Ultrafast dynamics of atoms and molecules with XFELs

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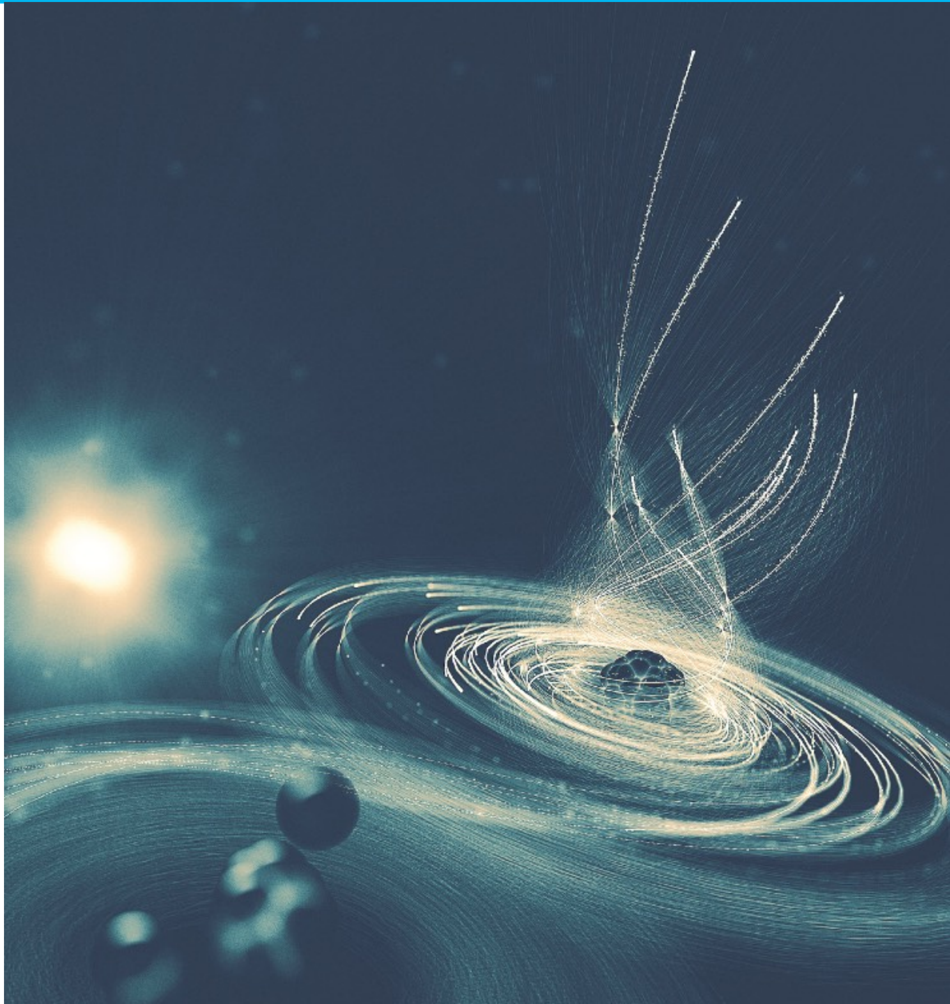


CFEL SCIENCE · DESY. · HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

Acknowledgment

XMOLECULE development

XATOM development

Yajiang Hao
Now at USTB
(Beijing)

Ludger Inhester

Kota Hanasaki
Now at Kyoto Univ.

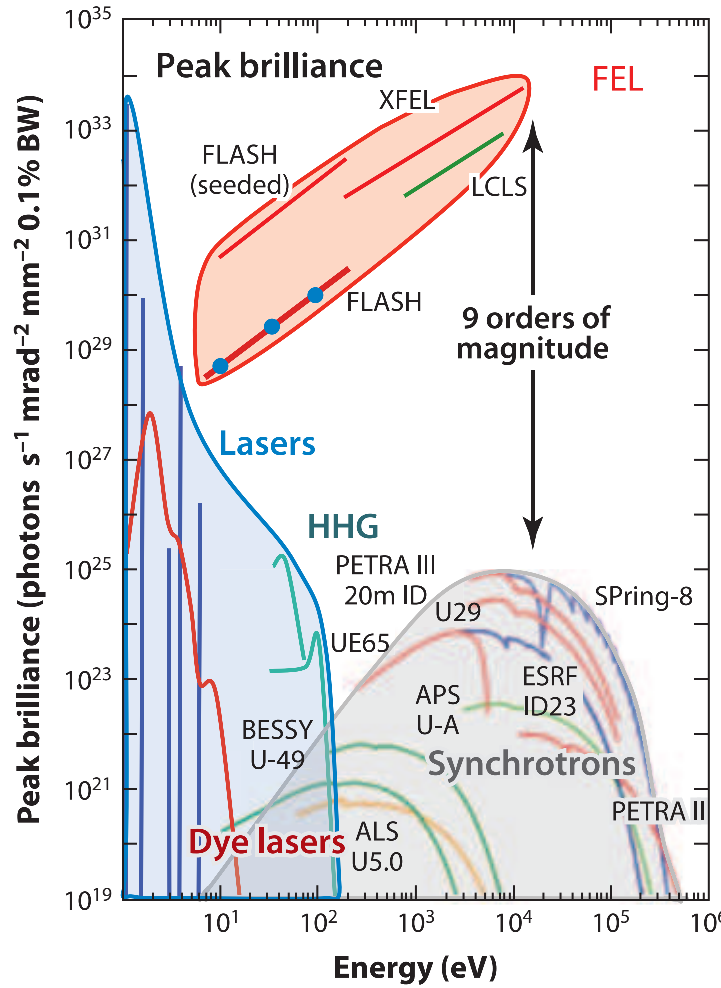
Koudai Toyota

Oriol Vendrell
Now at Heidelberg Univ.

Robin Santra

XFEL: X-ray free-electron laser

- XFEL: *ultraintense* and *ultrashort*
- X-ray beam parameters
  - photon energy: ~keV
  - focal size: ~submicron
  - pulse duration: ~few femtoseconds
  - ➔ peak intensity: **~10^{20} W/cm^2**
- Where are XFELs?
  - LCLS at SLAC, USA (2009)
  - SACLA at RIKEN Harima, Japan (2011)
  - PAL XFEL at Pohang, Korea (2017)
  - European XFEL, Germany (2017)



