

Ultrafast dynamics of atoms and molecules induced by intense XFEL pulses

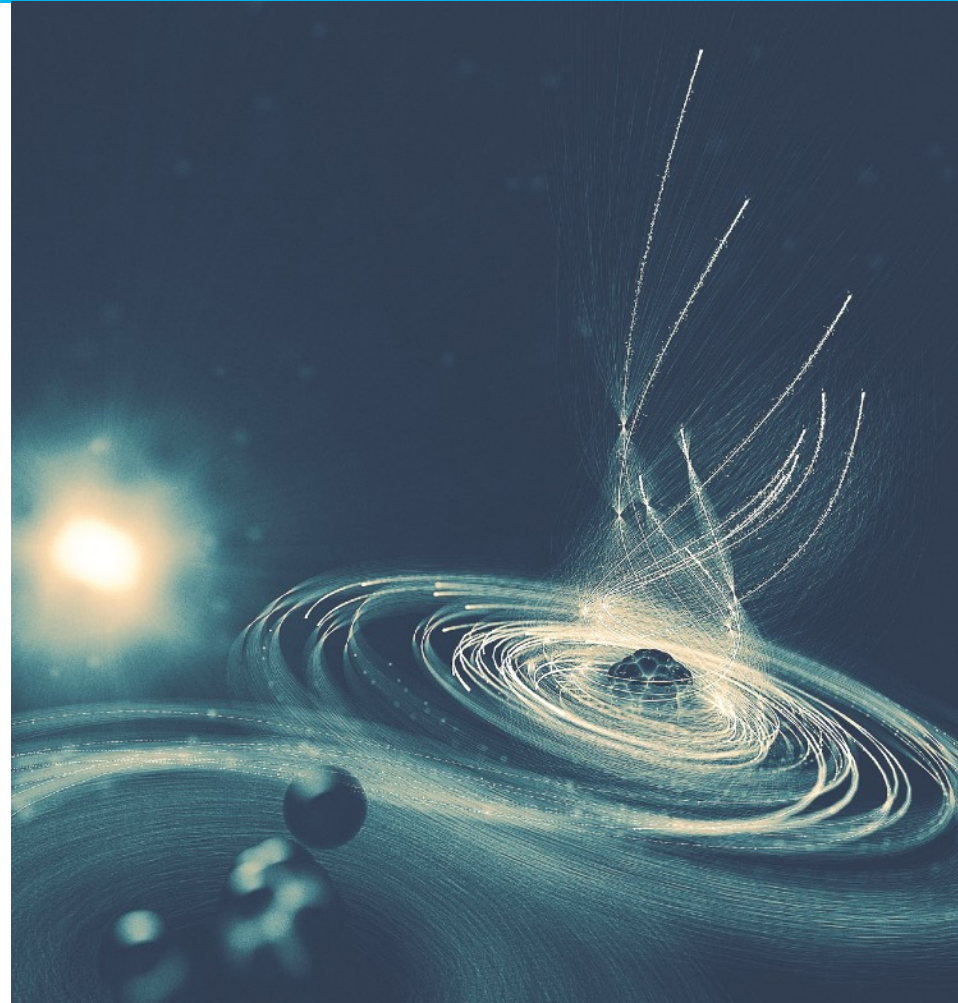
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Center for Free-Electron Laser Science,
DESY, Hamburg, Germany

28th Annual International Laser
Physics Workshop
HICO, Gyeongju, Korea
July 8–12, 2019



HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES



Acknowledgment

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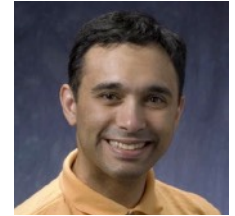
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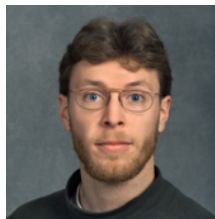
Experiment team



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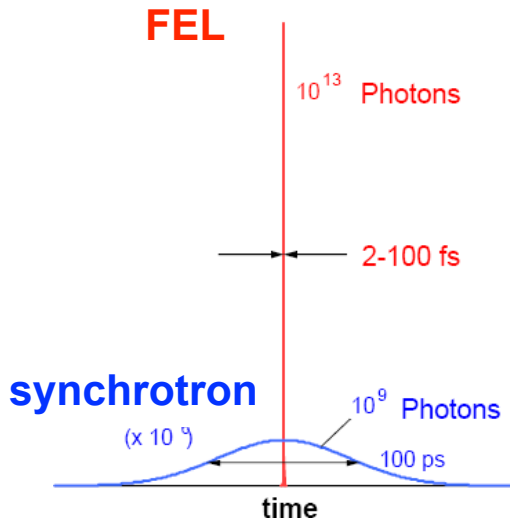


