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

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

---

Topical conference on Indian Society of Atomic and Molecular Physics
IISER/IIT Tirupati, India, January 6–8, 2018

XATOM and XMOLECULE developers

Yajiang Hao
Now at USTB (Beijing)

Ludger Inhester

Kota Hanasaki
Now at Tohoku Univ.

Koudai Toyota

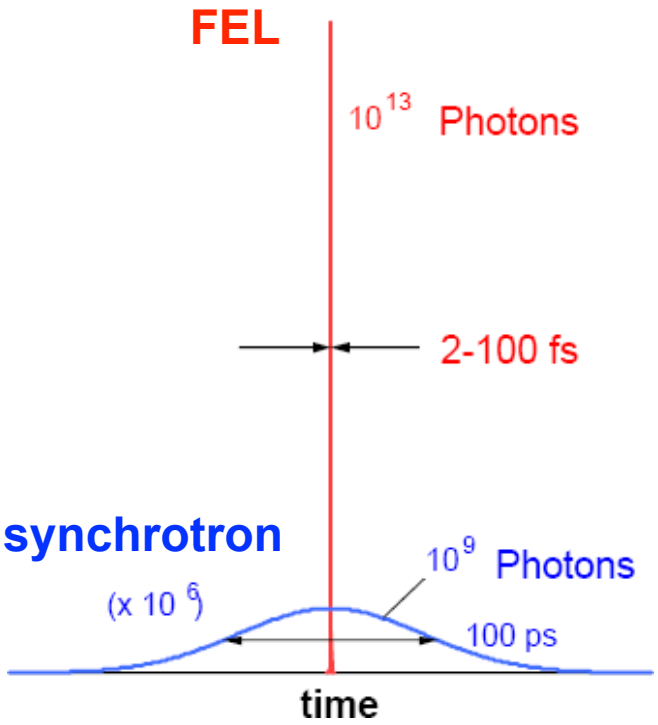
Sang-Kil Son

Oriol Vendrell
Now at Aarhus Univ.

