What happens to atoms and molecules during XFEL pulses?

Sang-Kil Son
Center for Free-Electron Laser Science, DESY, Hamburg, Germany

Physical Colloquium, Universtät Kassel, December 3, 2015

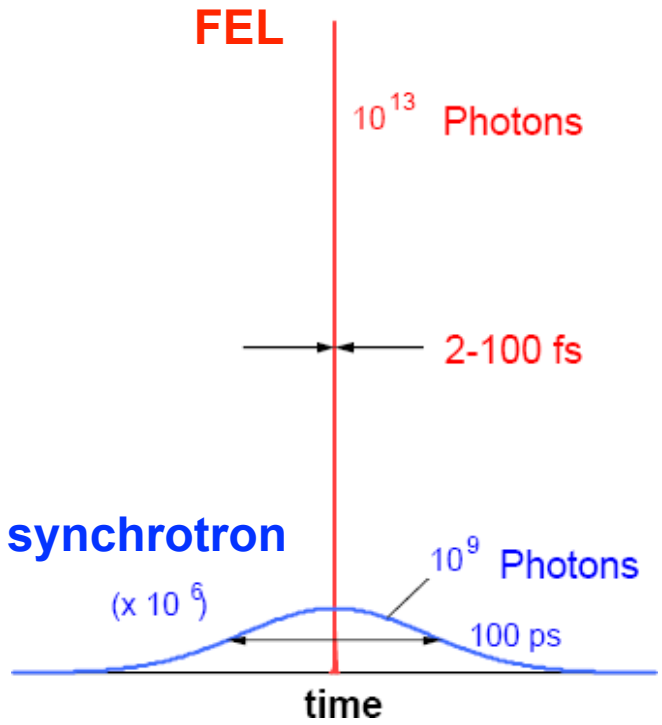
Overview

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

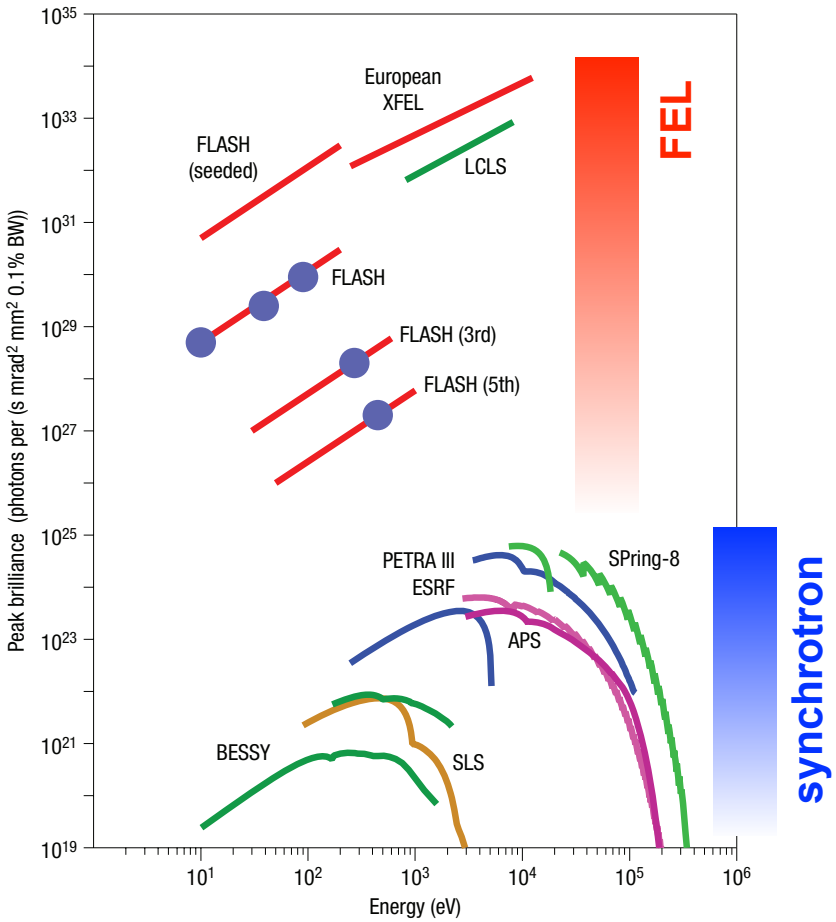
Introduction

XFEL: X-ray free-electron laser

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



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



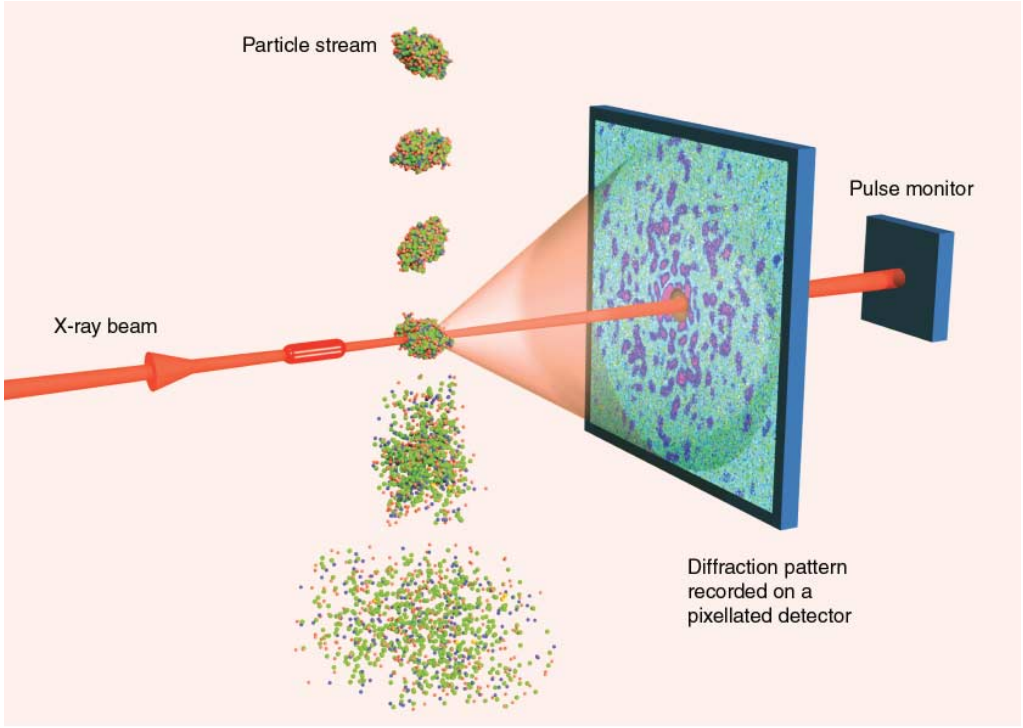
Ackermann *et al.*, *Nature Photon.* **1**, 336 (2007).

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
- Enough signals obtained from even single molecules by using *ultraintense* pulses
- Signals obtained before radiation damage by using *ultrafast* pulses



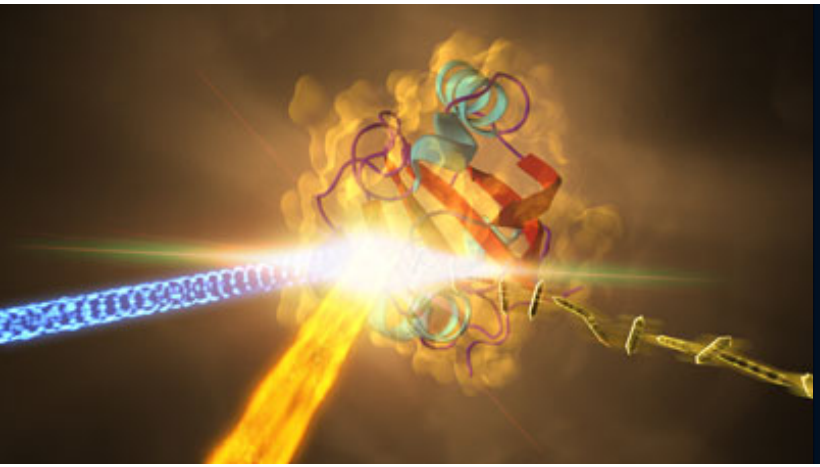
Gaffney & Chapman, *Science* **316**, 1444 (2007).

