Multiphoton multiple ionization dynamics of atoms and molecules at high x-ray intensity

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International Workshop on Intense-field Short-wavelength Atomic and Molecular Processes, ISWAMP-3
July 18–20, 2015

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X-ray multiphoton absorption

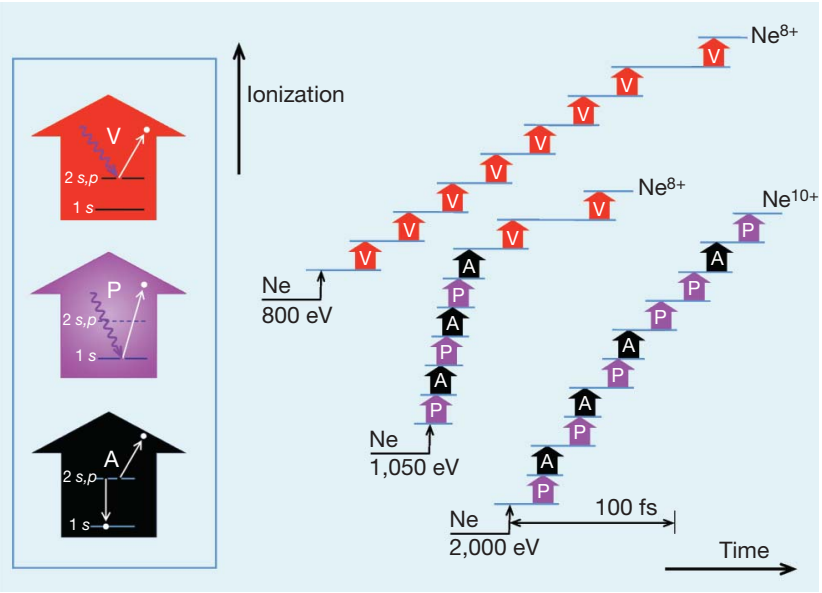
- High x-ray intensity beyond one-photon absorption saturation

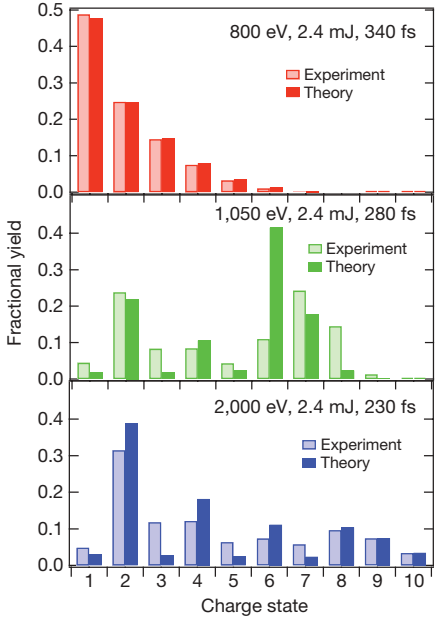
$$\mathcal{F} > \mathcal{F}_{\mathrm{sat}}, \text{ where } \sigma_{\mathrm{abs}}\mathcal{F}_{\mathrm{sat}} = 1$$

- Direct two-photon absorption cross section is very small

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

- Sequential multiphoton absorption is dominant

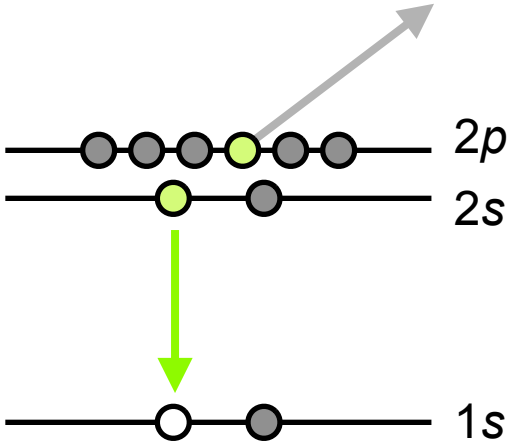




Young *et al.*, *Nature* **466**, 56 (2010).

