What happens to atoms, molecules, and dense plasmas at high x-ray intensity?

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

---

(Virtual) Seminar, Laboratory for Laser Energetics, Univ. of Rochester
September 14, 2021

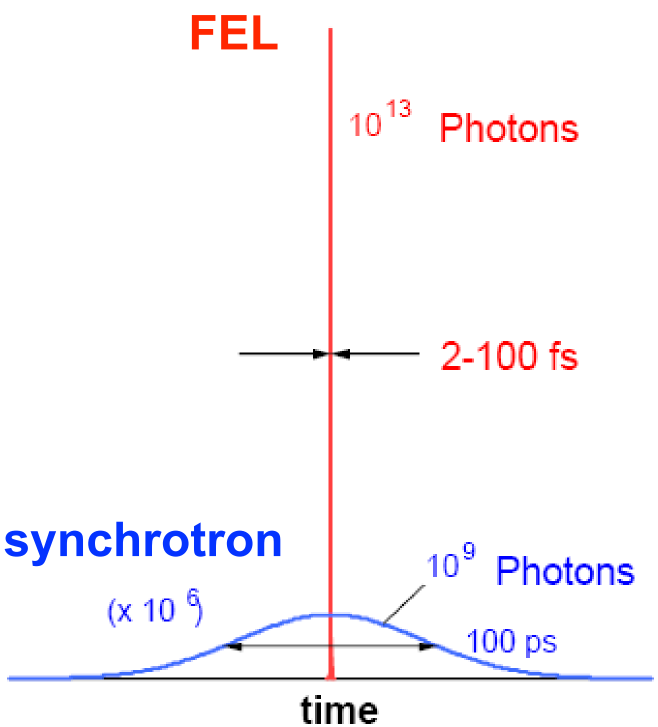
CFEL SCIENCE DESY. HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

Overview

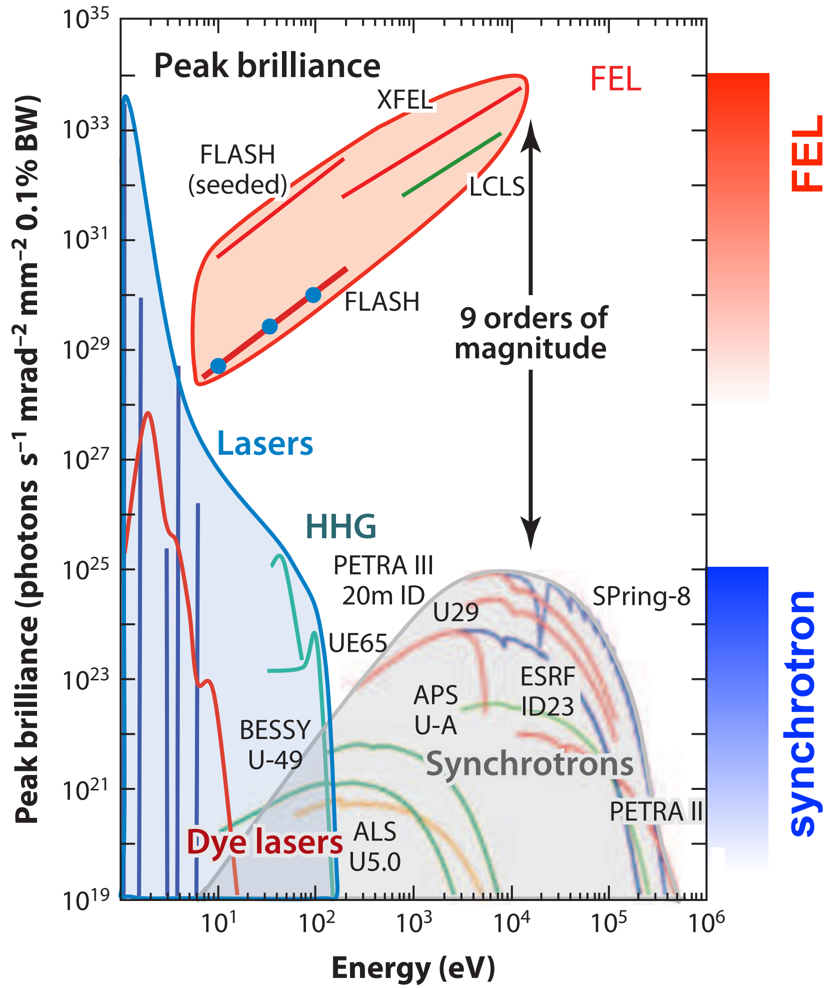
- Introduction to XFEL and XFEL–matter interaction
- XATOM and x-ray multiphoton multiple ionization dynamics of Xe
- XMOLECULE and x-ray-induced ultrafast explosion dynamics of CH_3I
- XMDYN and non-equilibrium warm-dense-matter dynamics of Al plasma
- Summary

XFEL: X-ray free-electron laser

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



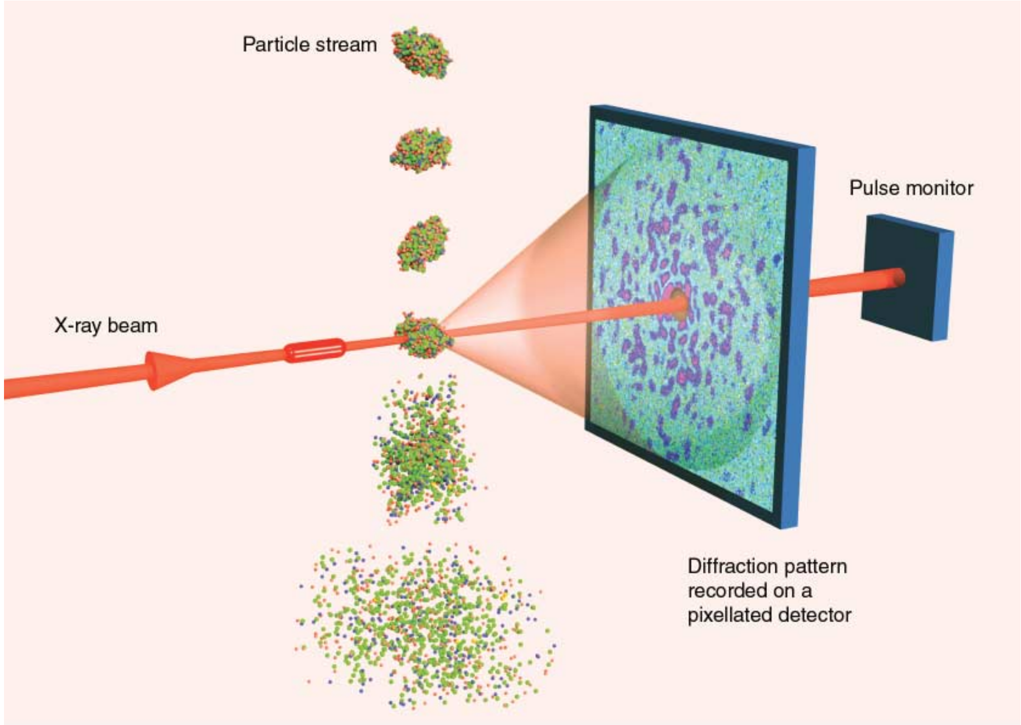
Schneider, *Rev. Accl. Sci. Tech.* **3**, 13 (2010).



Ullrich *et al.*, *Annu. Rev. Phys. Chem.* **63**, 635 (2012).

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?

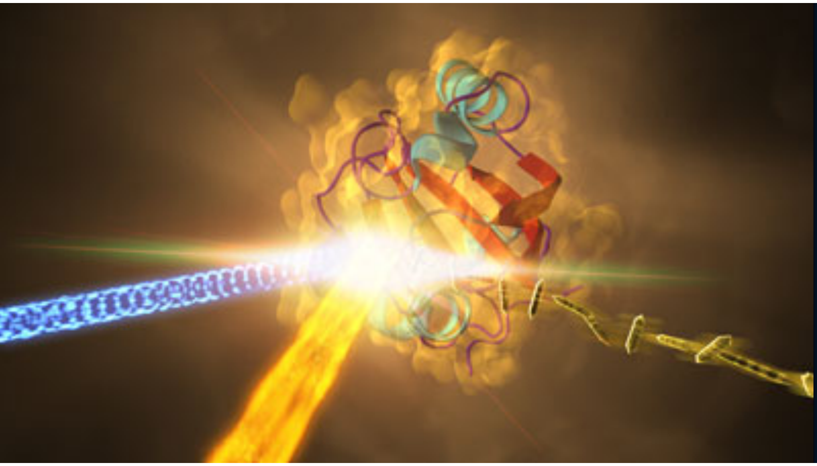
Where are XFELs?

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

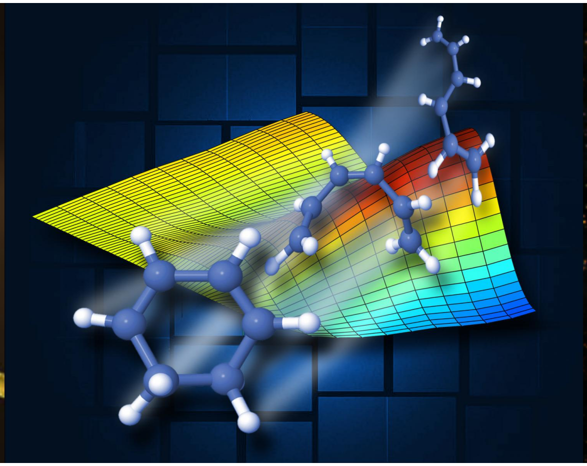
XFEL science

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

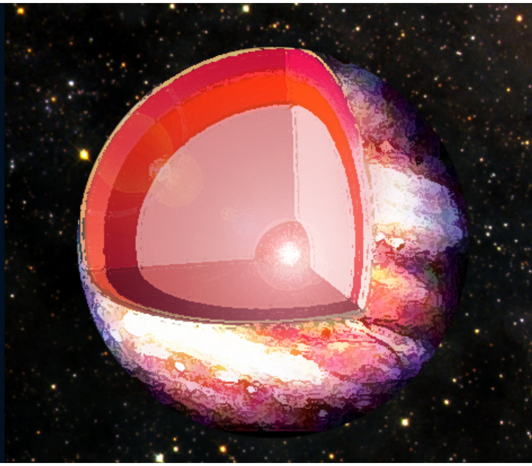
➔ XFEL applications waiting for increased theoretical support