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

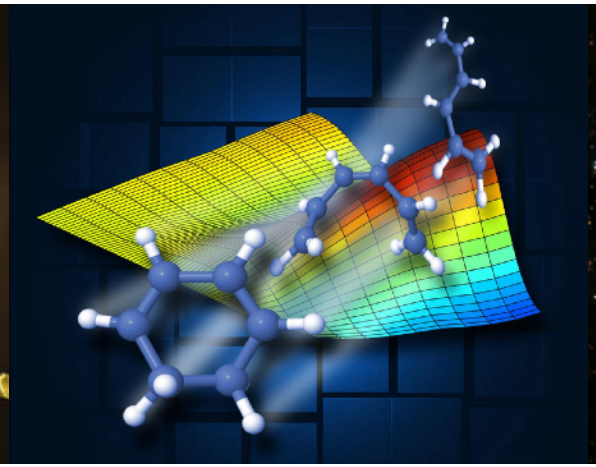
XFEL science

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

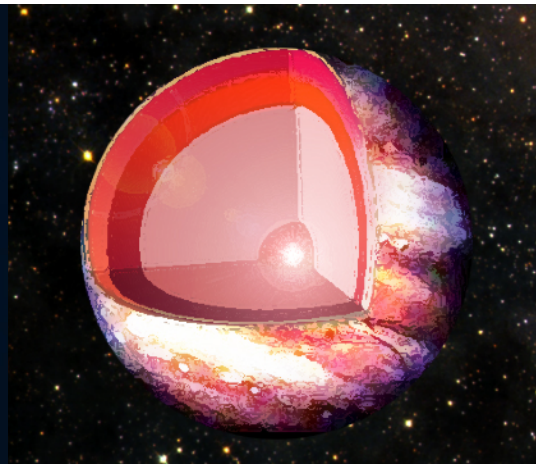
➔ XFEL applications waiting for increased theoretical support



SLAC



SLAC

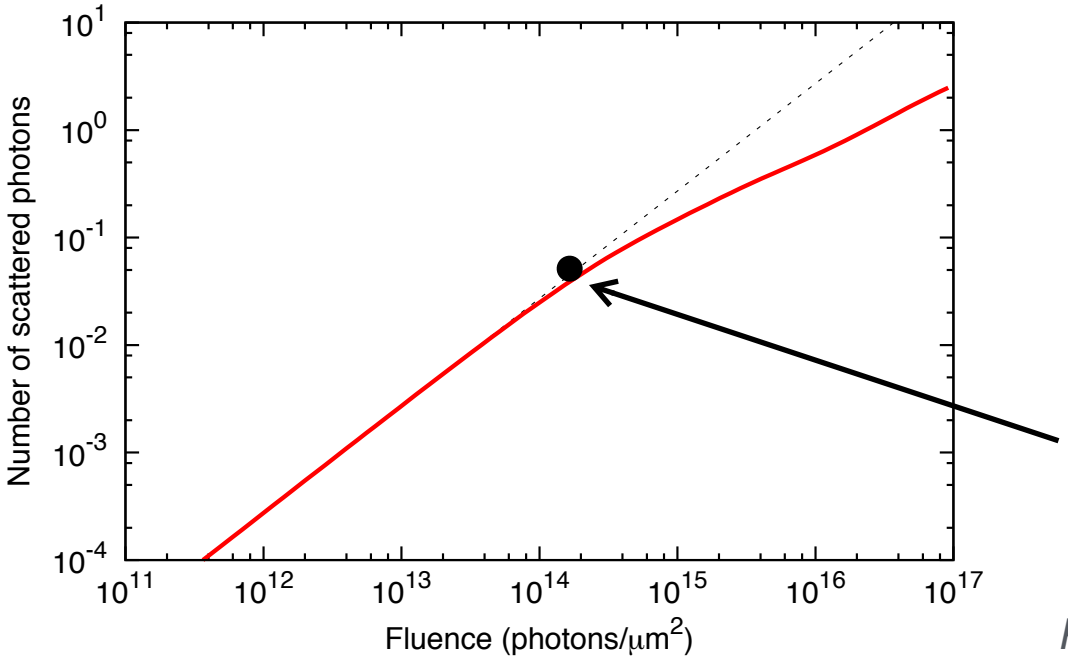


LBL

ATOM

What happens at high x-ray intensity?

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



Carbon @ 8 keV

σ_{abs} = 0.084 kbarns

⬇

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

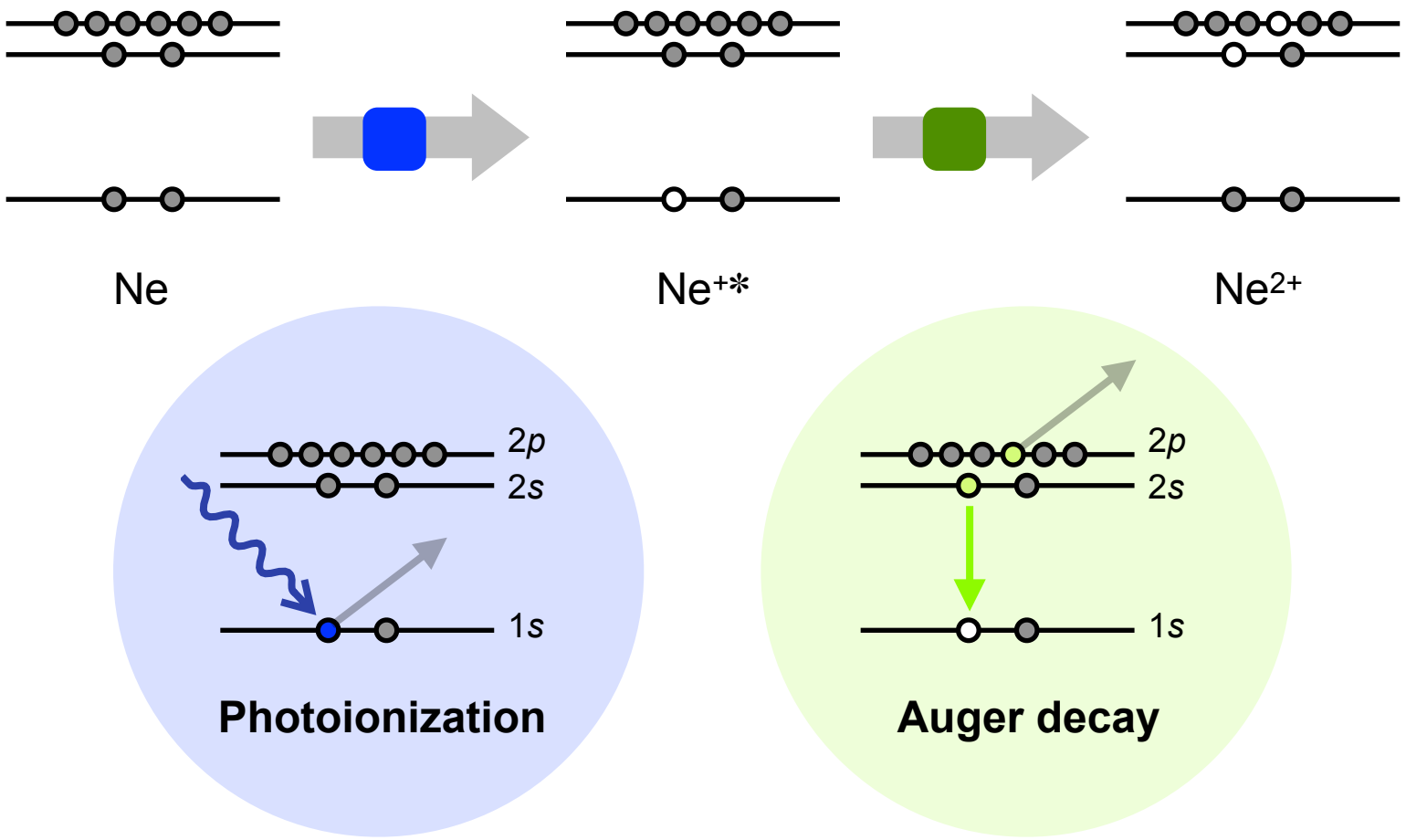
⬇

$F_{sat} = 1.2 \times 10^{14}$ 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

X-ray absorption (single photon)

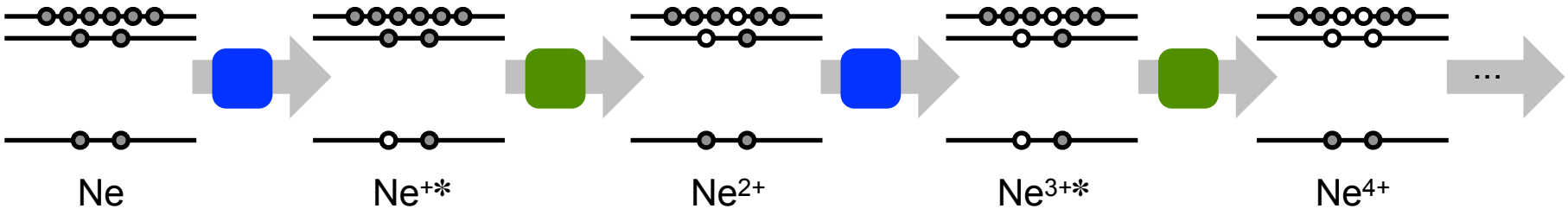


X-ray multiphoton absorption

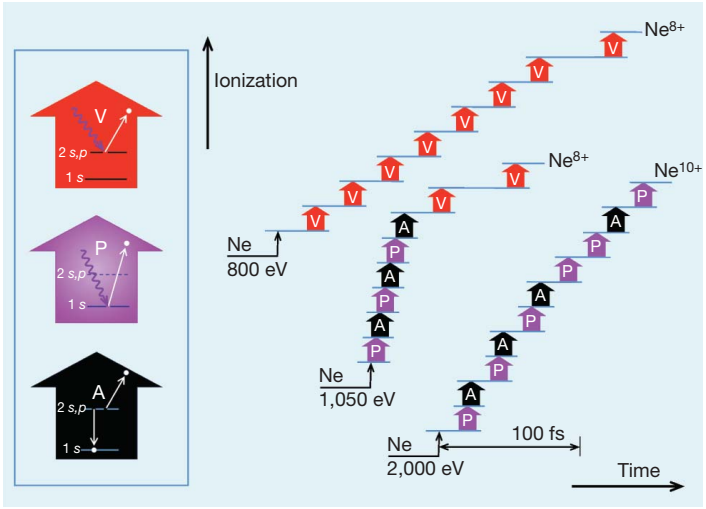
- Direct multiphoton absorption cross section is too small

  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).

