What happens to atoms and molecules during XFEL pulses?

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Center for Free-Electron Laser Science, DESY, Hamburg, Germany

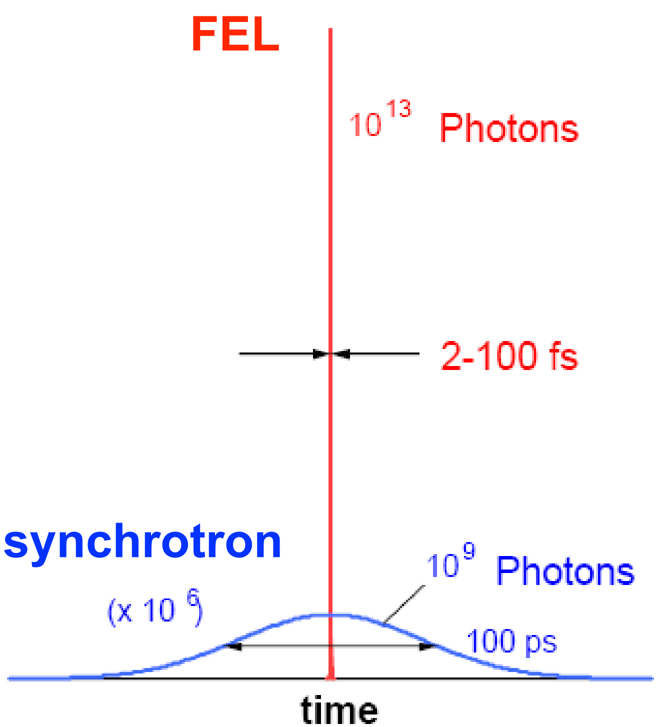
Physics and Photon Science Colloquium, GIST
Gwangju, South Korea, October 18, 2016

Overview

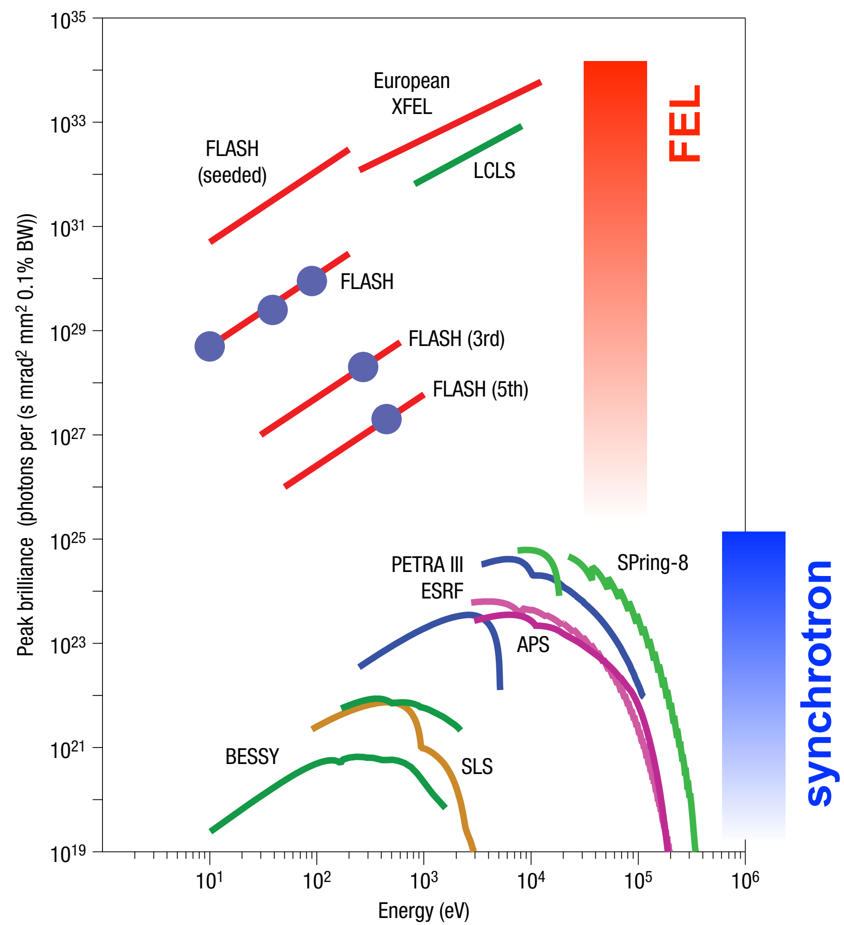
- Introduction to XFEL science
- Atom: x-ray multiphoton multiple ionization dynamics of Xe
- Molecule: x-ray ionization and fragmentation dynamics of CH_3I
- Toward complex systems
- Summary

XFEL: X-ray free-electron laser

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



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



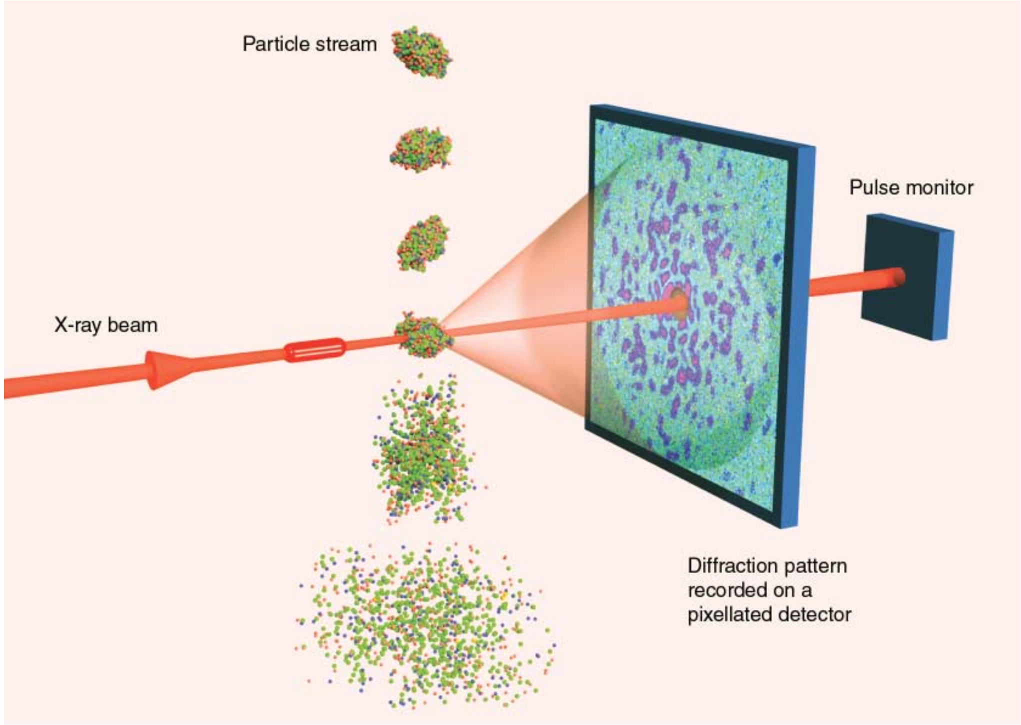
Ackermann *et al.*, *Nature Photon.* **1**, 336 (2007).

Where are XFELs?

- FLASH at DESY, Germany (2004)
- LCLS at SLAC, USA (2009)
- SACLA at RIKEN Harima, Japan (2011)
- PAL XFEL at Pohang, Korea (2016)
- European XFEL, Germany (2017)

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



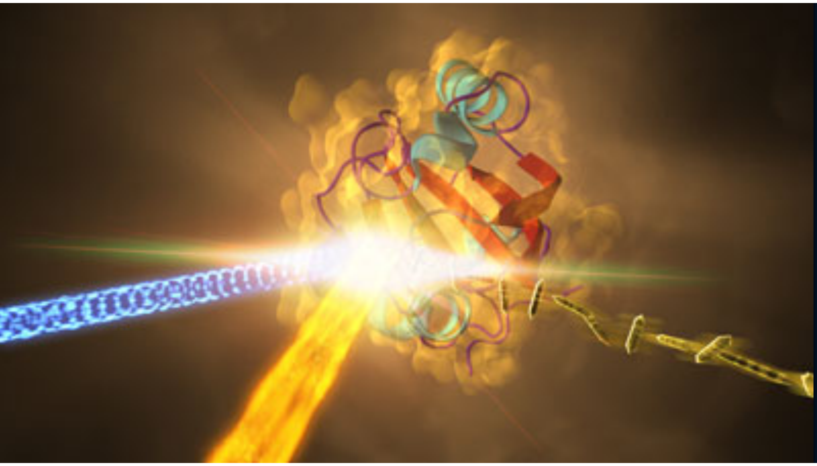
Gaffney & Chapman, *Science* **316**, 1444 (2007).

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

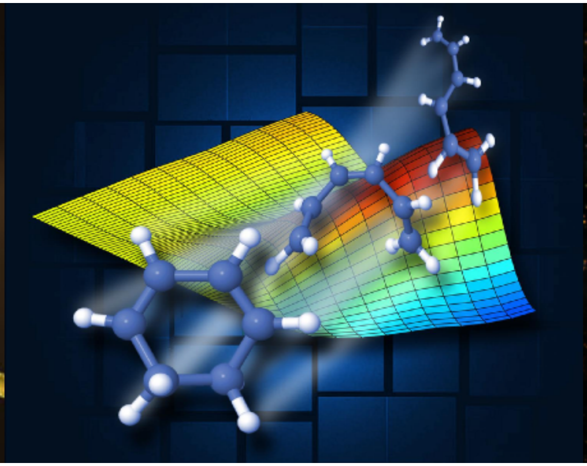
XFEL science

- Imaging of biomolecules for biology and life science
- Ultrafast dynamics for chemistry and material science
- Matter in extreme states for astrophysics and energy science

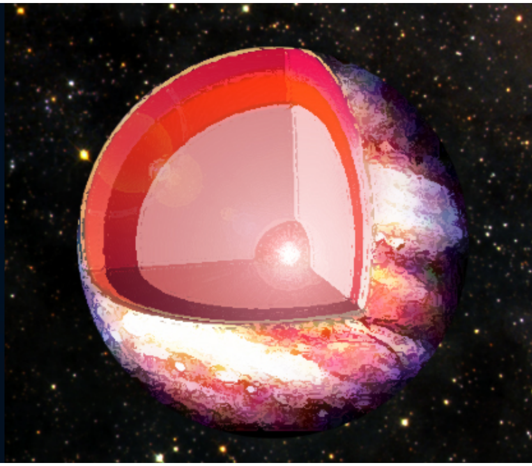
➔ XFEL applications waiting for increased theoretical support



