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

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HELMHOLTZ ASSOCIATION

CFEL SCIENCE

Center for Free-Electron Laser Science
CFEL is a scientific cooperation of the three organizations:
DESY – Max Planck Society – University of Hamburg

DESY

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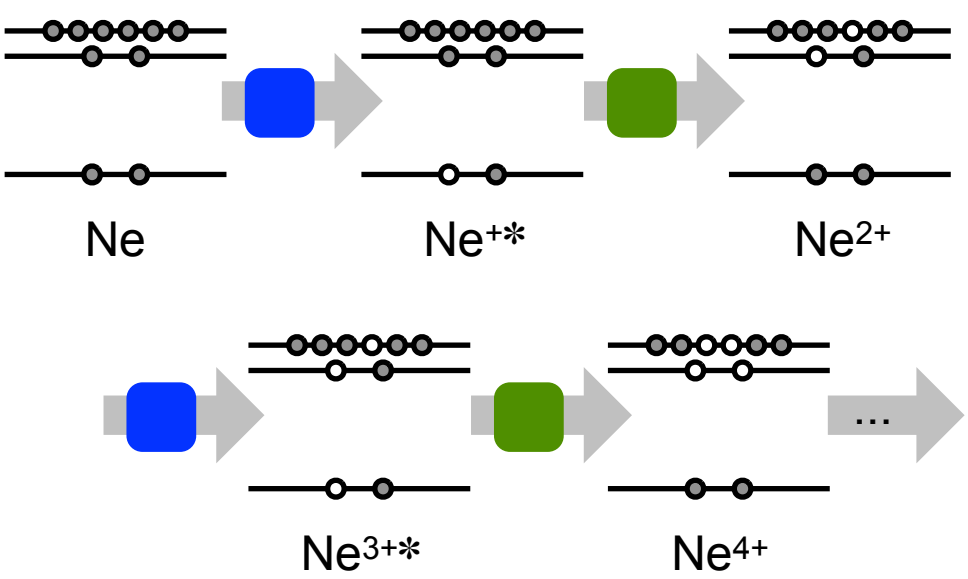
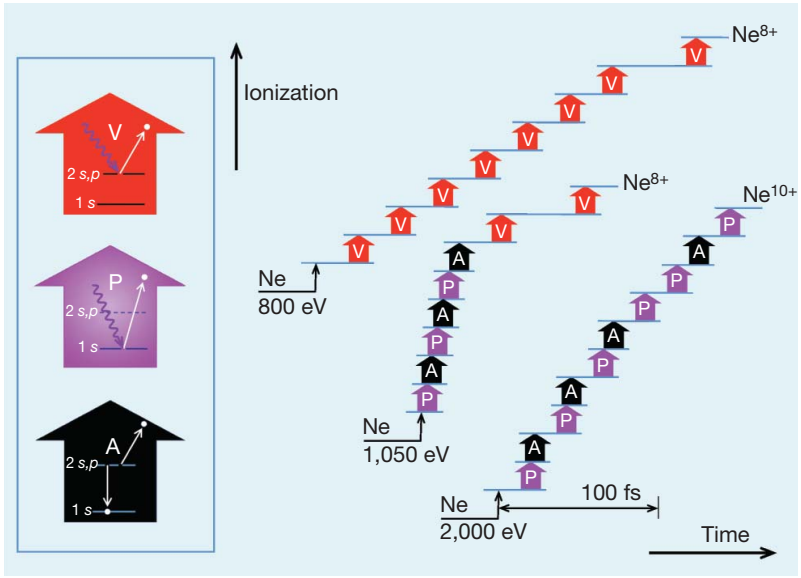
X-ray multiphoton absorption

- XFEL delivers ultraintense and ultrafast x-ray pulses.
- Direct multiphoton absorption cross section is too small.