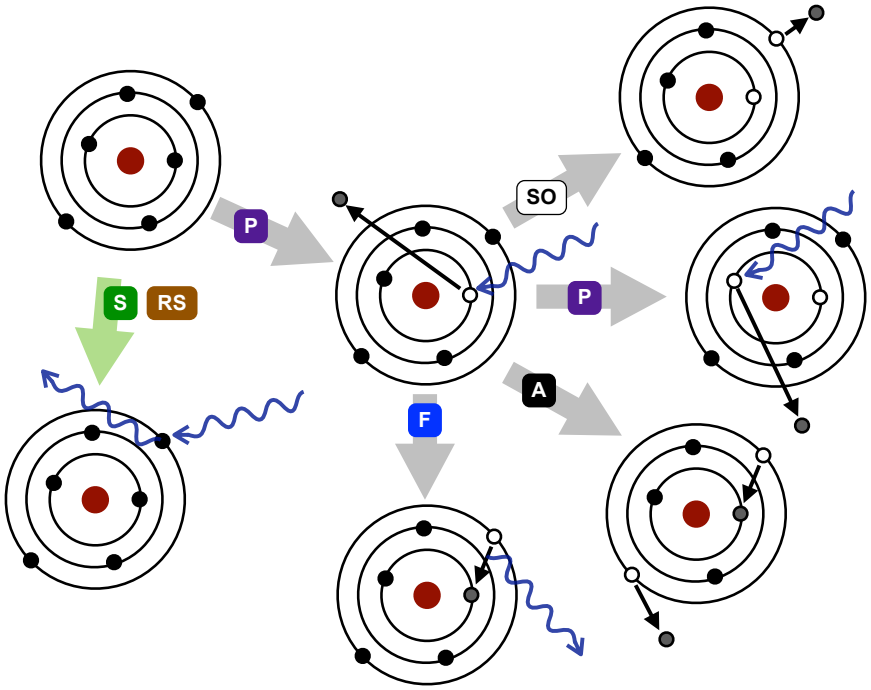
How to treat x-ray multiphoton dynamics?

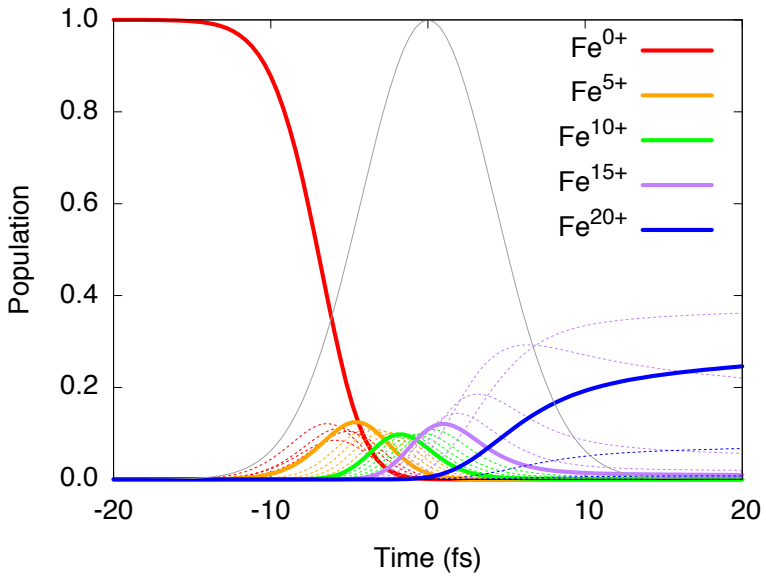
- No standard quantum chemistry code available

- Theoretical challenges
  - tremendously many hole states by x-ray multiphoton absorption
  - highly excited system far from the ground state
  - electronic continuum states
  - complex inner-shell ionization dynamics
  - coupled ionization dynamics and nuclear dynamics (for molecules)

XATOM

- XATOM: an integrated toolkit for x-ray and atomic physics
  - 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

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

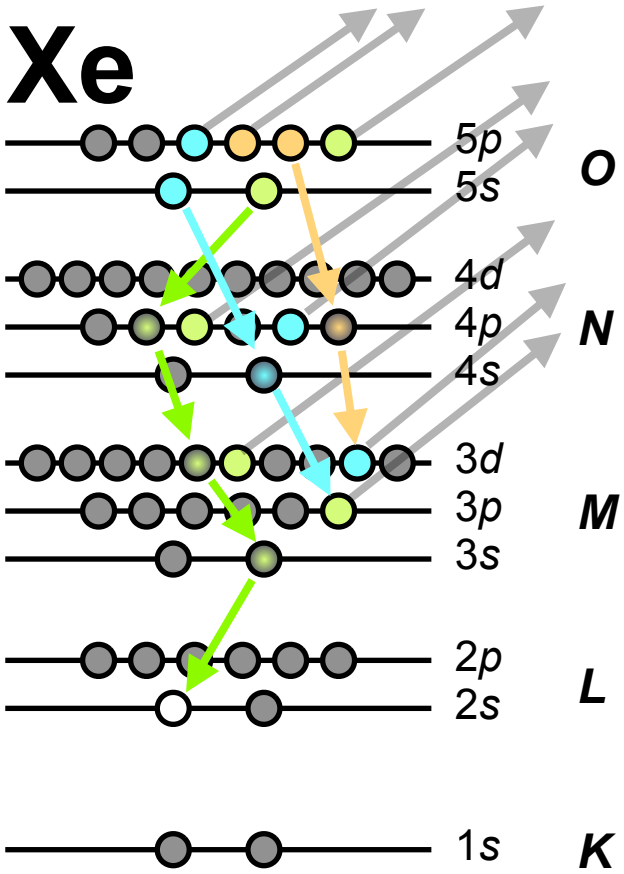
- Calculate all cross sections and rates of x-ray-induced processes based on the perturbation theory
- Solve coupled rate equations

$$\frac{d}{dt}P_I(t) = \sum_{I'\neq I}^{\text{all config.}}\left[\Gamma_{I'\to I}P_{I'}(t) - \Gamma_{I\to I'}P_I(t)\right]$$

- 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



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

Auger (Coster-Kronig) decay cascade

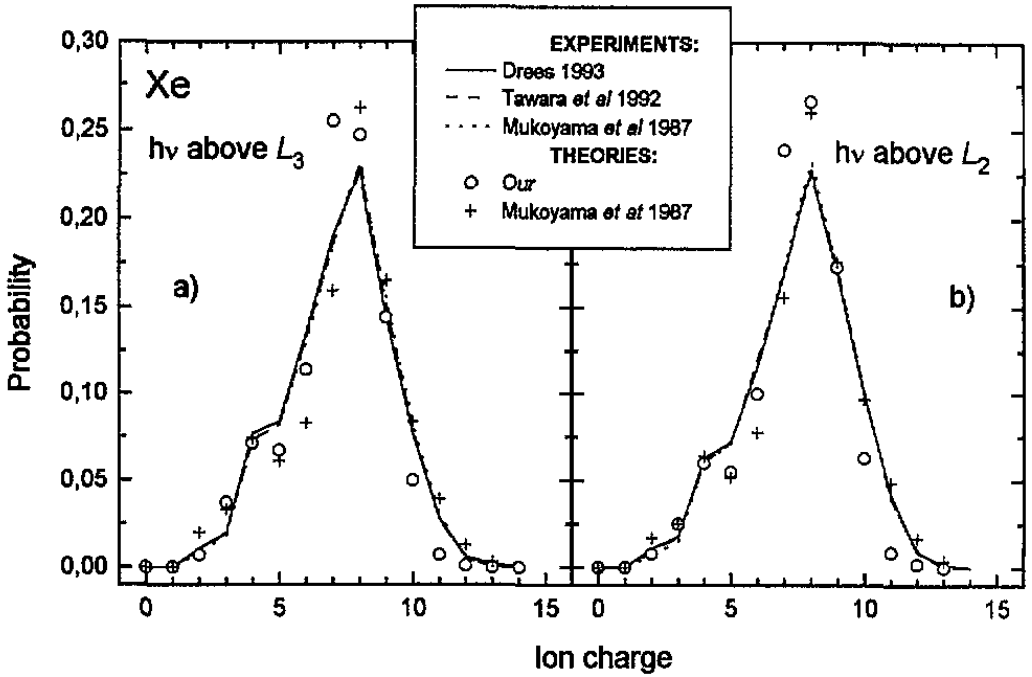


Figure 3. Xe^{i+} charge spectra produced by photoionization of Xe atoms above the L_3-threshold (*a*), and above the L_2-threshold (*b*). Drees (1993), Tawara *et al* (1992), this work—excitation energies 4.8 keV (*a*) and 5.2 keV (*b*); Mukoyama *et al* (1987)—excitation energies 4.9 keV (*a*) and 5.3 keV (*b*).

Kochur *et al.*, *J. Phys. B* **28**, 387 (1995).

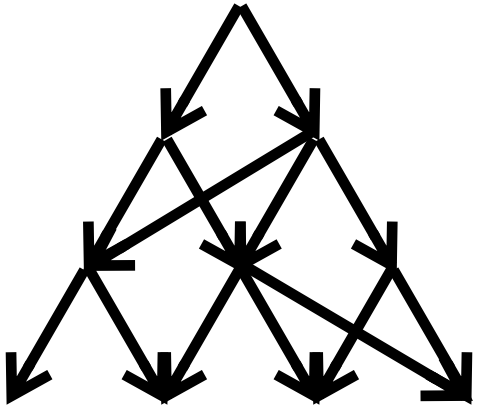
Prof. Demekhin's work of 20 years ago!

