Relativistic effects in x-ray multiphoton ionization dynamics

Sang-Kil Son
Center for Free-Electron Laser Science, DESY, Hamburg, Germany

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CFEL SCIENCE DESY. HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

Acknowledgment

CFEL-DESY Theory Division


Ludger Inhester


Zoltan Jurek


Robin Santra


Koudai Toyota


Yajiang Hao


Kota Hanasaki


Julia Schäfer


Benoît Richard

Experiment collaboration


Benedikt Rudek at PTB


Daniel Rolles at KSU

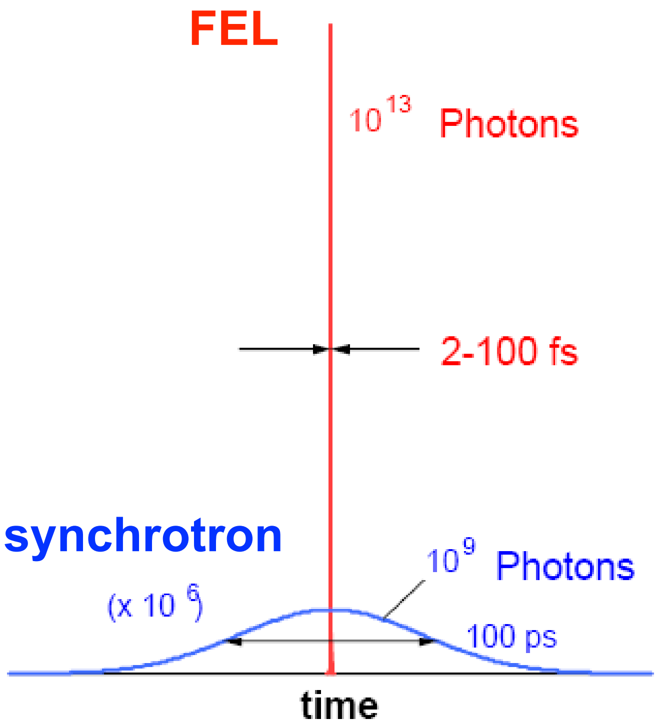

Artem Rudenko at KSU


Rebecca Boll at EuXFEL

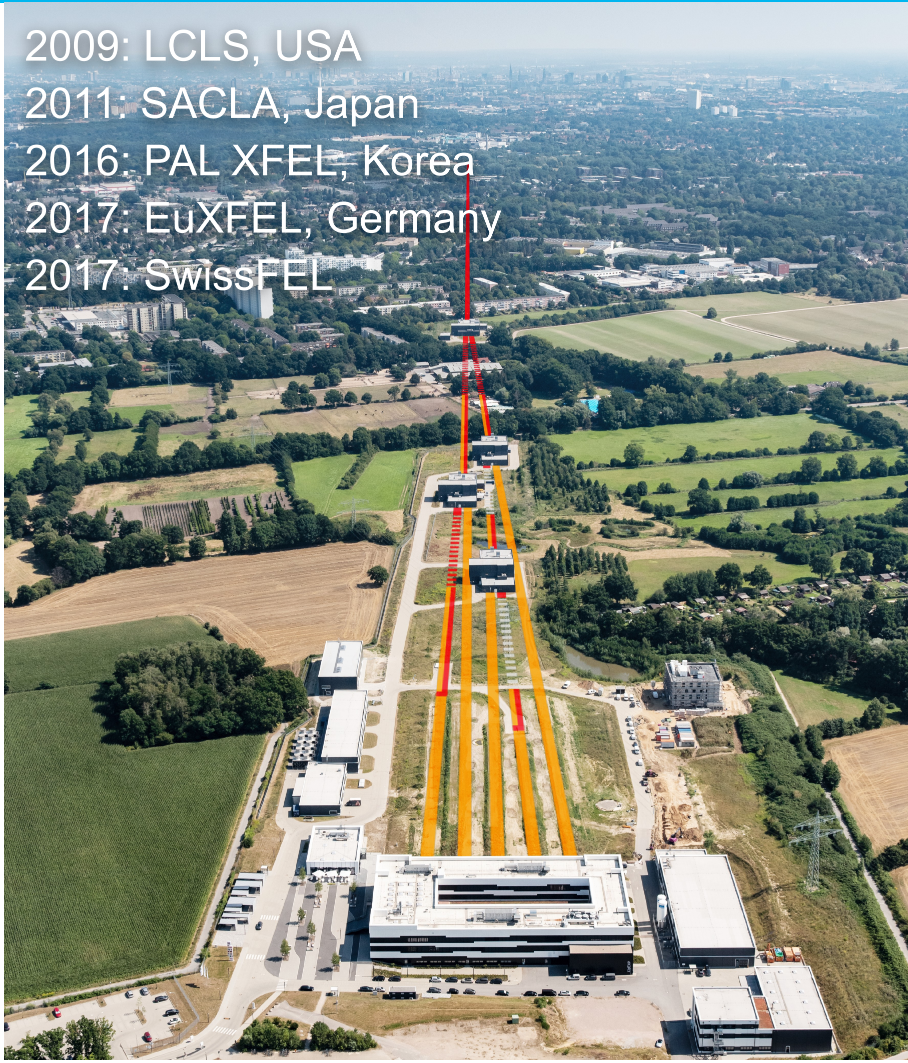

Till Jahnke at EuXFEL

XFEL: X-ray Free-Electron Laser

- *Ultraintense*: ~10^{13} photons
- *Ultrafast*: ~femtoseconds



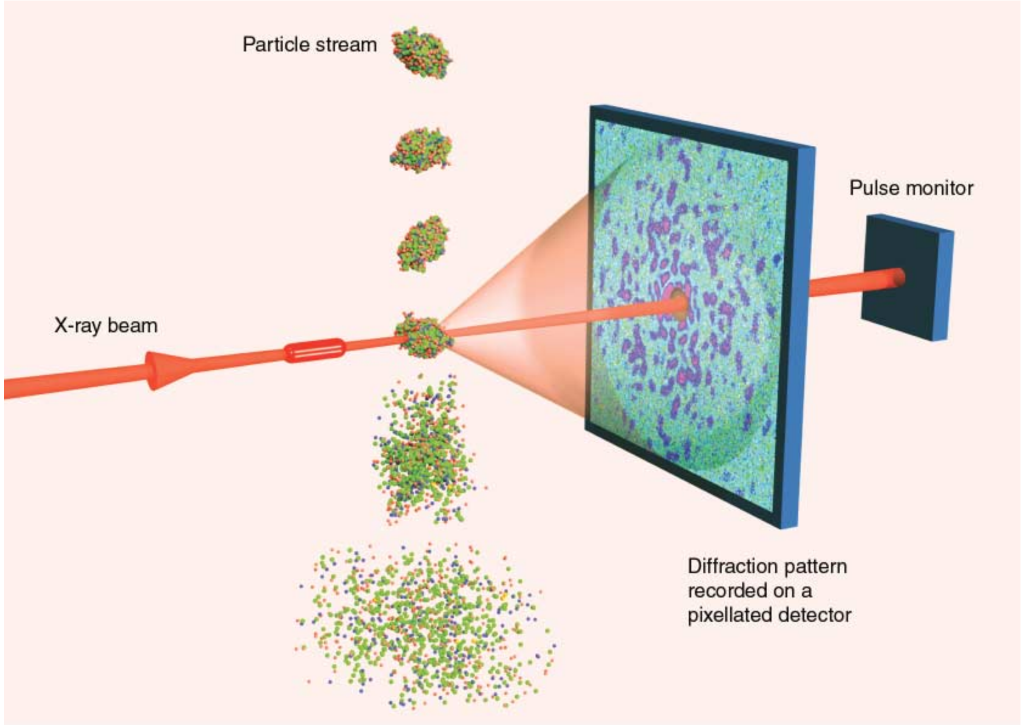
Schneider, *Rev. Accl. Sci. Tech.* **3**, 13 (2010).



Aerial view of the European XFEL

Why *ultraintense* and *ultrafast*?

