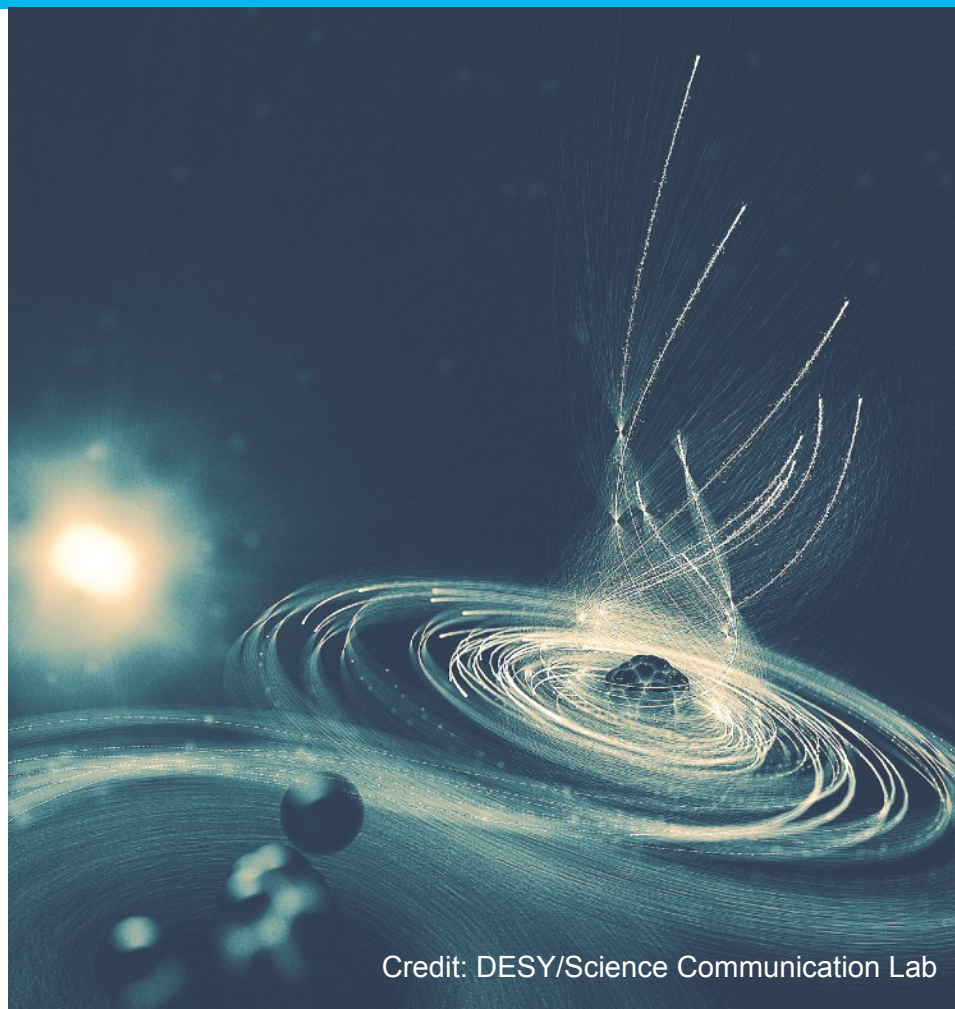
What happens to atoms and molecules during XFEL pulses?

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

European XFEL Theory Seminar
June 22, 2017



Credit: DESY/Science Communication Lab

XATOM and XMOLECULE developers

Yajiang Hao
Now at USTB (Beijing)

Ludger Inhester

Kota Hanasaki
Now at Tohoku Univ.

Koudai Toyota

Sang-Kil Son

Oriol Vendrell
Now at Aarhus Univ.

