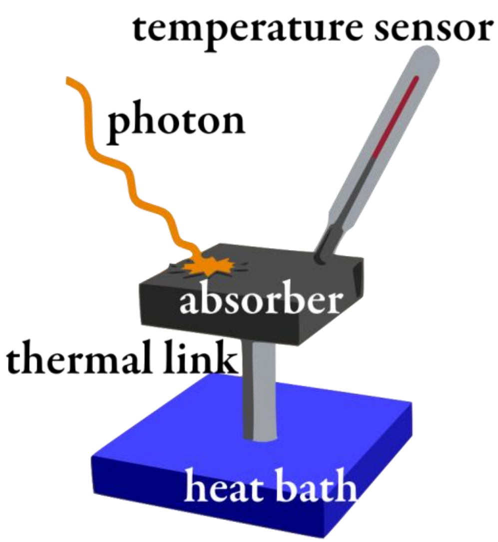
50Hz 25Kc/s =1.2MHz

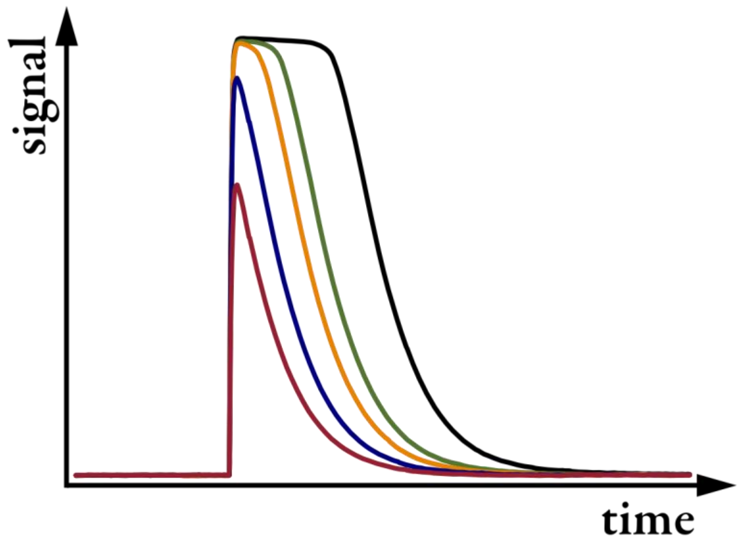


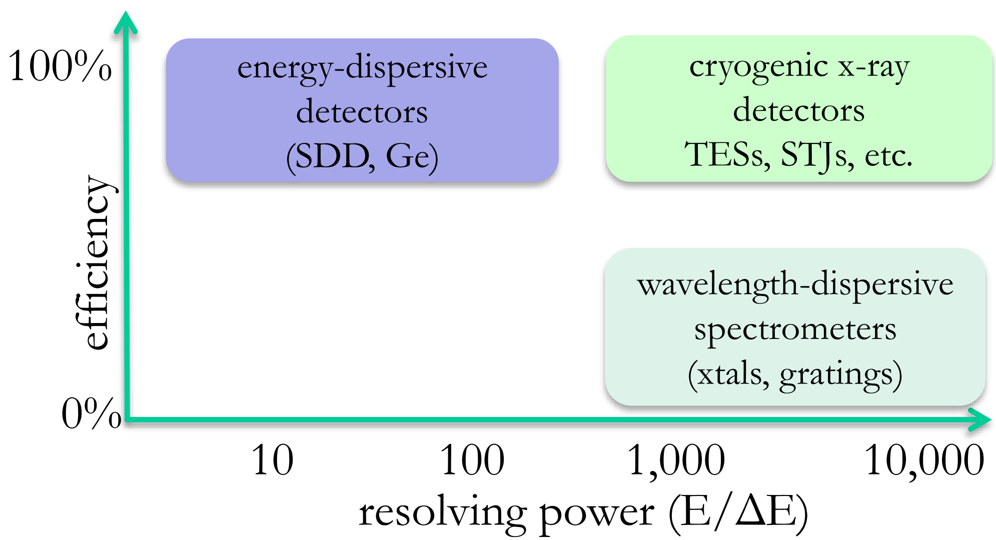
Spectrum at Eli

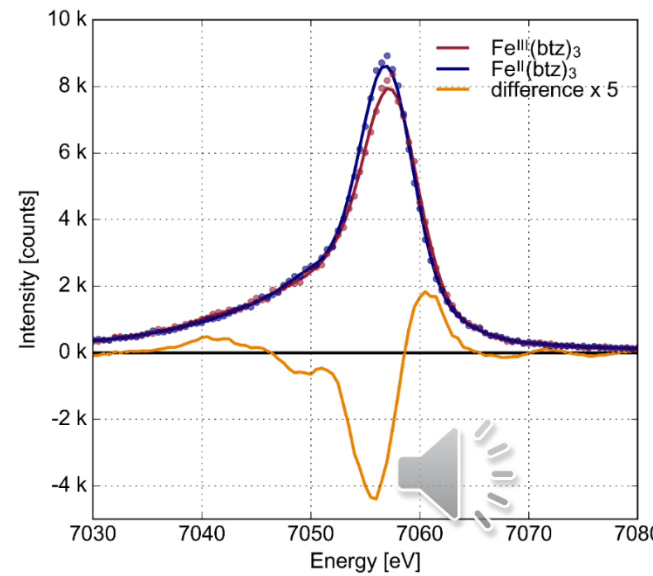


direct detection with calorimetric idea