Ionization dynamics: Monte Carlo method

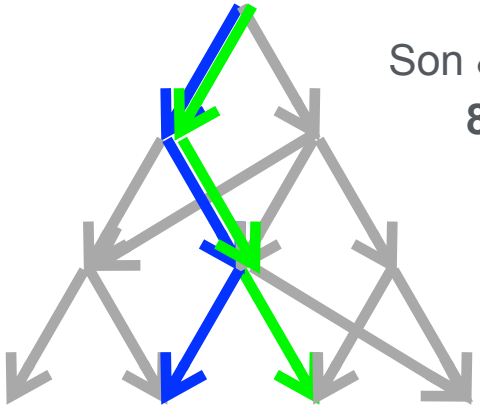
Xe: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$

- 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



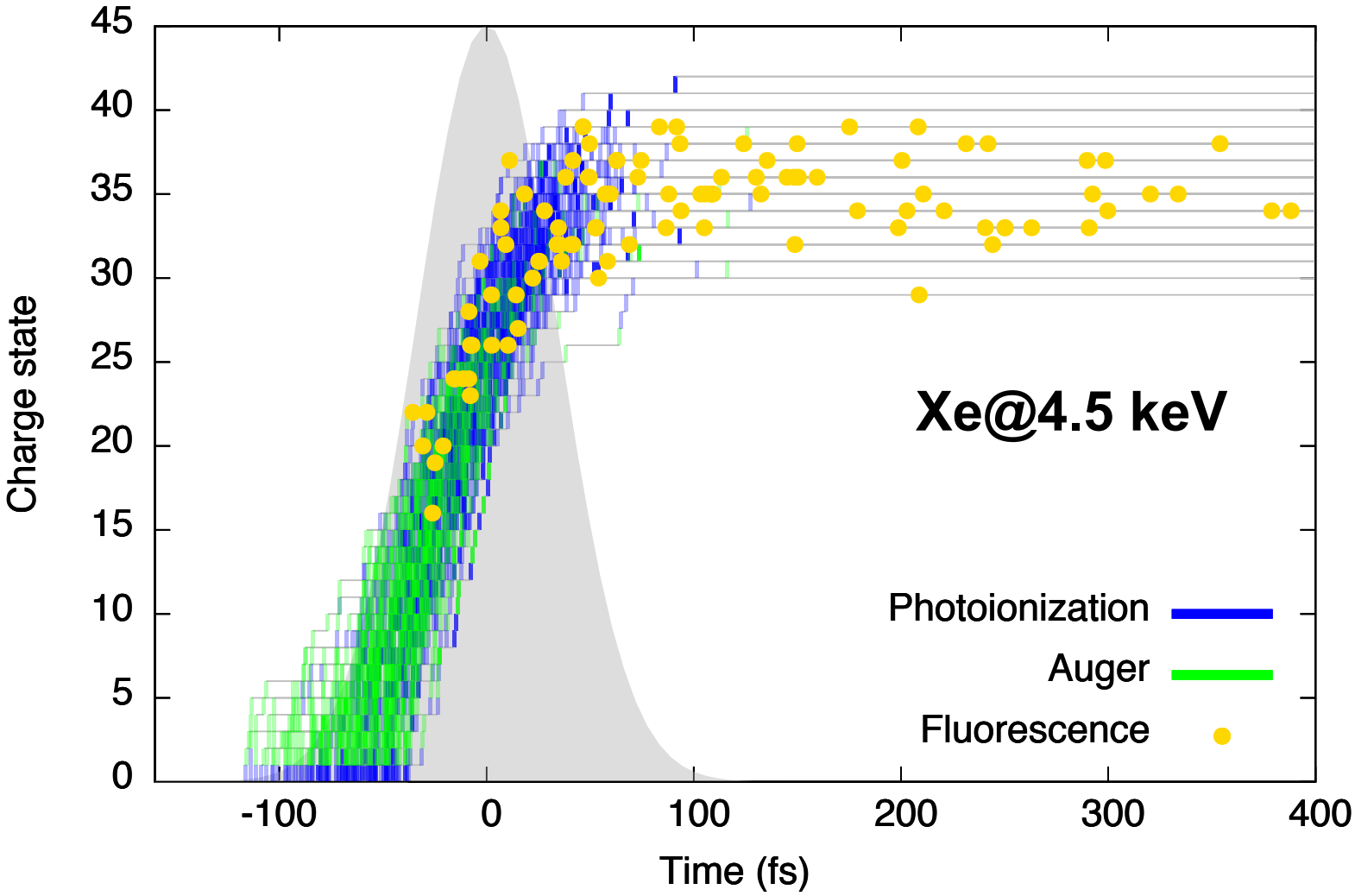
direct solution



Monte Carlo approach

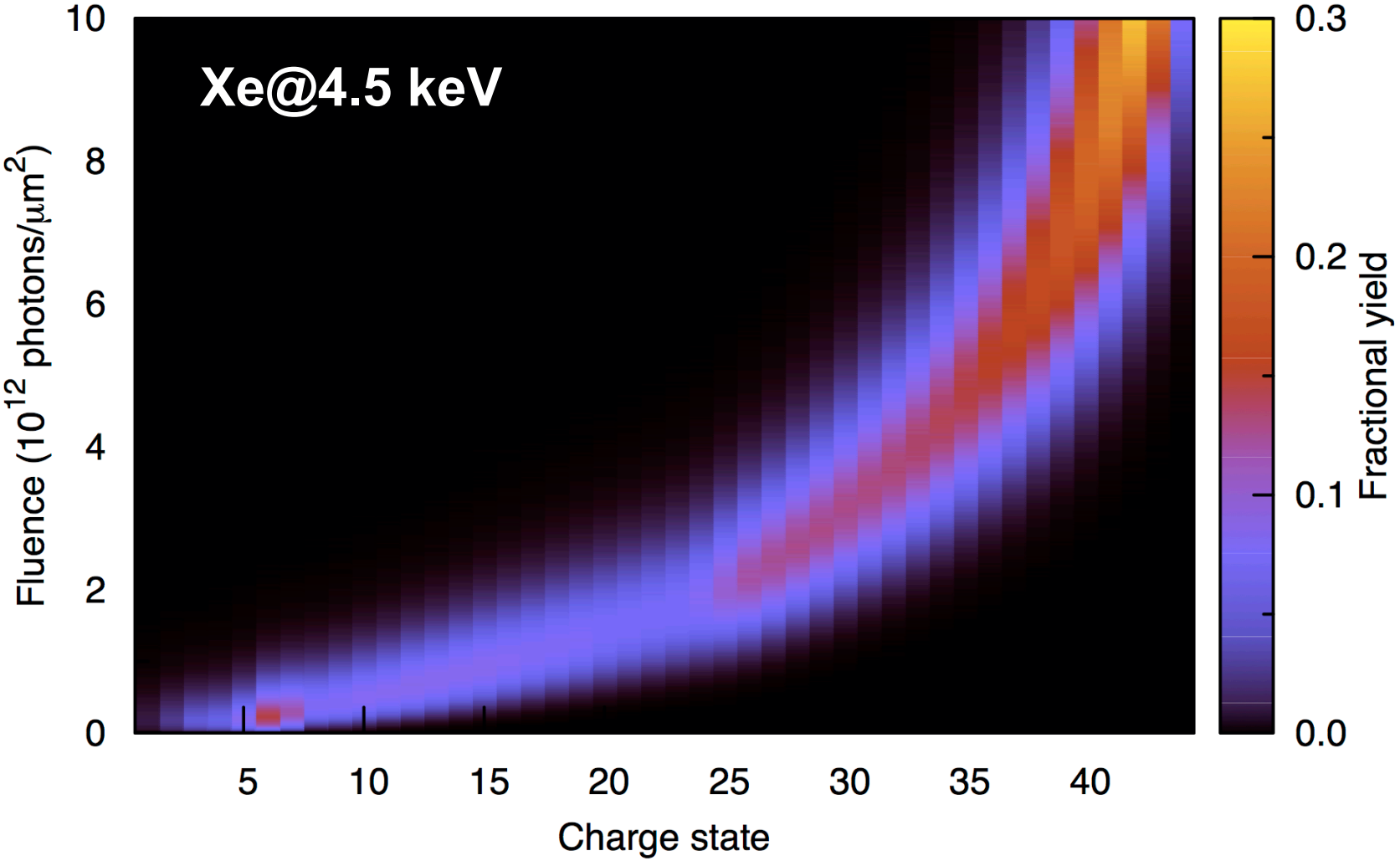
Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

