Ultrafast ionization and fragmentation dynamics of molecules at high x-ray intensity

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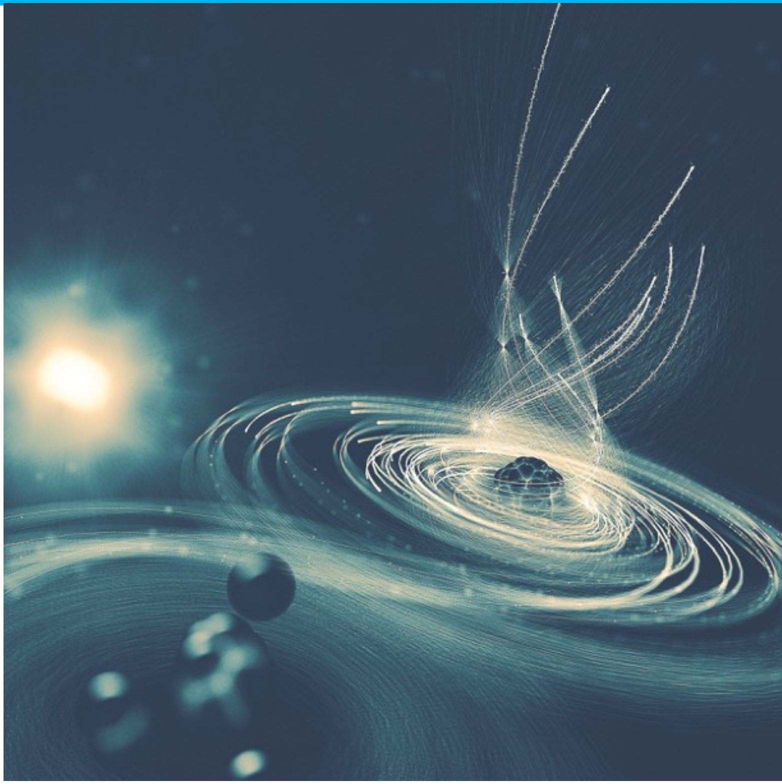
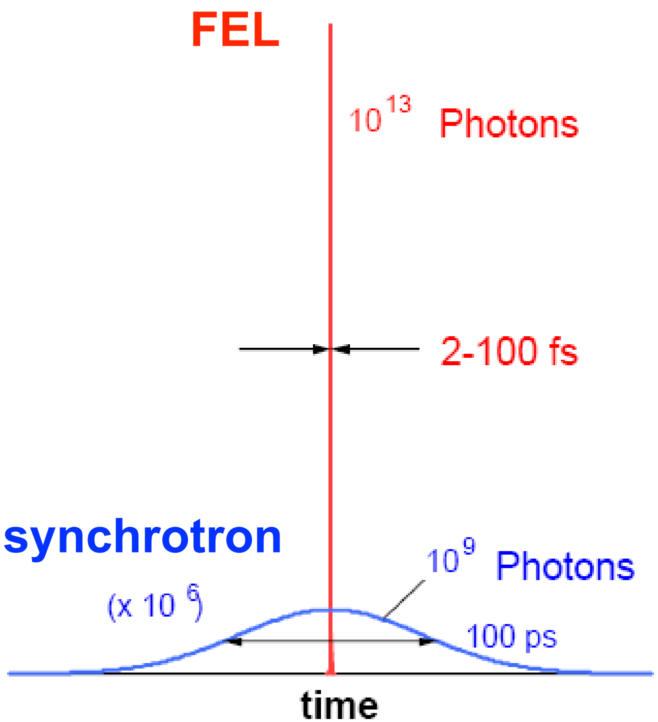
Light-Matter Interaction: Recent Advances in Theory
CFEL, Hamburg, Germany, January 25, 2018