SLAC



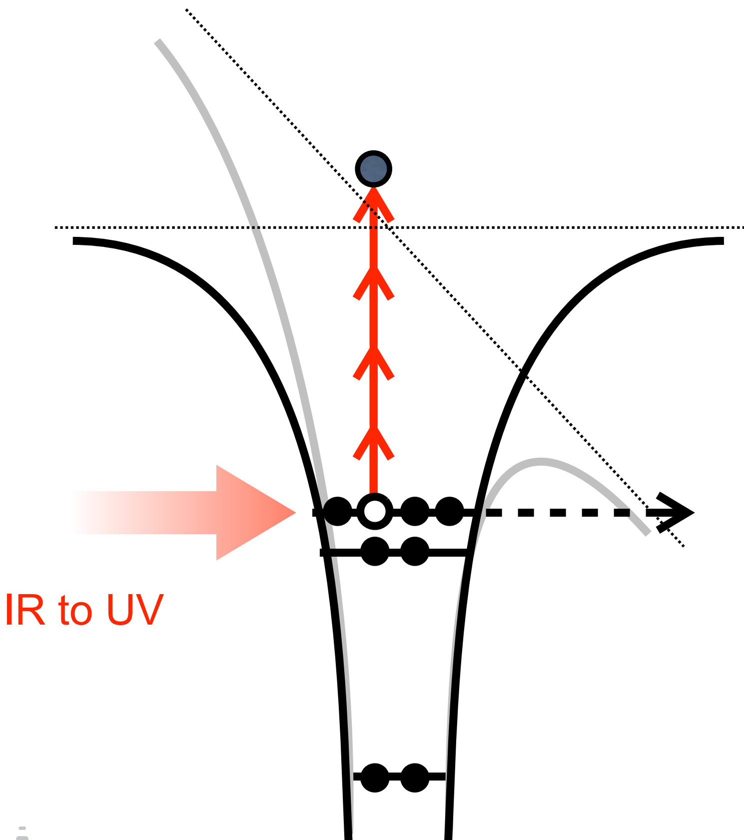
SLAC



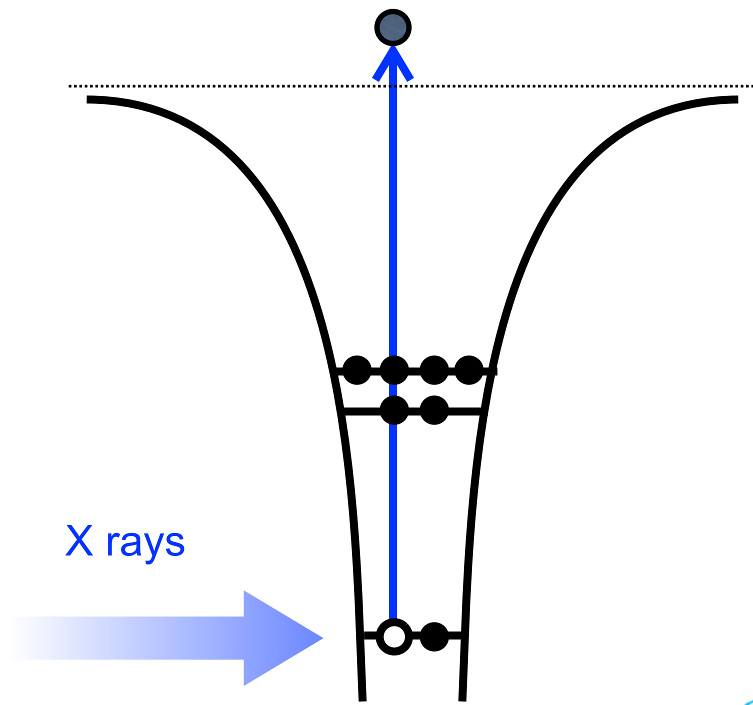
LBL

What differences from optical strong-field?

> Optical strong-field regime
- tunneling or multiphoton processes
- valence-electron ionization



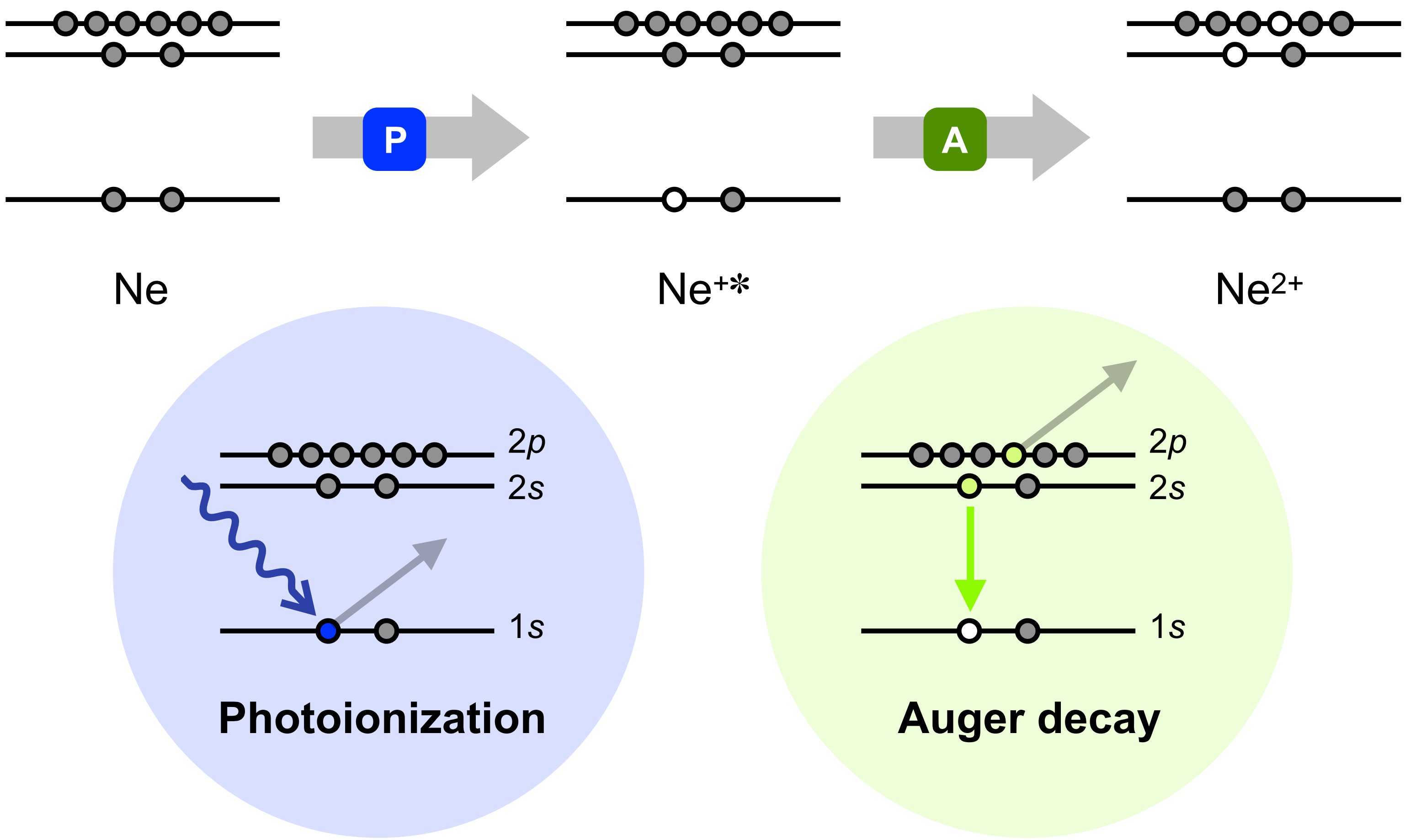
> Intense X-ray regime
- mainly one-photon processes
- core-electron ionization and relaxation
- multiphoton multiple ionization via a sequence of one-photon processes



CFEL SCIENCE

DESY

X-ray absorption (single photon)

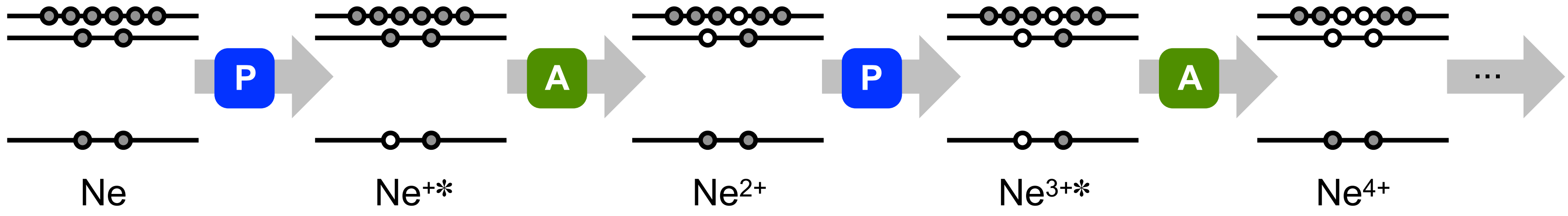


X-ray multiphoton absorption

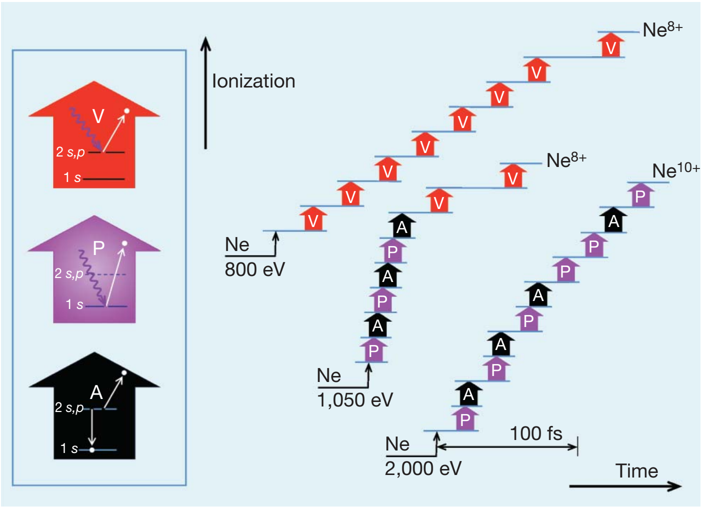
- Direct multiphoton absorption cross section is too small

Doumy *et al.*, *Phys. Rev. Lett.* **106**, 083002 (2011).

- Sequential multiphoton absorption is dominant

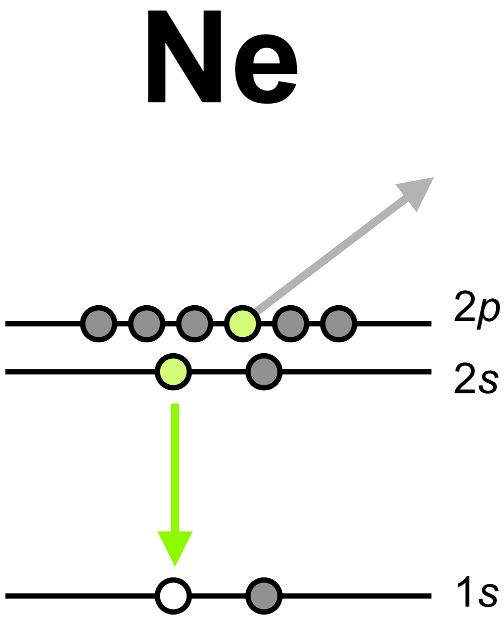


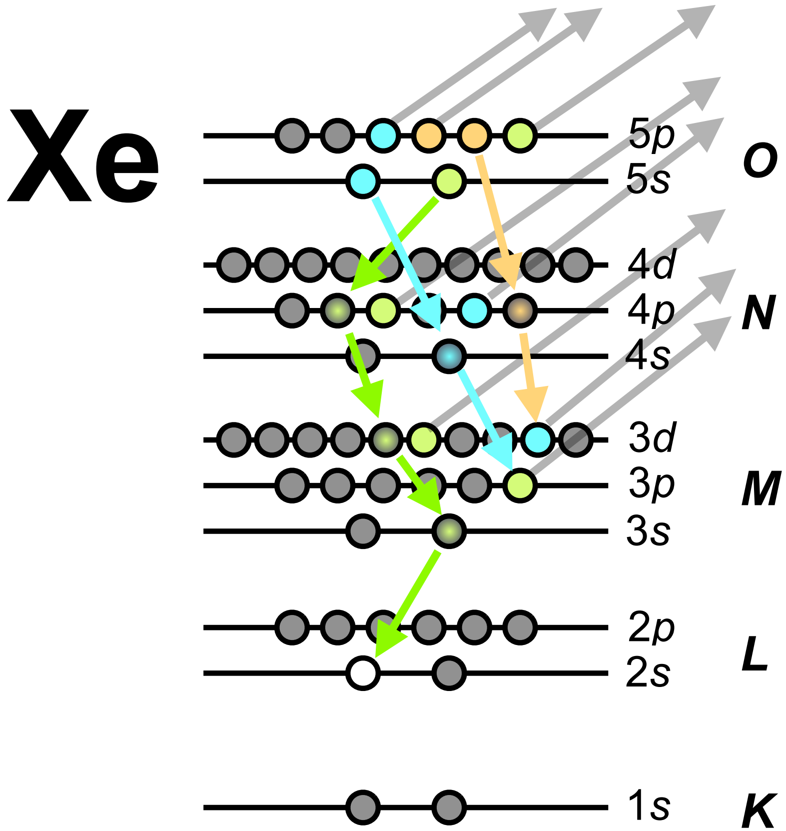
Sequential multiphoton multiple ionization dynamics



Young *et al.*, *Nature* **466**, 56 (2010).