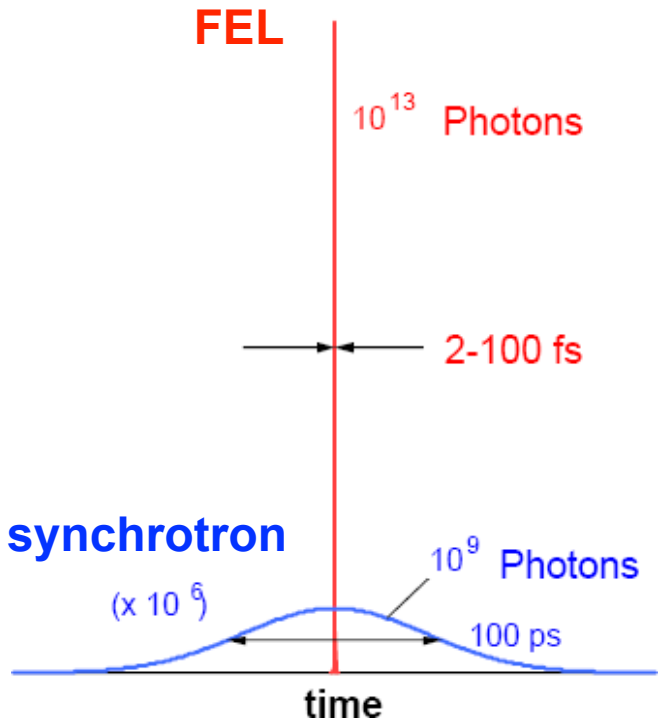
Robin Santra

Overview

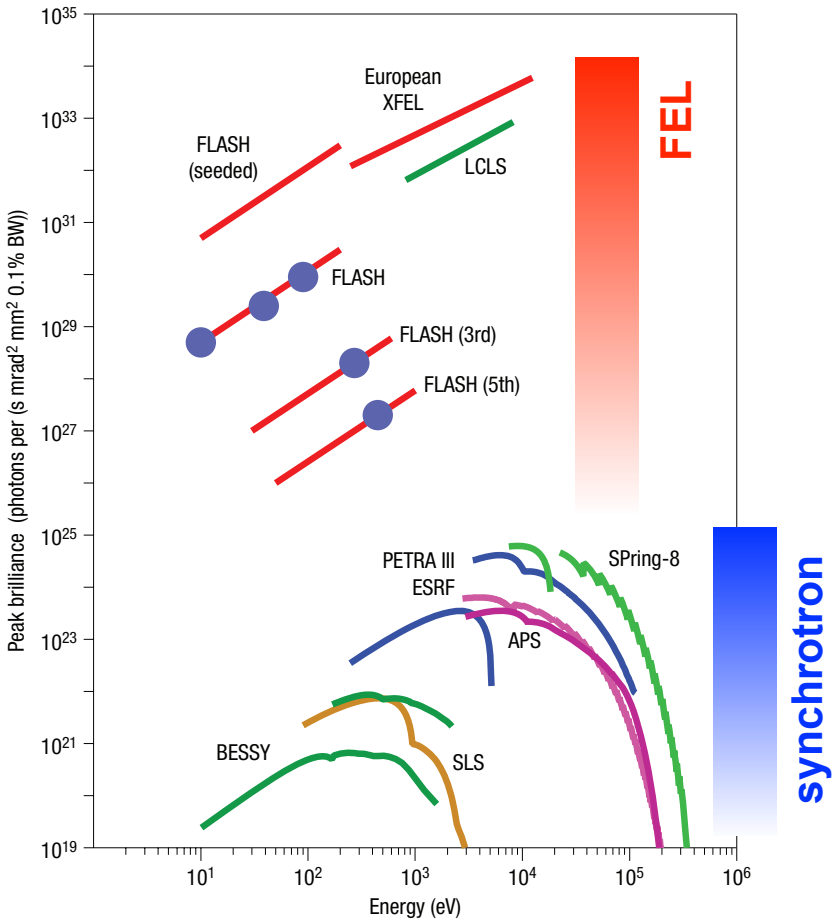
- Introduction to XFEL–matter interaction
- XATOM and x-ray multiphoton multiple ionization dynamics of Xe
- XMOLECULE and x-ray-induced ultrafast explosion dynamics of CH_3I
- Summary

XFEL: X-ray free-electron laser

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



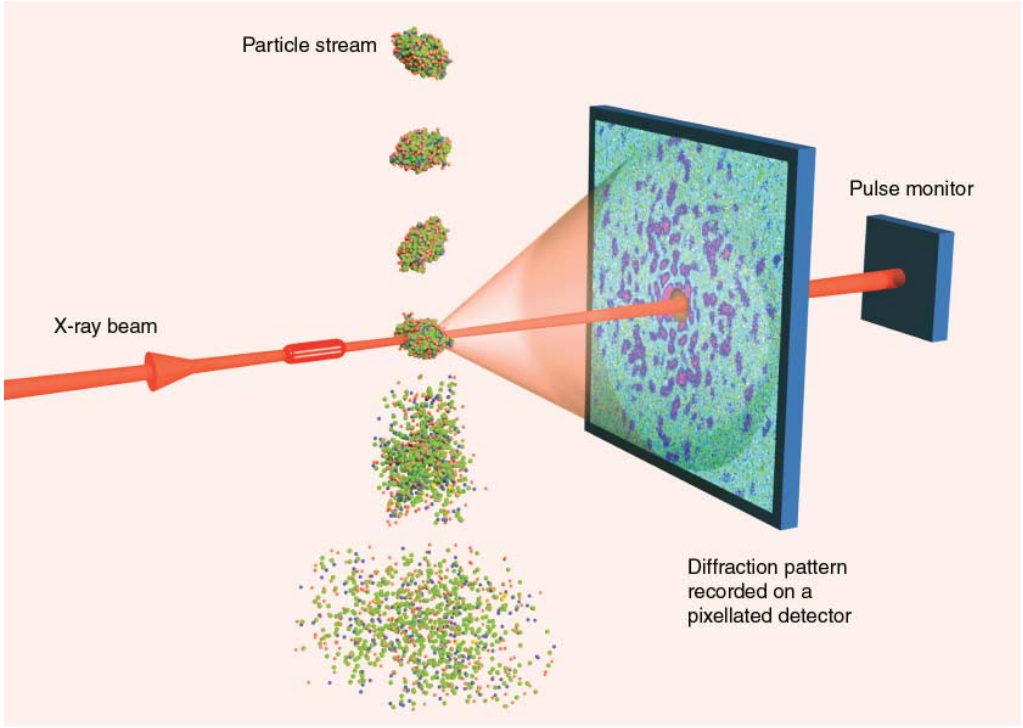
Schneider, *Rev. Accl. Sci. Tech.* **3**, 13 (2010).



