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

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Team X

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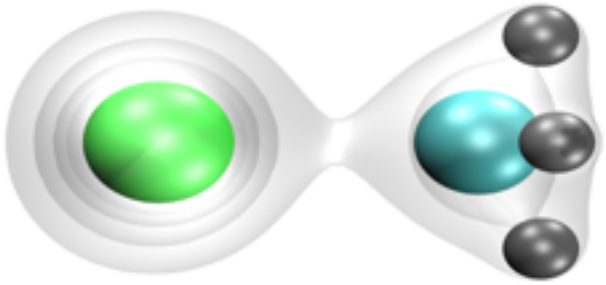
Coulomb explosion of iodomethane

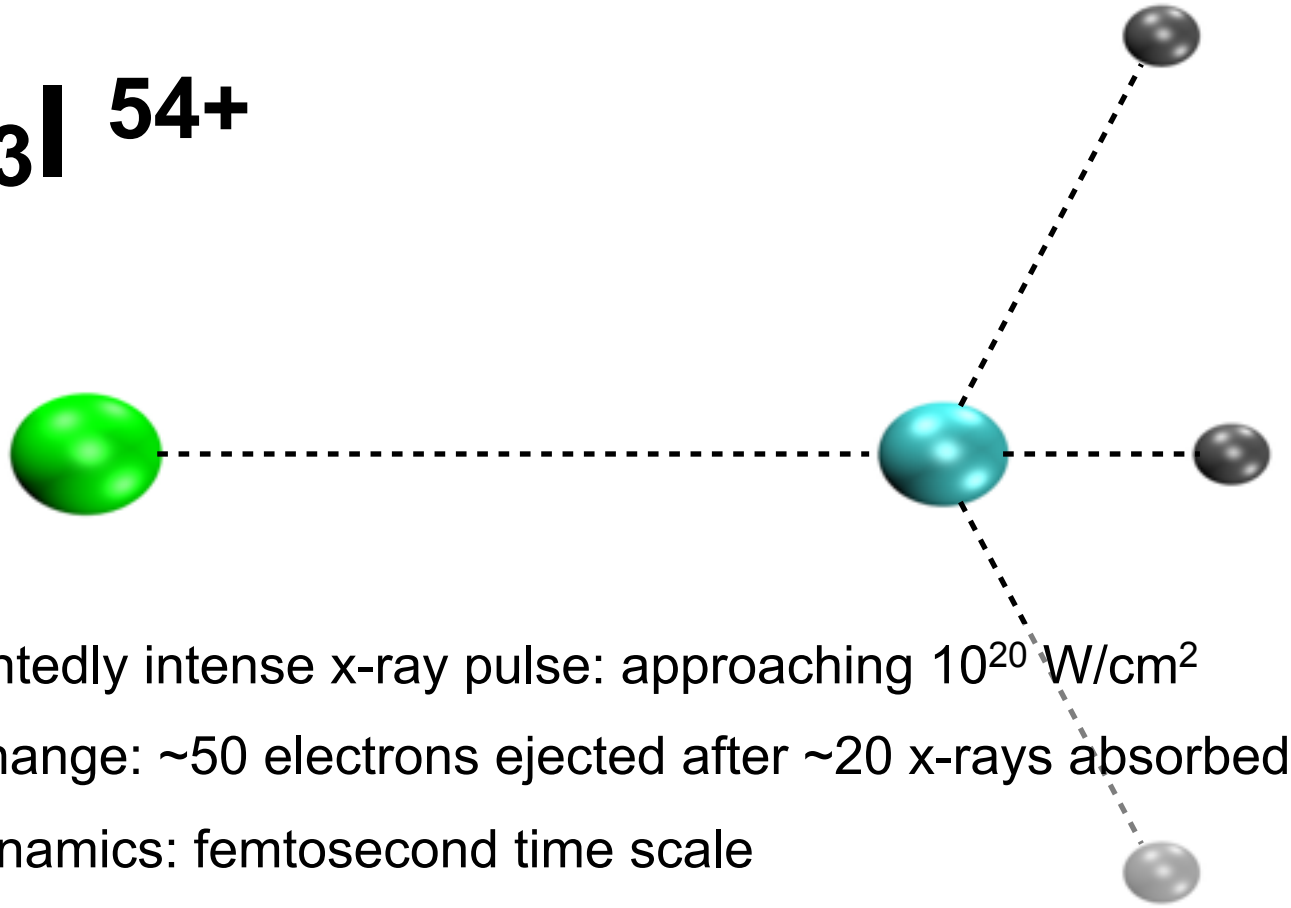
CH_3I

(t = 0 fs)



What happened?