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

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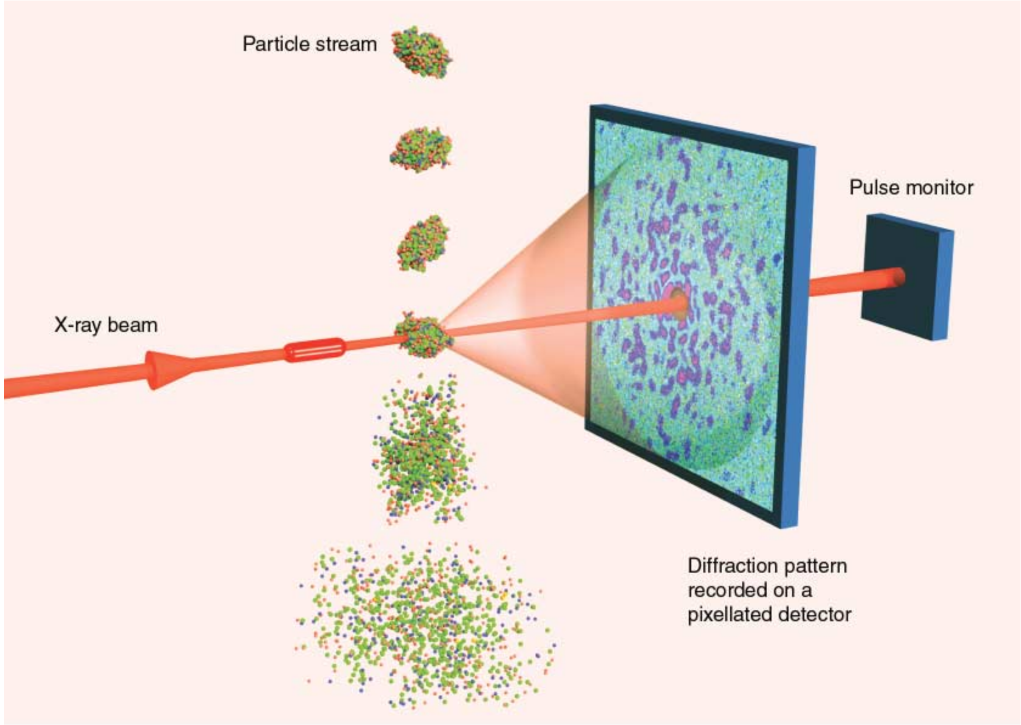
Why *ultraintense* and *ultrafast*?

- 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

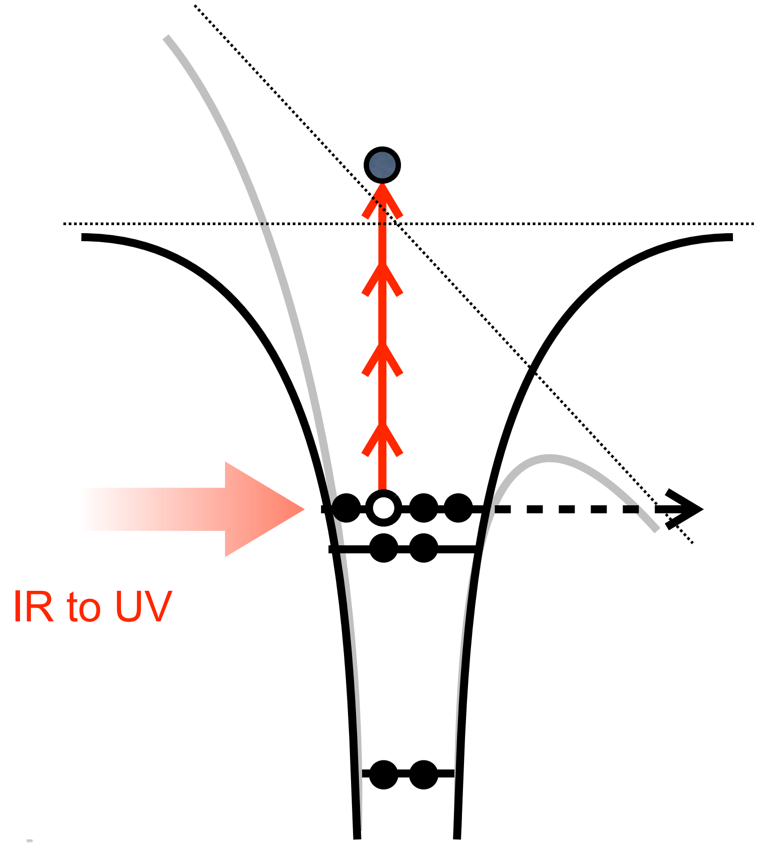


Gaffney & Chapman, *Science* **316**, 1444 (2007).

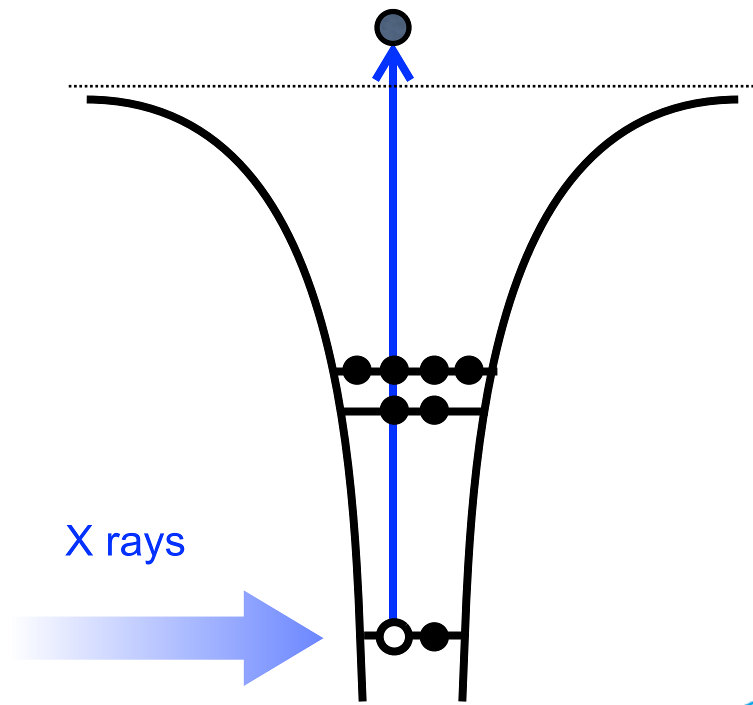
How does matter interact with *ultraintense* and *ultrafast* pulses?

Strong light-matter interaction

> Optical strong-field regime
- tunneling or multiphoton processes
- valence-electron ionization



> Intense X-ray regime
- mainly one-photon processes
- core-electron ionization and relaxation
- multiphoton multiple ionization via a sequence of one-photon processes

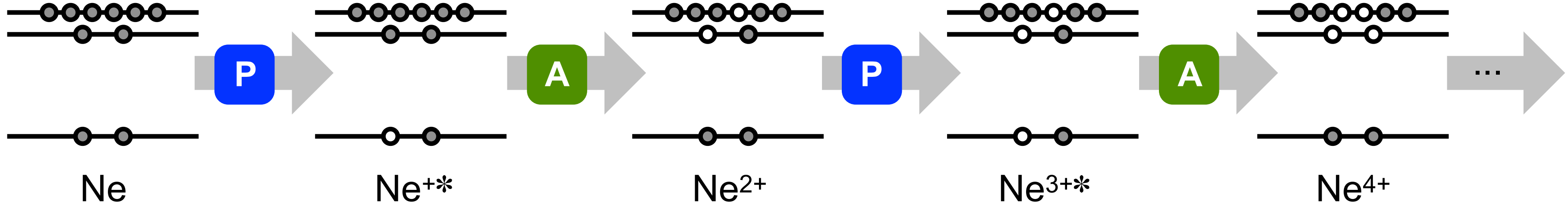


X-ray multiphoton absorption

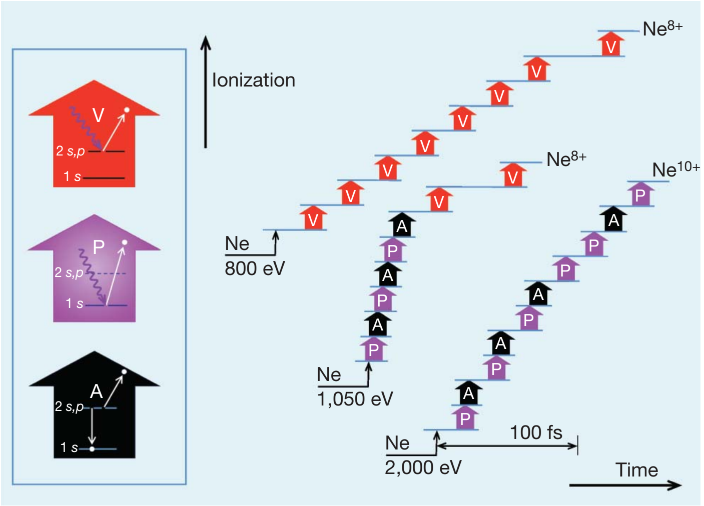
- Direct multiphoton absorption cross section is too small