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

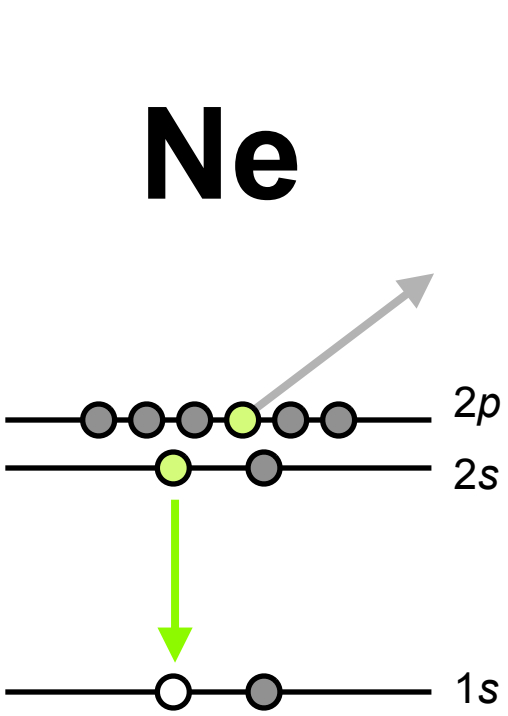
- Sequential multiphoton absorption is dominant.

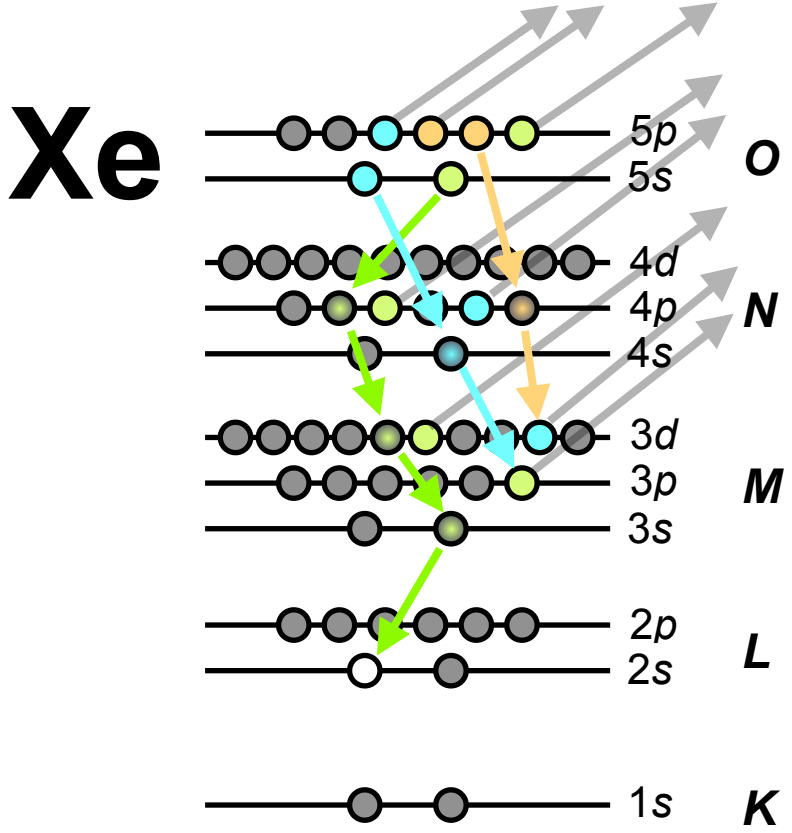




Young *et al.*, *Nature* **466**, 56 (2010).

Complex inner-shell decay cascade



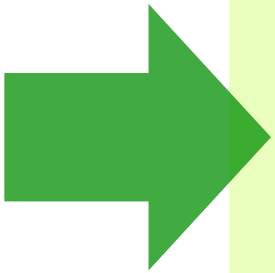


Multiphoton absorption after/during decay cascade

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

Challenges for x-ray multiphoton ionization

- No standard quantum chemistry code available
  - tremendously many hole states by x-ray multiphoton ionization
  - highly excited electronic structure / electronic continuum states
  - complex multiphoton multiple ionization dynamics