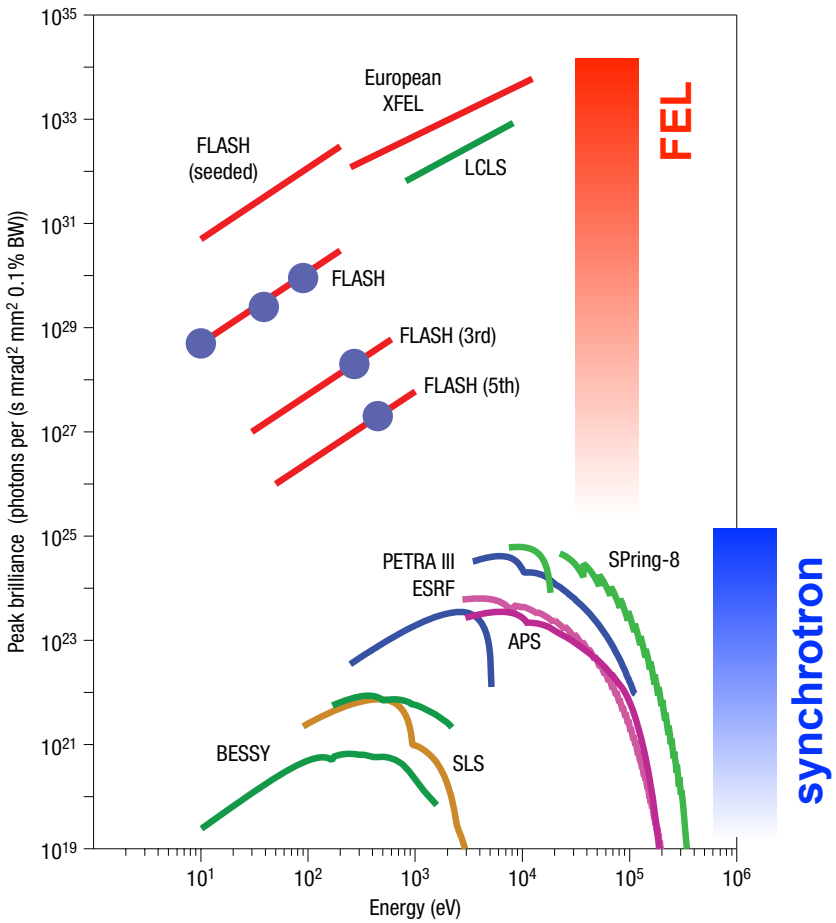
Robin Santra

XFEL: X-ray free-electron laser

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



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



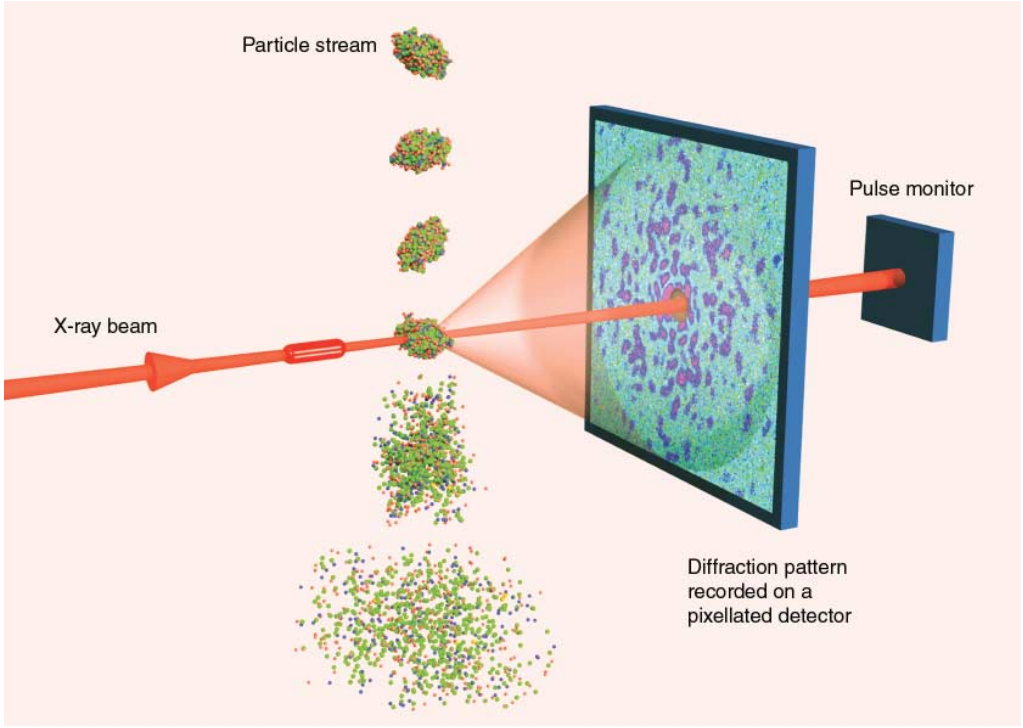
Ackermann *et al.*, *Nature Photon.* **1**, 336 (2007).

Where are XFELs?

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

Why *ultraintense* and *ultrafast*?

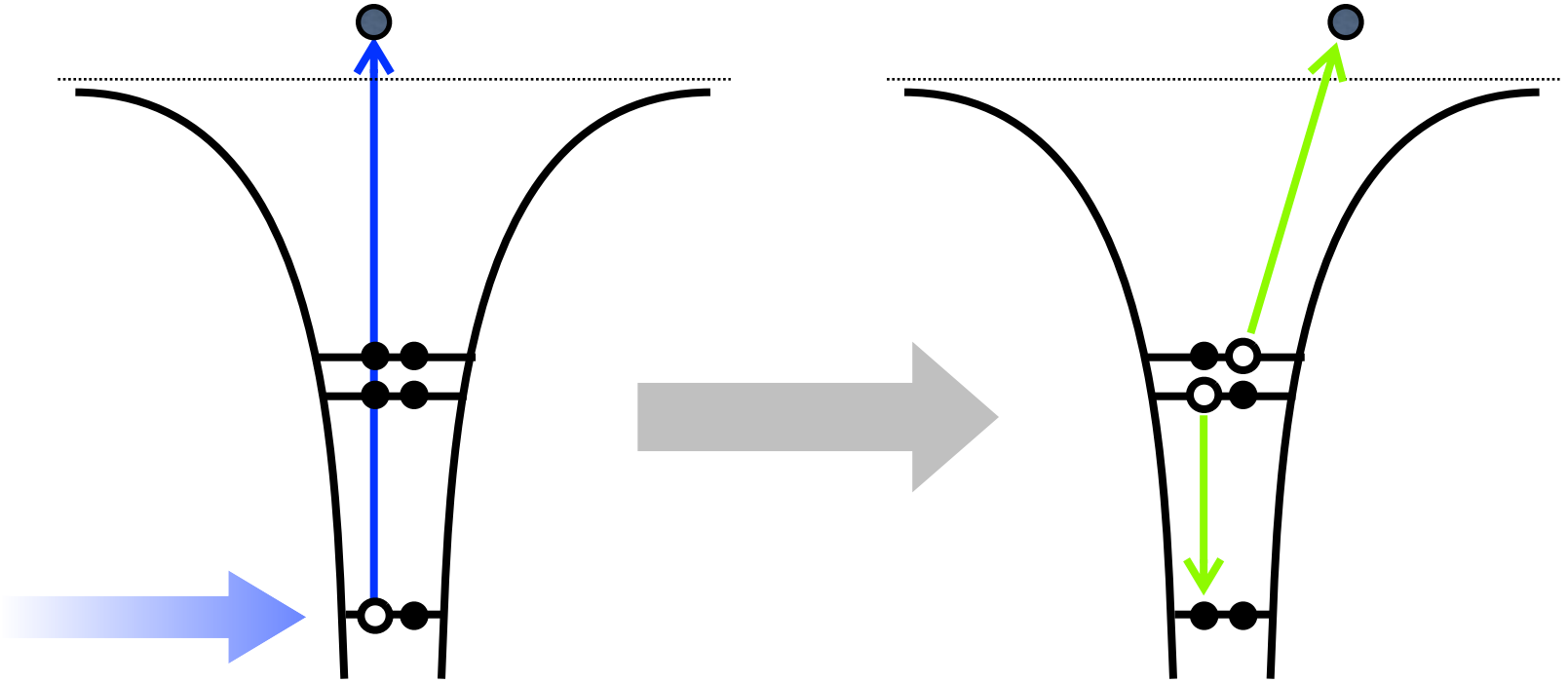
- Structural determination of biomolecules with x-rays
  ➔ X-ray crystallography
- Growing high-quality crystals is one of major bottlenecks
- Enough signals obtained from even single molecules by using *ultraintense* pulses
- Signals obtained before radiation damage by using *ultrafast* pulses