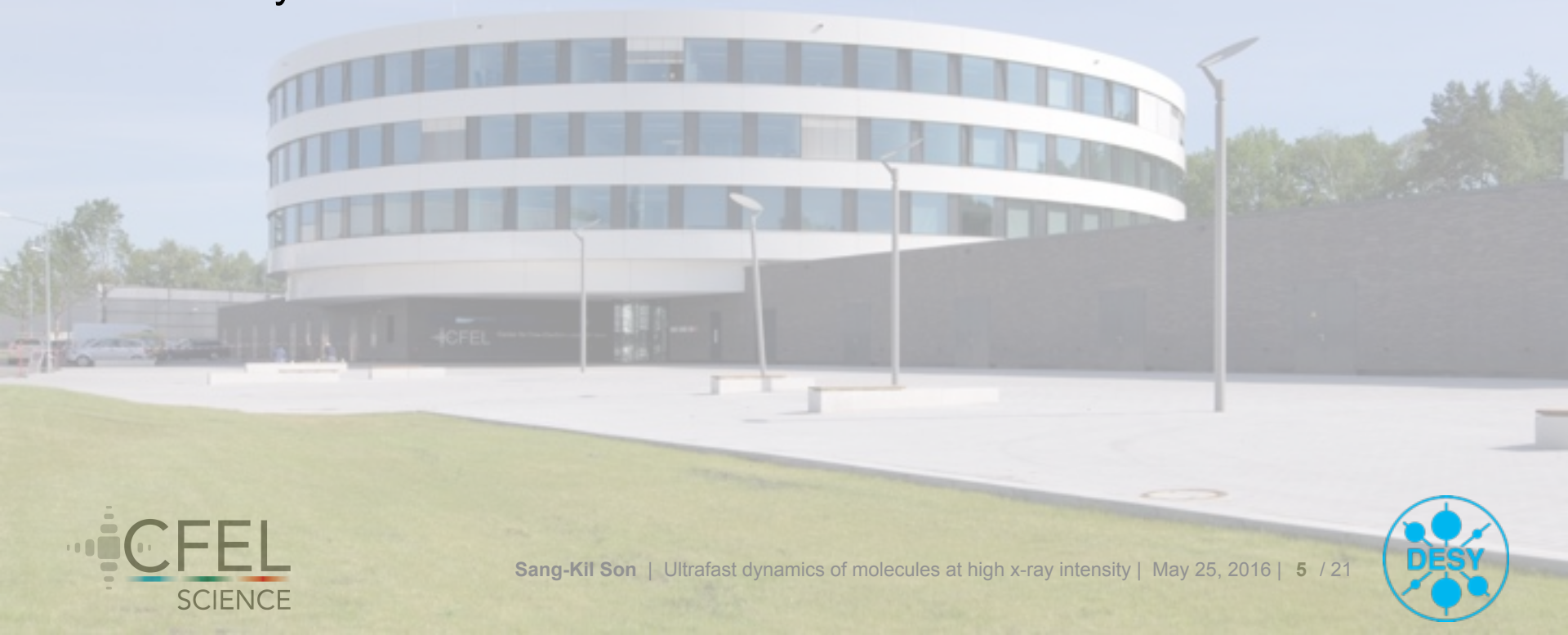
CH_3I^{54+}



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

Overview

- X-ray multiphoton ionization of atoms at high x-ray intensity
- Ultrafast ionization and fragmentation dynamics of molecules
- Towards complex systems
- Summary

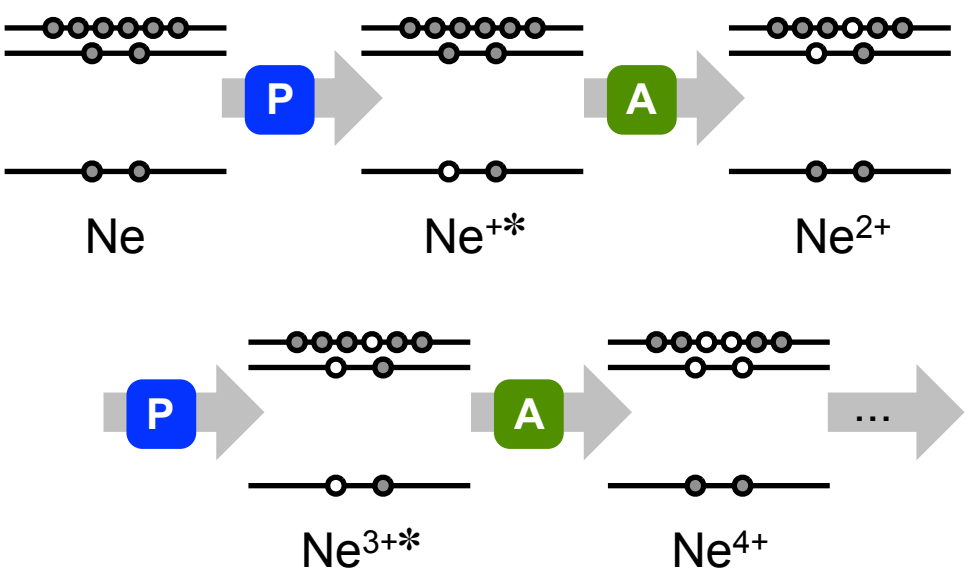


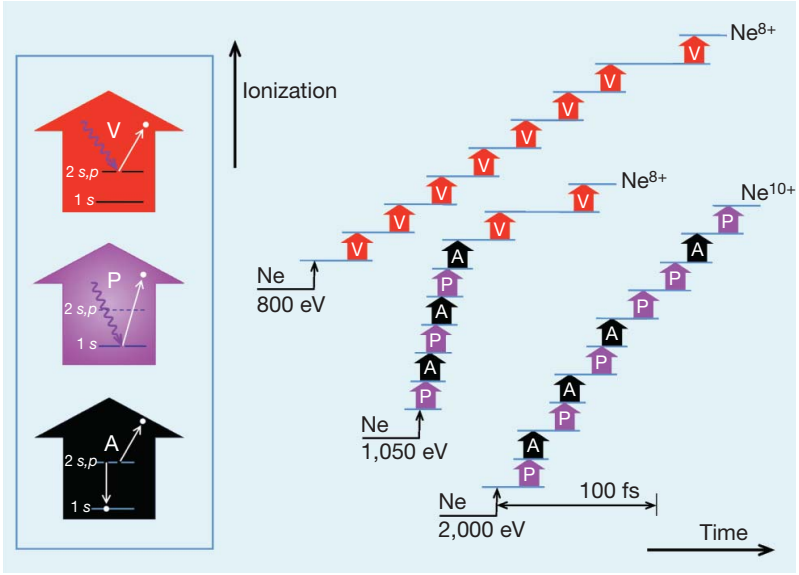
X-ray multiphoton absorption

- 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).