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

- Sequential multiphoton absorption is dominant



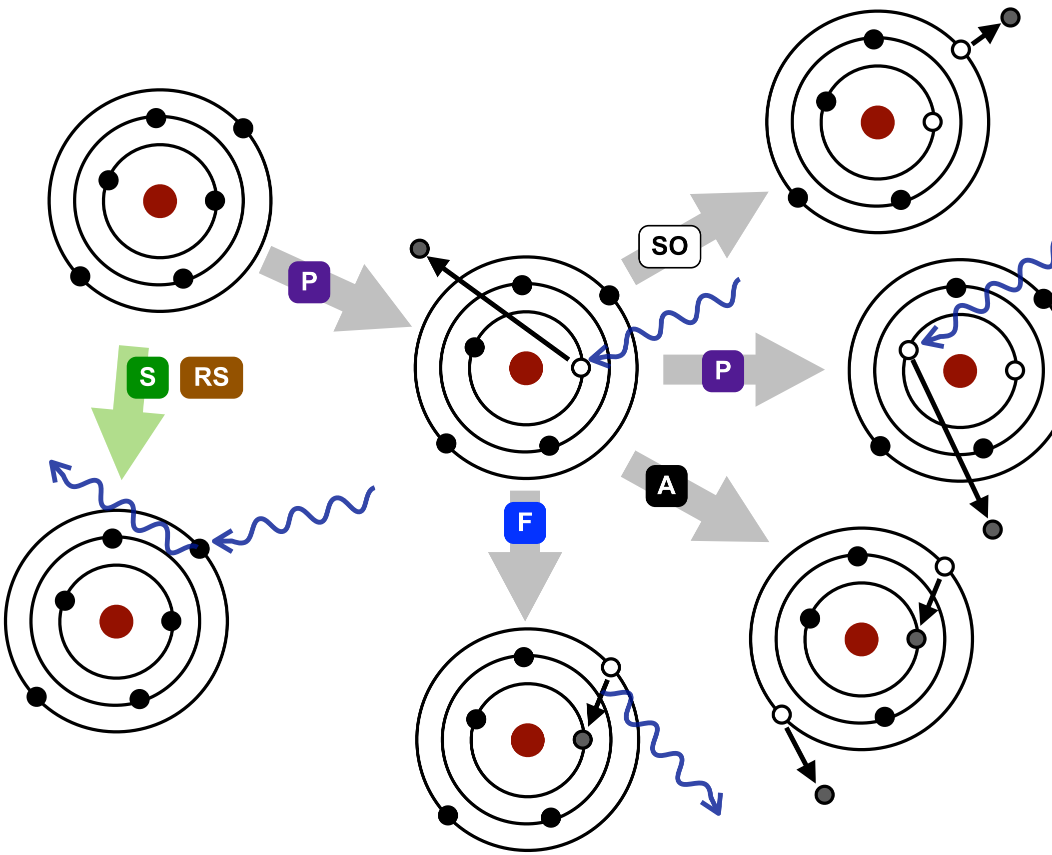
Sequential multiphoton multiple ionization dynamics



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

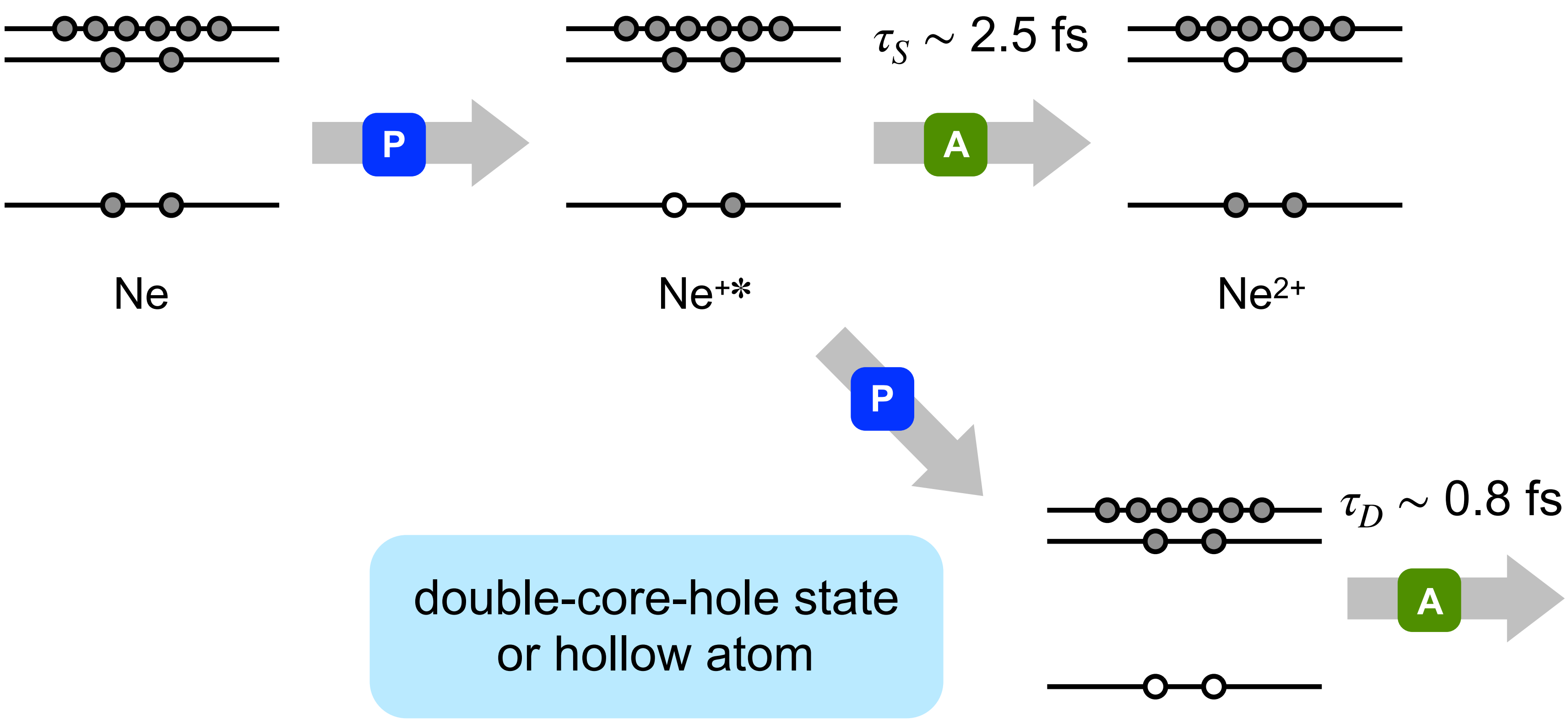
XATOM

- X-ray-induced atomic processes calculated for any given element and configuration
- Ionization dynamics solved by a rate-equation approach
- Sequential ionization model has been tested by a series of atomic XFEL experiments