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

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

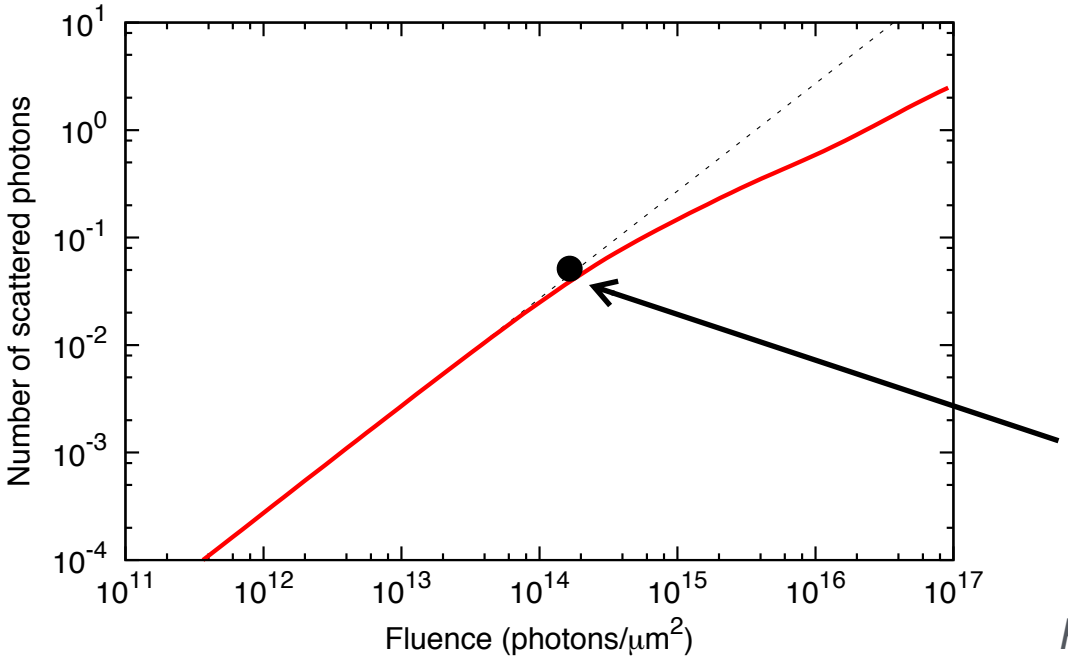


Gaffney & Chapman, *Science* **316**, 1444 (2007).

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

What high x-ray intensity means?