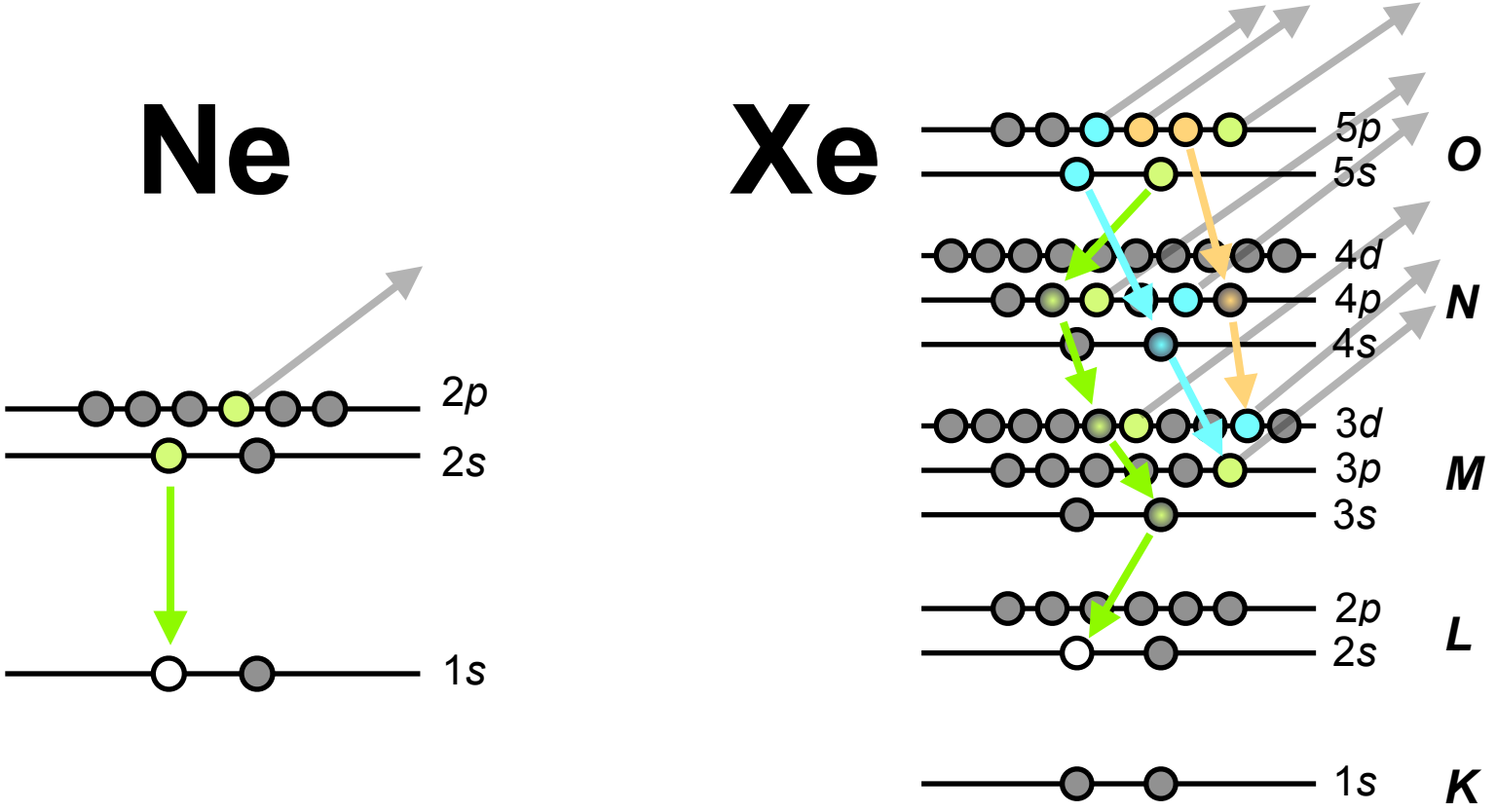
- Sequential multiphoton absorption is dominant.





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

Complex inner-shell decay cascade

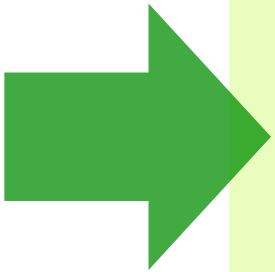


Multiphoton absorption after/during decay cascade

- More than 1 million multiple-hole states
- More than 40 million x-ray-induced processes

