What happens to atoms and molecules during XFEL pulses?

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Seminar on Dynamical Aspects of Theoretical Chemistry
Freie Universtät Berlin, November 19, 2015

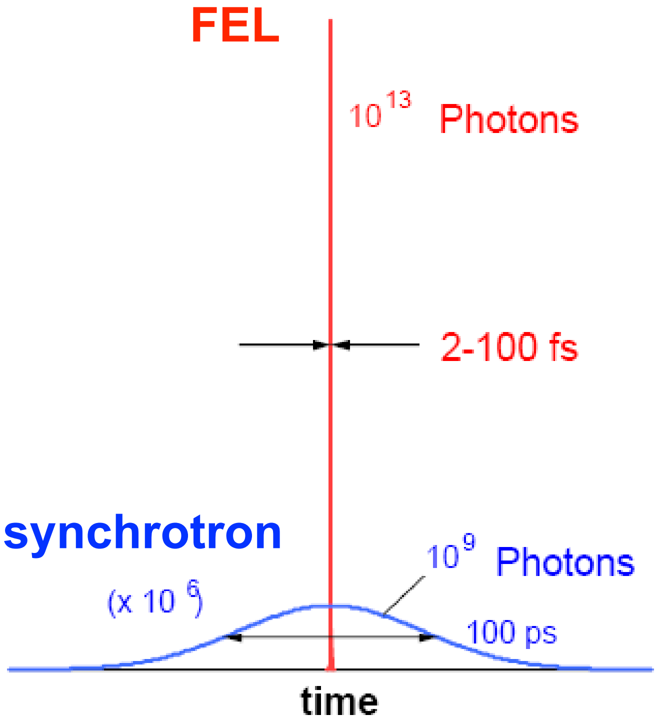
Overview

- Introduction to XFEL science
- Atom: x-ray multiphoton multiple ionization dynamics of Xe
- Molecule: x-ray ionization and fragmentation dynamics of CH_3I
- Summary

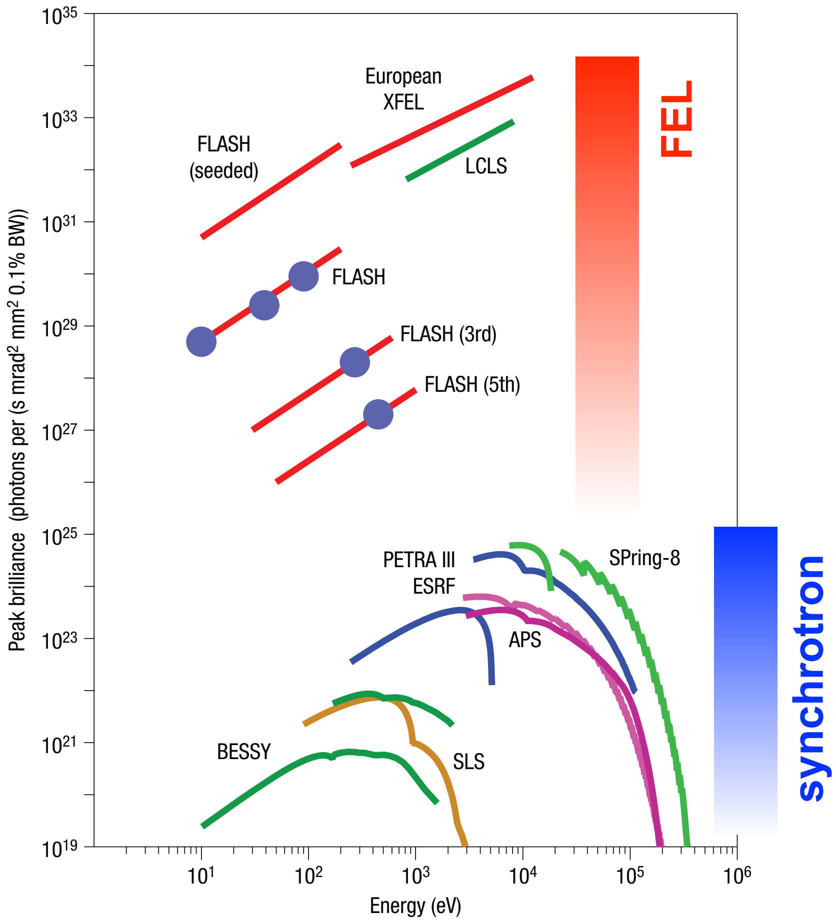
Introduction

XFEL: X-ray free-electron laser

- *Ultraintense*: ~10^{13} photons
- *Ultrafast*: ~femtoseconds



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



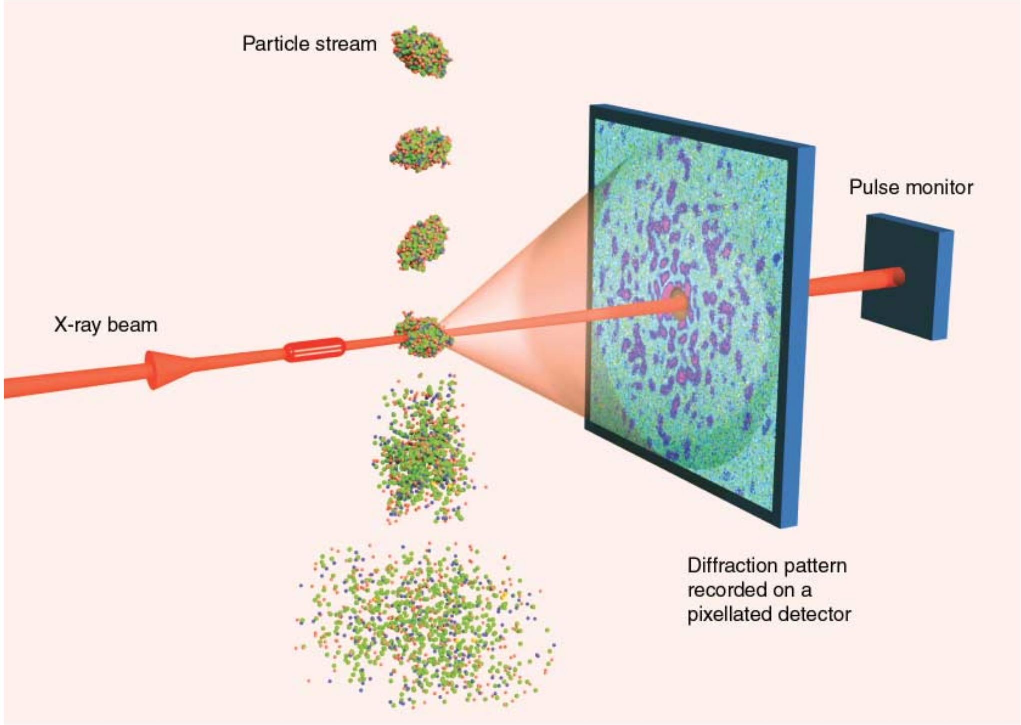
Ackermann *et al.*, *Nature Photon.* **1**, 336 (2007).

Where are XFELs?

- FLASH at DESY, Germany (2004)
- LCLS at SLAC, USA (2009)
- SACLA at RIKEN Harima, Japan (2011)
- PAL XFEL at Pohang, Korea (2016)
- 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
- XFEL provides *ultraintense* and *ultrafast* pulses
- Enough signals obtained from *nano-sized crystals* or even single molecules



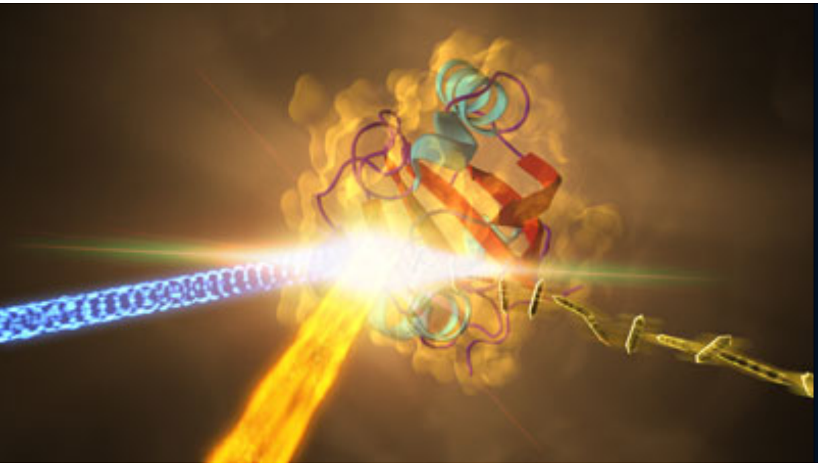
Gaffney & Chapman, *Science* **316**, 1444 (2007).