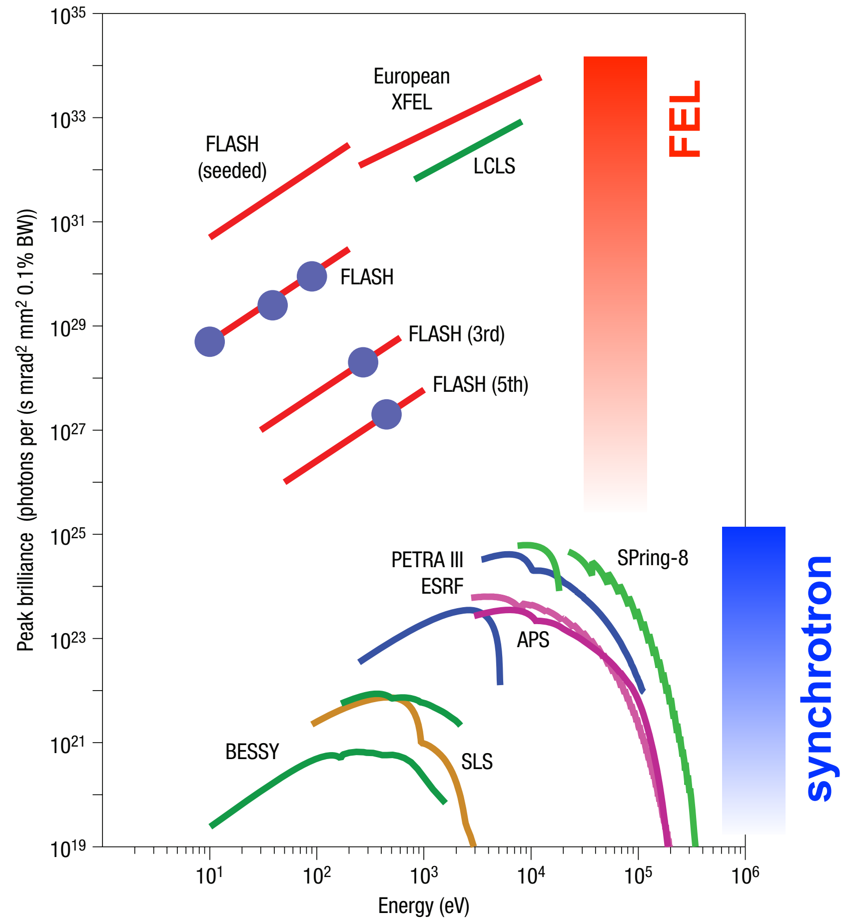


XFEL: X-ray free-electron laser

- *Ultraintense*: up to ~10^{20} W/cm^2
- *Ultrafast*: ~femtoseconds



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



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

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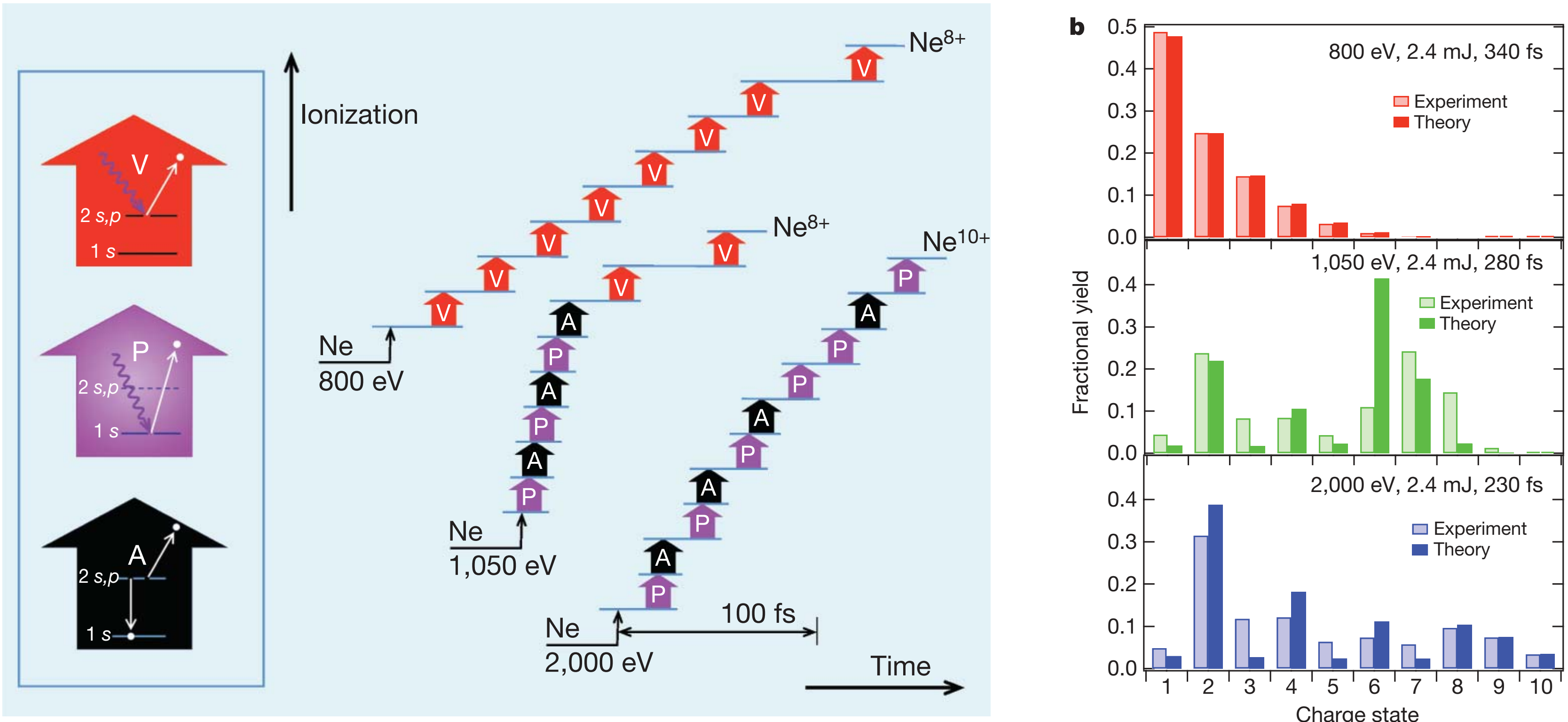
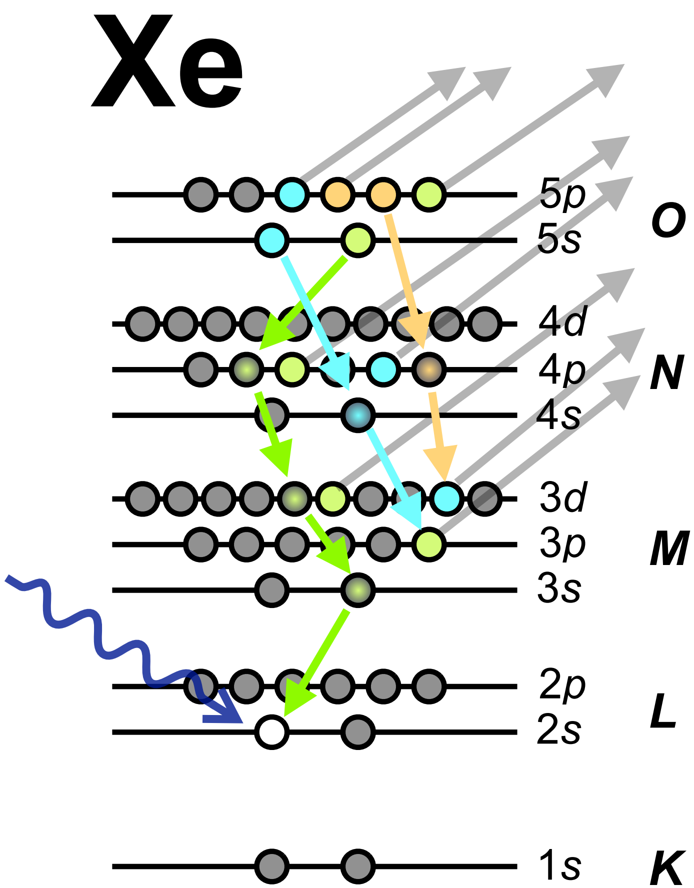
Interacting with *ultraintense* x-ray pulses



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

- First LCLS experiment: fundamental atomic physics in XFEL
- Lots of x-ray photons: repeated *K*-shell ionization (P) followed by Auger (A)

X-ray multiphoton ionization dynamics



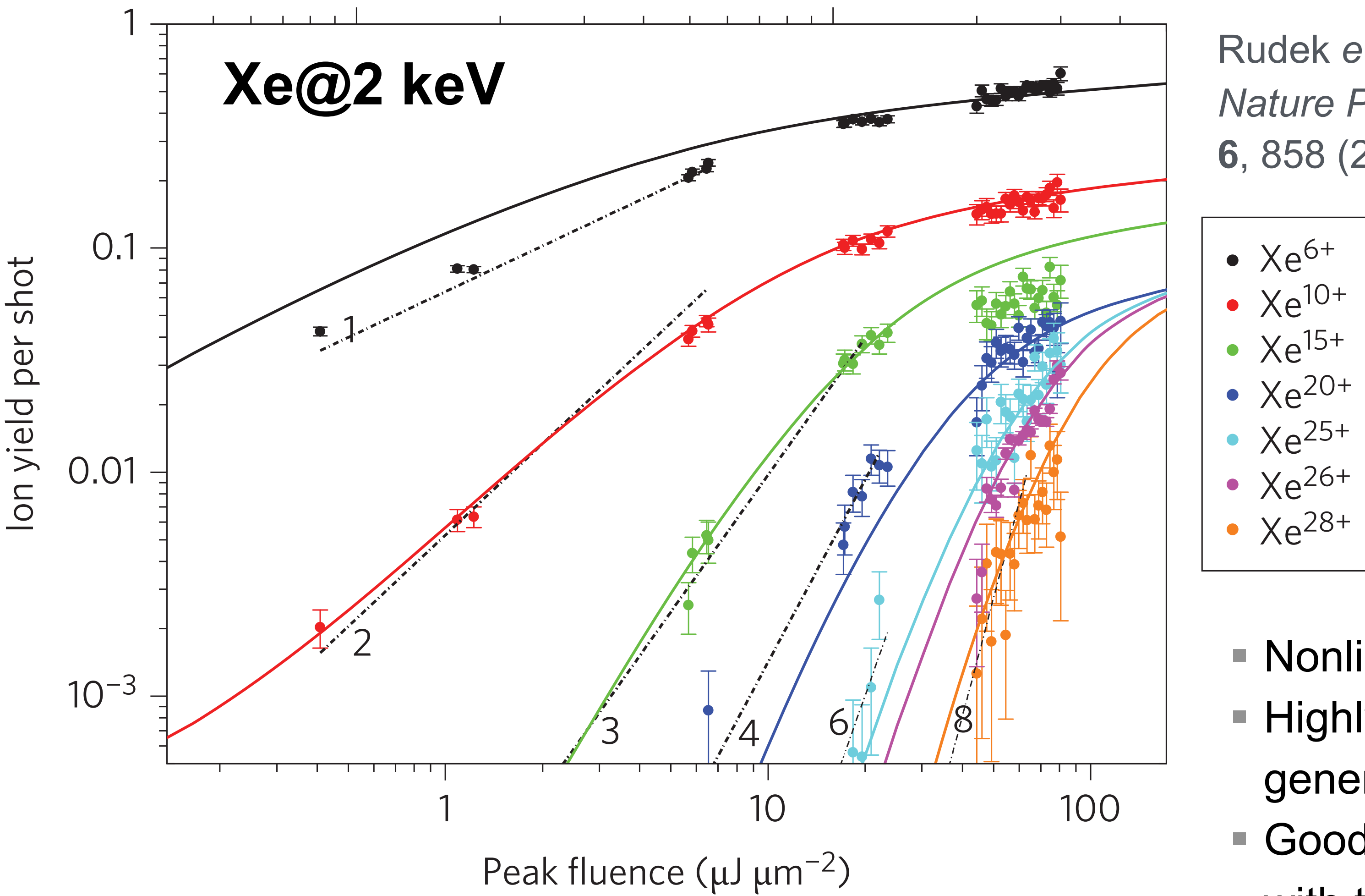
- Sequential multiphoton multiple ionization at high x-ray intensity
- Complicated ionization dynamics
- Highly excited electronic structure
- No standard code available