- Structural determination of biomolecules with x-rays
  ➔ X-ray crystallography
- Growing high-quality crystals is one of major bottlenecks
- Enough signals obtained from even single molecules by using *ultraintense* pulses
- Signals obtained before radiation damage by using *ultrafast* pulses



Gaffney & Chapman, *Science* **316**, 1444 (2007).

How does matter interact with *ultraintense* and *ultrafast* pulses?

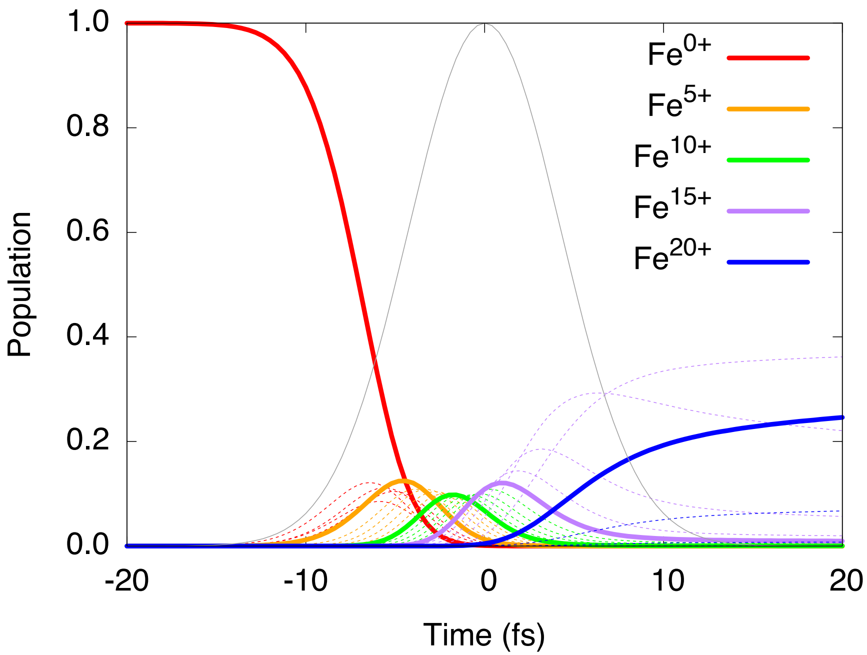
Why *heavy atom?*

- Serial femtosecond crystallography at XFELs: beyond proof-of-principle

  Chapman, *Annu. Rev. Biochem.* **88**, 35 (2019).
  Barends *et al.*, *Nat. Rev. Methods Primers* **2**, 59 (2022).

- Anomalous scattering of heavy atoms: marker for phasing
- Severe ionization on heavy atoms ➔ novel phasing at high x-ray intensity

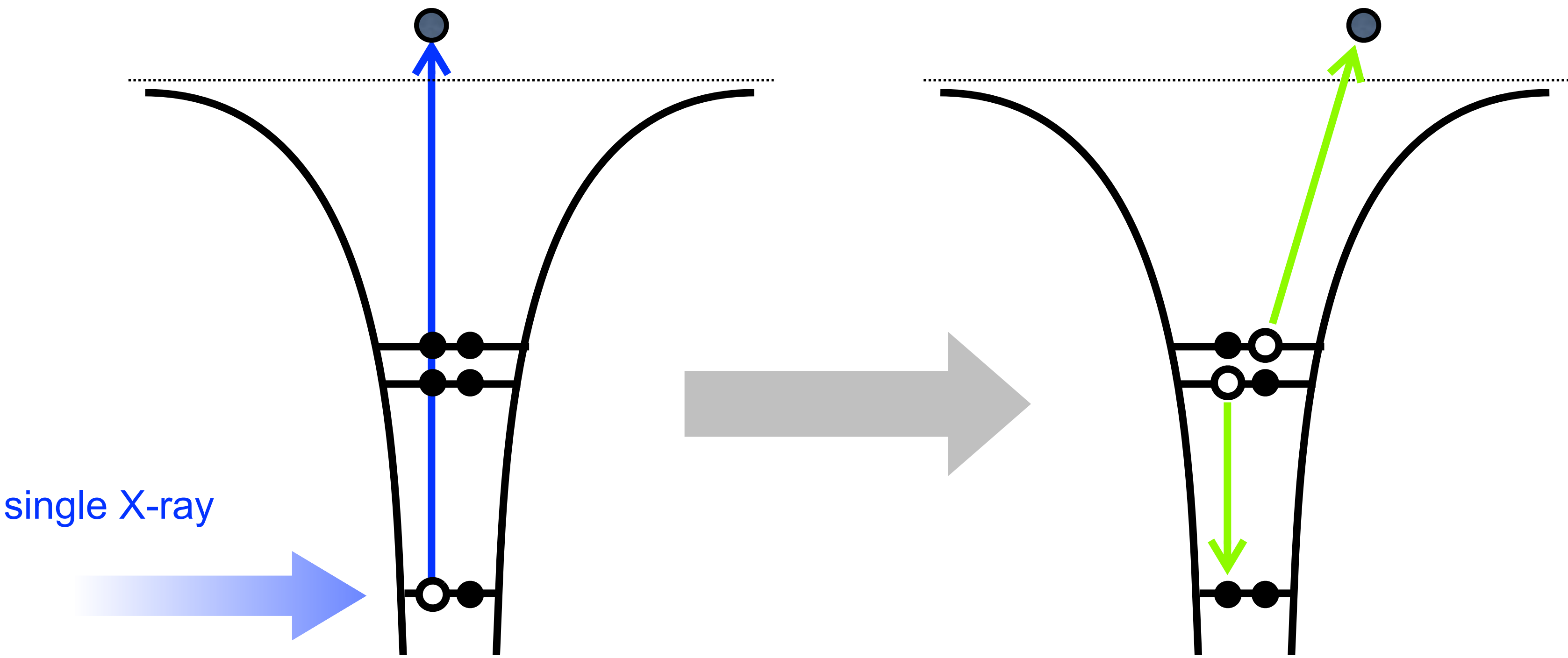
  Son, Chapman & Santra, *Phys. Rev. Lett.* **107**, 218102 (2011).
  Galli *et al.*, *IUCrJ* **2**, 627 (2015).



