X-ray-induced electronic damage of matter by post-ionization mechanisms

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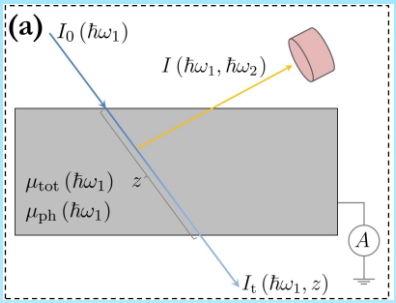
Introduction

Radiation damage

X-ray spectroscopy (XAS, XES)



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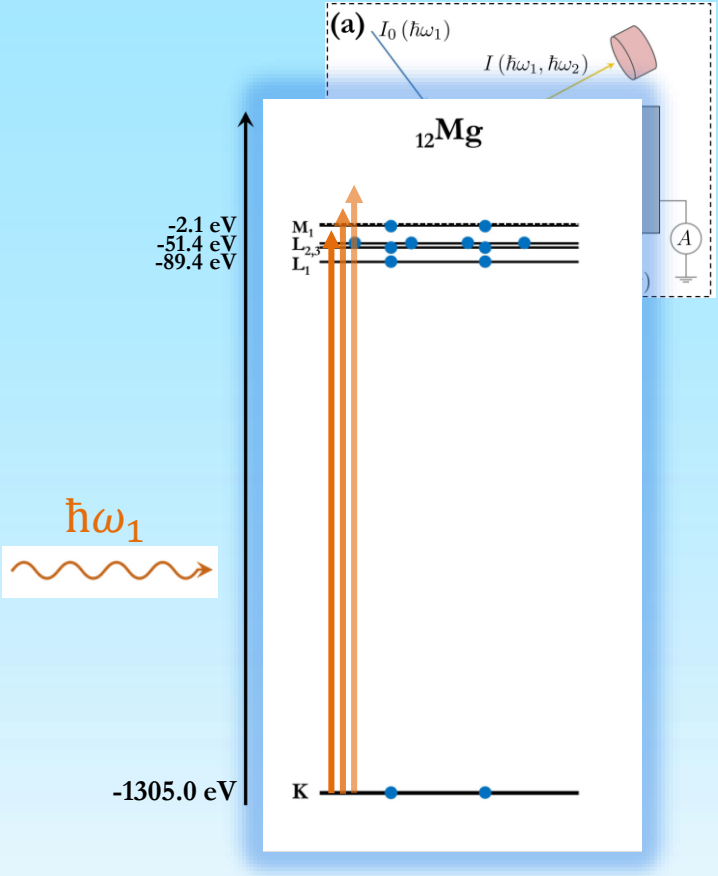

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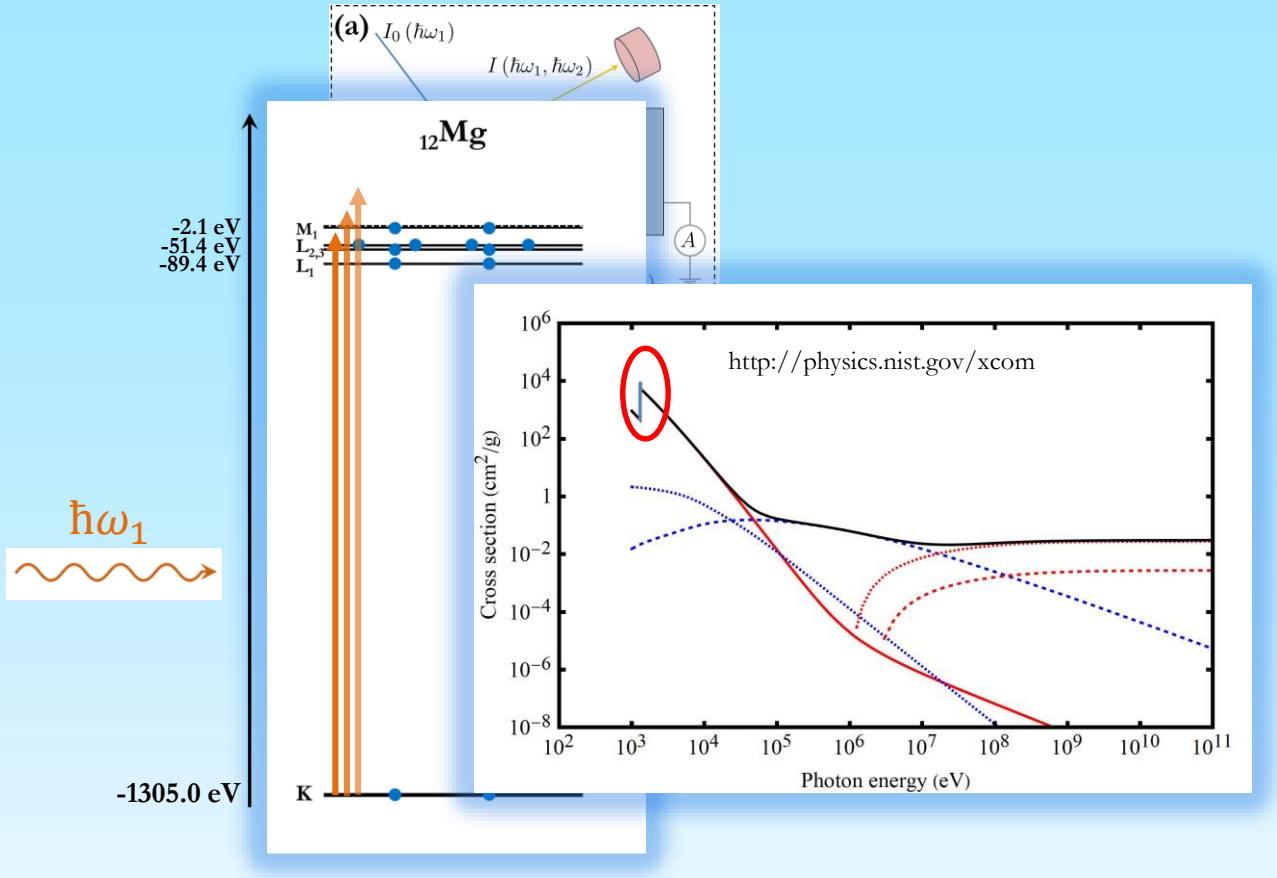

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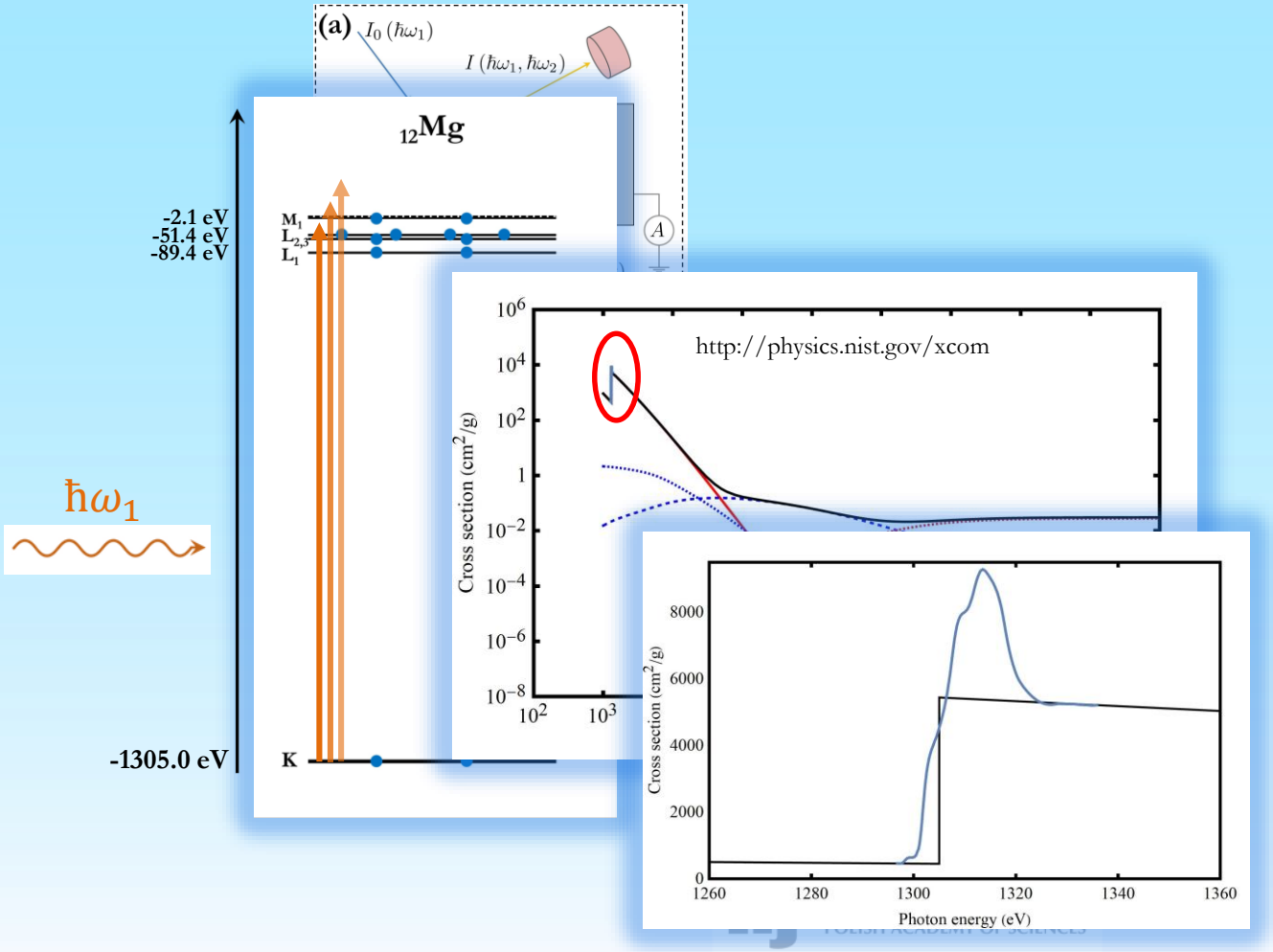