X-ray multiphoton ionization dynamics



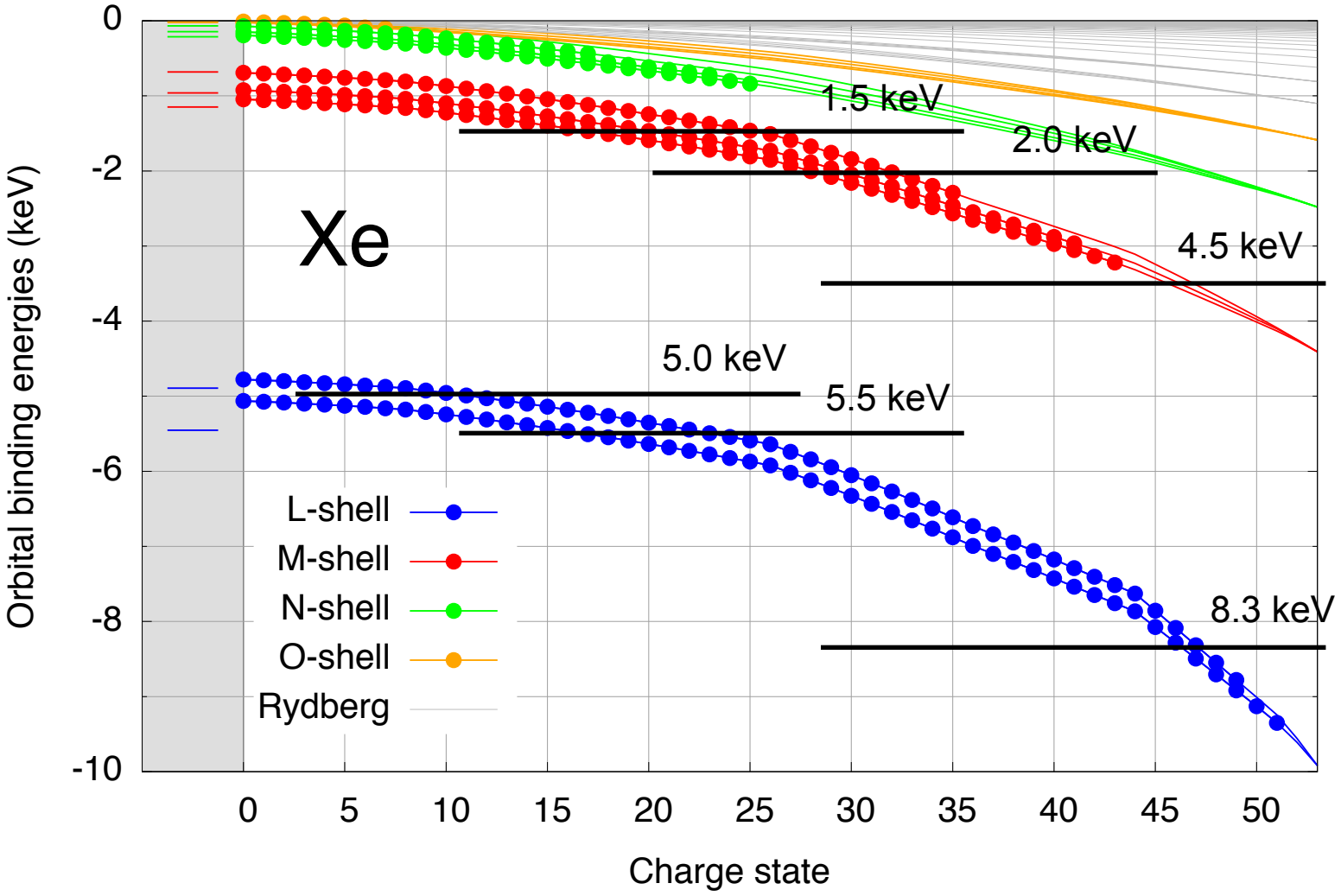
Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