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

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

Fundamental x-ray–matter interaction

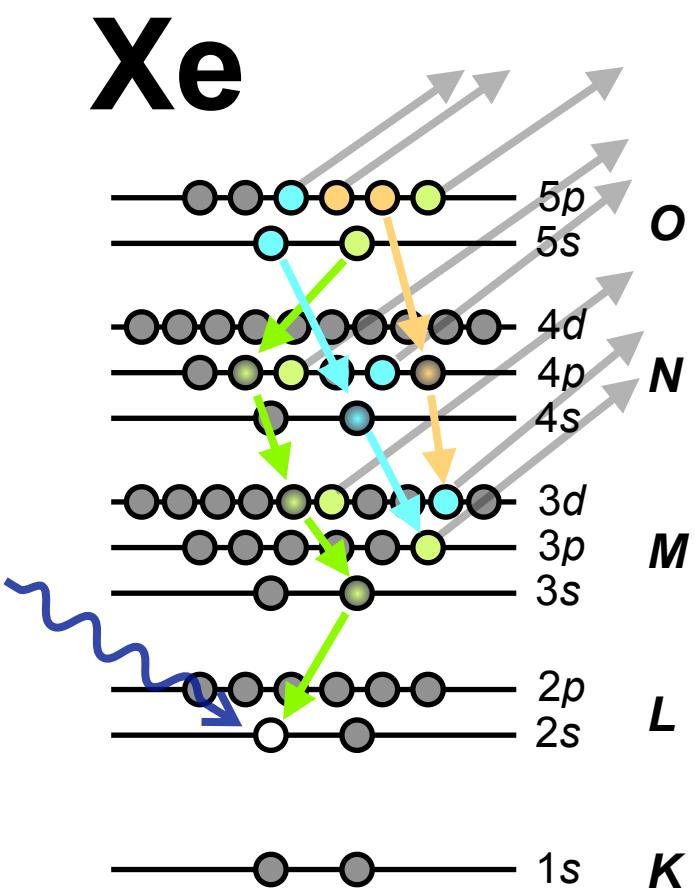


Photoionization: $C \rightarrow C^{*+} + e^-$

Auger decay: $C^{*+} \rightarrow C^{++} + e^-$

synchrotron: one-photon absorption ➔ **PA** ➔ C^{2+}
XFEL: many-photon absorption ➔ **PAPAPP** ➔ C^{6+}