Fe@8 keV
5×10^{12} ph/μm^2
10 fs FWHM

Son, Chapman & Santra, *Phys. Rev. Lett.* **107**, 218102 (2011).

Fundamental x-ray–matter interaction



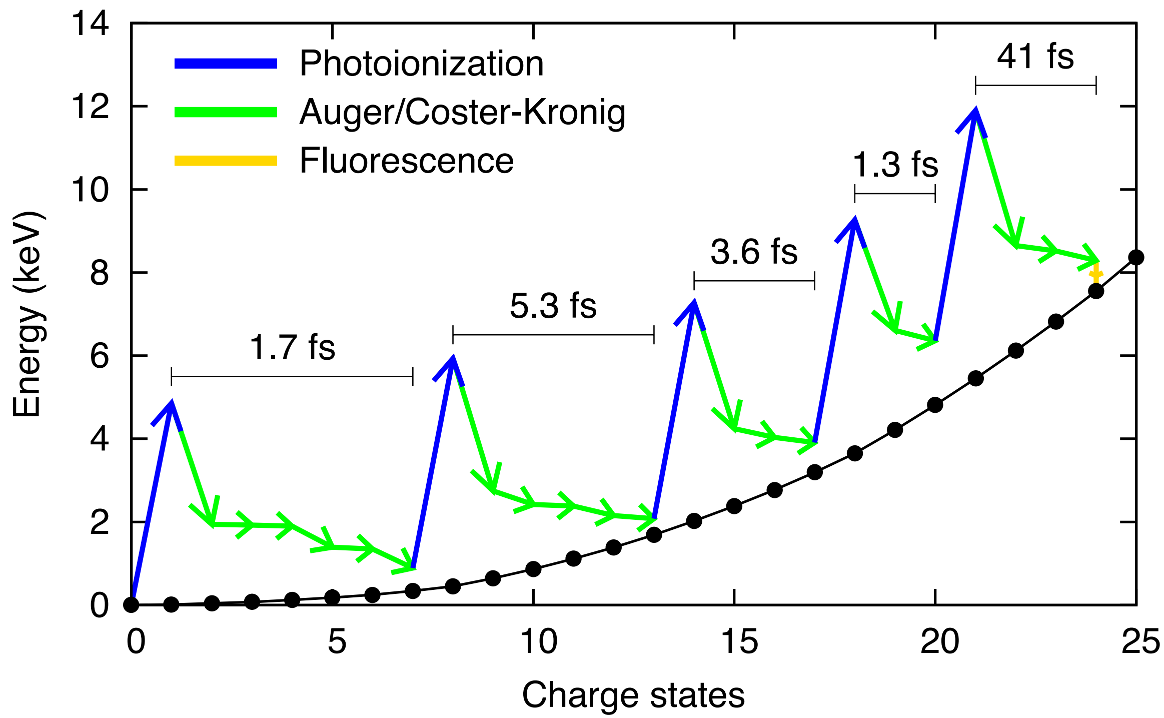
Photoionization: C → C^{*+} + e^-

Auger-Meitner decay: C^{*+} → C^{++} + e^-

synchrotron: one-photon absorption ➔ **PA** ➔ C^{2+}

XFEL: many-photon absorption ➔ **PAPAPP** ➔ C^{6+}

X-ray multiphoton ionization



Xe@5.5 keV

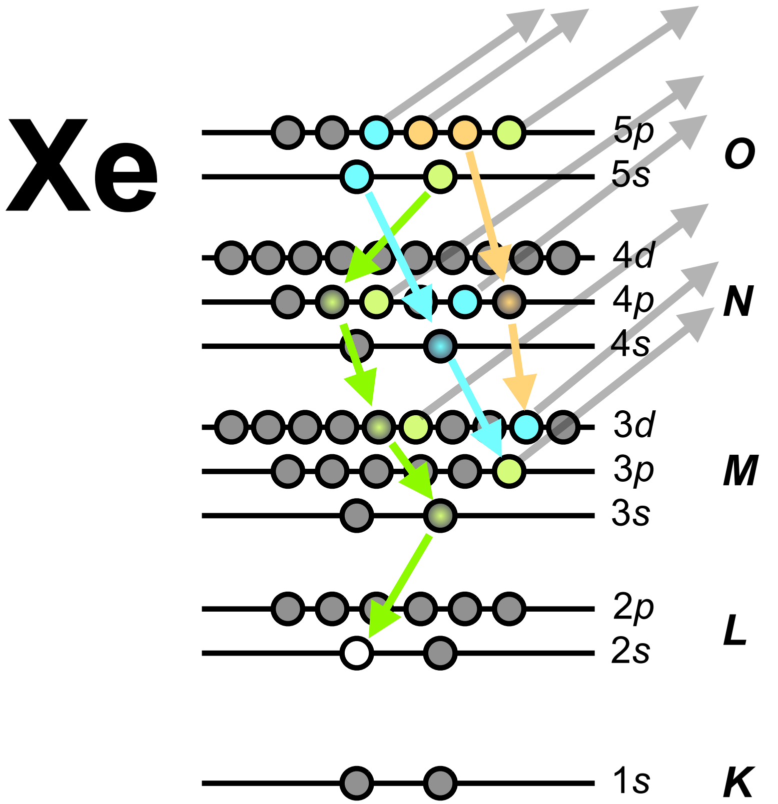
Fukuzawa *et al.*, *Phys. Rev. Lett.* **110**, 173005 (2013).