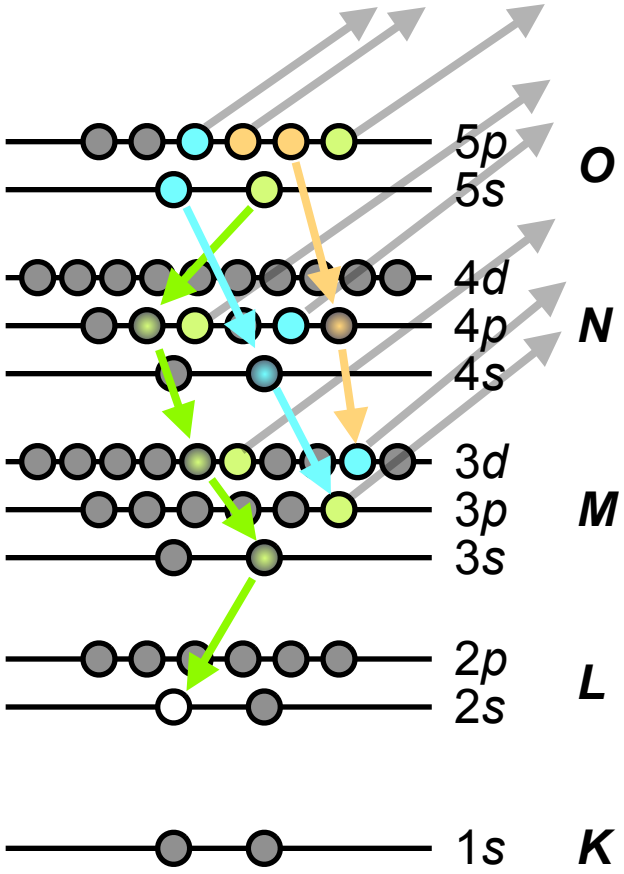
Complex inner-shell decay cascade

Ne



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

Xe



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

Auger (Coster-Kronig) decay cascade

XATOM: all about x-ray atomic physics

- Computer program suite dedicated to ionization dynamics of atoms
- 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
- Solve coupled rate equations to simulate ionization dynamics

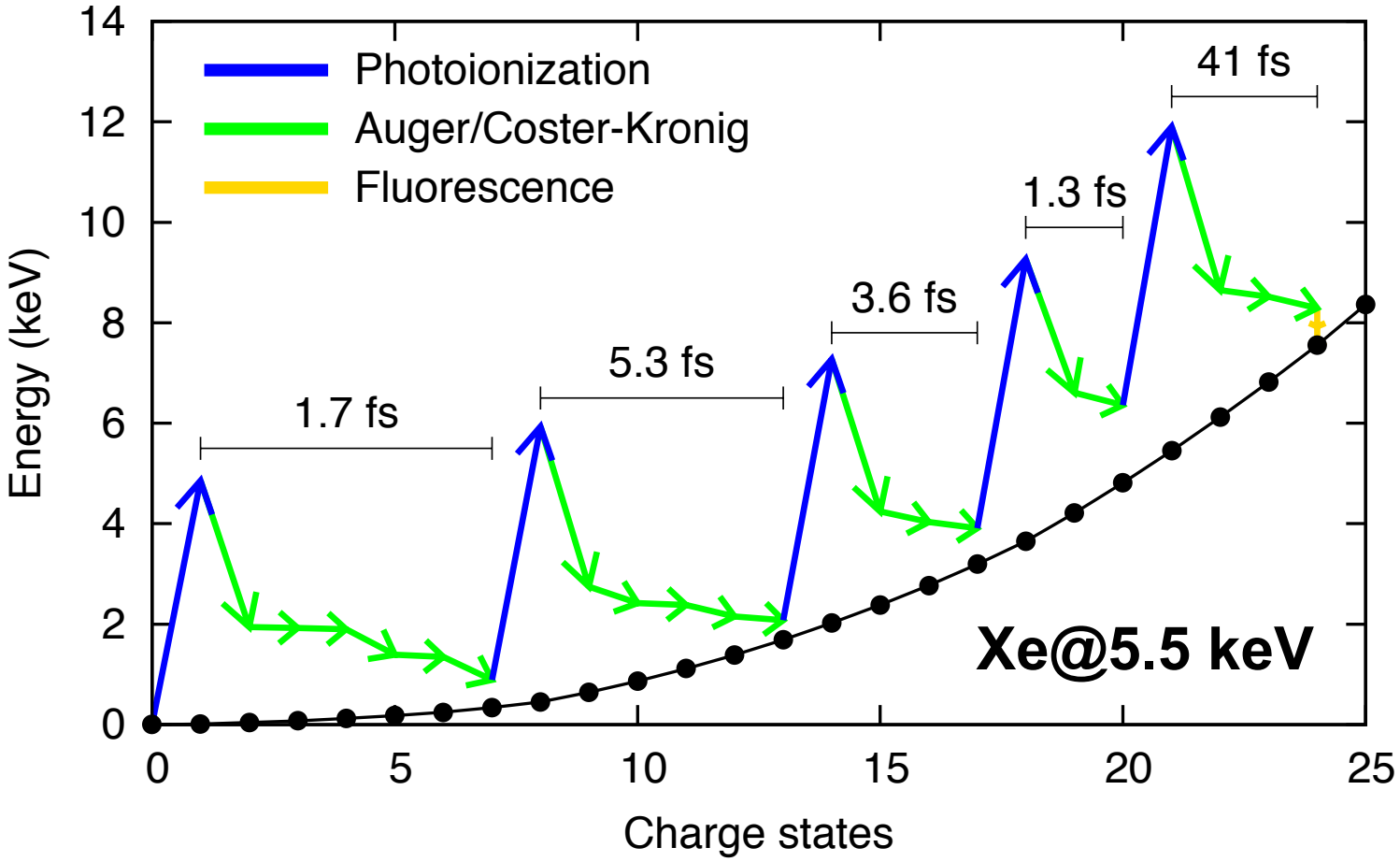
  For Xe *L*-shell, more than 20 million coupled rate equations