XATOM

- Efficient electronic structure calculation for every single electronic configuration
- Calculate all cross sections and rates
- Solve rate eqs for ionization dynamics

Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).
Jurek, Son, Ziaja & Santra, *J. Appl. Cryst.* **49**, 1048 (2016).

Quantitative comparison of ion yields



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

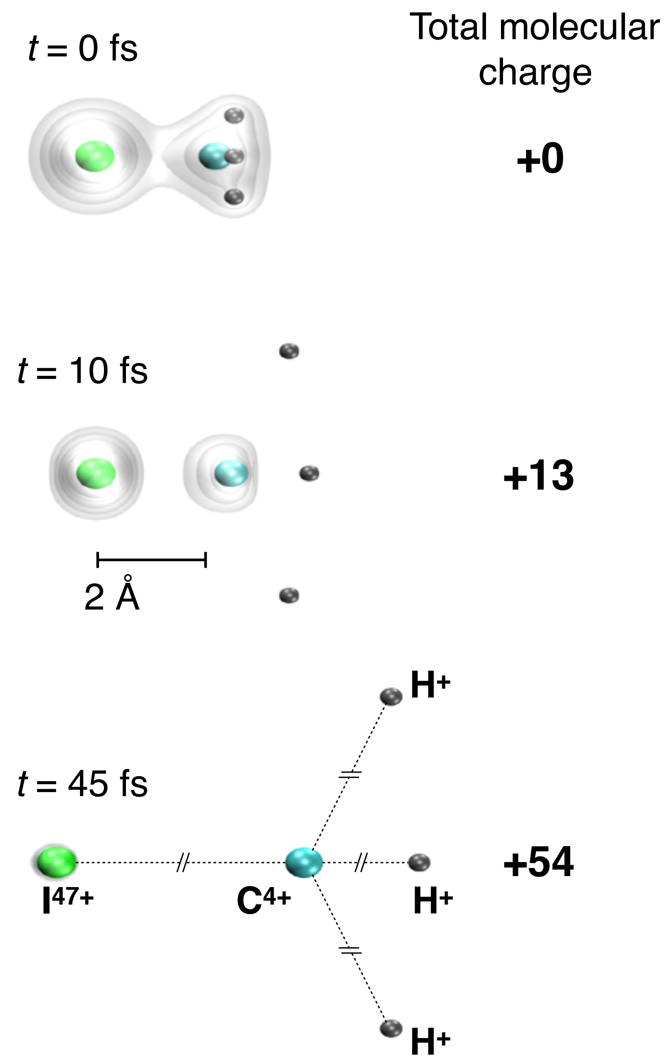
- Nonlinear behavior
- Highly charged ions generated
- Good agreement with theory

Challenges for molecular dynamics at XFEL

- No *ab initio* theoretical tools available
  - Coupled ionization and nuclear dynamics in the same time scales
  - Extremely complicated ionization dynamics
  - Highly excited electronic structure

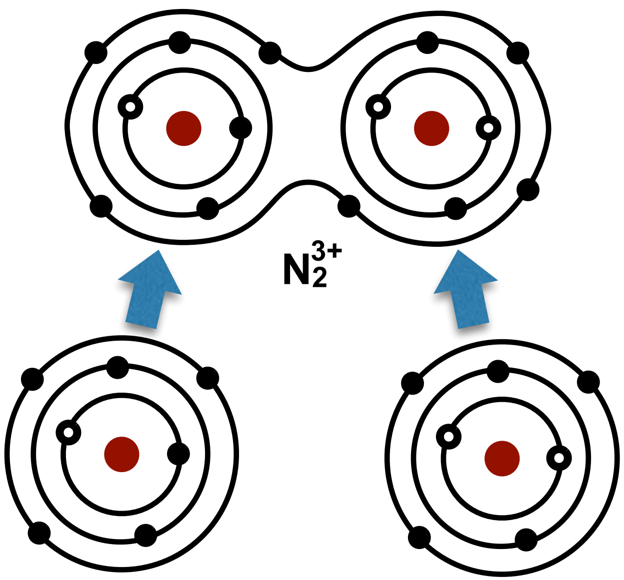
XMOLECULE

- Quantum electrons, classical nuclei
- Core-hole adapted basis functions
- Monte Carlo on the fly



XMOLECULE: Numerical details

- 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+}: $1s^0 2s^2 2p^3$

Yajiang Hao
Now at USTB (Beijing)

Kota Hanasaki
Now at Tohoku Univ.

Ludger Inhester

- Continuum states: approximated by atomic continuum calculated by XATOM
- Cross sections, rates, and gradients 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).