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

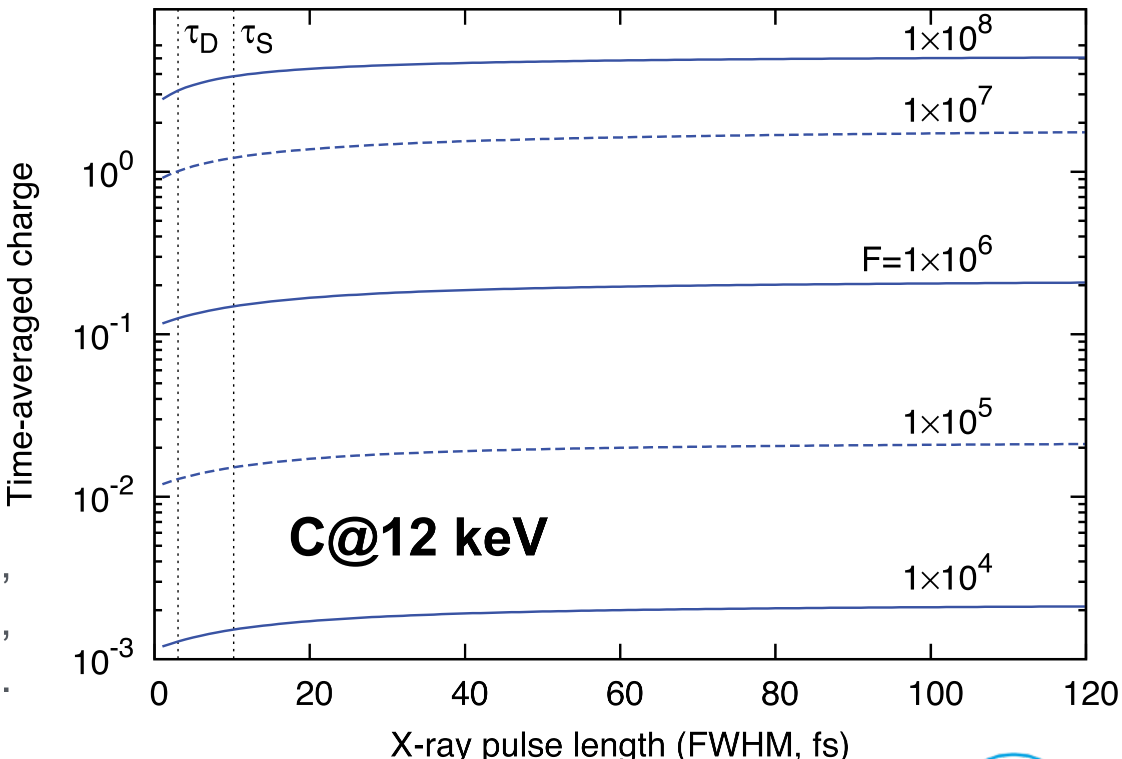
Hollow atom or double-core-hole state



No more *K*-shell absorption

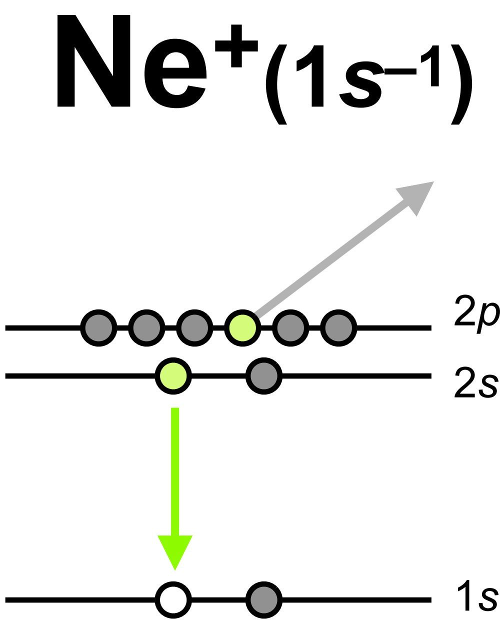
Shorter pulse induces less ionization

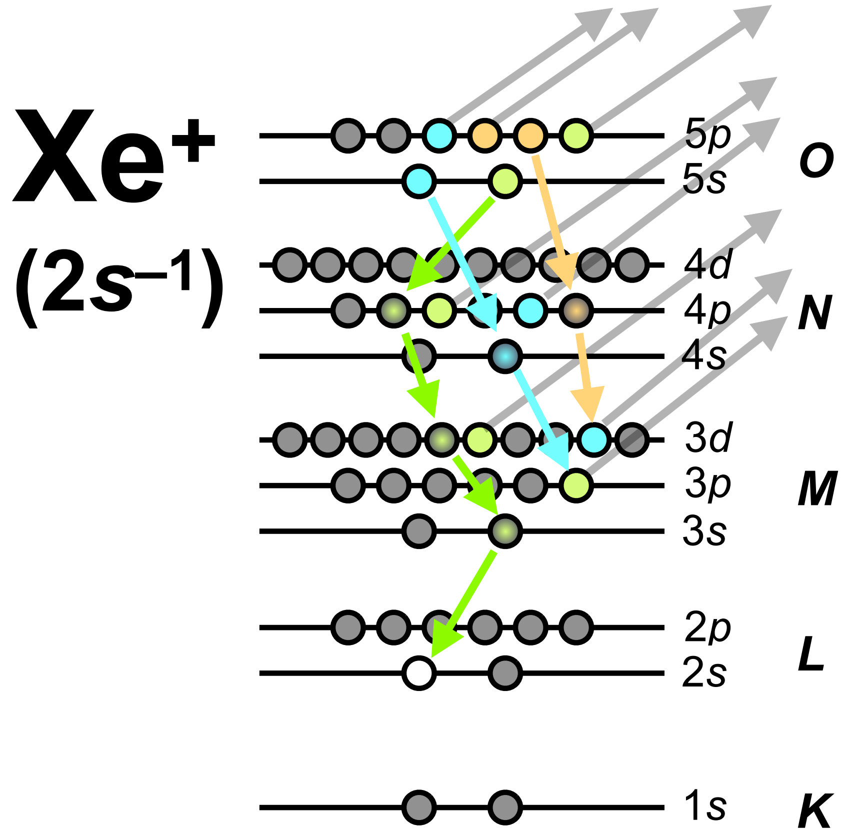
- When the pulse is short enough to compete with core-hole lifetimes
  - intensity-induced x-ray transparency — Young *et al.*, *Nature* **466**, 56 (2010).
  - frustrated absorption — Hoener *et al.*, *Phys. Rev. Lett.* **104**, 253002 (2010).
- *Higher intensity* (shorter pulse duration) of XFEL pulses induces *less ionization* due to hollow-atom formation