Complex inner-shell decay cascade





Multiphoton absorption after/during decay cascade

- More than 20 million multiple-hole configurations
- More than 2 billion x-ray-induced processes

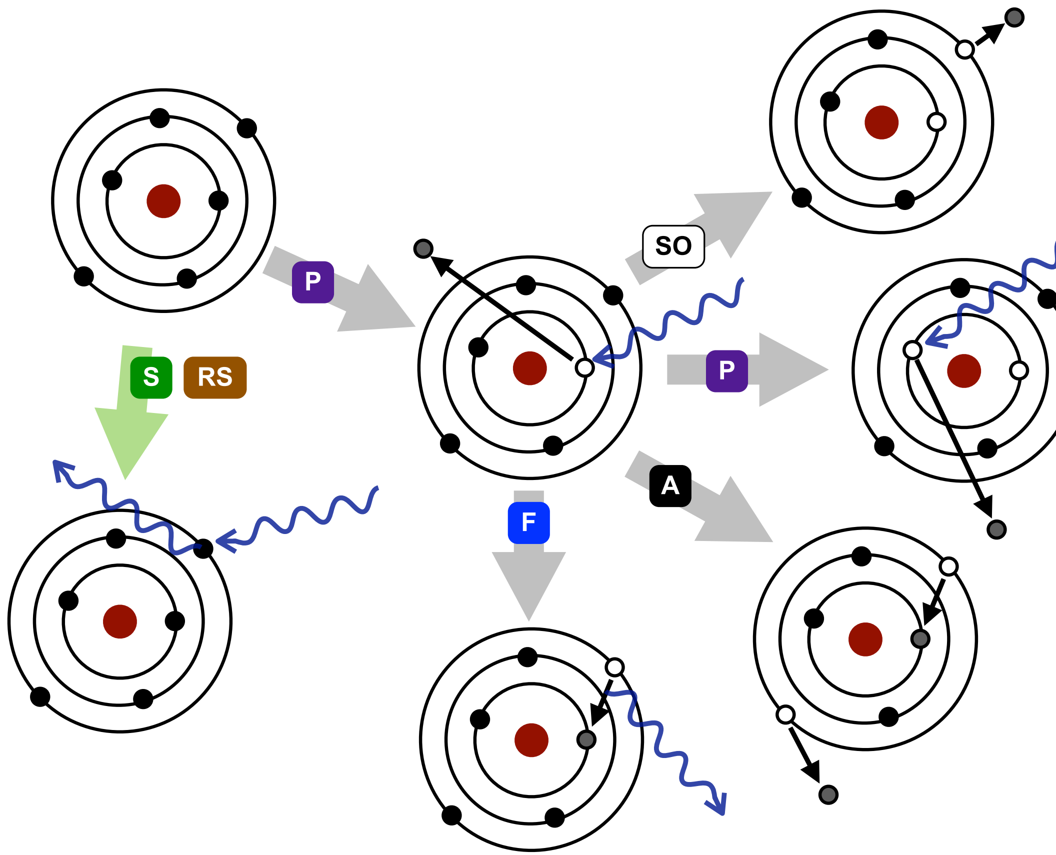
How to treat x-ray multiphoton dynamics?

- No standard quantum chemistry code available

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

XATOM

- XATOM: describes dynamical behaviors of atoms interacting with XFEL pulses
- X-ray-induced atomic processes for any given element and configuration
- Sequential ionization model has been tested by a series of atomic XFEL experiments: Ne, Ar, Kr, Xe, …



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

XATOM: Theoretical and numerical details

- Hartree-Fock-Slater method

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \int d^3r' \, \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{3}{2}\left\{\frac{3}{\pi}\rho(\mathbf{r})\right\}^{1/3}\right]\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

- Numerical grid: non-uniform for bound states and uniform for continuum

$$\psi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r} Y_{lm}(\theta,\varphi)$$

- Calculate all cross sections and rates of x-ray-induced processes based on the perturbation theory

Photoionization cross section

$$\sigma_{\mathrm{P}}(i,\omega) = \frac{4}{3}\alpha\pi^2\omega N_i \sum_{l_j=|l_i-1|}^{l_i+1} \frac{l_>}{2l_i+1} \left|\langle u_{n_i l_i}(r)|r|u_{\varepsilon l_j}(r)\rangle\right|^2$$

Fluorescence rate

$$\Gamma_{\mathrm{F}}(i,j) = \frac{4}{3}\alpha^3(I_i - I_j)^3 \frac{N_i^{\mathrm{H}} N_j}{4l_j+2} \cdot \frac{l_>}{2l_i+1} \left|\langle u_{n_i l_i}(r)|r|u_{n_j l_j}(r)\rangle\right|^2$$

Auger rate

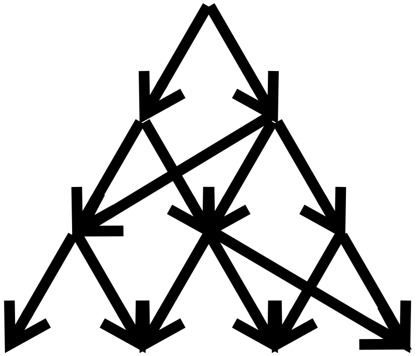
$$\Gamma_{\mathrm{A}}(i,jj') = \pi \frac{N_i^{\mathrm{H}} N_{jj'}}{2l_i+1} \sum_{L=|l_j-l_{j'}|}^{l_j+l_{j'}} \sum_{S=0}^{1} \sum_{l_{i'}} (2L+1)(2S+1)|M_{LS}(j,j',i,i')|^2$$

XATOM: Coupled rate equations

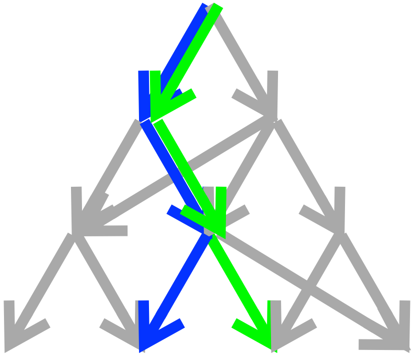
- Electronic structure, σ and Γ: calculated for every single configuration
- Solve coupled rate equations to simulate ionization dynamics

$$\frac{d}{dt}P_I(t) = \sum_{I' \neq I}^{\text{all config.}} \left[\Gamma_{I' \to I} P_{I'}(t) - \Gamma_{I \to I'} P_I(t)\right]$$

- Tremendously large coupled rate equations (~millions configurations)
  ➔ solved by Monte Carlo approach