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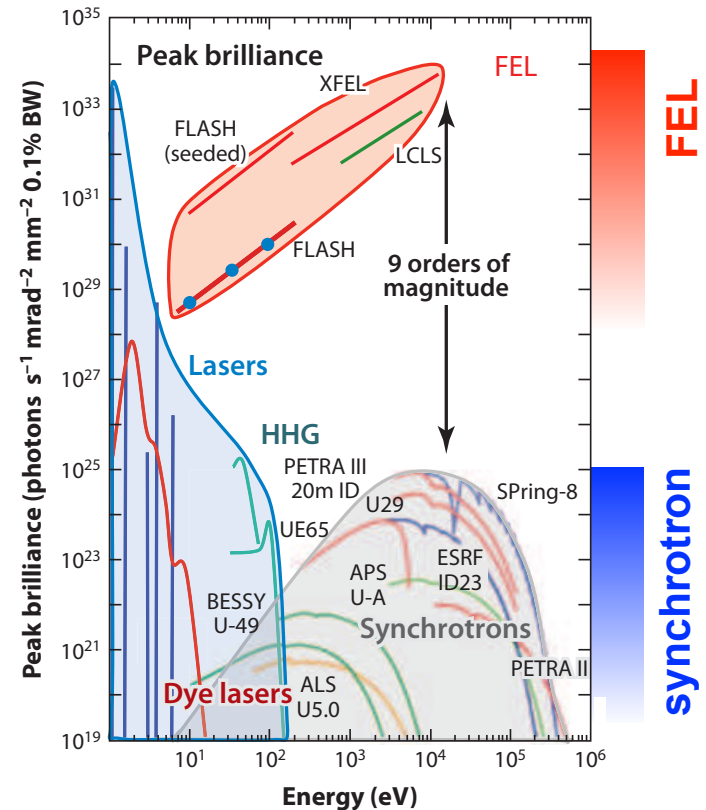
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XFEL: X-ray free-electron laser

- > *Ultraintense*: $\sim 10^{13}$ photons
- > *Ultrafast*: \sim femtoseconds
- > hard X-ray photon energy: \sim keV
 → peak intensity $\sim 10^{20}$ W/cm²



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

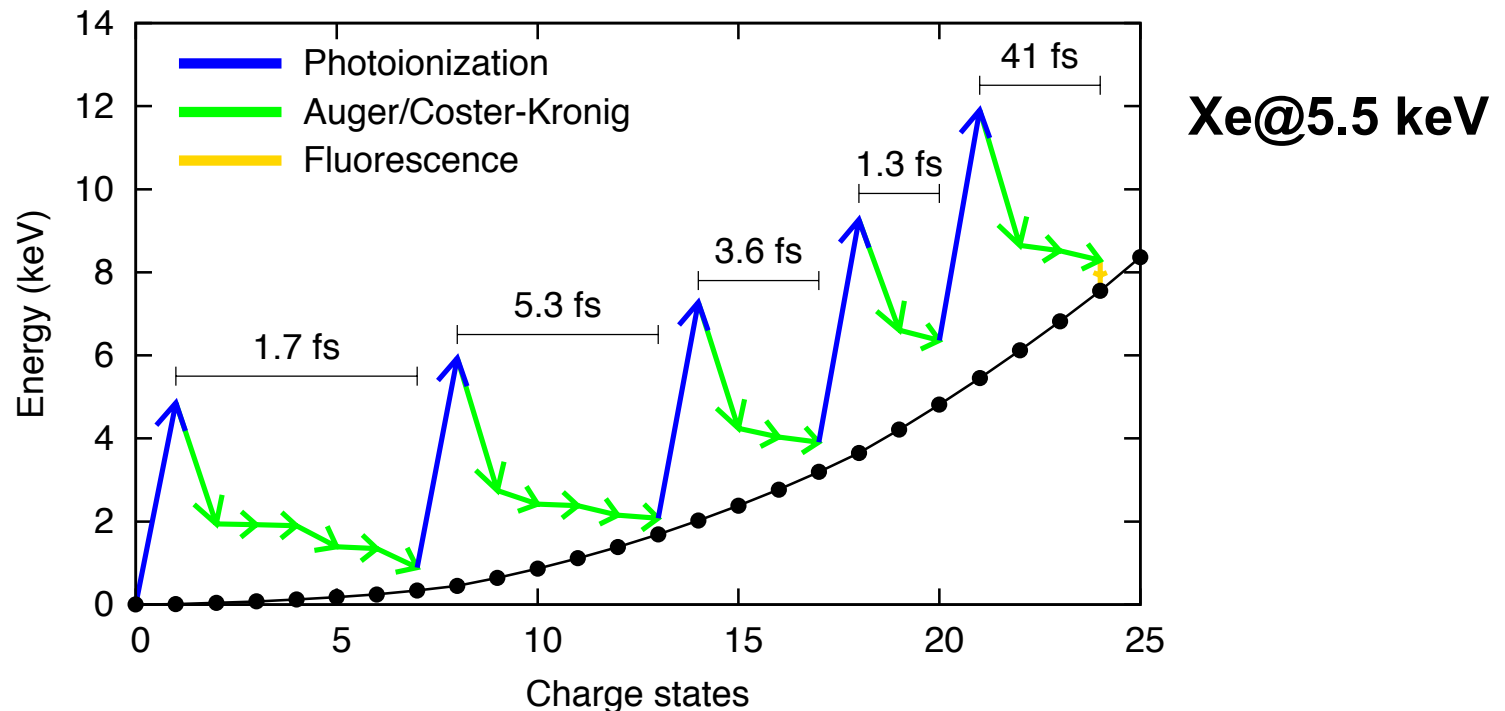


Ullrich et al., *Annu. Rev. Phys. Chem.* **63**, 635 (2012).