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



Carbon @ 8 keV

σ_{abs} = 0.084 kbarns

⬇

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

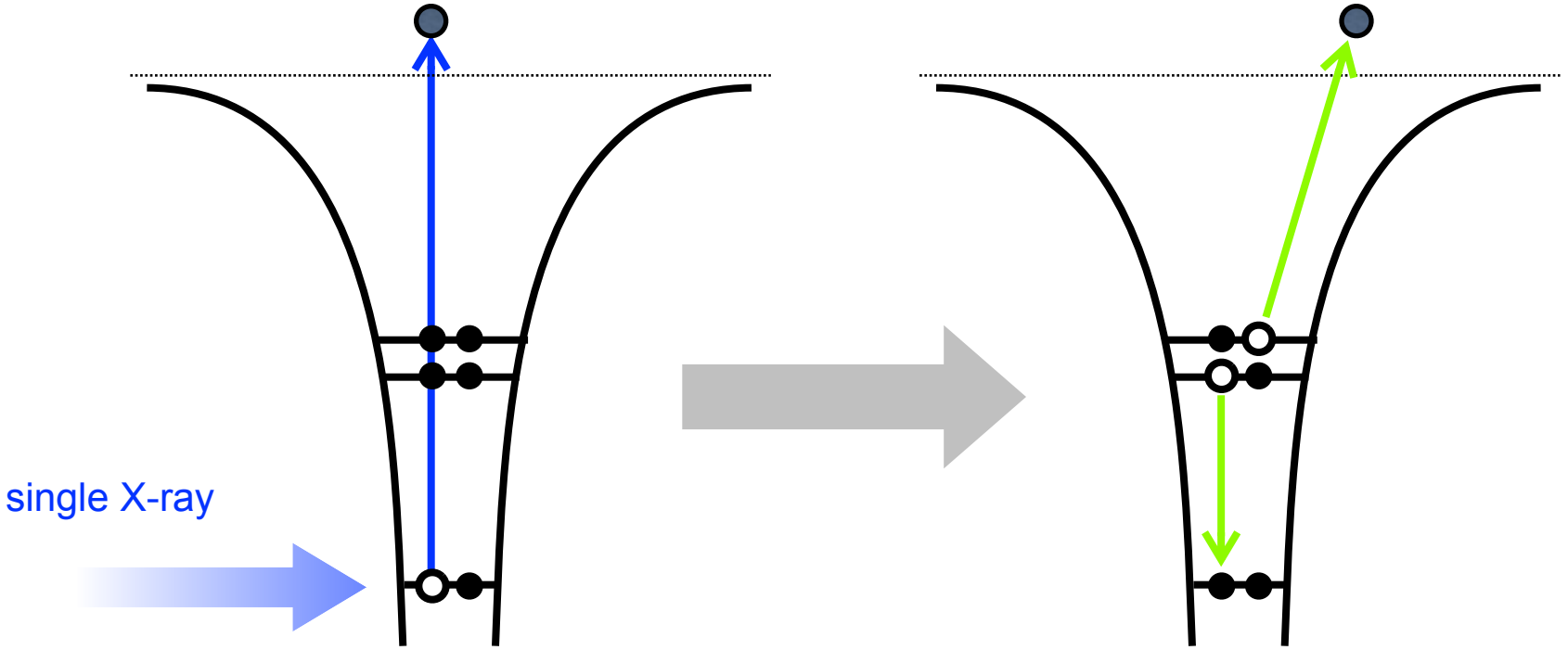
⬇

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

Fundamental x-ray–matter interaction

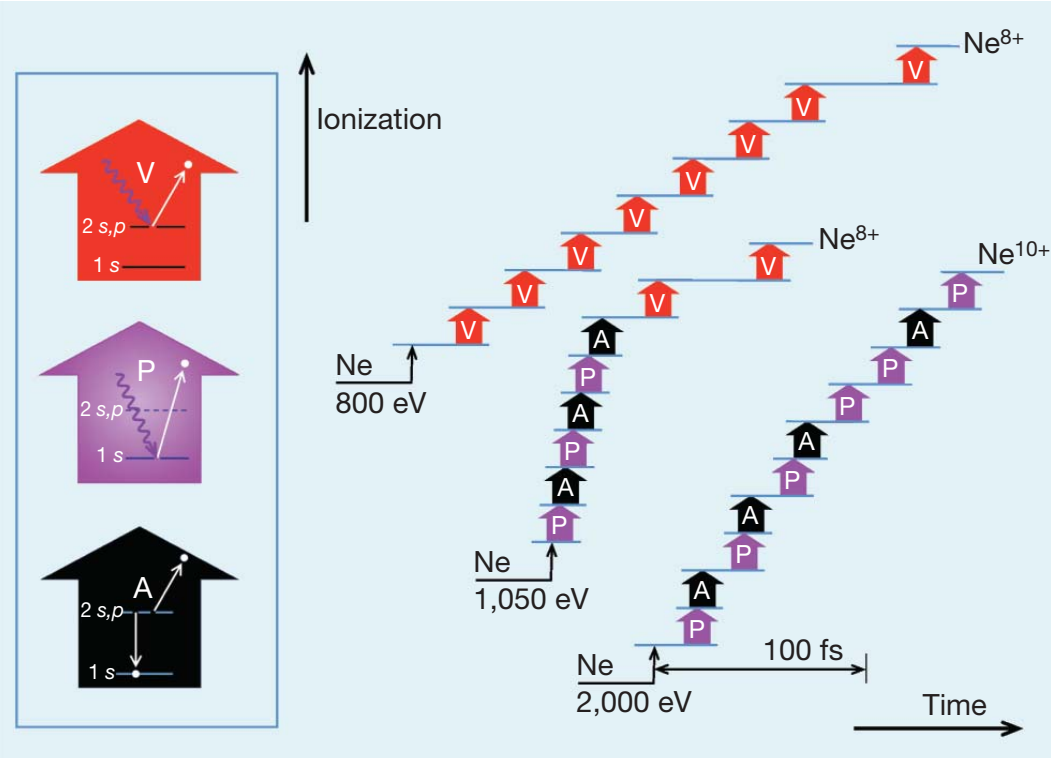


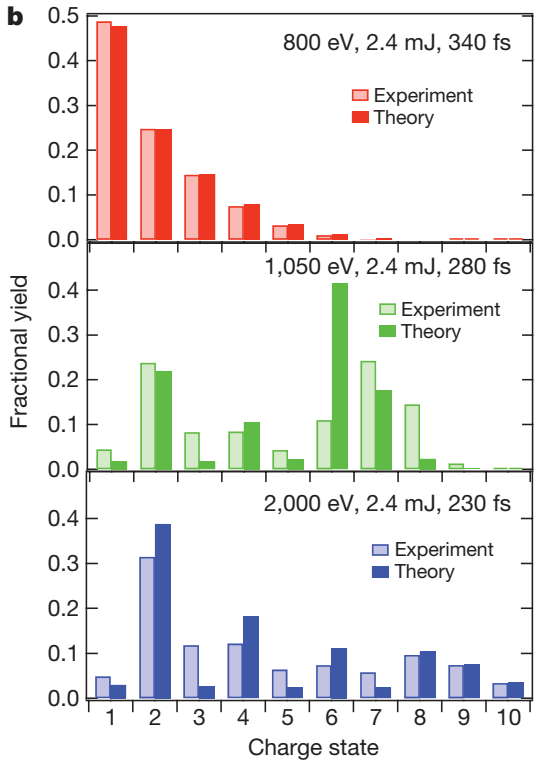
Photoionization: $C \rightarrow C^{*+} + e^-$

Auger decay: $C^{*+} \rightarrow C^{++} + e^-$

synchrotron: one-photon absorption ➔ **PA** ➔ C^{2+}
XFEL: many-photon absorption ➔ **PAPAPA** ➔ C^{6+}

Sequential multiphoton multiple ionization





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

- First LCLS experiment: fundamental atomic physics in XFEL
- Lots of x-ray photons: repeated *K*-shell ionization (P) followed by Auger (A)