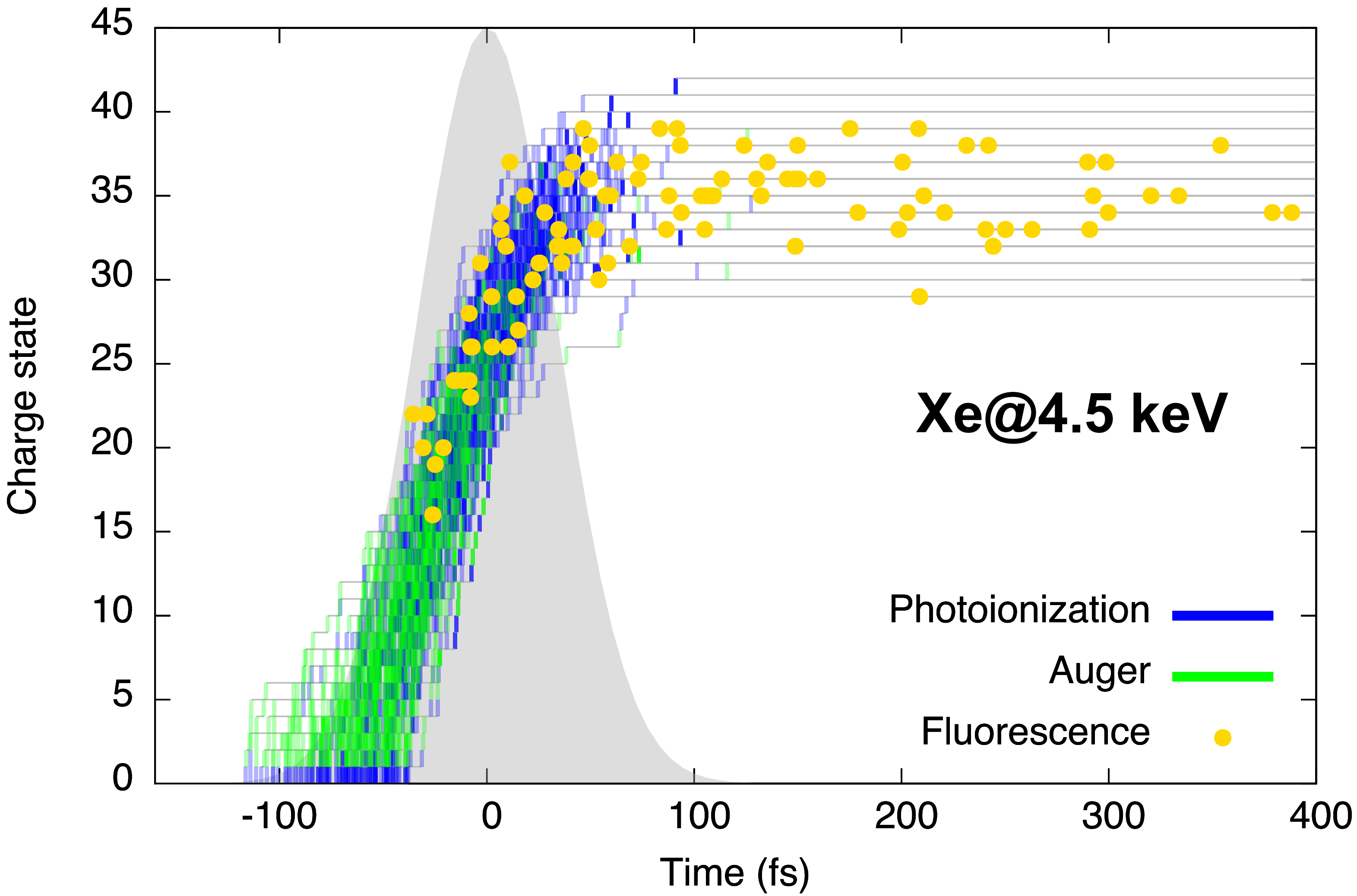
direct solution



Monte Carlo approach

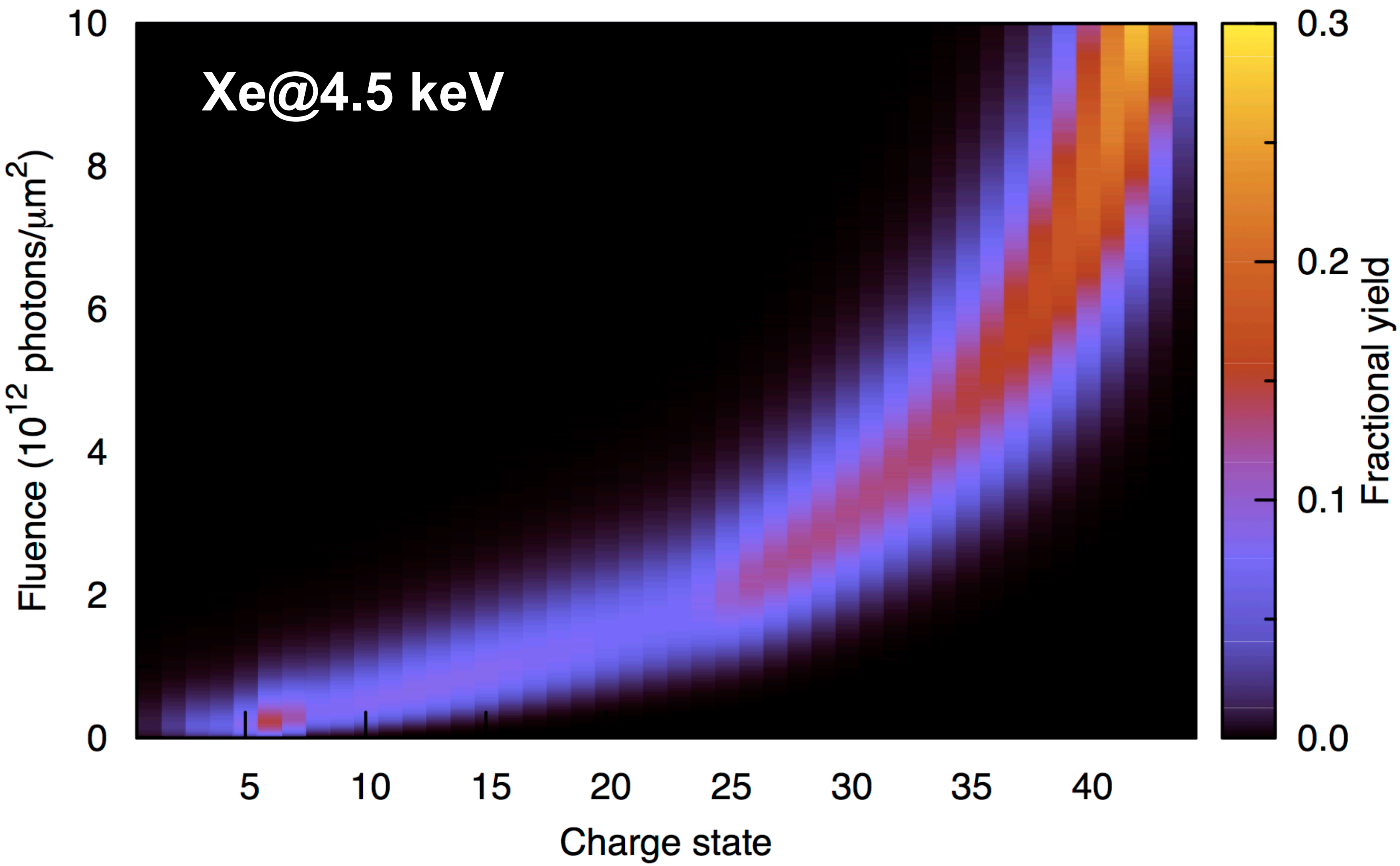
Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

X-ray multiphoton ionization dynamics



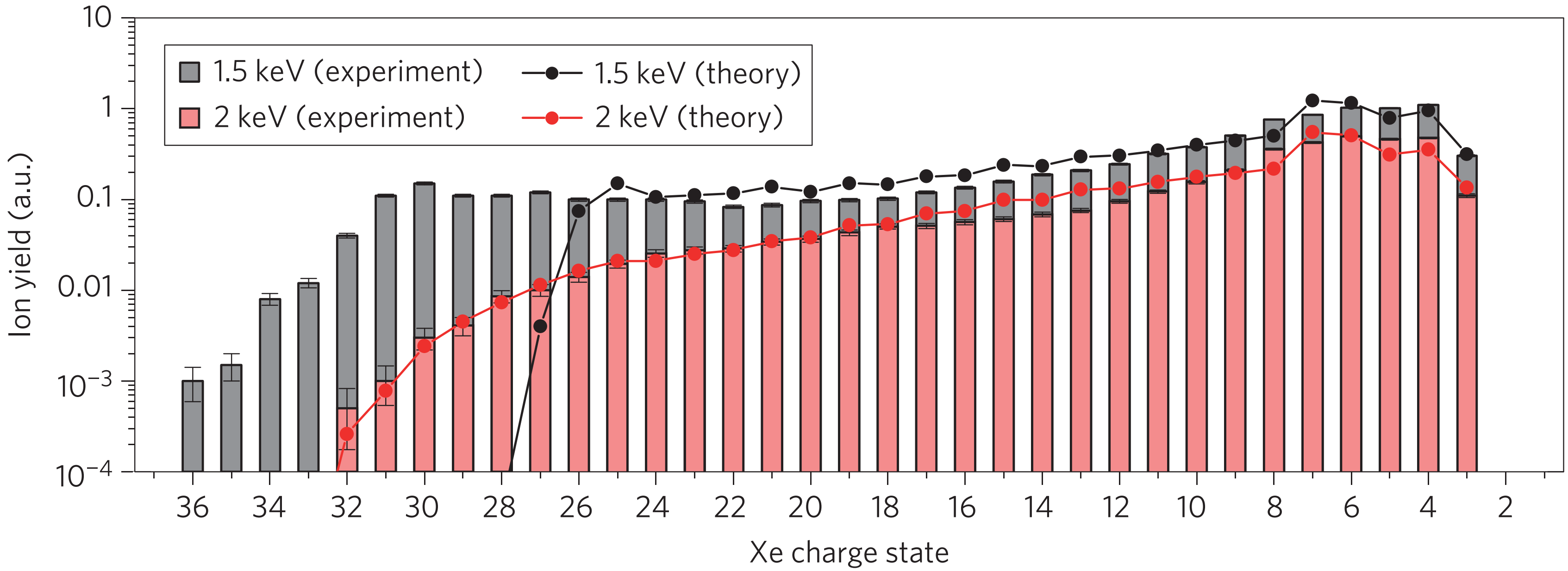
Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

Charge-state distributions of Xe



Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

Comparison with LCLS experiment



LCLS experiment

Daniel Rolles
at KSU

Artem Rudenko
at KSU

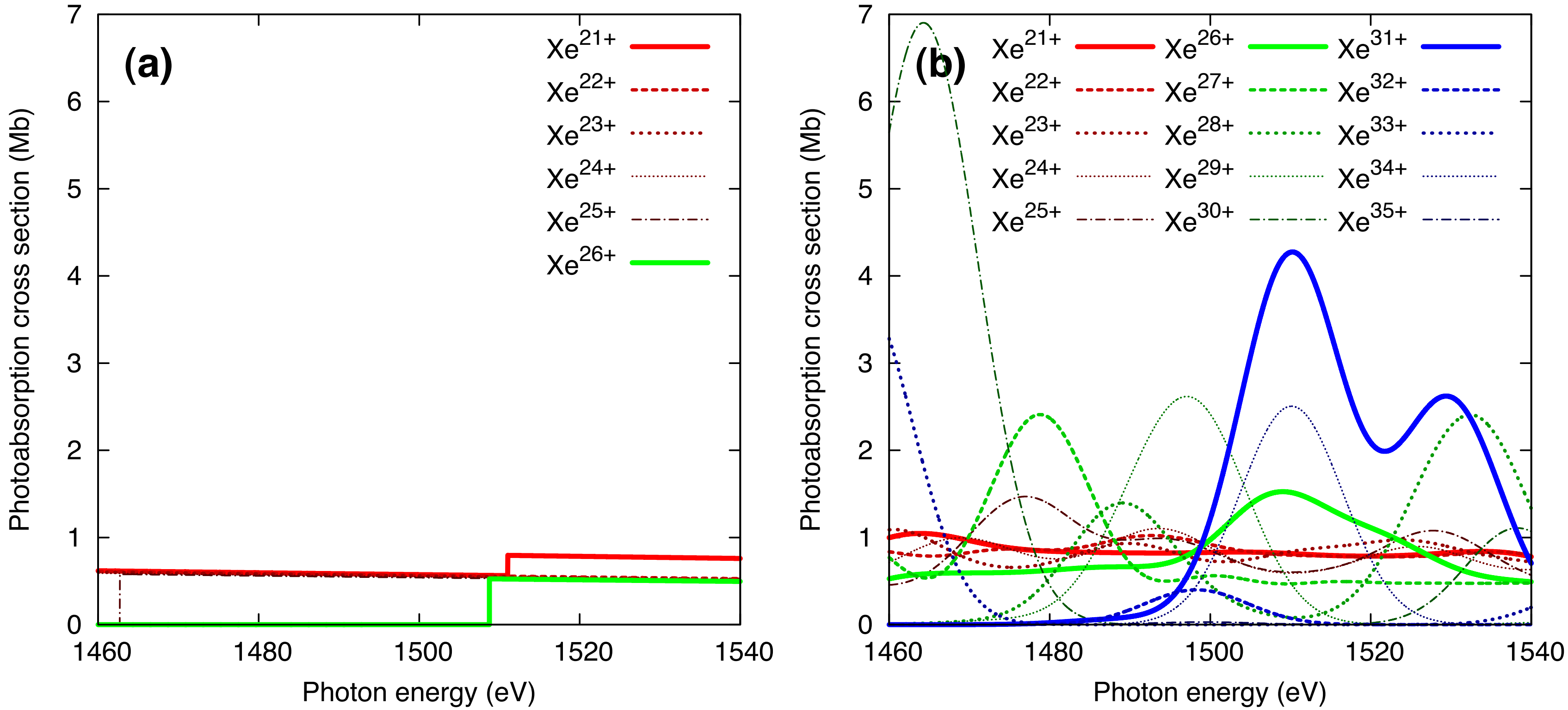
Benedikt Rudek
at PTB

Rudek *et al.*, *Nature Photon.* **6**, 858 (2012).