SLAC



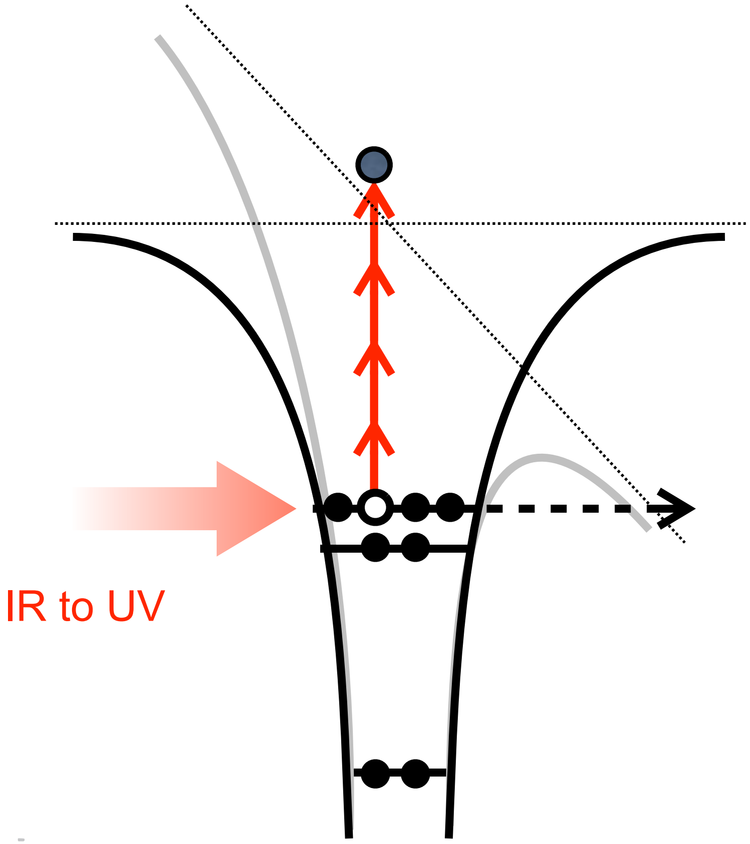
SLAC



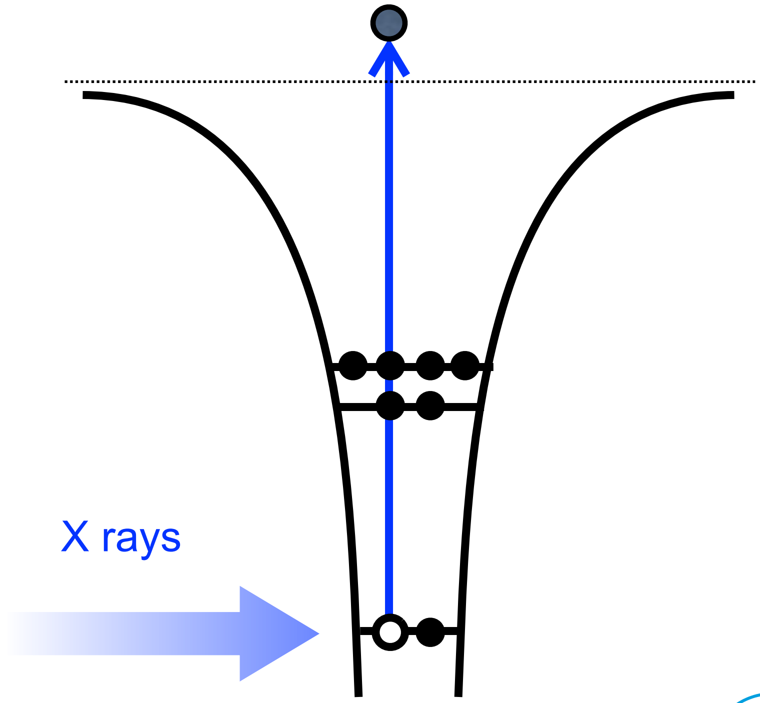
LBL

What differences from optical strong-field?

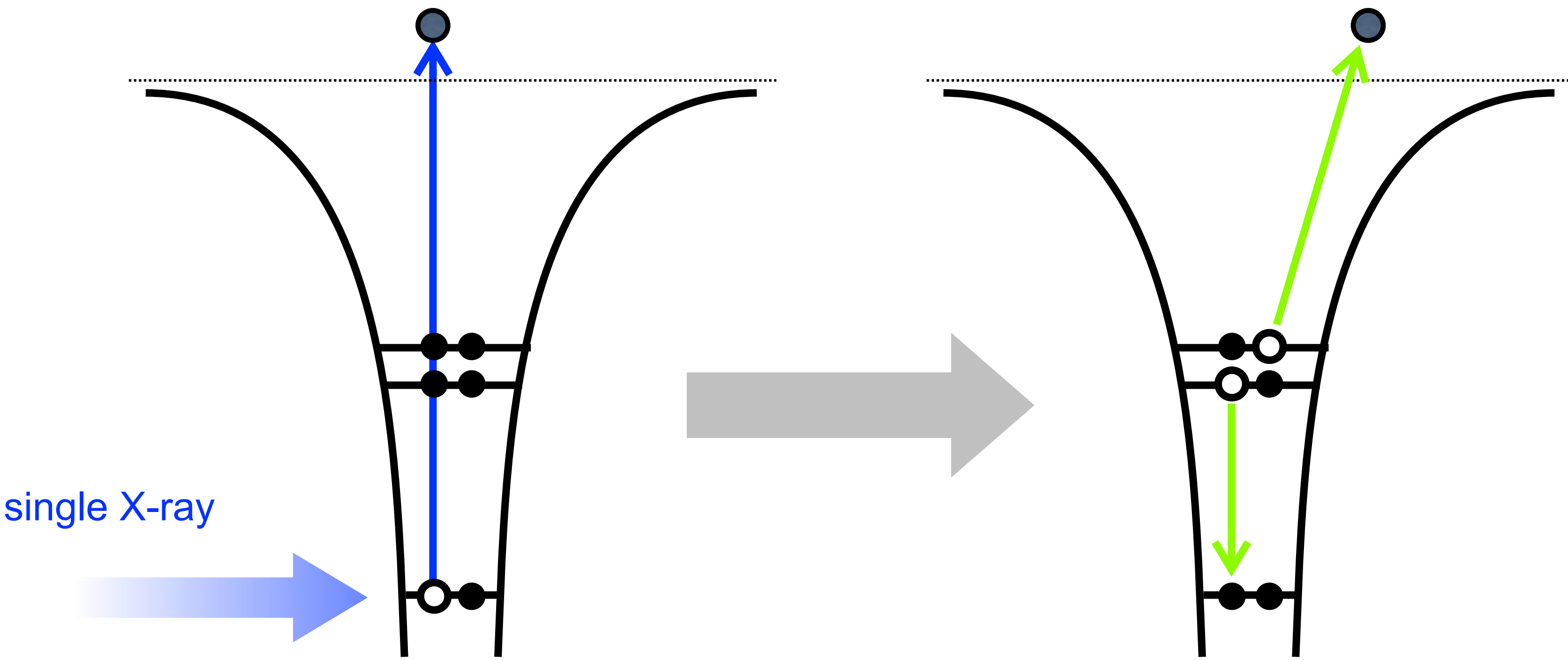
> Optical strong-field regime
  - tunneling or multiphoton processes
  - valence-electron ionization



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



Fundamental x-ray–matter interaction



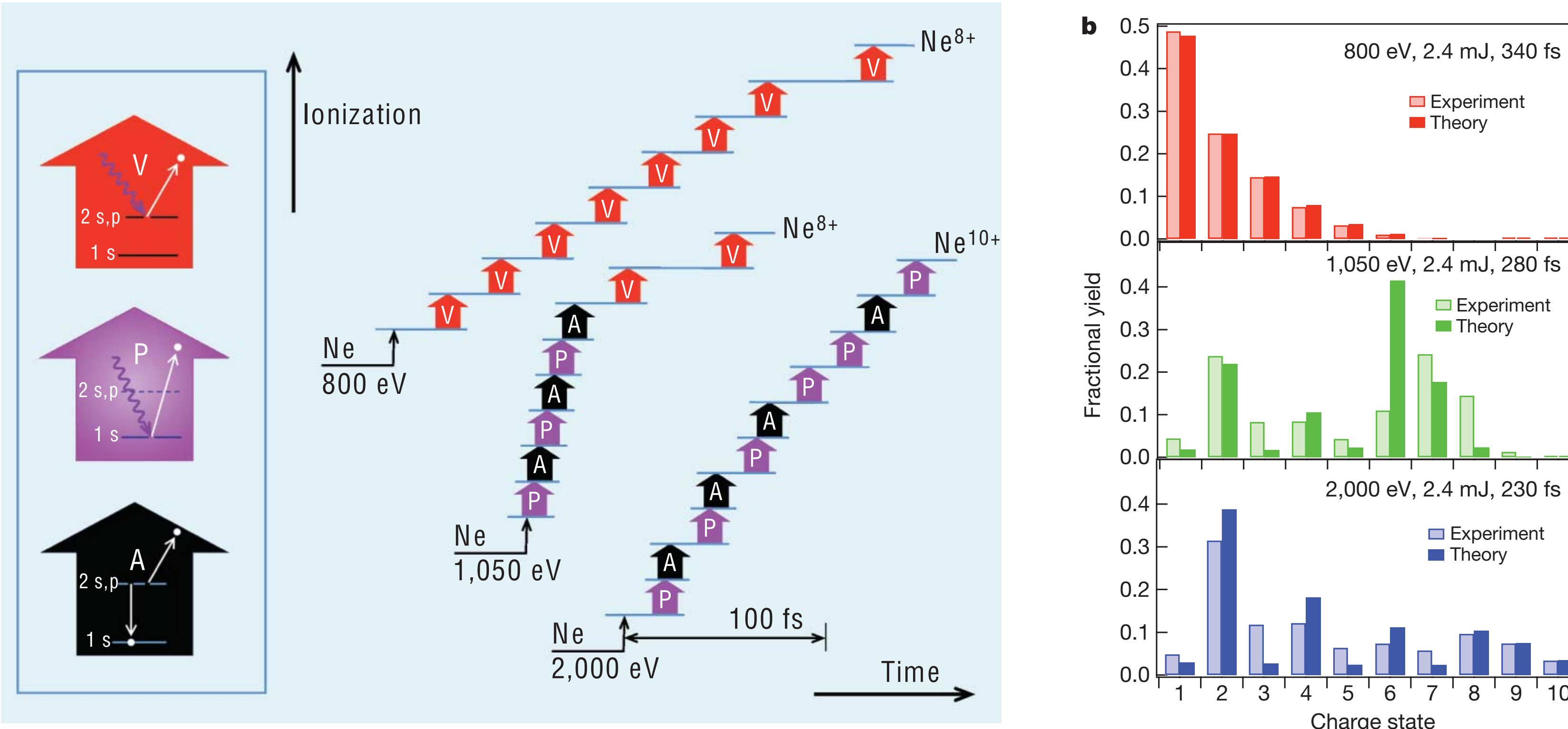
Photoionization: C → C^{*+} + e^-

Auger decay: C^{*+} → C^{++} + e^-

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

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

Sequential multiphoton multiple ionization



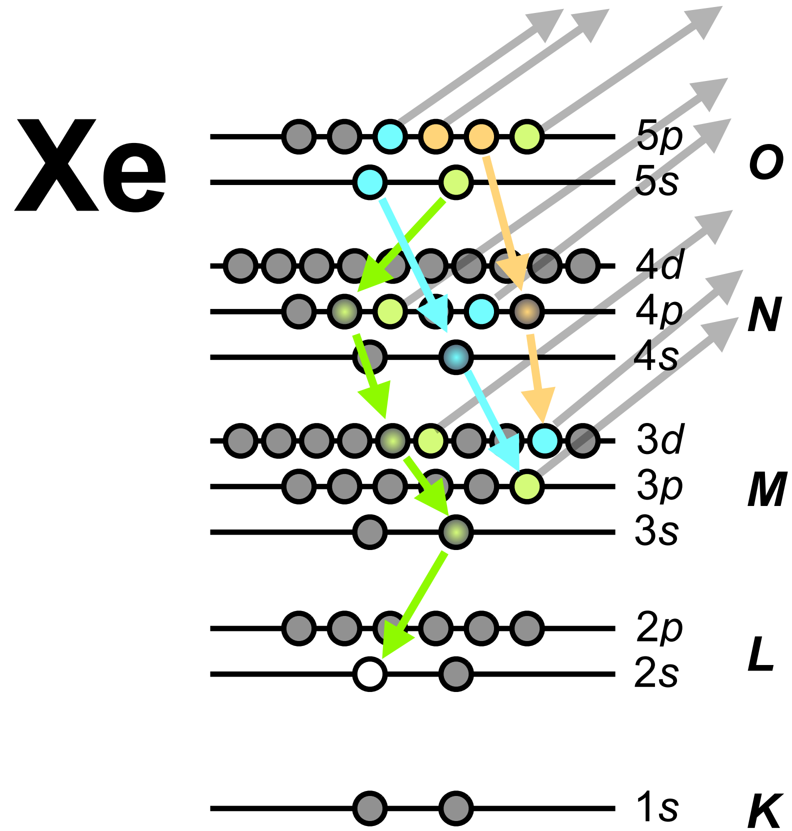
Young *et al.*, *Nature* **466**, 56 (2010).