  more than 2 billion processes ➔ Monte Carlo approach

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

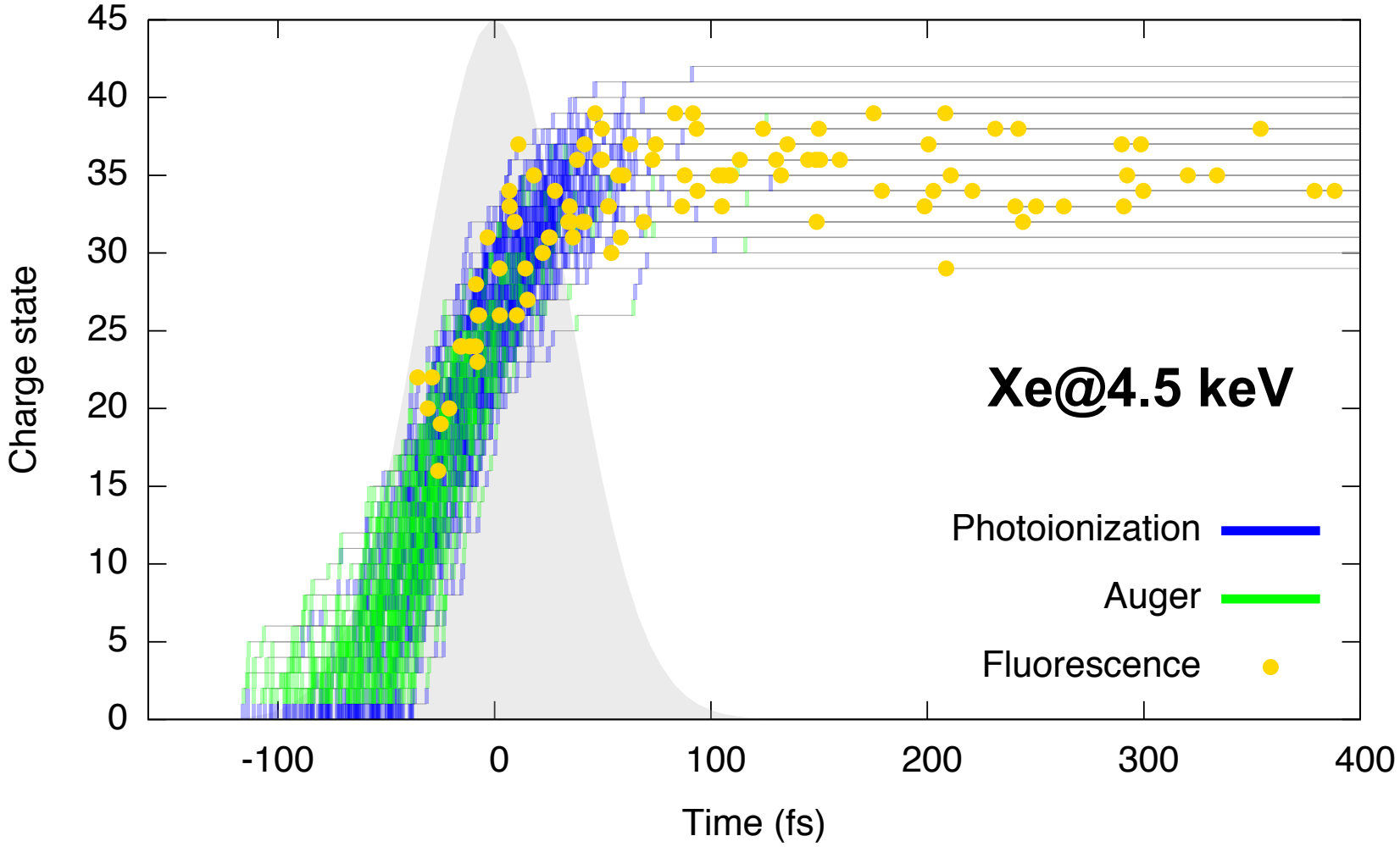
Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