- Xe *M*-shell ionization
- 2 keV: excellent agreement between theory and experiment
- 1.5 keV: further ionization via resonance

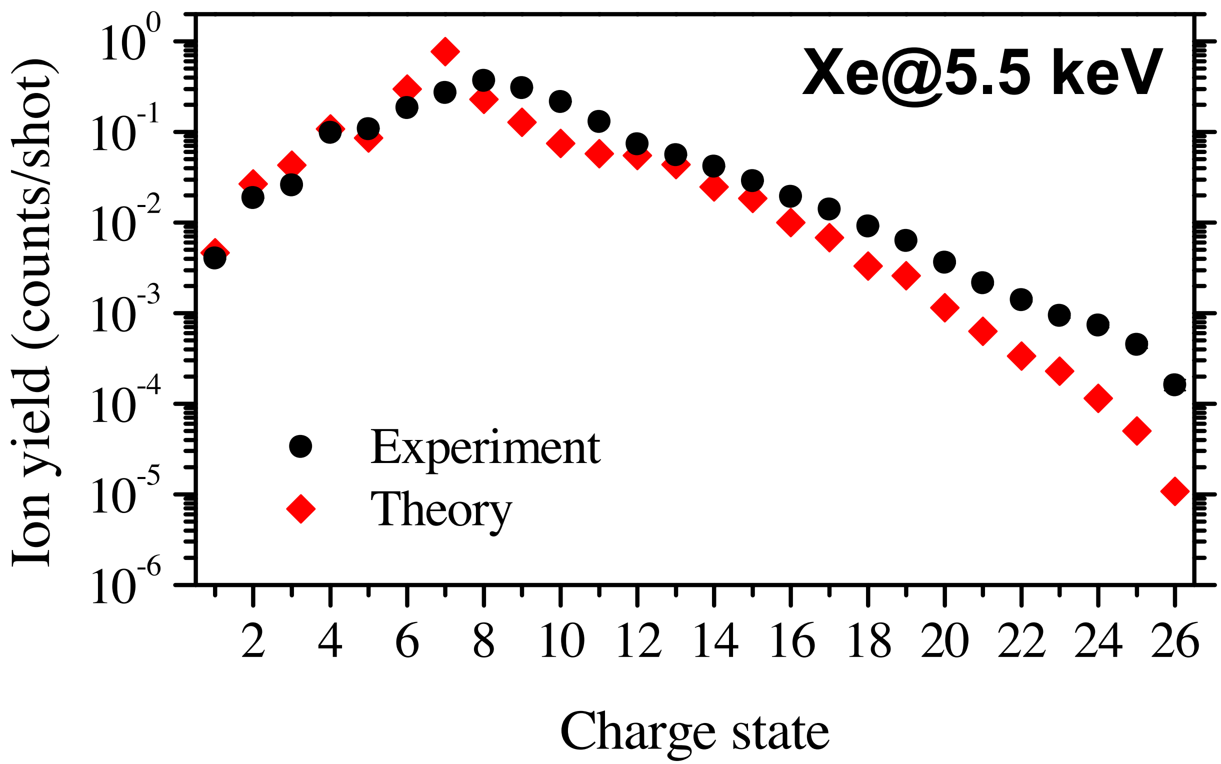
Ultra-efficient ionization by XFEL

- REXMI: Resonance-Enabled X-ray Multiple Ionization
- Broad bandwidth (~15 eV): resonances for many charge states



Rudek *et al.*, *Nature Photon.* **6**, 858 (2012).

Comparison with SACLA experiment



SACLA experiment

Kiyoshi Ueda
at Tohoku Univ.

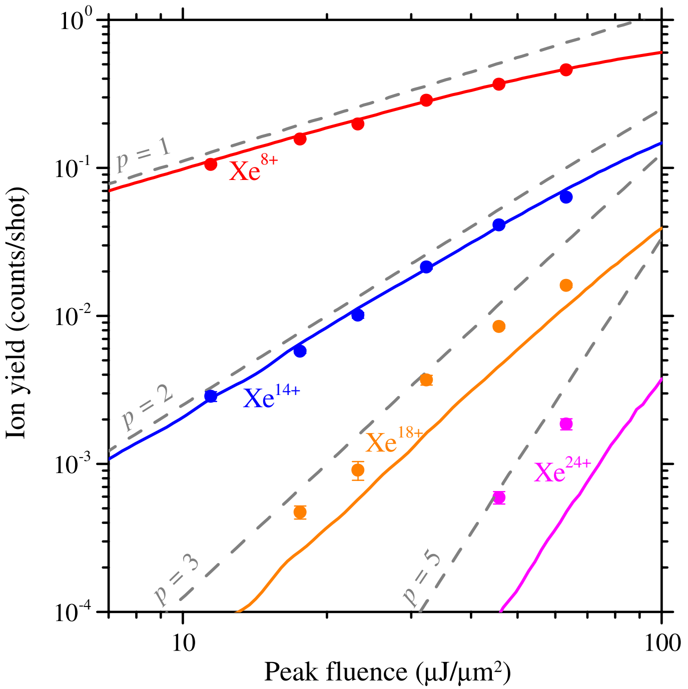
- Hironobu Fukuzawa
- Koji Motomura

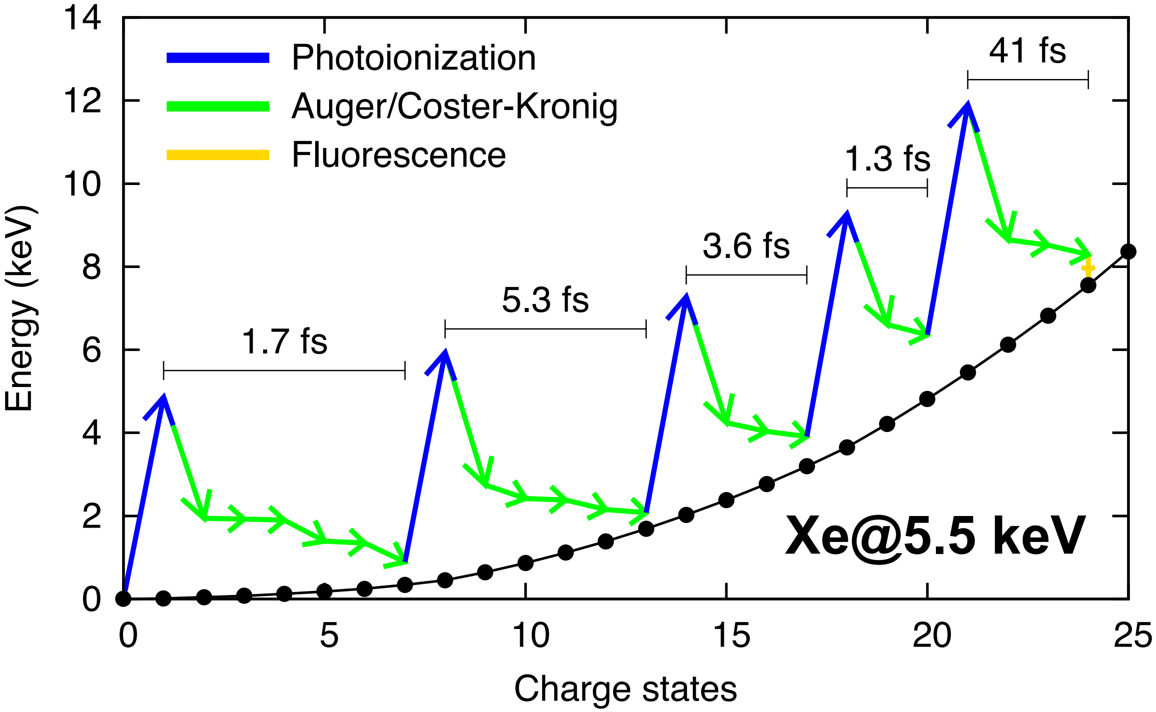
Fukuzawa *et al.*, *Phys. Rev. Lett.* **110**, 173005 (2013).

- Xe *L*-shell ionization: good agreement
- underestimation in theory: lack of relativity, shake-off, (and resonance)

Ionization dynamics described by theory

- To reach Xe^{24+}: 5 photons absorbed, 24 electrons ejected





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

XMOLECULE

- Challenges for molecular simulations at high x-ray intensity
  - coupled ionization and nuclear dynamics in the same time scales
  - formidable task: e.g. CH_3I ~ 200 trillion rate eqs at single geometry
- XMOLECULE: x-ray and molecular physics toolkit
  - quantum electrons, classical nuclei
  - efficient electronic structure calculation combined with XATOM
  - Monte Carlo on the fly

***Ab initio* ionization and fragmentation dynamics induced by intense XFEL pulses**

Hao, Inhester, Hanasaki, Son & Santra, *Struc. Dyn.* **2**, 041707 (2015).
Inhester, Hanasaki, Hao, Son & Santra, *Phys. Rev. A* **94**, 023422 (2016).