X-ray multiphoton multiple ionization



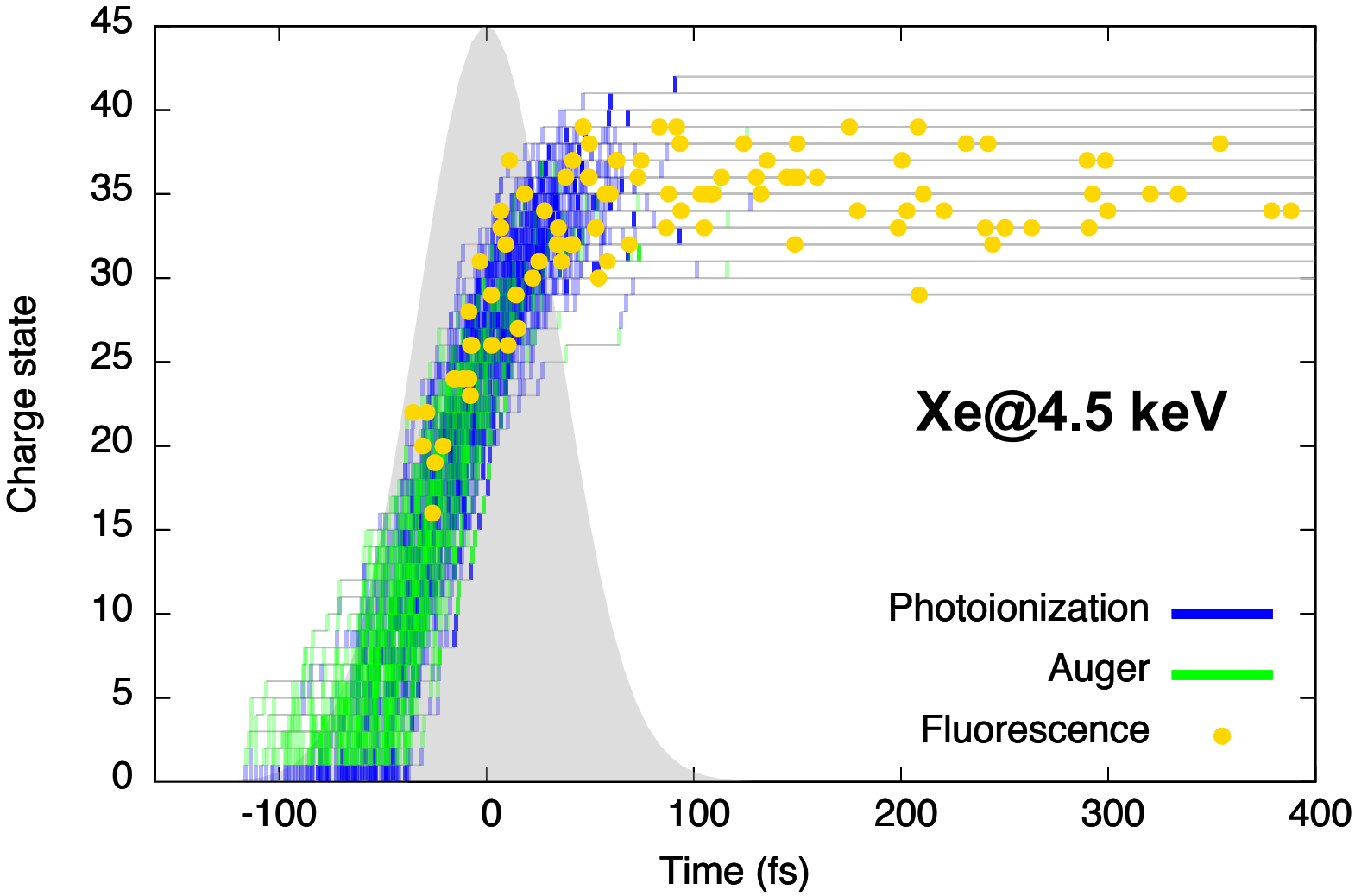
- Sequential multiphoton multiple ionization at high x-ray intensity
- Extremely complicated ionization dynamics
- Highly excited electronic structure
- No standard code available

XATOM

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

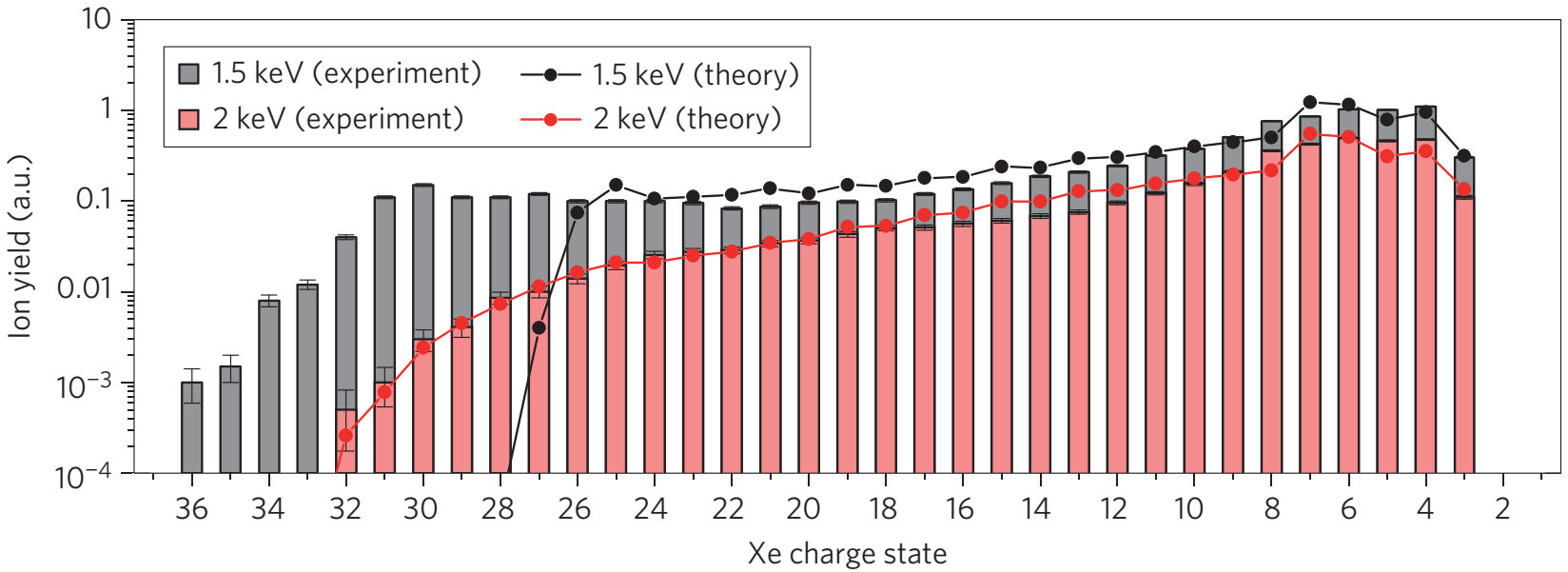
Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).
Jurek, Son, Ziaja & Santra, *J. Appl. Cryst.* **49**, 1048 (2016).