- First LCLS experiment: fundamental atomic physics in XFEL
- Direct multiphoton absorption cross section is too small

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

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

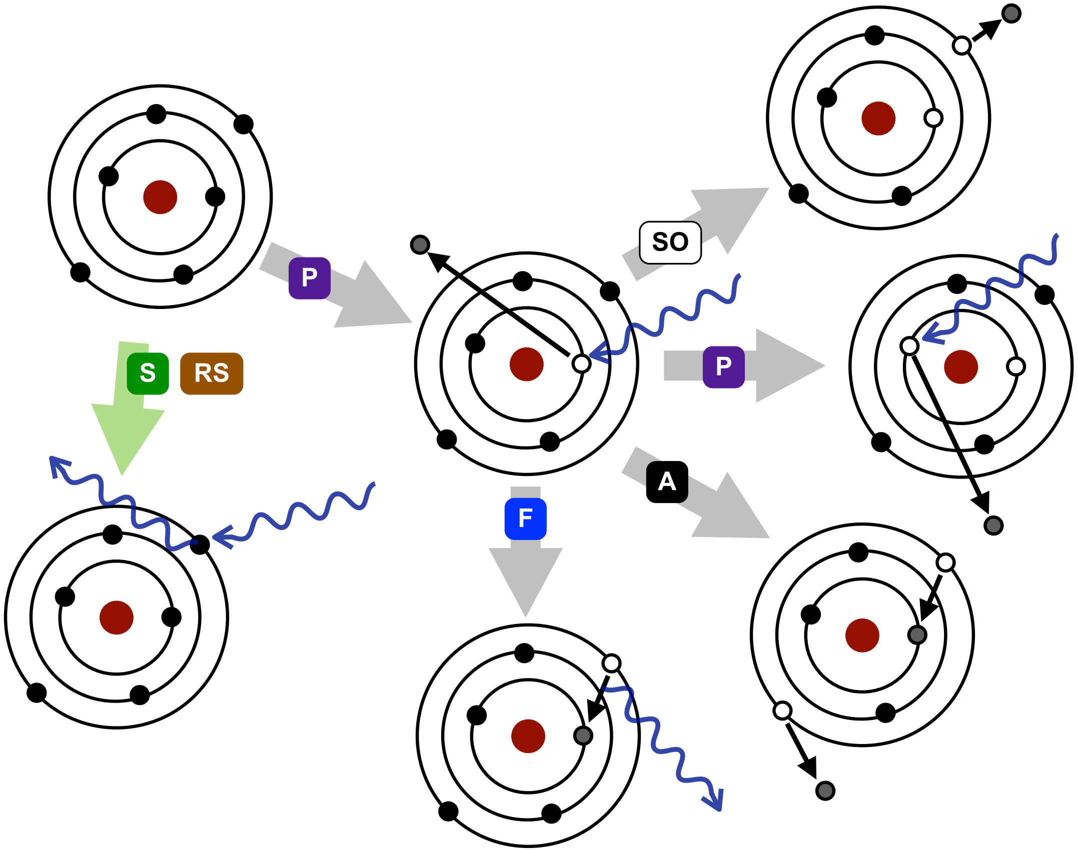


Multiphoton absorption after/during decay cascade creates:

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

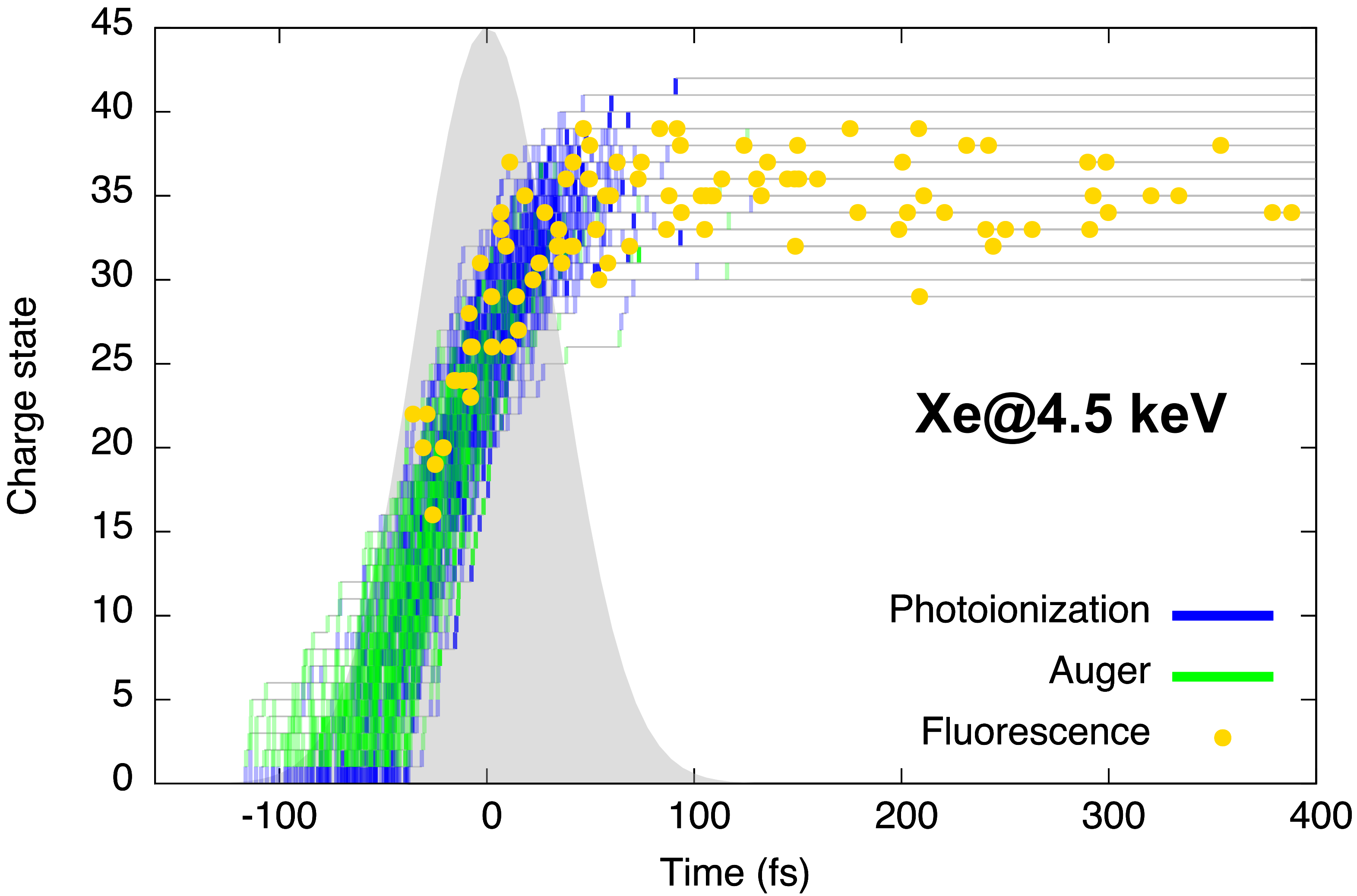
XATOM: all about x-ray atomic physics

- Hartree-Fock-Slater method for any given element and configuration
- X-ray-induced atomic processes for any given element and configuration
- Solve coupled rate equations to simulate ionization dynamics
- Sequential ionization model tested by a series of atomic XFEL experiments



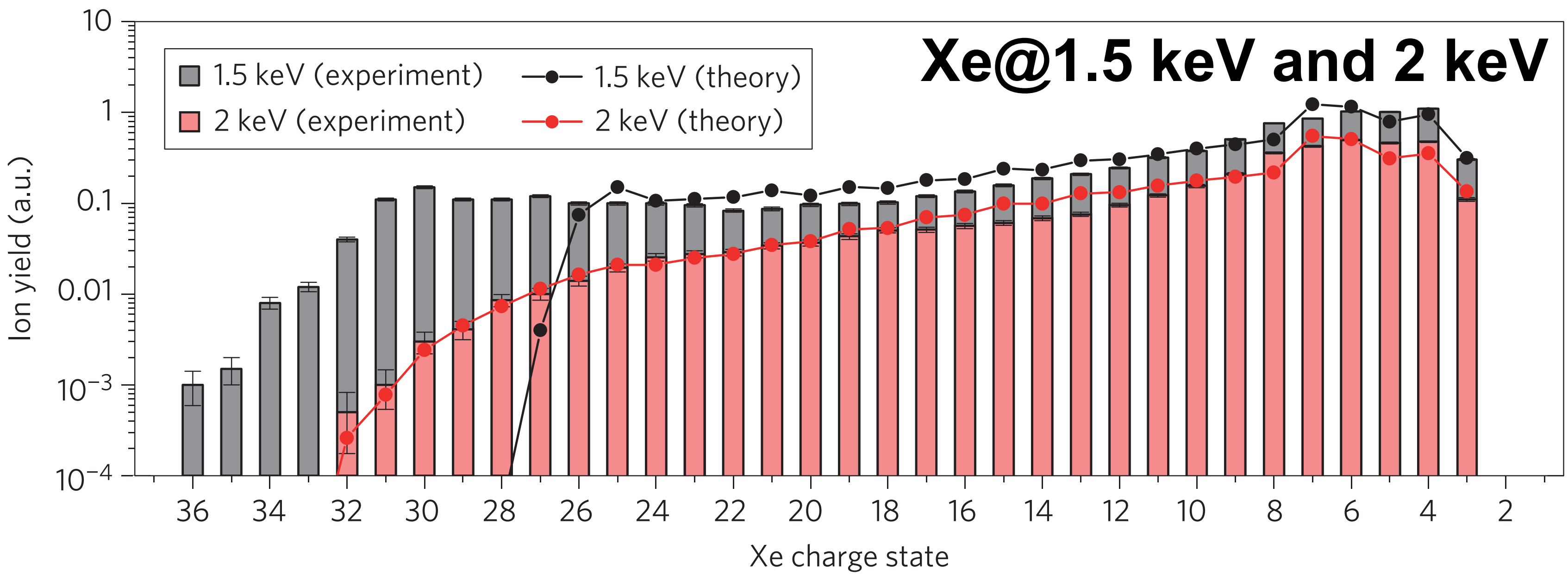
Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).
Jurek, Son, Ziaja & Santra, *J. Appl. Cryst.* **49**, 1048 (2016).
Download executables: http://www.desy.de/~xraypac