CFEL SCIENCE

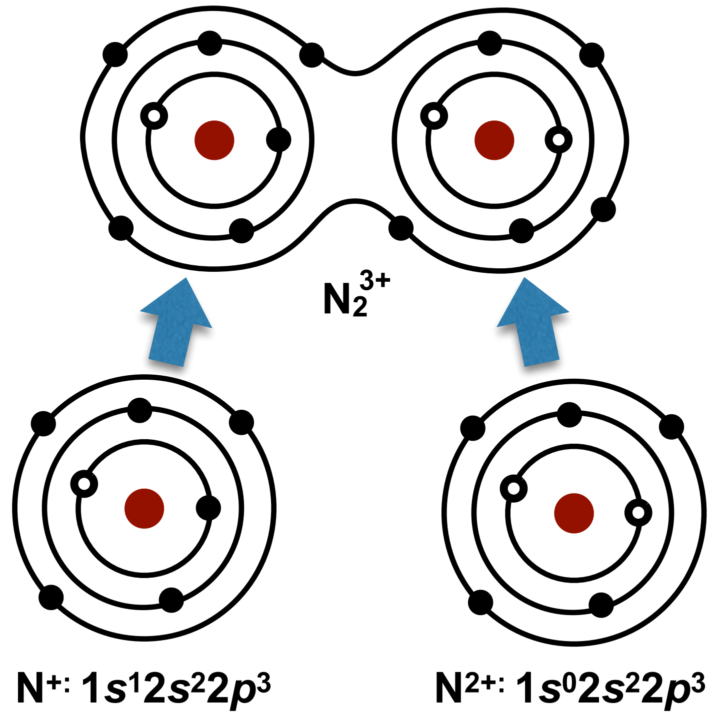
DESY

XMOLECULE: Numerical details

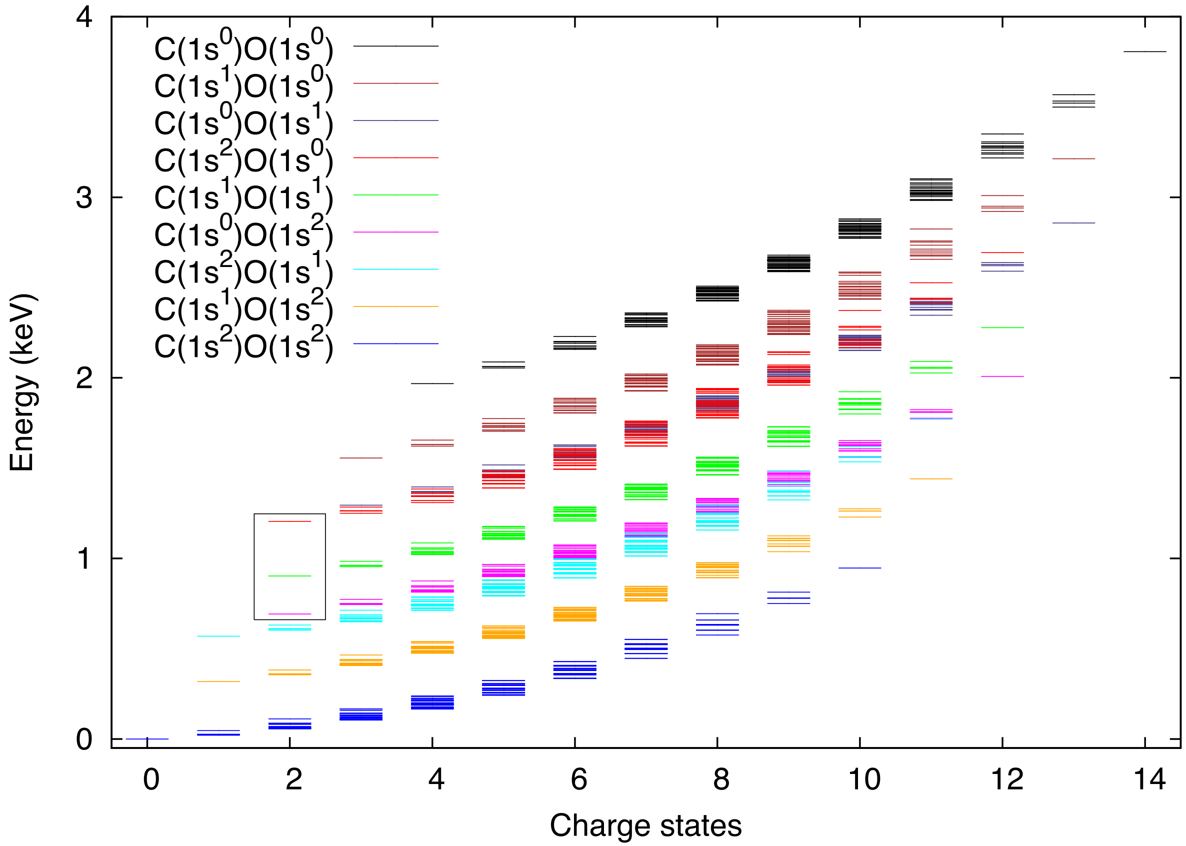
- Hartree-Fock-Slater method
- LCAO-MO for bound states

$$\psi_i(\mathbf{r}) = \sum_{\mu} C_{\mu i} \phi_{\mu}(\mathbf{r})$$

  - Core-hole-adapted numerical atomic orbitals calculated by XATOM
  - Good treatment for molecular core-hole states
- Molecular continuum approximated by atomic continuum
- Gradients calculated on the fly
- Various numerical techniques employed
  - multicenter integration on a molecular grid built from atomic grids
  - multicenter expansion and multipole expansion in direct Coulomb interaction
  - maximum overlap method to prevent variational collapse



Various multiple-hole states of CO

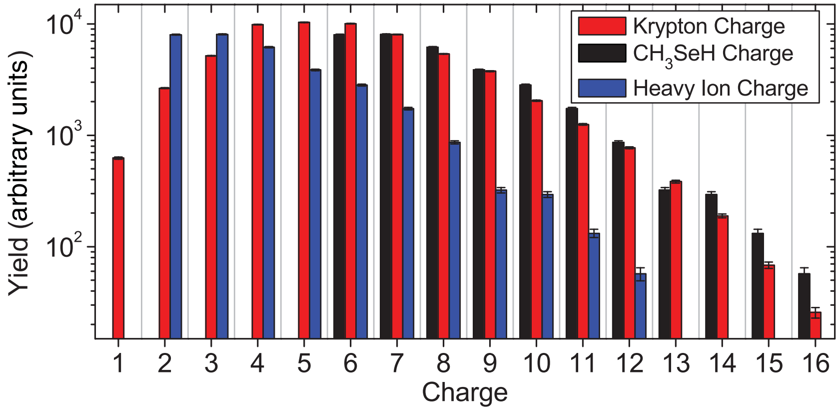


R=1.128Å

Hao, Inhester, Hanasaki, Son & Santra, *Struc. Dyn.* **2**, 041707 (2015)

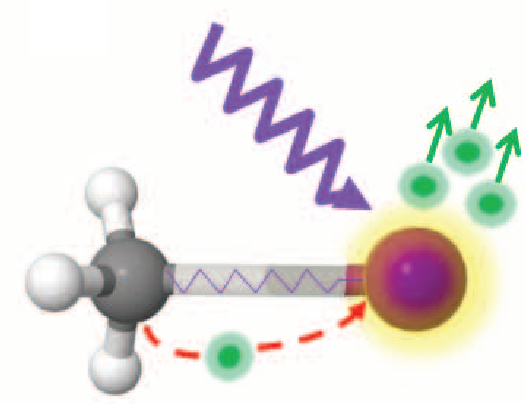
All possible multiple-hole configurations (*N*=2187) formed by x-ray multiphoton ionization

Earlier works on molecules at low intensity



Total charge: CH_3SeH vs. Kr

Erk *et al.*, *PRL* **110**, 053003 (2013).



CH_3I: charge rearrangement as a function of bond distance

Erk *et al., Science* **345**, 288 (2014).

Total charge of molecule is similar to atomic charge.
Heavy atom charges are reduced after charge rearrangement.

⬇

Still valid for high x-ray intensity?

Iodomethane at high x-ray intensity

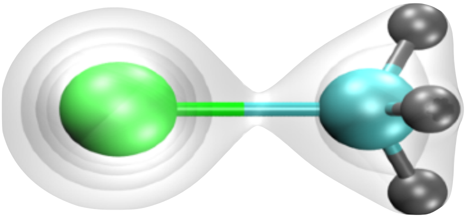
- New experimental setup:
  LCLS CXI using nano-focus
  → new realm of intensity
  approaching ~10^{20} W/cm^2
- Selective ionization on heavy atom

LCLS experiment

Daniel Rolles
at KSU

Artem Rudenko
at KSU

CH_3I @ 8.3 keV



σ(I)~50 kbarn

σ(C)~80 barn

σ(H)~8 mbarn

- X-ray multiphoton ionization occurs at high intensity
- Charge imbalance induces charge rearrangement
- Coulomb explosion after/during ionization & charge rearrangement

Collaboration of XFEL experiment

Experiment team

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

DESY, Hamburg B. Erk, R. Boll, C. Bomme, E. Savelyev

PTB, Braunschweig B. Rudek

MPI for Medical Research, Heidelberg L. Foucar

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

UPMC, Paris T. Marchenko, M. Simon

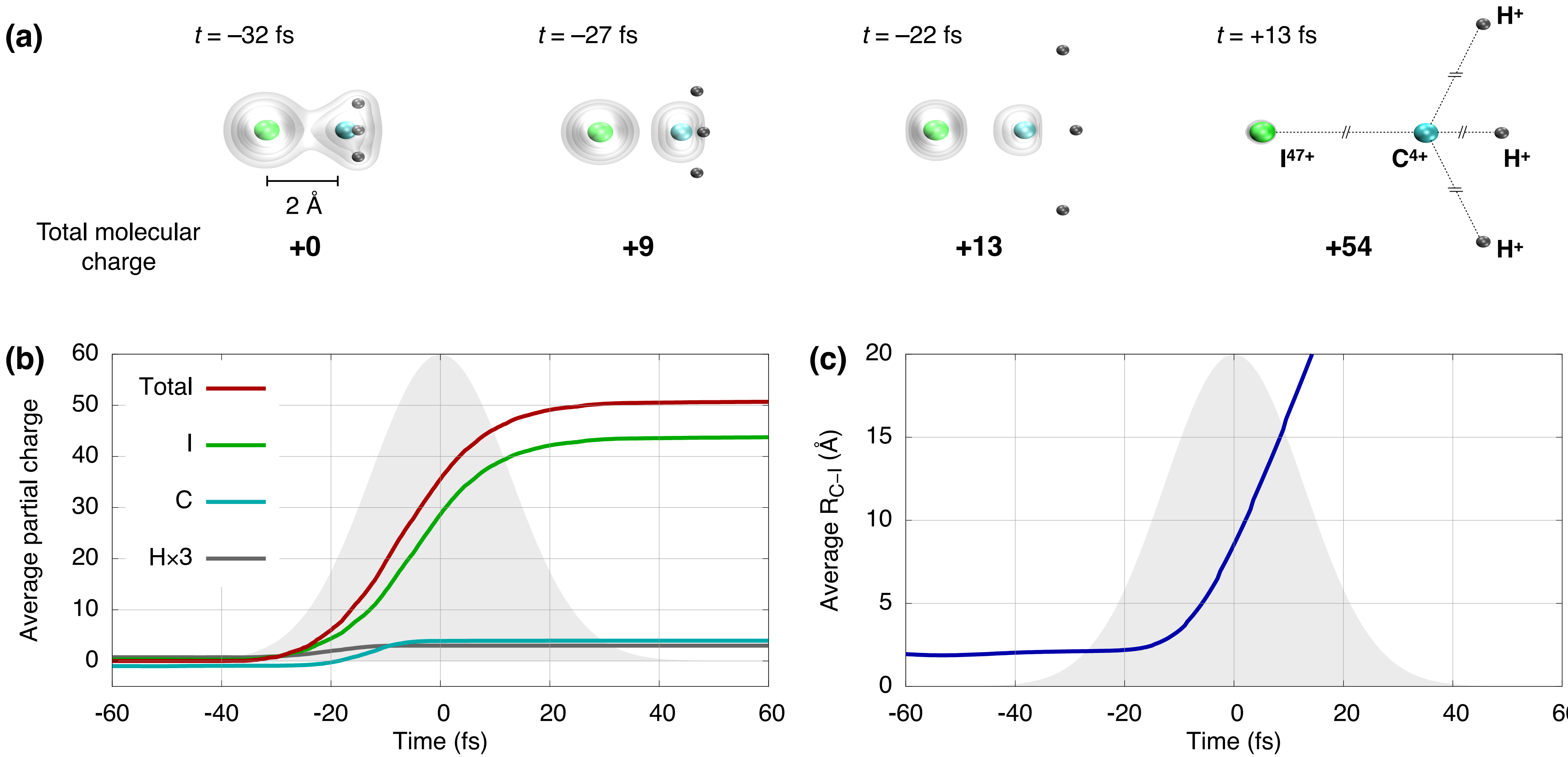
Tohoku University, Sendai K. Ueda

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

Theory team

CFEL, DESY L. Inhester, K. Hanasaki, K. Toyota, Y. Hao, O. Vendrell, S.-K. Son, R. Santra

Capturing ultrafast dynamics



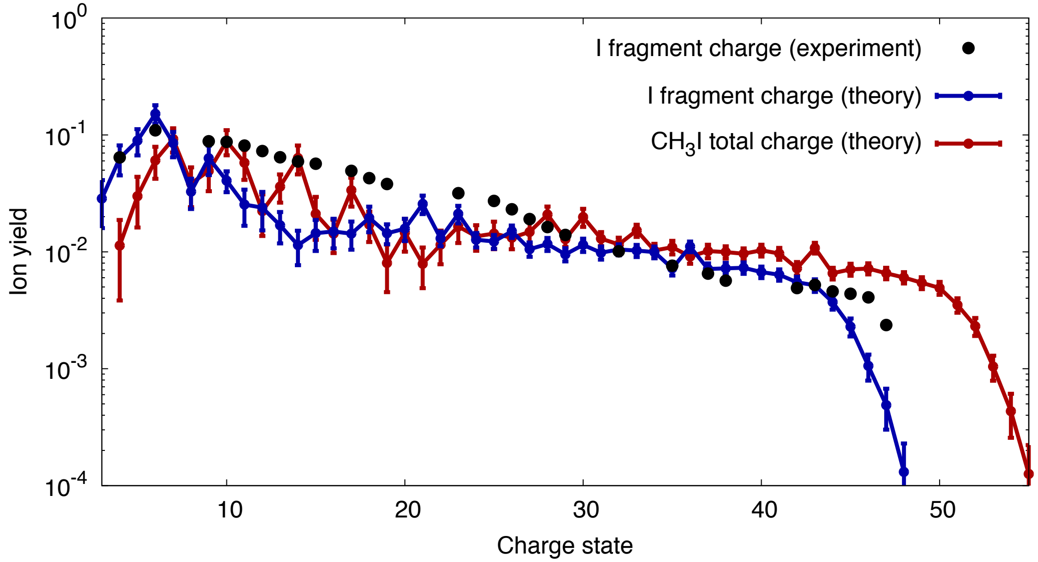
ionization & charge rearrangement dynamics

nuclear dynamics

Rudenko *et al.*, submitted.