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

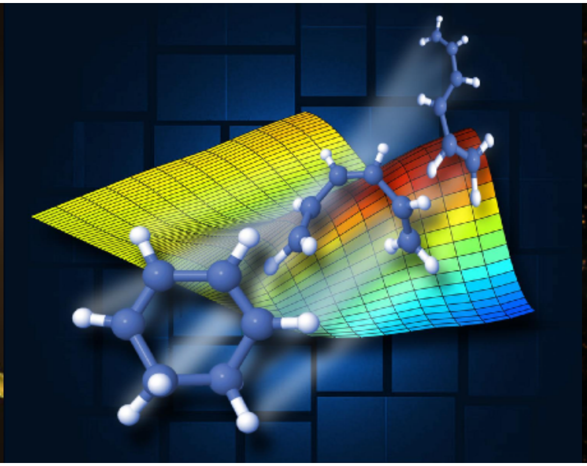
XFEL science

- Imaging of biomolecules for biology and life science
- Ultrafast dynamics for chemistry and material science
- Matter in extreme states for astrophysics and energy science

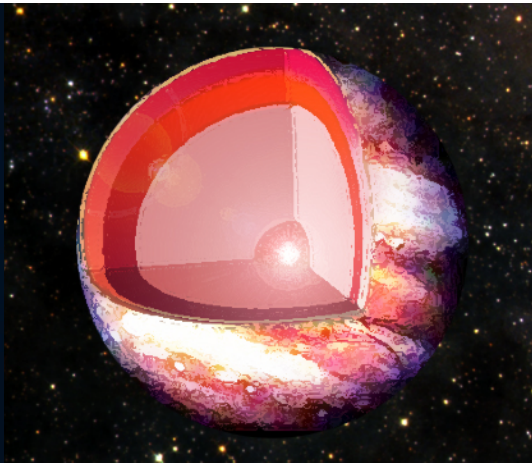
→ XFEL applications waiting for increased theoretical support



SLAC



SLAC

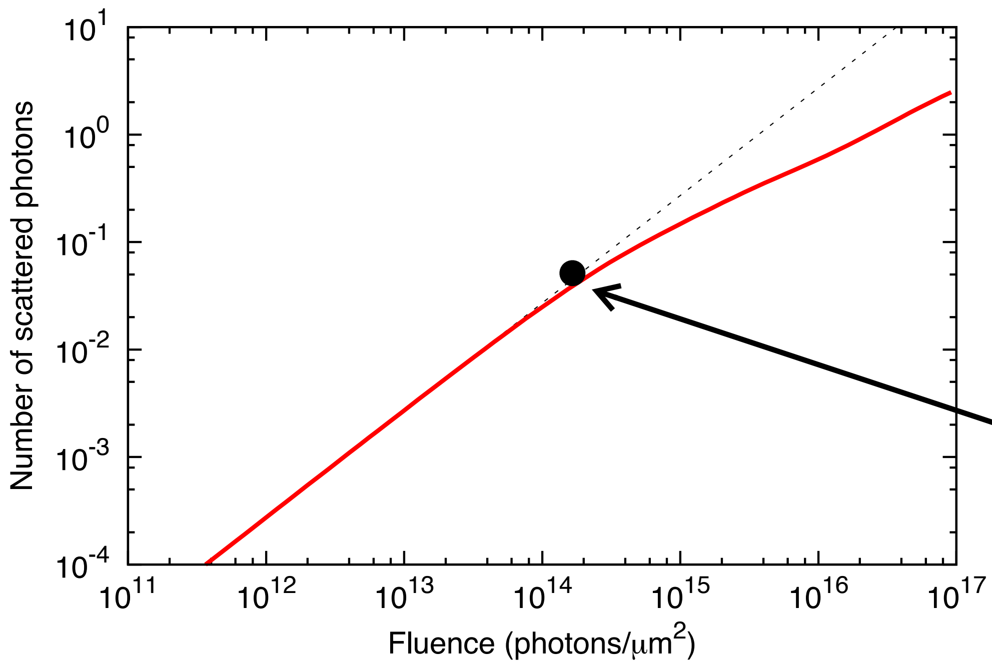


LBL

ATOM

What happens at high x-ray intensity?

- Fluence (photons/unit area) to saturate one-photon absorption



C @ 8 keV

σ_{abs} = 0.084 kbarns

⬇

prob. = $\sigma_{abs} \times F \sim 1$

⬇

$F_{sat} = 1.2\times10^{14}$ ph/μm^2

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

- High x-ray intensity beyond one-photon absorption saturation
  - synchrotron: at most one photon absorbed ➔ linear phenomena
  - XFEL: at least one photon absorbed ➔ nonlinear phenomena

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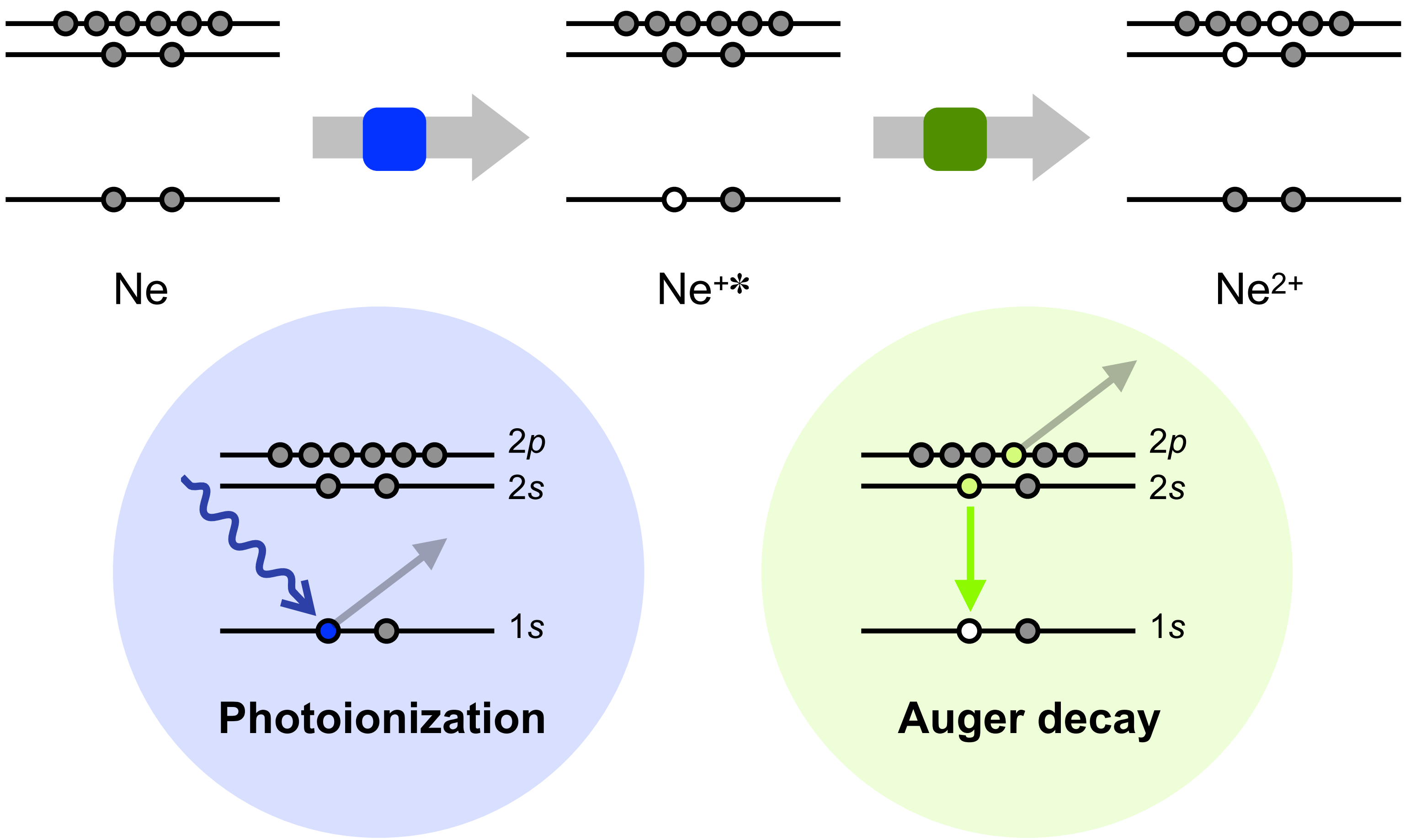
X-ray absorption (single photon)

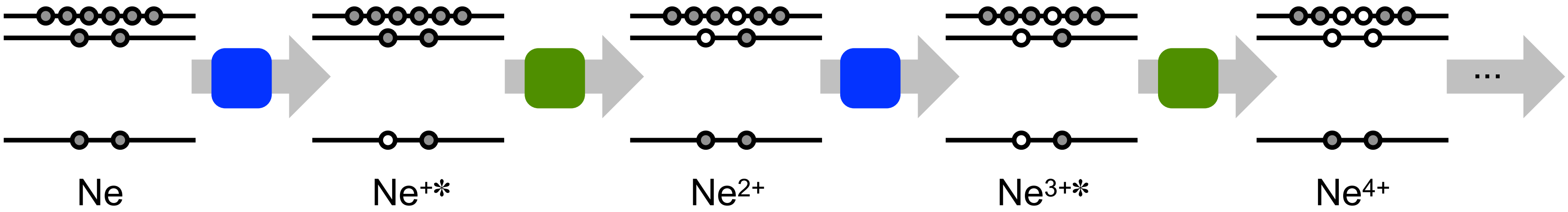


X-ray multiphoton absorption

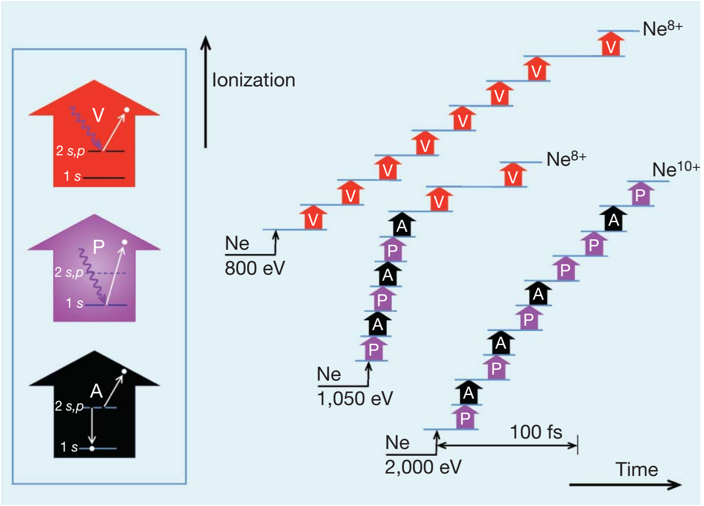
- Direct multiphoton absorption cross section is too small

  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).