X-ray multiphoton ionization mechanism



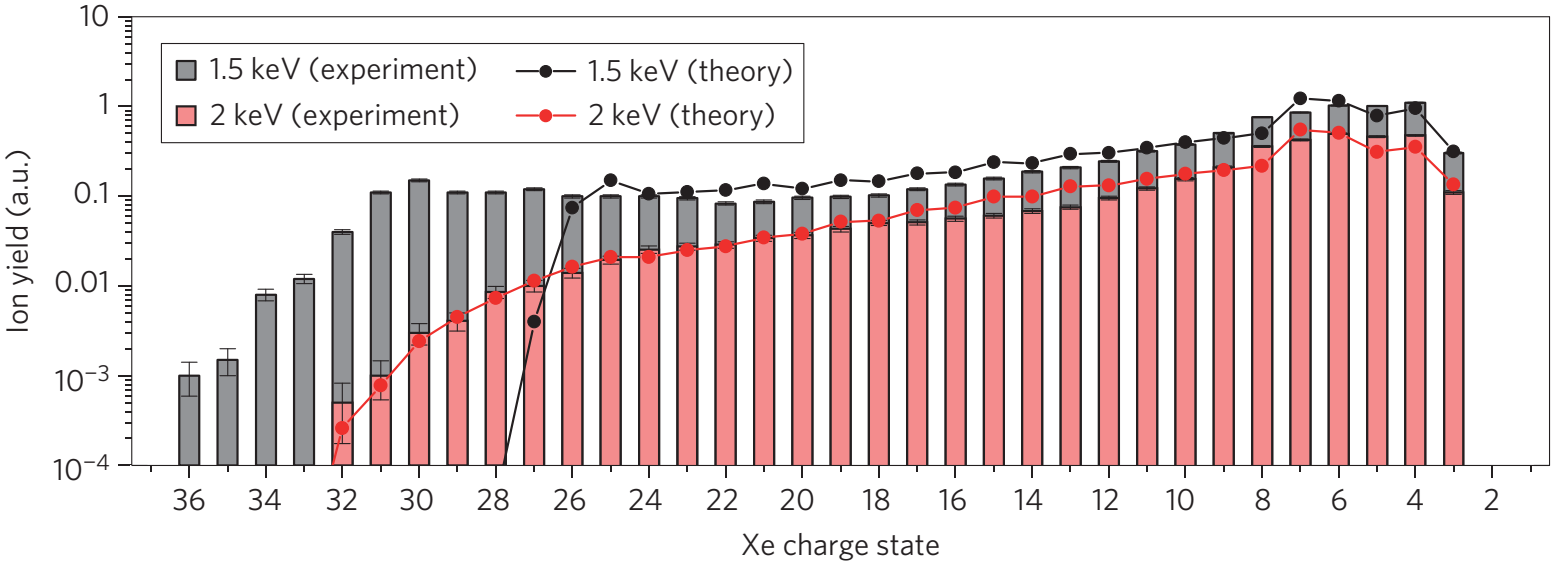
Fukuzawa *et al.*, *Phys. Rev. Lett.* **110**, 173005 (2013).