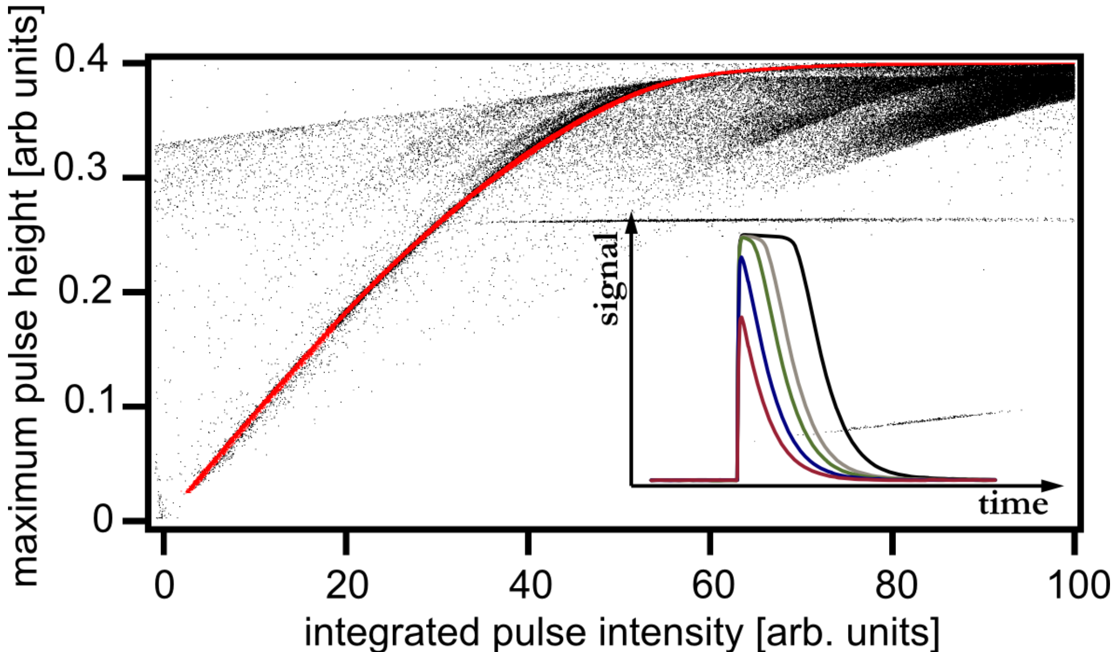




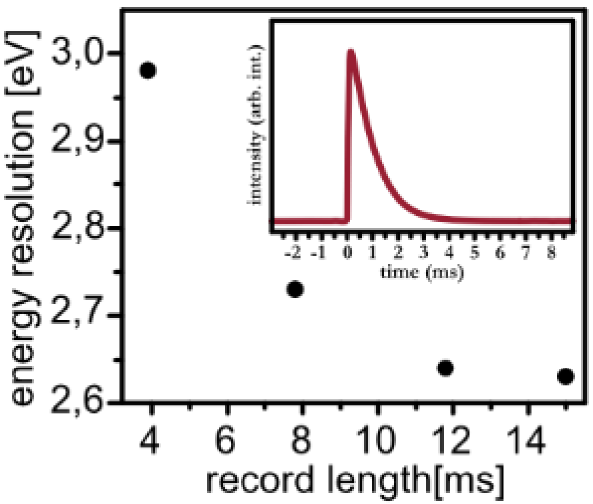


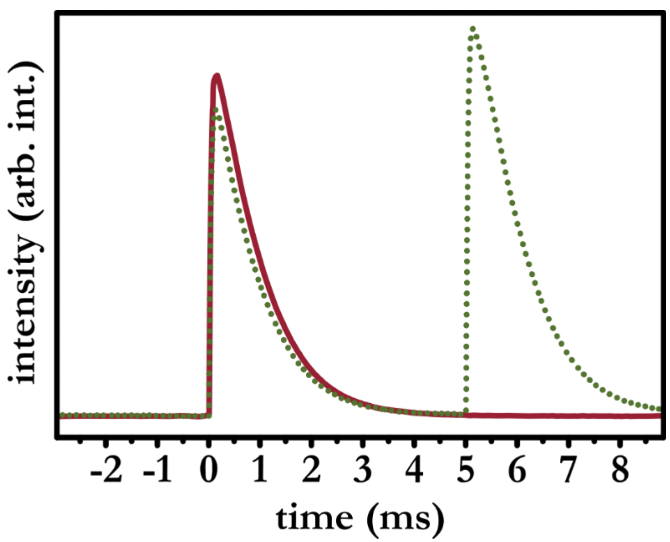


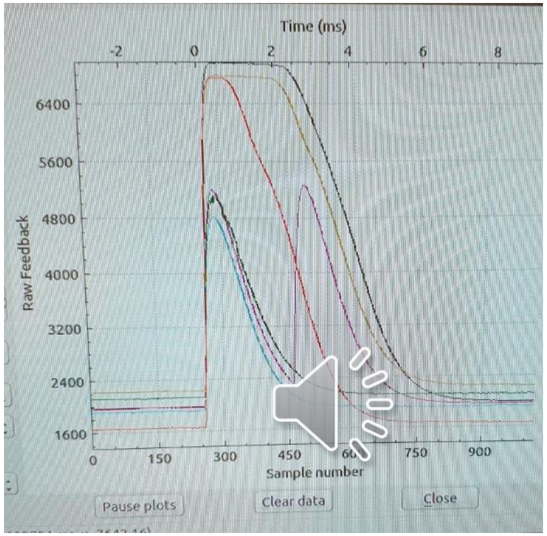
measure temperature



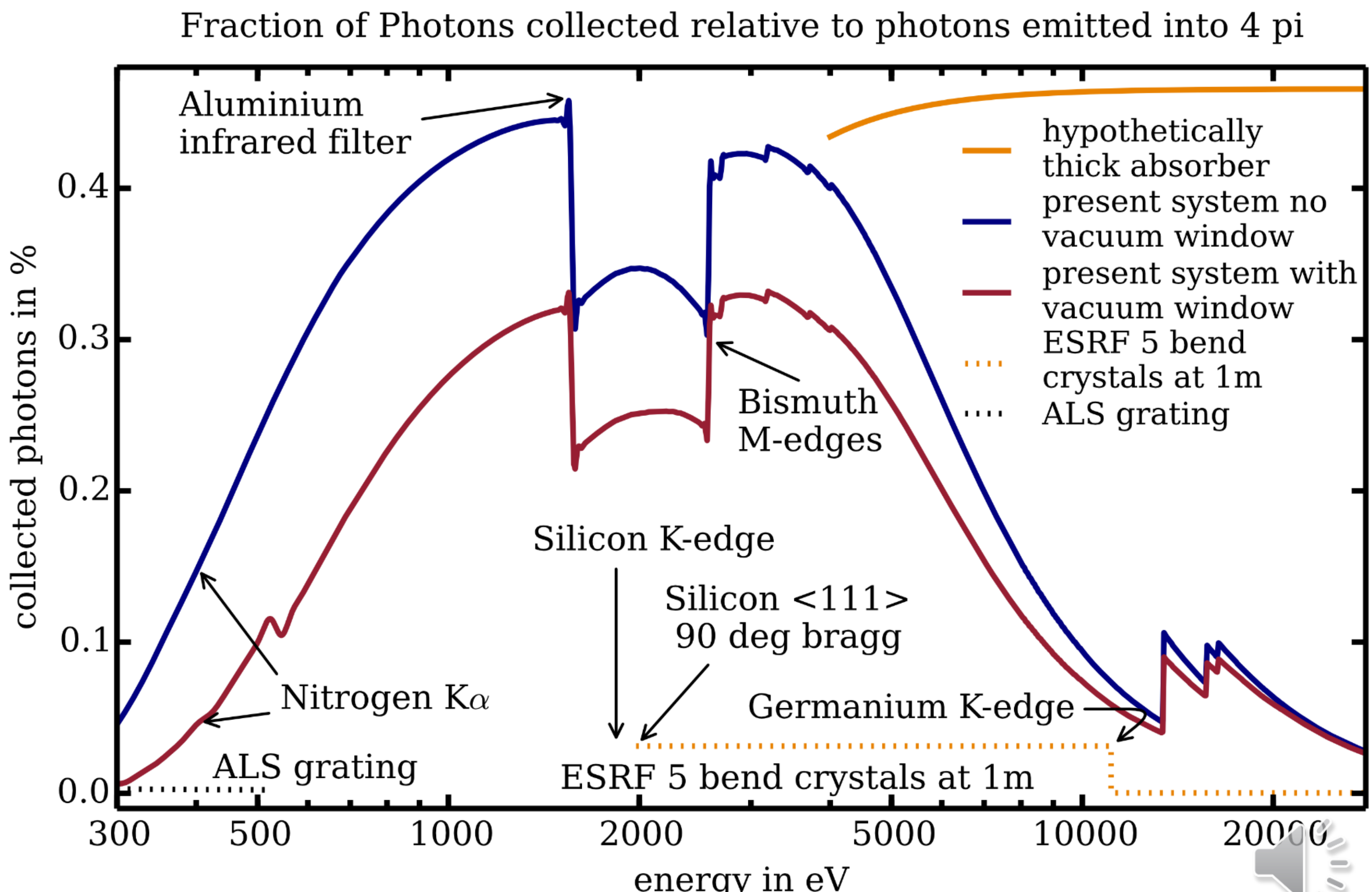
16kHz max