- Sequence of one-photon ionizations and relaxations
- 5 photons absorbed sequentially, 24 electrons ejected within 30 fs

Challenges for x-ray multiphoton ionization

> Theoretical challenges
  - tremendously many hole states by x-ray multiphoton absorption
  - highly excited system far from the ground state
  - electronic continuum states for ionization
  - complex inner-shell ionization dynamics, especially for heavy atoms

> No standard quantum chemistry code available

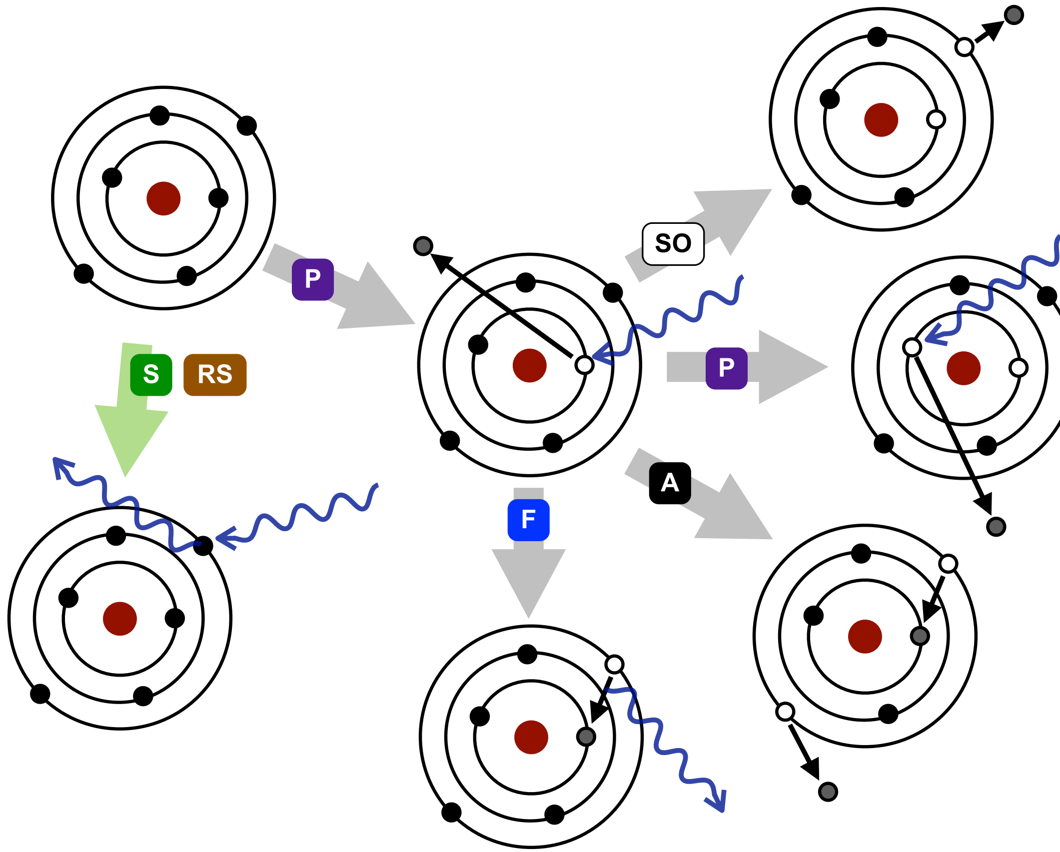


Multiphoton absorption after/during decay cascade creates:

- More than 20*M* multiple-hole config.
- More than 2*B* x-ray-induced processes

XATOM: all about x-ray atomic physics

- Hartree-Fock-Slater method for any given element and configuration
- X-ray-induced atomic processes based on perturbation theory
- Numerical grid method for bound and continuum states
- Solve coupled rate equations to simulate ionization dynamics (Monte Carlo on the fly)



Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).
Jurek, Son, Ziaja & Santra, *J. Appl. Cryst.* **49**, 1048 (2016).
Download executables: http://www.desy.de/~xraypac

Relativistic effects in x-ray processes

> Relativistic *E* correction within first-order perturbation theory

$$\hat{H} = \hat{H}_0 - \frac{\alpha^2}{8}\hat{p}^4 - \frac{\alpha^2}{4}\frac{dV}{dr}\frac{d}{dr} + \frac{\alpha^2}{2}\frac{1}{r}\frac{dV}{dr}\hat{l}\cdot\hat{s}$$

$$E_{nlj} = \varepsilon_{nl} + \Delta\varepsilon_{nl}^{\text{mass}} + \Delta\varepsilon_{nl}^{\text{Darwin}} + \Delta\varepsilon_{nlj}^{\text{so}}$$