Ionization pathway: many trajectories



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

Comparison with LCLS experiment



LCLS experiment

Daniel Rolles
at KSU

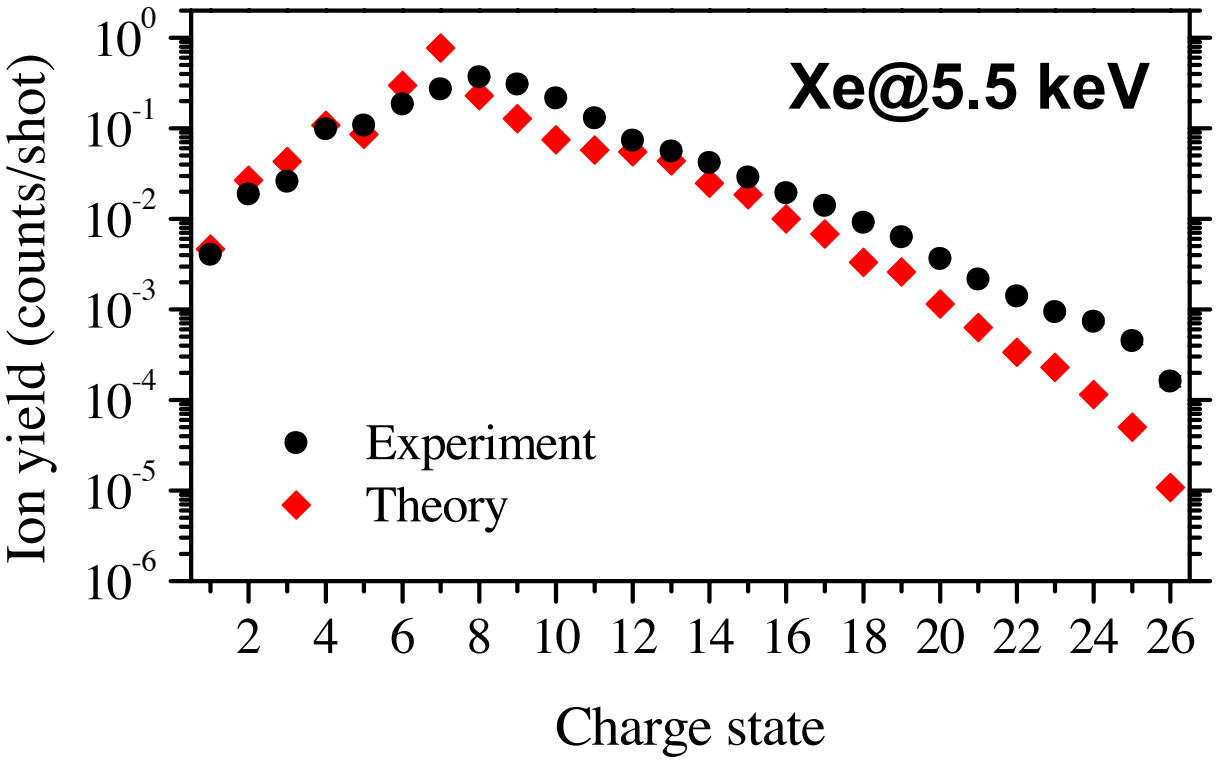
Artem Rudenko
at KSU

Benedikt Rudek
at PTB

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

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

Comparison with SACLA experiment



SACLA experiment

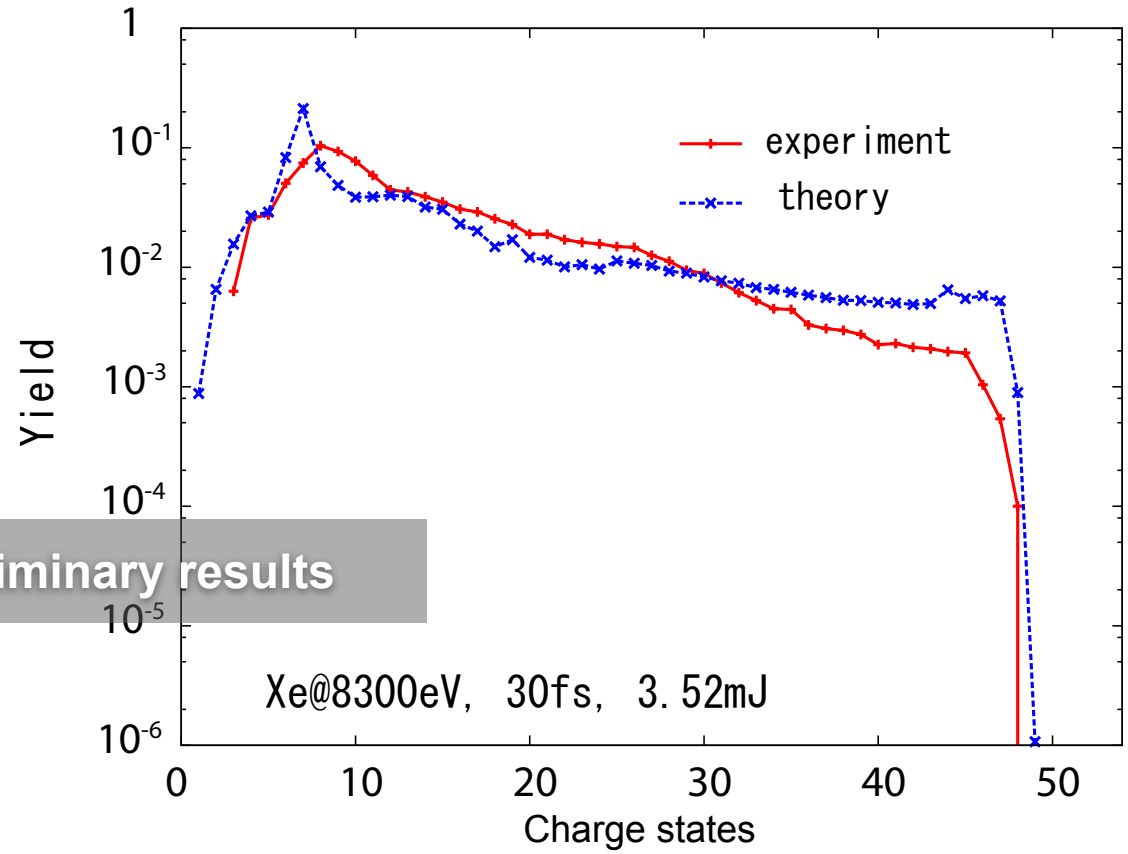
Kiyoshi Ueda
at Tohoku Univ.

- Hironobu Fukuzawa
- Koji Motomura

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

- Xe *L*-shell ionization: charged up to Xe^{26+}
- underestimation in theory: lack of relativistic effect and shake-off

Comparison with LCLS experiment



Preliminary results

LCLS experiment

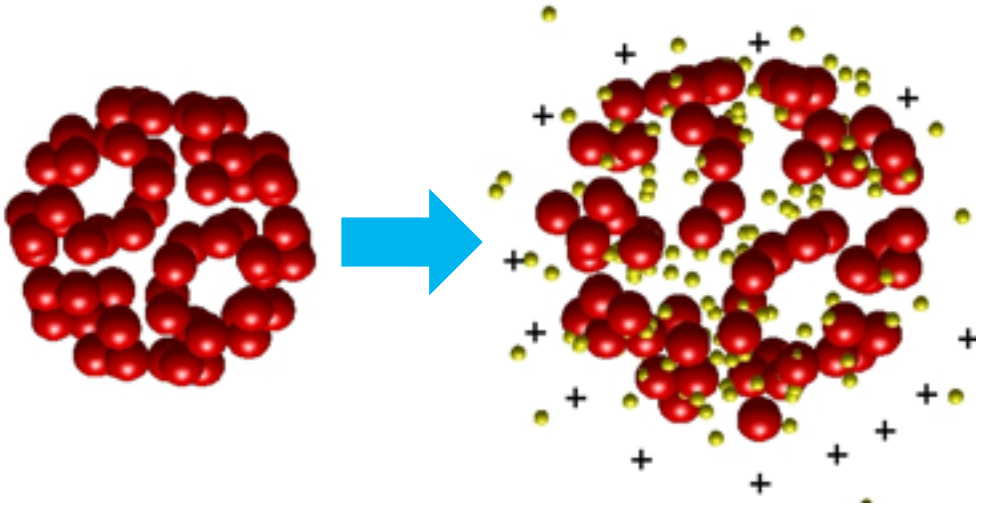
Daniel Rolles
Artem Rudenko
Benedikt Rudek