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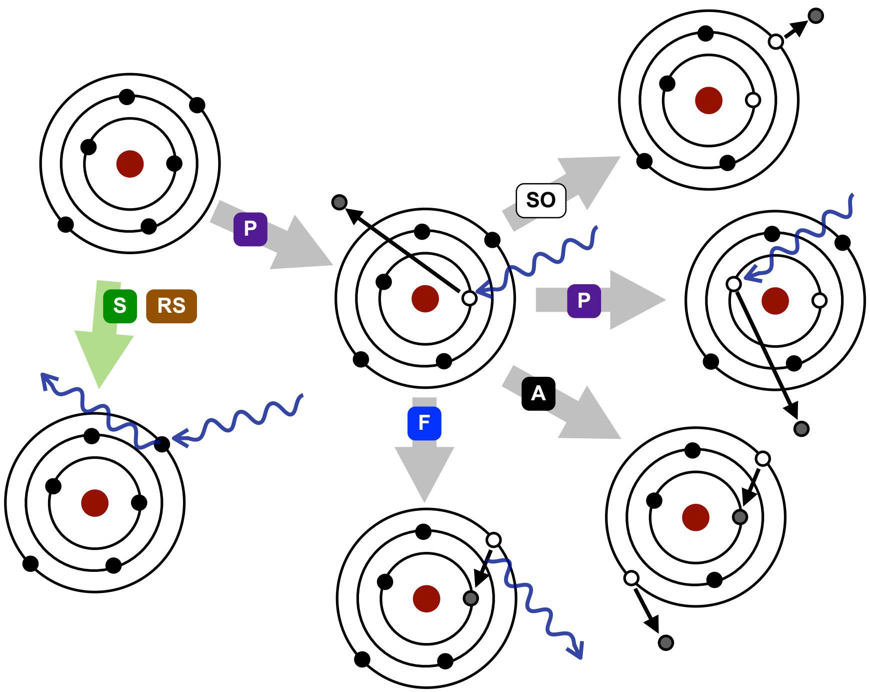
How to treat x-ray multiphoton dynamics?

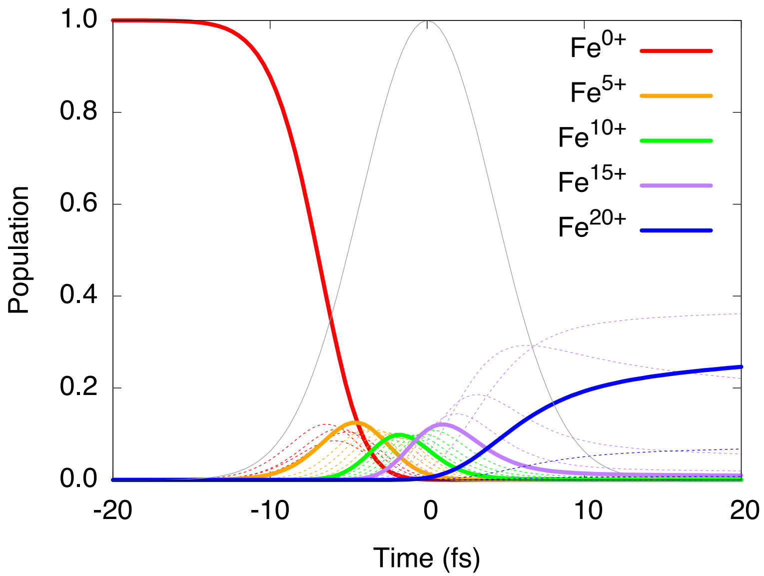
- No standard quantum chemistry code available

- Theoretical challenges
  - tremendously many hole states by x-ray multiphoton absorption
  - electronic continuum states
  - complex multiphoton multiple ionization dynamics
  - coupled ionization dynamics and nuclear dynamics (for molecules)

XATOM

- XATOM: x-ray and atomic physics toolkit
  - electronic structure: calculated for every single configuration
  - electronic dynamics: rate-equation model





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

XATOM: Numerical details

- Hartree-Fock-Slater method

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_X(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

- Numerical grid: non-uniform for bound states and uniform for continuum

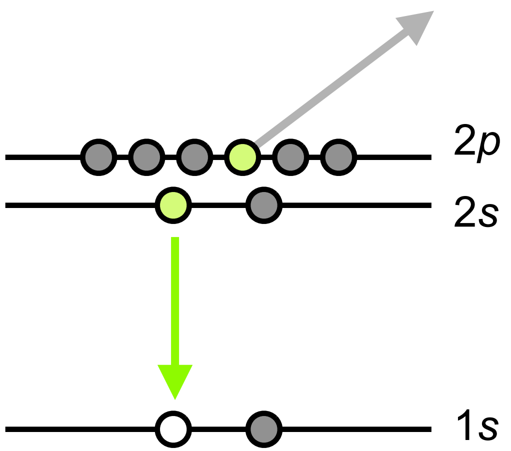
$$\psi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r}Y_{lm}(\theta,\varphi)$$

- Calculate all cross sections and rates of x-ray-induced processes using atomic continuum
- Solve coupled rate equations $\frac{d}{dt}P_I(t) = \sum_{I'\neq I}^{\text{all config.}}\left[\Gamma_{I'\to I}P_{I'}(t) - \Gamma_{I\to I'}P_I(t)\right]$
- Sequential ionization model has been tested by a series of atomic XFEL experiments: Ne, Ar, Kr, Xe, …