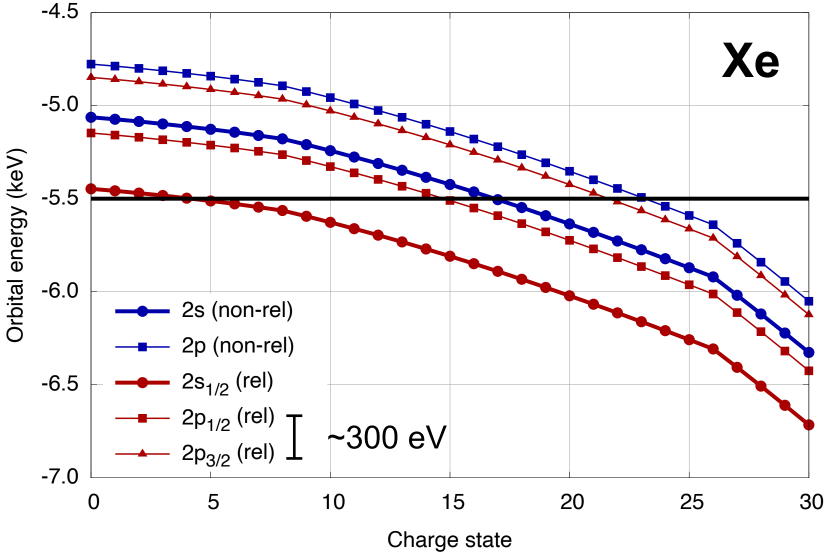
Koudai Toyota

> Open new Coster-Kronig decay channels due to spin-orbit splitting

Xe *L*-shell single vacancy

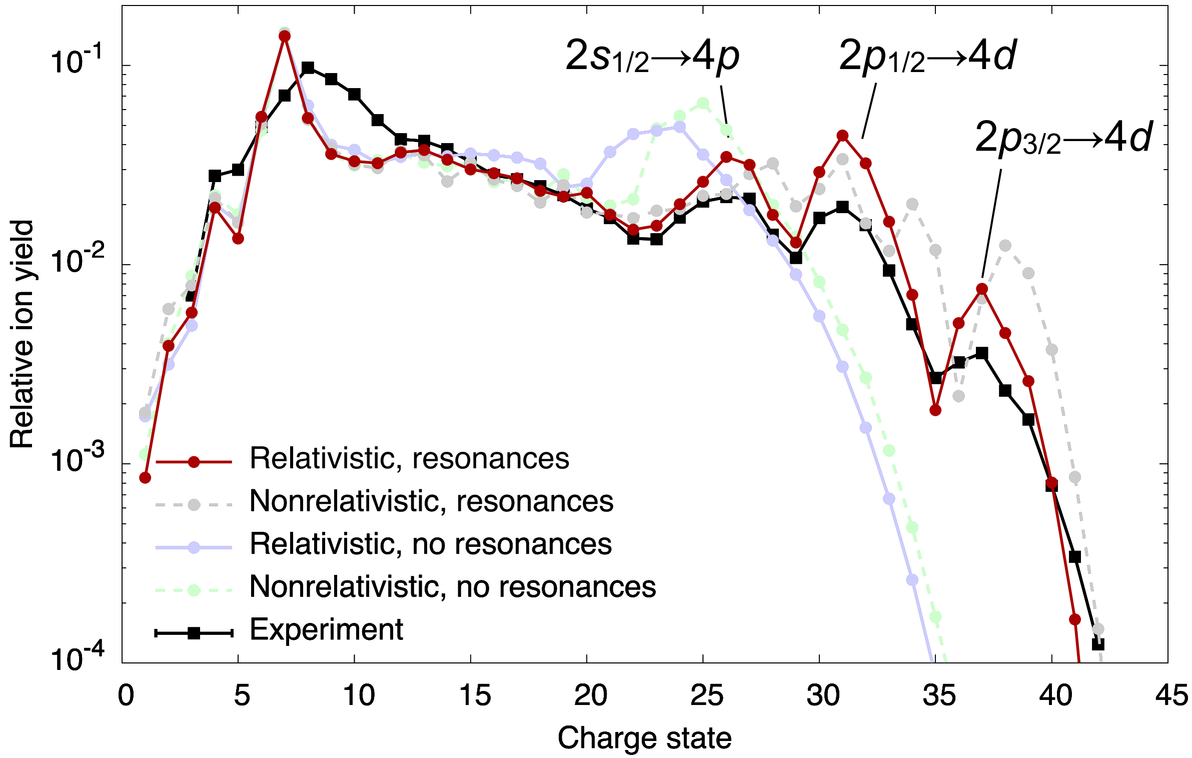
Group	Nonrel	Rel	DF [40]
$L_1 - X$	6.33×10^{-3}	8.03×10^{-3}	6.33×10^{-3}
$L_1 - XY$	6.07×10^{-2}	5.63×10^{-2}	6.50×10^{-2}
$L_1 - L_{23}X$	8.19×10^{-2}	6.76×10^{-2}	5.83×10^{-2}
$L_2 - X$	1.04×10^{-2}	1.32×10^{-2}	5.35×10^{-3}
$L_2 - XY$	9.38×10^{-2}	8.70×10^{-2}	4.86×10^{-2}
$L_2 - L_3X$	Forbidden	2.01×10^{-2}	6.82×10^{-3}
$L_3 - X$	$(=L_2 - X)$	1.08×10^{-2}	1.01×10^{-2}
$L_3 - XY$	$(=L_2 - XY)$	9.28×10^{-2}	1.10×10^{-1}

> Close photoionization at lower charges due to energy shifts



Toyota, Son & Santra, *Phys. Rev. A* **95**, 043412 (2017).

X-ray multiphoton ionization of Xe



Xe@5.5 keV

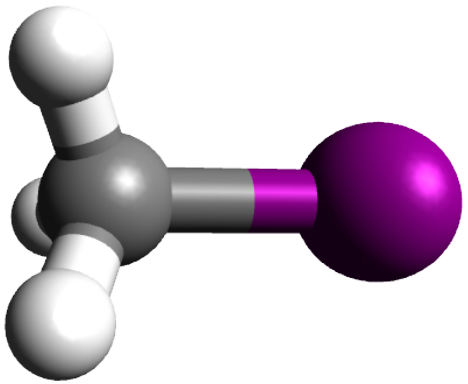
LCLS experiment led by Benedikt Rudek, Artem Rudenko, Daniel Rolles

Rudek *et al.*, *Nat. Commun.* **9**, 4200 (2018).