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

Complex inner-shell ionization dynamics

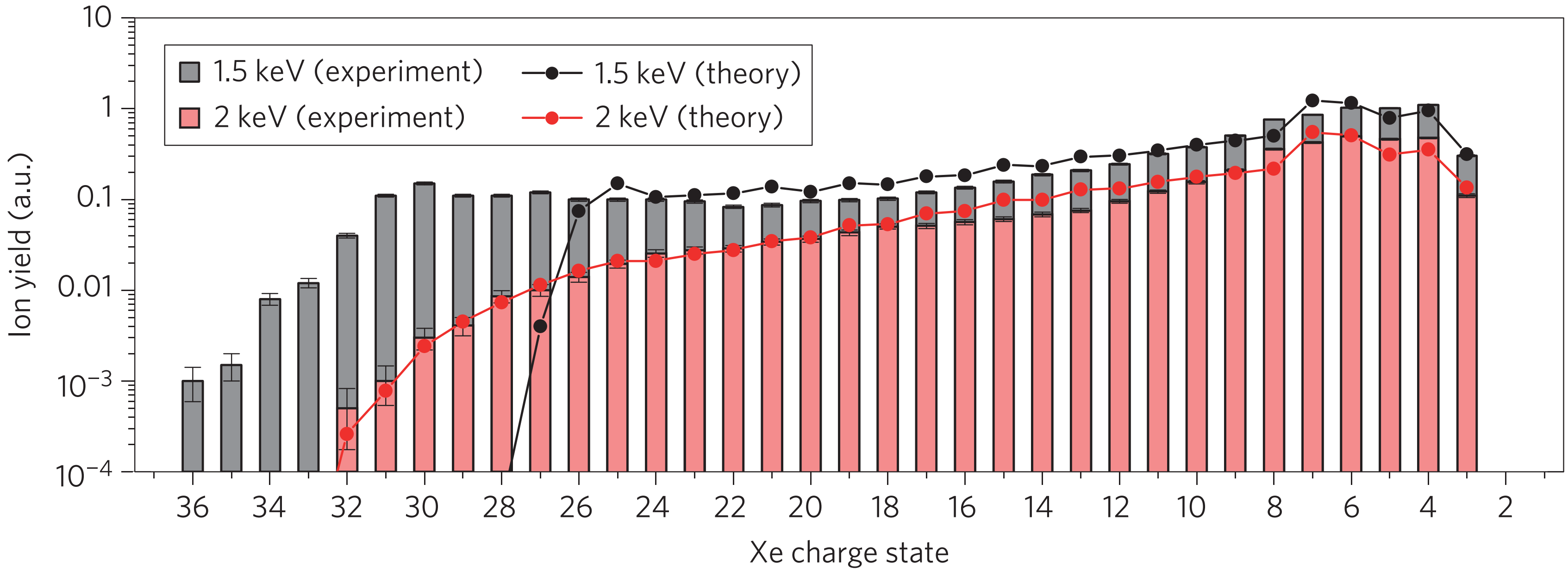




Multiphoton absorption after/during decay cascade

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

Ultra-efficient ionization by XFEL



LCLS experiment

Daniel Rolles at KSU

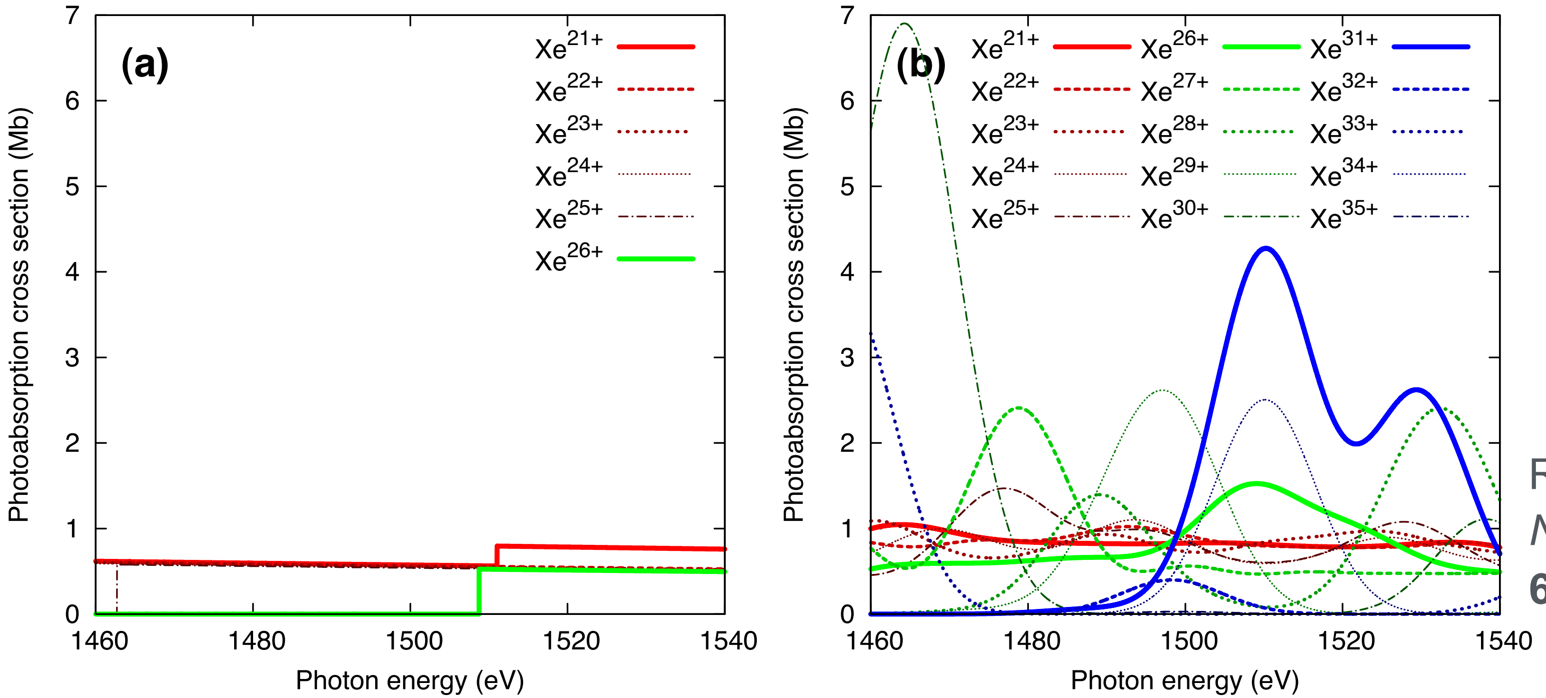
Artem Rudenko at KSU

Benedikt Rudek at PTB

- Xe *M*-shell ionization
- 2 keV: excellent agreement between theory and experiment
- 1.5 keV: further ionization via resonance