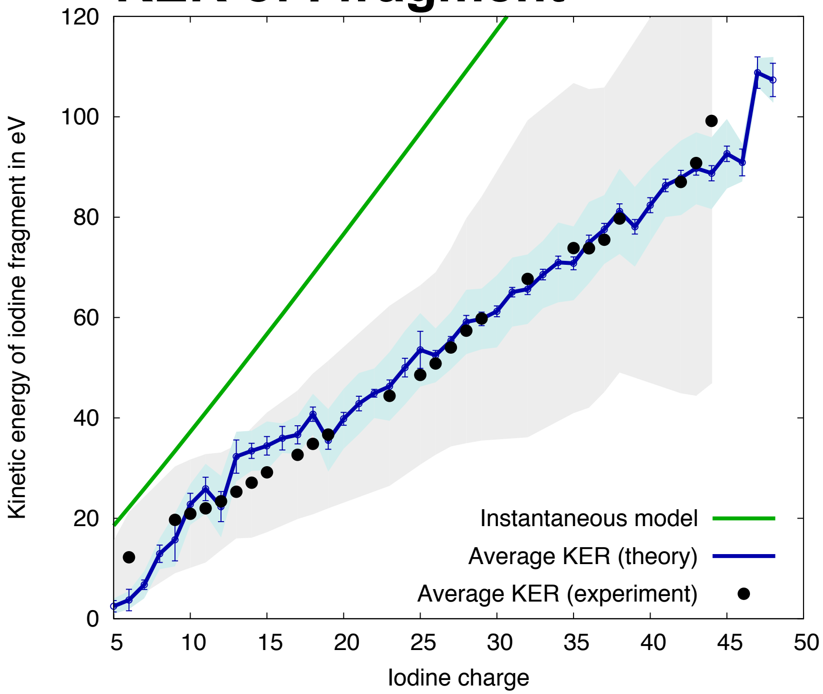
Comparison of CSD and KER

CSD of I and CH_3I



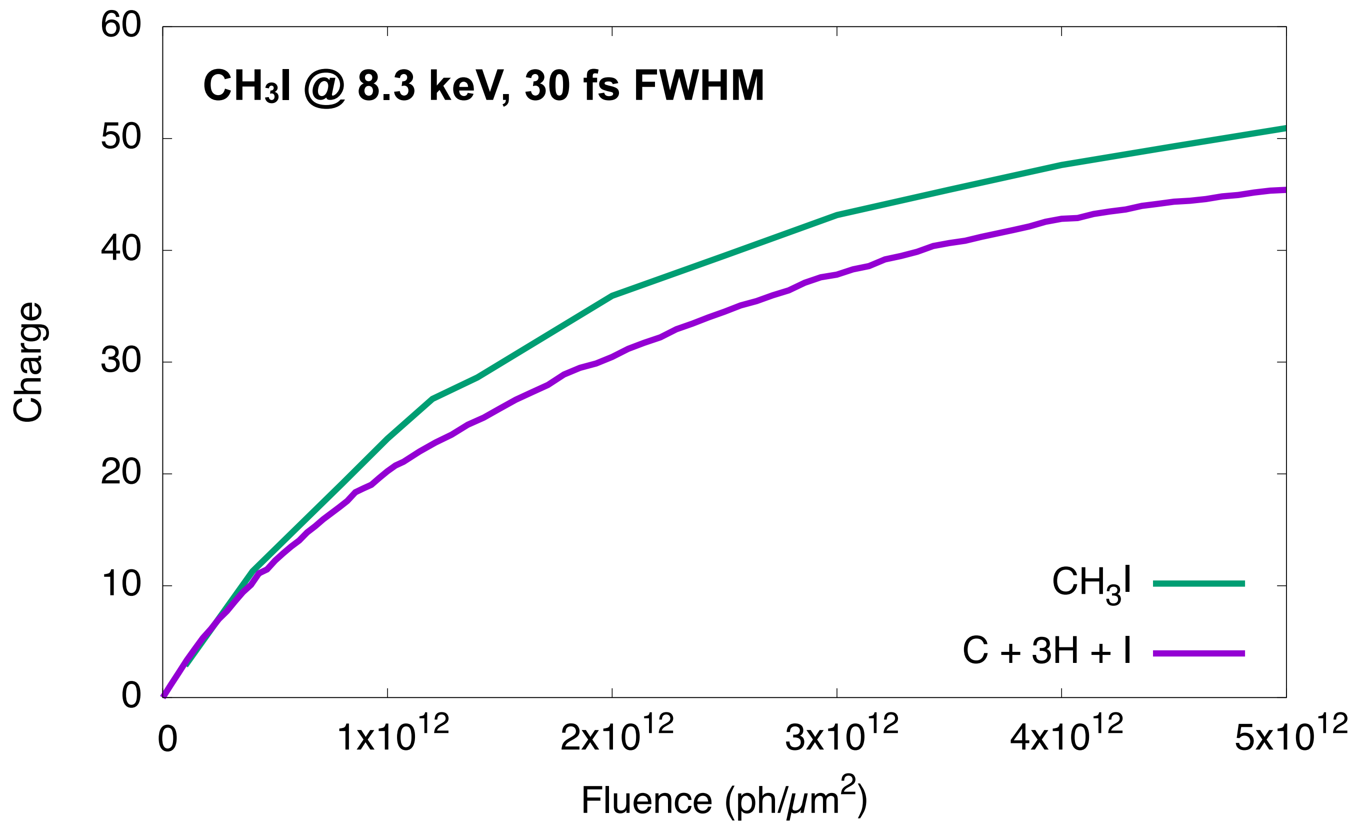
Rudenko *et al.*, to be submitted.

KER of I fragment



- Capturing ultrafast ionization and fragmentation dynamics
  - CSD (charge-state distribution): direct outcome of ionization dynamics
  - KER (kinetic energy release): molecular information when it breaks apart, influenced by detailed dynamical behaviors

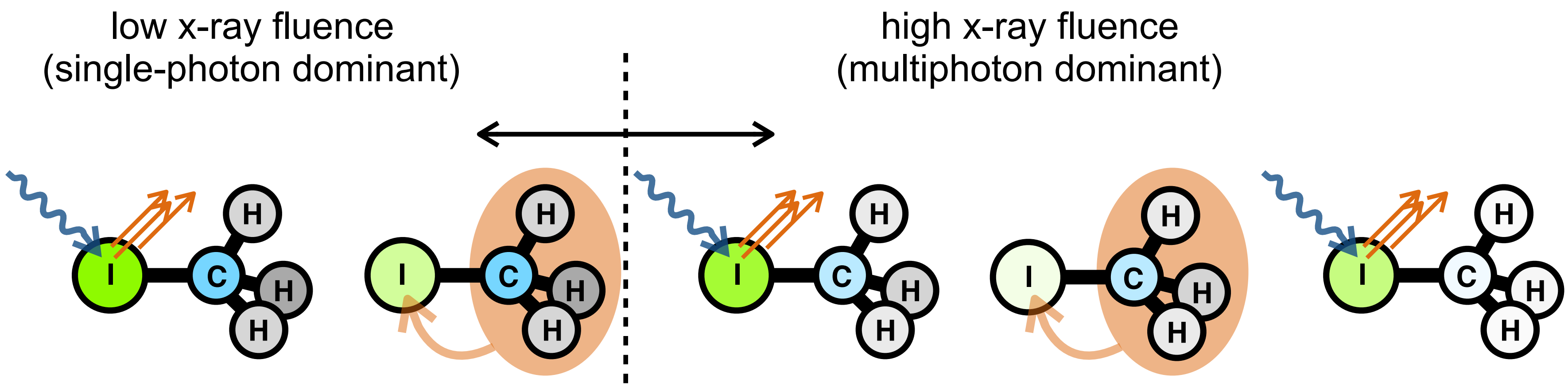
Molecular ionization enhancement



molecular charge > ∑(atomic charges): experimentally confirmed

Rudenko *et al.*, submitted.

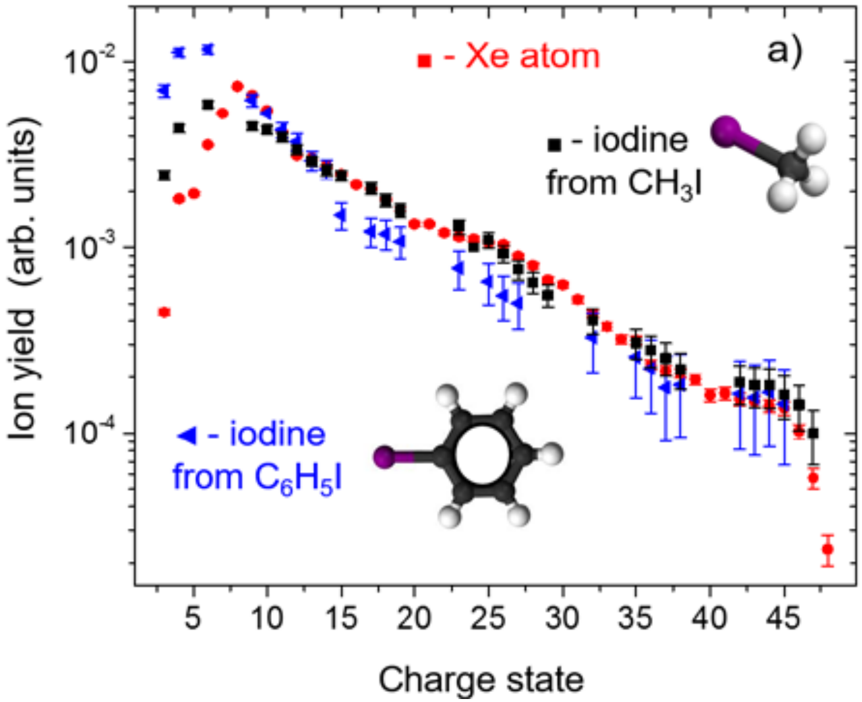
Ionization enhanced by charge rearrangement