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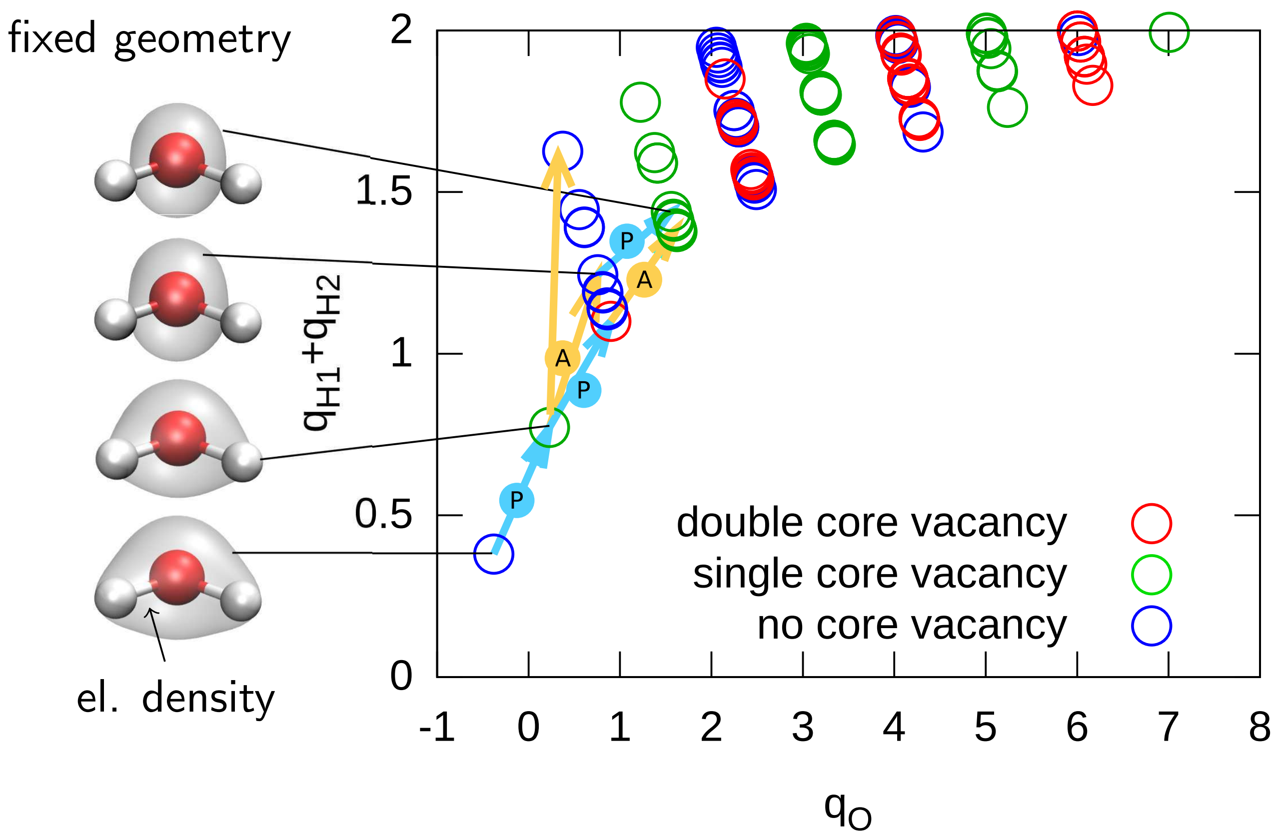
Ionization steps in a water molecule



Inhester, Hanasaki, Hao, Son & Santra, *Phys. Rev. A* **94**, 023422 (2016).

- *N* of electronic configurations for H_2O ➔ $3^5 = 243$
- *N* of electronic configurations for CH_3I ➔ 2×10^{14}

Iodomethane in *ultraintense* x-ray pulses

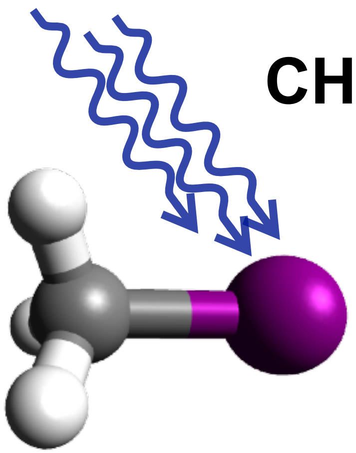
- New experimental setup: LCLS CXI using nano-focus
  ➔ new realm of intensity approaching ~2×10^{19} W/cm^2