3kHz normal





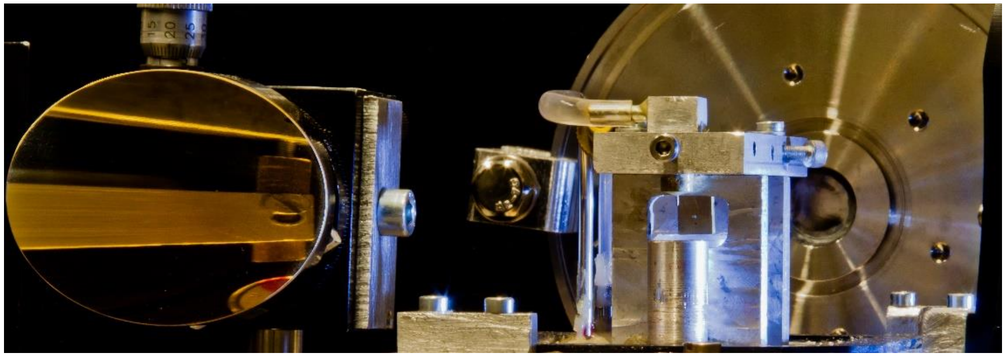


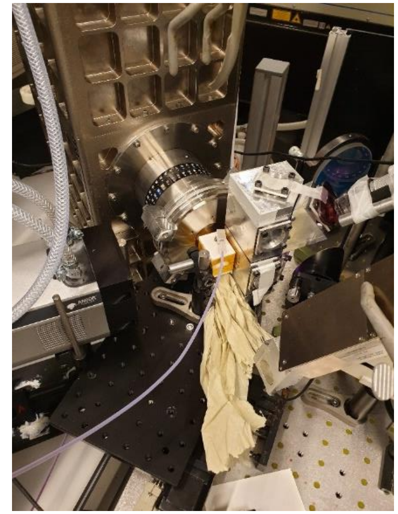
Efficiency

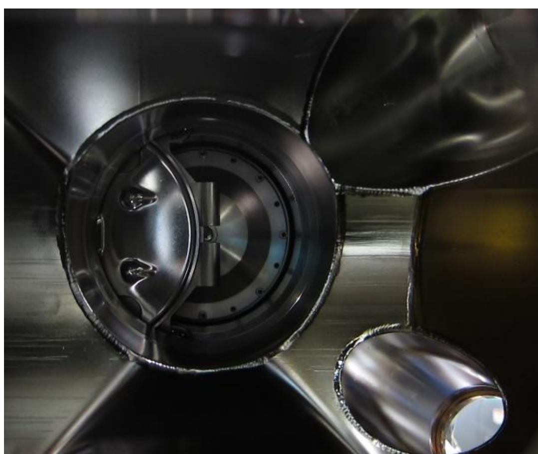


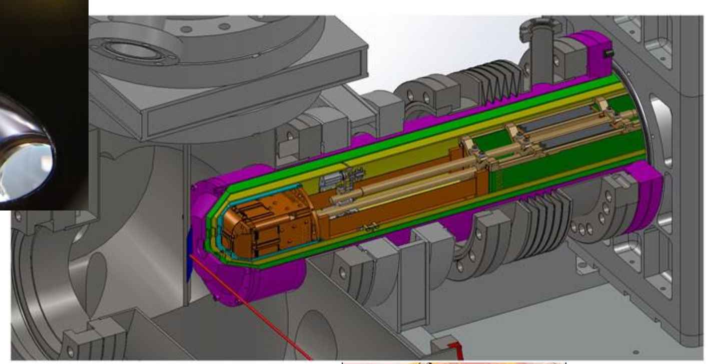
This data is 7 years old.
By now a factor 8 higher!