- Deep inner-shell (*L*-shell) ionization dynamics of Xe
- REXMI (Resonance-Enabled or -enhanced X-ray Multiple Ionization)

  Rudek *et al.*, *Nat. Photon.* **6**, 858 (2012).
- Highlighting the interplay between resonance and relativistic effects

Ultrafast dynamics of iodomethane



LCLS experiment:
Artem Rudenko,
Daniel Rolles

- σ(I) ~ 50,000 barn >>
  σ(C) ~ 80 barn at 8.3 keV
- severe ionization on iodine
  ➔ charge imbalance
  ➔ charge rearrangement
  ➔ fragmentation
- benchmark for heavy-atom-containing bio-molecule

XMOLECULE

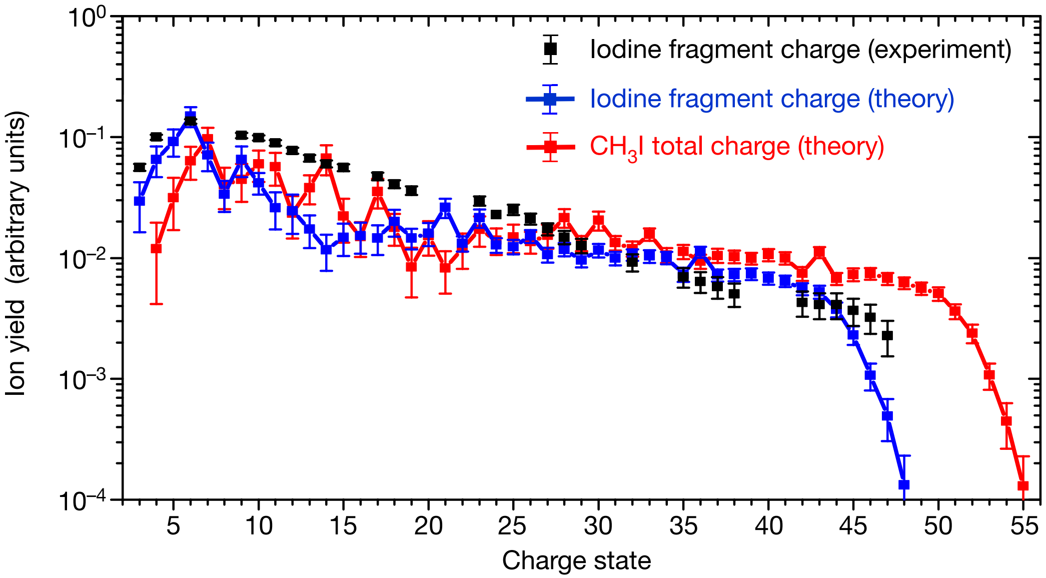
Ludger Inhester

- Quantum electrons, classical nuclei
- Efficient electronic structure calculation: core-hole adapted atomic basis functions obtained from XATOM
- Monte Carlo on the fly
- No relativistic effects implemented

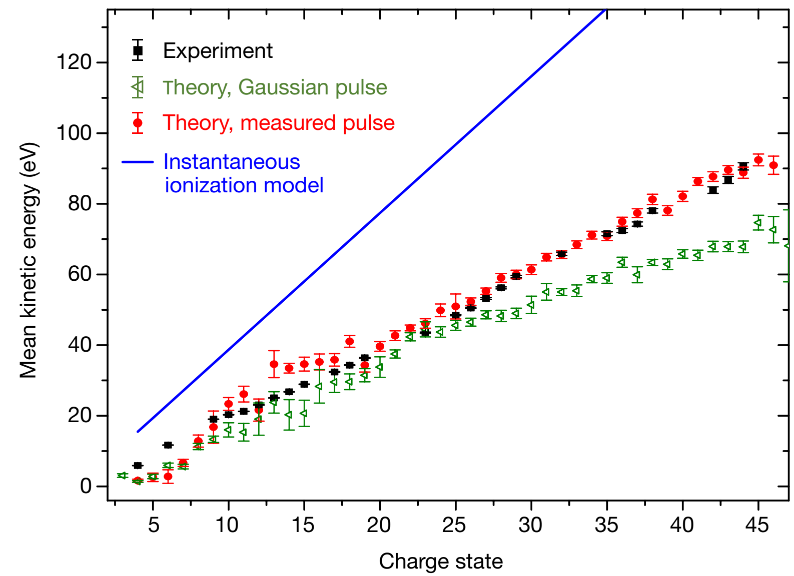
Hao *et al.*, *Struct. Dyn.* **2**, 041707 (2015).
Inhester *et al.*, *Phys. Rev. A* **94**, 023422 (2016).
Rudenko *et al.*, *Nature* **546**, 129 (2017).

Comparison with experimental data

CSD of I and CH_3I @8.3 keV



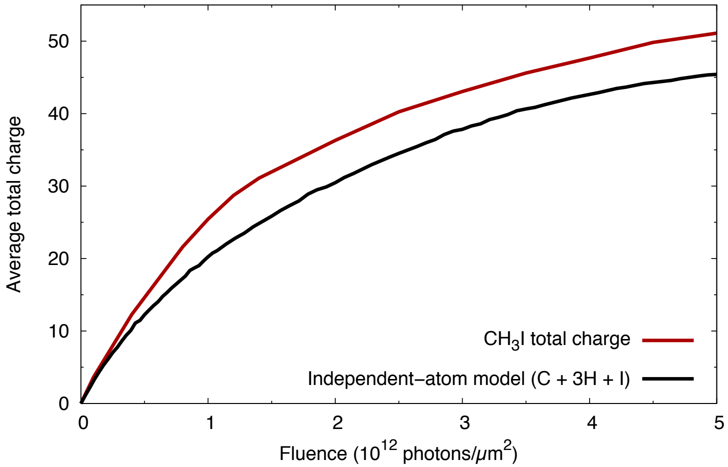
KER of I fragment



- CSD (charge-state distribution) & KER (kinetic energy release): Capturing detailed ionization and fragmentation dynamics
- First quantitative comparison for the behaviors of polyatomic molecules (including heavy element) under XFEL irradiation

Rudenko *et al.*, *Nature* **546**, 129 (2017).