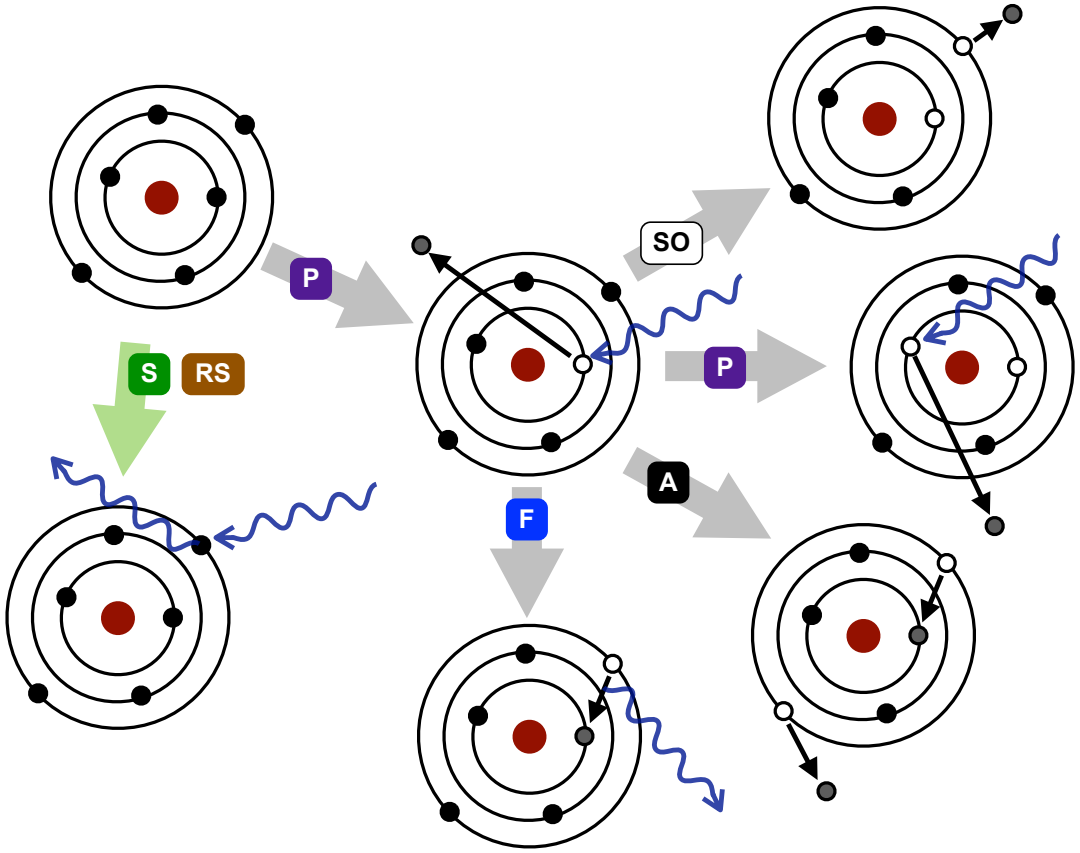
Challenges for x-ray multiphoton ionization

- 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 for ionization
  - complex inner-shell ionization dynamics, especially for heavy atoms

XATOM

- XATOM: describes dynamical behaviors of atoms interacting with XFEL pulses
- X-ray-induced atomic processes for any given element and configuration
- Sequential ionization model has been tested by a series of atomic XFEL experiments: Ne, Ar, Kr, Xe, …



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

XATOM: Electronic structure

- Efficient electronic structure calculation required
- Hartree-Fock-Slater method

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \int d^3r' \, \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{3}{2}\left\{\frac{3}{\pi}\rho(\mathbf{r})\right\}^{1/3}\right]\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

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

- Bound states ➔ generalized pseudospectral method on *nonuniform* grid
- Continuum states: calculated with the same potential as used in bound states ➔ 4th-order Runge-Kutta method on *uniform* grid

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

XATOM: Cross sections and rates

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

$$\Gamma_{FI} = 2\pi\delta\left(E_F - E_I\right)\left|\langle F|\hat{H}_{\rm int}|I\rangle\right|^2$$

- Photoionization cross section

$$\sigma_{\rm P}(i,\omega) = \frac{4}{3}\alpha\pi^2\omega N_i \sum_{l_j=|l_i-1|}^{l_i+1} \frac{l_>}{2l_i+1}\left|\langle u_{n_i l_i}(r)|r|u_{\varepsilon l_j}(r)\rangle\right|^2$$

- Fluorescence rate

$$\Gamma_{\rm F}(i,j) = \frac{4}{3}\alpha^3(I_i - I_j)^3\frac{N_i^{\rm H}N_j}{4l_j+2}\cdot\frac{l_>}{2l_i+1}\left|\langle u_{n_i l_i}(r)|r|u_{n_j l_j}(r)\rangle\right|^2$$

- Auger rate

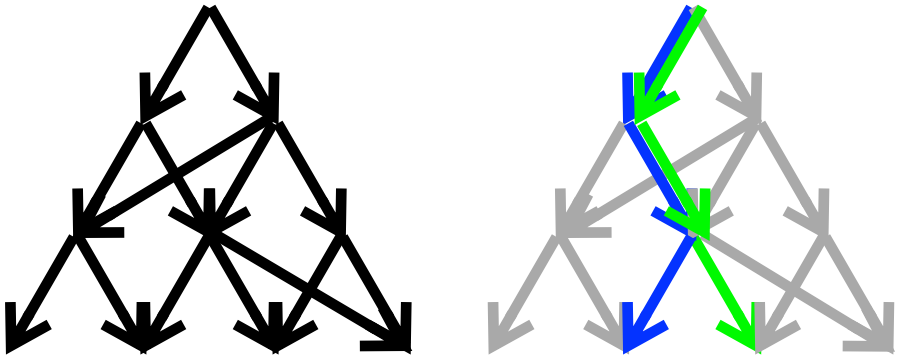
$$\Gamma_{\rm A}(i,jj') = \pi\frac{N_i^{\rm H}N_{jj'}}{2l_i+1}\sum_{L=|l_j-l_{j'}|}^{l_j+l_{j'}}\sum_{S=0}^{1}\sum_{l_{i'}}(2L+1)(2S+1)|M_{LS}(j,j',i,i')|^2$$