X-ray multiphoton ionization dynamics



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

Xe: Comparison with experiment



LCLS experiment

Daniel Rolles
at KSU

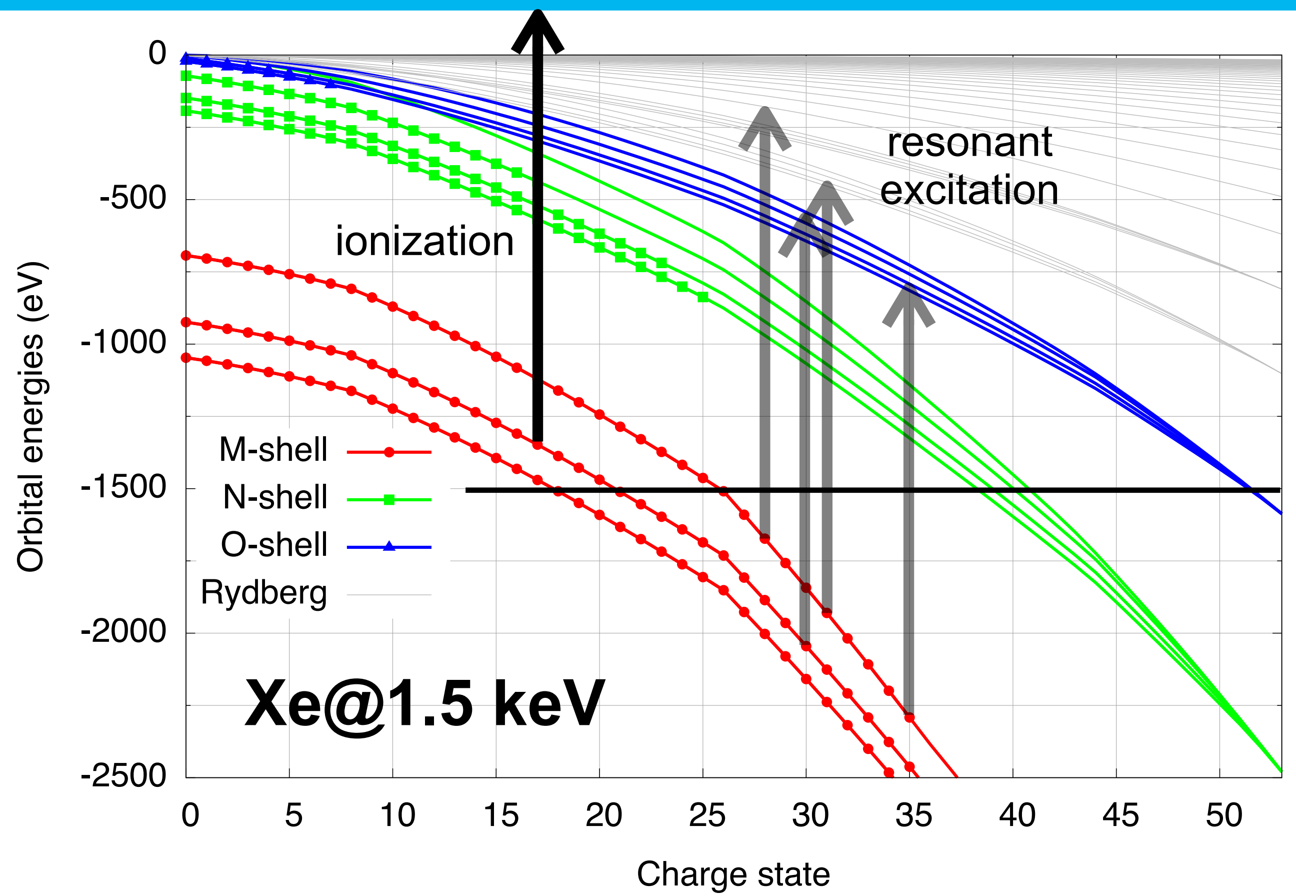
Artem Rudenko
at KSU

Benedikt Rudek
at PTB

- Xe *M*-shell ionization
- 2 keV: excellent agreement between theory and experiment
- 1.5 keV: big discrepancy between theory and experiment

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

Ionization enhanced by resonances



REXMI:
Resonance-Enabled X-ray Multiple Ionization

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

- At 1500 eV: single-photon ionization stops at Xe^{26+}
- Multiple resonant excitation: densely-spaced Rydberg states + broad bandwidth (~1%) ➔ further ionization via Auger-like autoionization

Resonance and relativistic effects

- Beyond straightforward ionization dynamics: resonance effect observed
- Deep inner-shell dynamics driven by hard x-rays: relativistic effects expected ($2p_{1/2}$–$2p_{3/2}$ splitting ~300 eV)
- XATOM extended to include both relativistic energy corrections and resonant excitations

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

XATOM extension

Koudai Toyota

- N of coupled rate equations = N of multiple-hole config.
  - Ne: $1s^2\ 2s^2\ 2p^6$ ➔ 63 config.
  - Xe: $[1s^2\ 2s^2\ 2p^6]\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$ ➔ 1,120,581 config.
  - Xe: $[1s^2]\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$

    nonrelativistic, no resonance ➔ 23,532,201 config.

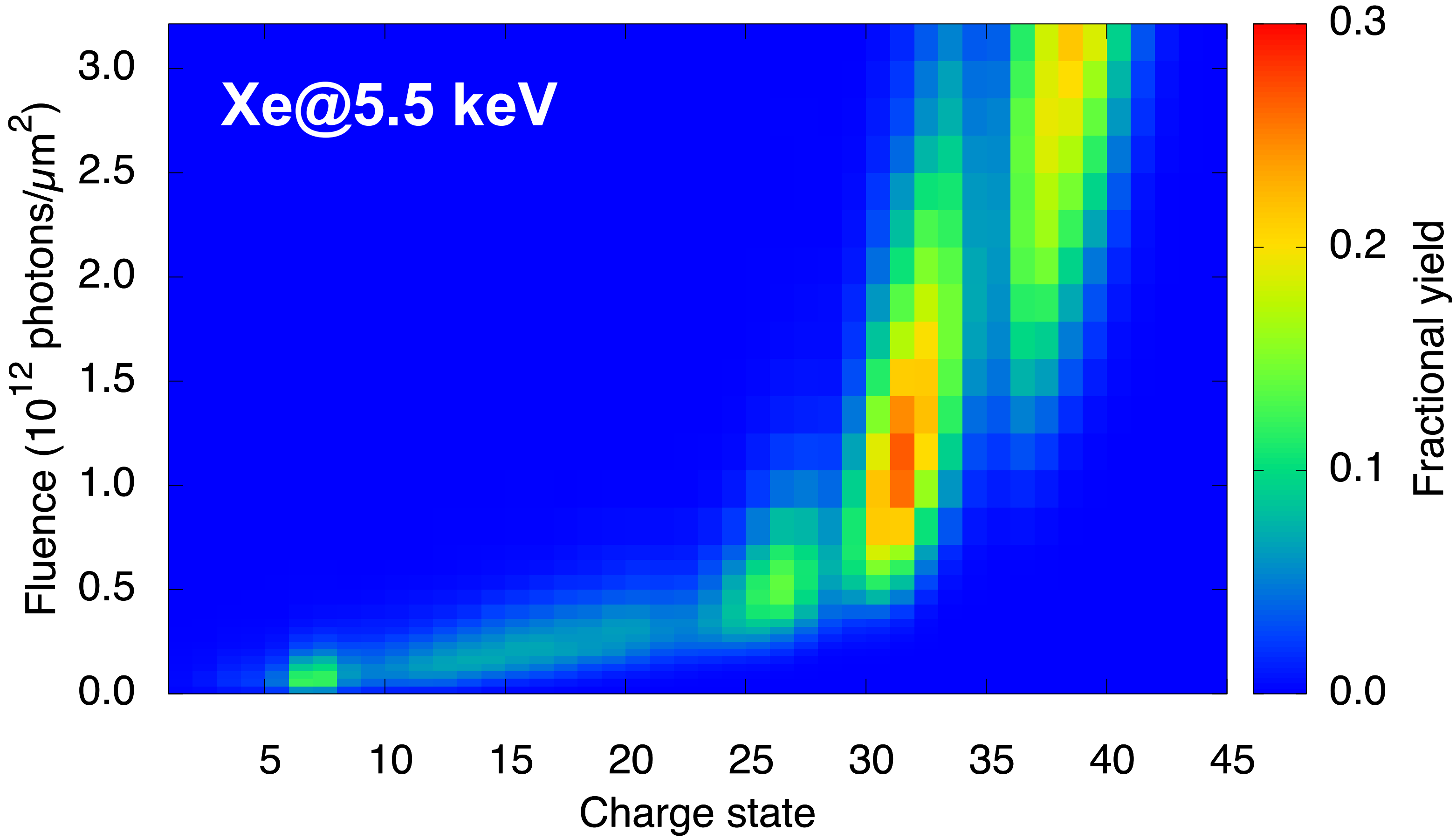
    relativistic, no resonance ➔ 5,023,265,625 config.

    relativistic, resonance (n_{max}=30, l_{max}=7) ➔ 2.6×10^{68} config.