Theory

Koudai Toyota

- higher photon energy and higher fluence: charged up to Xe^{48+}
- inclusion of the relativistic effect in progress

Need for molecular treatment in fullerene



Murphy *et al.*, *Nature Commun.* **5**, 4281 (2014).

XMDYN simulation

Zoltan Jurek
at CFEL-DESY Theory

- C_{60}-specific force field for neutral; Coulomb force for charged ions
- Molecular Auger effect: removing one from a neighboring atom and one from its own
- No first-principle treatment of electron impact ionization

XMOLECULE

- An *ab initio* electronic-structure approach dedicated to ionization dynamics of polyatomic molecules
- Theoretical challenges
  - complex ionization dynamics involving tremendously many hole configurations
  - ionization dynamics coupled with fragmentation dynamics
  - self-consistent-field calculation for every electronic and nuclear configuration
  - no rigorous treatment of highly excited, polyatomic system


Yajiang Hao


Ludger Inhester


Kota Hanasaki

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

Molecular multiple-hole state calculation

- 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

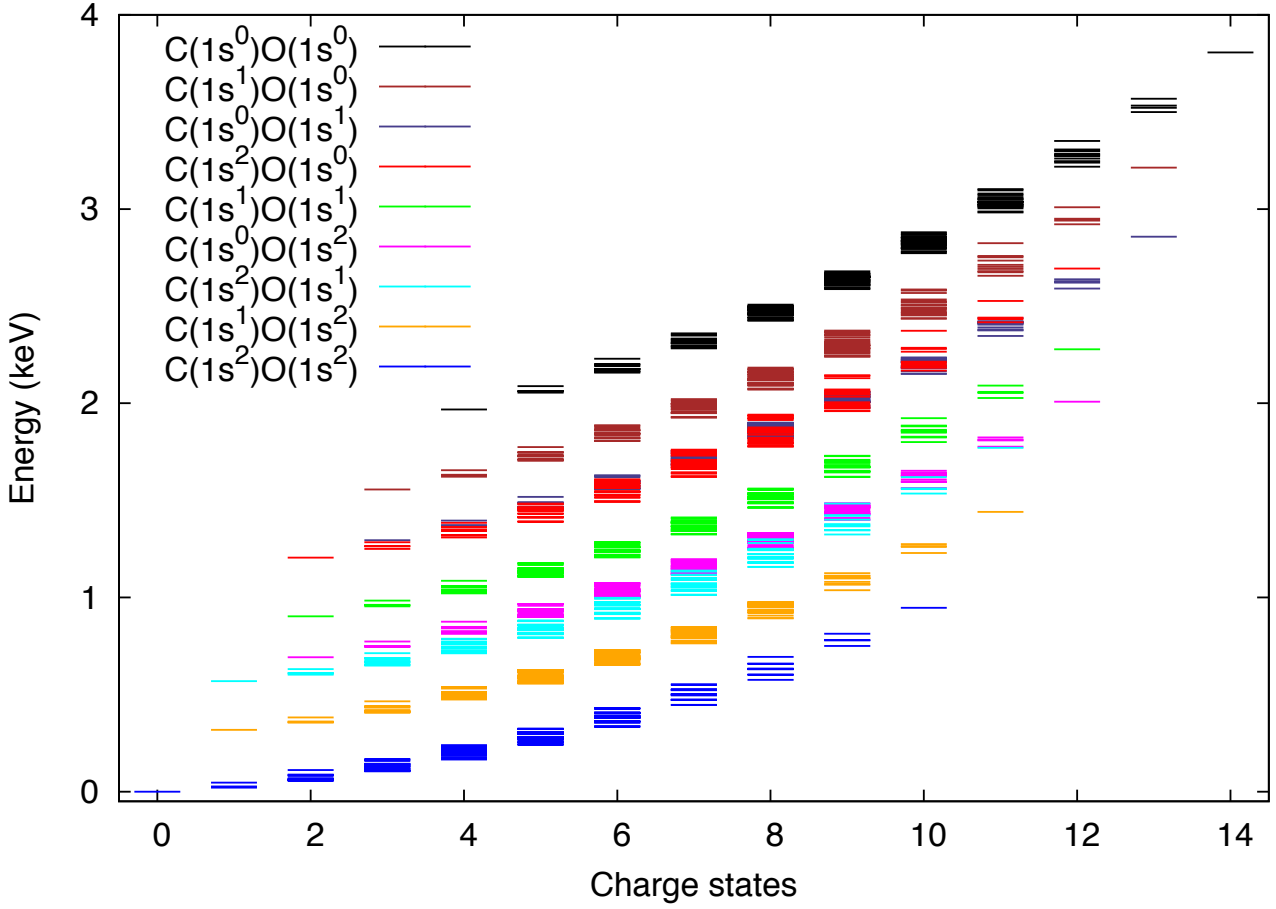
$$\phi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r}Y_{lm}(\theta,\varphi)$$ calculated by XATOM