X-ray multiphoton ionization dynamics



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

Comparison between theory & experiment

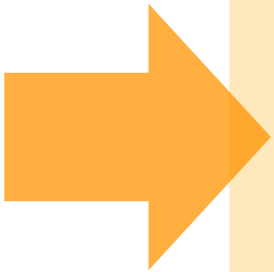


- Xe at LCLS: *M*-shell ionization — Rudek *et al.*, *Nature Photon.* **6**, 858 (2012).
  - 2 keV: excellent agreement between theory and experiment
  - 1.5 keV: further ionization via resonance (REXMI)
- Xe at SACLA: deeper inner-shell — Fukuzawa *et al.*, *PRL* **110**, 173005 (2013).
- Recent study of interplay between resonance and relativistic effects

  Toyota, Son & Santra, *PRA* **95**, 043412 (2017); Rudek *et al.*, in preparation.

Challenges for molecular dynamics at XFEL

- No *ab initio* theoretical tools available for 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
  - 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

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

Iodomethane in *ultraintense* x-ray pulses

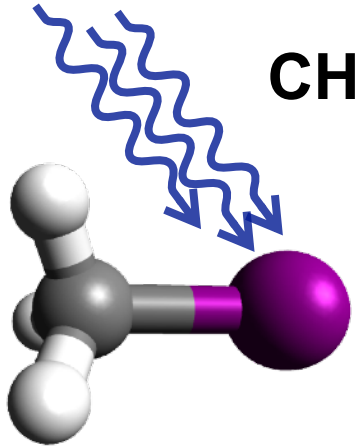
- New experimental setup:
  LCLS CXI using nano-focus
  ➔ new realm of intensity
  approaching ~2×10^{19} W/cm^2