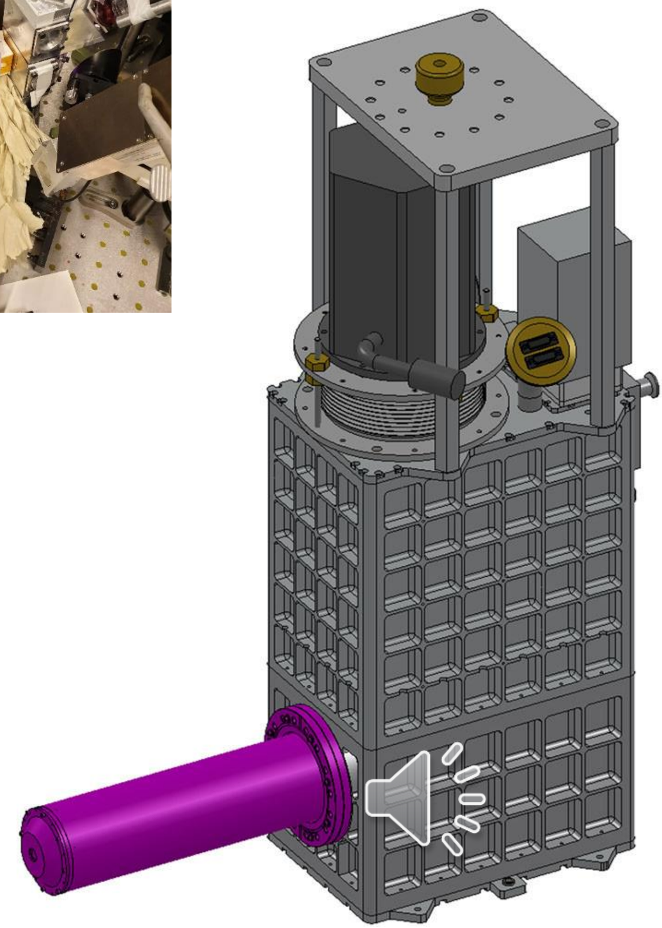
J. Synchrotron Radiat., vol. 22, no. 3, pp. 766–775, May 2015, doi: 10.1107/S1600577515004312.