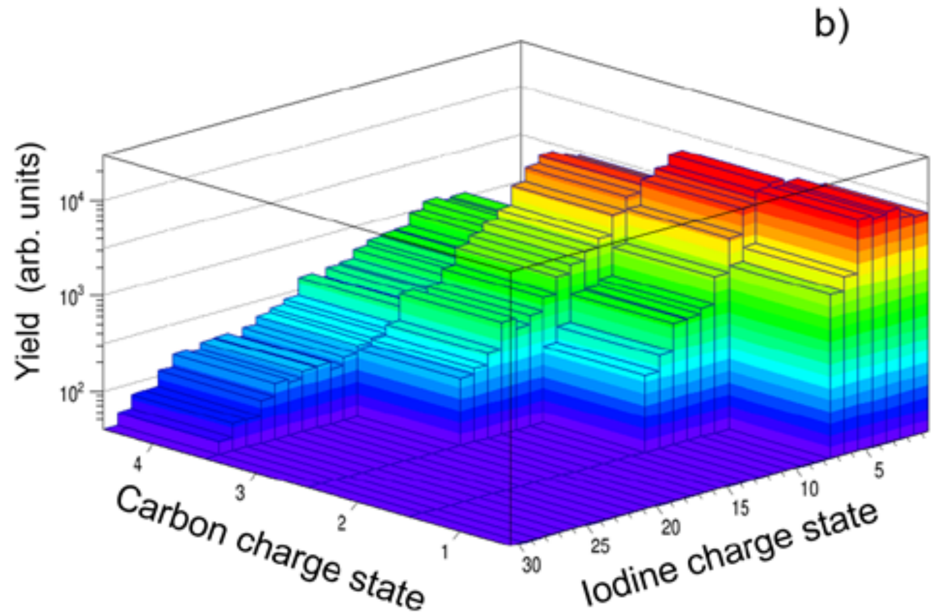


- Electrons from light atoms become available for further ionization on heavy atoms after charge rearrangement.
- CREXIM: Charge-Rearrangement-Enhanced X-ray Ionization of Molecules
- Impact on molecular imaging: not reducing partial charges of heavy atoms due to charge rearrangement, but inducing more ionization overall

Rudenko *et al.*, submitted.

The bigger molecule, the larger effect

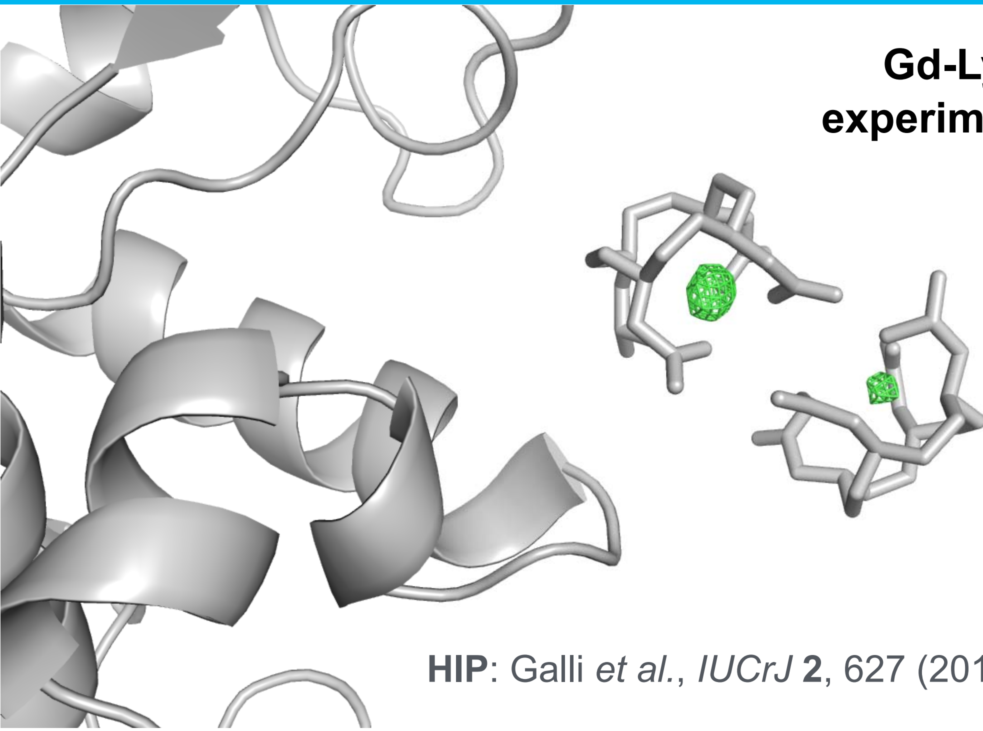




- Coincidence measurement at intermediate intensity: higher iodine charge always along with highest carbon charge
- Estimated molecular charge: Xe^{48+}, CH_3I^{54+}, and $C_6H_5I^{>54+}$

Rudenko *et al.*, submitted.

Application: x-ray molecular imaging

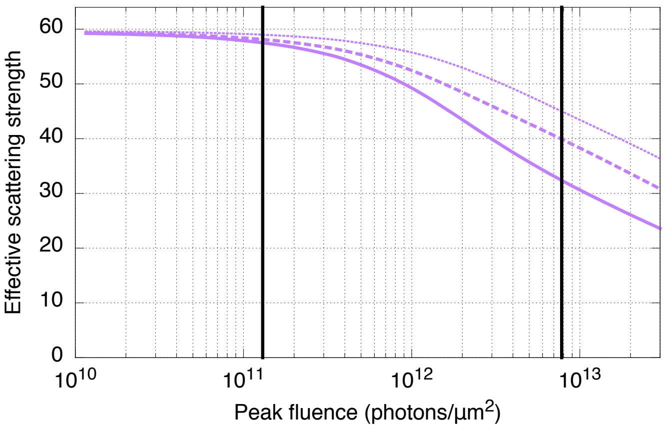


Gd-Lysozyme experiment at LCLS

HIP: Galli *et al.*, *IUCrJ* **2**, 627 (2015).

Henry Chapman at CFEL

Lorenzo Galli at CFEL



- Another bottleneck of x-ray crystallography: **phasing**
- Proposals of novel phasing methods: utilizing selective ionization of heavy atoms at high x-ray intensity

HI-MAD: Son *et al.*, *PRL* **107**, 218102 (2011).
HI-RIP: Galli *et al.*, *J. Synch. Rad.* **22**, 249 (2015).

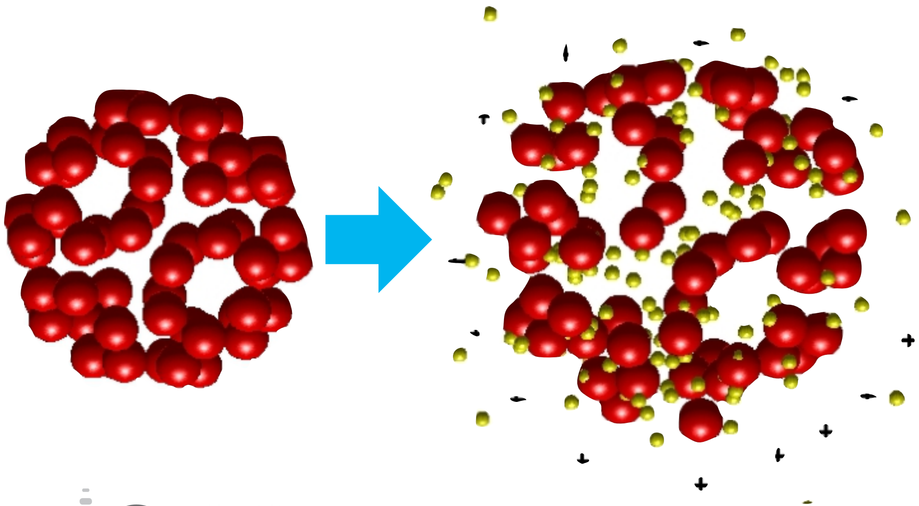
- Based on knowledge of dynamical behaviors of heavy atoms within a molecule

Toward complex systems

- **XMDYN**: X-ray molecular dynamics
  - Classical dynamics for ions and free electrons
  - Quantum treatment for bound electrons
    ➔ combined with XATOM
- Coulomb explosion of C_{60} at high x-ray intensity
- Nanoplasma formation of Ar & Xe clusters (~1000 atoms)
- *Ab initio* treatment of molecular effect ➔ to be combined with XMOLECULE

XMDYN development

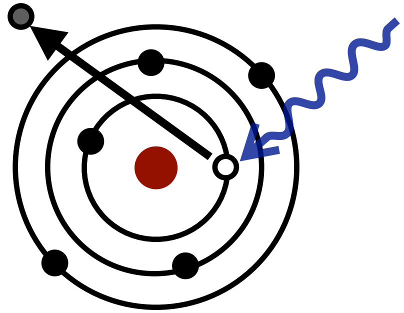
Zoltan Jurek
at CFEL-DESY Theory

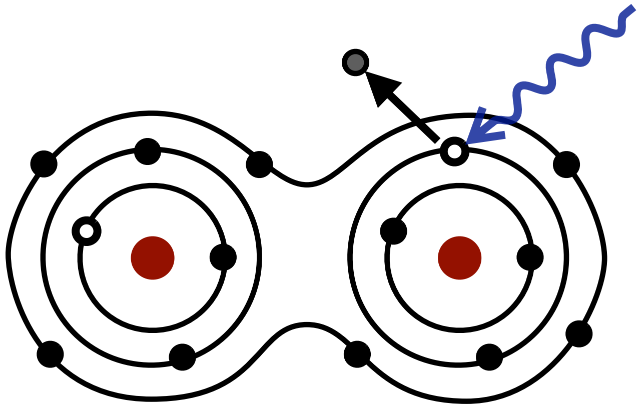


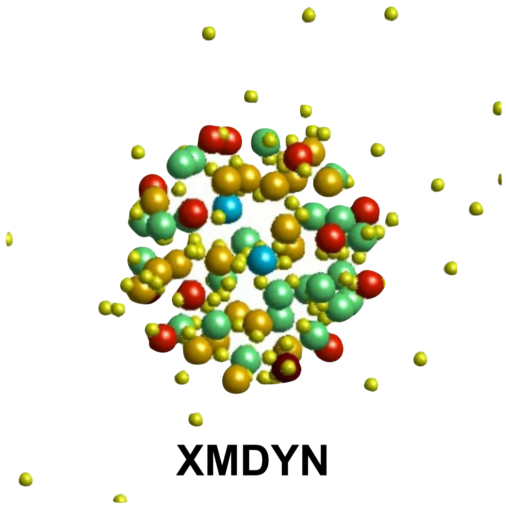
Murphy *et al.*, *Nature Commun.* **5**, 4281 (2014).
Jurek *et al.*, *J. Phys. B* **47**, 124036 (2014).
Berrah *et al.*, *Faraday Discuss.* **171**, 471 (2014).
Tachibana *et al.*, *Sci. Rep.* **5**, 10977 (2015).
Saxena *et al.*, *HEDP* **15**, 93 (2015).
Yoon *et al.*, *Sci. Rep.* **6**, 24791 (2016).
Jurek *et al.*, *J. Appl. Cryst.* **49**, 1048 (2016).

Download exec.: http://www.desy.de/~xraypac

Summary







- XATOM, XMOLECULE, and XMDYN: enabling tools to investigate x-ray multiphoton physics of atoms, molecules, and clusters exposed to high intensity x-ray pulses
- Sequential ionization model: good agreements with experimental data
- X-ray multiphoton ionization dynamics of Xe: REXMI
- Ultrafast explosion dynamics of CH_3I: highest charge state ever, CREXIM: molecular ionization enhancement

CFEL-DESY Theory Division

Prof. Dr. Robin Santra
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