Example: Xe atom

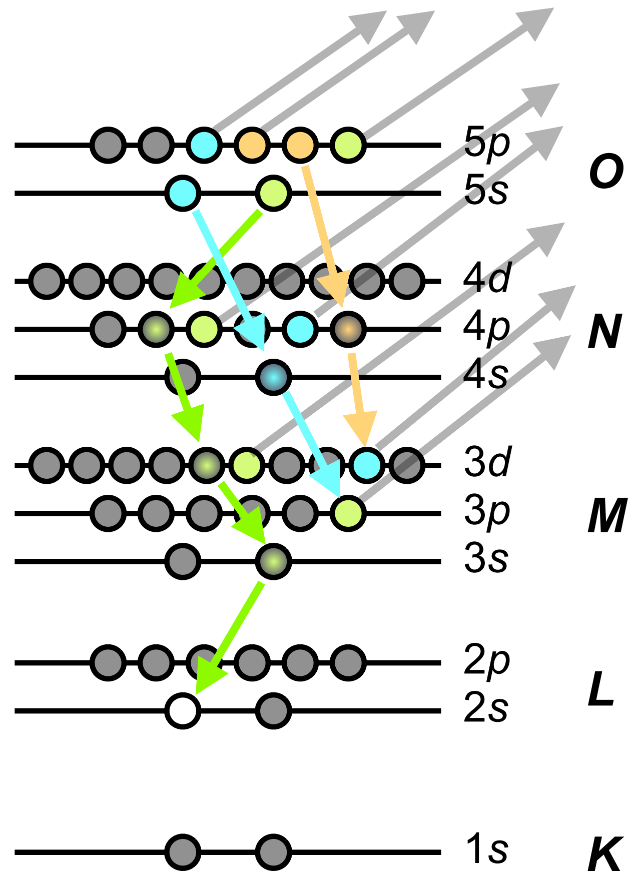
Complex inner-shell decay cascade

Ne



$Ne^{+*} \rightarrow Ne^{2+} + e^{-}$

Xe



$Xe^{+*} \rightarrow Xe^{(n+1)+} + ne^{-}$

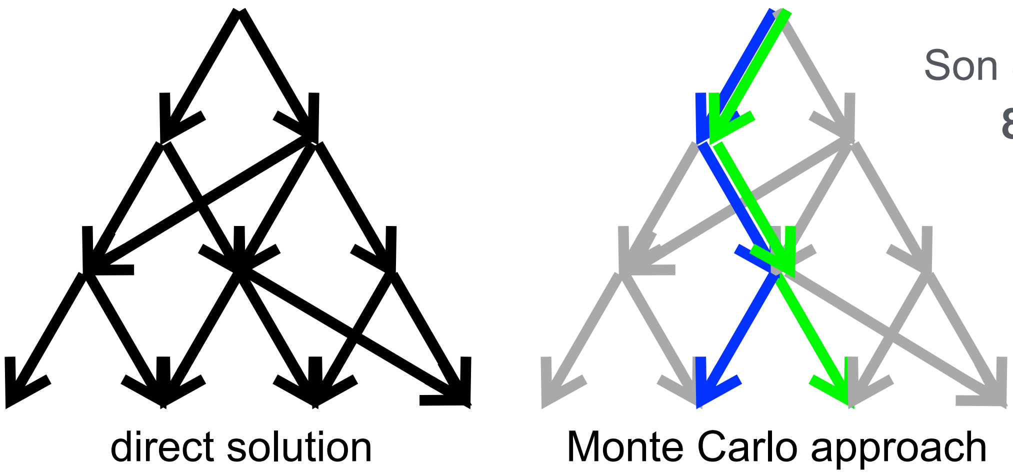
Auger (Coster-Kronig) decay cascade

Ionization dynamics: Monte Carlo method

Xe: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$

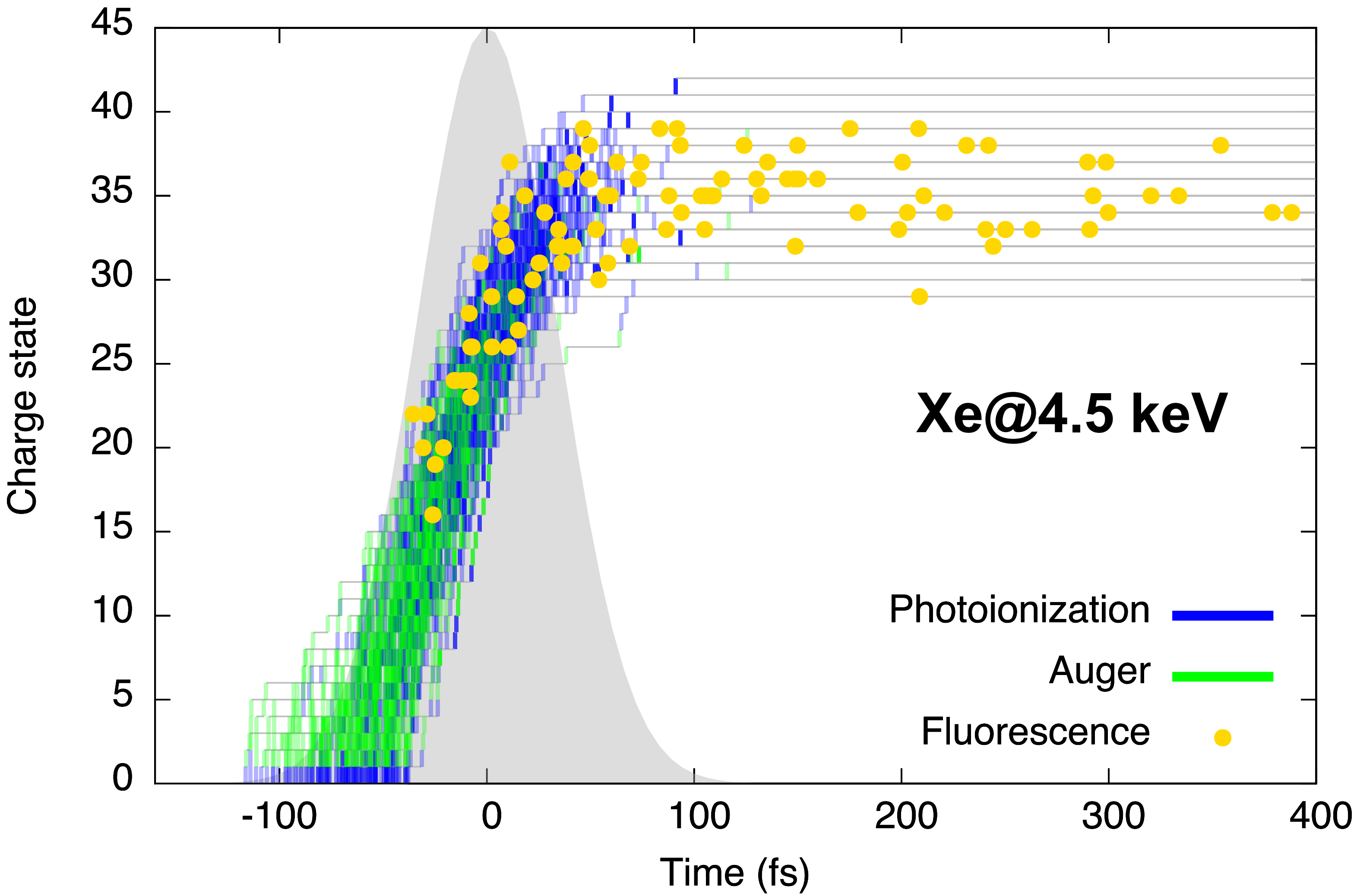
- More than 1 million coupled rate equations to be considered
- More than 40 million x-ray-induced processes to be considered

➔ solved by the Monte Carlo method



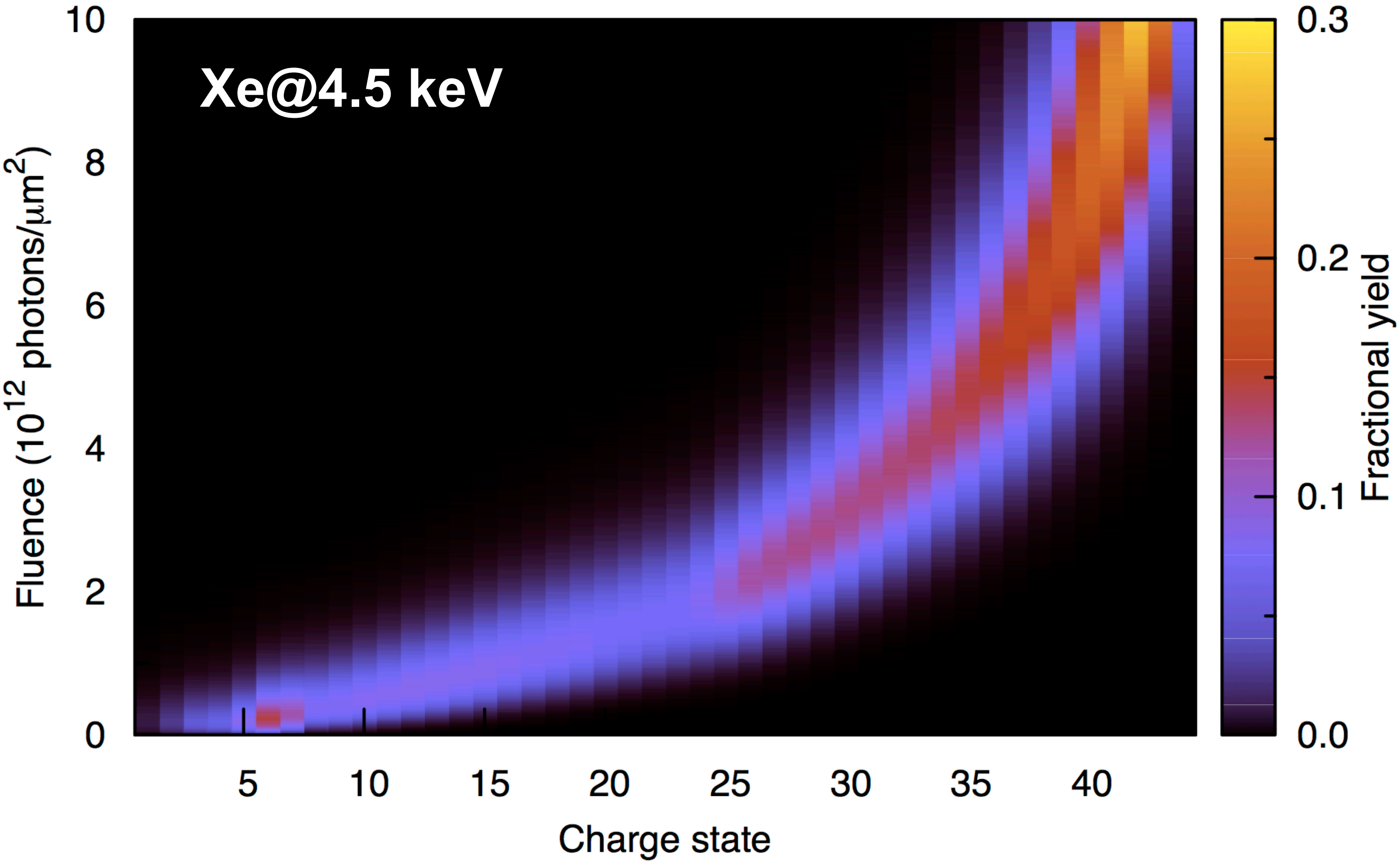
Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

X-ray multiphoton ionization dynamics



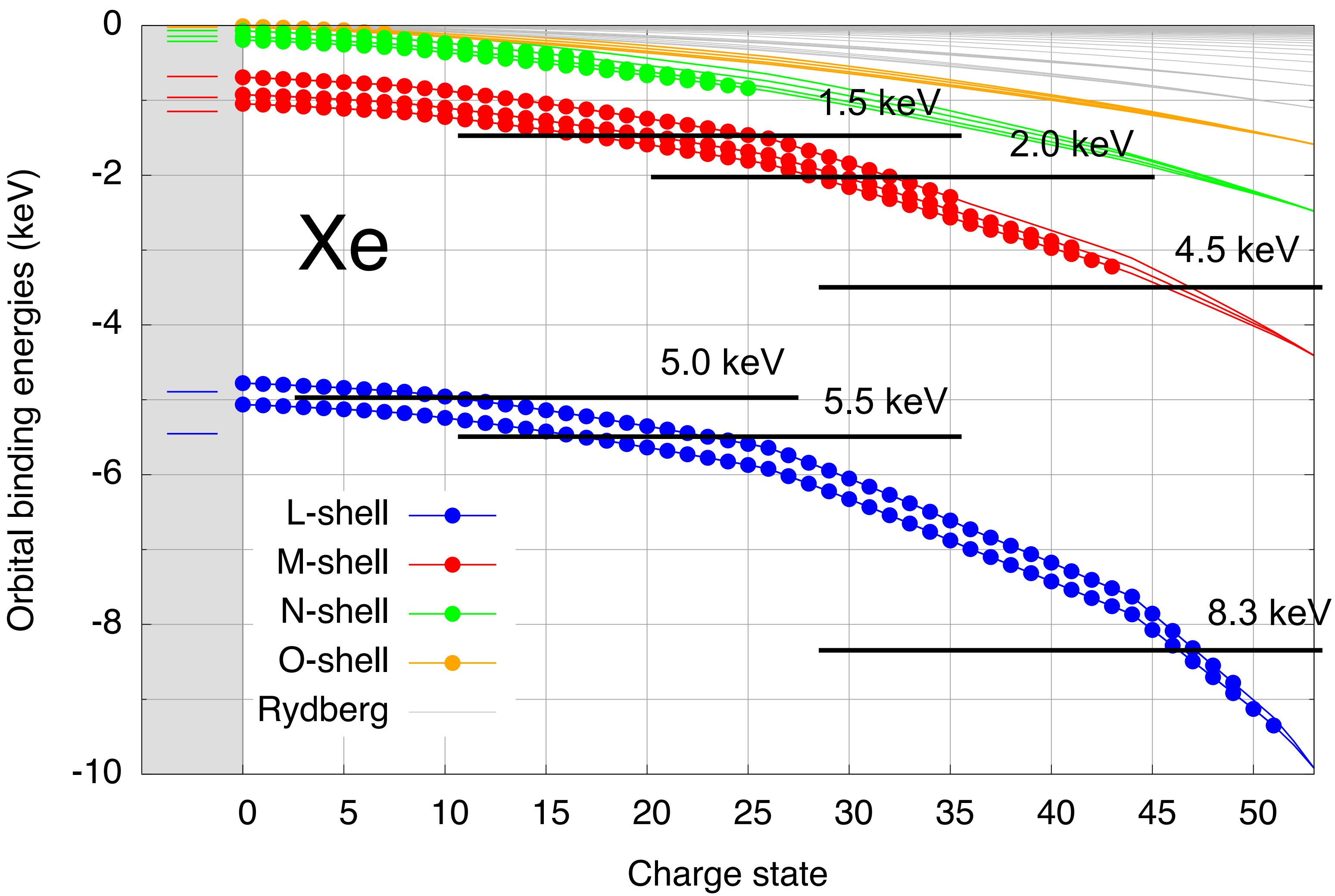
Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