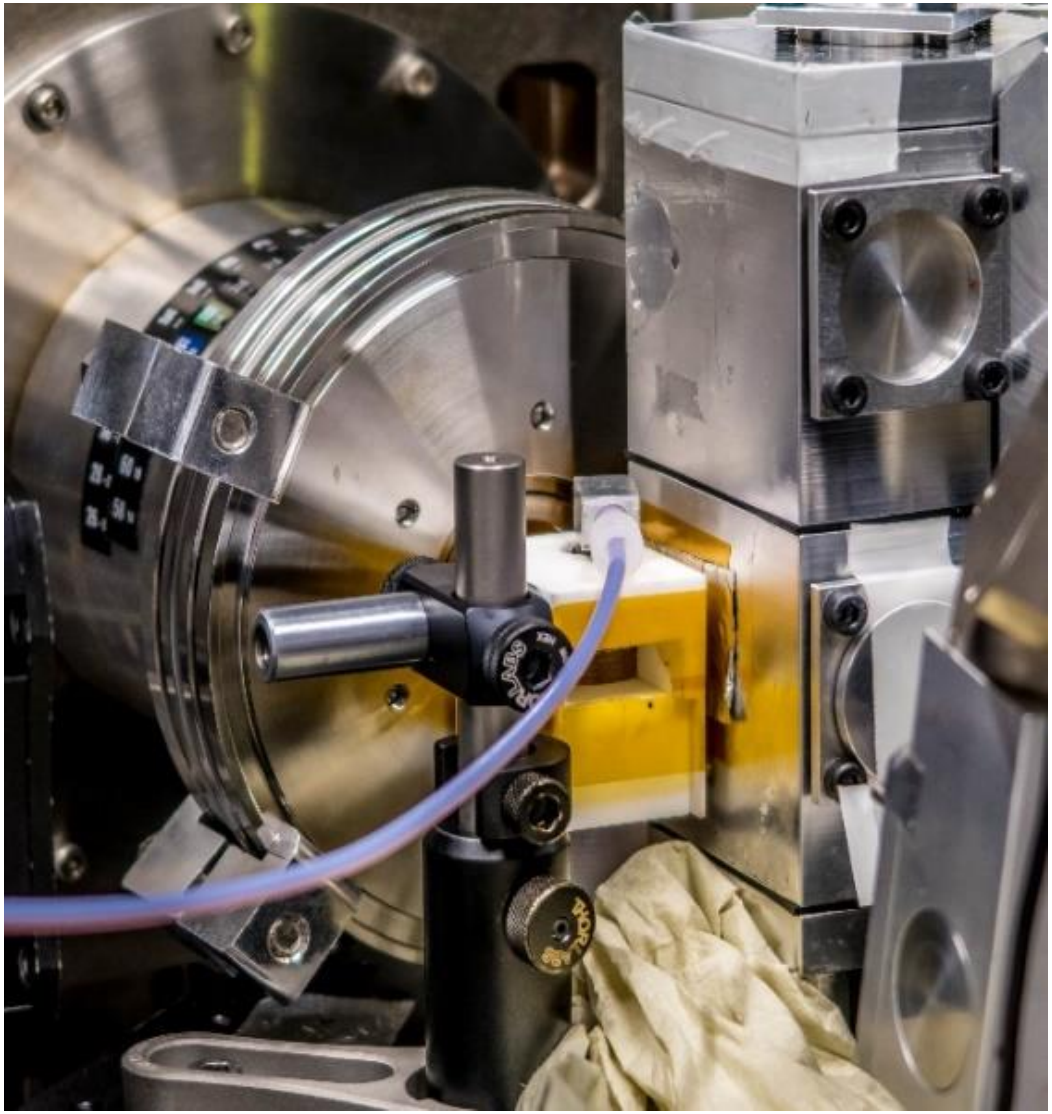


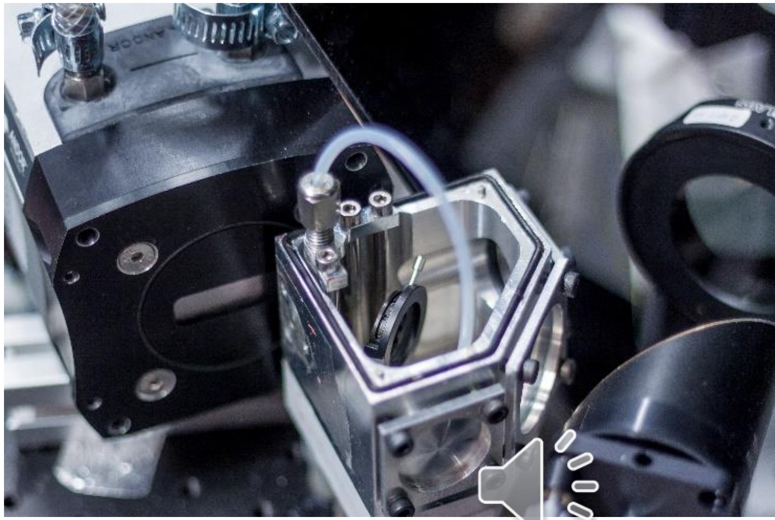




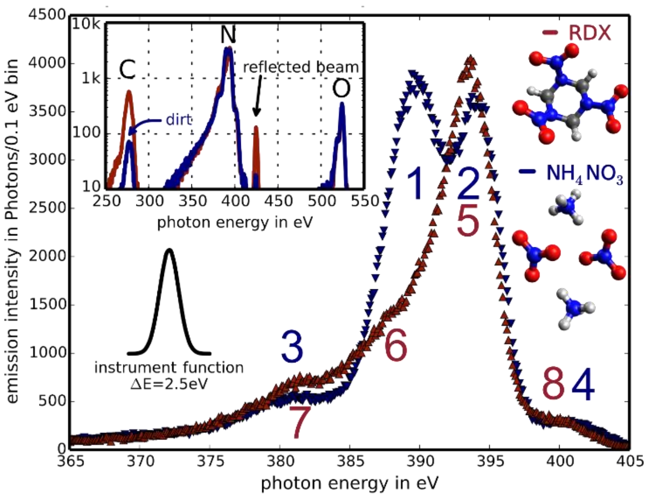


Freestanding laboratory use

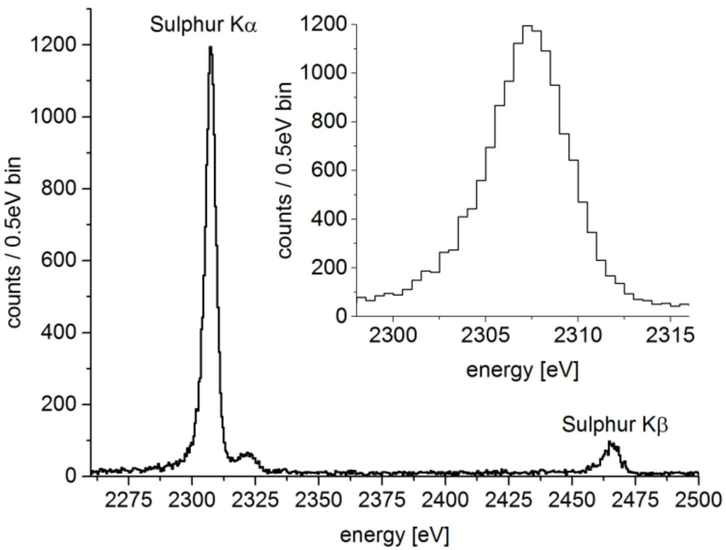


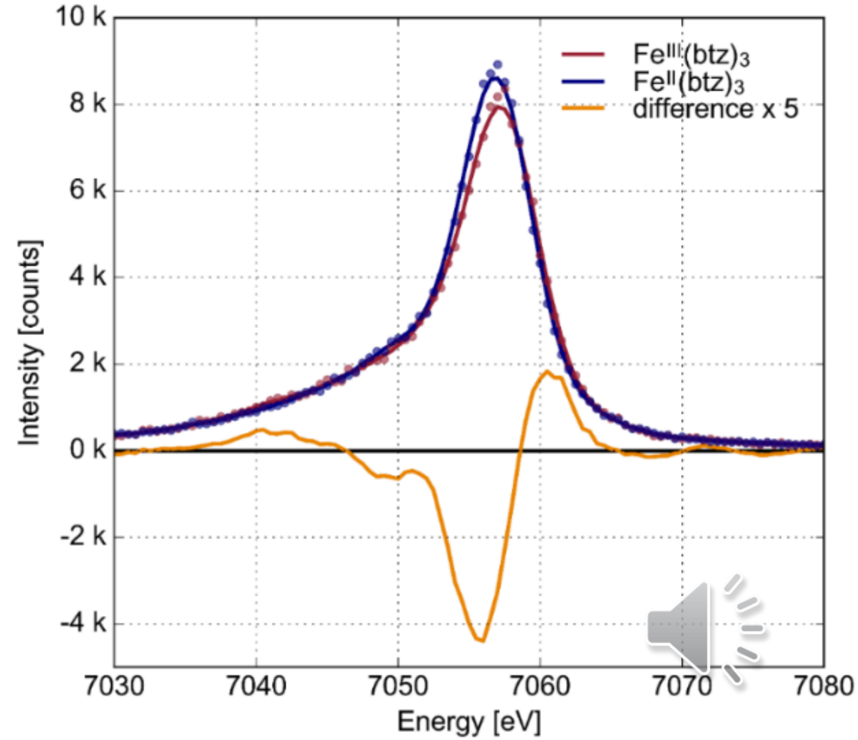


XANES/XES

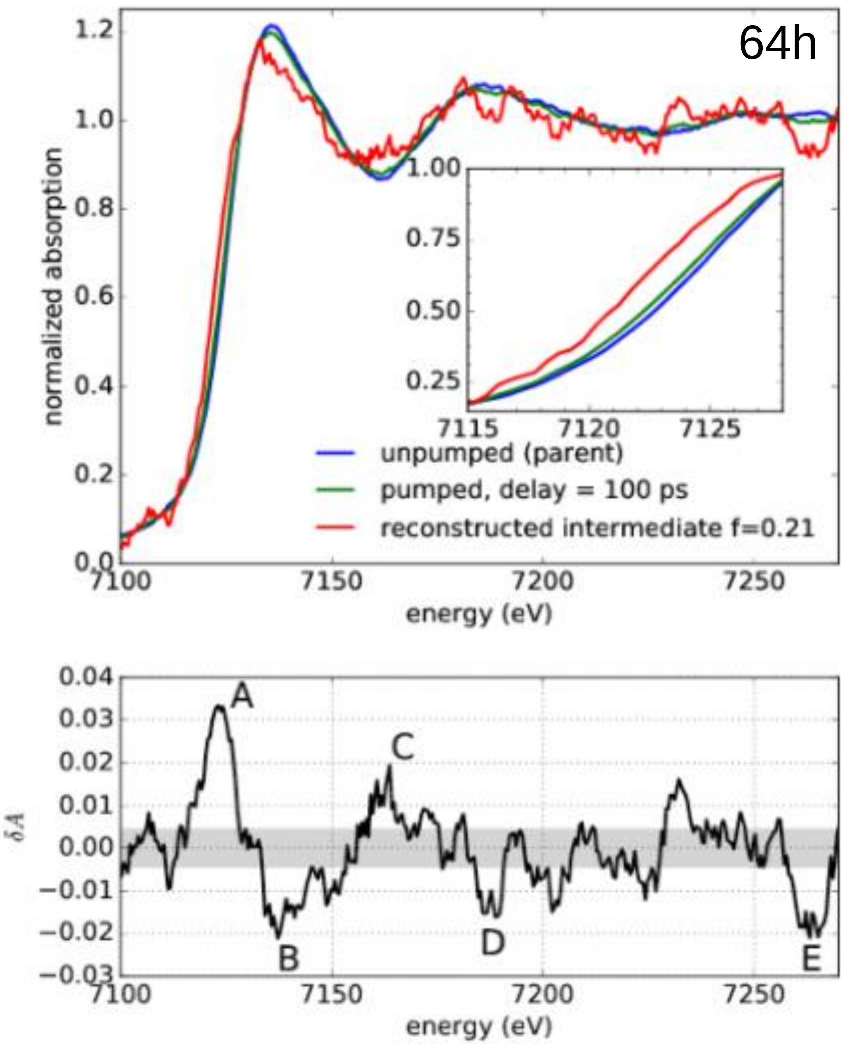