Charge-state distributions of Xe

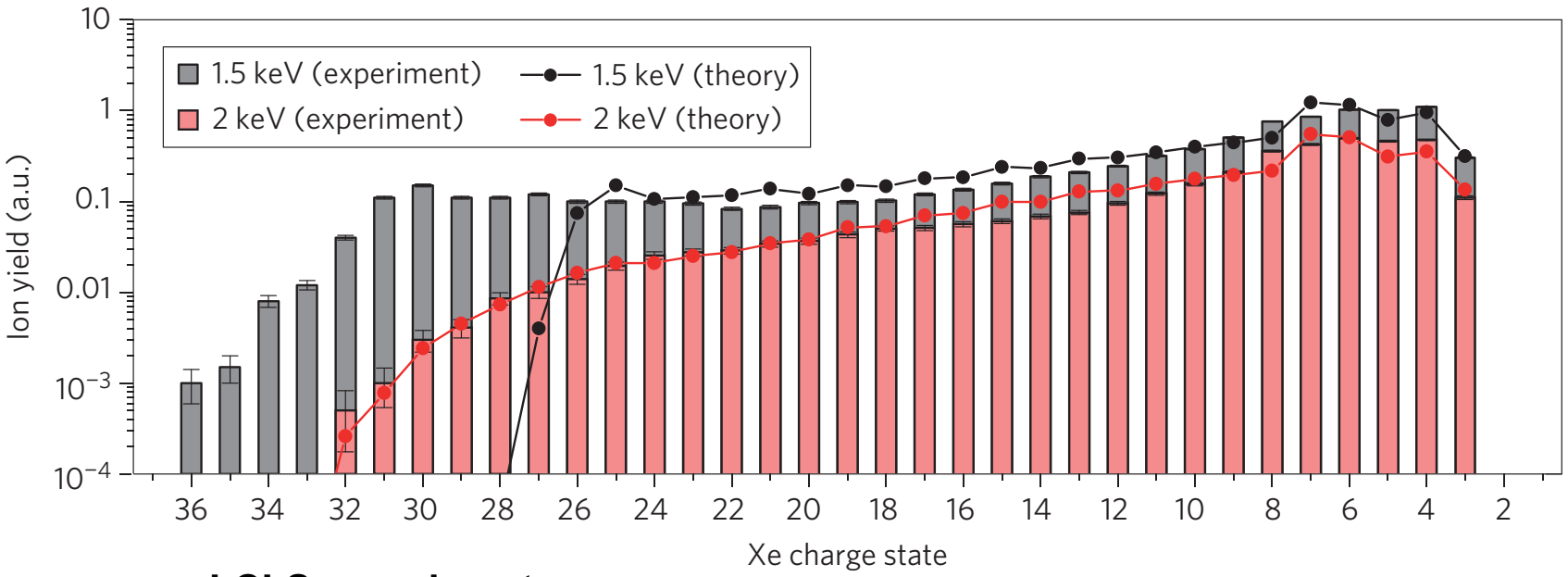


Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

Ionization thresholds of Xe ions



Comparison with LCLS experiment



LCLS experiment

Daniel Rolles
at KSU

Artem Rudenko
at KSU

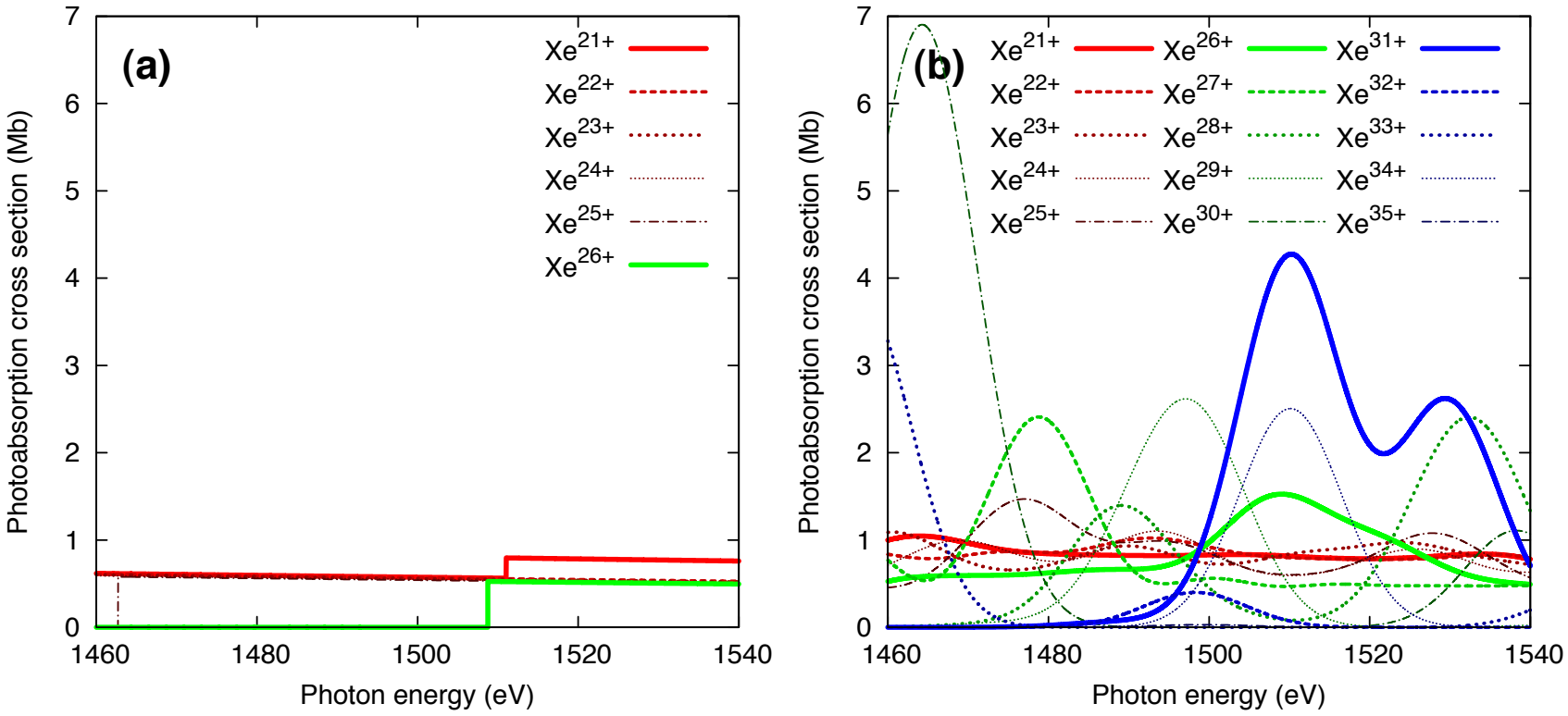
Benedikt Rudek
at PTB

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

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

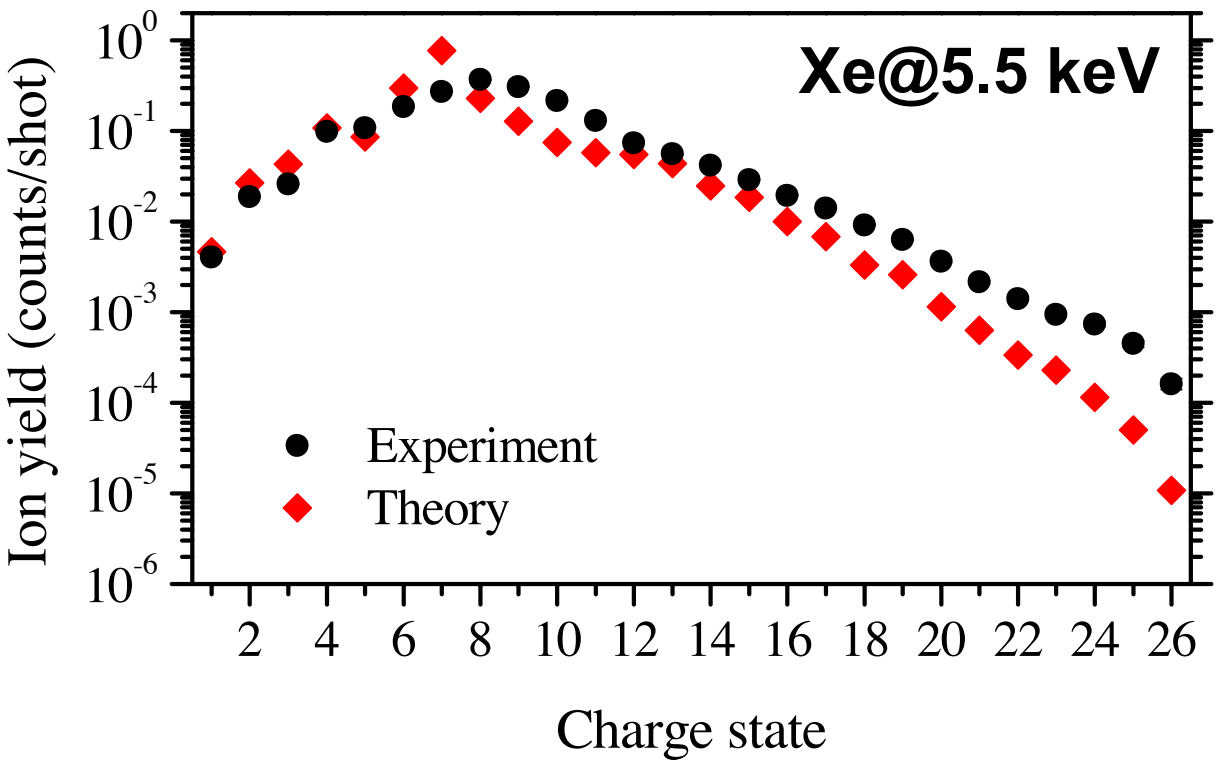
Ultra-efficient ionization by XFEL

- REXMI: Resonance-Enabled X-ray Multiple Ionization
- Broad bandwidth (~15 eV): resonances for many charge states



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

Comparison with SACLA experiment



SACLA experiment

Kiyoshi Ueda
at Tohoku Univ.

- Hironobu Fukuzawa
- Koji Motomura

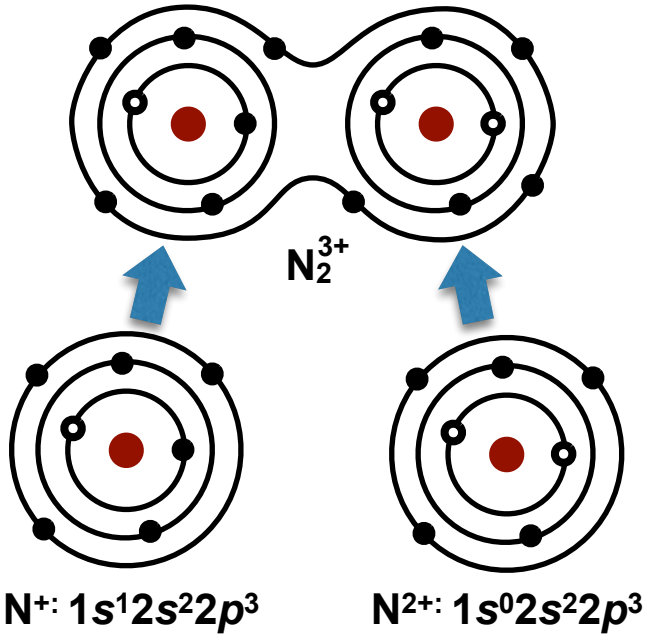
Fukuzawa *et al.*,
Phys. Rev. Lett.
110, 173005 (2013).

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

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

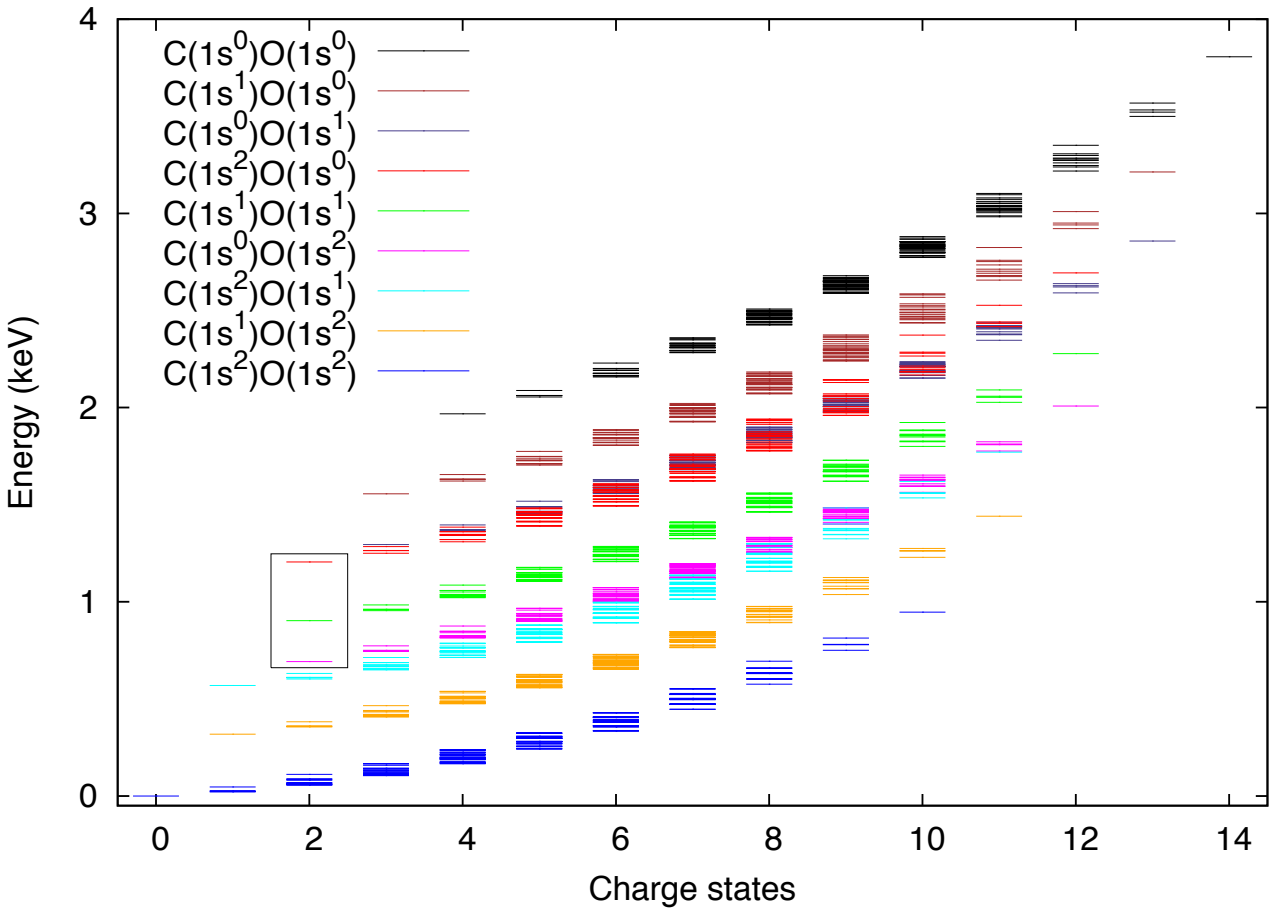
$$\phi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r}Y_{lm}(\theta,\varphi)$$ calculated by XATOM