Daniel Rolles
at KSU

Artem Rudenko
at KSU

Benjamin Erk
at DESY

Selective ionization on heavy atom



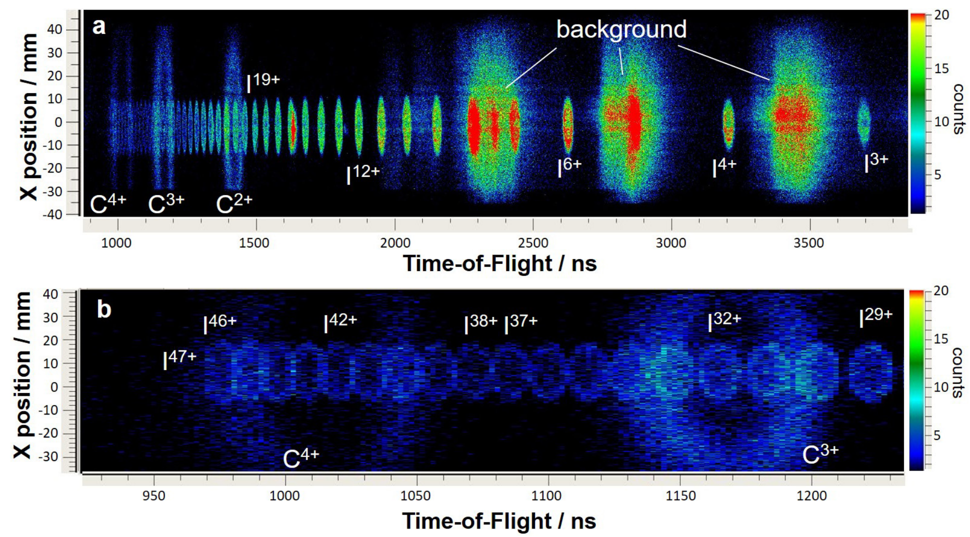
CH_3I @ 8.3 keV

σ(I)~50 kbarn

σ(C)~80 barn

σ(H)~8 mbarn

Measurement of ion ToF and hit position



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

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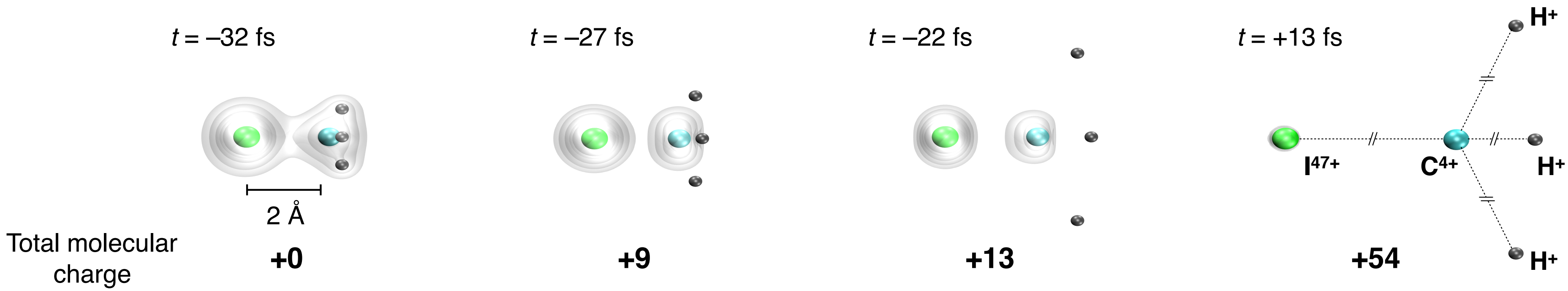
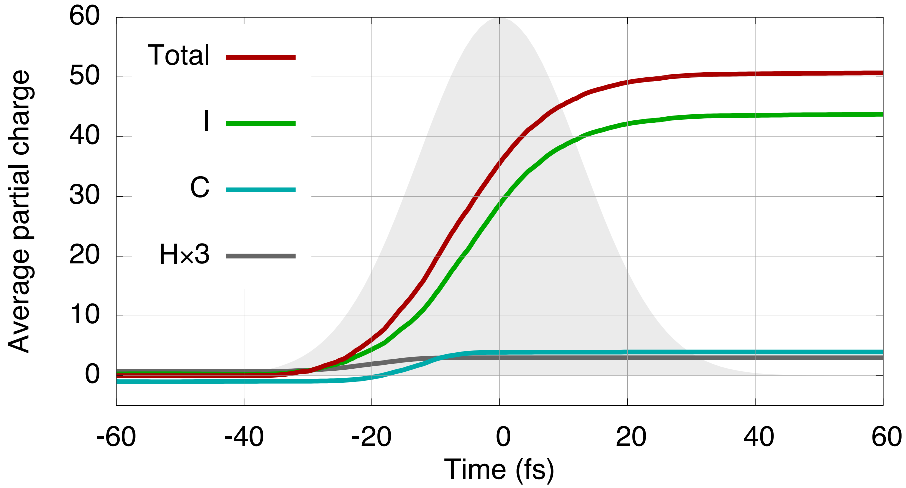
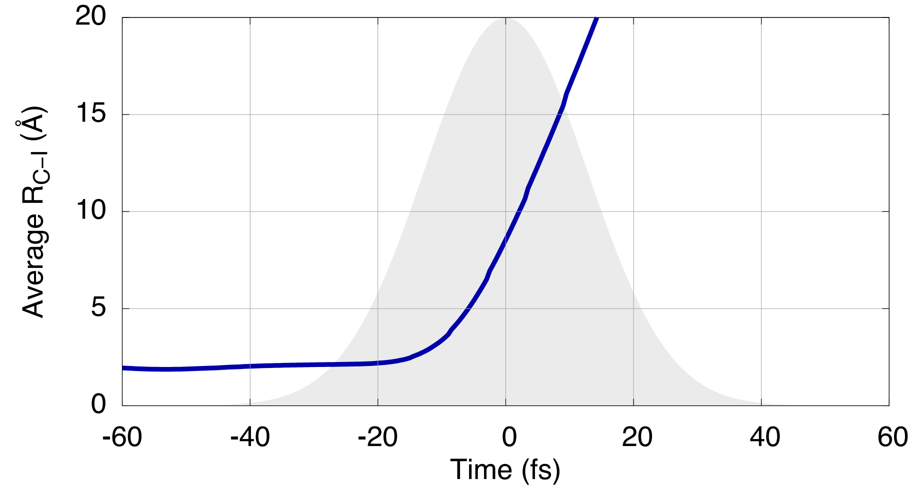
Capturing ultrafast explosion dynamics



Ionization dynamics



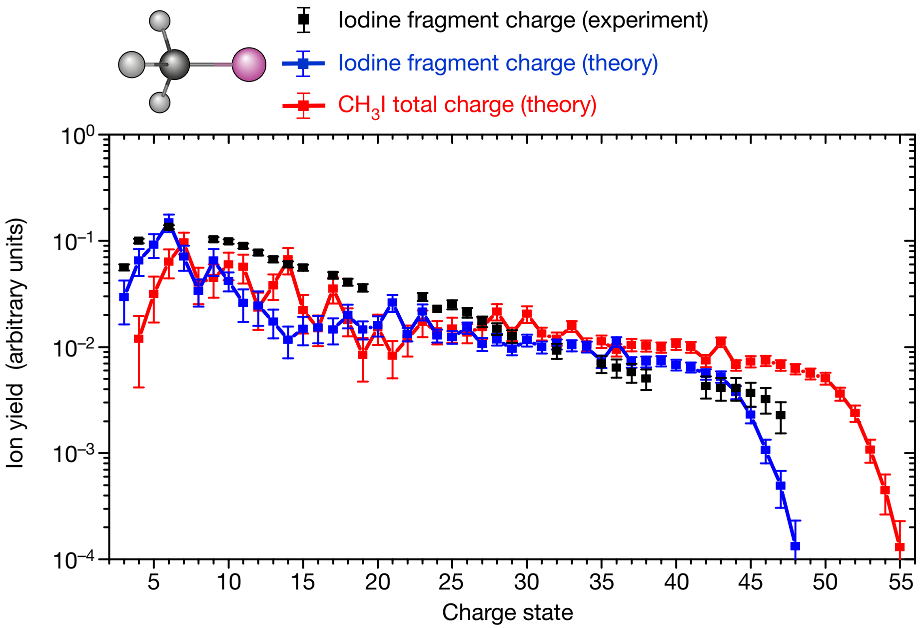
Nuclear dynamics



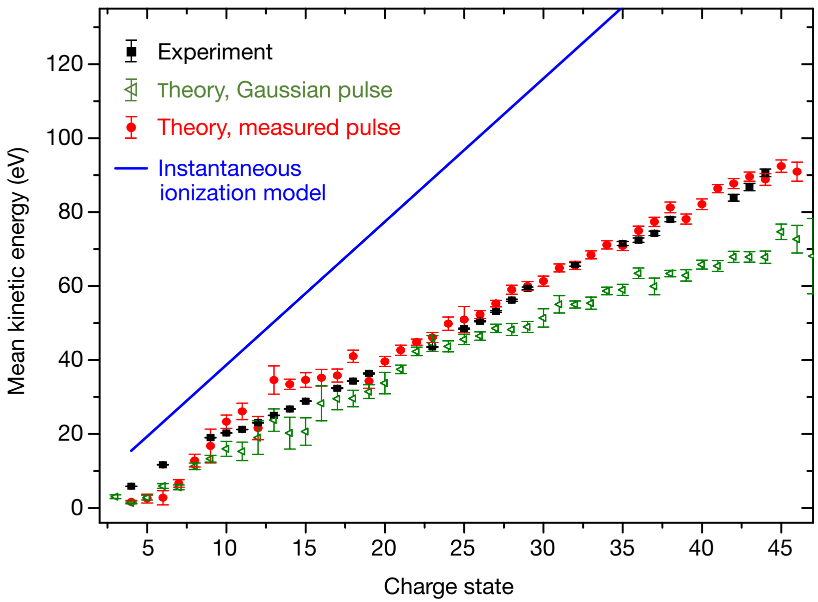
Rudenko *et al.*, *Nature* **546**, 129 (2017).

Comparison between theory & experiment

CSD of I and CH_3I



KER of I fragment



- CSD (charge-state distribution) and KER (Kinetic energy releases): sensitive to detailed ionization and fragmentation dynamics
- Capturing the essence of ionization and fragmentation dynamics of molecules at high x-ray intensity

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

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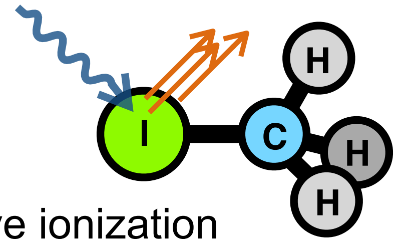
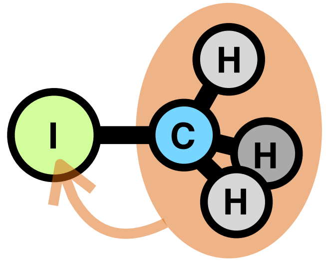
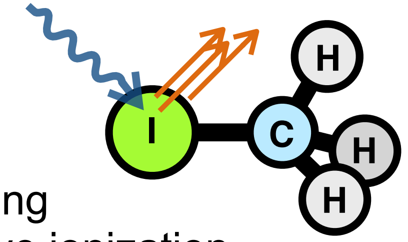
Ionization enhanced by charge rearrangement