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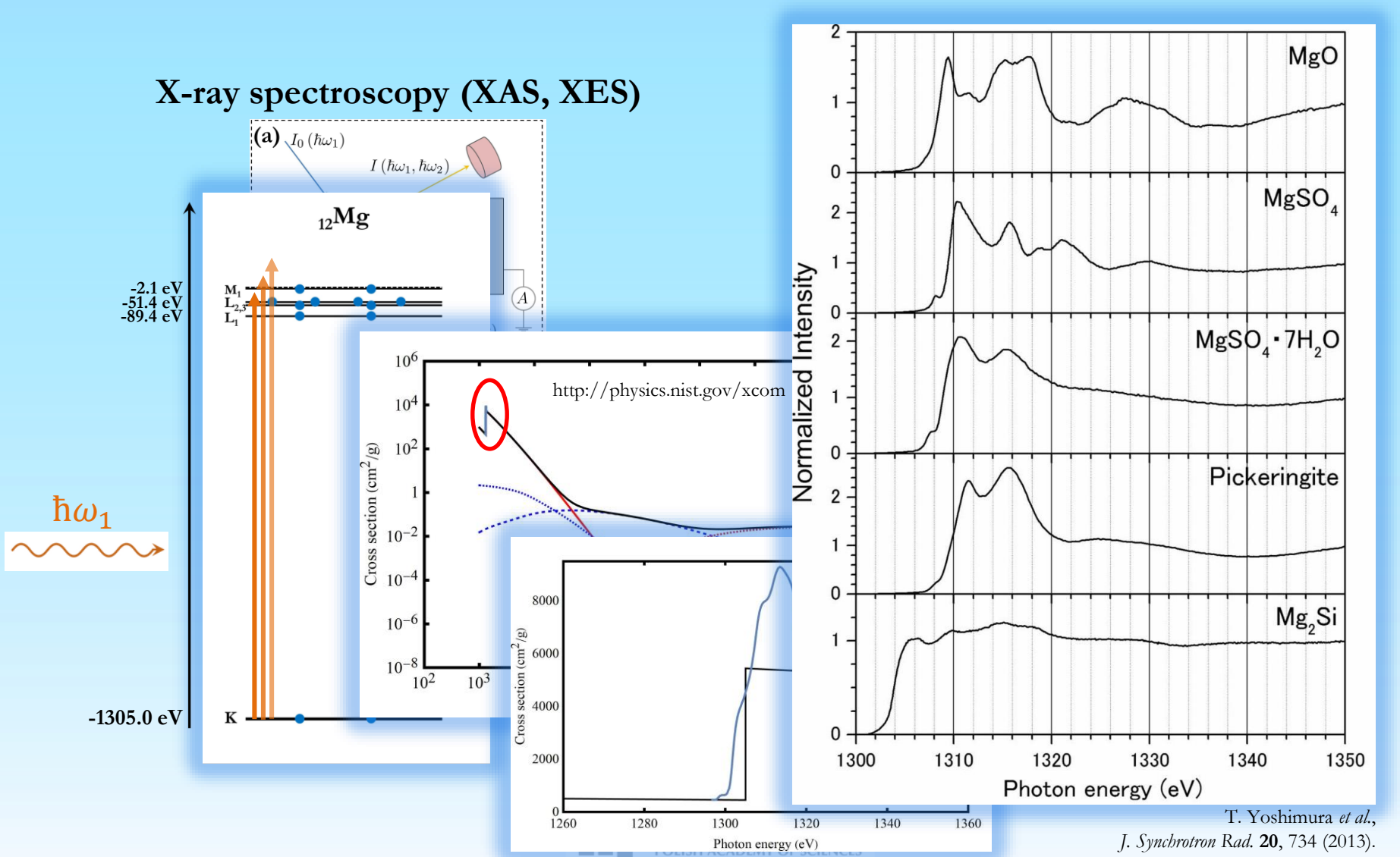

T. Yoshimura *et al.*, *J. Synchrotron Rad.* **20**, 734 (2013).

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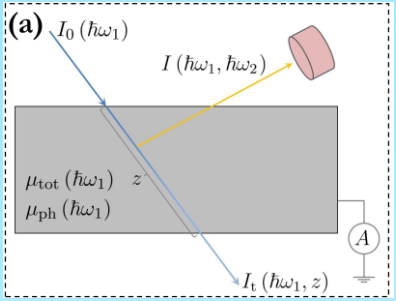
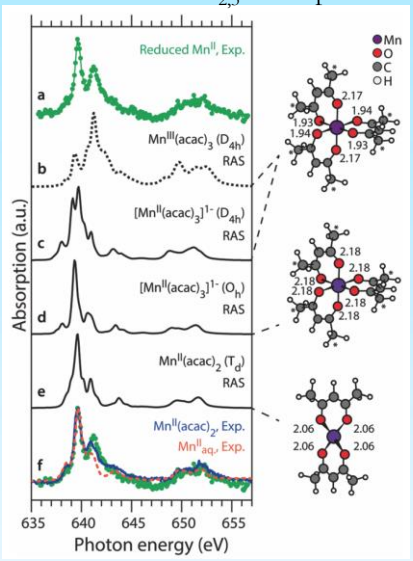


Mn $L_{2,3}$ XAS spectrum



M. Kubin *et al.*,
Phys. Chem. Chem. Phys. **20**, 1681 (2018).

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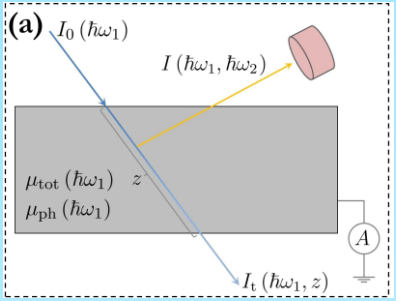

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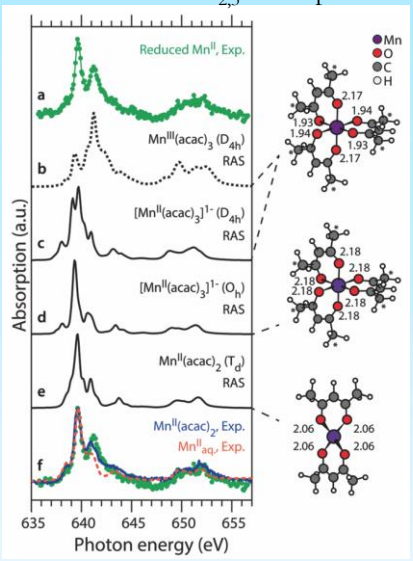

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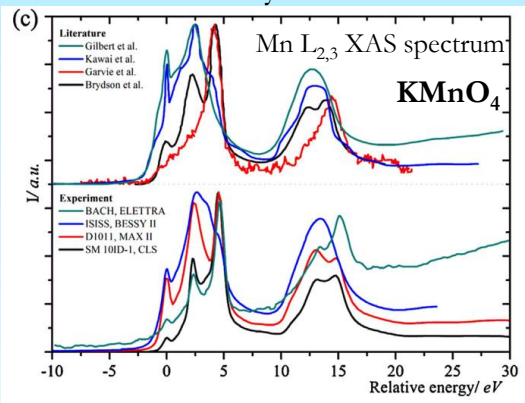

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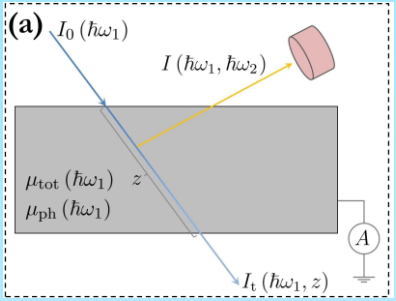

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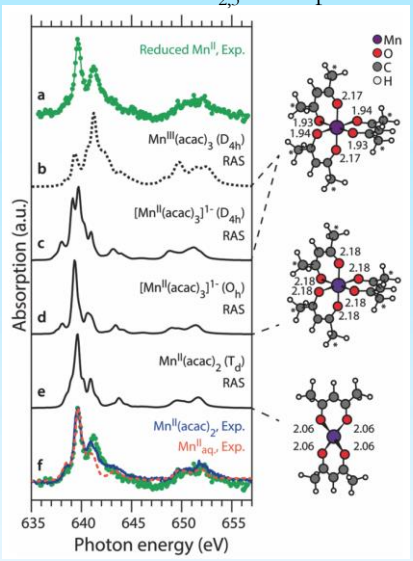

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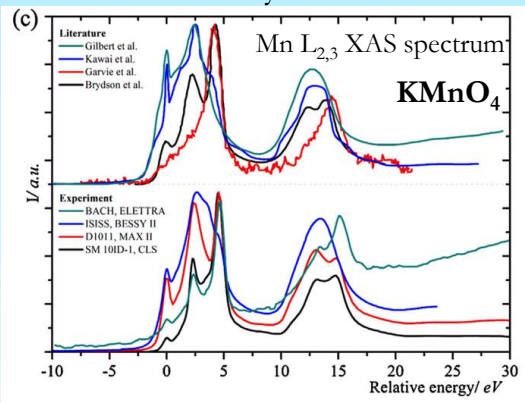

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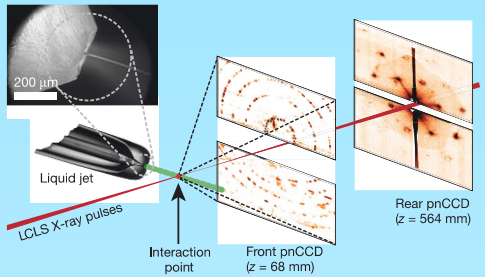

H. N. Chapman *et al.*, *Nature* **470**, 73–77 (2011).

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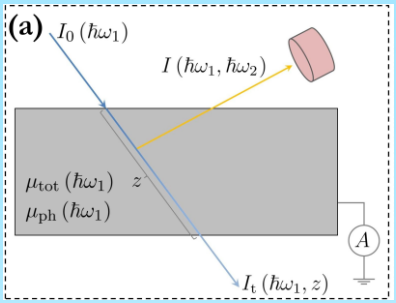

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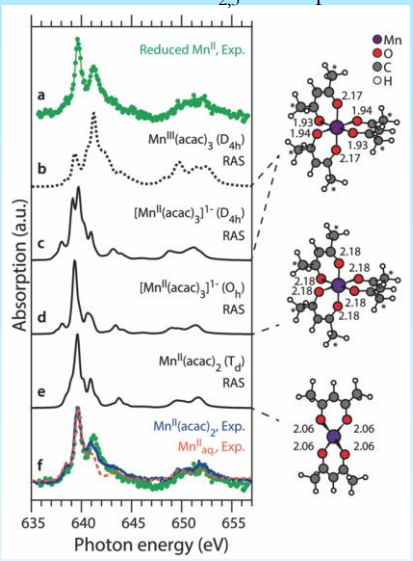

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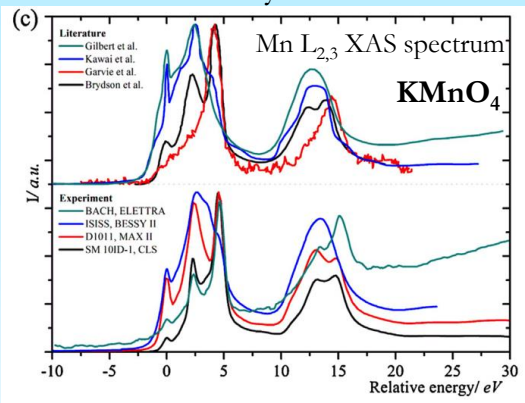

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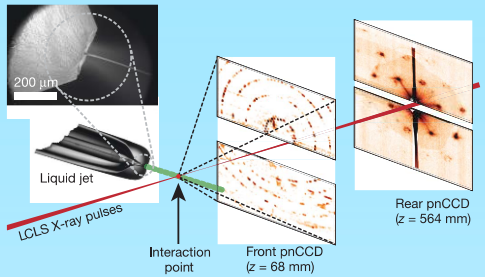

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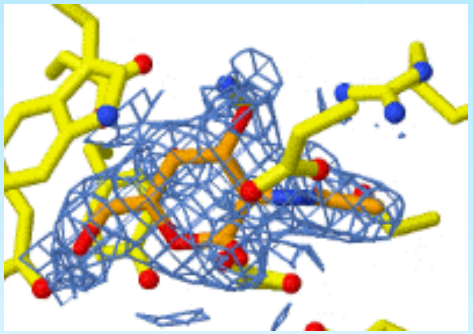

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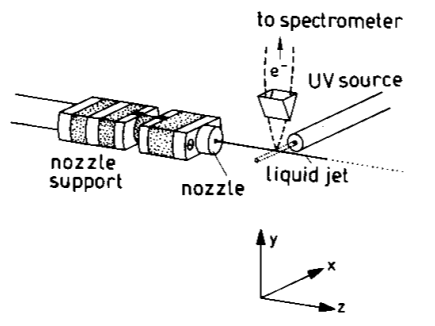
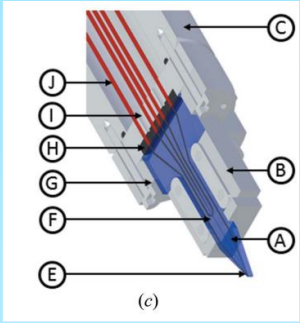
Introduction