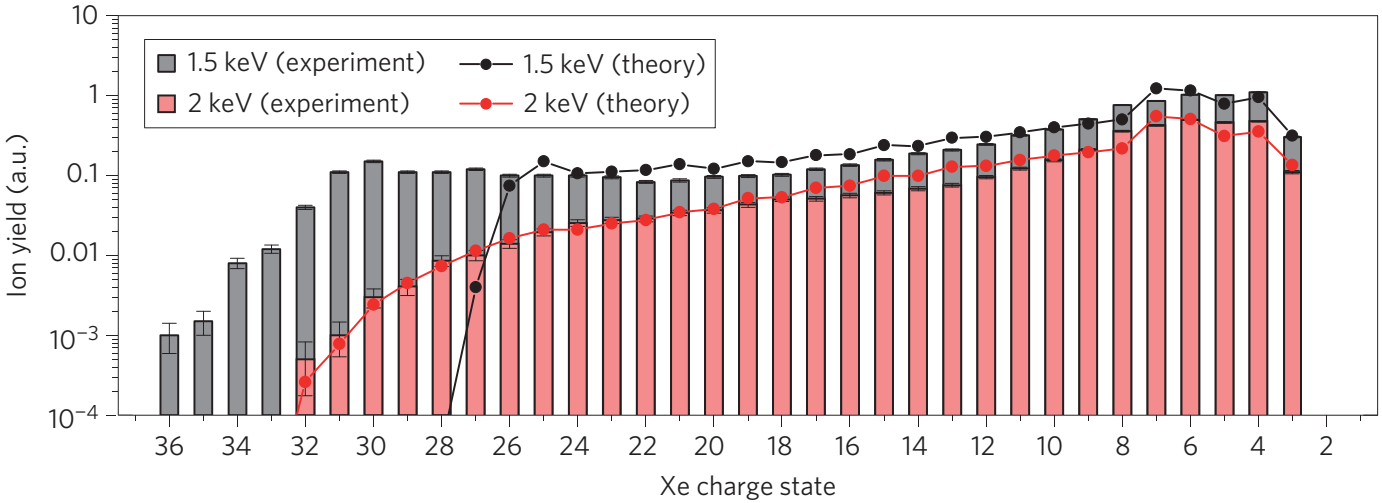


XATOM

- Hartree-Fock-Slater method for every single configuration
- numerical grid method for both bound and continuum states
- rate-equation model for ionization dynamics
- Monte Carlo approach to solve a huge set of rate equations

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

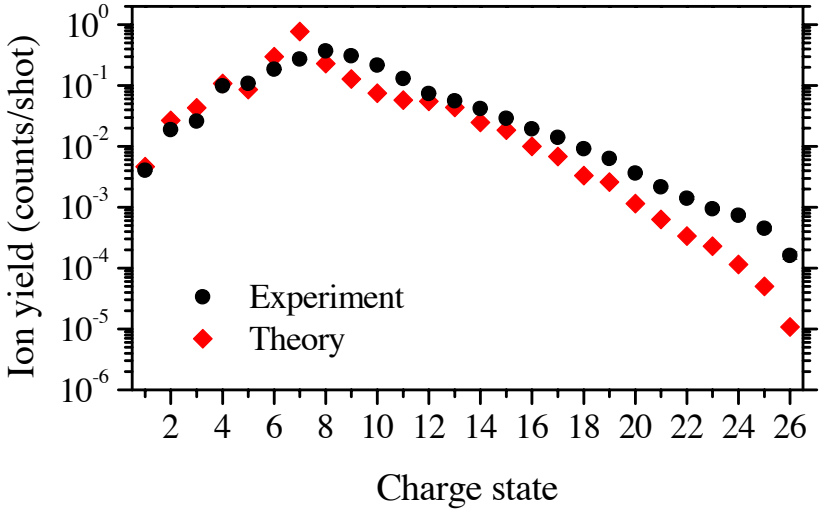
Comparison b/w theory and experiment



Xe at LCLS

- 1.5 keV: ~Xe^{36+}
- 2.0 keV: ~Xe^{32+}

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



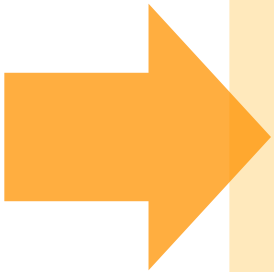
Xe at SACLA, 5.5 keV: ~Xe^{26+}

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

Sequential multiphoton multiple ionization model has been tested by a series of gas-phase XFEL experiments: Ne, Ar, Kr, Xe, …

Challenges for molecular dynamics at XFEL

- No *ab initio* theoretical tools available for high x-ray intensity
  - formidable task: e.g. CH_3I ~ 200 trillion coupled rate equations
  - highly excited molecular electronic structure
  - coupled ionization and nuclear dynamics in the same time scales