XATOM: Coupled rate equations

- Electronic structure: calculated for every single configuration
- Cross sections and rates: calculated for every single configuration
- Solve coupled rate equations to simulate ionization dynamics

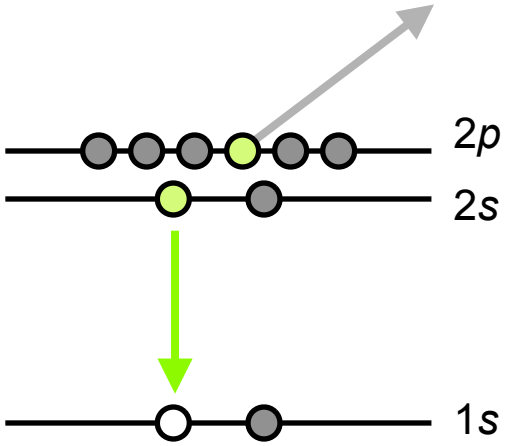
$$\frac{d}{dt}P_I(t) = \sum_{I' \neq I}^{\text{all config.}} \left[\Gamma_{I' \to I} P_{I'}(t) - \Gamma_{I \to I'} P_I(t)\right]$$

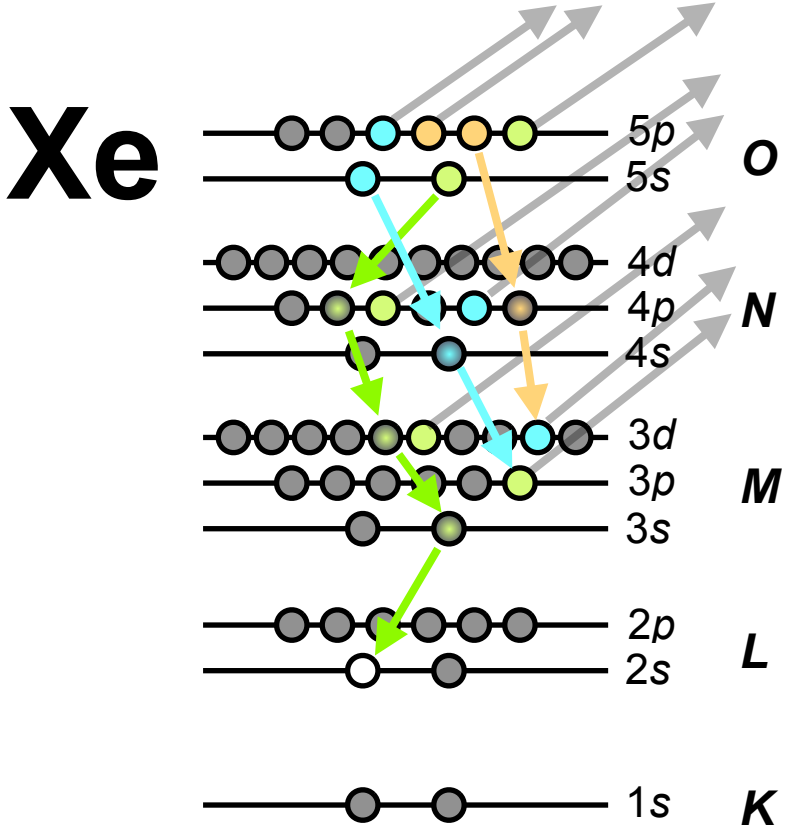
- Tremendously large coupled rate equations (~millions configurations)
  ➔ solved by Monte Carlo approach