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

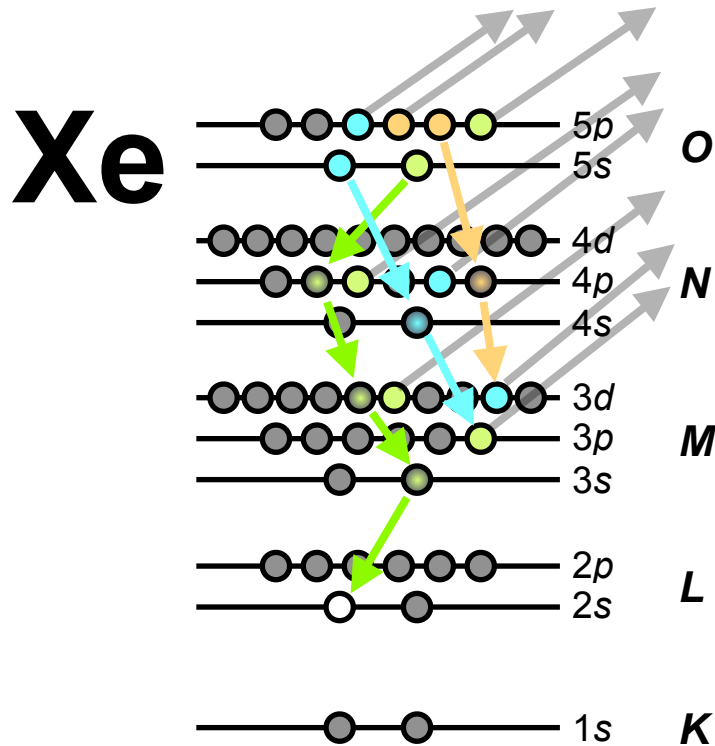
Sequential multiphoton multiple ionization

- SACLA experiment: Xe at 5.5 keV, $\sim 50 \mu\text{J}/\mu\text{m}^2$ ($\sim 2 \times 10^{17} \text{ W}/\text{cm}^2$)
- 5 photons absorbed sequentially, 24 electrons ejected within 30 fs

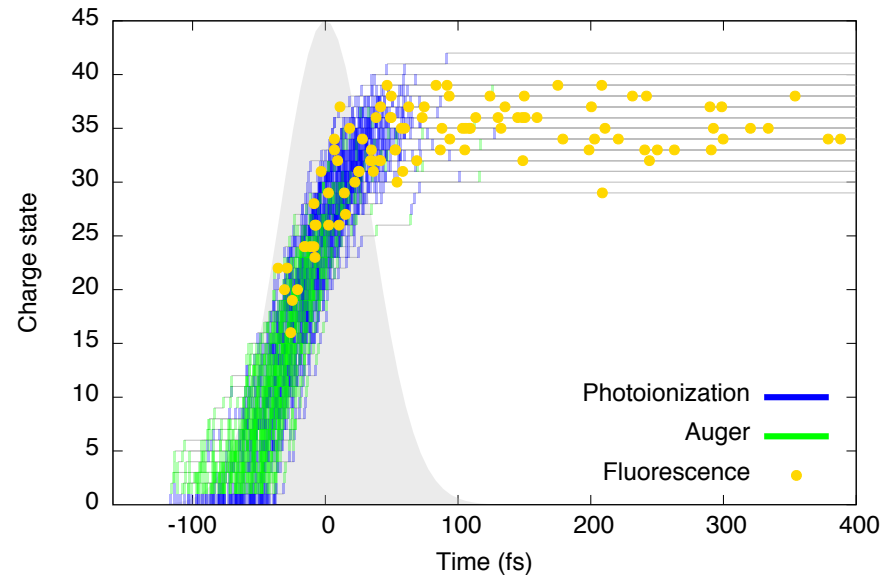


Fukuzawa *et al.*, *Phys. Rev. Lett.* **110**, 173005 (2013).

How to describe atoms in XFEL pulses



- Extremely complicated multiphoton multiple ionization dynamics: $\sim 20M$ coupled rate equations to be solved
- No standard quantum chemistry code available