- 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

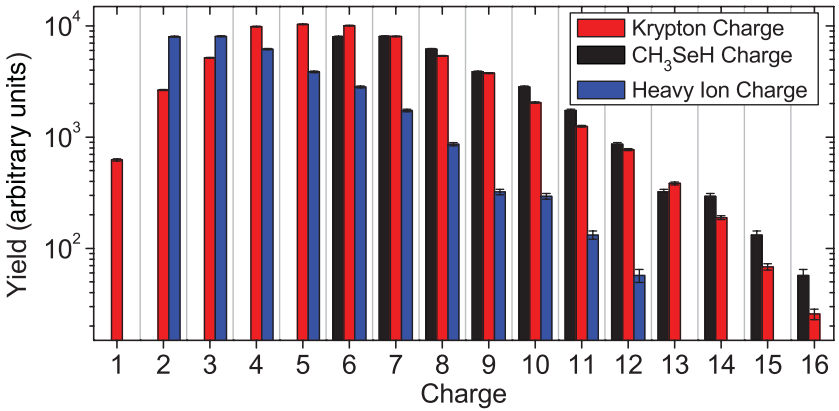
Various multiple-hole states of CO



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

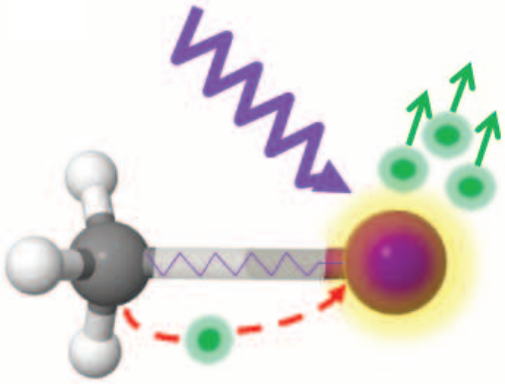
Example: CH_3I

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.

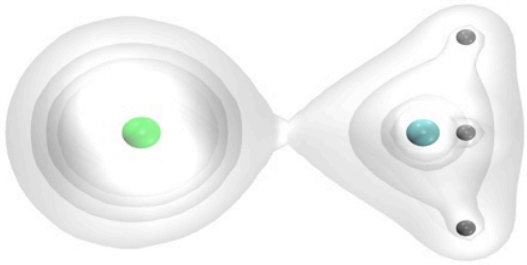
⬇

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/μm^2
- 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/μm^2