CFEL SCIENCE

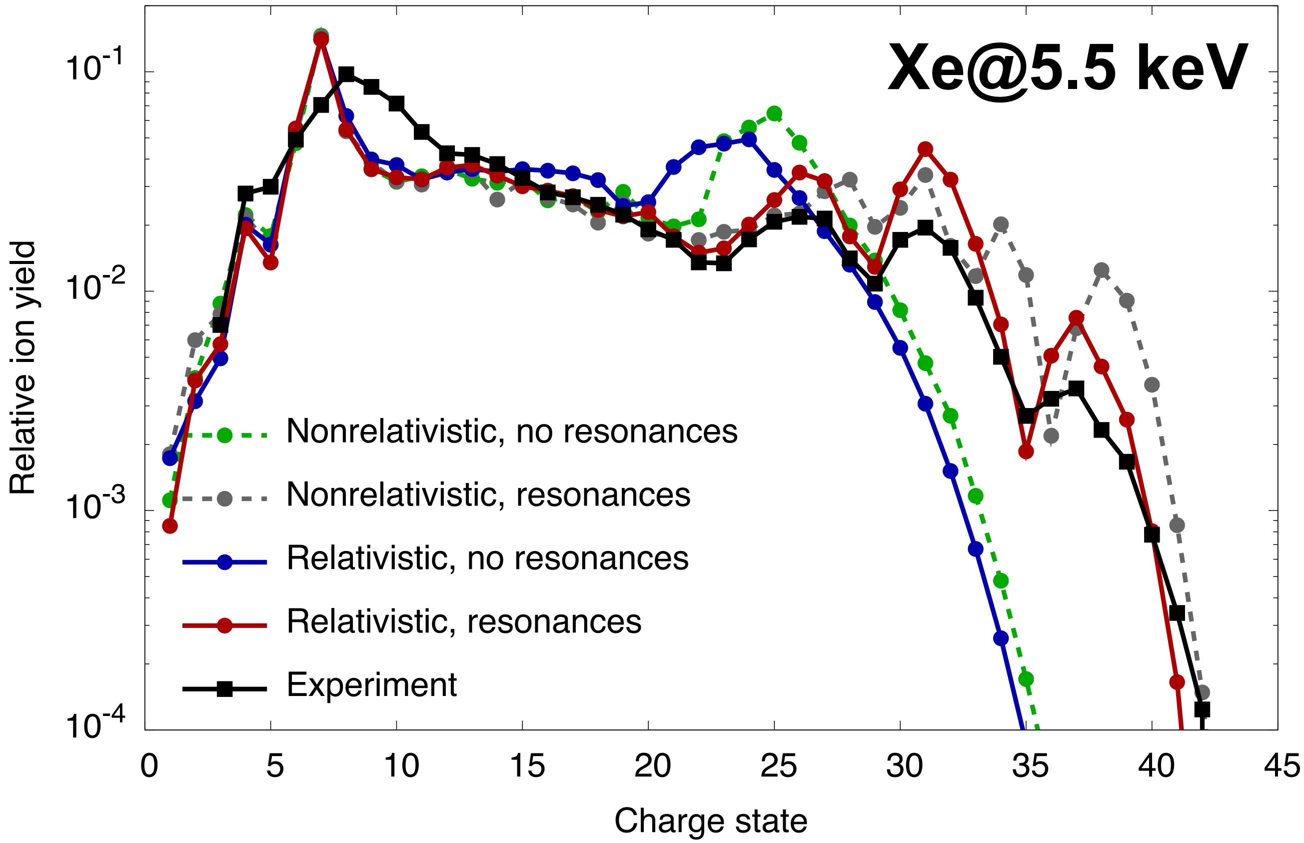
DESY.

CSD with resonance & relativity



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

Xe: Comparison with new LCLS data



> Highlighting the interplay between resonance and relativistic effects

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

Challenges for molecular dynamics at XFEL

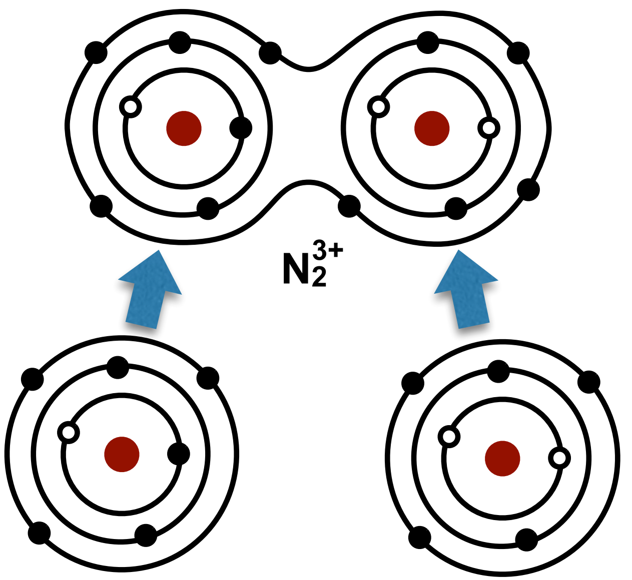
- No *ab initio* theoretical tools available for high x-ray intensity
  - Extremely complicated dynamics:
    e.g. CH_3I ~ 200 trillion rate equations at single geometry
  - Coupled ionization and nuclear dynamics in the same time scales
  - Highly excited molecular electronic structure

XMOLECULE

- Quantum electrons, classical nuclei
- Efficient electronic structure calculation: core-hole adapted basis functions calculated by XATOM
- Monte Carlo on the fly

XMOLECULE: Elec. structure & dynamics

- Hartree-Fock-Slater method
- Bound states: LCAO-MO with core-hole-adapted numerical atomic orbitals calculated by XATOM



N^{+}: $1s^1 2s^2 2p^3$ N^{2+}: $1s^0 2s^2 2p^3$

XMOLECULE development

Yajiang Hao
Now at USTB (Beijing)

Kota Hanasaki
Now at Kyoto Univ.

Ludger Inhester

- Continuum states: approximated by atomic continuum calculated by XATOM
- Cross sections, rates, and molecular forces calculated on the fly for given electronic and nuclear configuration

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

Iodomethane in an *ultraintense* x-ray pulse

- New experimental setup:
  LCLS CXI using nano-focus
  ➔ new realm of intensity
  approaching ~10^{20} W/cm^2