Molecular ionization enhancement

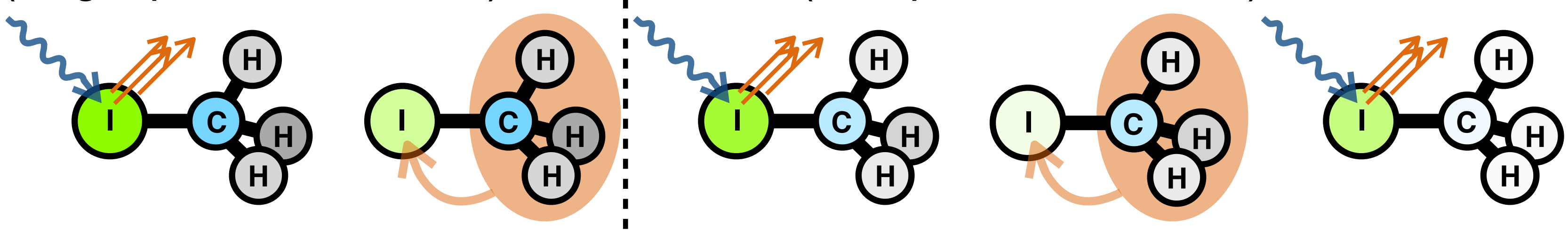


Total molecular charge > Sum of individual atomic charges

How? Note that charge rearrangement does not increase total molecular charge!

low x-ray fluence (single-photon dominant)

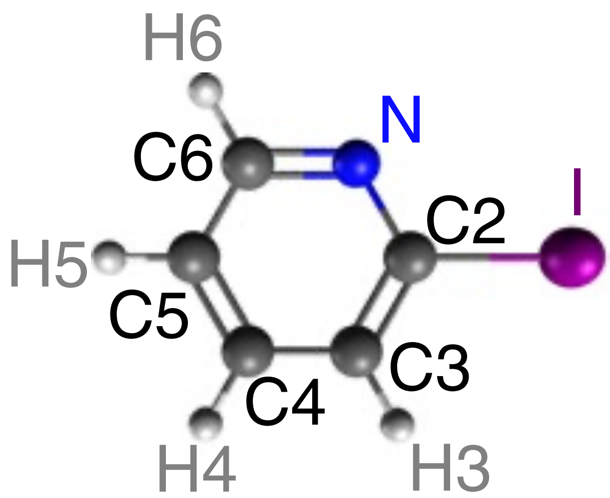
high x-ray fluence (multiphoton dominant)



CREXIM: Charge-Rearrangement-Enhanced X-ray Ionization of Molecules

Rudenko *et al.*, *Nature* **546**, 129 (2017).

Coulomb explosion of iodopyridine



- σ(C,N,H) < σ(I) at 2.0 keV
- ionization and intra-molecular electron arrangement together
- rapid and complete Coulomb explosion

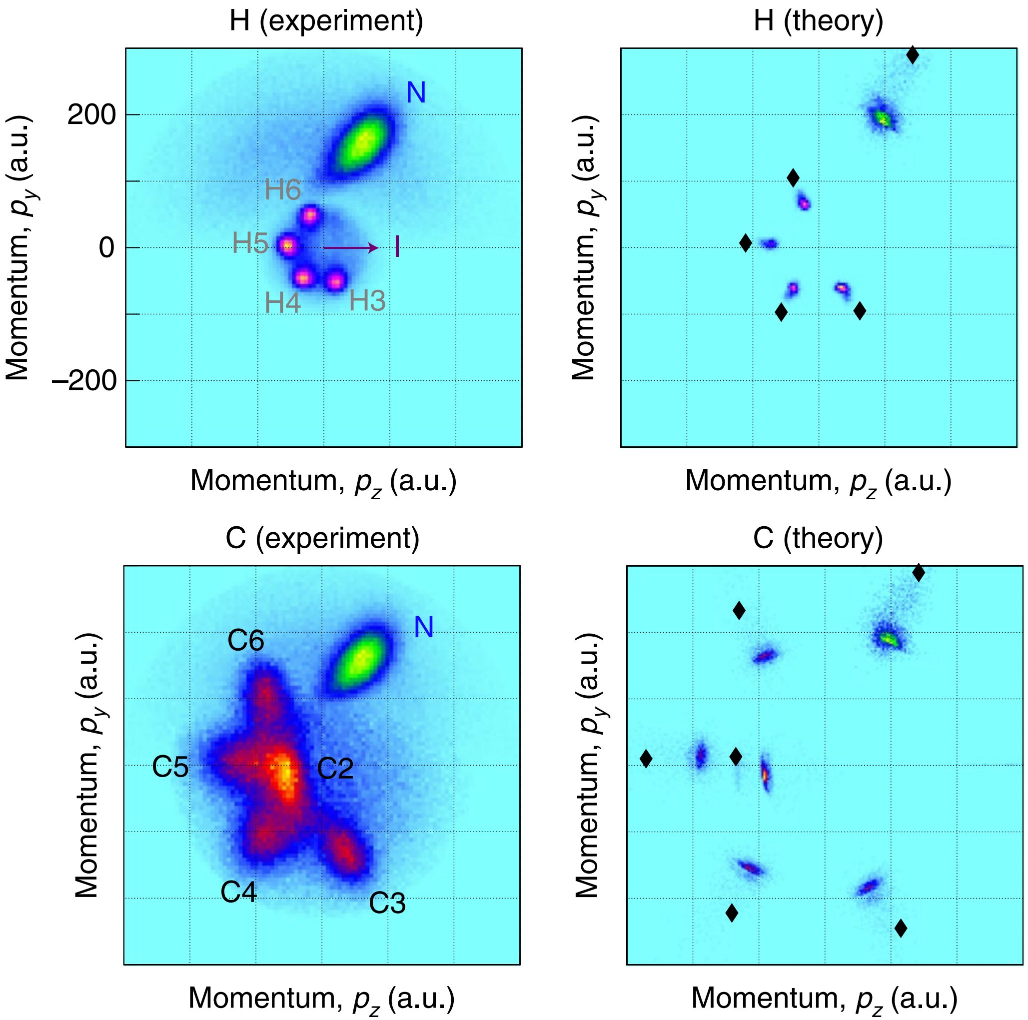
XMDYN

Zoltan Jurek

- Monte-Carlo Molecular Dynamics (MCMD)
- Quantum treatment for bound electrons of individual atoms ➔ combined with XATOM
- Classical dynamics for ions and free elec.
- Charge transfer model based on the over-the-barrier model
- No first-principles treatment for chemical bonding and molecular Auger
- No relativistic effects implemented

Murphy *et al.*, *Nature Commun.* **5**, 4281 (2014).
Jurek *et al.*, *J. Appl. Cryst.* **49**, 1048 (2016).