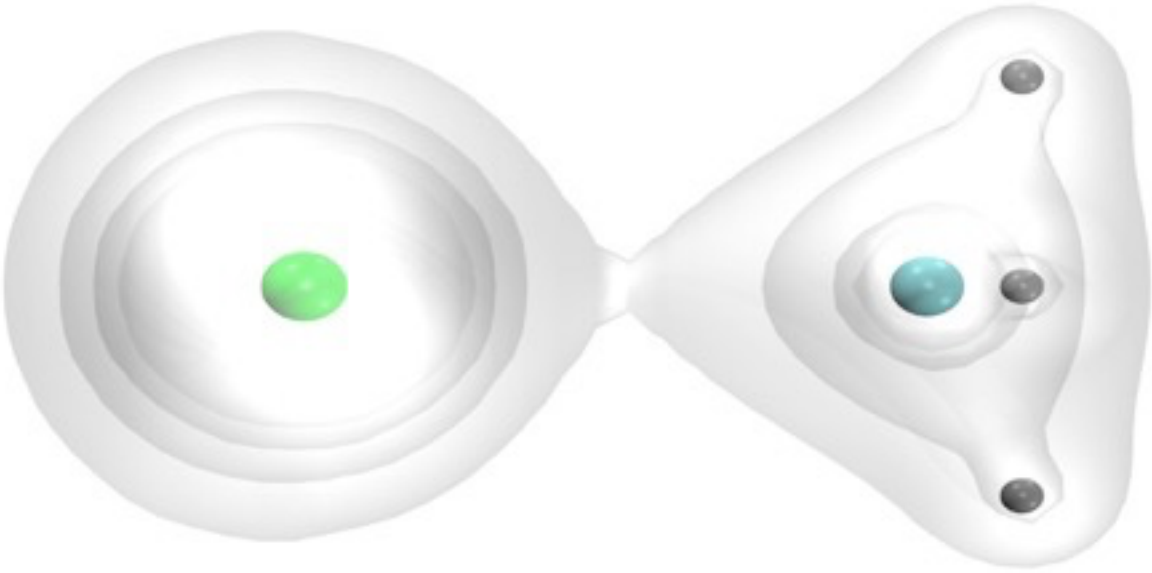
LCLS experiment

Daniel Rolles
at KSU

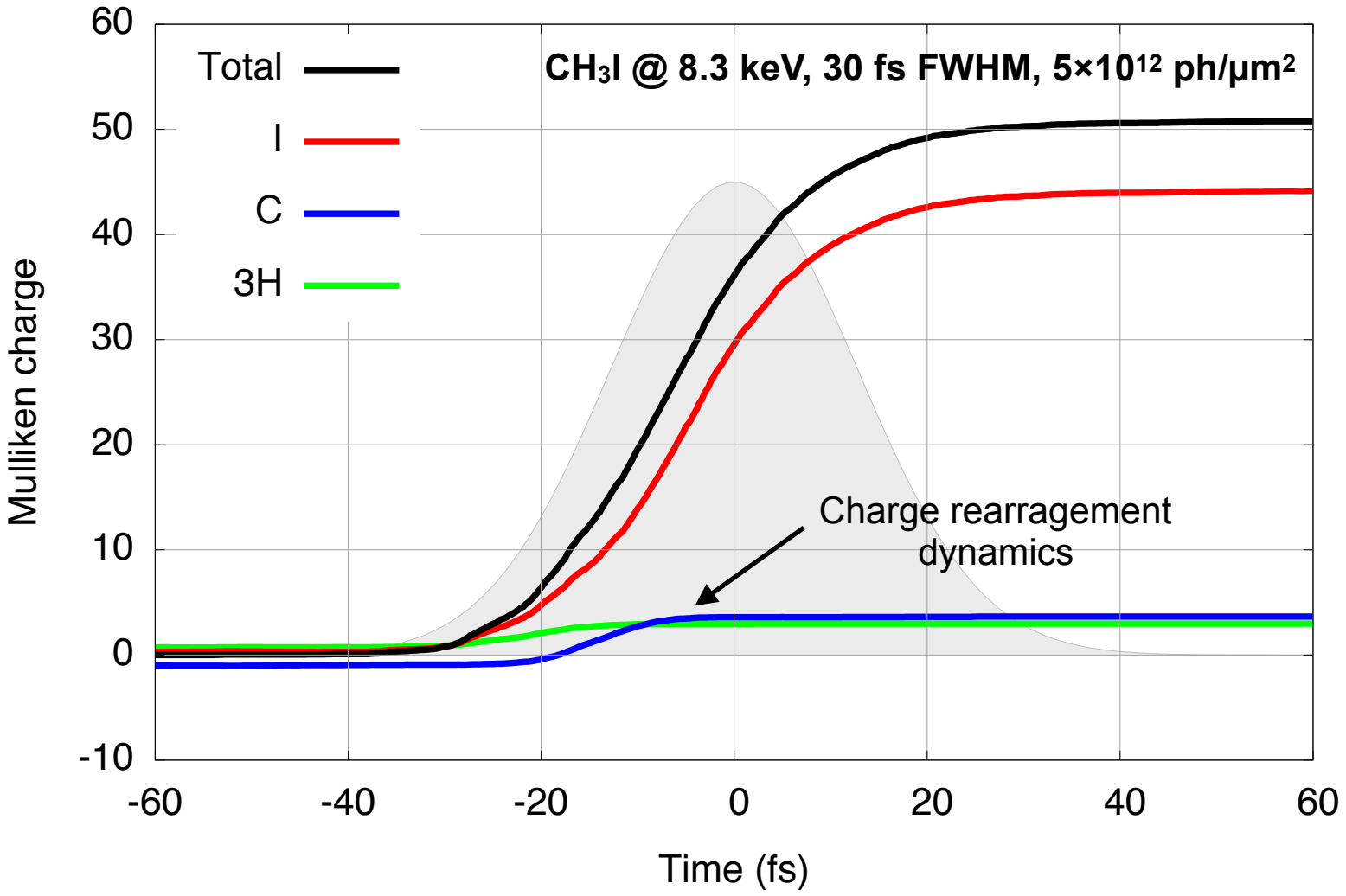
Artem Rudenko
at KSU

Ionization & fragmentation dynamics

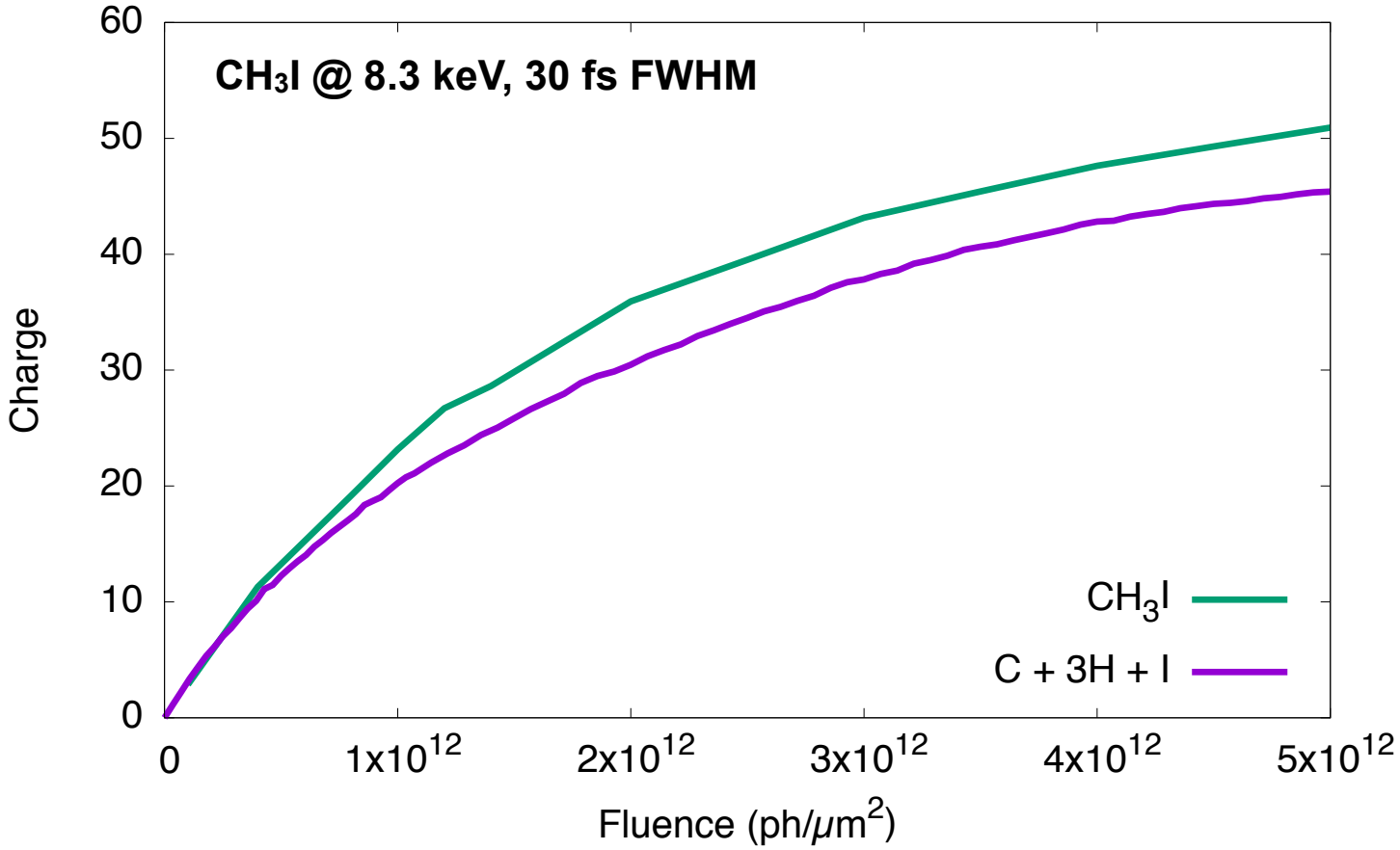
CH_3I



Time evolution of partial charge population



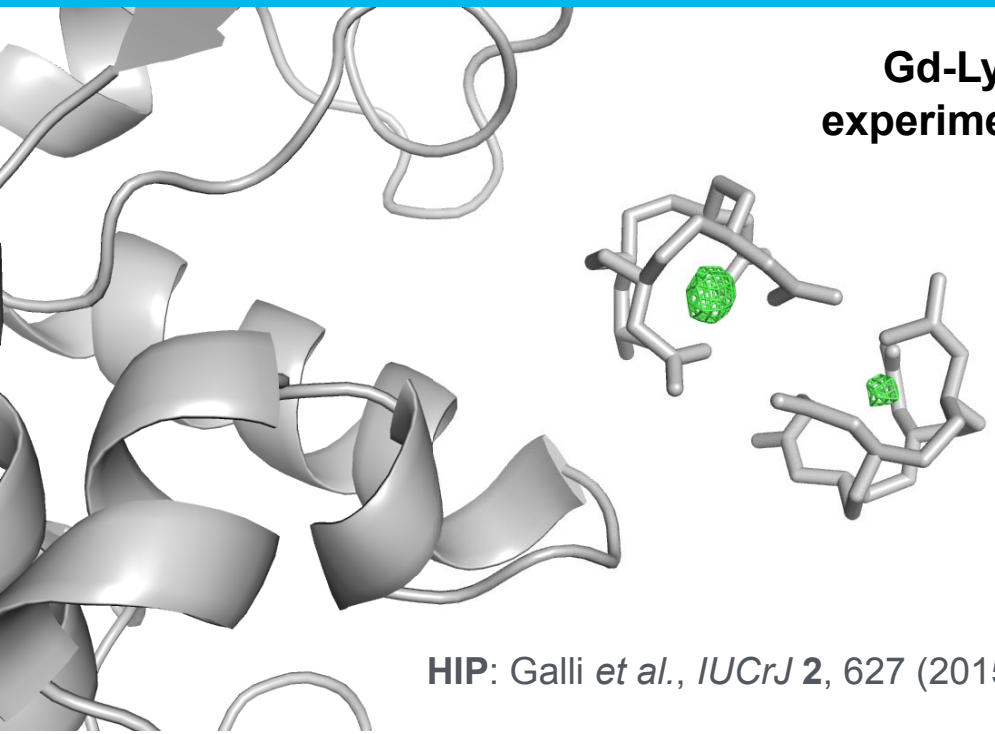
Molecular ionization enhancement



total molecular charge > atomic charges: experimentally confirmed

Rudenko *et al.*, (in preparation).

Application: x-ray molecular imaging

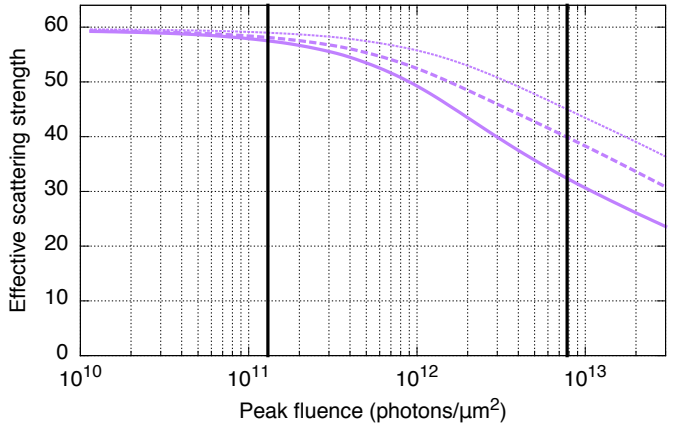


Gd-Lysozyme experiment at LCLS

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

Henry Chapman at CFEL

Lorenzo Galli at CFEL

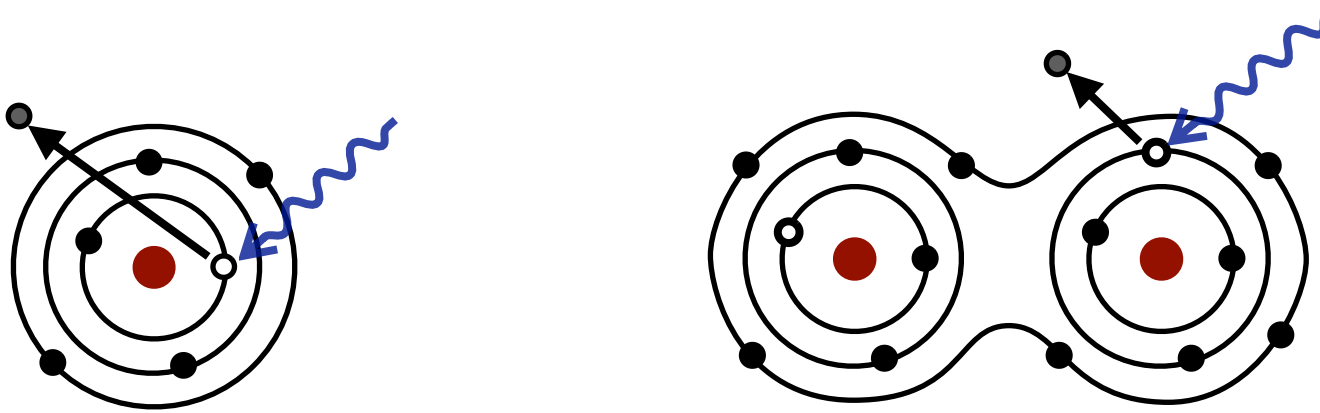


- Another bottleneck of x-ray crystallography: **phasing**
- Proposals of novel phasing methods:
  utilizing selective ionization of heavy atoms
  at high x-ray intensity

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

CFEL-DESY Theory Division

November 2015

Prof. Dr. Robin Santra
Dr. Sang-Kil Son
Dr. Oriol Vendrell
Prof. Dr. Beata Ziaja-Motyka
Dr. Daria Gorelova
Dr. Kota Hanasaki
Dr. Ludger Inhester
Dr. Zoltan Jurek
Dr. Antonia Karamatskou
Dr. Zheng Li
Dr. Nikita Medvedev
Dr. Pankaj Kumar Mishra
Dr. Vikrant Saxena
Dr. Koudai Toyota
Malik M. Abdullah
Caroline Arnold
Sophia Bazzi
Yi-Jen Chen
Athiya M. Hanna
Murali Krishna
Victor Tkachenko

CFEL SCIENCE

DESY

Team X

Yajiang Hao
Now at USTB (Beijing)

Ludger Inhester

Kota Hanasaki

Koudai Toyota

Sang-Kil Son

Oriol Vendrell

Robin Santra

Collaboration: Benedikt Rudek (PTB), Daniel Rolles (KSU), Artem Rudenko (KSU), Kiyoshi Ueda (Tohoku), Henry Chapman (CFEL), Lorenzo Galli (CFEL)

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DESY

Thank you for your attention!

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DESY