Charge-state distributions of Xe

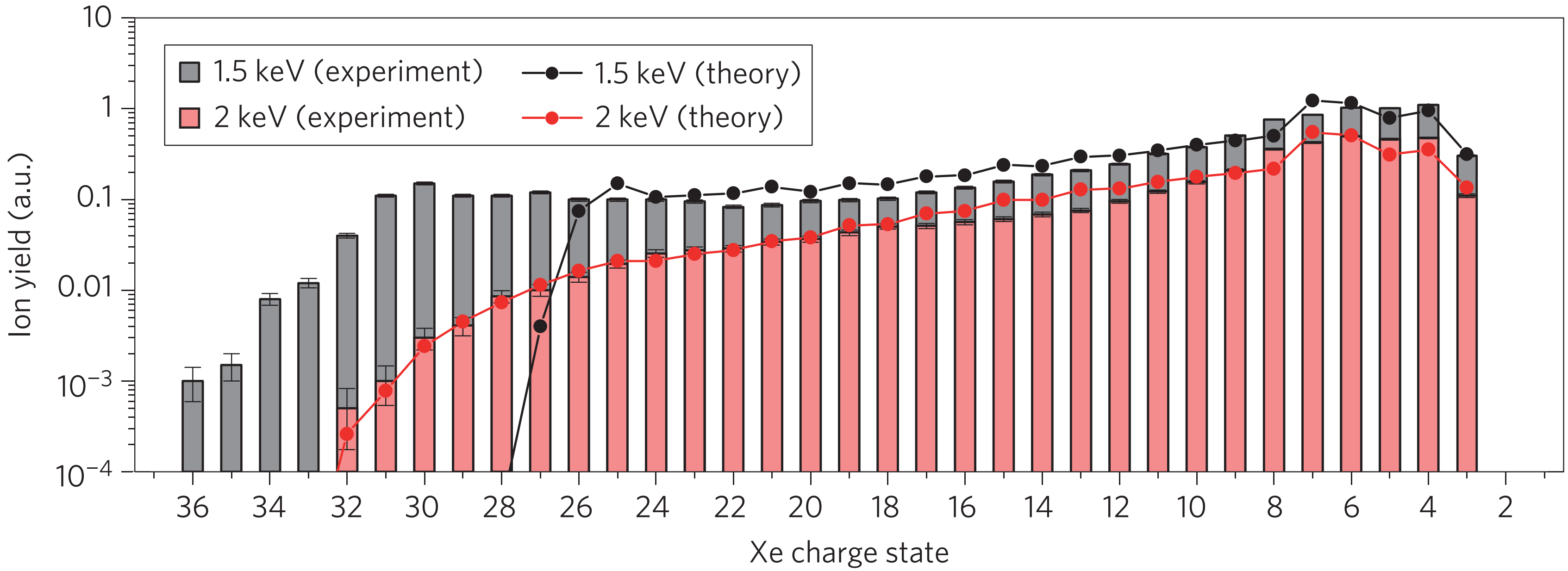


Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

Ionization thresholds of Xe ions



Comparison with LCLS experiment



LCLS experiment

Daniel Rolles
at KSU

Artem Rudenko
at KSU

Benedikt Rudek
at PTB

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

- Xe *M*-shell ionization
- 2 keV: excellent agreement between theory and experiment
- 1.5 keV: resonance-enabled x-ray multiple ionization (REXMI)

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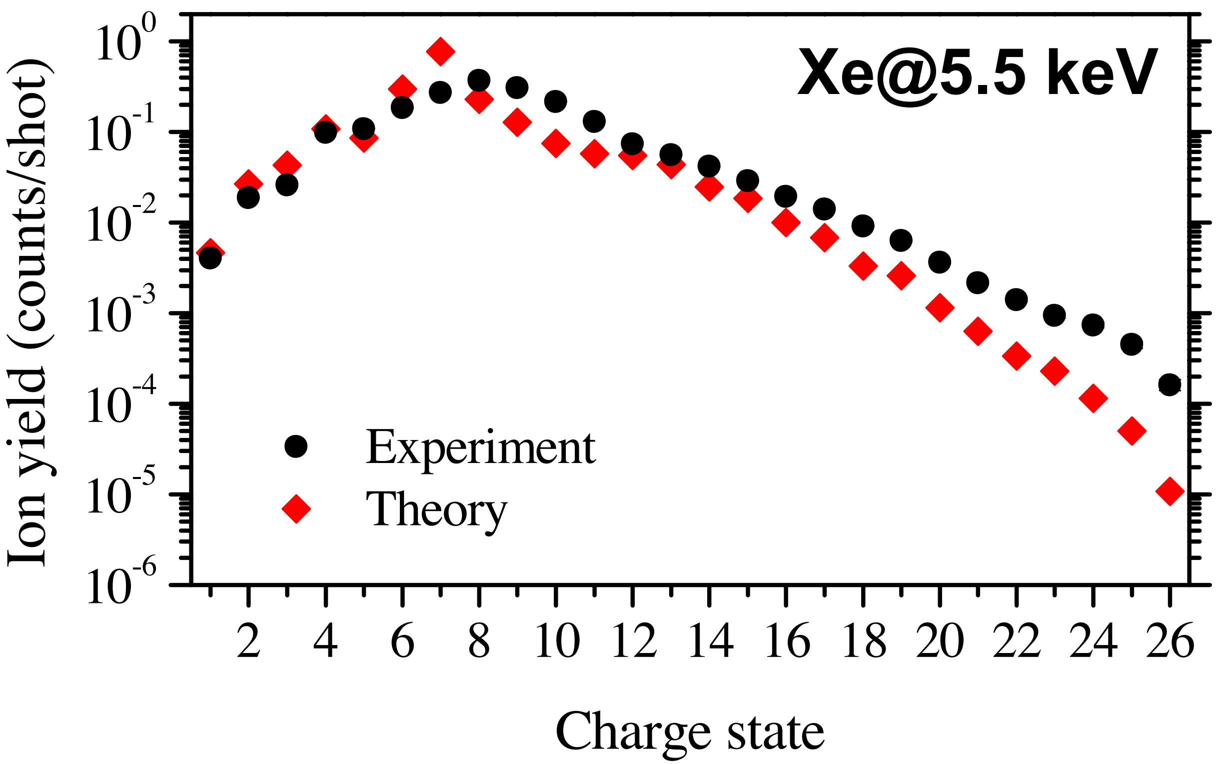
Comparison with SACLA experiment



SACLA experiment

Kiyoshi Ueda
at Tohoku Univ.