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

Complex inner-shell decay cascade

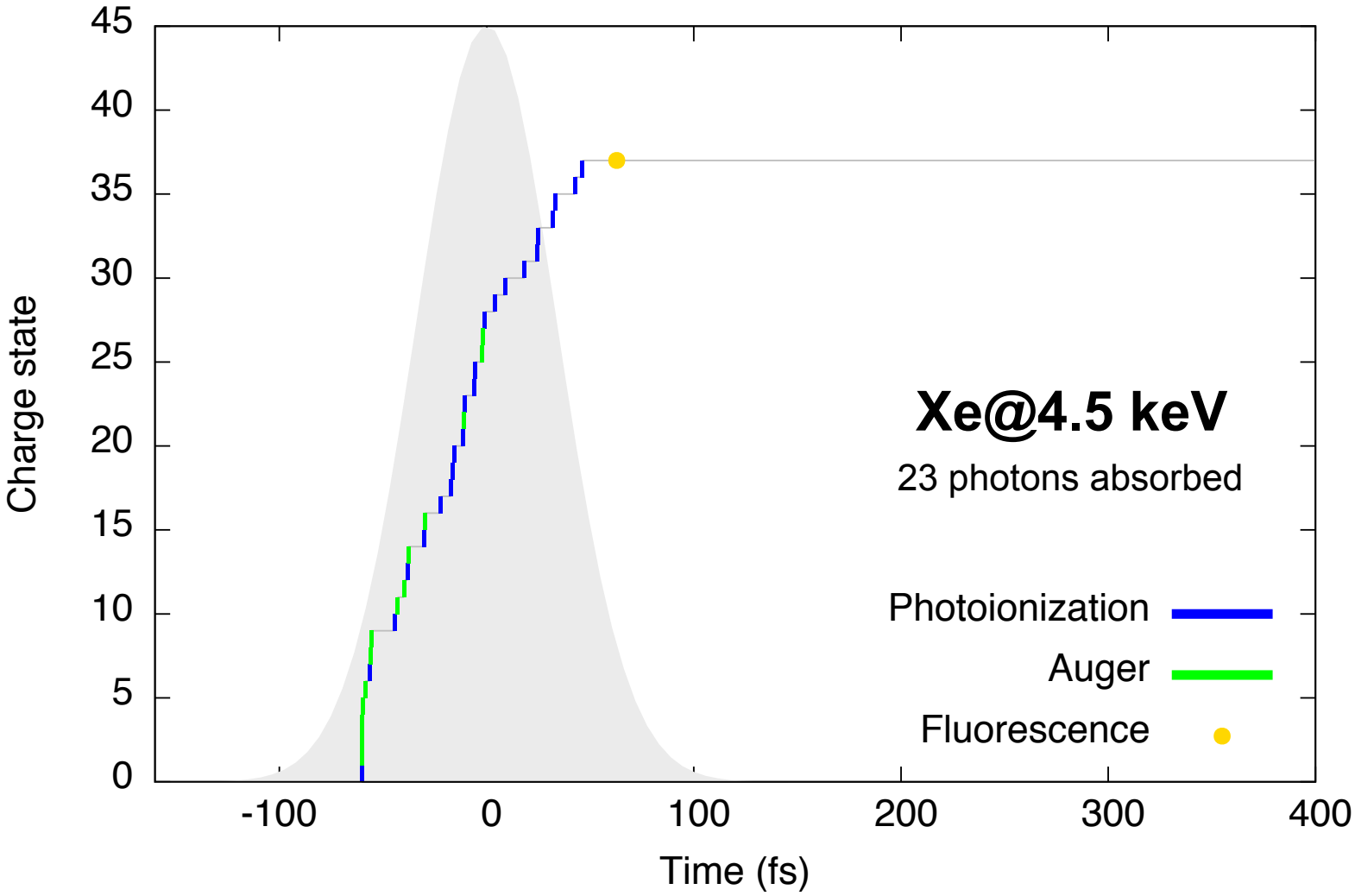




Multiphoton absorption after/during decay cascade

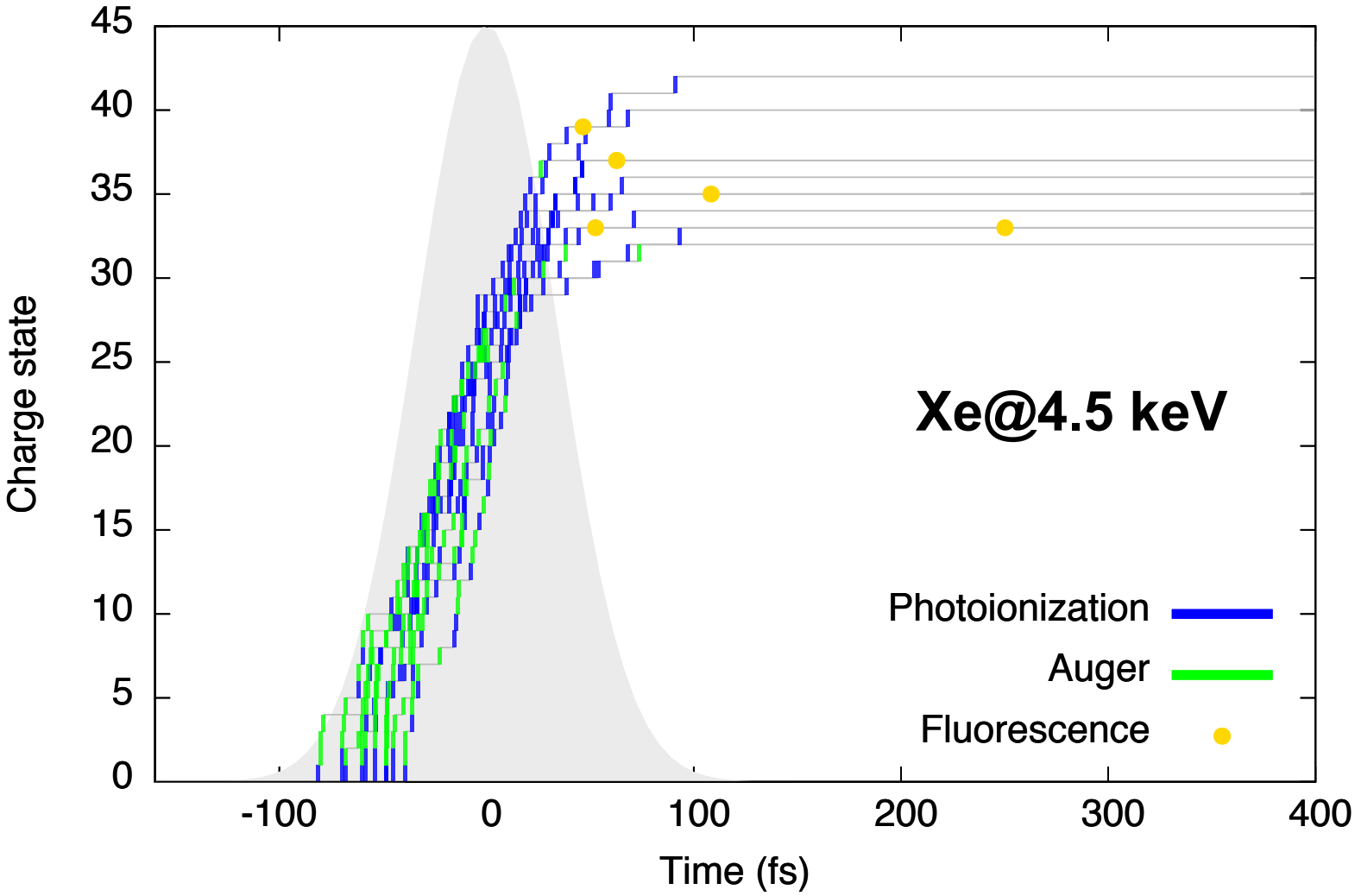
- More than 20 million multiple-hole configurations
- More than 2 billion x-ray-induced processes