Comparison with experimental data



diamonds: instantaneous model

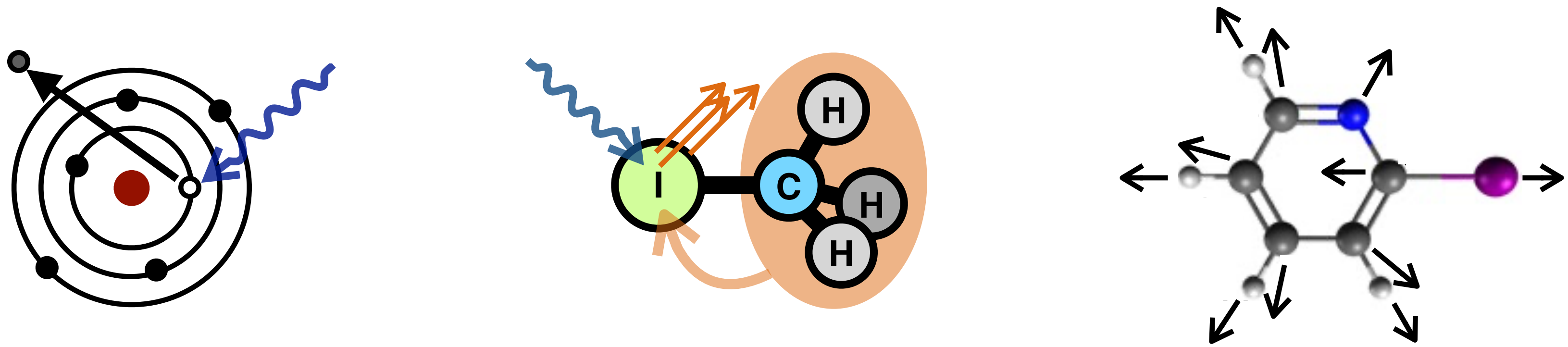
iodopyridine@2.0 keV

European XFEL experiment led by Rebecca Boll and Till Jahnke

> Multi-coincident momentum imaging, including H
> Highest-quality Coulomb explosion imaging with high-repetition rate of EuXFEL
> Quantitative comparison between theory and experiment

Boll *et al.*, *Nat. Phys.* **18**, 423 (2022).

Conclusion



XATOM

XMOLECULE

XMDYN

- Enabling tools to investigate x-ray multiphoton physics of atoms, molecules, and complex systems exposed to high-intensity x-ray pulses
- XFEL–matter interaction: sequential multiphoton multiple ionization
  - Xe: ionization enhanced via resonances and modulated by relativity
  - iodomethane: ultrafast ionization & fragmentation of small molecules
  - iodopyridine: Coulomb explosion imaging of complex systems
- Relativistic effects are important for XFEL-induced dynamics of heavy-atom-containing systems

Collaborations

Experiment team (Xe, CH_3I, and C_5H_4NI)

Kansas State University S. J. Robatjazi, X. Li, D. Rolles, A. Rudenko

DESY, Hamburg B. Erk, C. Bomme, E. Savelyev, J. Correa, C. Passow, N. Rennhack

PTB, Braunschweig B. Rudek

European XFEL R. Boll, T. M. Baumann, A. De Fanis, P. Grychtol, M. Ilchen, K. Kubicek, T. Mazza, J. Montano, V. Music, Y. Ovcharenko, D. E. Rivas, P. Schmidt, R. Wagner, P. Ziolkowski, M. Meyer, T. Jahnke

MPI for Medical Res., Heidelberg L. Foucar, I. Schlichting

Argonne National Lab. Ch. Bostedt, S. Southworth, C. S. Lehmann, B. Krässig, L. Young

UPMC, Paris T. Marchenko, M. Simon

Tohoku University, Sendai K. Ueda

LCLS, SLAC National Accelerator Laboratory K. R. Ferguson, M. Bucher, T. Gorkhover, S. Carron, R. Alonso-Mori, J. E. Koglin, G. J. Williams, S. Boutet, P. Walter

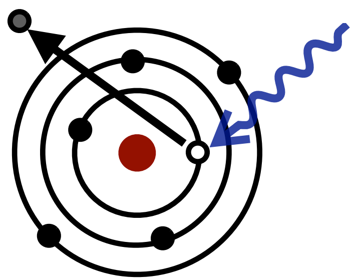
Goethe-Uni., Frankfurt K. Fehre, G. Kastirke, M. S. Schöffler, N. Anders, S. Eckart, R. Dörner, S. Grundmann, A. Hartung, M. Hofmann, C. Janke, M. Kircher, M. Kunitski, N. Melzer, G. Nalin, A. Pier, J. Rist, L. Ph. H. Schmidt, J. Siebert, N. Strenger, D. Trabert, F. Trinter, I. Vera-Ferez, M. Weller

MPI for Nuclear Physics, Heidelberg S. Meister

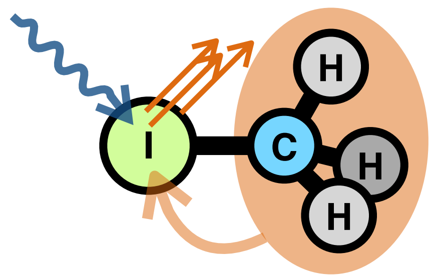
Theory team

CFEL, DESY M. M. Abdullah (now DESY), K. Hanasaki (now UC Riverside), Y. Hao (now USTB Beijing), R. Jin (now MPIK), J. Schäfer (now Heliatek), K. Toyota (now Amada), O. Vendrell (now Uni. Heidelberg), B. Richard, L. Inhester, Z. Jurek, S.-K. Son, R. Santra

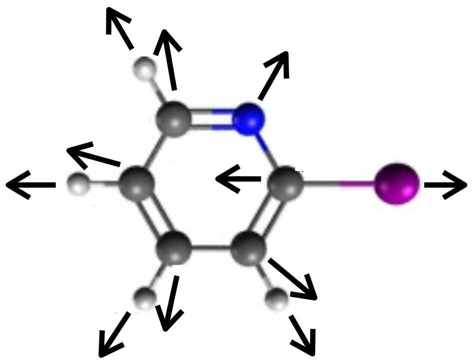
Conclusion with QR codes



XATOM



XMOLECULE



XMDYN

Thank you for your attention!