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

Ionization enhanced by resonances

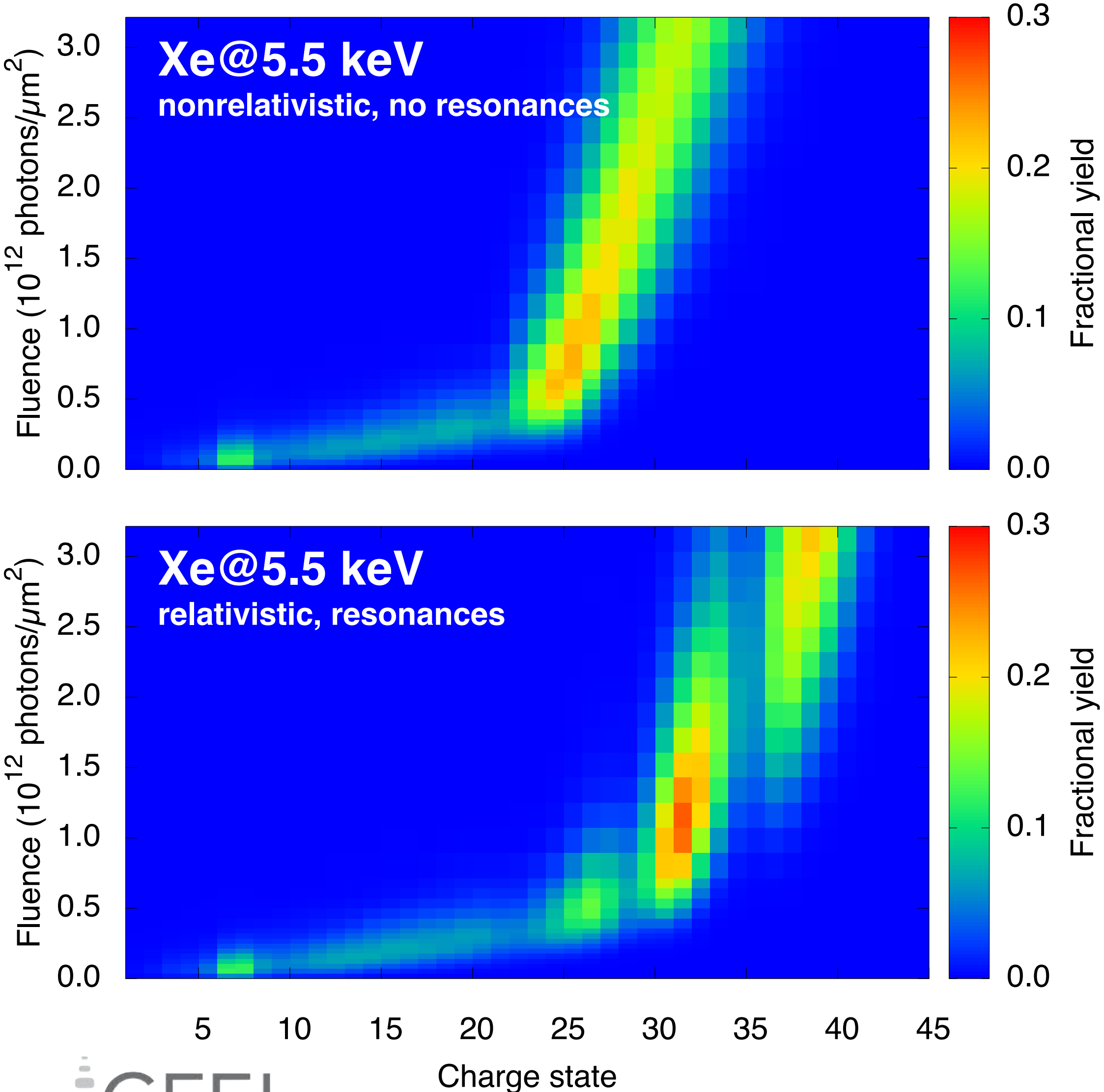


Rudek *et al.*, *Nature Photon.* **6**, 858 (2012).

REXMI: Resonance-Enabled X-ray Multiple Ionization

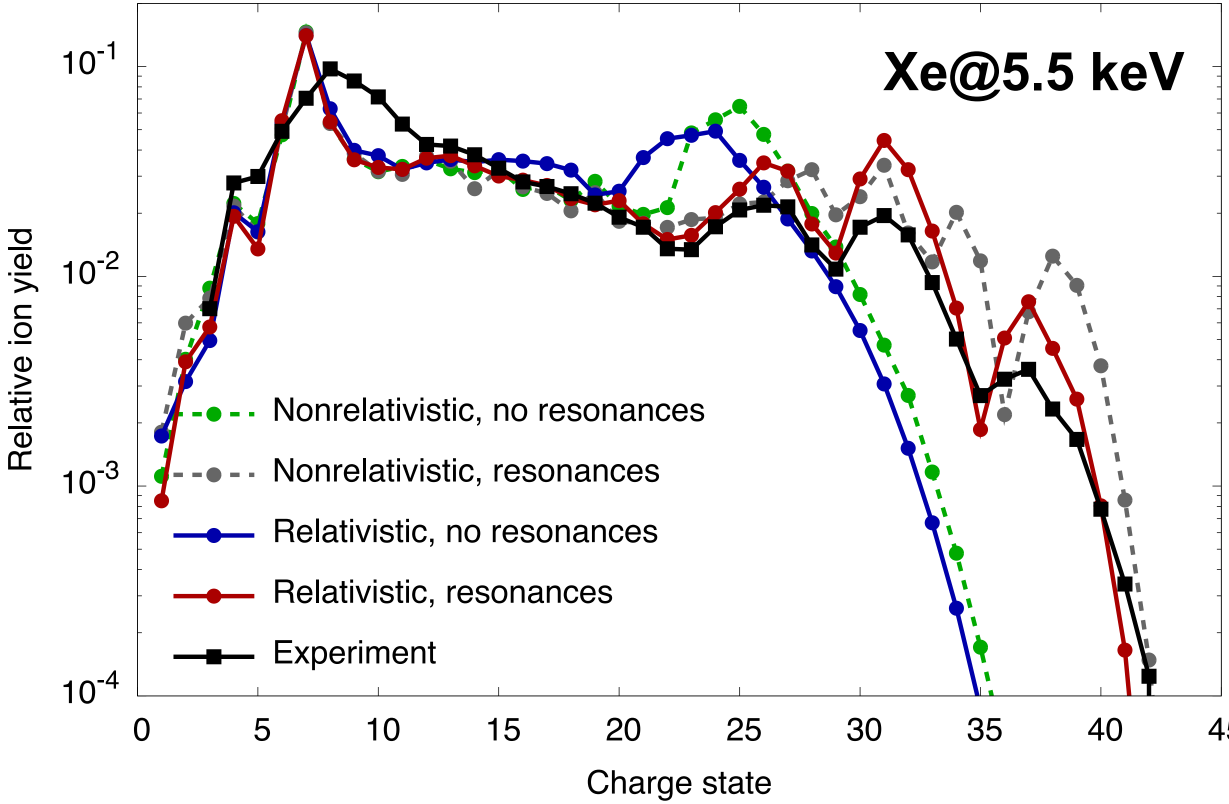
- Multiple resonant excitations occur in a range of charge states
- A broad bandwidth required (typical XFEL bandwidth: ~1%)

Interplay between resonance and relativity



- Harder x-rays drive *L*-shell ionization of Xe
- Spin-orbit splitting: $2p \rightarrow 2p_{1/2}$ and $2p_{3/2}$
- XATOM extended to treat both resonant and relativistic effects
- *N* of coupled rate equations to be solved: ~20M (non-relativistic) ➔ ~5B (relativistic) ➔ ~10^{68} (including both resonant and relativistic effects)

REXMI with relativistic effects



LCLS experiment:
Benedikt Rudek,
Daniel Rolles,
Artem Rudenko

- Excellent agreement between theory and experiment
- Distinctive bumps in the charge states ➔ *L*-shell spin-orbit splitting

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

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
  - Extremely complicated dynamics:
    e.g. CH_3I ~ 200 trillion rate equations 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, *Phys. Rev. A* **94**, 023422 (2016).