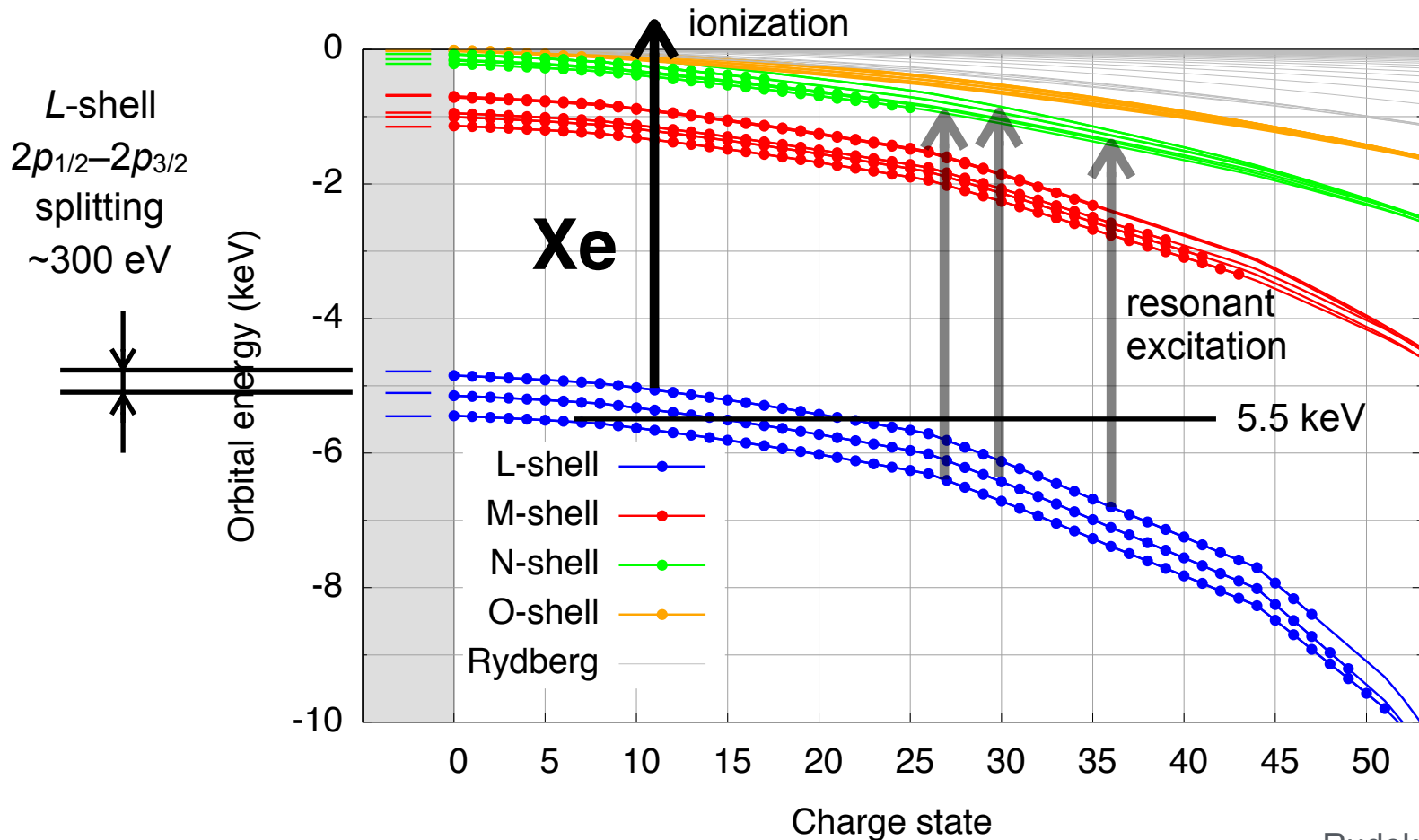
Monte Carlo: Son & Santra, *PRA* **85**, 063415 (2012).

XATOM: computer program suite to describe dynamical behavior of atoms interacting with XFEL pulses

Jurek, Son, Ziaja & Santra, *J. Appl. Cryst.* **49**, 1048 (2016).