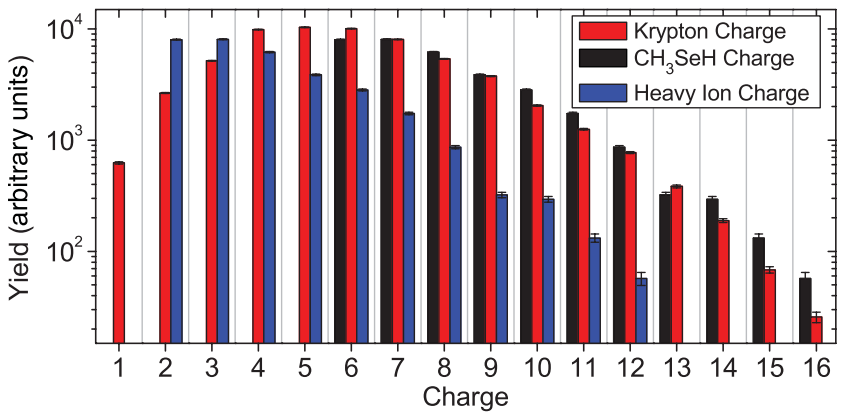


XMOLECULE

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

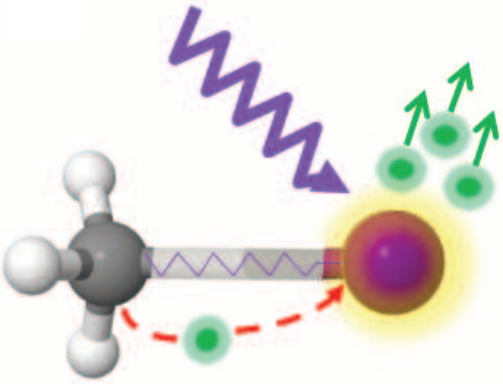
Hao, Inhester, Hanasaki, Son & Santra, *Struc. Dyn.* **2**, 041707 (2015).
Inhester, Hanasaki, Hao, Son & Santra, *Phys. Rev. A* **94**, 023422 (2016).

Molecules at low x-ray 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

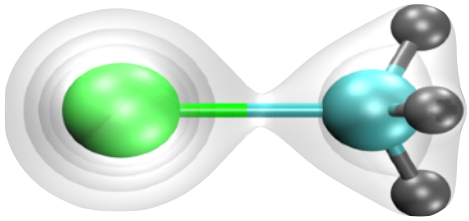
- New experimental setup:
  LCLS CXI using nano-focus
  ➔ new realm of intensity
  approaching ~10^{20} W/cm^2
- Selective ionization on heavy atom