Challenges for x-ray multiphoton ionization

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

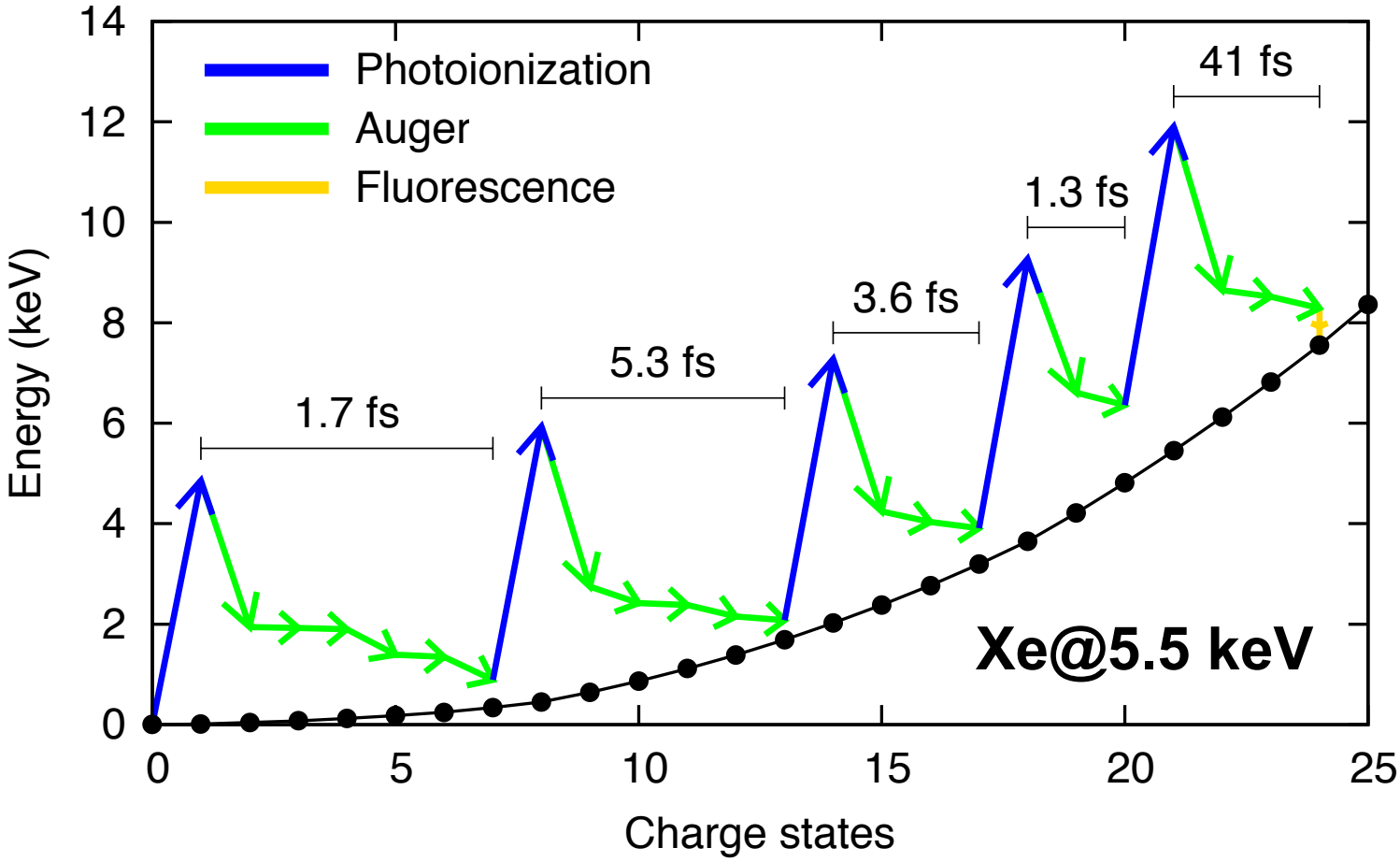


XATOM

- 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

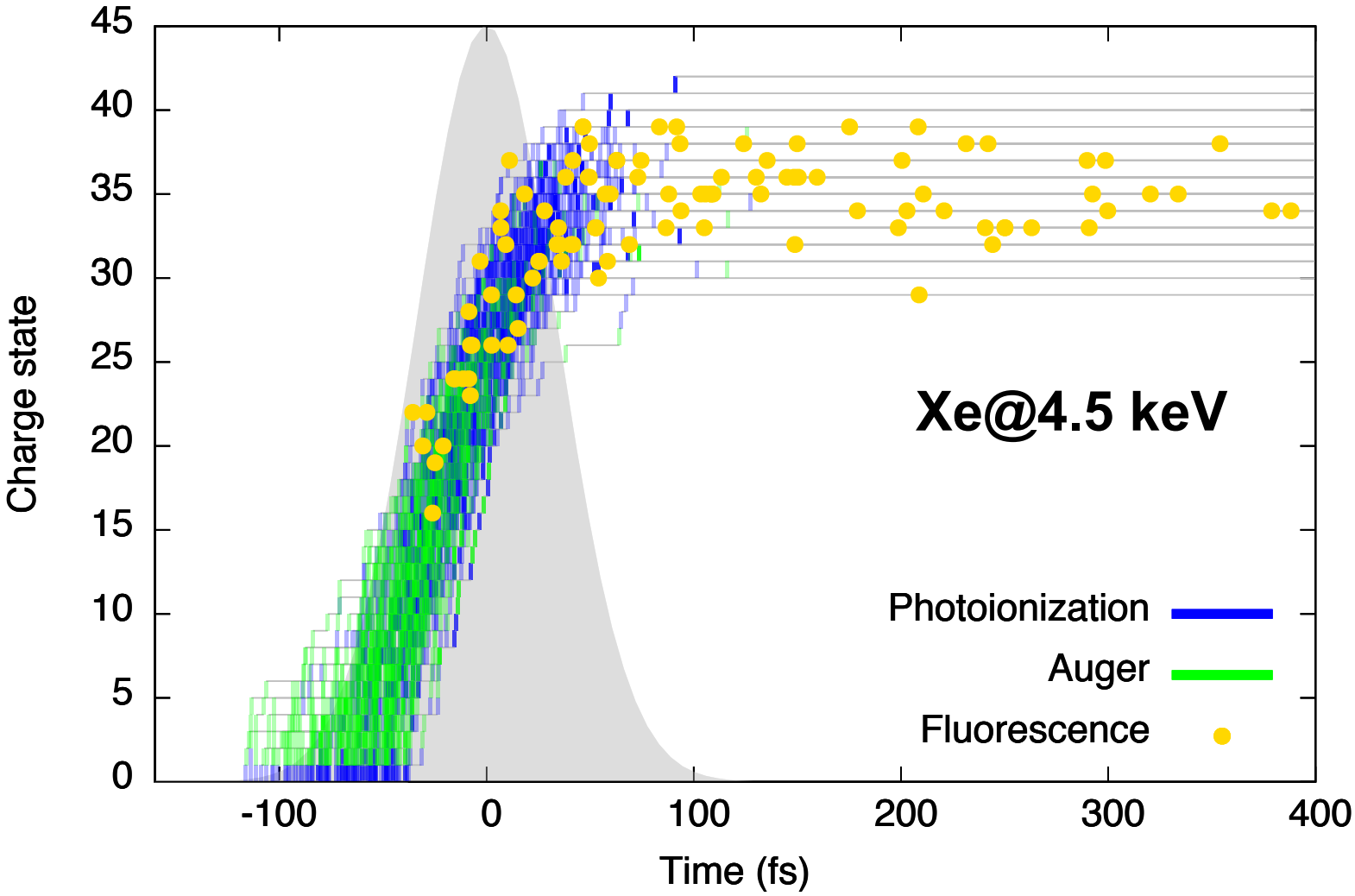
Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).
Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

X-ray multiphoton ionization mechanism



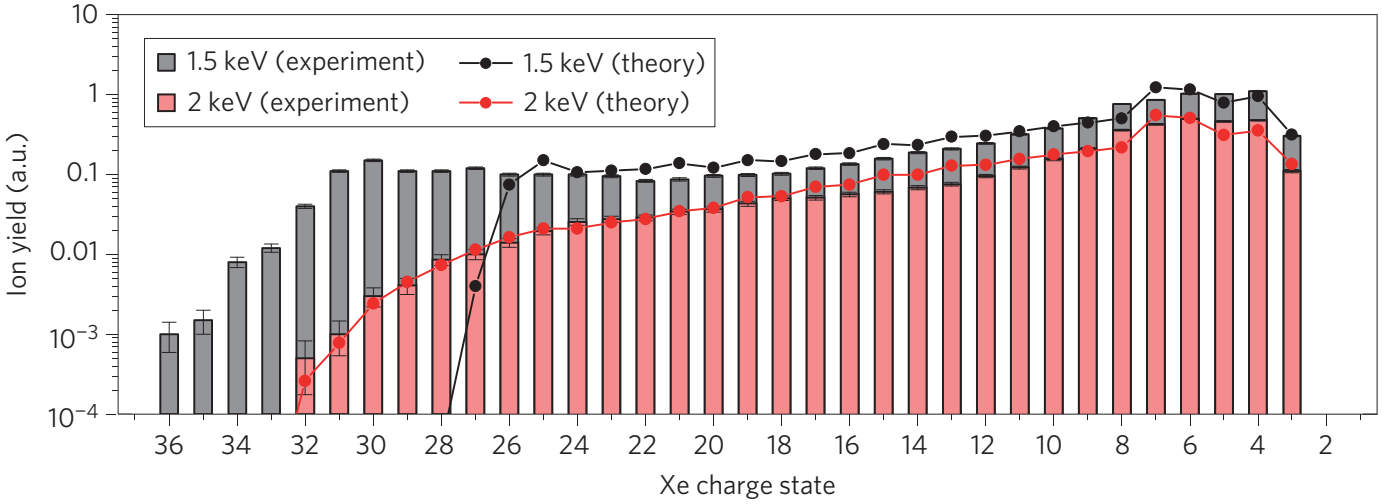
Fukuzawa *et al.*, *Phys. Rev. Lett.* **110**, 173005 (2013).