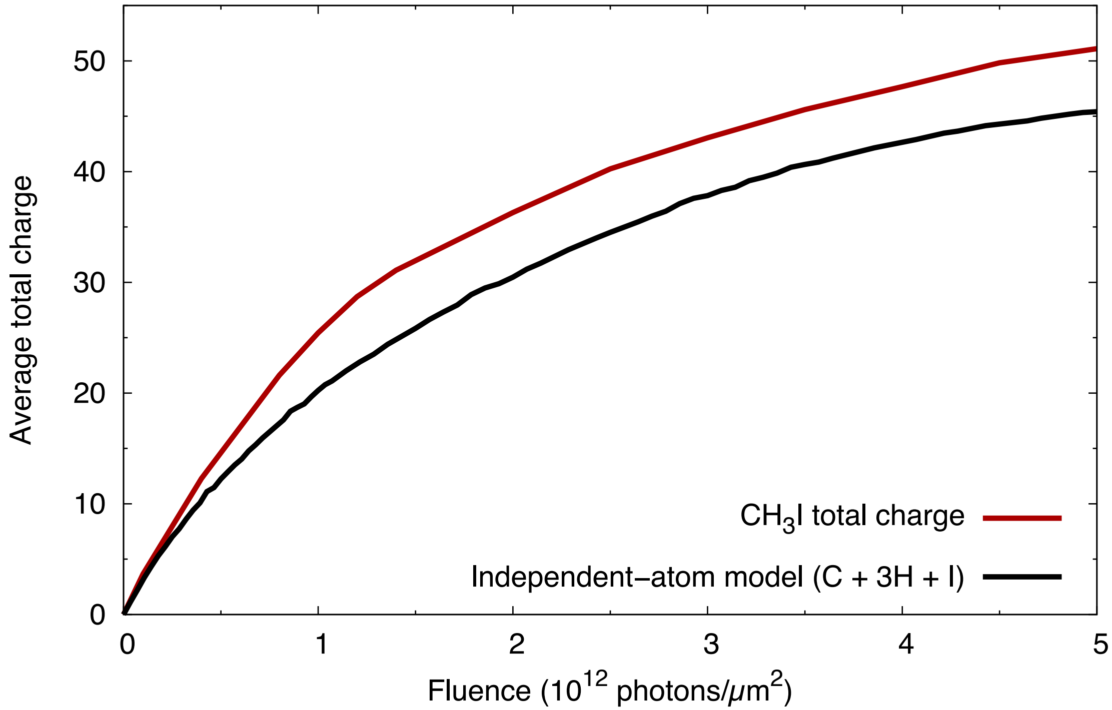
selective ionization
induces charge imbalance



charge rearrangement



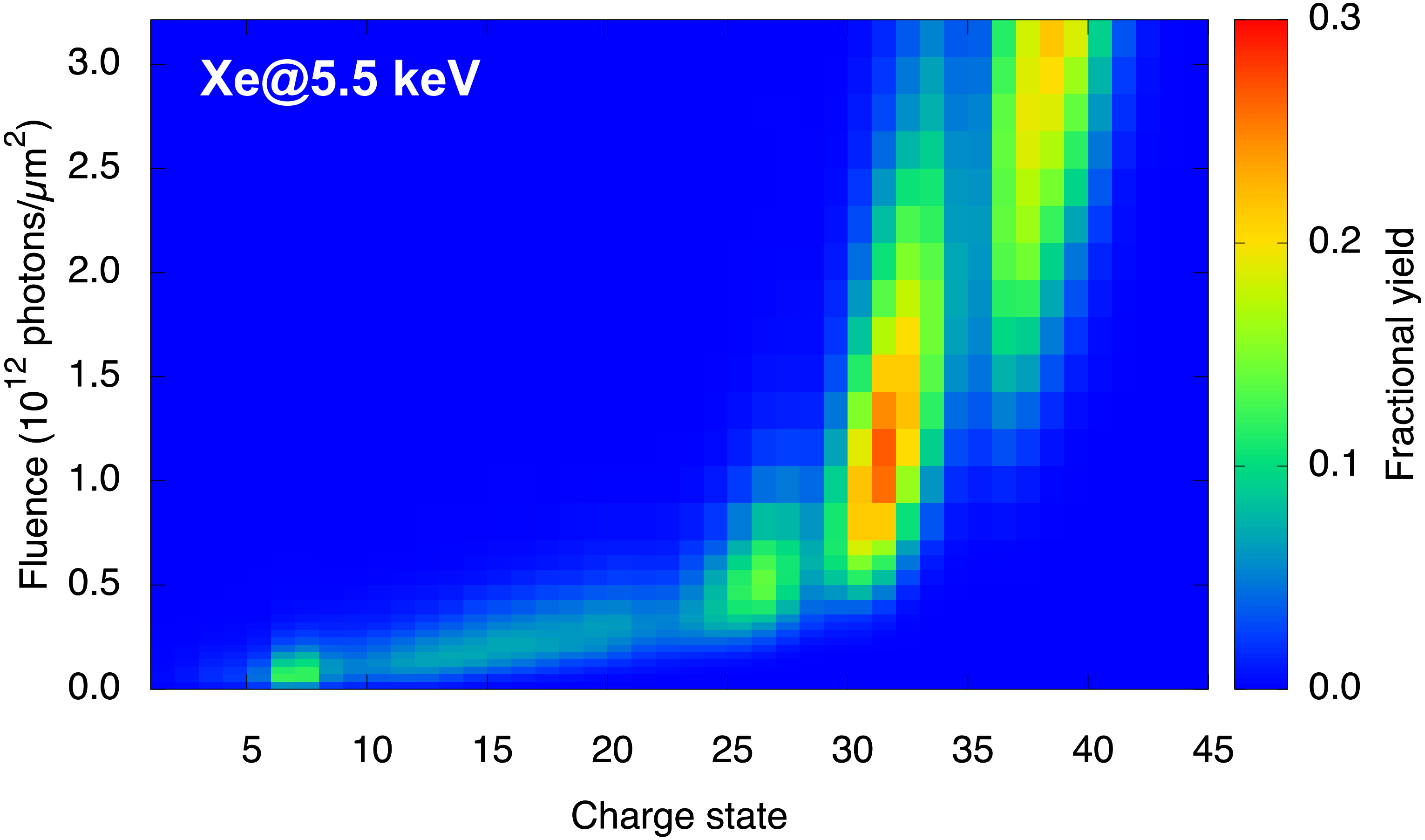
repeating
selective ionization



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

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

Back to the atom: resonance and relativity



Rudek, Toyota, *et al.*, (in preparation).