Radiation damage - prevention

Liquid sample delivery systems



M. Faubel, B. Steiner, J. P. Toennies, *J. Chem. Phys.* **106**, 9013 (1997).



J. Schulz *et al.*, *J. Synchrotron Rad.* **26**, 339 (2019).

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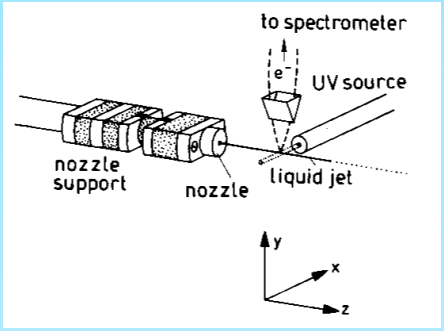

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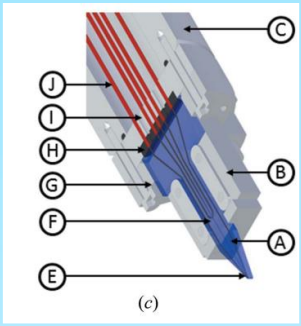
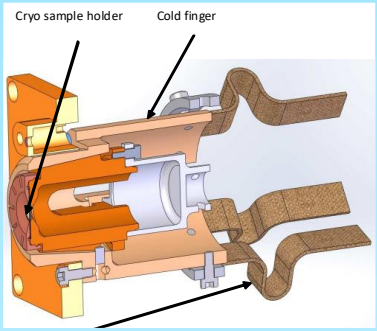


J. Schulz *et al.*, *J. Synchrotron Rad.* **26**, 339 (2019).

Cryo-cooling techniques



M. Salome *et al., J. Phys* **425**, 182004 (2013).

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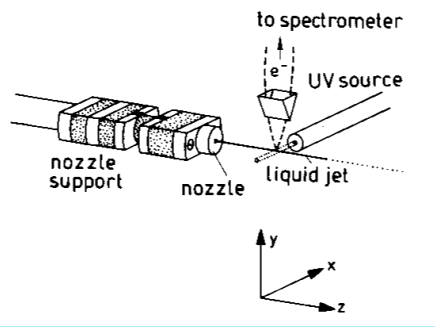

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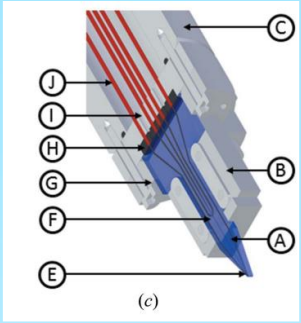

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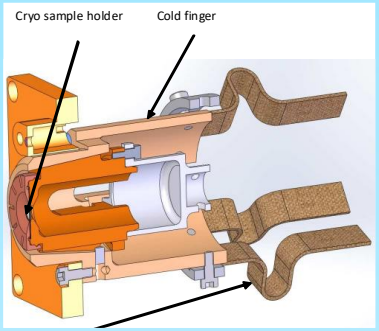

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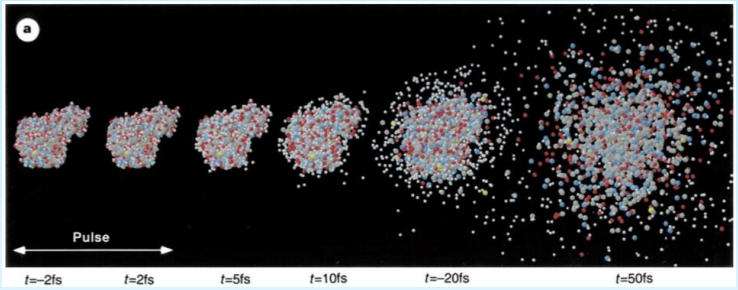
"Probe-before-destroy" approach



R. Neutze *et al., Nature* **406**, 752 (2000).

Introduction

X-ray free-electron laser (XFEL) beam interaction with matter

Nature **466**, 56 (2010)

Femtosecond electronic response of atoms to ultra-intense X-rays

L. Young[1], E. P. Kanter[1], B. Krässig[1], Y. Li[1], A. M. March[1], S. T. Pratt[1], R. Santra[1,2], S. H. Southworth[1], N. Rohringer[3], L. F. DiMauro[4], G. Doumy[4], C. A. Roedig[4], N. Berrah[5], L. Fang[5], M. Hoener[5,6], P. H. Bucksbaum[7], J. P. Cryan[7], S. Ghimire[7], J. M. Glownia[7], D. A. Reis[7], J. D. Bozek[8], C. Bostedt[8] & M. Messerschmidt[8]

[...] At this fluence, the neon target inevitably changes during the course of a single femtosecond-duration X-ray pulse—by sequentially ejecting electrons—to produce fully-stripped neon through absorption of six photons. Rapid photoejection of inner-shell electrons produces 'hollow' atoms and an intensity-induced X-ray transparency. Such transparency, due to the presence of inner-shell vacancies, can be induced in all atomic, molecular and condensed matter systems [...]

beam parameters:
2000 eV (above Ne *K* edge)
pulse duration: 40 fs
10^{11} – 10^{12} photons per pulse
beam spot size: 1.0 × 1.0 μm^2

Science **340**, 491 (2013)

Simultaneous Femtosecond X-ray Spectroscopy and Diffraction of Photosystem II at Room Temperature

Jan Kern[1,2], Roberto Alonso-Mori[2], Rosalie Tran[1], Johan Hattne[1], Richard J. Gildea[1], Nathaniel Echols[1], Carina Glöckner[3], Julia Hellmich[3], Hartawan Laksmono[4], Raymond G. Sierra[4], Benedikt Lassalle-Kaiser[1,‡], Sergey Koroidov[5], Alyssa Lampe[1], Guangye Han[1], Sheraz Gul[1], Dörte DiFiore[3], Despina Milathianaki[2], Alan R. Fry[2], Alan Miahnahri[2], Donald W. Schafer[2], Marc Messerschmidt[2], M. Marvin Seibert[2], Jason E. Koglin[2], Dimosthenis Sokaras[6], Tsu-Chien Weng[6], Jonas Sellberg[6,7], Matthew J. Latimer[6], Ralf W. Grosse-Kunstleve[1], Petrus H. Zwart[1], William E. White[2], Pieter Glatzel[8], Paul D. Adams[1], Michael J. Bogan[2,4], Garth J. Williams[2], Sébastien Boutet[2], Johannes Messinger[5], Athina Zouni[3], Nicholas K. Sauter[1], Vittal K. Yachandra[1,*], Uwe Bergmann[2,*], and Junko Yano[1,*]

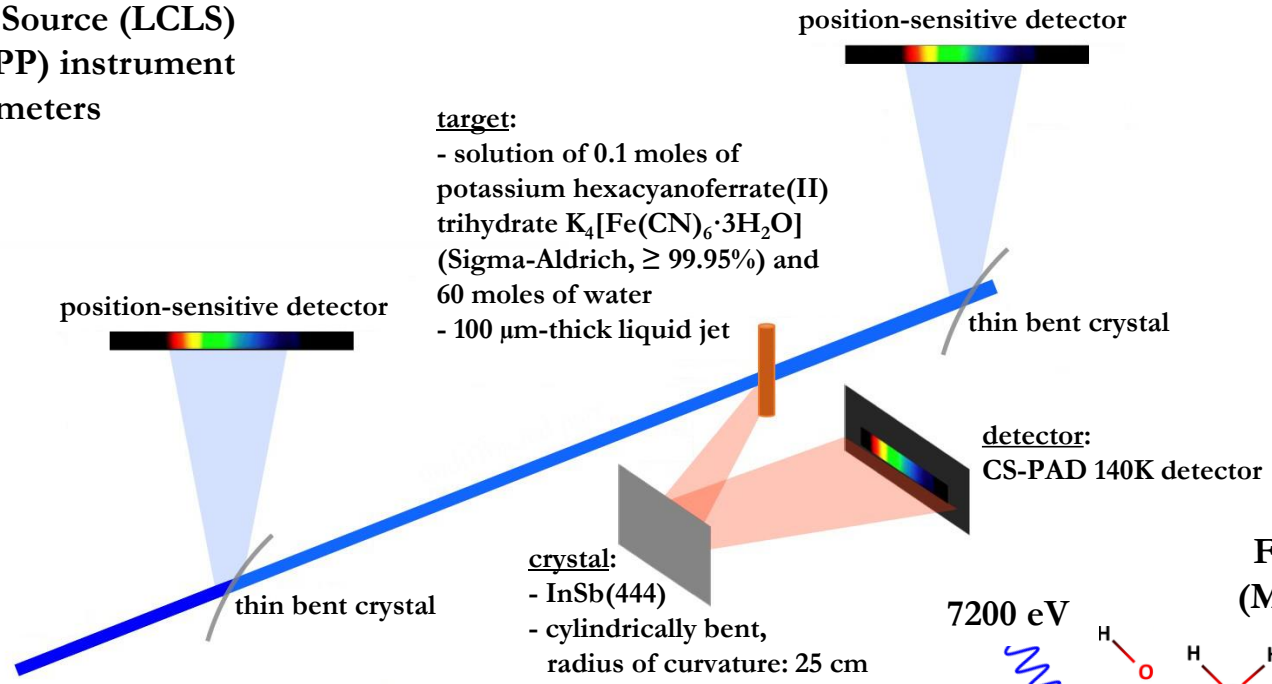
[…] Our simultaneous XRD/XES study shows that the PS II crystals are intact during our measurements at the LCLS, not only with respect to the structure of PS II, but also with regard to the electronic structure of the highly radiation sensitive Mn_4CaO_5 cluster, opening new directions for future dynamics studies.

beam parameters:
7000 eV (above Mn *K* edge)
pulse duration: 45 fs
3 – 6 ×10^{11} photons per pulse
beam spot size: 1.5 × 1.5 μm^2

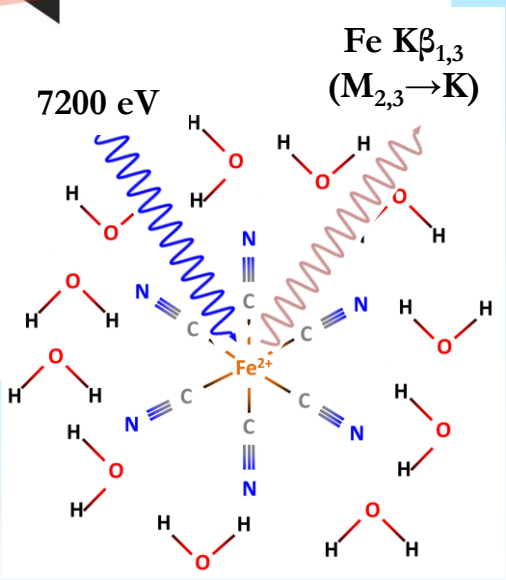
Experimental

Fe Kβ X-ray emission spectroscopy (XES) at X-ray free-electron laser (XFEL) for changing photon flux

Linac Coherent Light Source (LCLS)
X-ray pump-probe (XPP) instrument
typical operation parameters



X-ray beam:
- self-amplified spontaneous emission (SASE)
- repetition rate: 120 Hz
- mean photon energy: 7200 eV (88 eV above Fe K-edge binding energy)
- pulse duration: 30 fs
- number of photons per pulse: 4×10^{11}
- beam spot area on the target changed from 6 to 241 μm^2 with Be lenses