X-ray multiphoton ionization dynamics



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

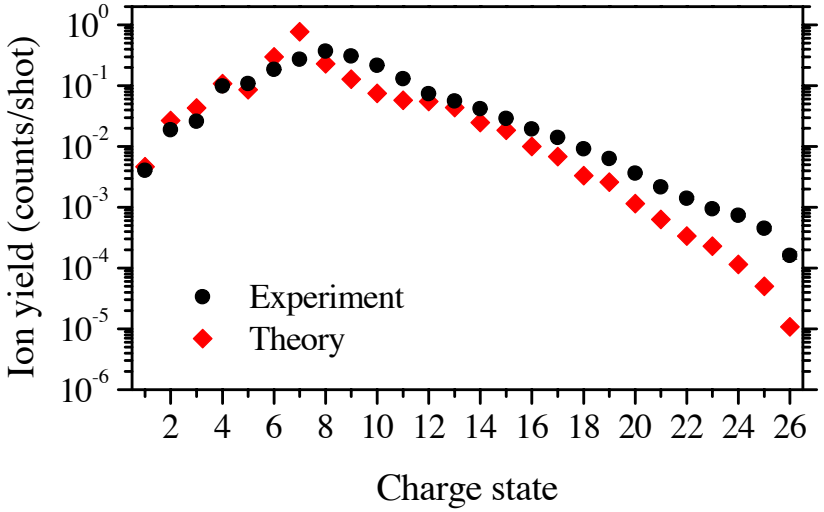
Comparison b/w experiment and theory



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



Yajiang Hao, Ludger Inhester, Kota Hanasaki, Son & Santra, *Struc. Dyn.* **2**, 041707 (2015).
Inhester *et al.*, in preparation.

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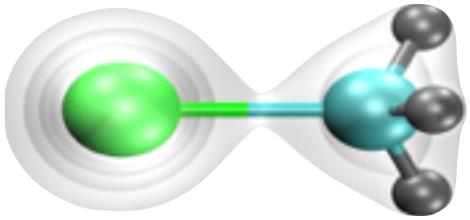
Iodomethane at high x-ray intensity

- Selective ionization on heavy atom

CH_3I @ 8.3 keV



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

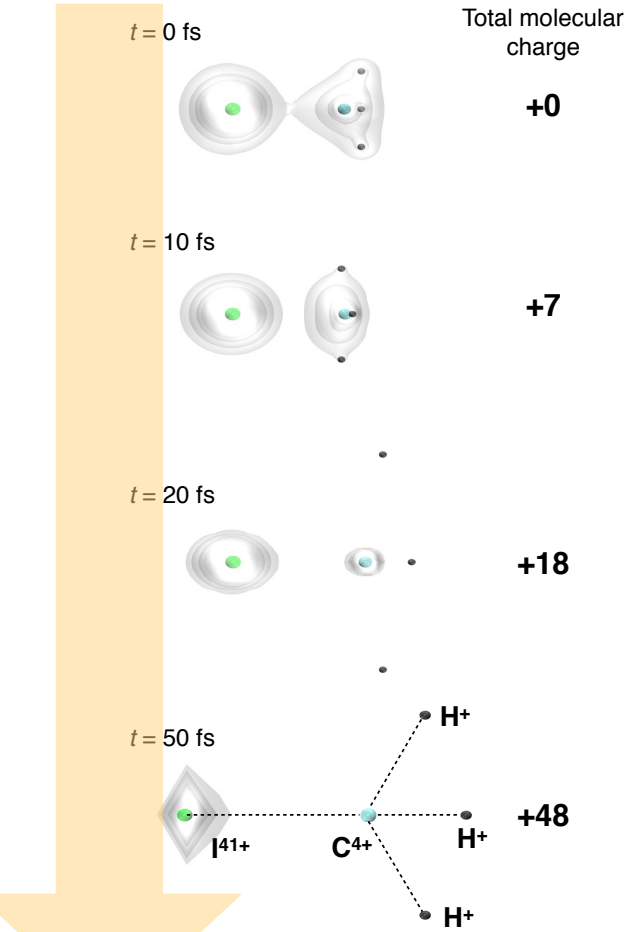
- X-ray multiphoton ionization occurs at high intensity
- Charge imbalance induces charge rearrangement
- Coulomb explosion after/during ionization & charge rearrangement
- New experimental setup:
  LCLS CXI using nano-focus
  ➔ new realm of intensity
  approaching ~10^{20} W/cm^2