LCLS experiment

Daniel Rolles
at KSU

Artem Rudenko
at KSU

Selective ionization on heavy atom



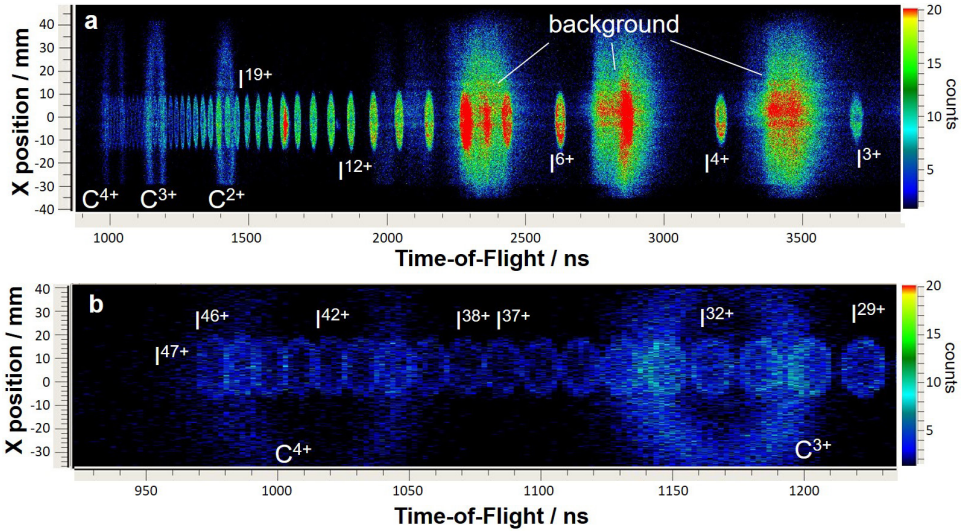
CH_3I @ 8.3 keV

σ(I)~50 kbarn

σ(C)~80 barn

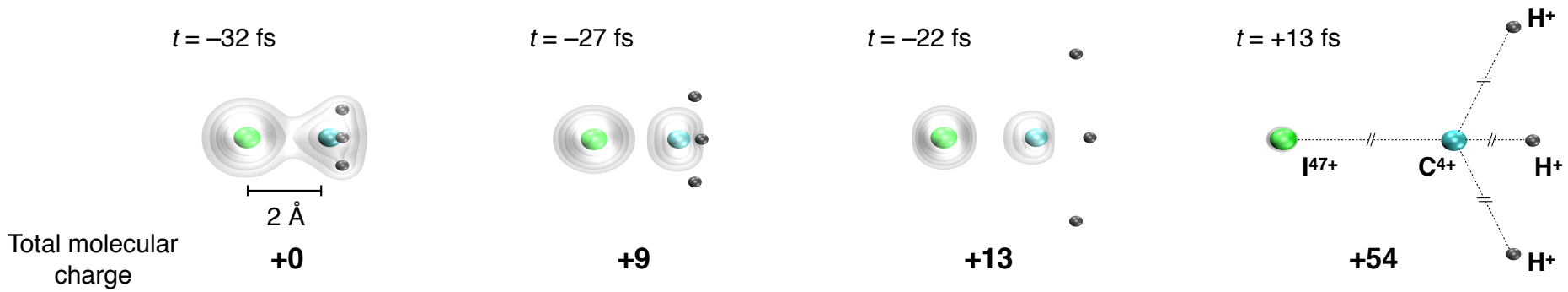
σ(H)~8 mbarn

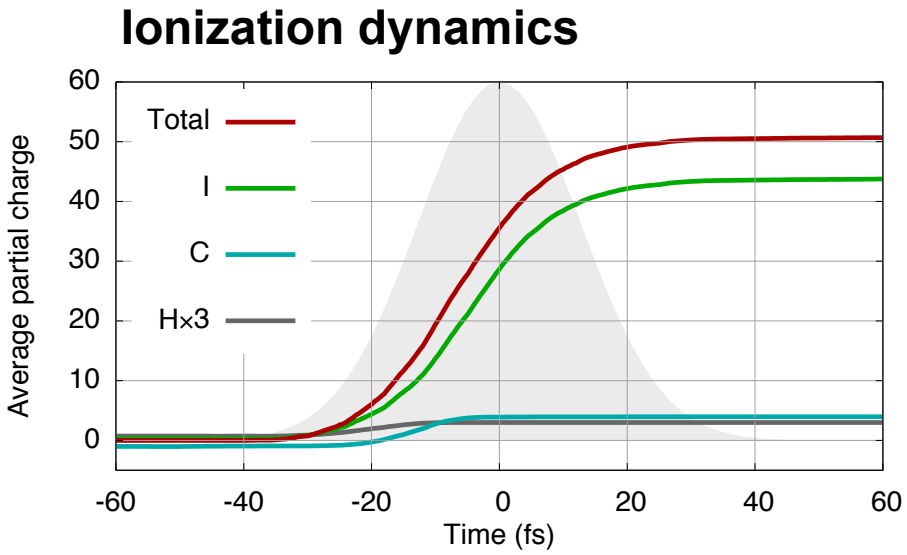
Measurement of ion ToF and hit position

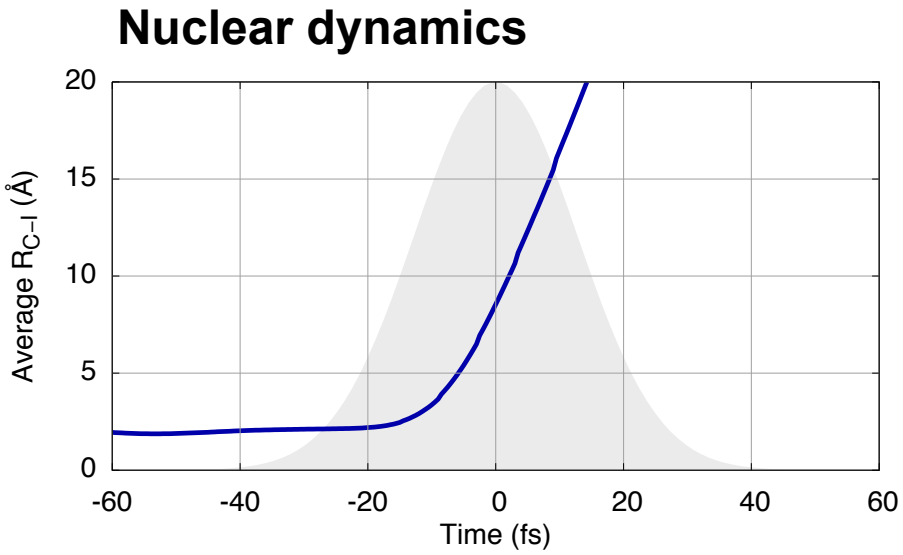


Rudenko *et al.*, *Nature* **546**, 129 (2017).