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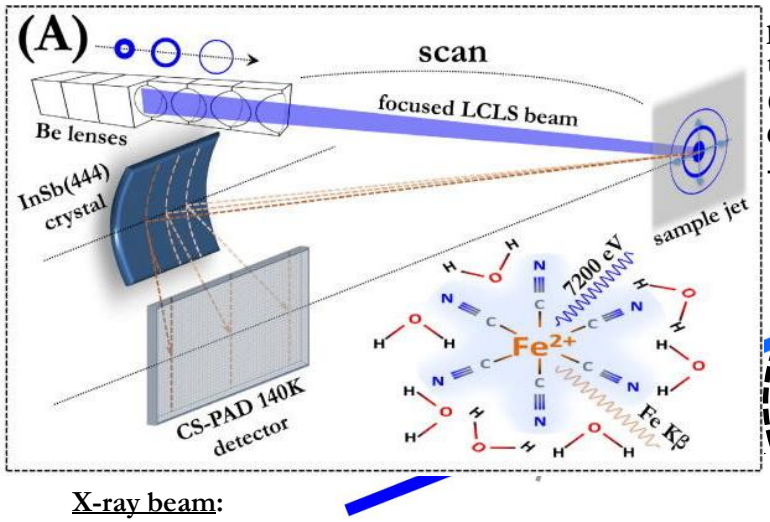

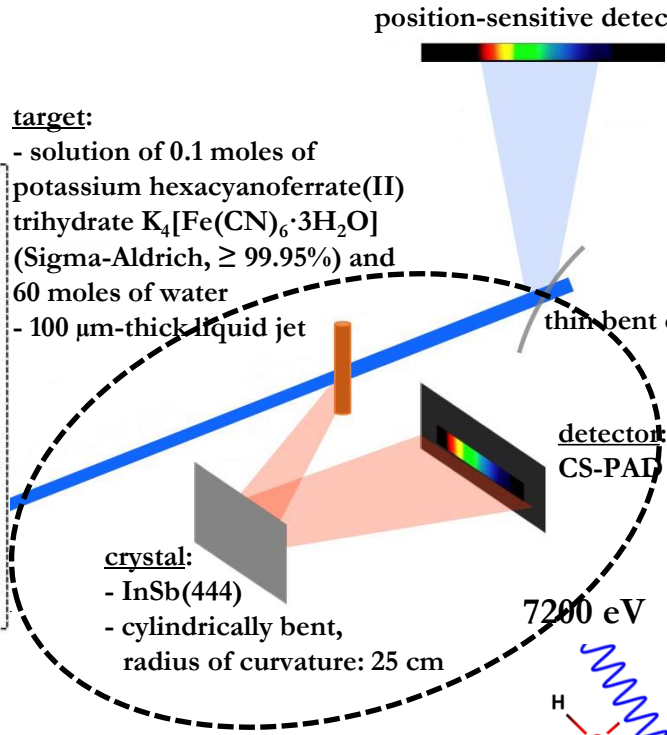

target:
- solution of 0.1 moles of potassium hexacyanoferrate(II) trihydrate $K_4[Fe(CN)_6 \cdot 3H_2O]$ (Sigma-Aldrich, ≥ 99.95%) and 60 moles of water
- 100 µm-thick liquid jet

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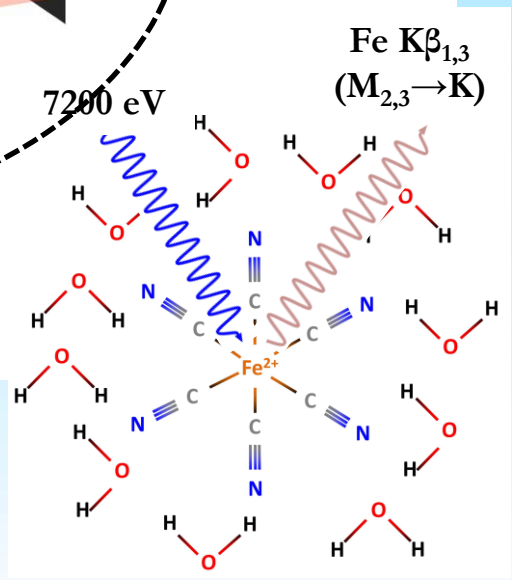
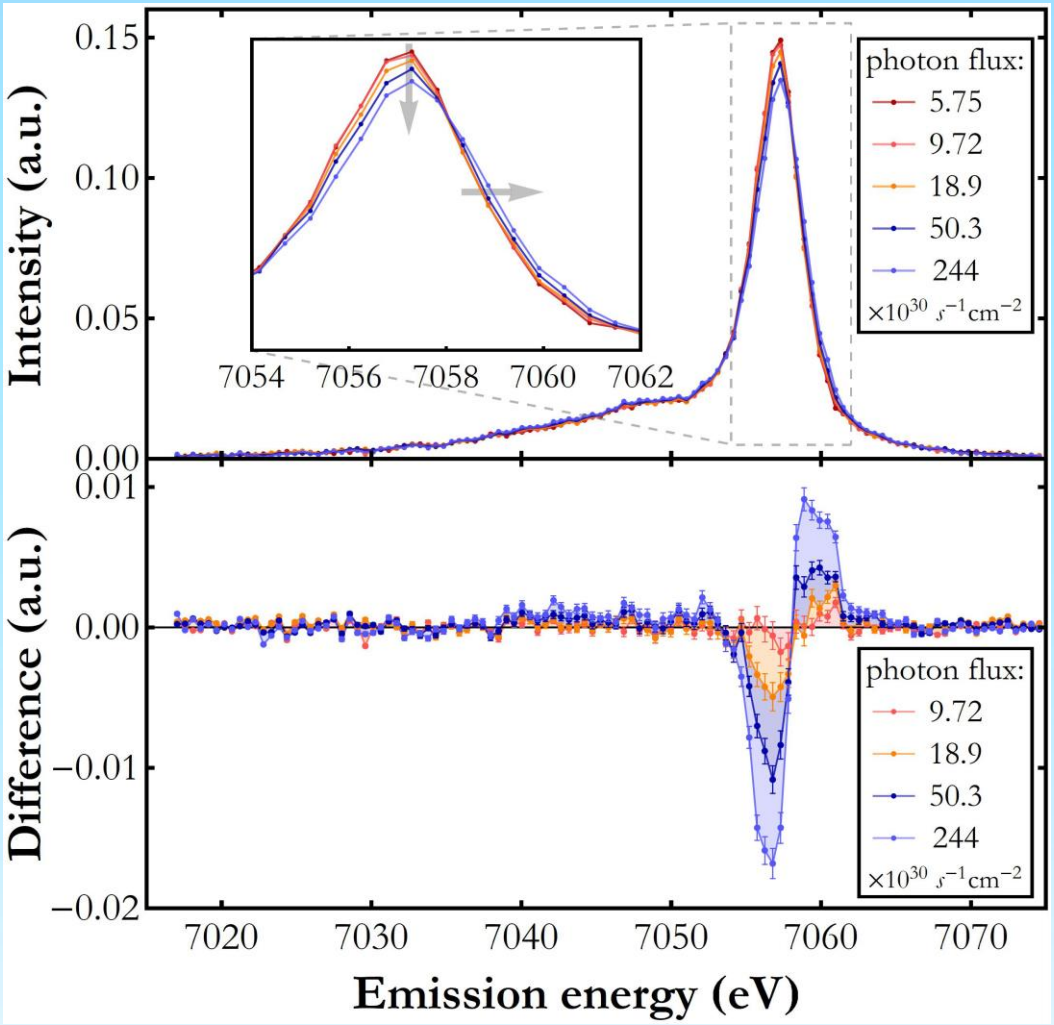


Results and discussion

Fe Kβ dependence on the incident photon flux



The Fe Kβ X-ray emission spectra measured for $K_4[Fe(CN)_6 \cdot 3H_2O]$ water solution for different fluxes of the incident photon beam.

The spectra were scaled to obtain the integral over entire studied energy domain equal to 1 to ensure constant $1s$ shell ionization cross section and the $3p \rightarrow 1s$ transition fluorescence yield and is supported by experimental studies showing that the influence of oxidation state change on the ratio of Fe Kα to Kβ fluorescence yields is below 10 %. The intensity measurement uncertainty does not exceed 2 % in the energy range 7054 – 7062 eV.

S. K. Kulshreshtha, D. N. Wagh, H. N. Bajpei, *X-Ray Spectrom.* **34**, 200-202 (2005).

O. K. Köksal, G. Apaydın, E. Cengiz, K. Karabulut, *J. Phys.: Conf. Ser.* **707**, 012004 (2016).

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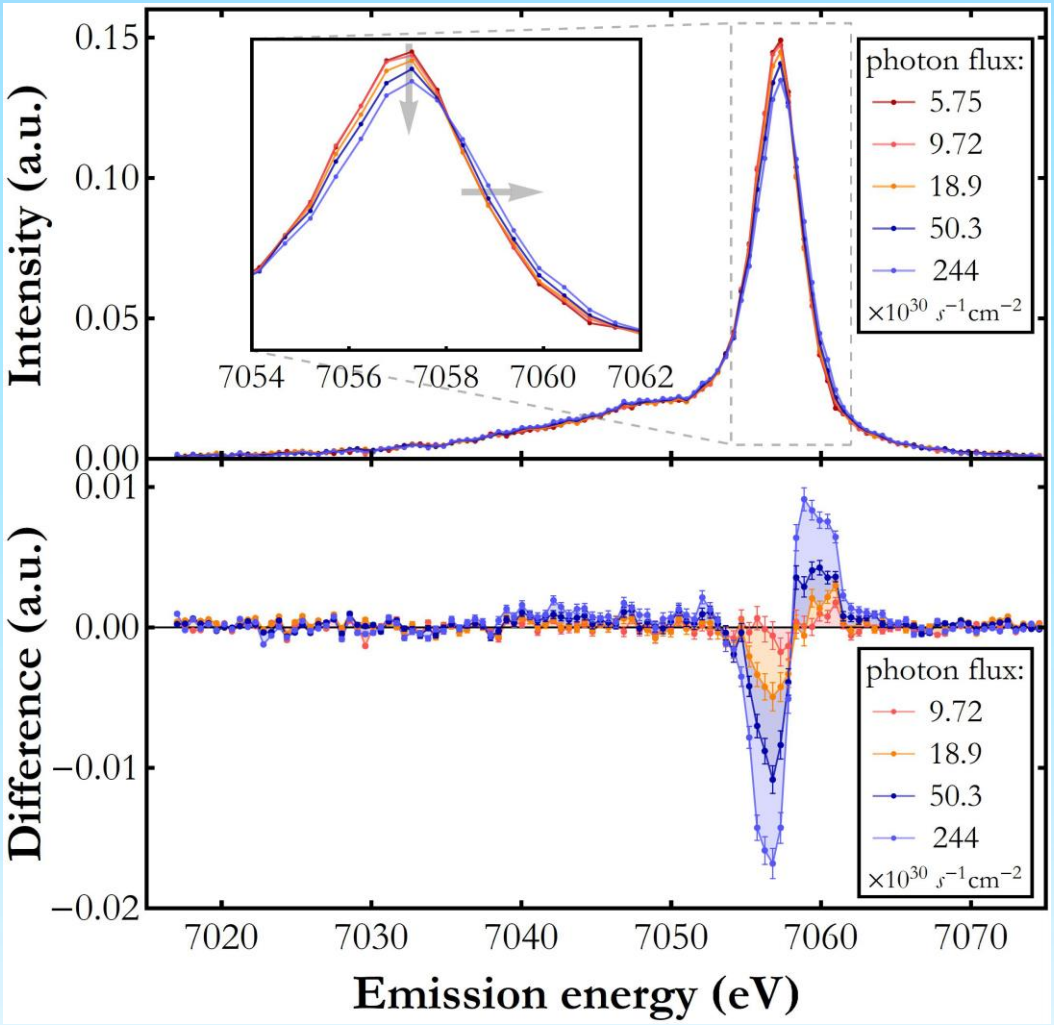

- not caused by the molecule's spin change as in W. Zhang *et al.*, *Nature* **509**, 345 (2014).

- not caused by sequential photoionization as, e.g., in A. Rudenko *et al.*, *Nature* **546**, 129 (2017).

Understanding the mechanism

Motivation

15 % of the incident photons are absorbed, 82 % of the photoabsorption events result in O 1*s* photoionization.