XATOM extended to resonance & relativity

- Relativistic energy correction within first-order perturbation theory

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

  - open new Coster-Kronig decay channels
  - close photoionization channels earlier
  - the closer to photon energy, the higher cross sections

XATOM development

Koudai Toyota

- Resonant photoexcitation cross section (REXMI)

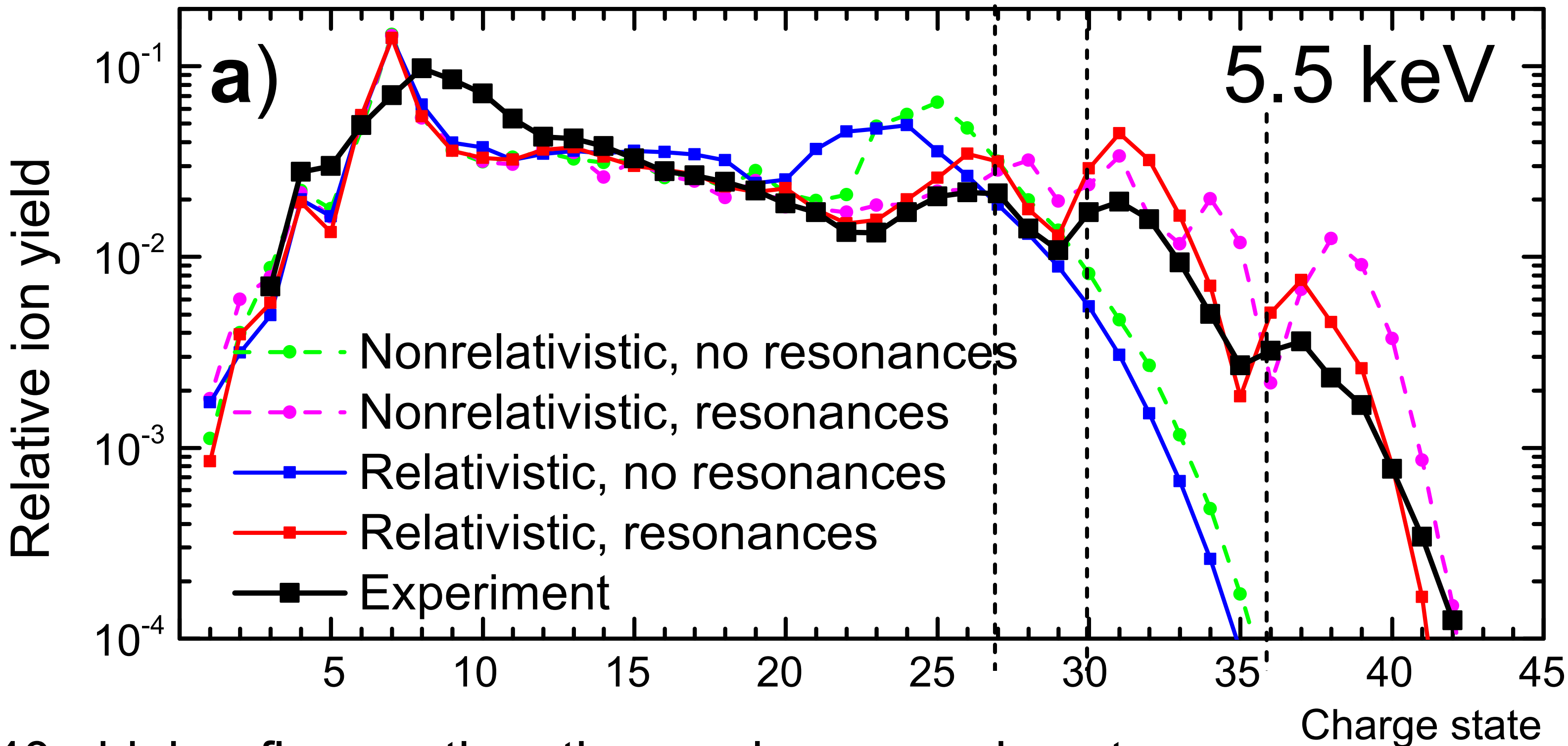
$$\sigma_{\mathrm{R}}(i,f,\omega_{\mathrm{in}}) = \frac{4}{3}\pi^2\alpha\omega_{\mathrm{in}} l_{>} N_i N_f^H \left\{ \begin{array}{ccc} l_i & s & j_i \\ j_f & 1 & l_f \end{array} \right\}^2 |\langle u_{n_f l_f}(r)|r|u_{n_i l_i}(r)\rangle|^2$$
$$\times\delta(E - E_{n_f l_f j_m} + E_{n_i l_i j_i})$$

- Numerical complexity for Xe with n_{max}=30 and l_{max}=7

➔ 10^{68} electronic configurations to be considered!

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

Comparison between theory & experiment



- ~40× higher fluence than the previous experiment
- REXMI shows characteristic three peak structure
- Importance of interplay between resonance and relativistic effects

Rudek, Toyota, *et al.*, (in preparation).

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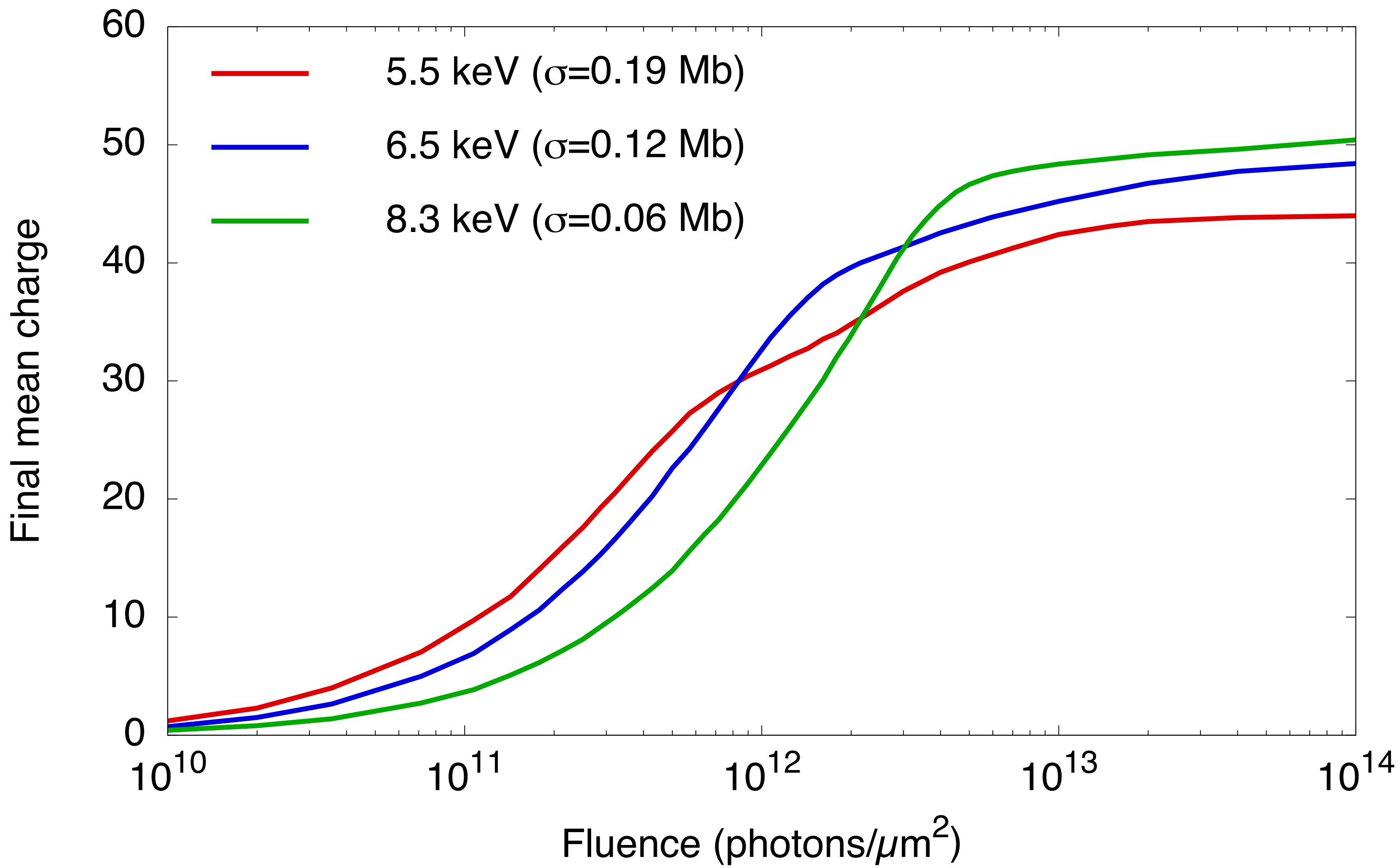
Predictive power of the ionization degree