Capturing ultrafast explosion dynamics



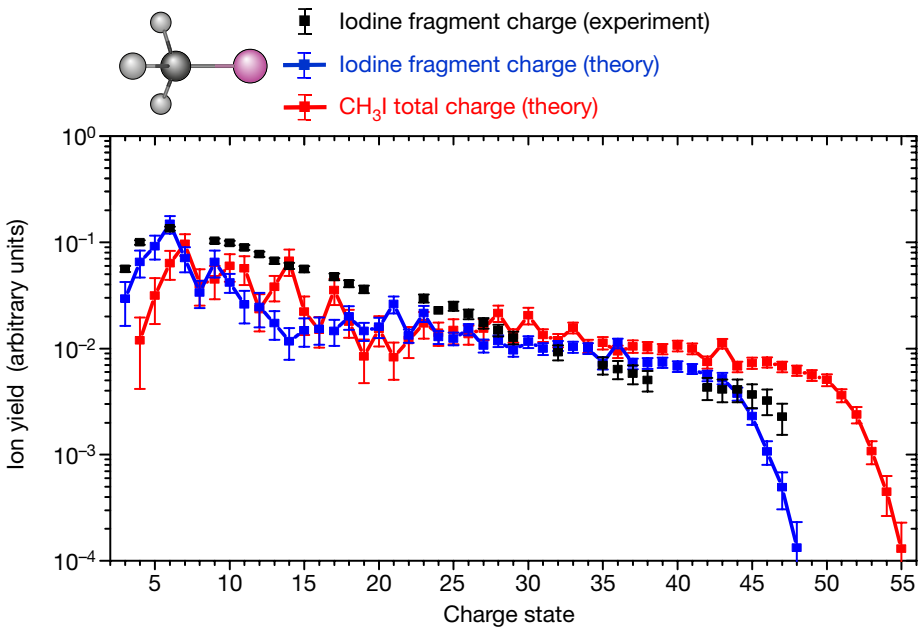




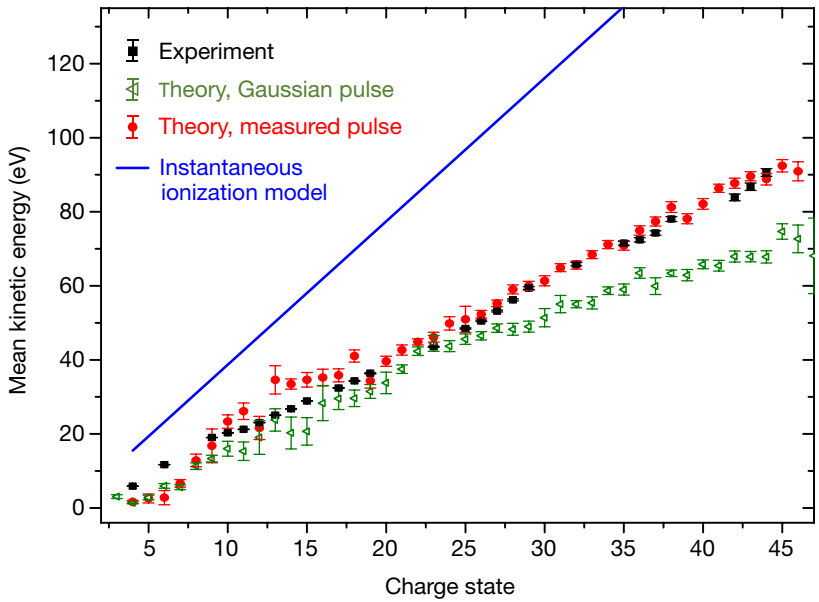
Rudenko *et al.*, *Nature* **546**, 129 (2017).