- 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

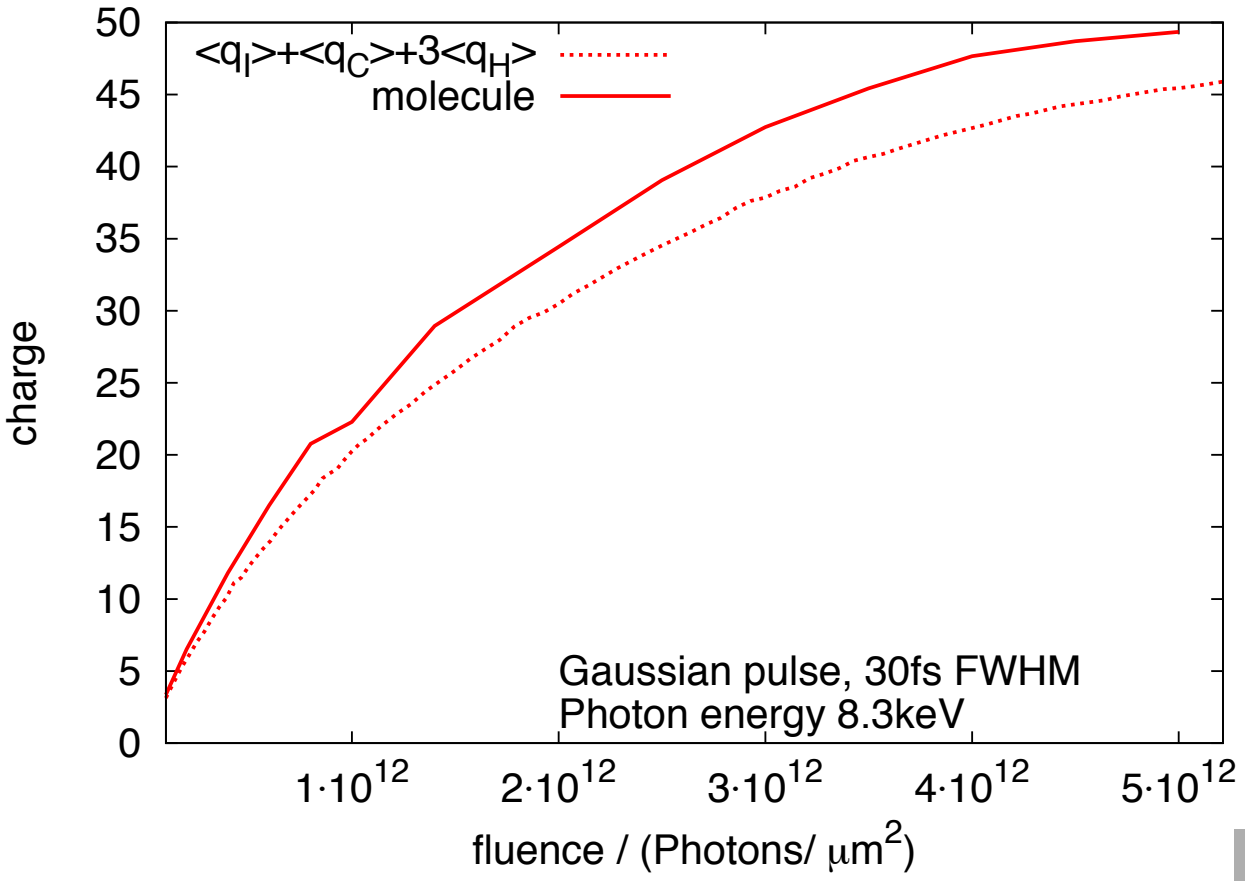
Various electronic states of CO



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

Methyl iodide at high x-ray intensity

molecular model vs. independent atomic model

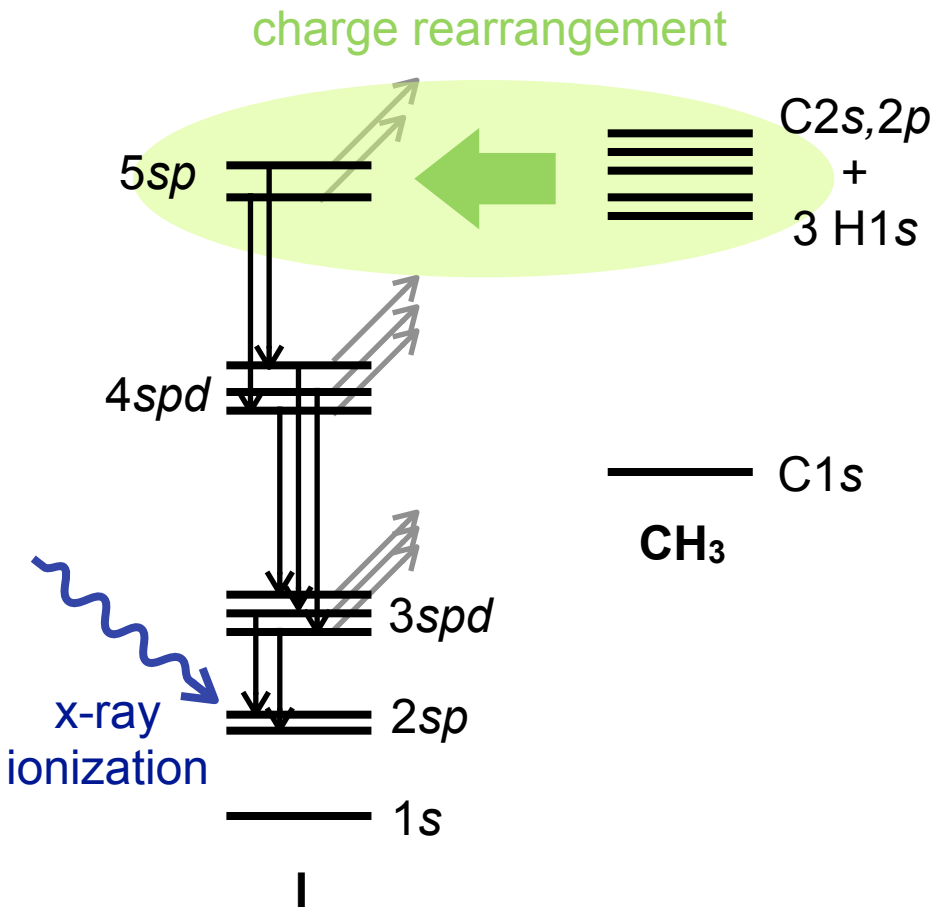


CH_3I @ 8.3 keV
(fixed geometry)

Collaboration with
Daniel Rolles
Artem Rudenko
Benjamin Erk
Rebecca Boll

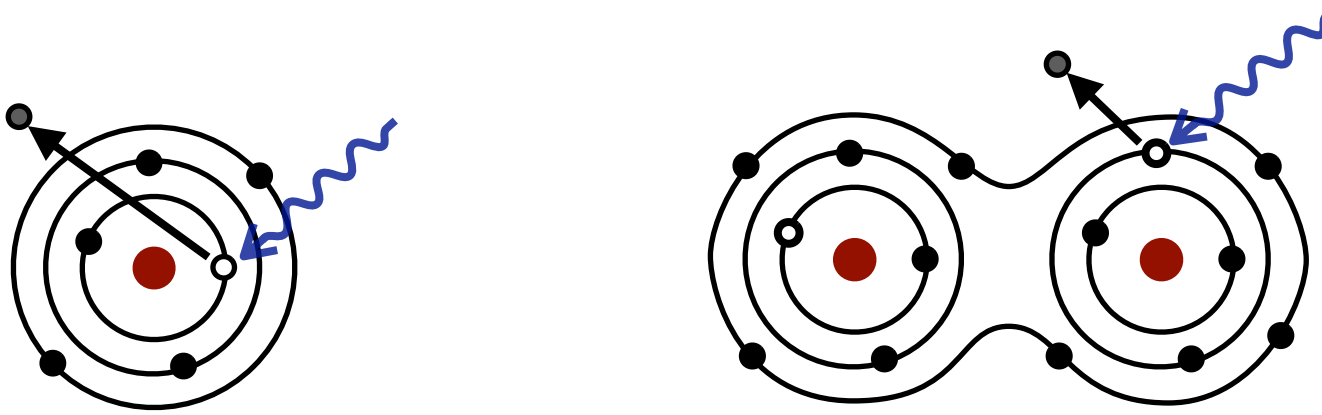
Preliminary results

Ionization enhanced by charge rearrangement



- At low intensity, $Q_{molecule} \sim Q_{atom}$
  Erk *et al.*, *PRL* **110**, 053003 (2013).
- At high intensity, $Q_{molecule} > Q_{atom}$ ionization enhancement due to charge rearrangement
- Charge shifted by orbital relaxation and molecular Auger decay
- More charge rearrangement via valence orbitals when highly charged: larger basis set needed
- Less charge rearrangement by bond breaking: molecular dynamics needed

Conclusions



- Atoms and molecules are highly ionized when exposed to XFEL pulses
- Multiphoton multiple ionization dynamics described by a sequence of one-photon ionizations and accompanying relaxations
- Tested by a series of atomic experiments at LCLS and SACLA
- Ionization enhanced by molecular environment: detailed electronic structure and dynamics calculations required