Download executables: <http://www.desy.de/~xraypac>

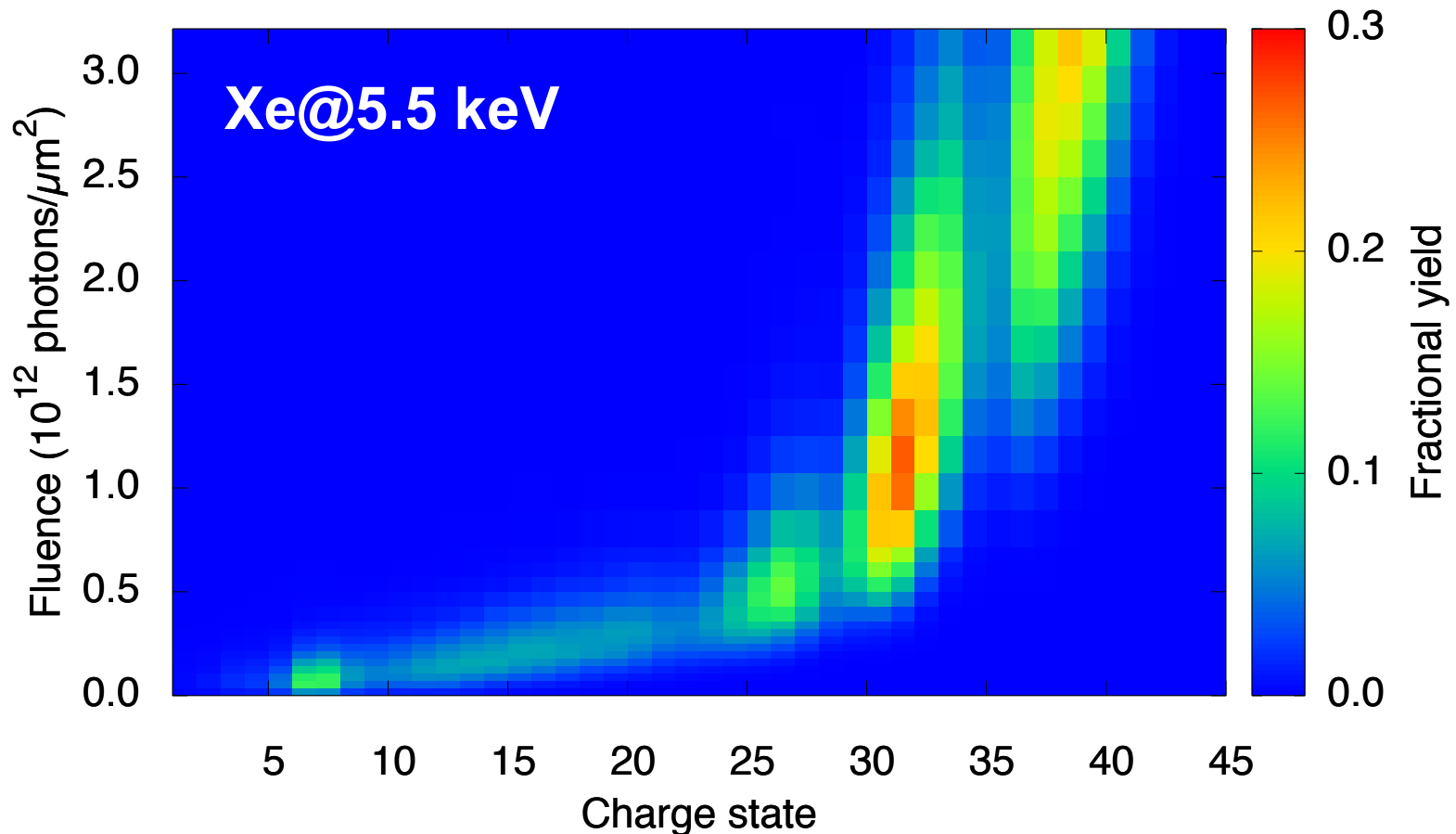
Resonance and relativistic effects



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

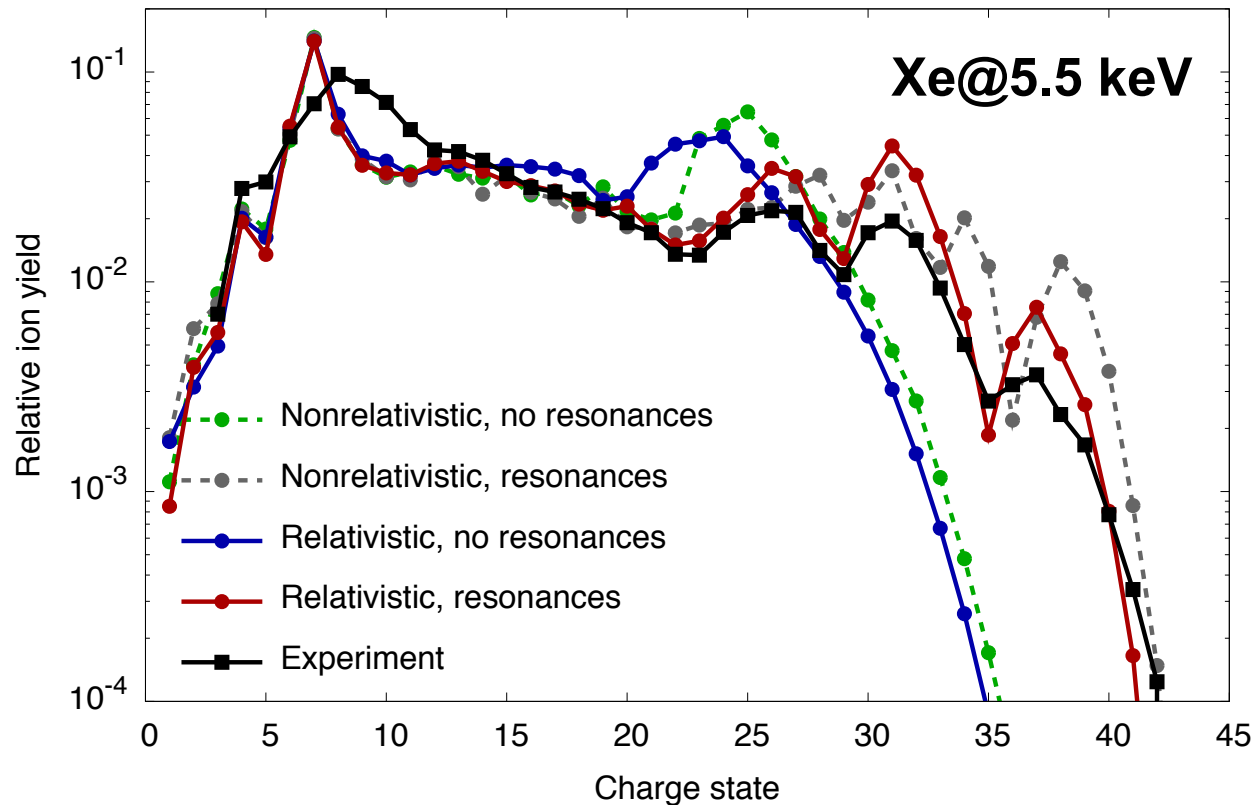
- > **REXMI**: multiple resonant excitation and Auger-like decay
- > N of rate eqs: $\sim 20M$ (non-rel) $\rightarrow \sim 5B$ (rel) $\rightarrow \sim 2.6 \times 10^{68}$ (resonance+rel)