Comparison between theory & experiment

CSD of I and CH_3I



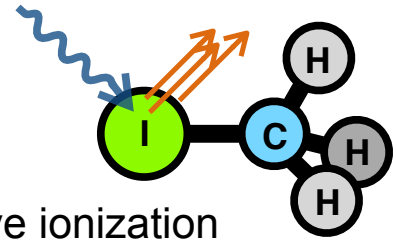
KER of I fragment



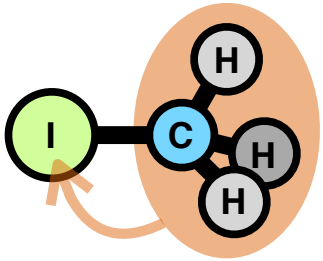
- CSD (charge-state distribution) and KER (Kinetic energy releases): sensitive to detailed ionization and fragmentation dynamics
- Capturing the essence of ionization and fragmentation dynamics of molecules at high x-ray intensity

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

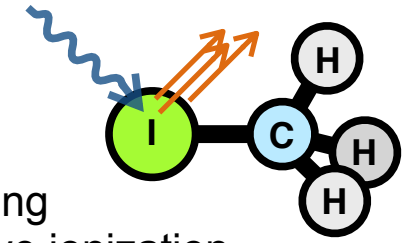
Ionization enhanced by charge rearrangement



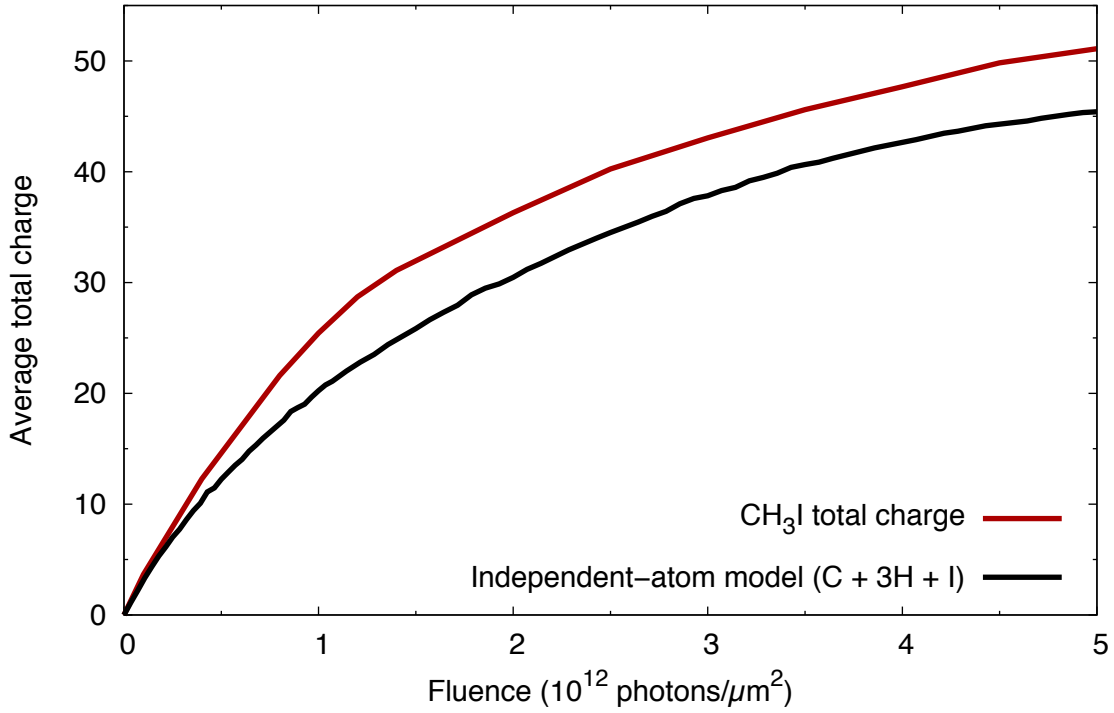
selective ionization
induces charge imbalance



charge rearrangement



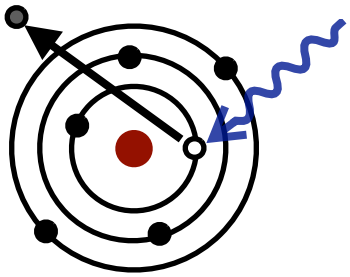
repeating
selective ionization

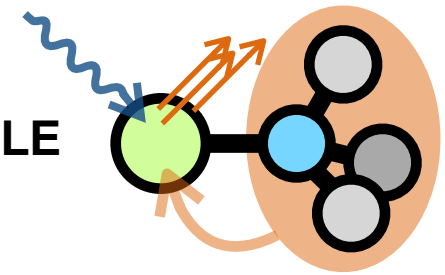


CREXIM: Charge-Rearrangement-Enhanced X-ray Ionization of Molecules

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

Conclusion

XATOM 

XMOLECULE 

- Enabling tools to investigate x-ray multiphoton physics of atoms and molecules exposed to high intensity x-ray pulses
- X-ray-induced ultrafast explosion dynamics of CH_3I:
  First quantitative comparison for molecules under XFEL irradiation
- Observed a new phenomenon, CREXIM, and identified its mechanism
- Impact on molecular imaging: not reducing partial charges of heavy atoms due to charge rearrangement, but inducing more ionization overall
  ➔ To be taken into account for future XFEL applications

Collaboration of this project

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

Thank you for your attention!

CFEL SCIENCE

DESY