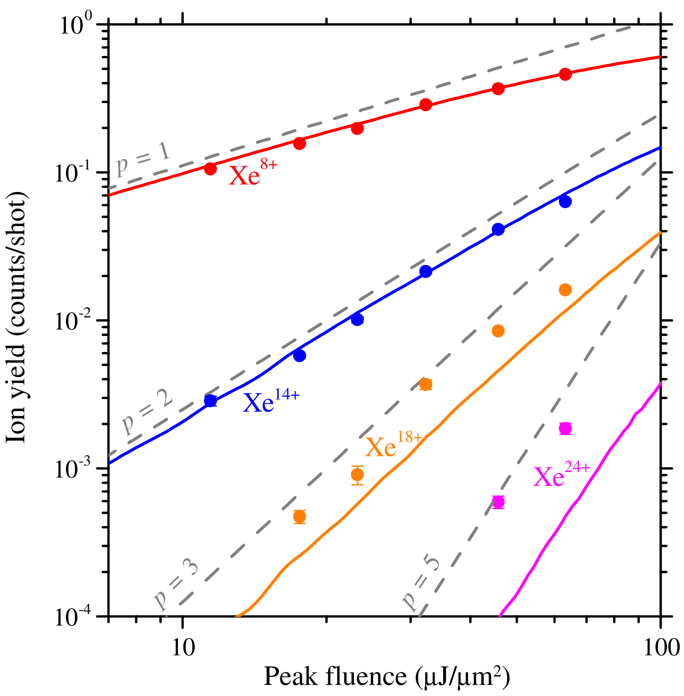
- Hironobu Fukuzawa
- Koji Motomura

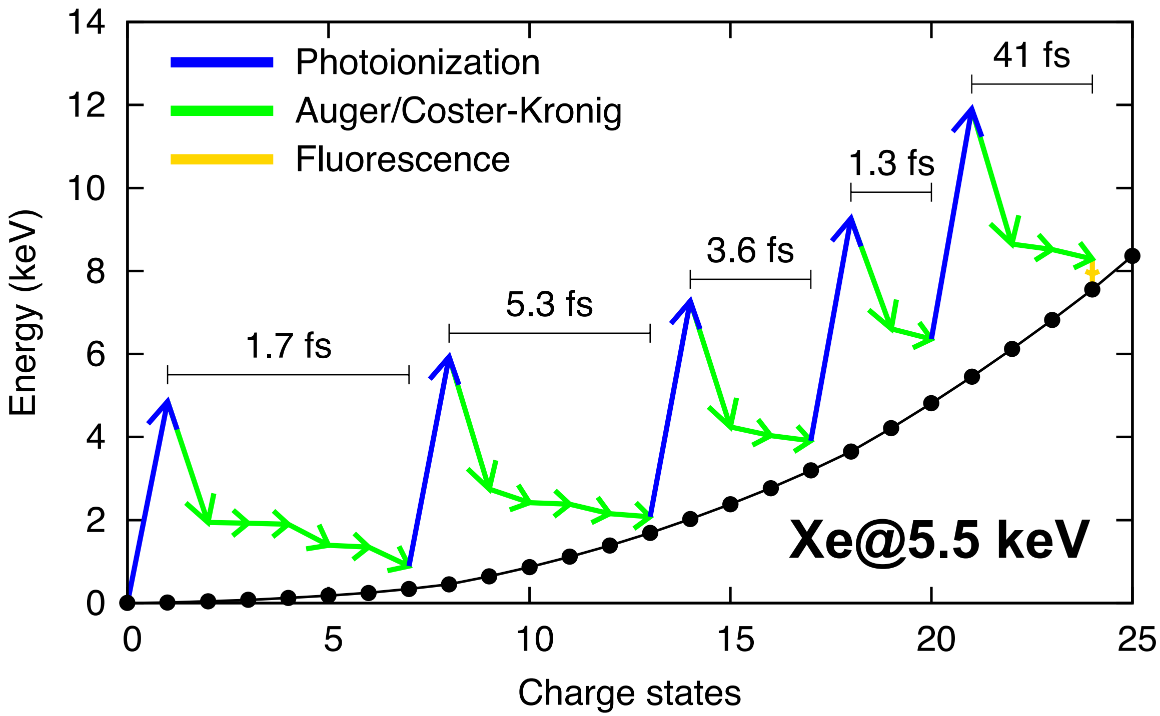
Fukuzawa *et al.*, *Phys. Rev. Lett.* **110**, 173005 (2013).

- Xe *L*-shell ionization: good agreement
- underestimation in theory: lack of relativistic effect, shake-off, and resonance effect

X-ray multiphoton ionization mechanism

- To reach Xe^{24+}: 5 photons absorbed, 24 electrons ejected



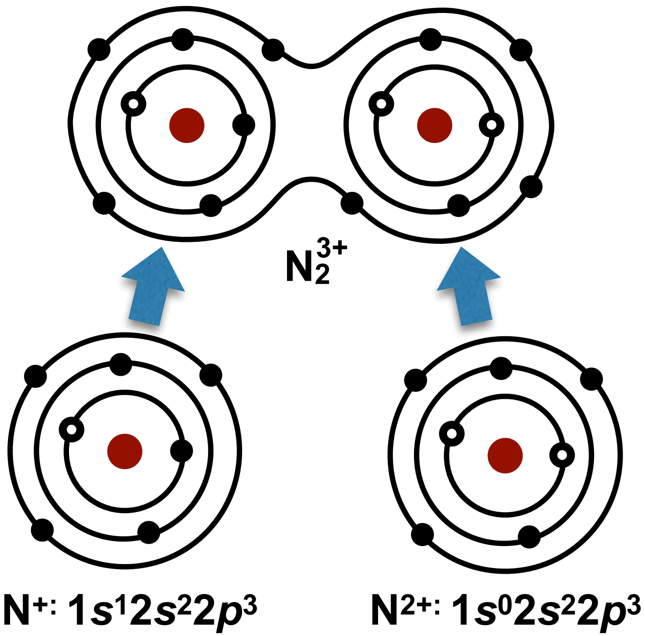


Fukuzawa *et al.*, *Phys. Rev. Lett.* **110**, 173005 (2013).

MOLECULE

XMOLECULE

- XMOLECULE: x-ray and molecular physics toolkit
  - quantum electrons, classical nuclei
  - efficient electronic structure calculation: core-hole adapted basis functions calculated XATOM
  - Monte Carlo on the fly



***Ab initio* ionization and fragmentation dynamics induced by intense XFEL pulses**

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

XMOLECULE: Numerical details

- Hartree-Fock-Slater method

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_X(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- MO represented by linear combination of AO: $\psi_i(\mathbf{r}) = \sum_\mu C_{\mu i}\phi_\mu(\mathbf{r})$
- AO: numerical solutions of corresponding atomic core-hole states

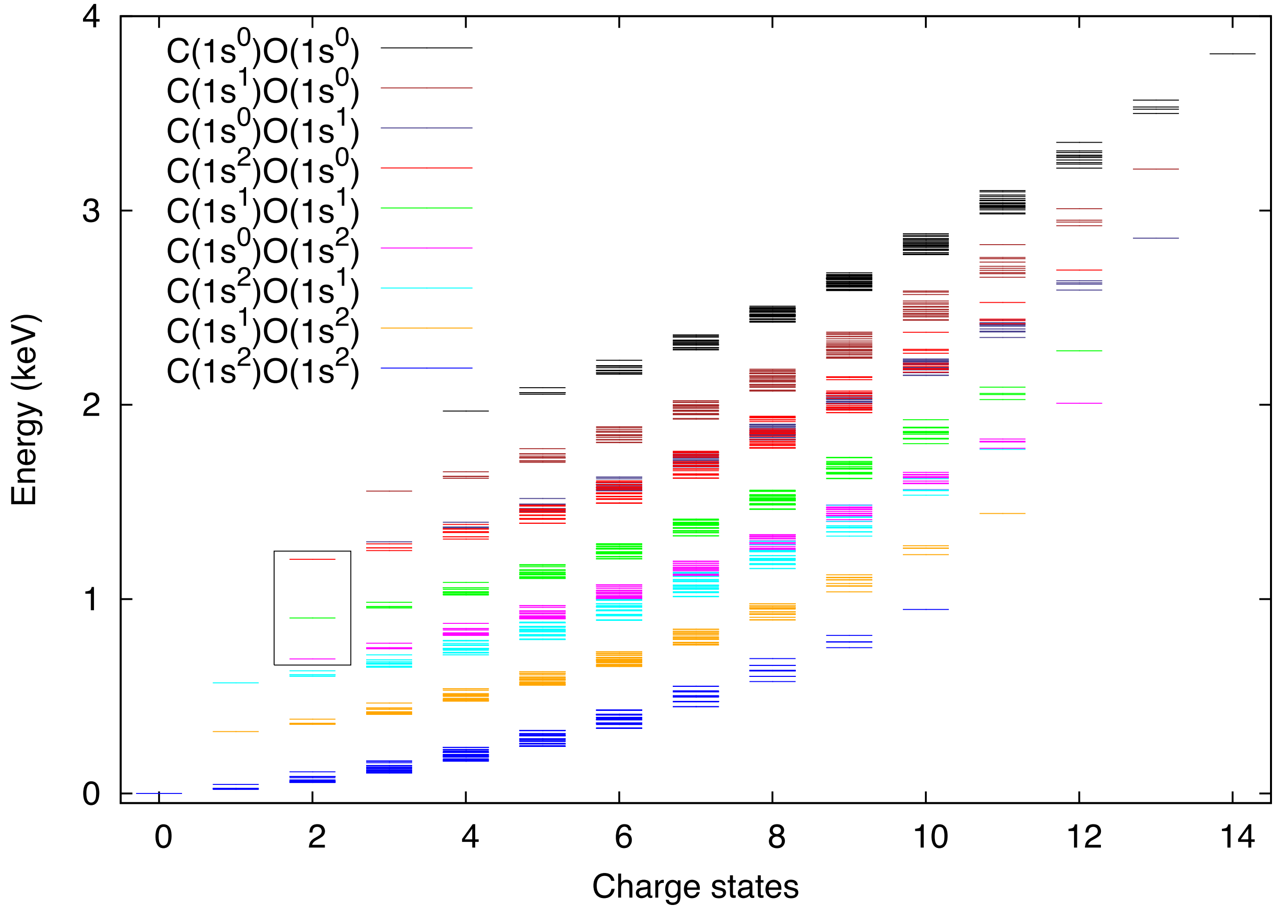
$$\phi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r} Y_{lm}(\theta, \varphi)$$ calculated by XATOM

- Matrix eigenvalue problem $\mathbf{HC} = \mathbf{SCE}$

$$H_{\mu\nu} = \int d^3r\, \phi_\mu(\mathbf{r}) \left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right] \phi_\nu(\mathbf{r}), \quad S_{\mu\nu} = \int d^3r\, \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})$$

- Various numerical techniques employed
  - multicenter integration on a molecular grid built from atomic grids
  - multicenter expansion and multipole expansion in direct Coulomb interaction
  - maximum overlap method to prevent variational collapse