T. Schoonjans *et al.*, *Spectrochim. Acta, Part B* **66**, 776-784 (2011).

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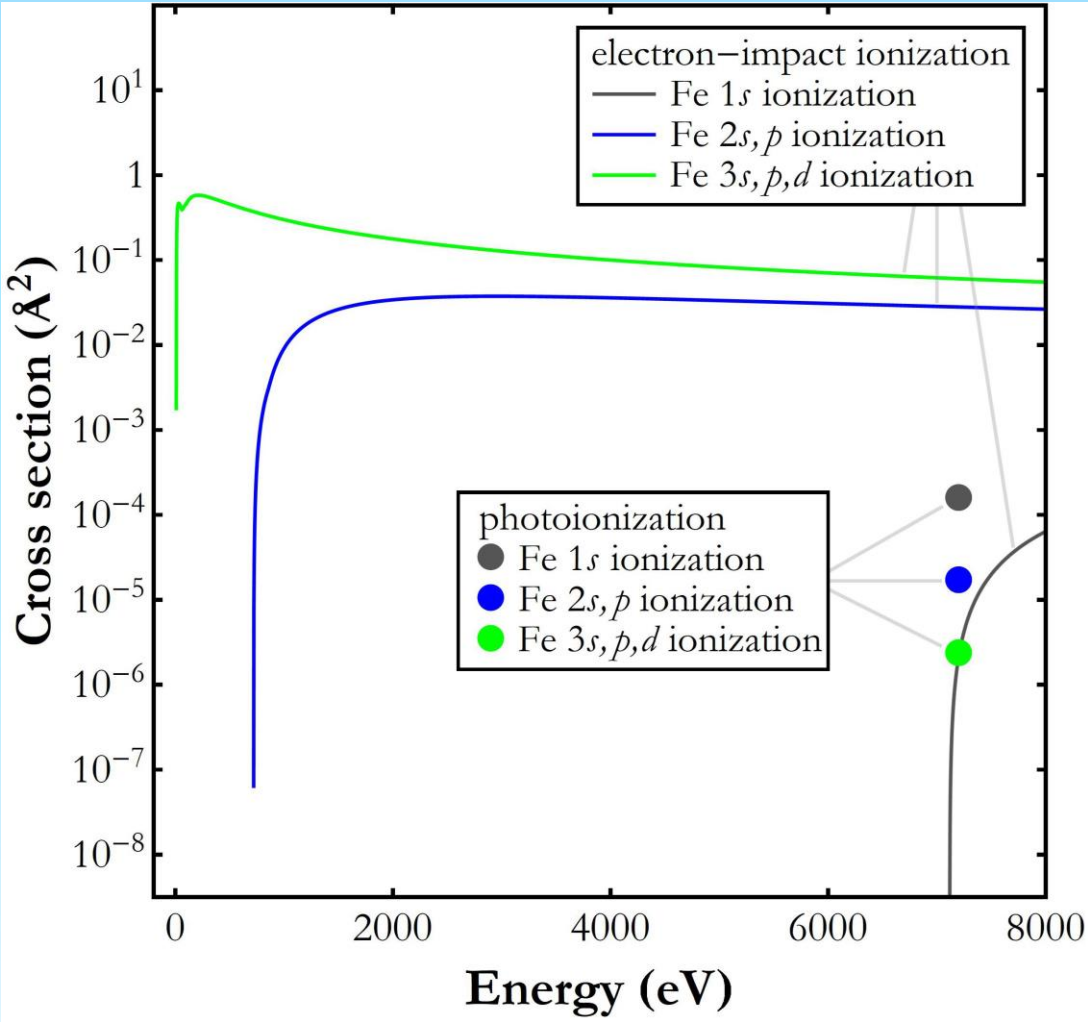
The cross section for electron-impact Fe ionization is up to the order of 10^4 larger than the Fe 1*s* shell photoionization cross section.



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B. Tsipinyuk, A. Bekkerman, E. Kolodney, https://arxiv.org/abs/physics/0407030 (2005).

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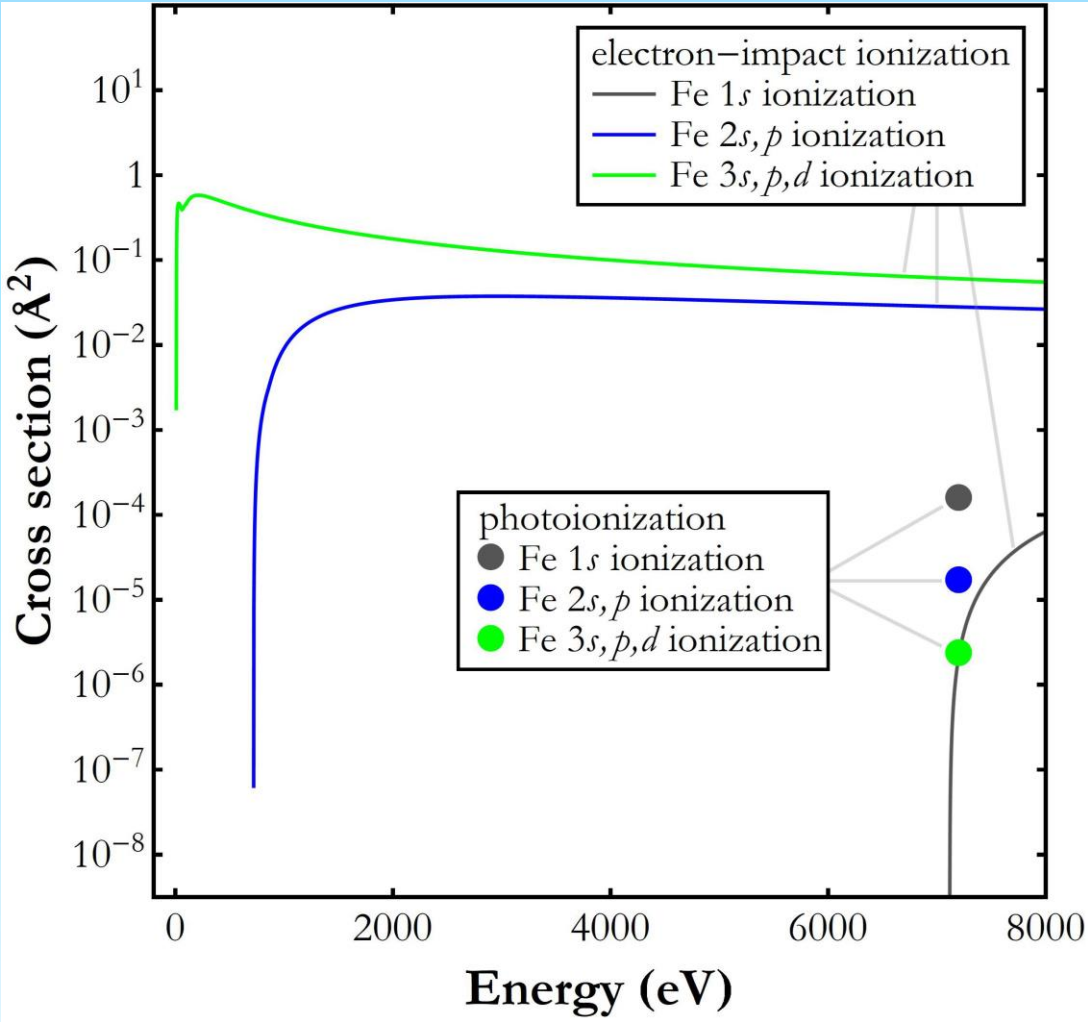
Photoelectrons and Auger electrons travel in average tens of nm between interactions and may reach the nearest Fe atoms in less than 1 fs.

Unlike photons, free electrons interact with the material multiple times losing the energy gradually.



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H. Shinotsuka *et al.*, *Surf. Interface Anal.* **49**, 238-252 (2016).

Understanding the mechanism

Energy and time distribution of photons and electrons, Fe ionization probability

$$\mathrm{d}E = -\overline{E_{loss,e\leftrightarrow a}}(E) f_e(E)\, dt$$

E - electron energy, t - time

$f_e(E)$ - average collision frequency per electron

$\overline{E_{loss,e\leftrightarrow a}}(E)$ - average energy loss per interaction

P. M. Banks, *Planet. Space Sci.* **14**, 1085-1103 (1966).
V. Vinogradov, V. P. Shevel'ko, *Sov. Phys. JETP* **44**, 542 (1976).

Understanding the mechanism

Energy and time distribution of photons and electrons, Fe ionization probability

$$\mathrm{d}E = -\overline{E_{loss,e\leftrightarrow a}}(E) f_e(E)\, dt$$

E - electron energy, t - time

$f_e(E)$ - average collision frequency per electron

$\overline{E_{loss,e\leftrightarrow a}}(E)$ - average energy loss per interaction

$$f_e(E) = n_a \sigma_{i,e\leftrightarrow a}(E) \bar{v}_e(E)$$

n_a - concentration of atoms a

$\sigma_{i,e\leftrightarrow a}(E)$ - cross section for inelastic electron-atom interaction

$\bar{v}_e(E)$ - average electron speed

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$$S_a(E) = n_a \sigma_{i,e\leftrightarrow a}(E) \overline{E_{loss,e\leftrightarrow a}}(E)$$

$S_a(E)$ - linear stopping power for a

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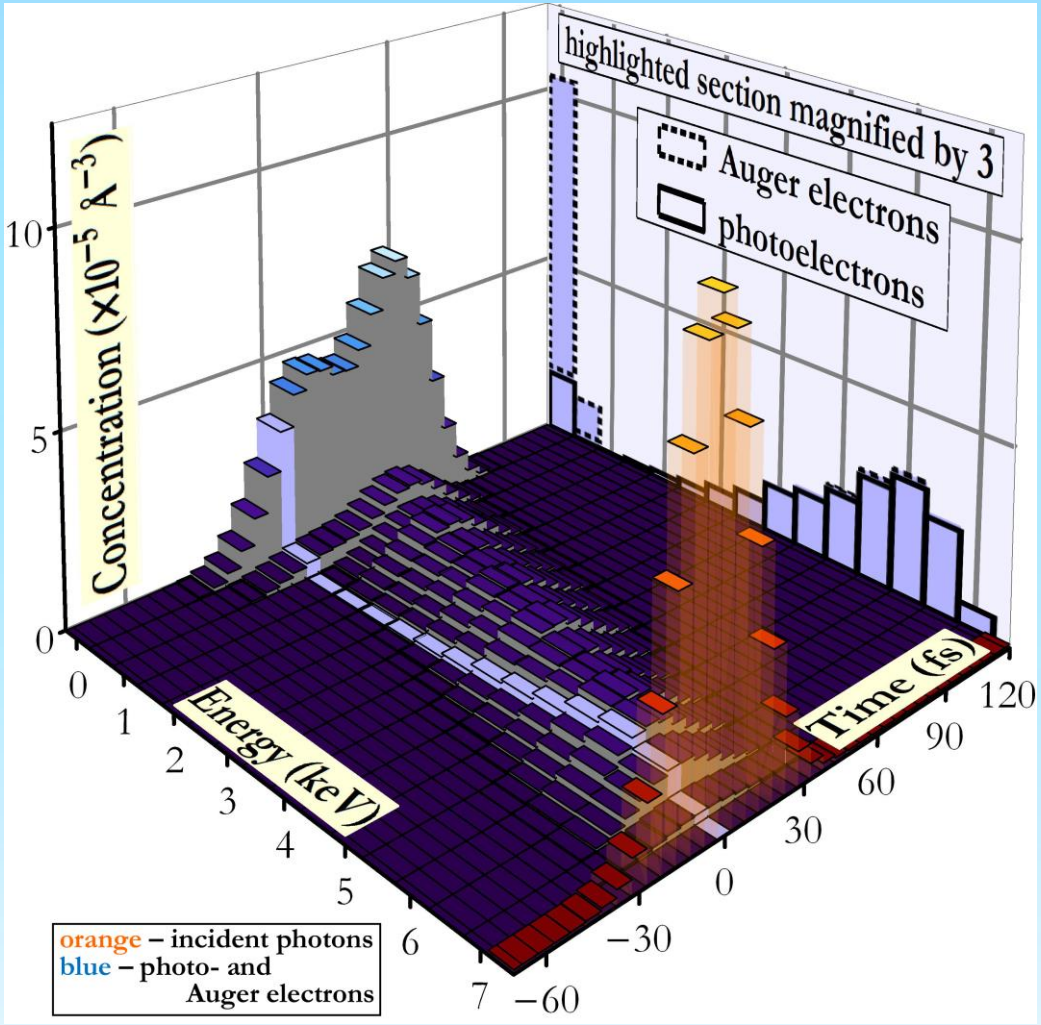