LCLS experiment

Daniel Rolles
at KSU

Artem Rudenko
at KSU

CH_3I @ 8.3 keV



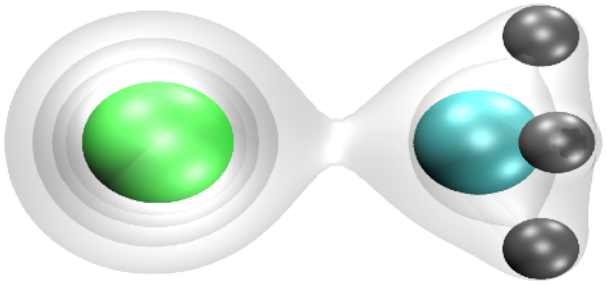
σ(I)~50 kbarn
σ(C)~80 barn
σ(H)~8 mbarn

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

Coulomb explosion of iodomethane

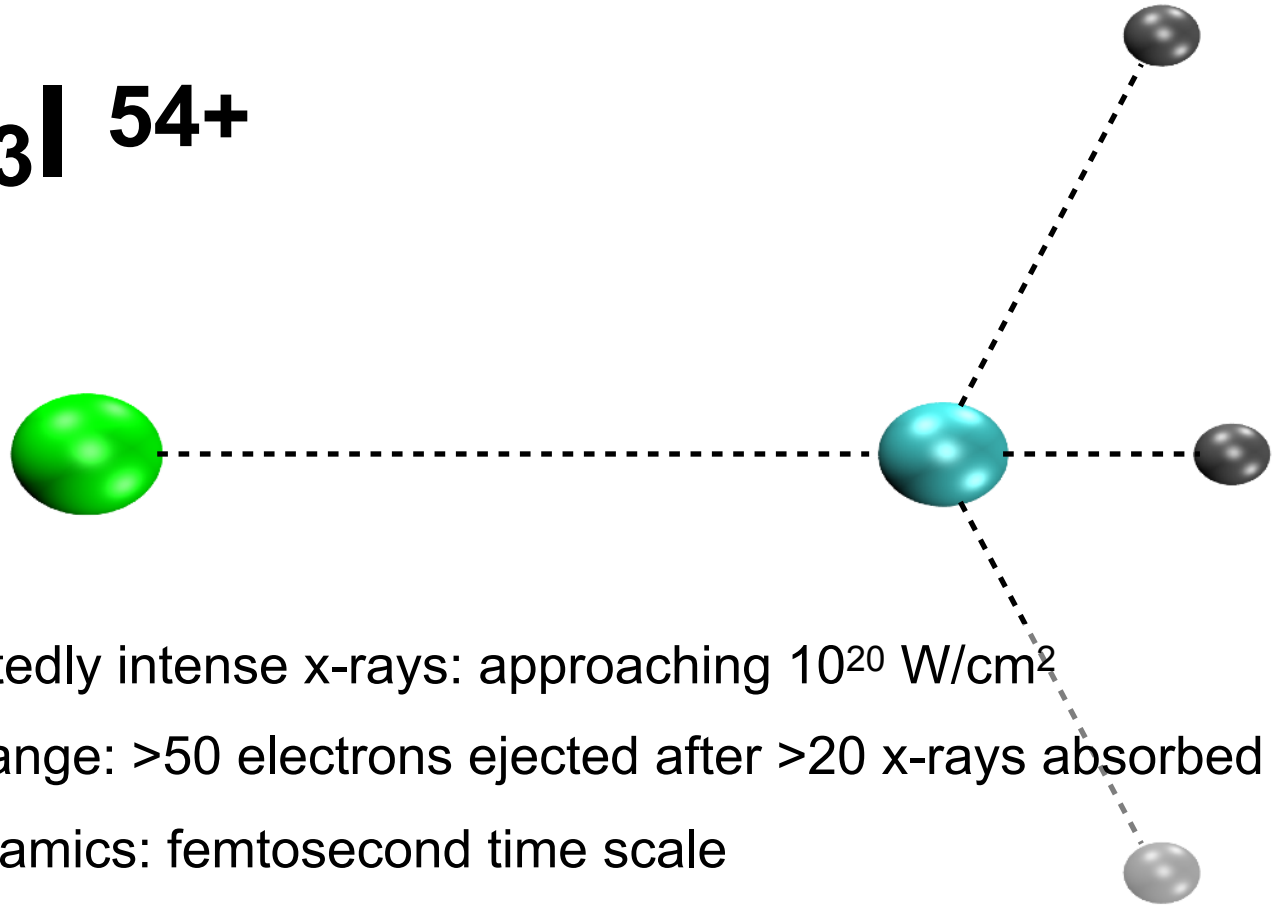
CH_3I

(t = 0 fs)



What happened?