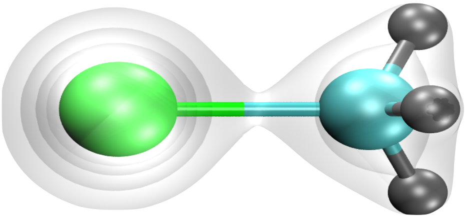
LCLS experiment

Daniel Rolles at KSU

Artem Rudenko at KSU

- Selective ionization on heavy atom

CH_3I @ 8.3 keV



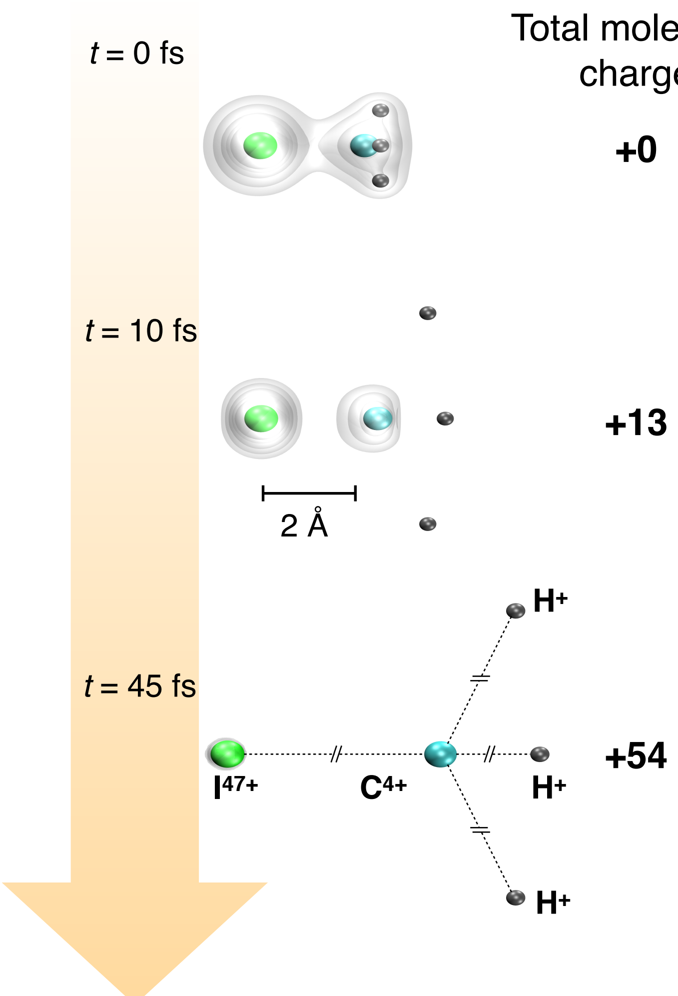
σ(I) ~ 50,000 barn

σ(C) ~ 80 barn

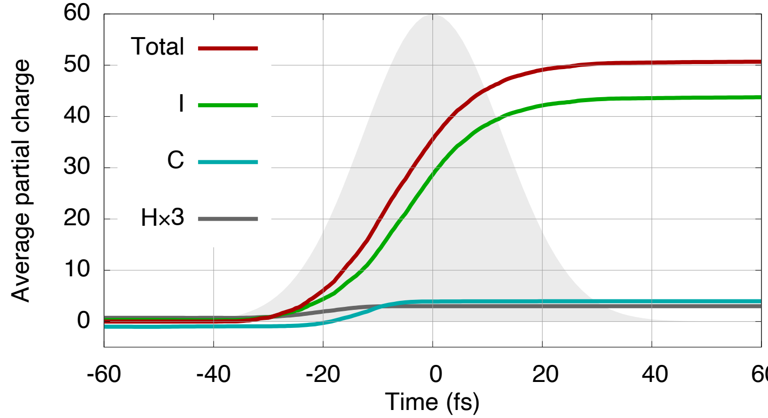
σ(H) ~ 0.008 barn

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

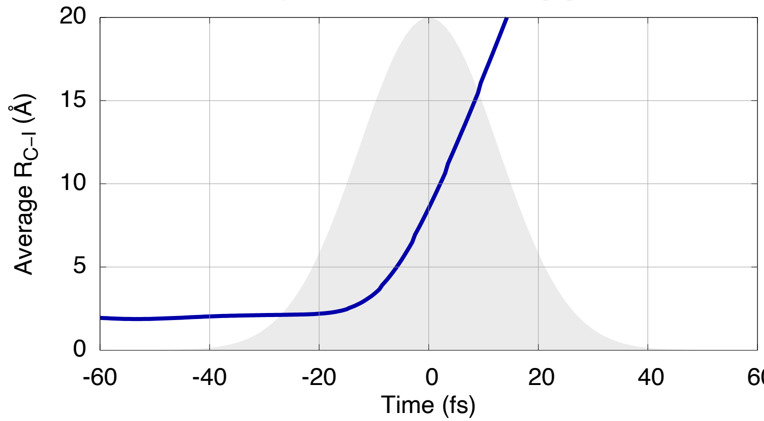
Ionization and fragmentation dynamics



Ionization dynamics: $Q(t)$



Nuclear dynamics: $R(t)$



CSD

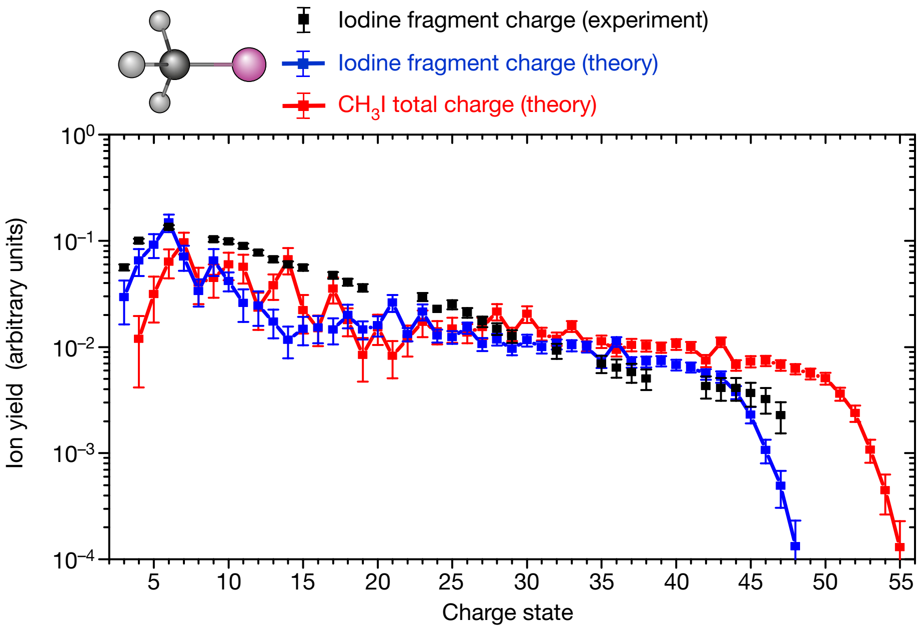
Charge-State Distribution

KER

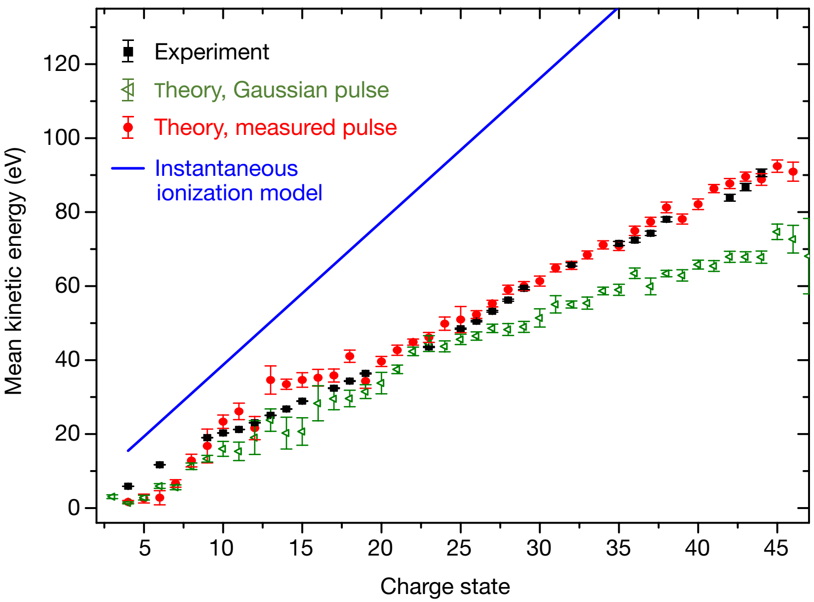
Kinetic Energy Release

CH_3I: Comparison of CSD and KER

CSD of I and CH_3I



KER of I fragment

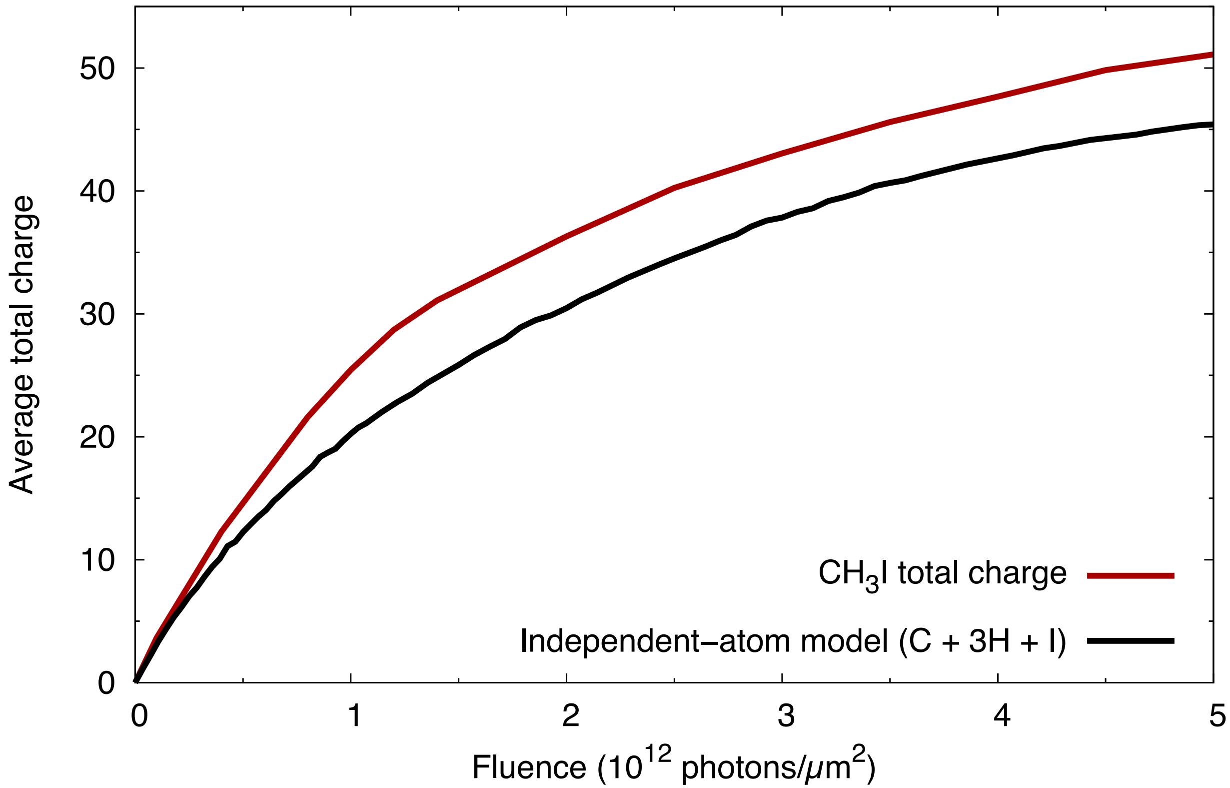


> CSD & KER: Capturing detailed ionization and fragmentation dynamics

> First quantitative comparison for the behaviors of polyatomic molecules under XFEL irradiation

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

Molecular ionization enhancement



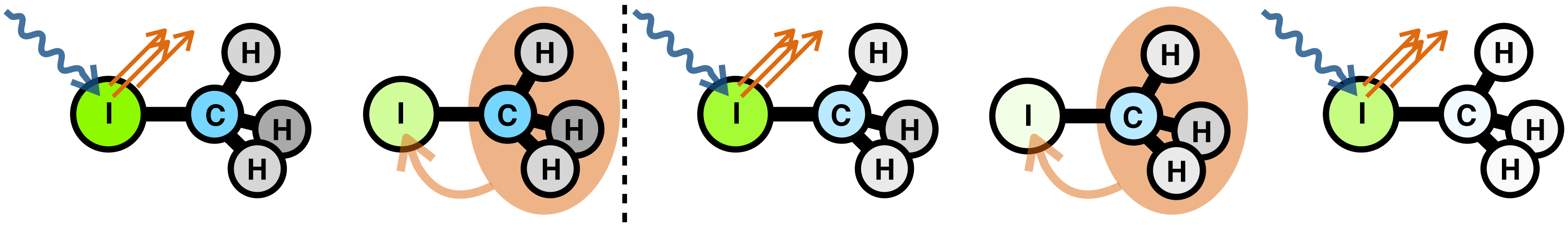
- At low fluence, molecular total charge = sum of individual atomic charges
- At high fluence, molecular total charge > sum of individual atomic charges

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

Ionization enhanced by charge rearrangement

low x-ray fluence
(single-photon dominant)

high x-ray fluence
(multiphoton dominant)



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

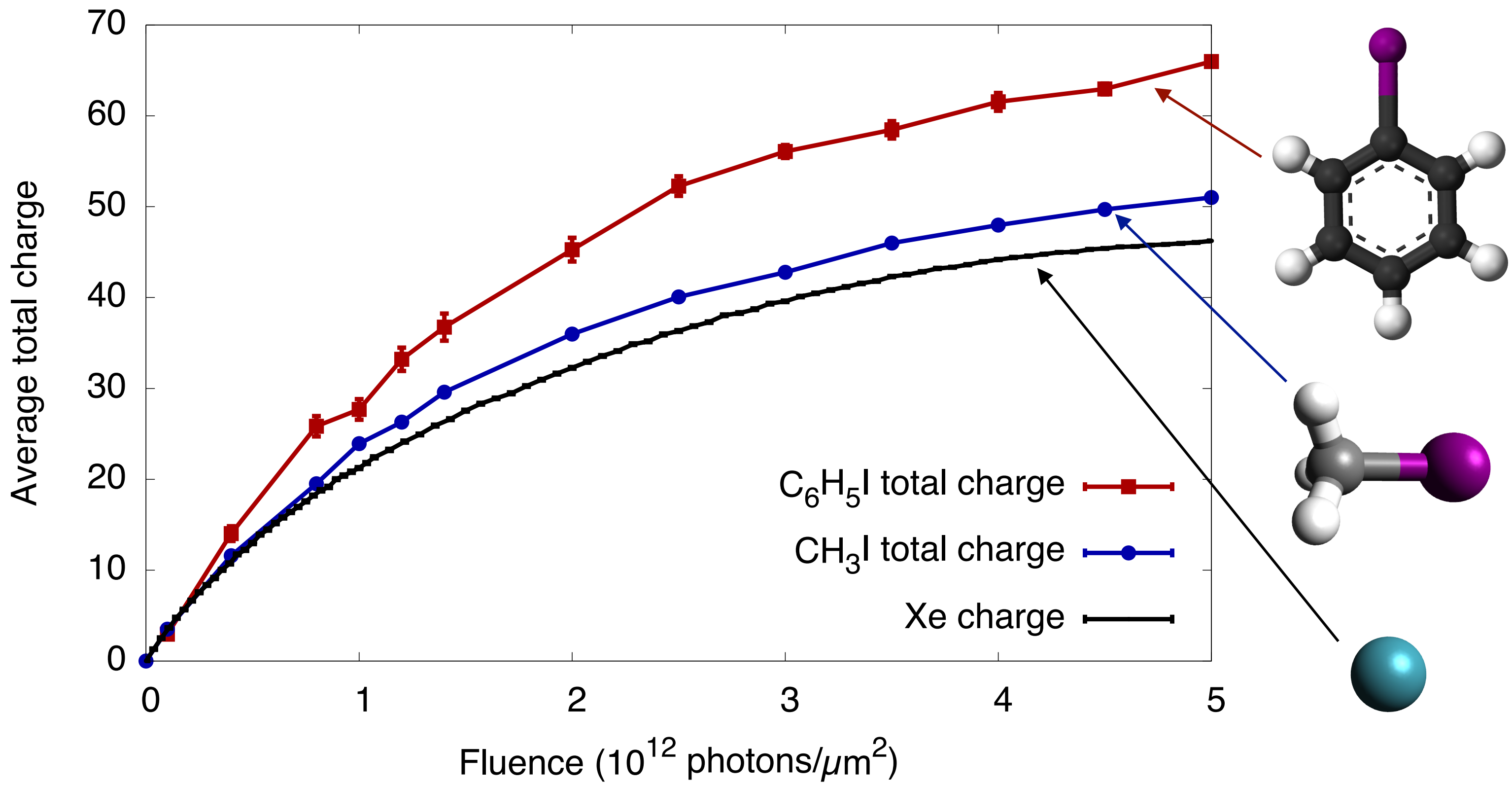
- Impact on molecular imaging: not reducing partial charges of heavy atoms due to charge rearrangement, but inducing more ionization overall

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

CFEL SCIENCE

DESY.