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Understanding the mechanism

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$$f_{Fe}(t) = \int \sigma_{i,e\leftrightarrow Fe}(E)\overline{v_e}(E)n_e(E,t)\,dE$$

$f_{Fe}(t)$ - electron-impact ionization frequency for single Fe atom

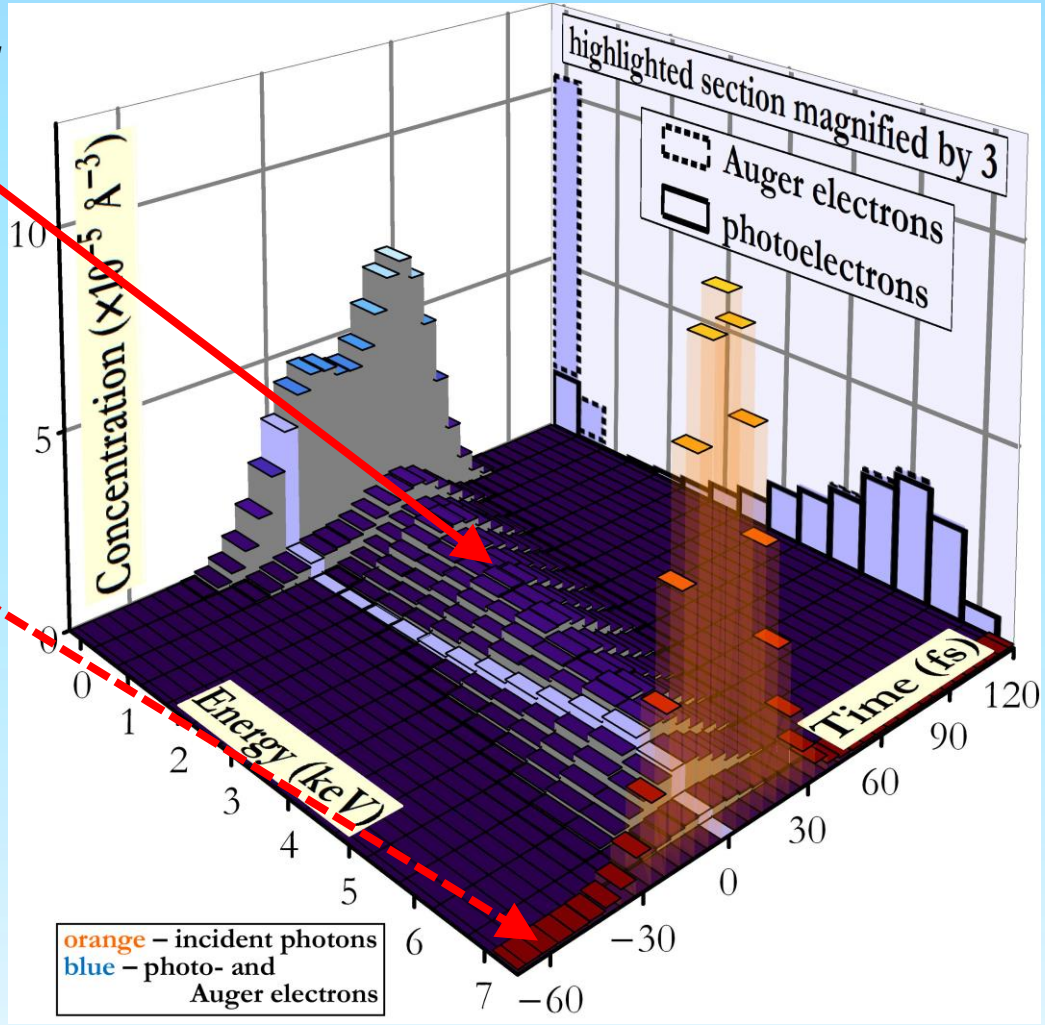
$n_e(E,t)$ - simulated energy and time evolution of the energetic electrons

$$F_{Fe}(t) = \frac{\sigma_{ph\leftrightarrow Fe}}{S} n_{ph}(t)$$

$F_{Fe}(t)$ - Fe 1*s* photoabsorption ionization frequency for single Fe atom

$\sigma_{ph\leftrightarrow Fe}$ - Fe 1*s* photoabsorption cross section

$n_{ph}(t)$ - simulated time evolution of the incident photons



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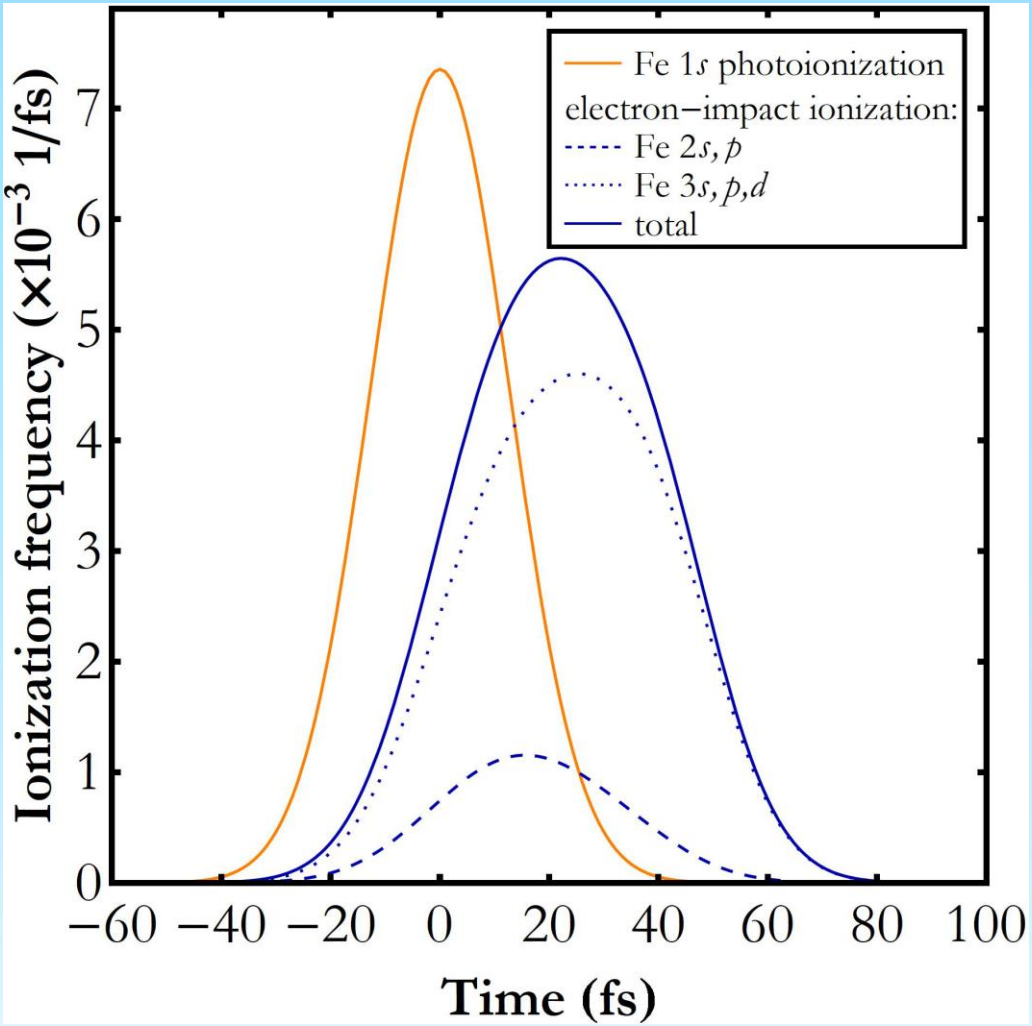

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Understanding the mechanism

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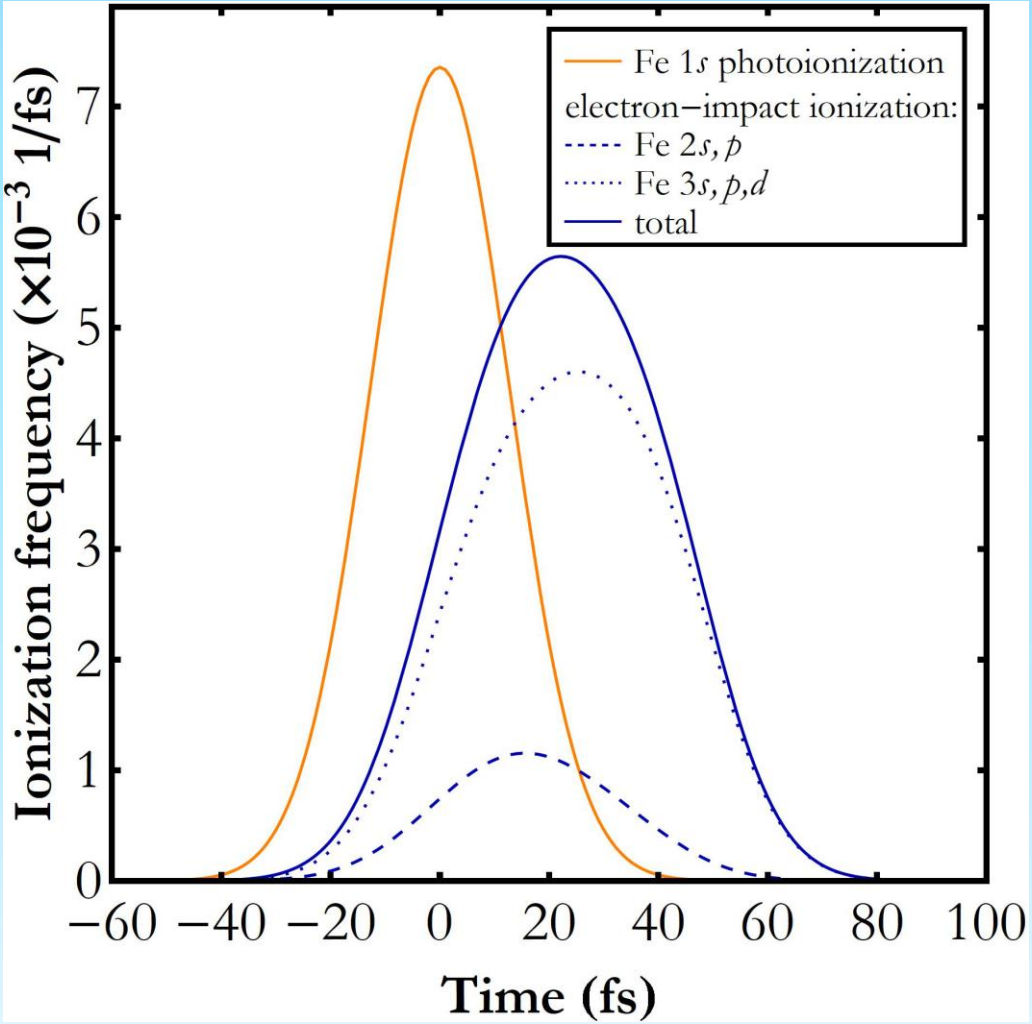
$n_{ph}(t)$ - simulated time evolution of the incident photons

$$\frac{\int_{-\infty}^{\infty} F_{Fe}(t)\left[\int_{-\infty}^{t} f_{Fe}(t')\,dt'\right]dt}{\int_{-\infty}^{\infty} F_{Fe}(t)\,dt} \approx 5\%$$