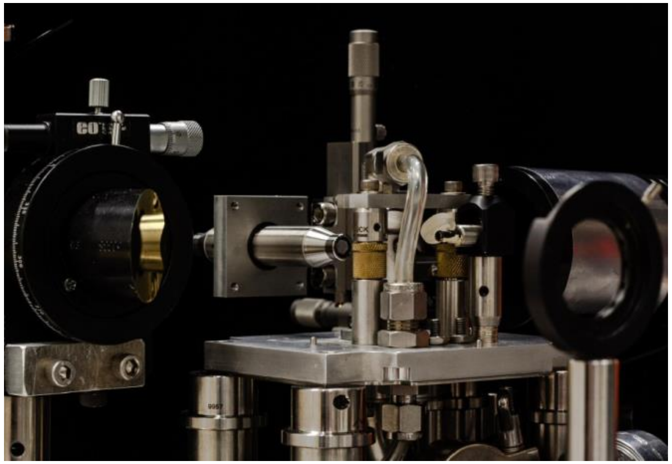
Journal of Synchrotron Radiation **22** 3, 766 (2015);
https://doi.org/10.1107/S1600577515004312.





time-resolved XAFS and XES at low excitation yield





NIST
National Institute of
Standards and Technology
Quantum Devices Group

Wrong Experiment!!!