Iodomethane in an *ultraintense* x-ray pulse

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

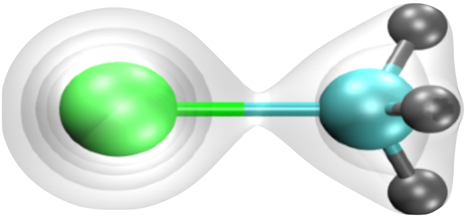
LCLS experiment

Daniel Rolles at KSU

Artem Rudenko at KSU

- Selective ionization on heavy atom

CH_3I @ 8.3 keV

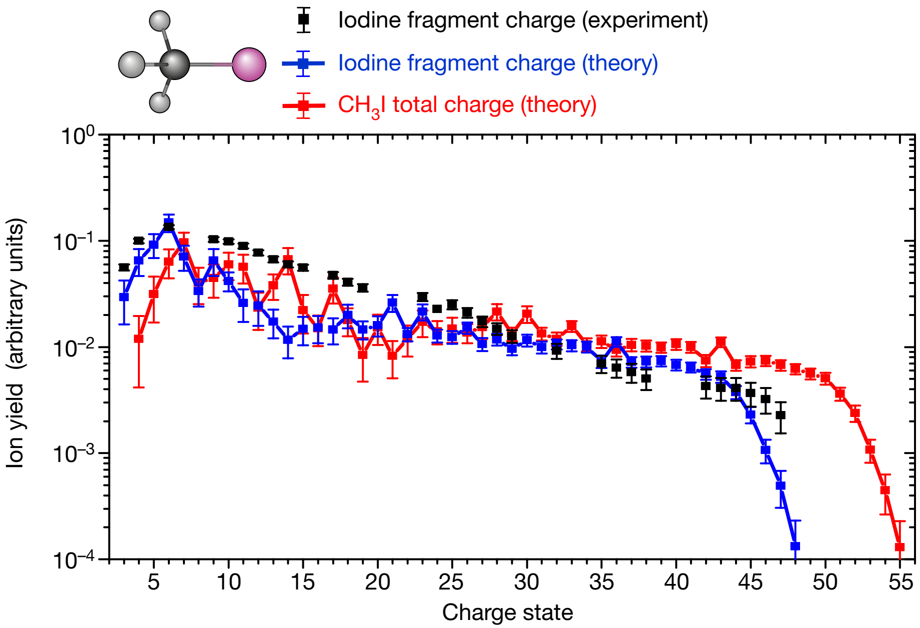


σ(I)~50 kbarn
σ(C)~80 barn
σ(H)~8 mbarn

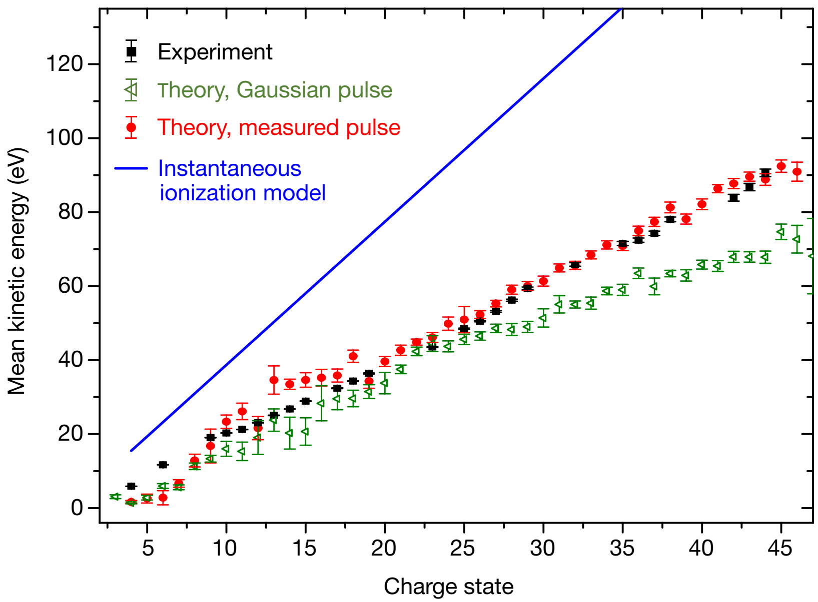
- X-ray multiphoton ionization occurs at high intensity
- Charge imbalance induces charge rearrangement
- Coulomb explosion after/during ionization & charge rearrangement