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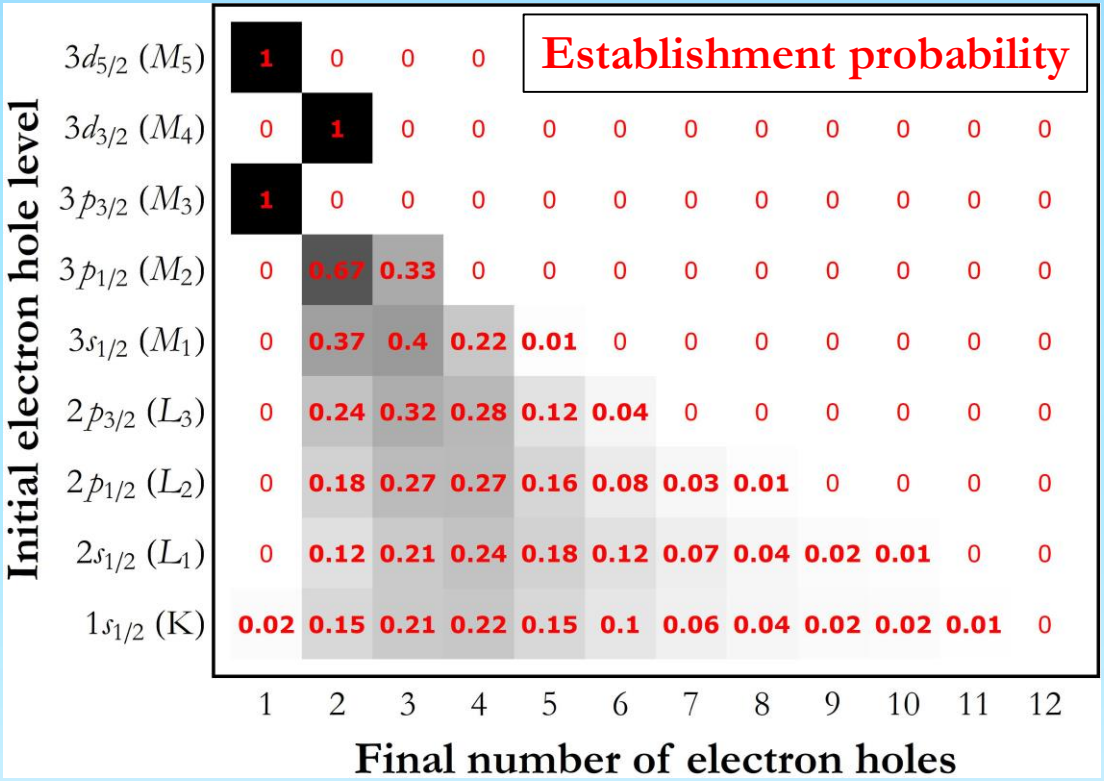
Understanding the mechanism

Multiple ionization of Fe atoms through Auger decays – probability



Fe atoms' ionization due to only the Auger decays induced by a single electron-impact ionization reaches more than 6 electron holes on the valence levels which results in oxidation state of Fe atoms in $Fe^{2+}(CN)_6$ of more than 8+.

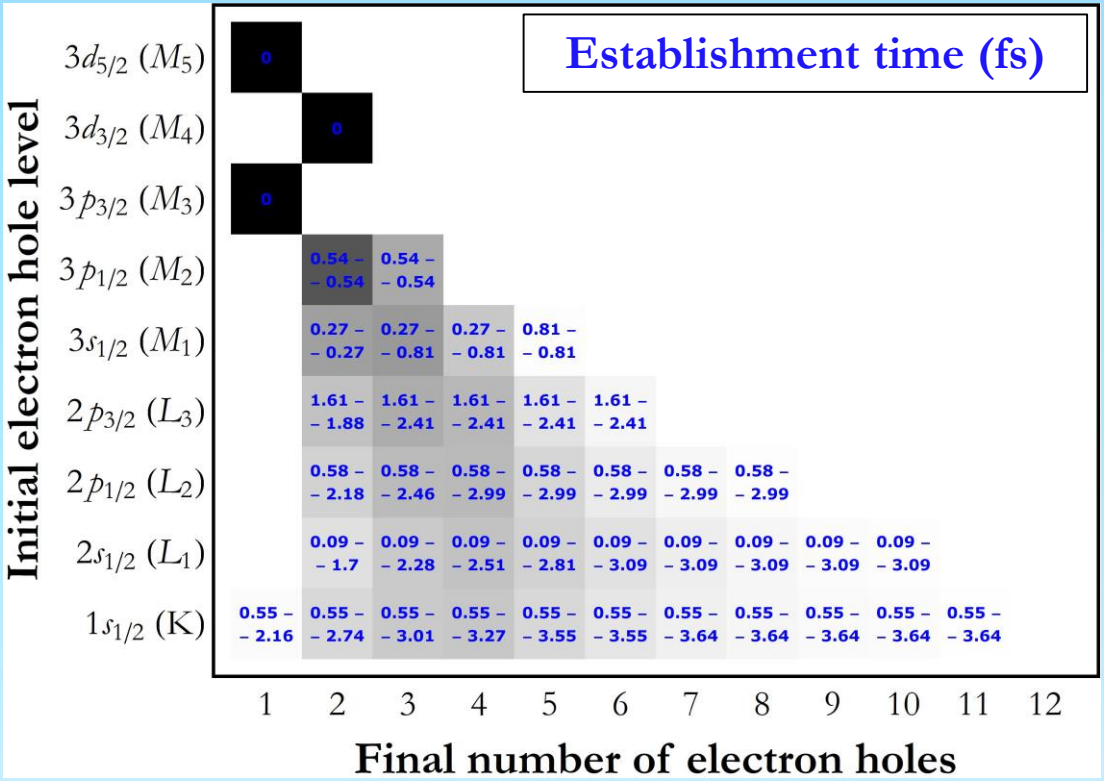
Fe: $1s_{1/2}^2$
$2s_{1/2}^2\ 2p_{1/2}^2\ 2p_{3/2}^4$
$3s_{1/2}^2\ 3p_{1/2}^2\ 3p_{3/2}^4\ 3d_{3/2}^4\ 3d_{5/2}^2$
$4s_{1/2}^2$

The estimated multiple electron hole-states' relative occurrences are approximately
0.29 : 0.32 : 0.21 : 0.12 : 0.04 : 0.02 for respectively
1, 2, 3, 4, 5 and 6 electron holes or equivalently for
Fe oxidation state 3+, 4+, 5+, 6+, 7+, 8+.

T. Schoonjans *et al.*, *Spectrochim. Acta, Part B* **66**, 776-784 (2011).
A. Thompson, X-ray Data Booklet (Lawrence Berkeley Laboratory, Berkeley, USA, ed. 3, 2009), pp. 9-64.

Understanding the mechanism

Multiple ionization of Fe atoms through Auger decays – time



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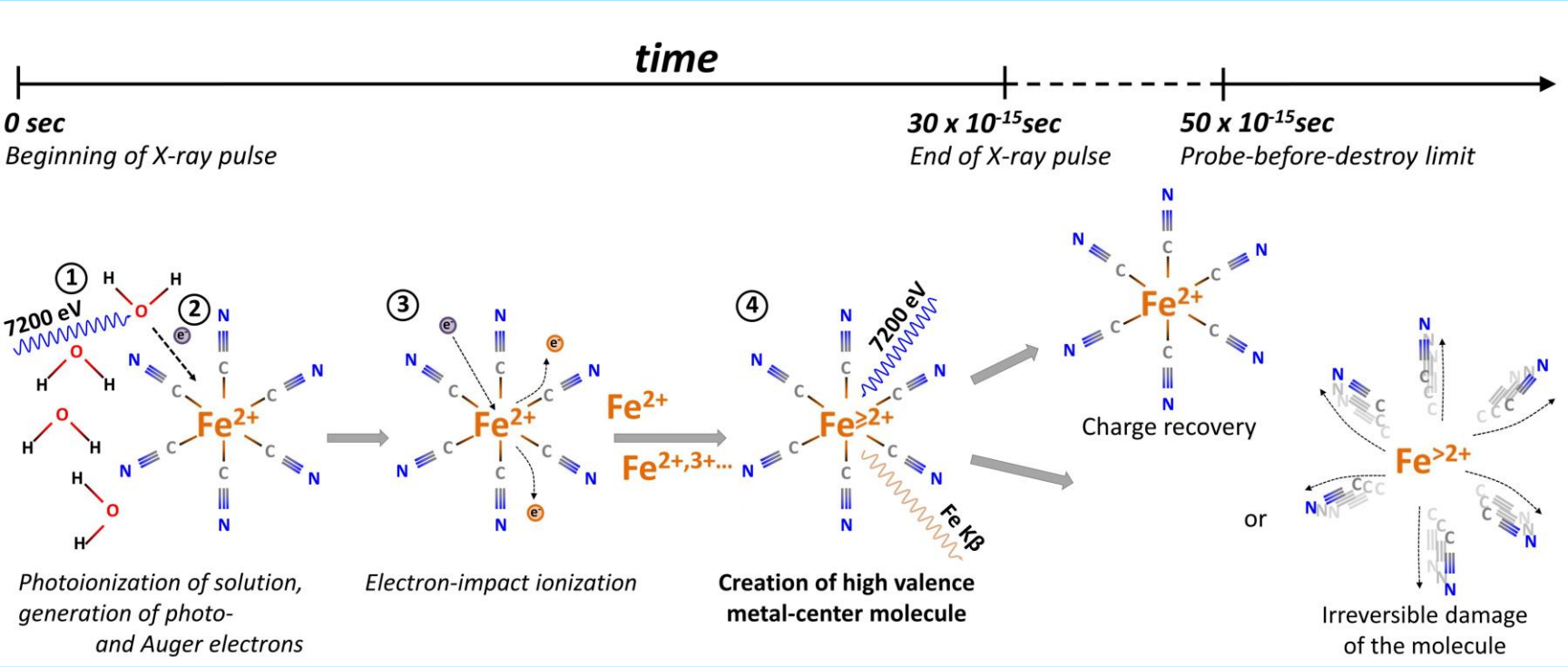
Understading the mechanism