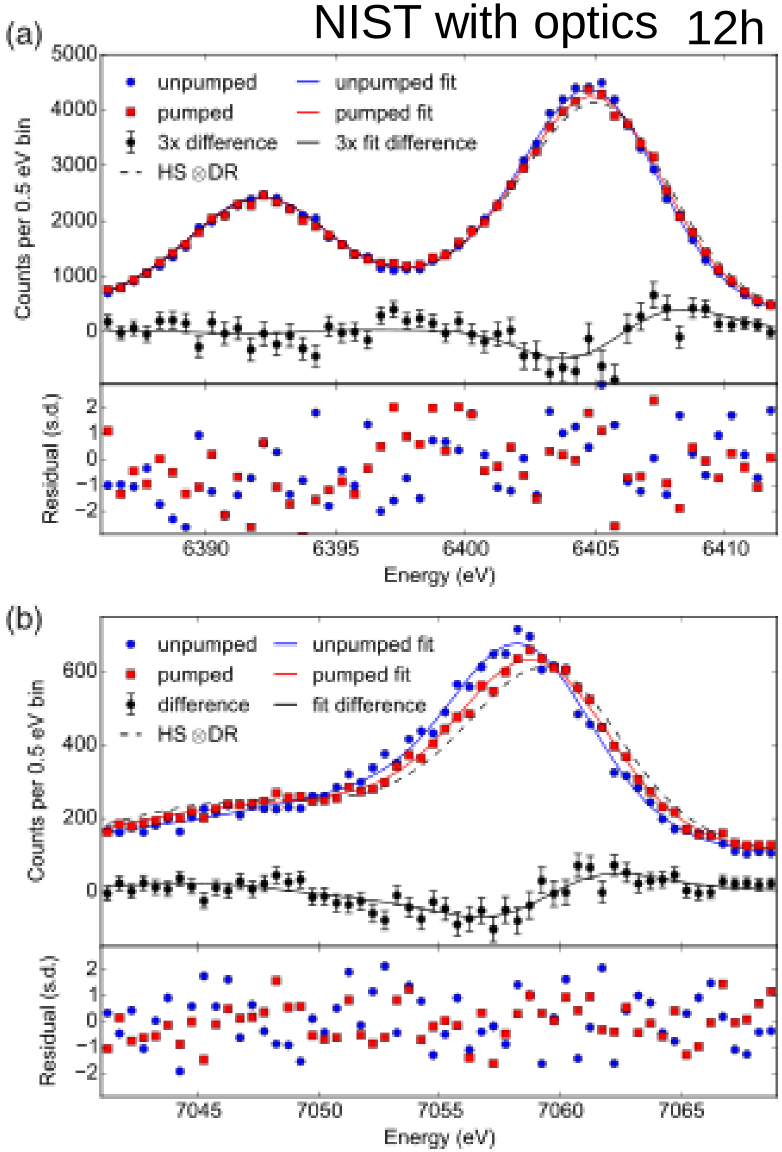
5e9ph/str/eV/h @4mJ

XES:
5e12ph/str/h (1000eV absorbed)
No detector saturation

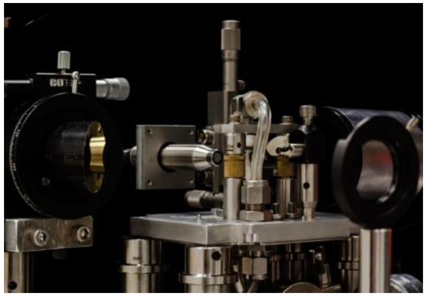
The Journal of Physical Chemistry Letters, vol. 8, no. 5, pp. 1099–1104, Feb. 2017, doi: 10.1021/acs.jpclett.7b00078.

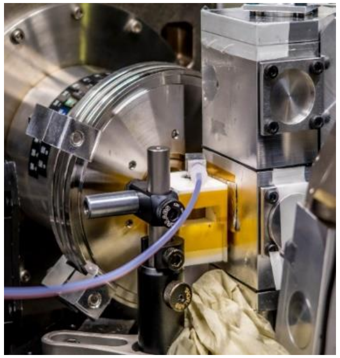
time-resolved XAFS and XES at low excitation yield

NIST with optics 12h

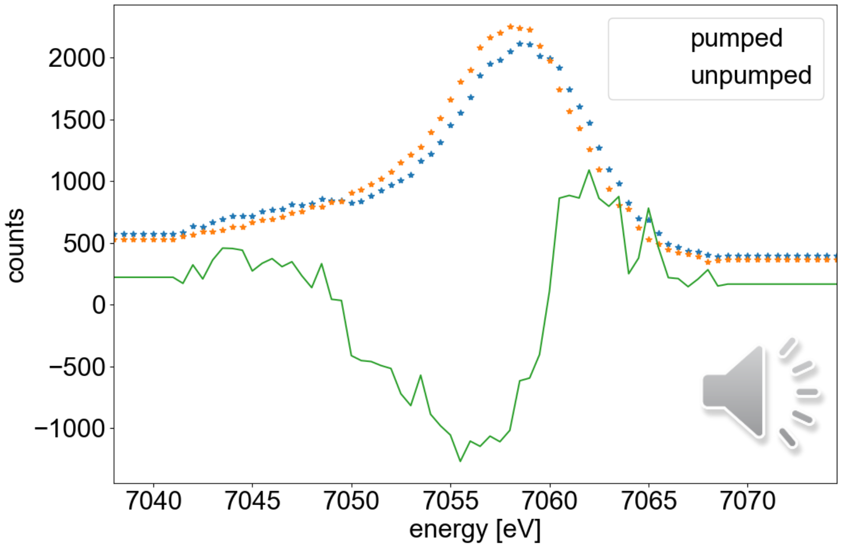


Physical Review X, vol. 6, no. 3, Sep. 2016, doi: 10.1103/physrevx.6.031047.