Xe CSD with resonance & relativity



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

Comparison with experimental CSD



- > Compared with LCLS CXI nanofocus experiment ($\sim 10^{19}$ W/cm²)
- > Structured CSD: interplay of resonance and relativistic effects verified

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

How to describe molecules in XFEL pulses

> Challenges

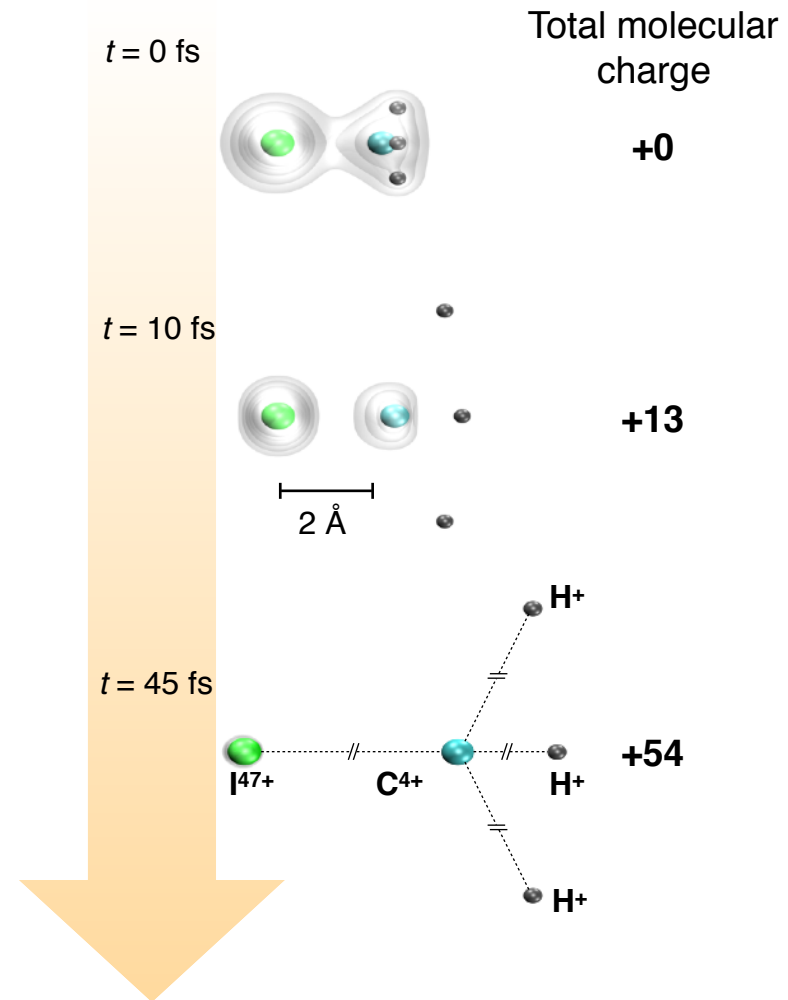
- Coupled ionization and nuclear dynamics in the same time scales
- Extremely complicated dynamics: e.g. CH₃I ~ 200 trillion rate equations at single geometry
- More difficult for highly excited elec. structure
- No *ab initio* theoretical tools available

XMOLECULE

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

Hao *et al.*, *Struc. Dyn.* **2**, 041707 (2015).

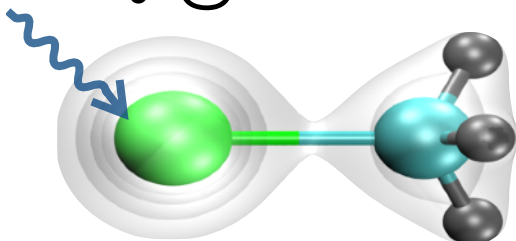
Inhester *et al.*, *Phys. Rev. A* **94**, 023422 (2016).



Iodomethane in ultraintense hard x-rays

- > LCLS CXI using nano-focus
→ approaching $\sim 10^{20}$ W/cm²
- > Selective ionization on heavy atom