Comparison between theory & experiment

CSD of I and CH_3I



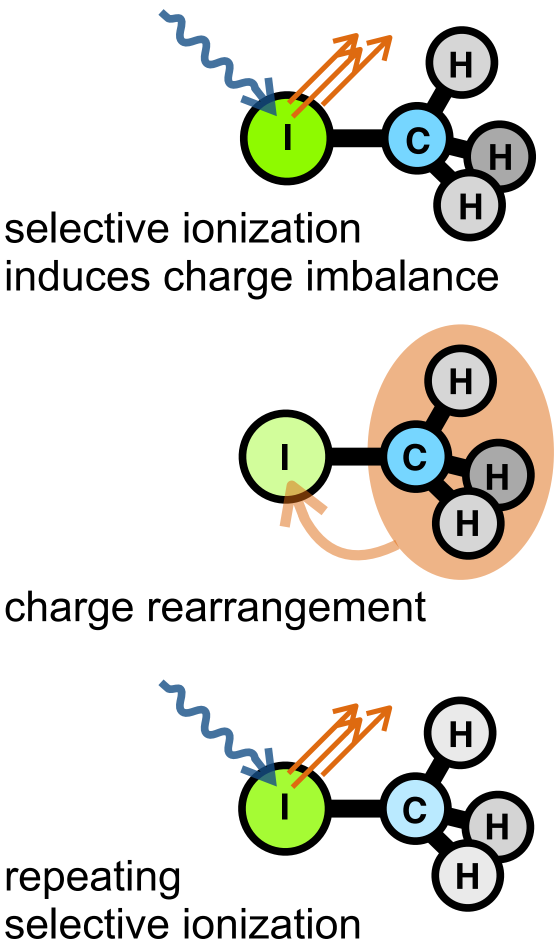
KER of I fragment

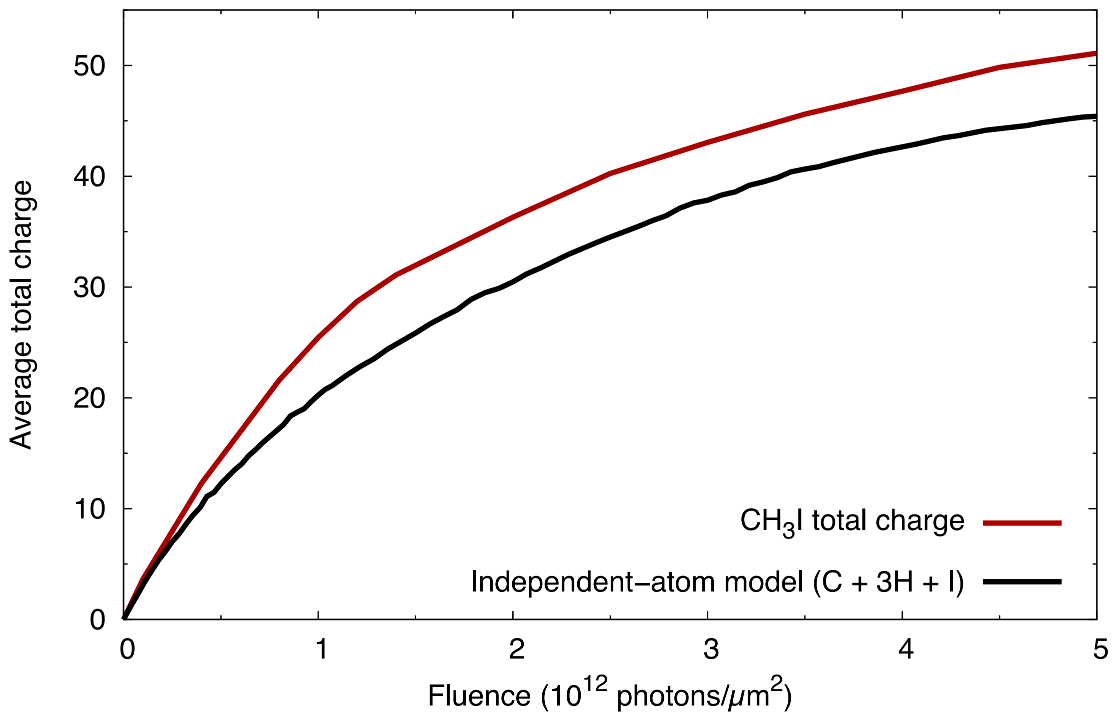


- CSD (charge-state distribution) and KER (Kinetic energy releases): sensitive to detailed ionization and fragmentation dynamics
- Capturing the essence of ionization and fragmentation dynamics of molecules at high x-ray intensity

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

Ionization enhanced by charge rearrangement

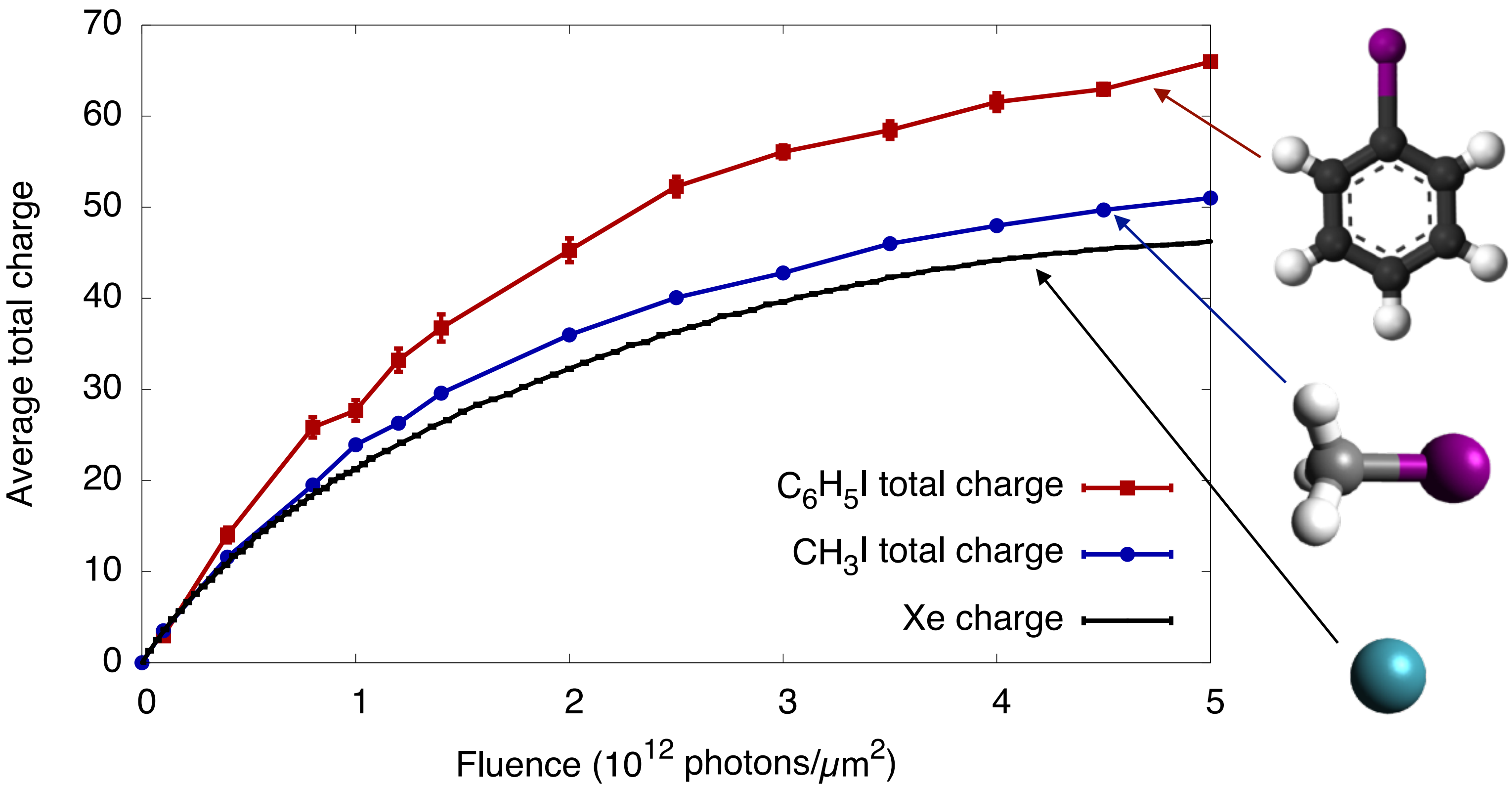




CREXIM: Charge-Rearrangement-Enhanced X-ray Ionization of Molecules

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

Bigger molecule, larger enhancement



- Xe, iodomethane, iodobenzene: similar cross section at 8.3 keV
- The stronger ionization for the larger molecule

Hao, Inhester, Son & Santra, (in preparation).

Conclusion

- XFEL provides *ultraintense* and *ultrashort* x-ray pulses
- XATOM & XMOLECULE: Enabling tools to investigate x-ray multiphoton physics of atoms and molecules exposed to high-intensity x-ray pulses
- Intriguing phenomena of atoms and molecules with intense XFEL pulses
  - Shorter pulse duration reduces ionization ➔ frustrated absorption
  - Multiple resonance enhances ionization ➔ REXMI
  - Charge rearrangement enhances ionization ➔ CREXIM
- Theory provides crucial insights of the XFEL–matter interaction

Thank you for your attention!

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