Summary

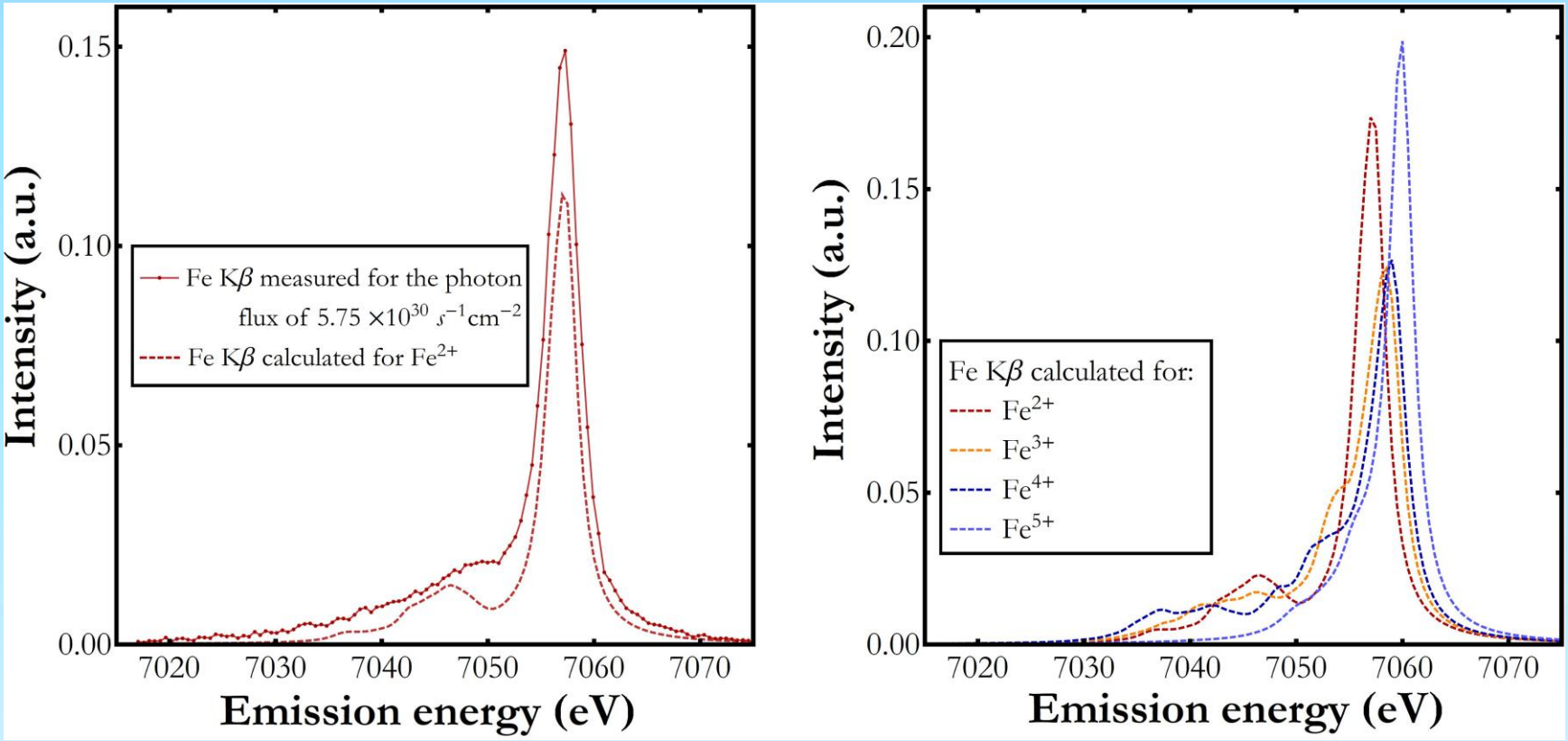


J. Kern *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **109**, 9721-9726 (2012).

S. M. Durbin, T. Clevenger, T. Graber, R. Henning, *Nat. Photonics* **6**, 111-114 (2012).

Fe Kβ X-ray emission spectrum calculation

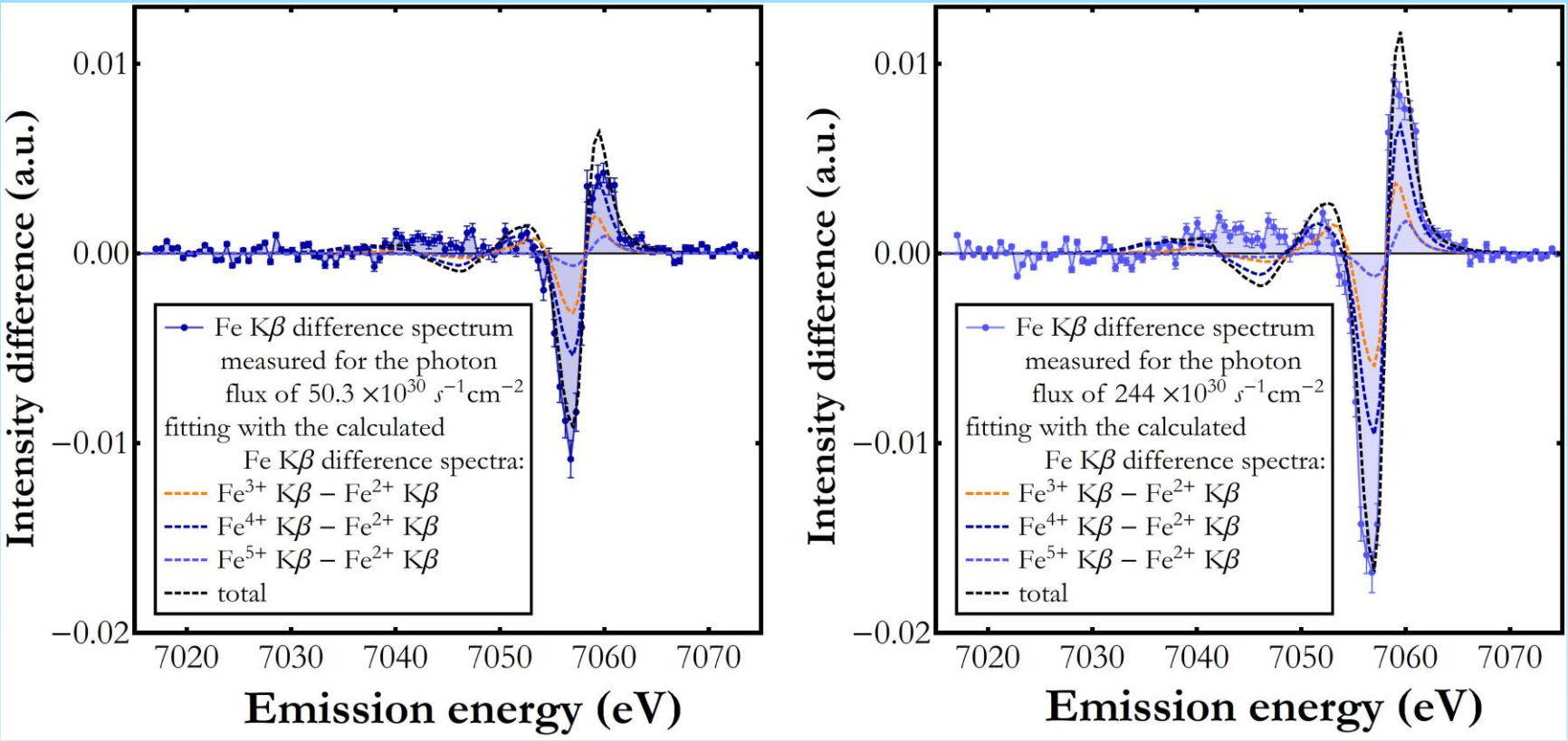
Effect of Fe oxidation state in $Fe(CN)_6$



The spectra were calculated within density functional theory (DFT). The field splitting parameter 10 Dq of 4.2 eV was used in the multiplet calculations and metal-to-ligand charge transfer was not included.

Fe Kβ X-ray emission spectrum calculation

Extraction of populations of different Fe oxidation states



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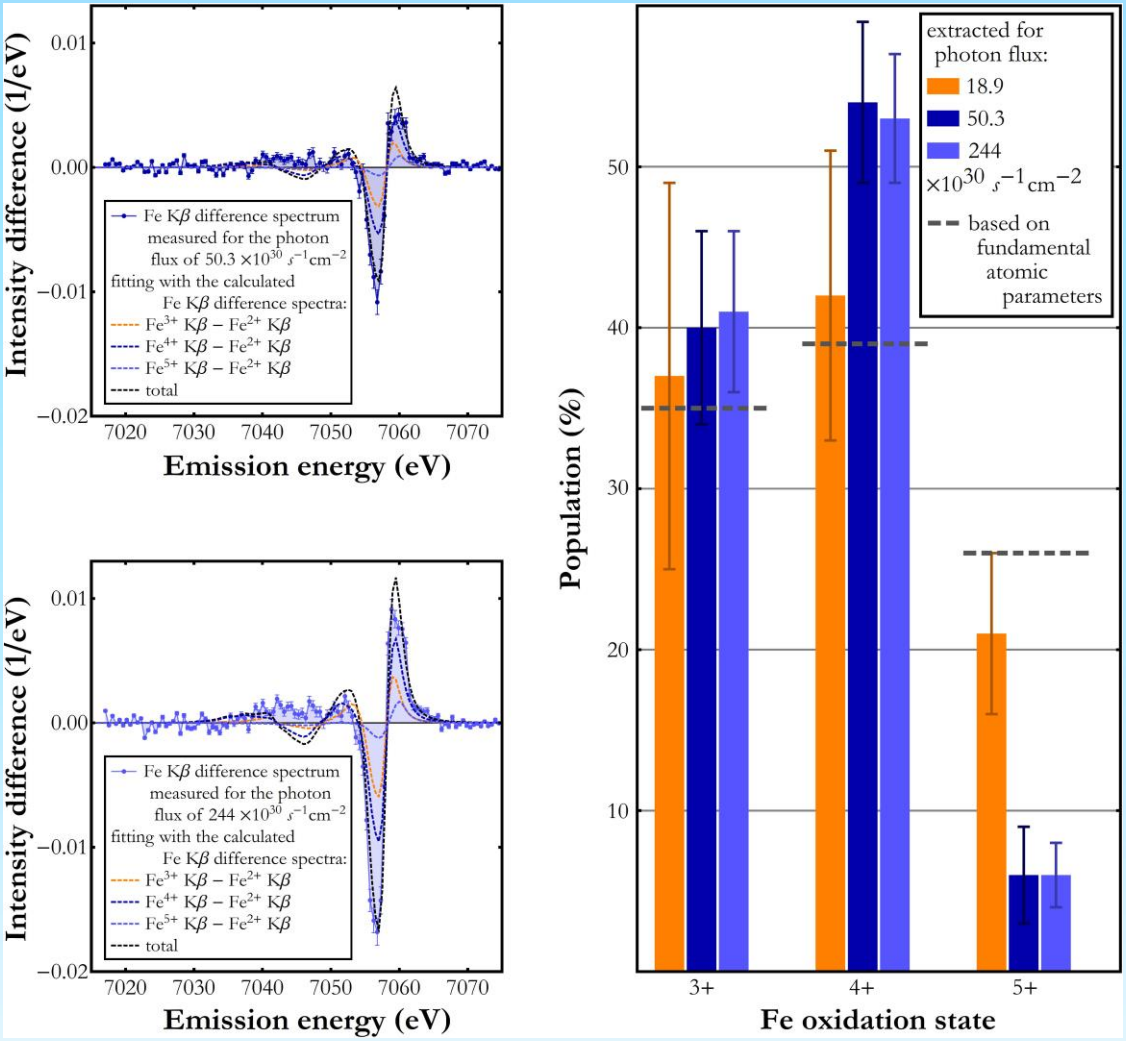

Summary

- Fe Kβ XES for $K_4[Fe^{2+}(CN)_6 \cdot 3H_2O]/H_2O$ solution at XFEL
- 30 fs-short pulses of 4×10^{11} 7200 eV-photons at the repetition rate of 120 Hz (typical operation parameters), beam focusing with movable Be lenses

- Observed: monotonic dependence of Fe Kβ XES spectra on the incident XFEL beam flux
- Mechanism: multiple ionization on the molecule's Fe site caused by electron impact and Auger decays
- The molecule at this short moment (< 50 fs) is in a unique high valence state where the bonds between Fe and C atoms are broken but the molecule's constituents have not moved yet.
- The effect is solvent dependent.

Thank you for your attention.

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Y. Kayser[2]
J. Czapla-Masztafiak[1]
M. Guo[3]
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E. Källman[3]
G. Knopp[4]
M. Lundberg[3]
C. Milne[4]
J. Rehanek[4]
J. Sá[3,6]
J. Szlachetko[1]

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[6] Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

W. Błachucki *et al.*, *Structural Dynamics* **6**, 024901 (2019).

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