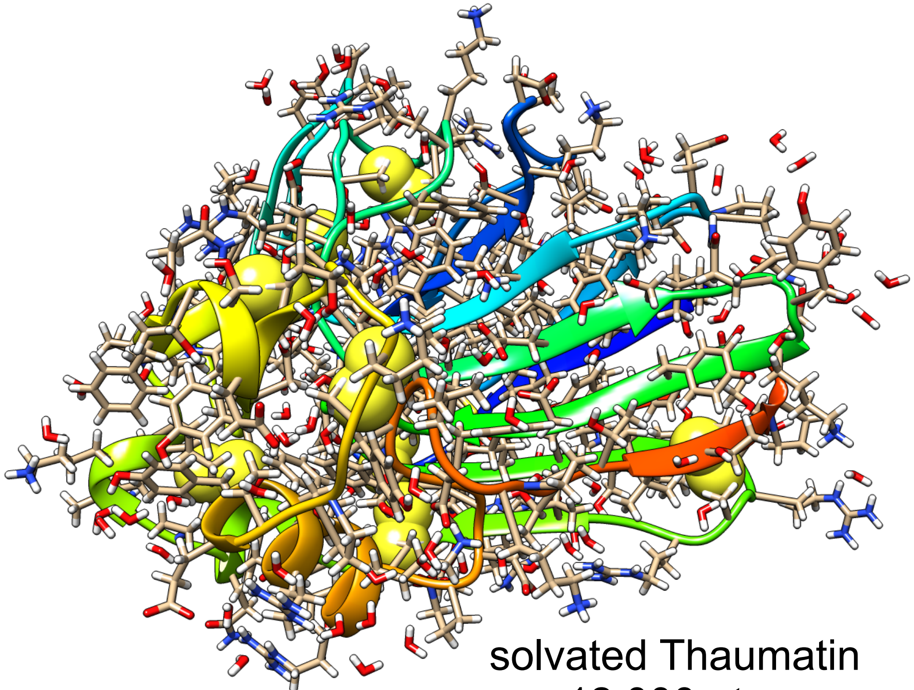


Rudek, Toyota, *et al.*, (in preparation).

Towards complex systems: XMDYN

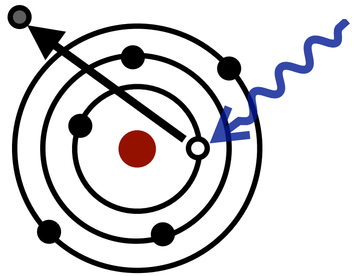
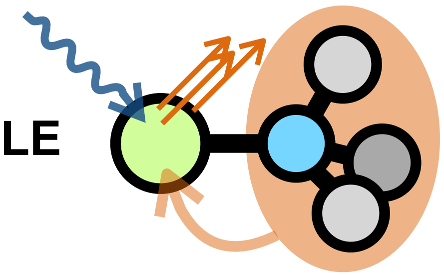

Zoltan Jurek


Malik M. Abdullah


solvated Thaumatin
~ 12,000 atoms

- **XMDYN**: X-ray molecular dynamics
  - Classical dynamics for ions and free electrons
  - Quantum treatment for bound electrons ➔ combined with XATOM
- First validation with LCLS (C_{60}) and SACLA (Ar/Xe clusters) experiments
  - Murphy *et al.*, *Nature Commun.* **5**, 4281 (2014).
  - Tachibana *et al.*, *Sci. Rep.* **5**, 10977 (2015).
- 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).

Conclusion

XATOM  XMOLECULE 

- Enabling tools to investigate x-ray multiphoton physics of atoms and molecules exposed to intense XFEL pulses
- Nonlinear behavior of atomic and molecular responses to intense x-rays
- Molecular ionization enhancement (CREXIM) for CH_3I:
  First quantitative comparison for molecules under XFEL irradiation
- Interplay of resonance and relativistic effects for Xe:
  First quantitative comparison for REXMI in atoms under XFEL irradiation
- New phenomena to be taken into account for future XFEL applications

Collaboration of CH_3I and Xe projects

Experiment team

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

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

PTB, Braunschweig B. Rudek

MPI for Medical Research, Heidelberg L. Foucar

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

UPMC, Paris T. Marchenko, M. Simon

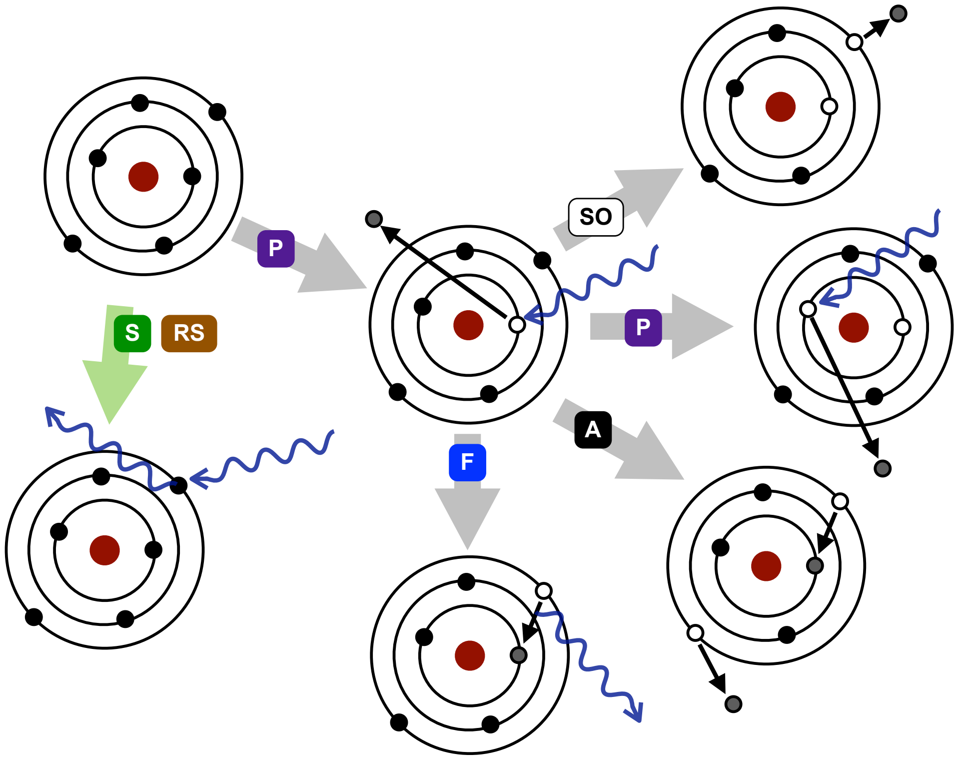
Tohoku University, Sendai K. Ueda

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

Theory team

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

XATOM and XMDYN are available



Jurek, Son, Ziaja & Santra,
J. Appl. Cryst. **49**, 1048 (2016).
Download executables of
XATOM and XMDYN:
https://www.desy.de/~xraypac/

Thank you for your attention!

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DESY