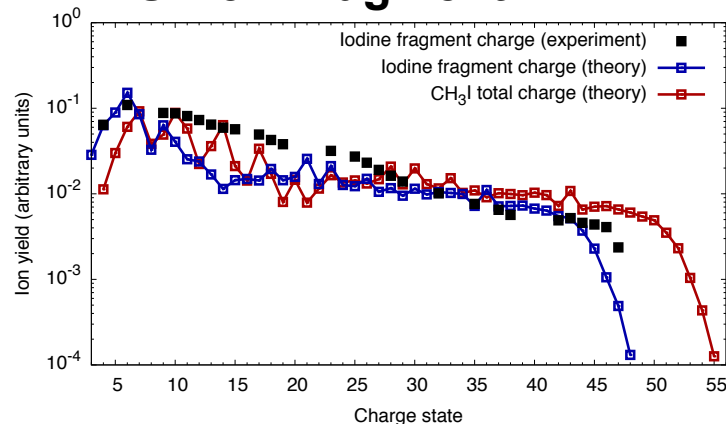
CH₃I @ 8.3 keV



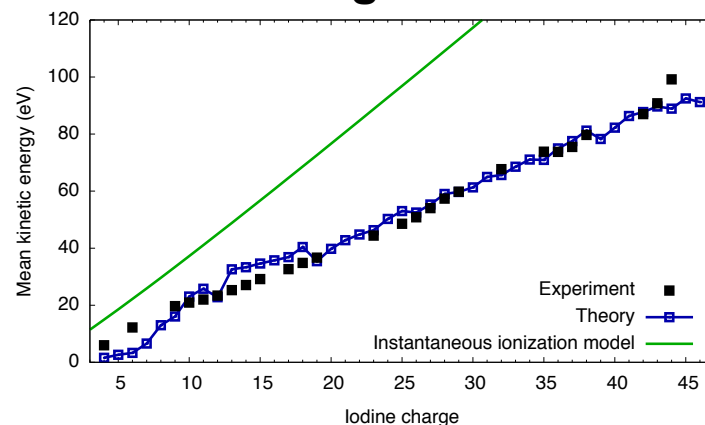
$\sigma(\text{I}) \sim 50$ kbarn
 $\sigma(\text{C}) \sim 80$ barn
 $\sigma(\text{H}) \sim 8$ mbarn

- > Coulomb explosion after/during ionization & charge rearrangement
- > First quantitative comparison for the behaviors of polyatomic molecules under XFEL irradiation

CSD of I fragment

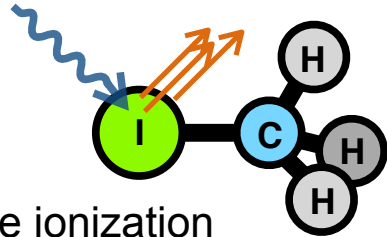


KER of I fragment

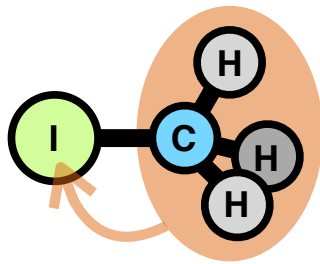


Rudenko *et al.*, *Nature* **546**, 129 (2017).

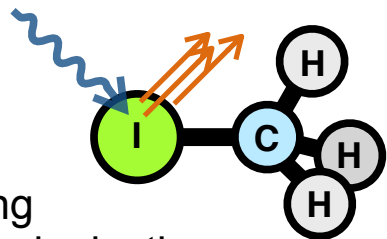
Ionization enhanced by charge rearrangement



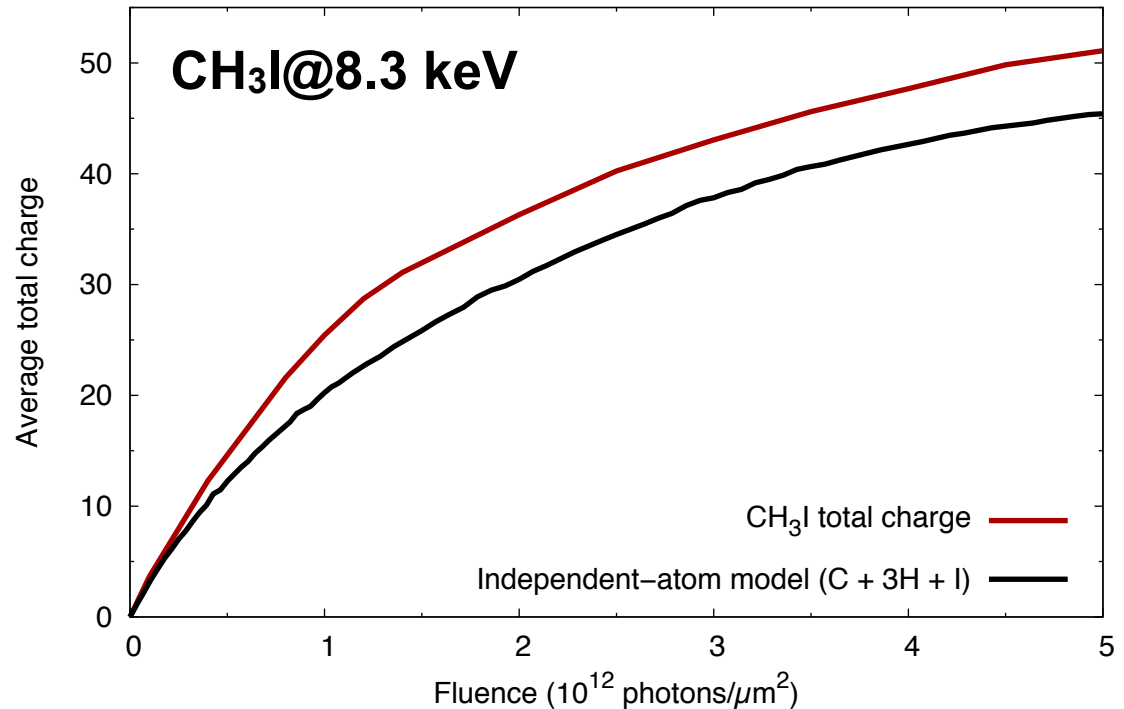
selective ionization
induces charge imbalance