The bigger molecule, the larger CREXIM



- Xe, iodomethane, iodobenzene: similar cross section at 8.3 keV
- The stronger ionization for the larger molecule at high intensity

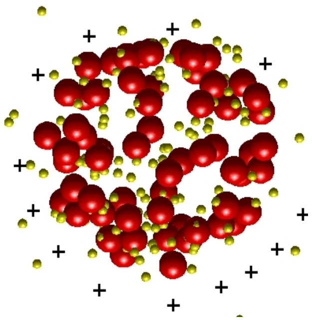
Hao, Inhester, Son & Santra, *PRA* **100**, 013402 (2019).

XMDYN: Towards complex systems

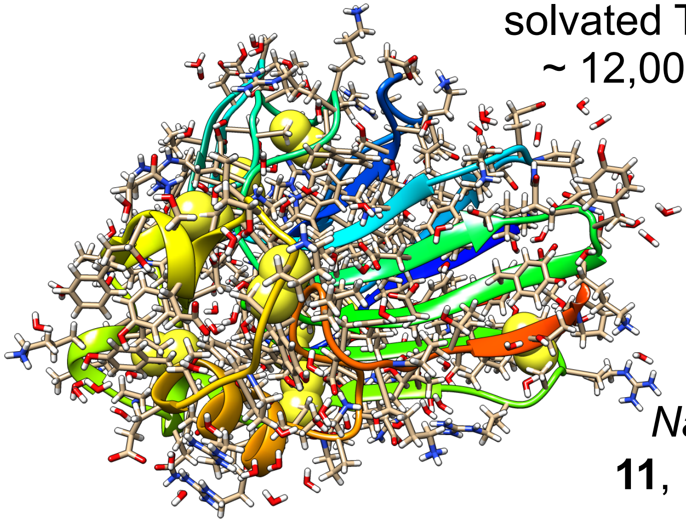
- Monte-Carlo Molecular Dynamics (MCMD)
  - Quantum treatment for bound electrons of individual atoms ➔ combined with XATOM
  - Classical dynamics for ions and free electrons
- No first-principles treatment for molecular effects (molecular Auger, chemical bond & charge transfer)
- Part of start-to-end simulation for single-particle imaging at European XFEL
  - Yoon *et al.*, *Sci. Rep.* **6**, 24791 (2016).
  - Fortmann-Grote *et al.*, *IUCrJ* **4**, 560 (2017).

XMDYN development

Zoltan Jurek



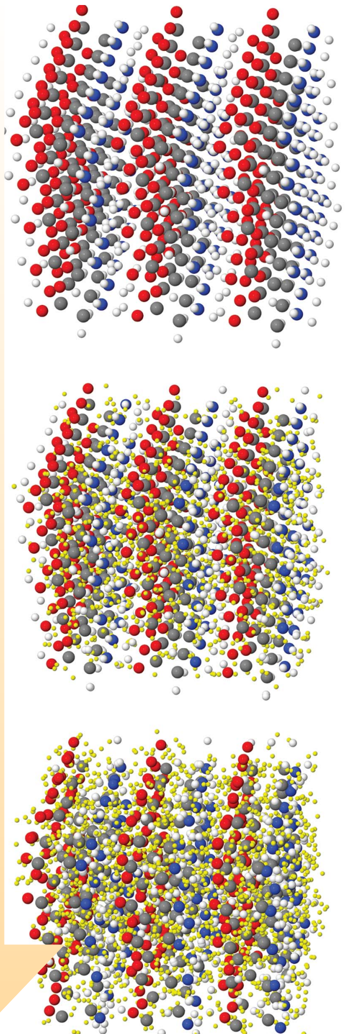
C_{60} explosion dynamics
- Murphy *et al.*, *Nat. Commun.* **5**, 4281 (2014).
- Berrah *et al.*, *Nat. Phys.* **15**, 1279 (2019).



solvated Thaumatin
~ 12,000 atoms

Nass *et al.*, *Nat. Commun.* **11**, 1814 (2020).

XMDYN with periodic boundary condition



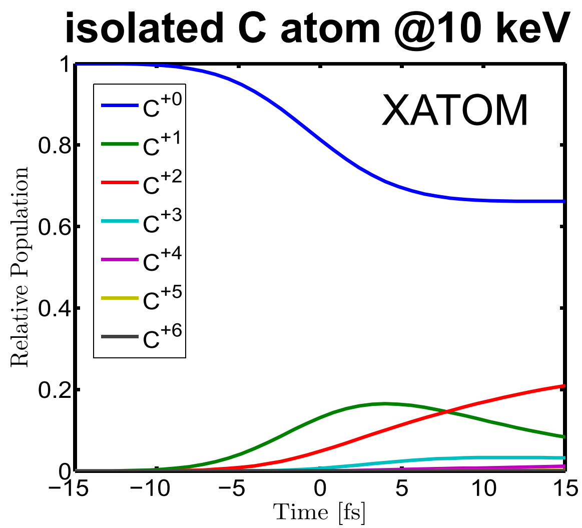
105 glycine molecules in a supercell @10 keV

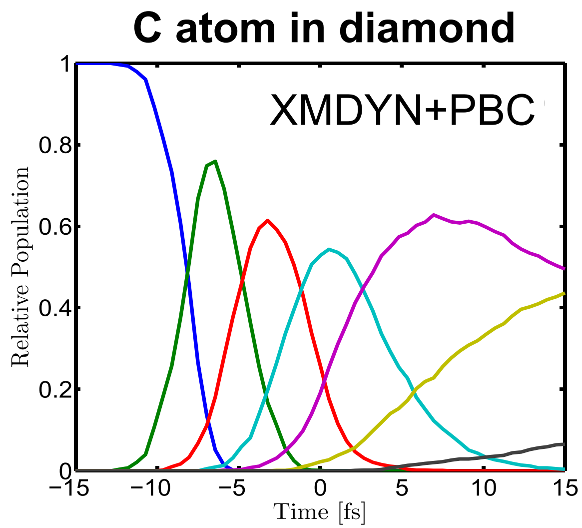
Abdullah *et al.*, *IUCrJ* **5**, 699 (2018).

XMDYN development

Zoltan Jurek

Malik M. Abdullah





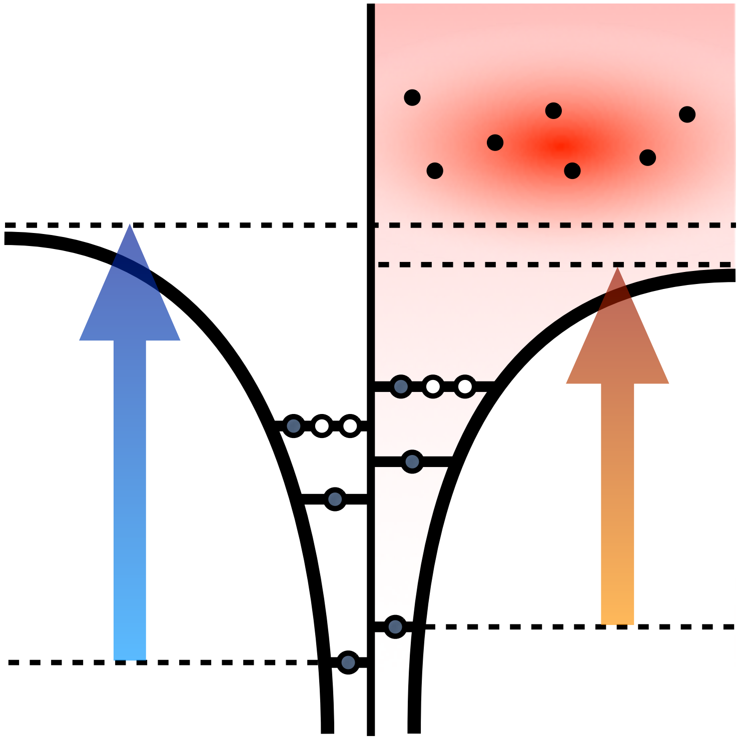
Ionization enhanced by collisional ionization in a dense electron plasma

Abdullah *et al.*, *Struct. Dyn.* **3**, 054101 (2016).

Electronic structure with dense plasma env.

isolated atom

- Coulomb potential by the nucleus
- screening by bound electrons



solid / plasma

Dense environment

+ screening by free electrons

+ pressure ionization

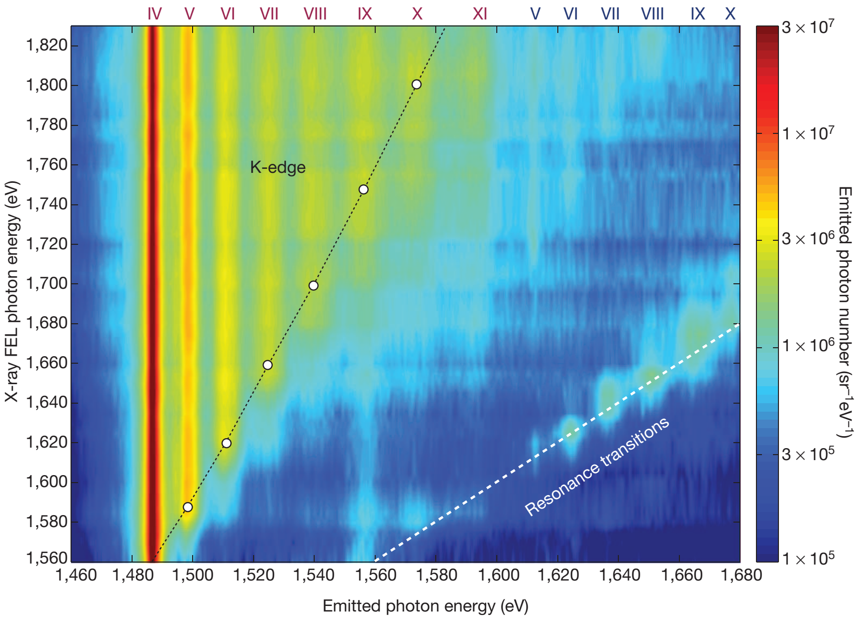
➔ IP lowering

Ionization potential depression (IPD): $\Delta E_i = \mathrm{IP}_i^{\mathrm{iso}} - \mathrm{IP}_i^{\mathrm{pla}}$

One of the most fundamental physics for atomic processes in a dense plasma

IPD in warm dense Al plasma

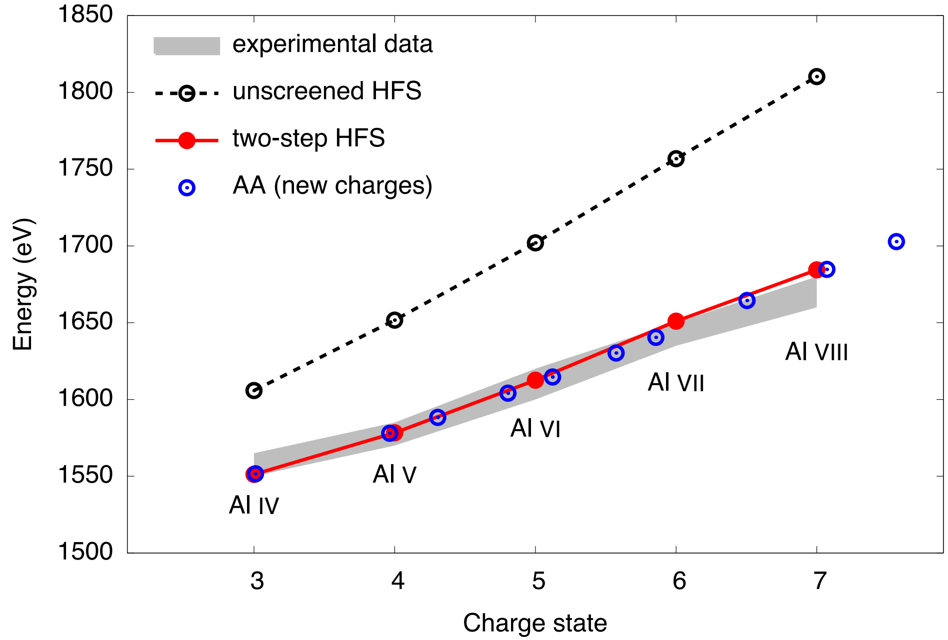
Al WDM created by XFEL: *T* < 200 eV, solid density (2.7 g/cm³)



Vinko *et al.*, *Nature* **482**, 59 (2012);

Ciricosta *et al.*, *Phys. Rev. Lett.* **109**, 065002 (2012).