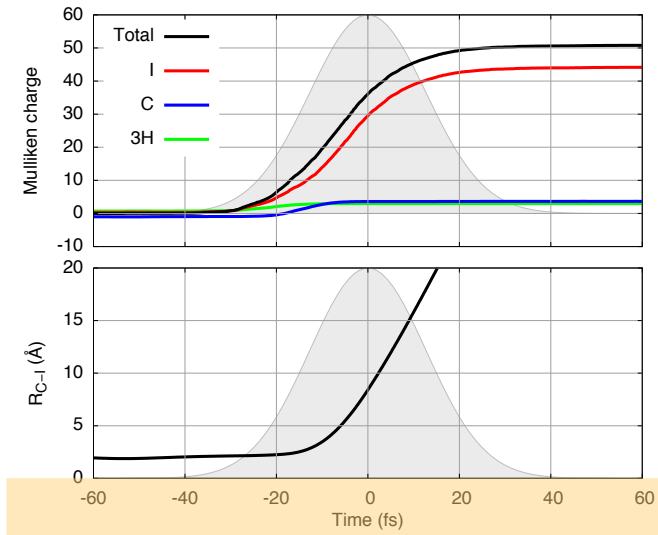
LCLS experiment

Daniel Rolles
at KSU

Artem Rudenko
at KSU

Capturing ultrafast dynamics





ionization dynamics &
charge rearrangement dynamics

nuclear dynamics

femtosecond time scale

- Theory can provide molecular movies
- How to observe ultrafast dynamics?
  - Charge state distribution (CSD)
  - Kinetic energy release (KER):
    molecular information when it breaks apart,
    influenced by detailed dynamical behaviors

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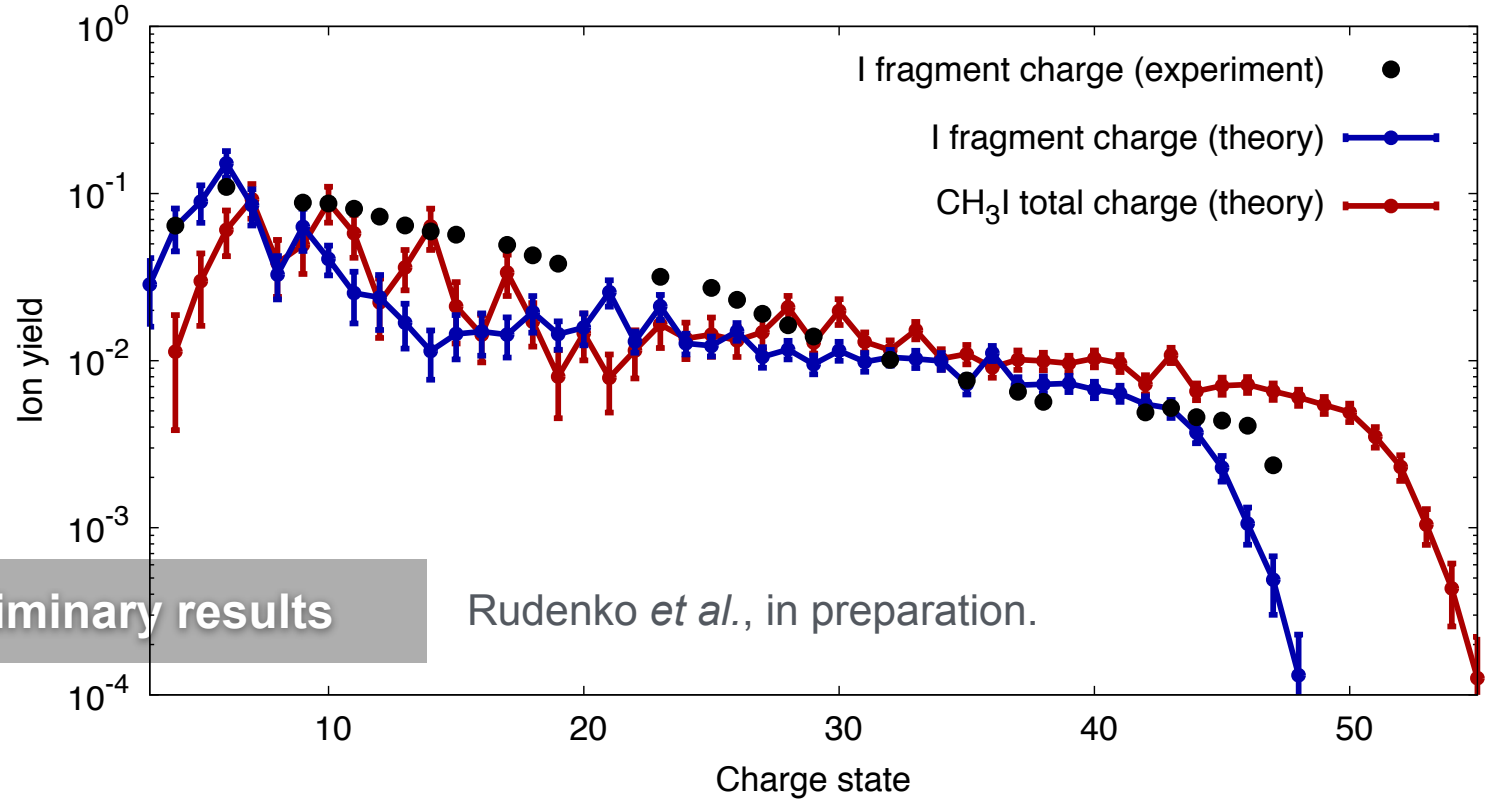
Charge state distribution (CSD)