charge rearrangement



repeating
selective ionization

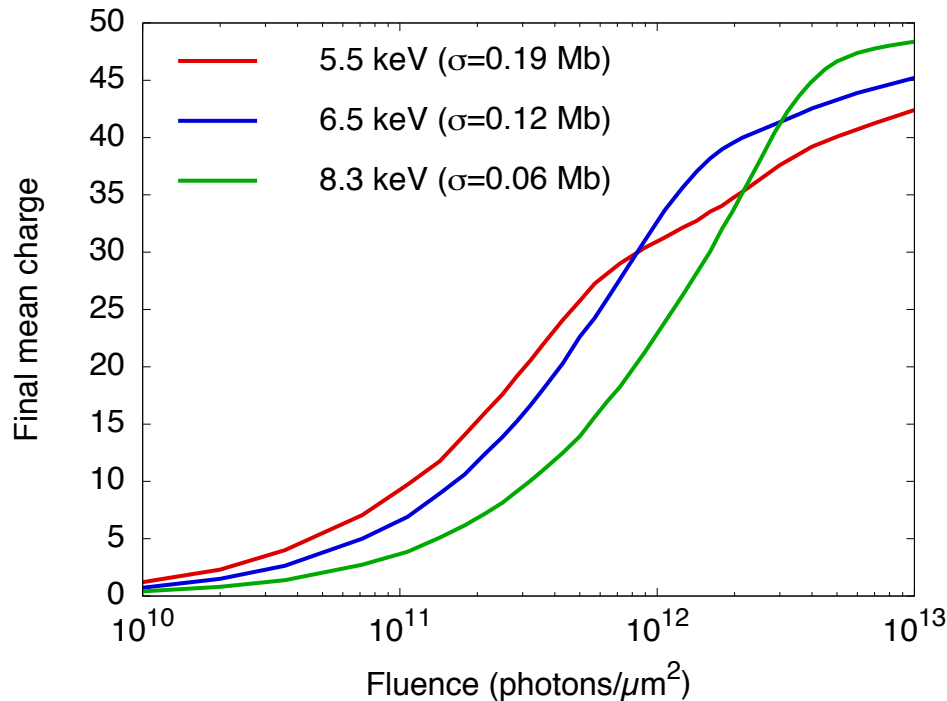


CREXIM: Charge-Rearrangement-Enhanced X-ray Ionization of Molecules

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

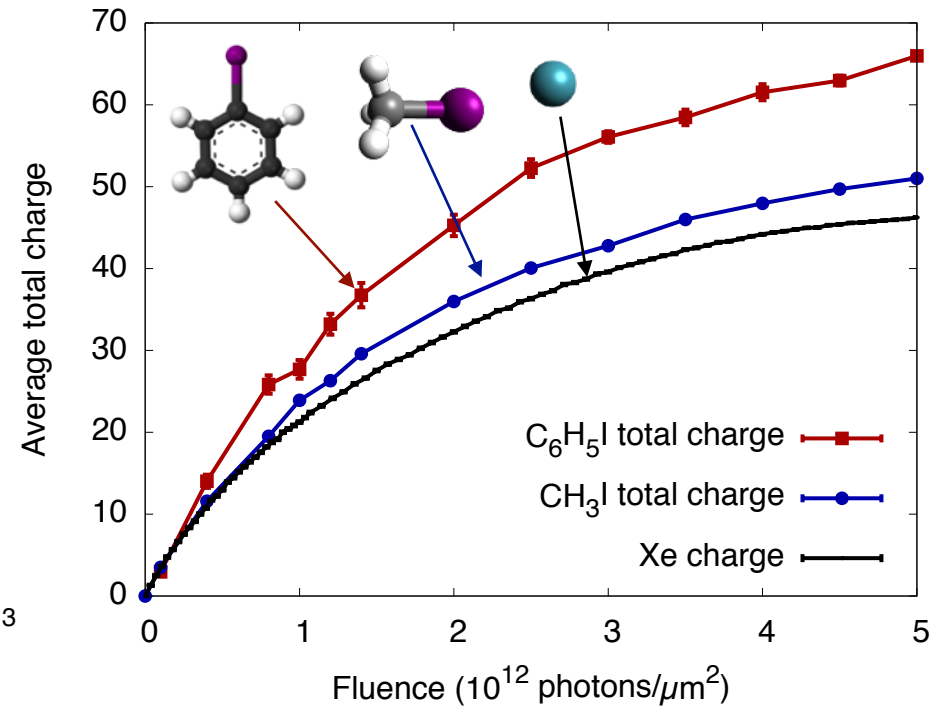
Multiphoton ionization at high x-ray intensity

Xe@different photon energies



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

I-containing molecules@8.3 keV



Hao *et al.*, *PRA* **100**, 013402 (2019).

- > At low fluence: ionization linearly proportional to cross section
- > At high fluence: need for tools to predict x-ray multiphoton processes

Conclusion

- XATOM & XMOLECULE: Enabling tools for investigating x-ray multiphoton physics of atoms and molecules exposed to high-intensity x-ray pulses
- XFEL–matter interaction: sequential multiphoton multiple ionization
- Intriguing phenomena of atoms and molecules with intense XFEL pulses
 - Xe: ionization enhanced via resonances (REXMI) and modulated by relativity
 - CH₃I: ionization enhanced via intramolecular charge rearrangement (CREXIM)
- Theory provides the predictive power for x-ray multiphoton ionization

Thank you for your attention!