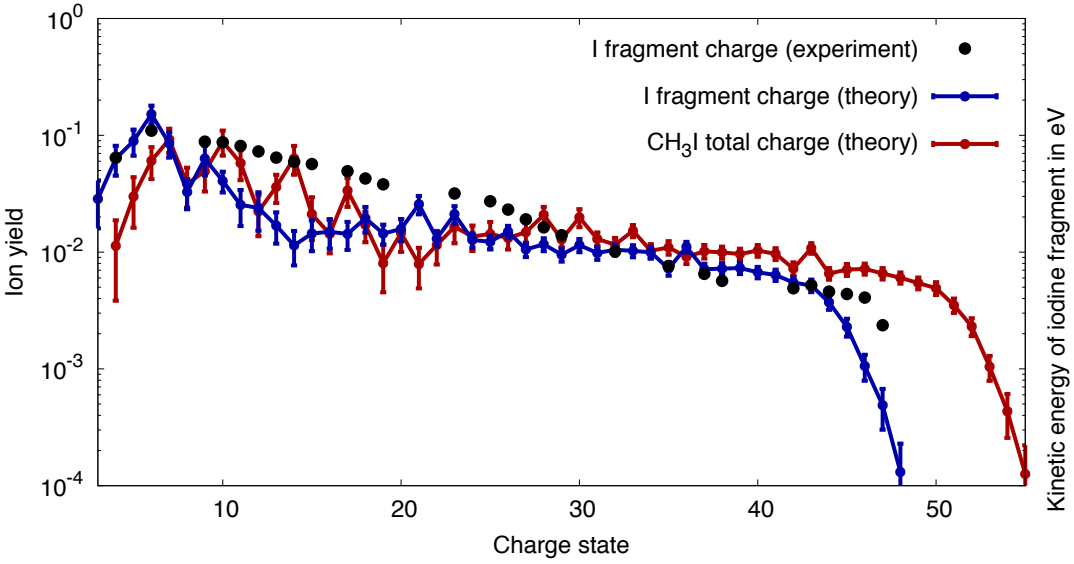
CH_3I^{54+}



- Unprecedentedly intense x-rays: approaching 10^{20} W/cm^2
- Dramatic change: >50 electrons ejected after >20 x-rays absorbed
- Ultrafast dynamics: femtosecond time scale