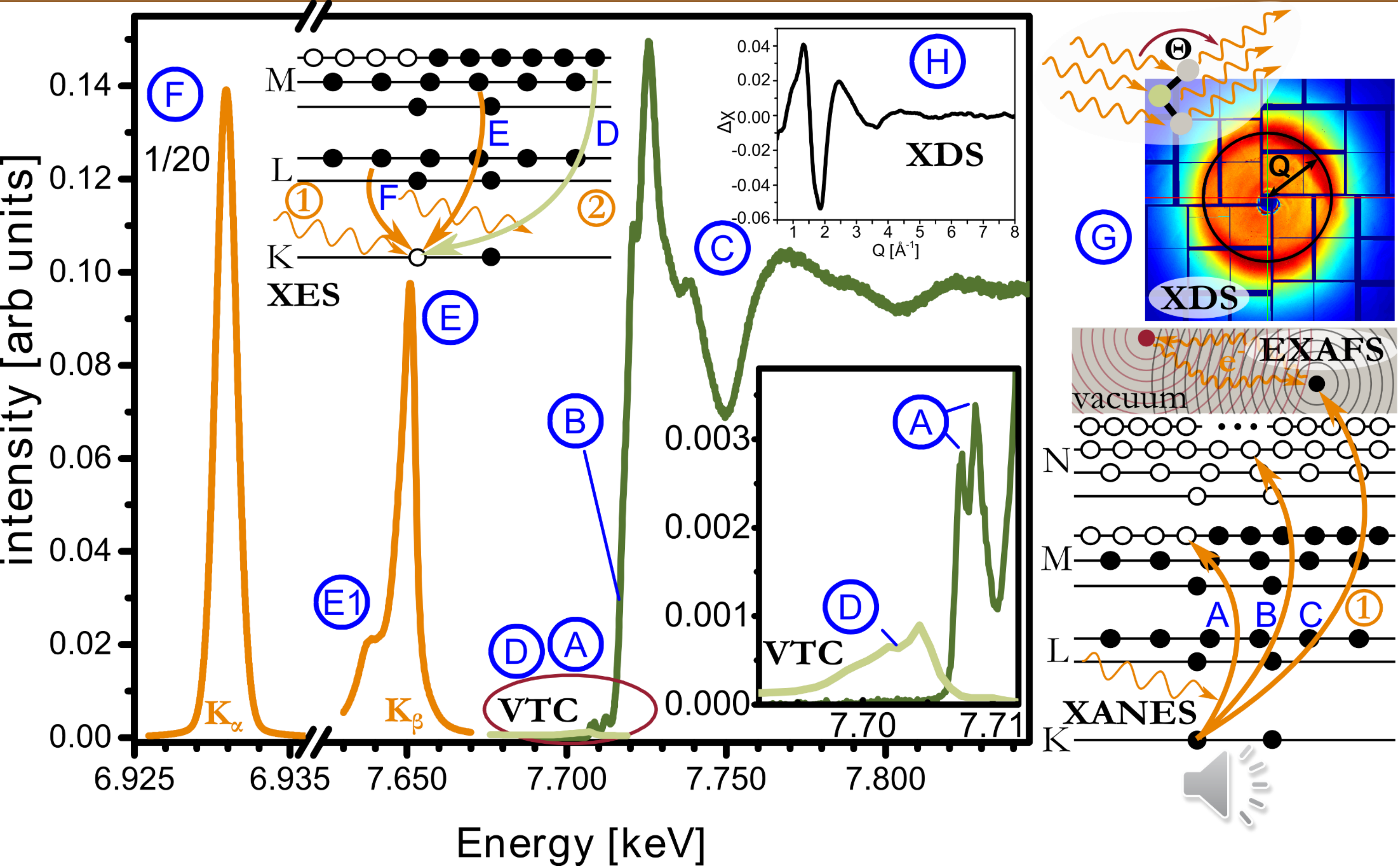




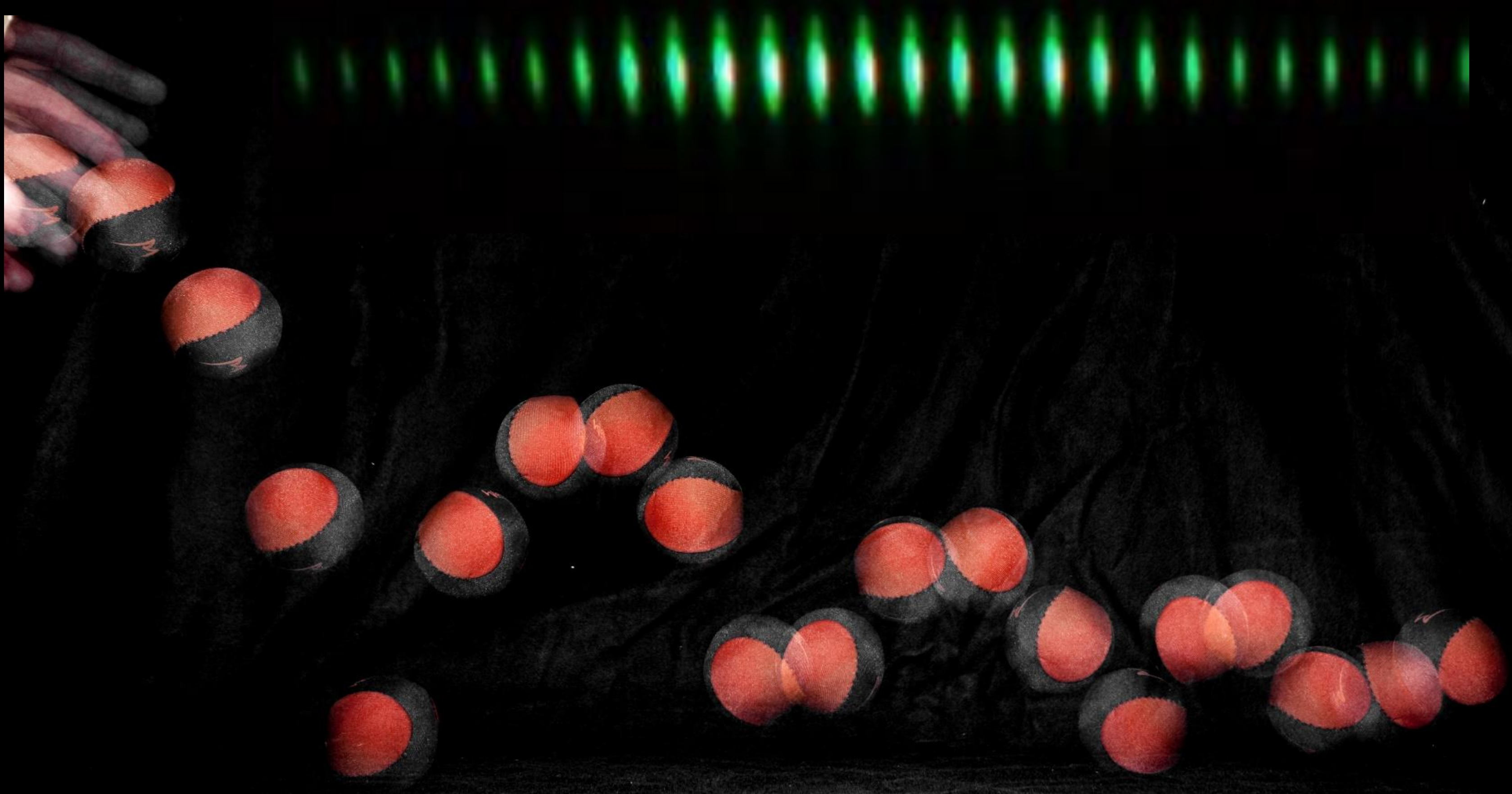
1 person setup and run,
4h accumulation,
3d printed chamber
NO optics
8ml at 6m/s, 10mMol, 15%



Lecture in a slide summary

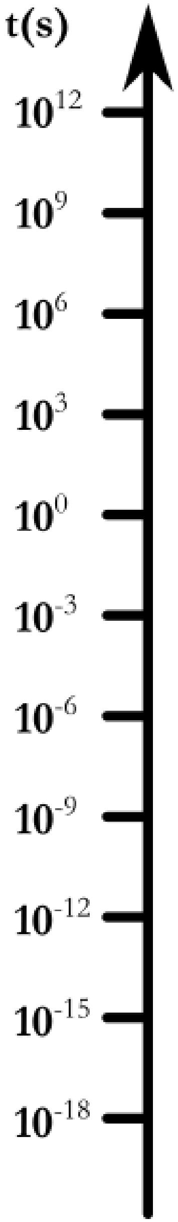


Stroboscopic effect



Focus on optical pump – x-ray probe
Other methods are been developed

Times for processes, do at home



Acid - Base equilibrium

Half time for a good synthesis reaction

Time to ferment with bacteria

Time for absorbing light in a molecule

Typical time to transfer an electron between close molecules

Time to fully oxidize a fresh copper surface to Cu(OH)2 and CuCO3 outdoors

Fluoresence lifetime of a typical organic dye molecule

Time for a molecule to diffuse about 100 nm

first step of energy transfer in photosynthesis

Half life time of ^{14}C

Phosphoresence lifetime of a Ruthenium base metal-organic complex