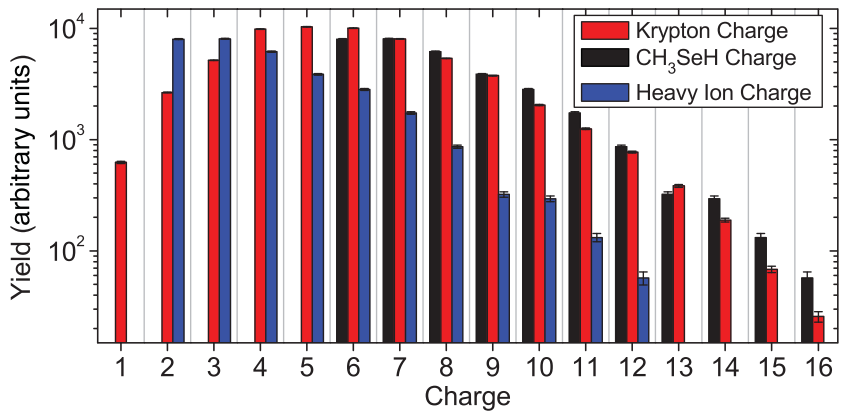
Various multiple-hole states of CO



All possible multiple-hole configurations formed by x-ray multiphoton ionization

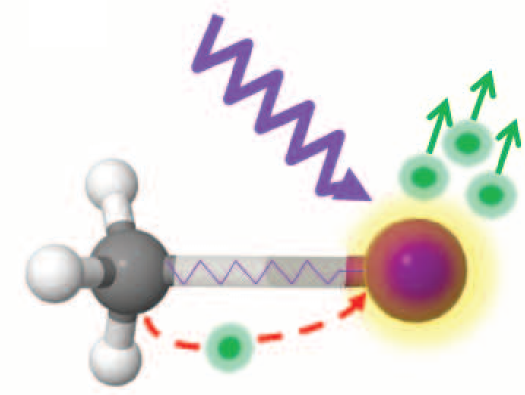
Example: CH_3I

Earlier works on molecules at low 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.

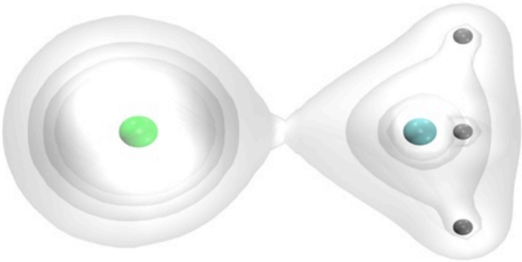
⬇

Still valid for high x-ray intensity?

Methyl iodide 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

- Multiphoton ionization occurs at high fluence: $F > F_{sat} \sim 2\times10^{11}$ ph/μm²
- Charge imbalance induces charge rearrangement
- Coulomb explosion after/during ionization & charge rearrangement
- New experimental results:
  LCLS CXI using nano-focus
  ➔ peak fluence ~ 5×10^{12} ph/μm²

LCLS experiment

Daniel Rolles at KSU

Artem Rudenko at KSU

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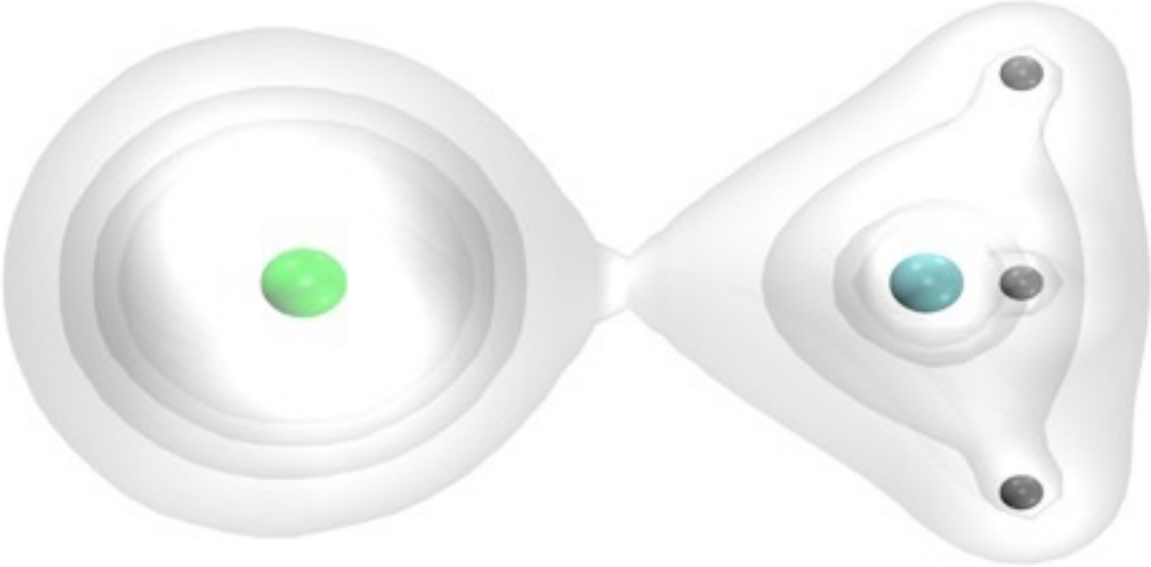
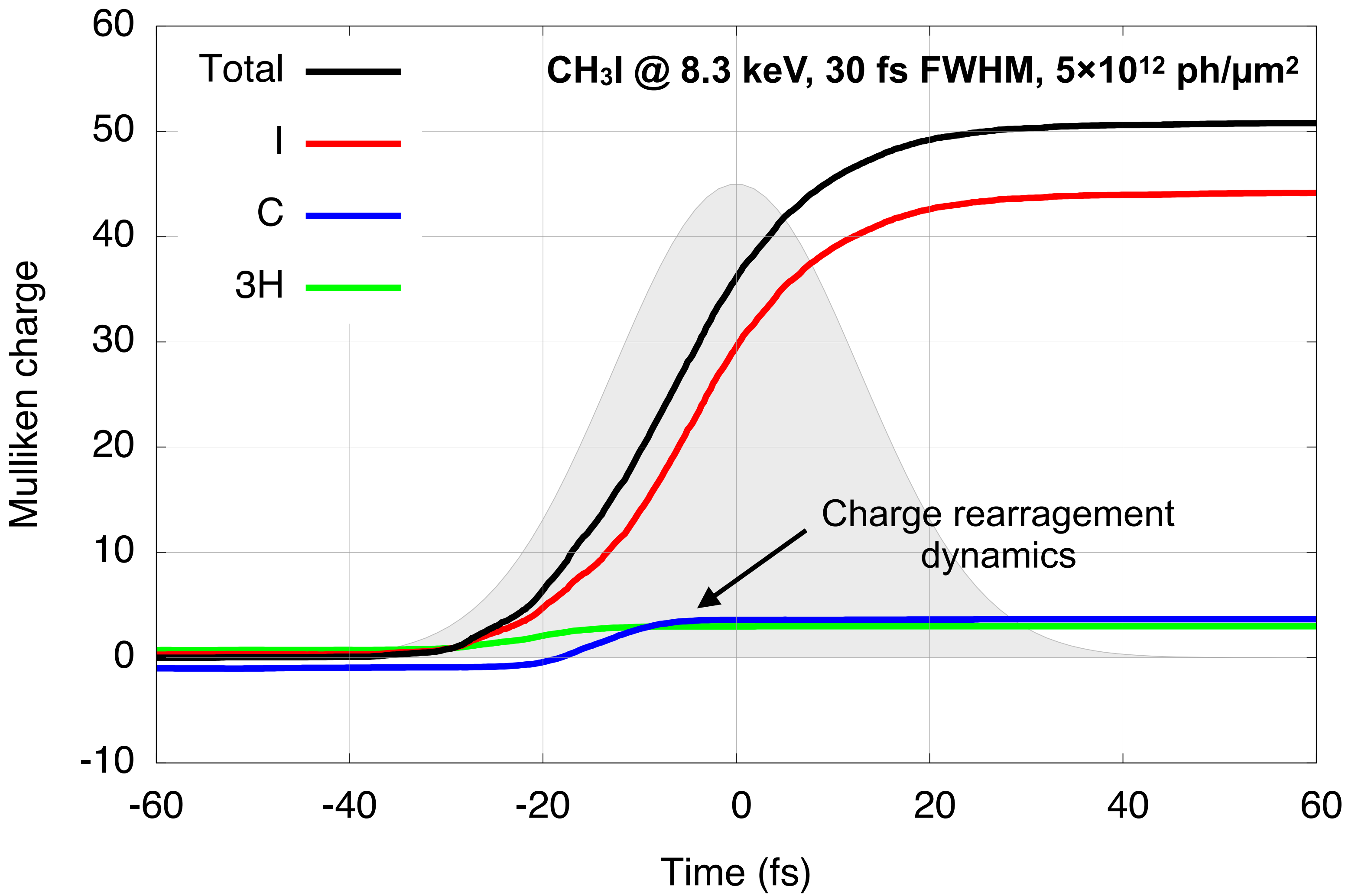
Ionization & fragmentation dynamics