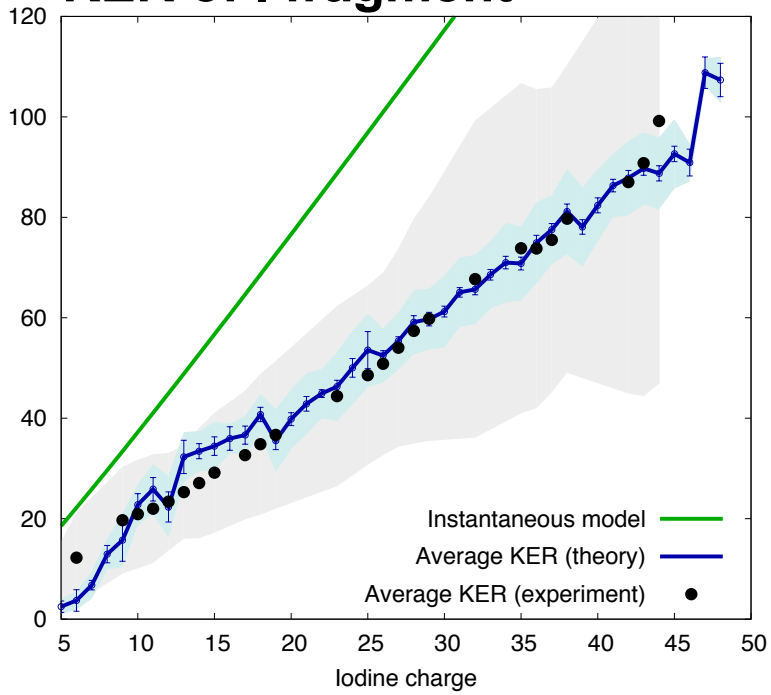
Comparison of CSD and KER

CSD of I and CH_3I



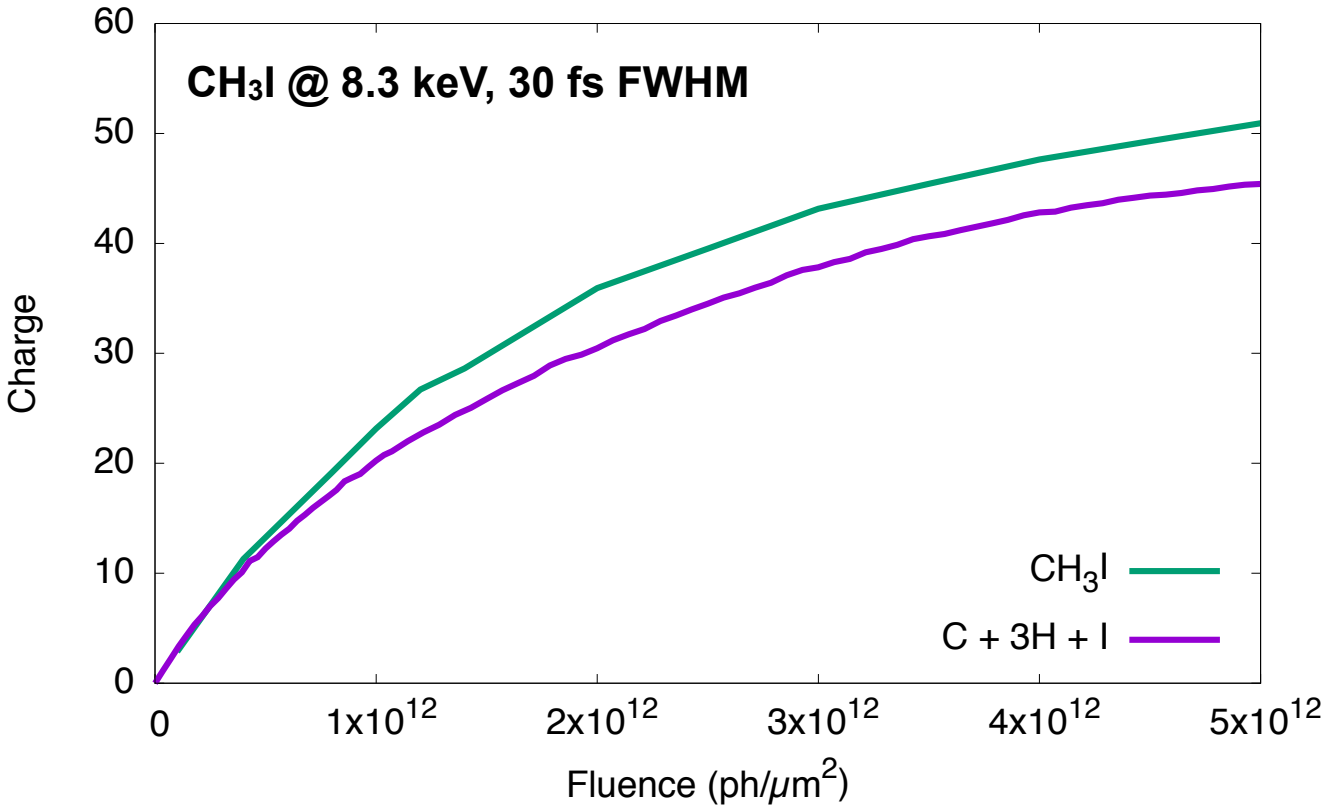
Rudenko *et al.*, submitted.

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

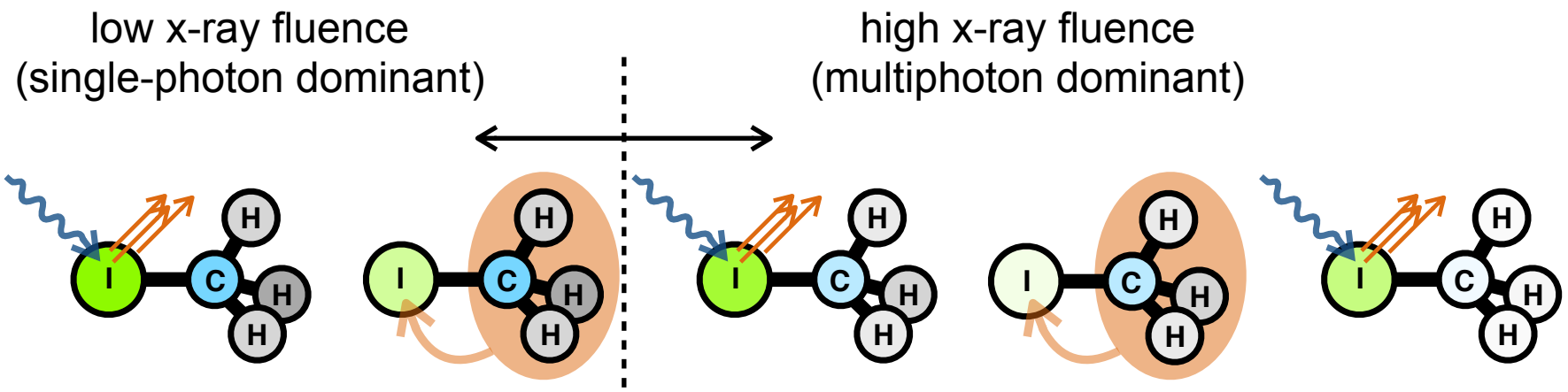
Molecular ionization enhancement



molecular charge > ∑(atomic charges): at high x-ray intensity theoretically anticipated and experimentally confirmed

Rudenko *et al.*, submitted.