IPD calculation at thermal equilibrium



Son *et al.*, *Phys. Rev. X* **4**, 031004 (2014);

Bekx *et al.*, *Phys. Rev. Res.* **2**, 033061 (2020).

Finite-temperature Hartree-Fock-Slater

➔ For a given *T*, IP evaluated at $\bar{Q}$ or at *Q* with a specific config.

Nonequilibrium WDM dynamics

> **XMDYN** Abdullah *et al.*, *Phys. Rev. E* **96**, 023205 (2017).

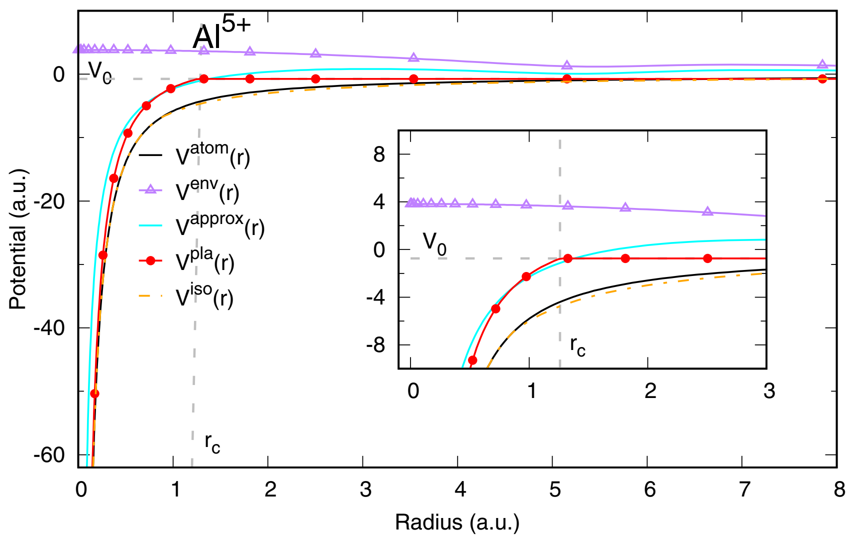
- no thermal equilibrium assumption employed
- no treatment for electronic structure with a plasma environment (XATOM for isolated atoms)

XMDYN+XPOT development

Rui Jin

> **XPOT**: extends XMDYN to include a plasma environment in XATOM calculation at any given time snapshot

- soft Coulomb potential for all classical particles
- spherical averaging for a given atom
- charge-selective averaging
- muffin-tin-like approximation

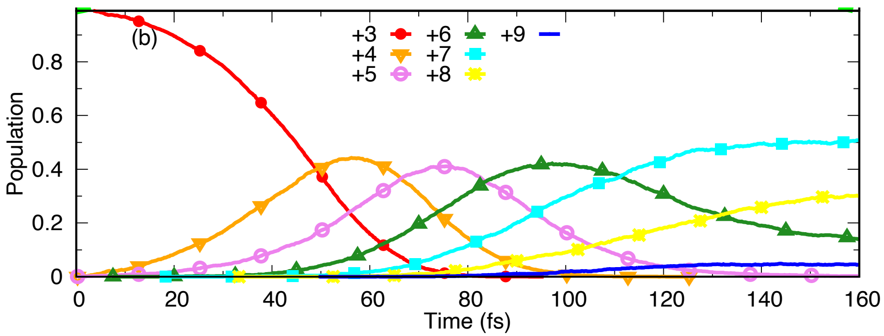


Jin *et al.*, *Phys. Rev. E* **103**, 023203 (2021).

$$V_A^{\rm pla}(\mathbf{r}) = \begin{cases} V_A^{\rm atom}(\mathbf{r}) + V_A^{\rm env}(\mathbf{r}) & \text{for } r < r_c, \\ V_0 & \text{for } r \geqslant r_c. \end{cases}$$

Transient IPD in nonthermal dense plasmas

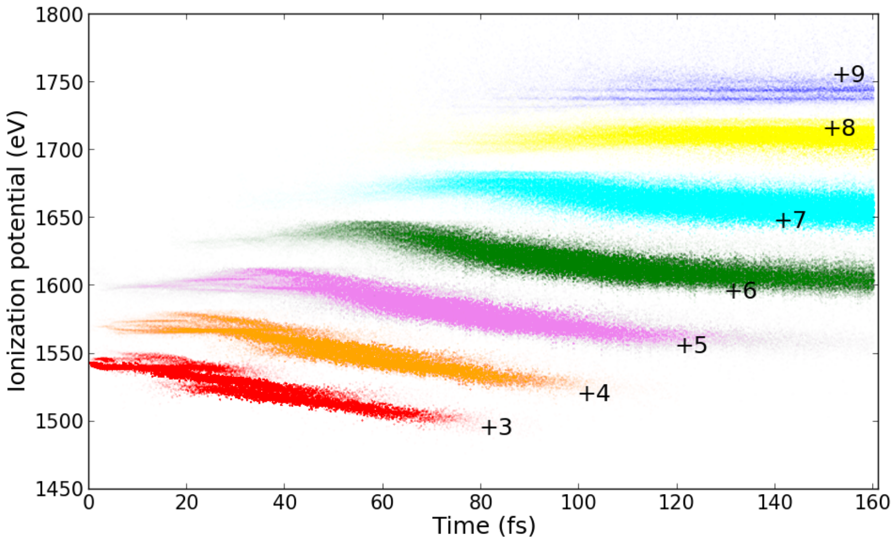
Time-evolution of charge-state population



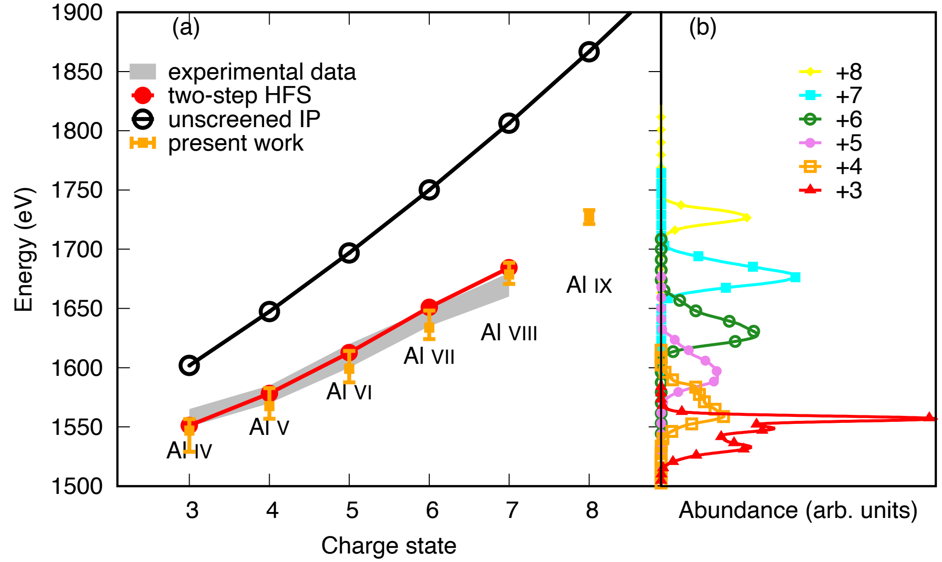
Al@1850 eV, 80 fs XFEL pulse

500 Al atoms in a supercell with a lattice constant of 20.23 Å containing 5×5×5 fcc unit cells

Time-resolved IP

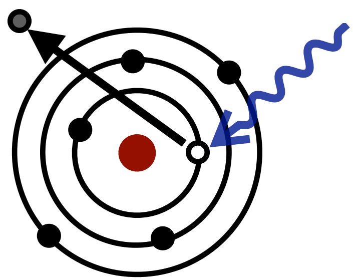


Comparison for time-integrated IP

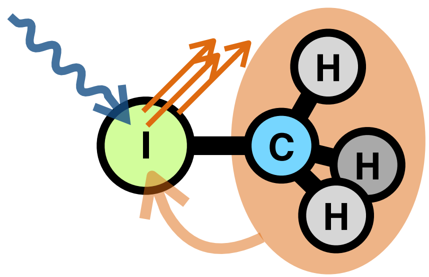


Jin *et al.*, *Phys. Rev. E* **103**, 023203 (2021).

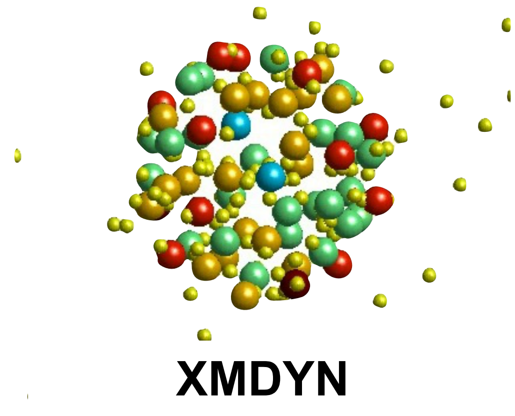
Conclusion



XATOM



XMOLECULE



XMDYN

- Enabling tools to investigate x-ray multiphoton physics of atoms, molecules, clusters, and plasmas exposed to high-intensity x-ray pulses
- XFEL–matter interaction: sequential multiphoton multiple ionization
- Intriguing phenomena with intense XFEL pulses
  - Xe: ionization enhanced via REXMI and modulated by relativity
  - CH_3I: molecular ionization enhancement via CREXIM
  - Al plasma: IPD and WDM formation dynamics
- Theory provides crucial insights of the XFEL–matter interaction

Collaborations

Experiment team (Xe and CH_3I)

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

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

PTB, Braunschweig B. Rudek

European XFEL R. Boll

MPI for Medical Res., Heidelberg L. Foucar

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

Theory team

CFEL, DESY M. M. Abdullah (now DESY), K. Hanasaki (now Kyoto Univ.), Y. Hao (now USTB Beijing), O. Vendrell (now Heidelberg Univ.), K. Toyota, R. Jin, L. Inhester, Z. Jurek, S.-K. Son, R. Santra

Robin Santra