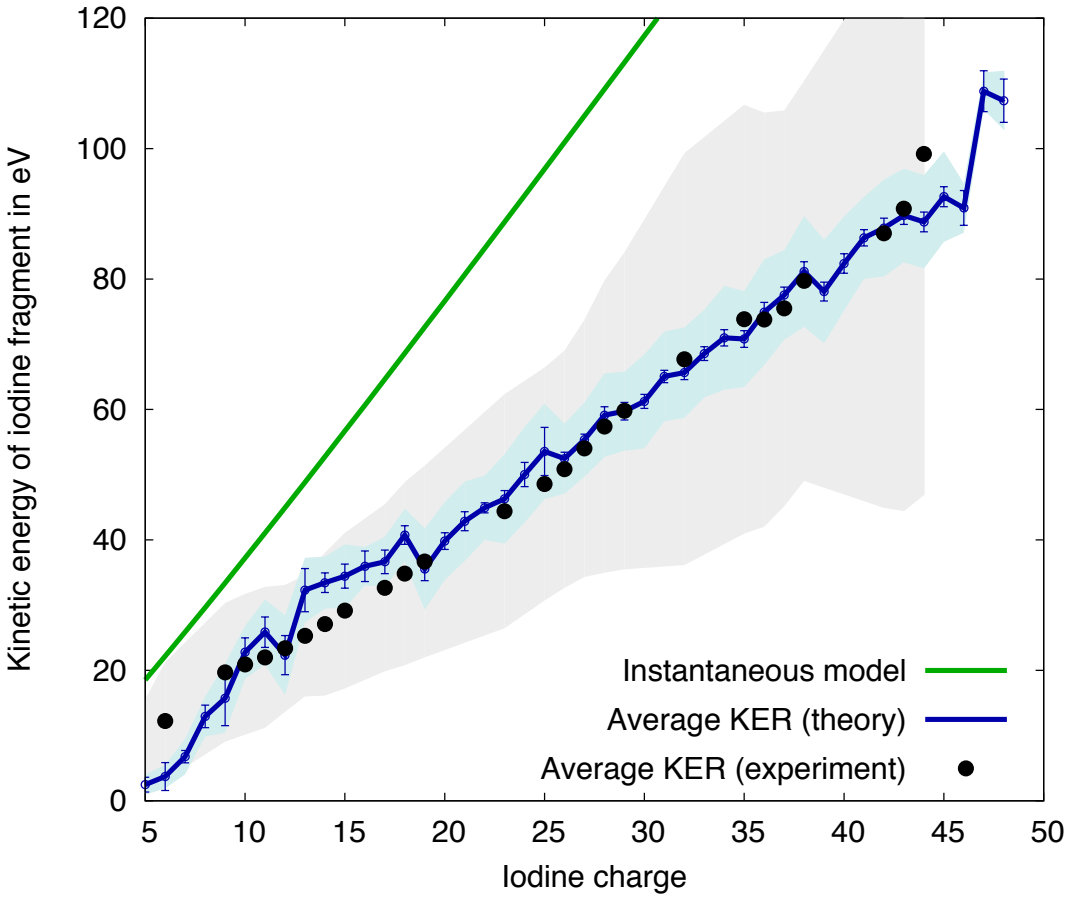


Preliminary results

Rudenko *et al.*, in preparation.

- Coincident measurement at intermediate intensity confirms that high I charges are along with C^{4+} and $3H^{+}$.
- Total charge ~ I fragment charge + 7 ➔ highest charge up to CH_3I^{54+}

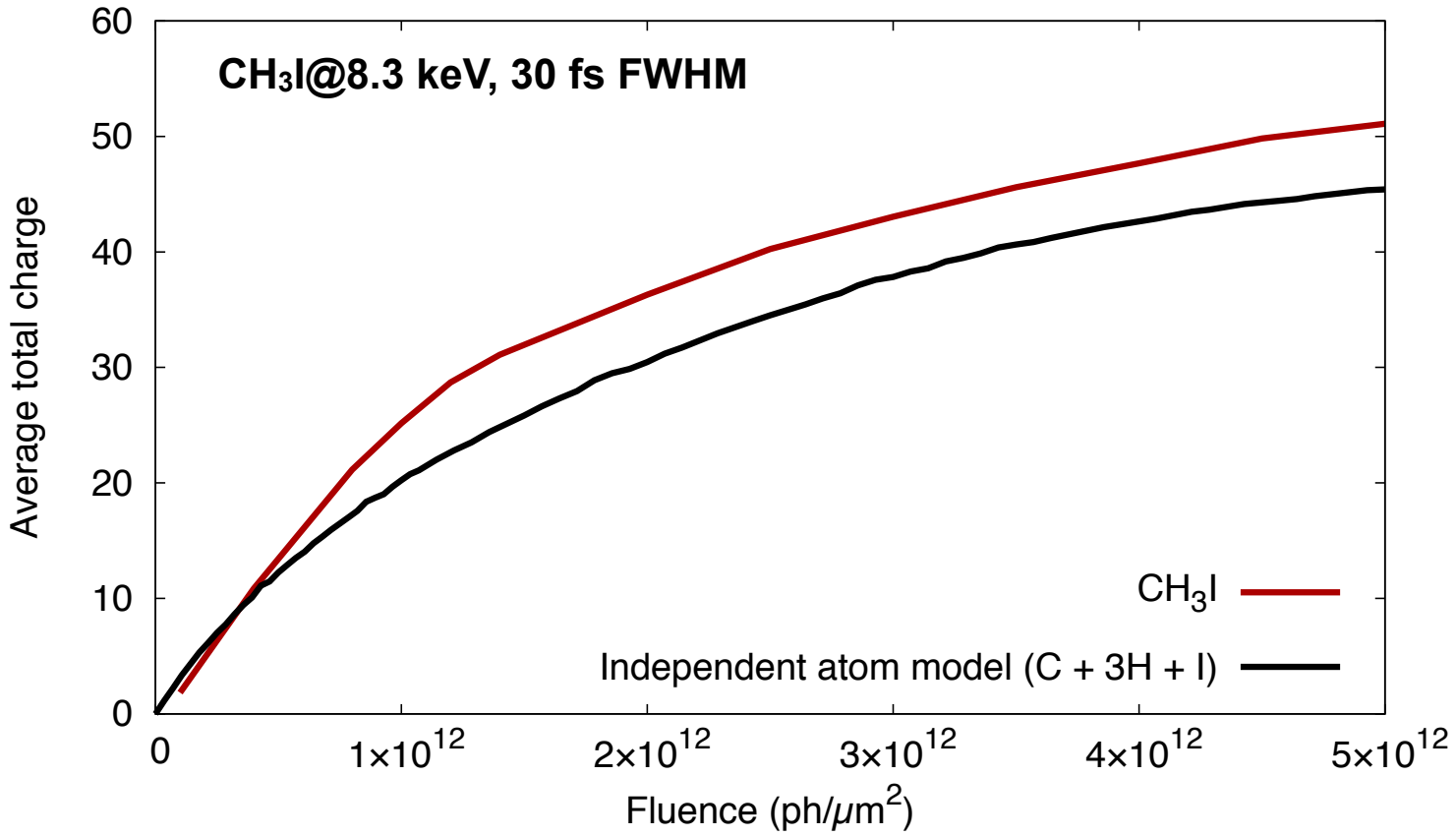
Kinetic energy release (KER)



- KER depends on time scales of relevant dynamics ➔ sensitive to pulse duration.
- KER distribution has a wide width because of many different channels.
- Theoretical width is narrower than experimental width. ➔ further theoretical development required (e.g. beyond config-based rates)

Rudenko *et al.*, in preparation.