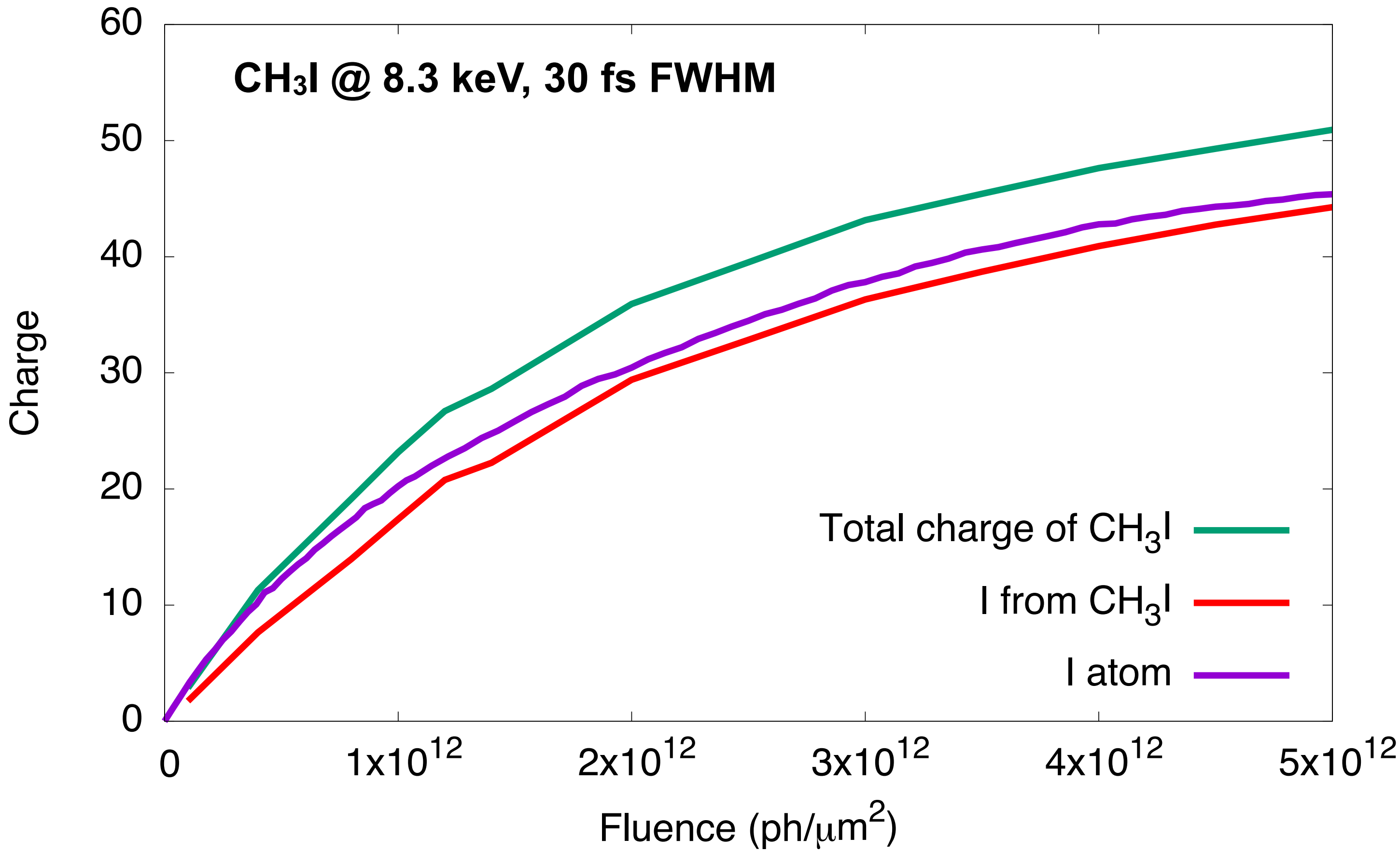
CH_3I



Time evolution of partial charge population

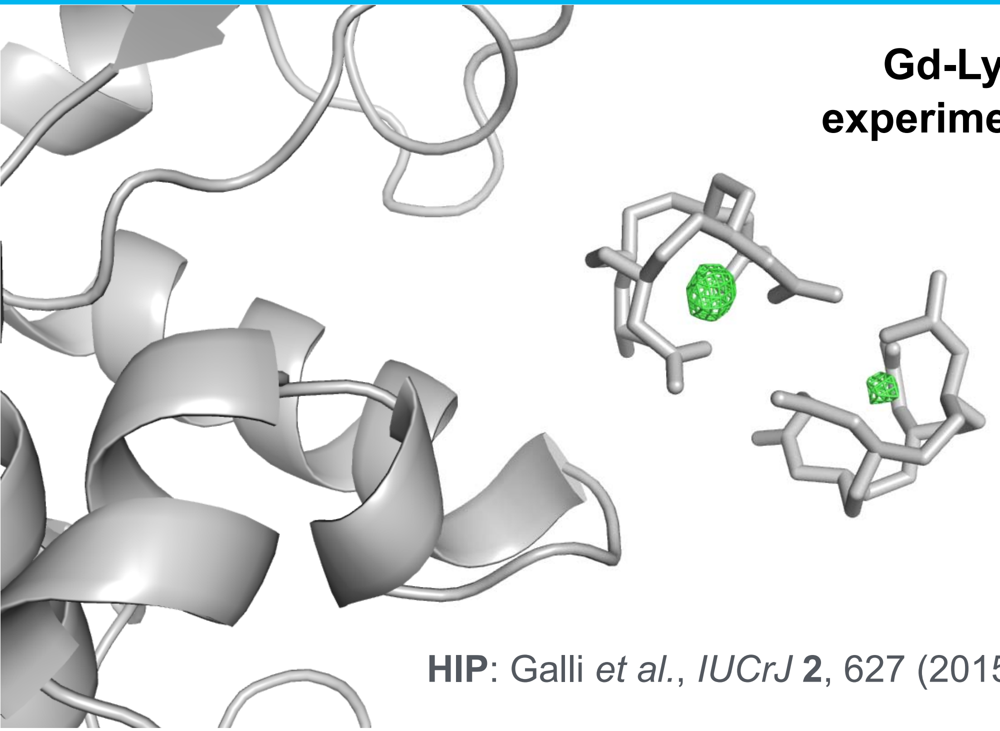


Molecular ionization enhancement



molecular total charge > atomic charge: experimentally confirmed

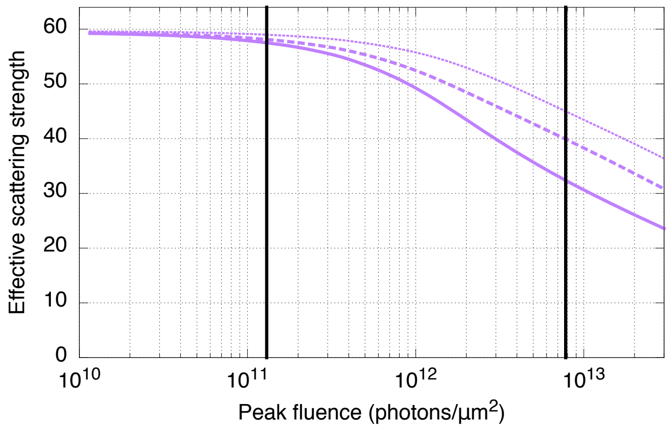
Application: x-ray molecular imaging



HIP: Galli *et al.*, *IUCrJ* **2**, 627 (2015).

Henry Chapman
at CFEL

Lorenzo Galli
at CFEL

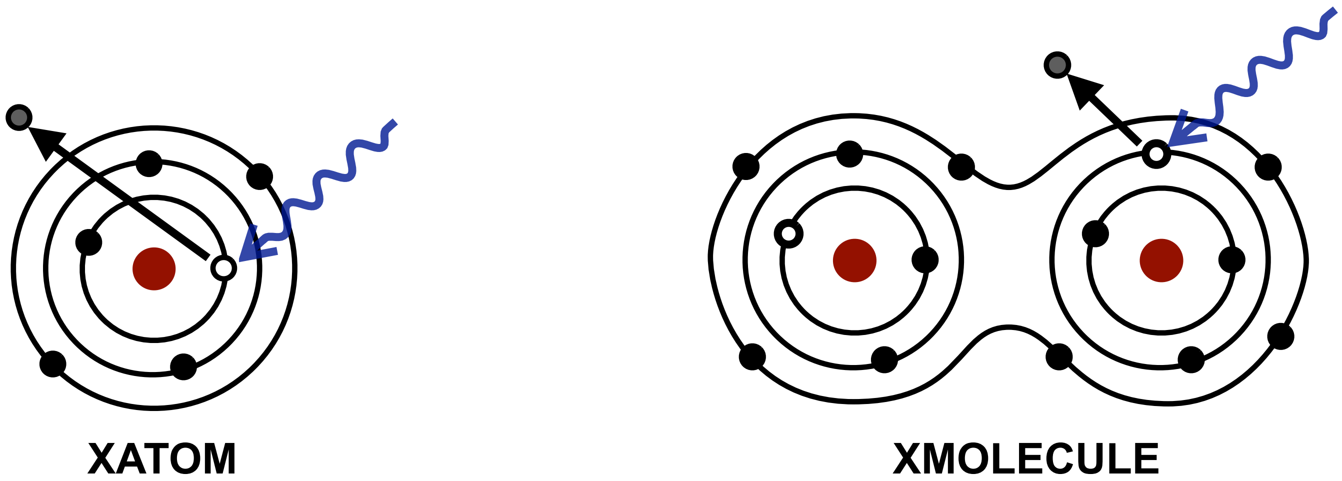


- Another bottleneck of x-ray crystallography: **phasing**
- Proposals of novel phasing methods:
  utilizing selective ionization of heavy atoms
  at high x-ray intensity

HI-MAD: Son *et al.*, *PRL* **107**, 218102 (2011).
HI-RIP: Galli *et al.*, *J. Synch. Rad.* **22**, 249 (2015).

- Based on knowledge of dynamical behaviors of heavy atoms within a molecule

Summary



- XATOM and XMOLECULE provide a physical insight of fundamental interactions between matter and intense XFEL pulses
- Multiphoton multiple ionization dynamics of Xe:
  a sequence of photoionization and accompanying relaxation processes
- Charge rearrangement dynamics of CH_3I:
  molecular ionization enhancement at high x-ray intensity

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Thank you for your attention!

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