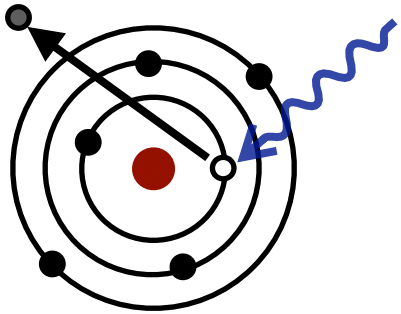
Ionization enhanced by charge rearrangement



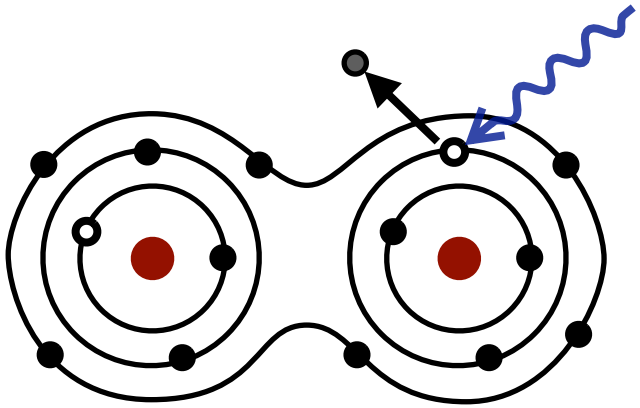
- Electrons from light atoms become available for further ionization on heavy atoms after charge rearrangement.
- CREXIM: Charge-Rearrangement-Enhanced X-ray Ionization of Molecules
- Impact on molecular imaging: not reducing partial charges of heavy atoms due to charge rearrangement, but inducing more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

Rudenko *et al.*, submitted.

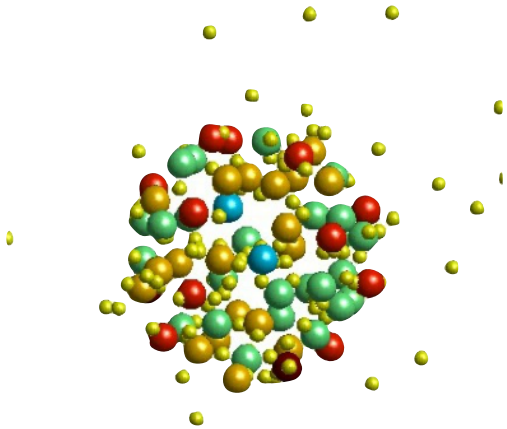
Summary



XATOM



XMOLECULE



XMDYN (Zoltan Jurek)

- XATOM, XMOLECULE, and XMDYN: enabling tools to investigate x-ray multiphoton physics of atoms, molecules, and clusters in intense XFEL pulses
- Femtosecond response of CH_3I to hard x-rays, recently conducted at LCLS
- Map of electronic and nuclear dynamics by a combined experimental and theoretical analysis
- Molecular ionization enhancement at high x-ray intensity: CREXIM

Acknowledgment

Experiment team

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

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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

UXSS: Ultrafast X-ray Summer School

UXSS 2015

- CFEL, Hamburg
- Giorgio Margaritondo
- Robin Santra
- David Reis
- Linda Young
- Markus Gühr
- Simone Techert
- Thomas White
- Wilfried Wurth
- Ulf Zastrau

UXSS 2016

- SLAC, Stanford
- Agostino Marinelli
- Philippe Wernet
- Matthias Fuchs
- Nora Berrah
- Louis DiMauro
- Steve Johnson
- Sigfried Glenzer
- Ian Robinson
- James Holton

UXSS 2017

- CFEL, Hamburg
- Probably June 2017
- Coming up soon…
- Stay tuned!

http://conferences.cfel.de/uxss_2017/
to be opened soon