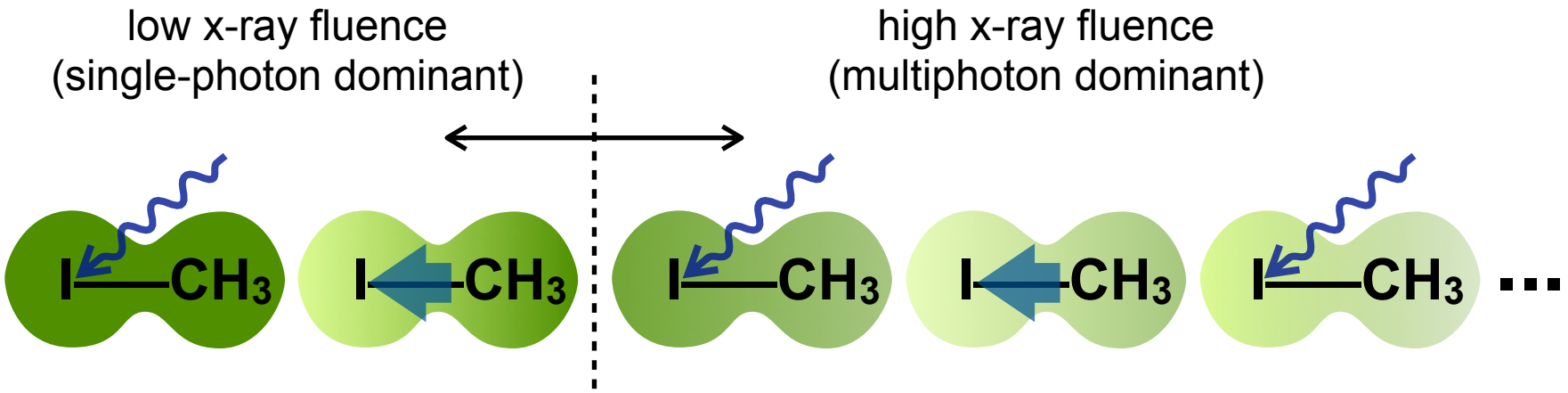
Molecular ionization enhancement



molecular charge > ∑(atomic charges): experimentally confirmed

Rudenko *et al.*, in preparation.

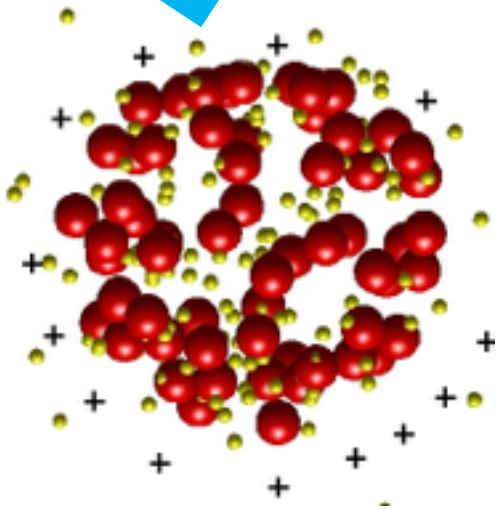
Ionization enhanced by charge rearrangement



- 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.*, in preparation.

Towards complex systems



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.* (in press).

XMDYN development

Zoltan Jurek
at CFEL-DESY Theory

- **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

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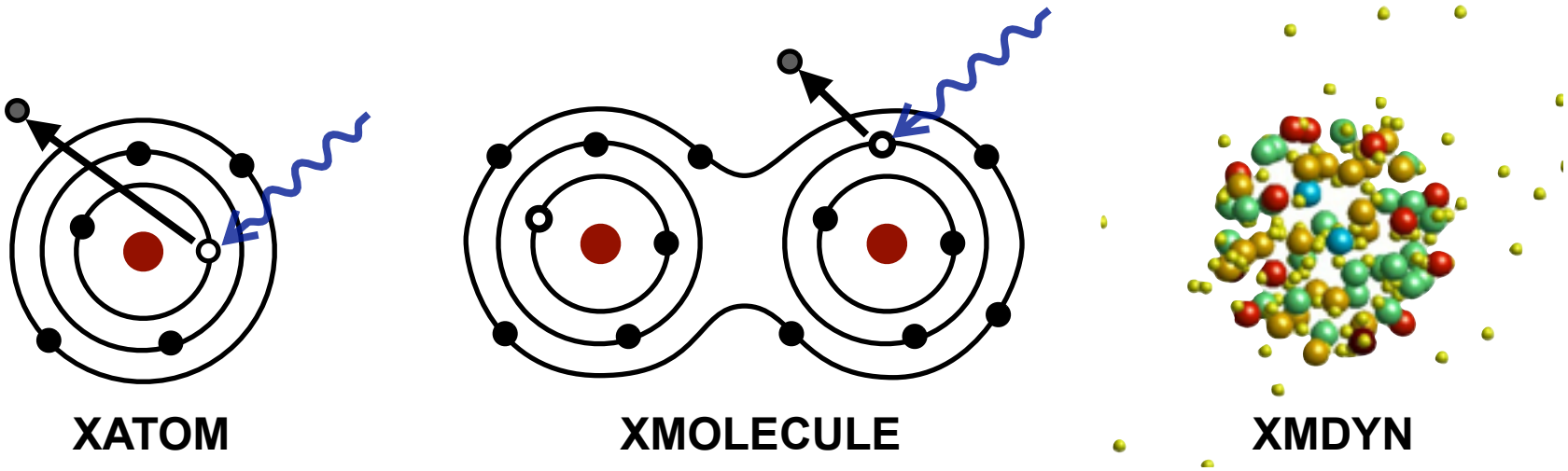
Summary



- XATOM, XMOLECULE, and XMDYN: enabling tools to investigate x-ray multiphoton physics of atoms, molecules, and clusters exposed to high intensity x-ray pulses
- X-ray multiphoton ionization dynamics of Xe atom
- Ultrafast explosion dynamics of CH_3I exposed to an XFEL pulse: x-ray ionization of molecules enhanced by charge rearrangement

Acknowledgment

Experimental team

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

Poster by
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Thank you for your attention!

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