X-ray multiphoton ionization dynamics



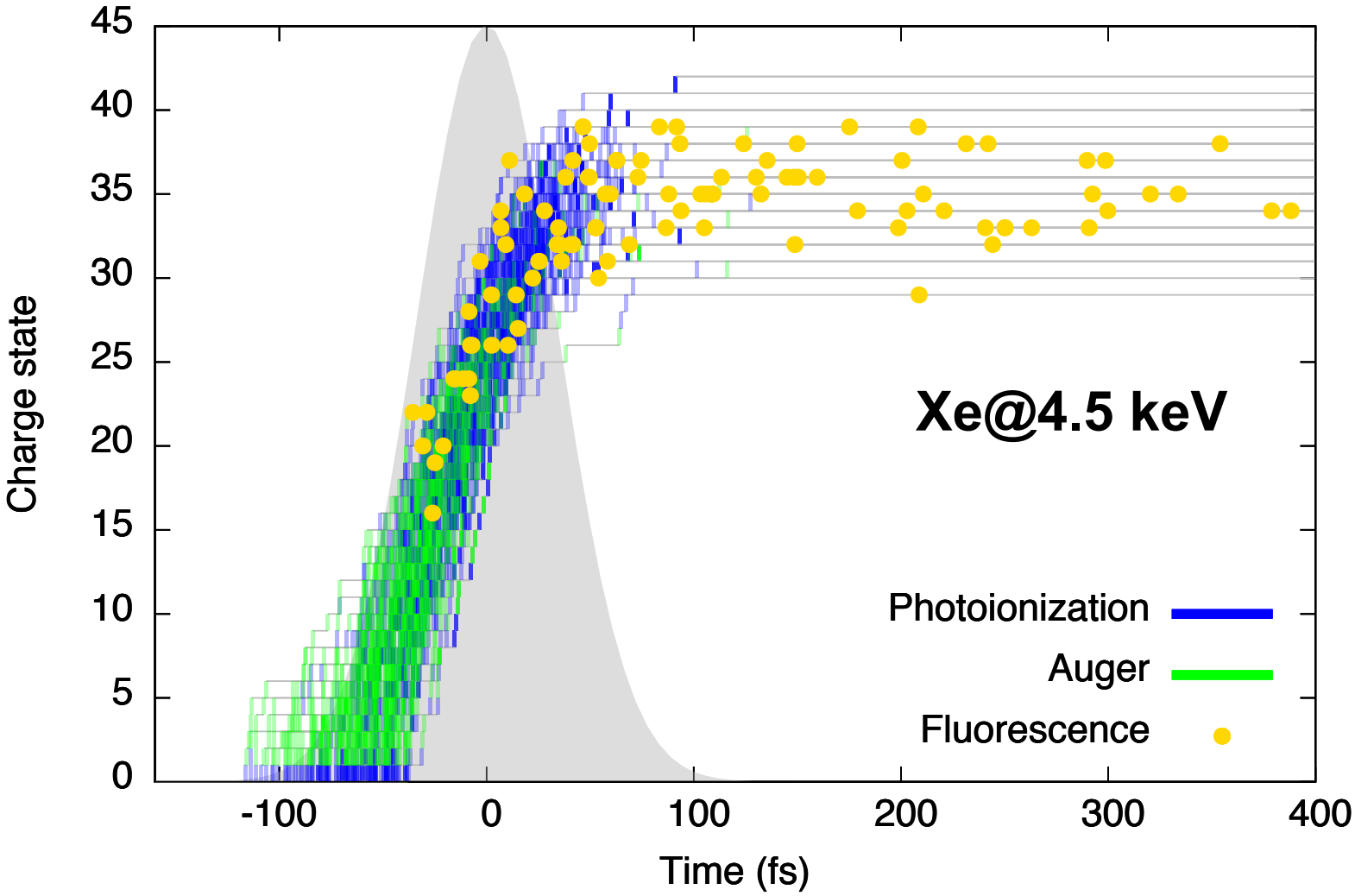
Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

X-ray multiphoton ionization dynamics



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

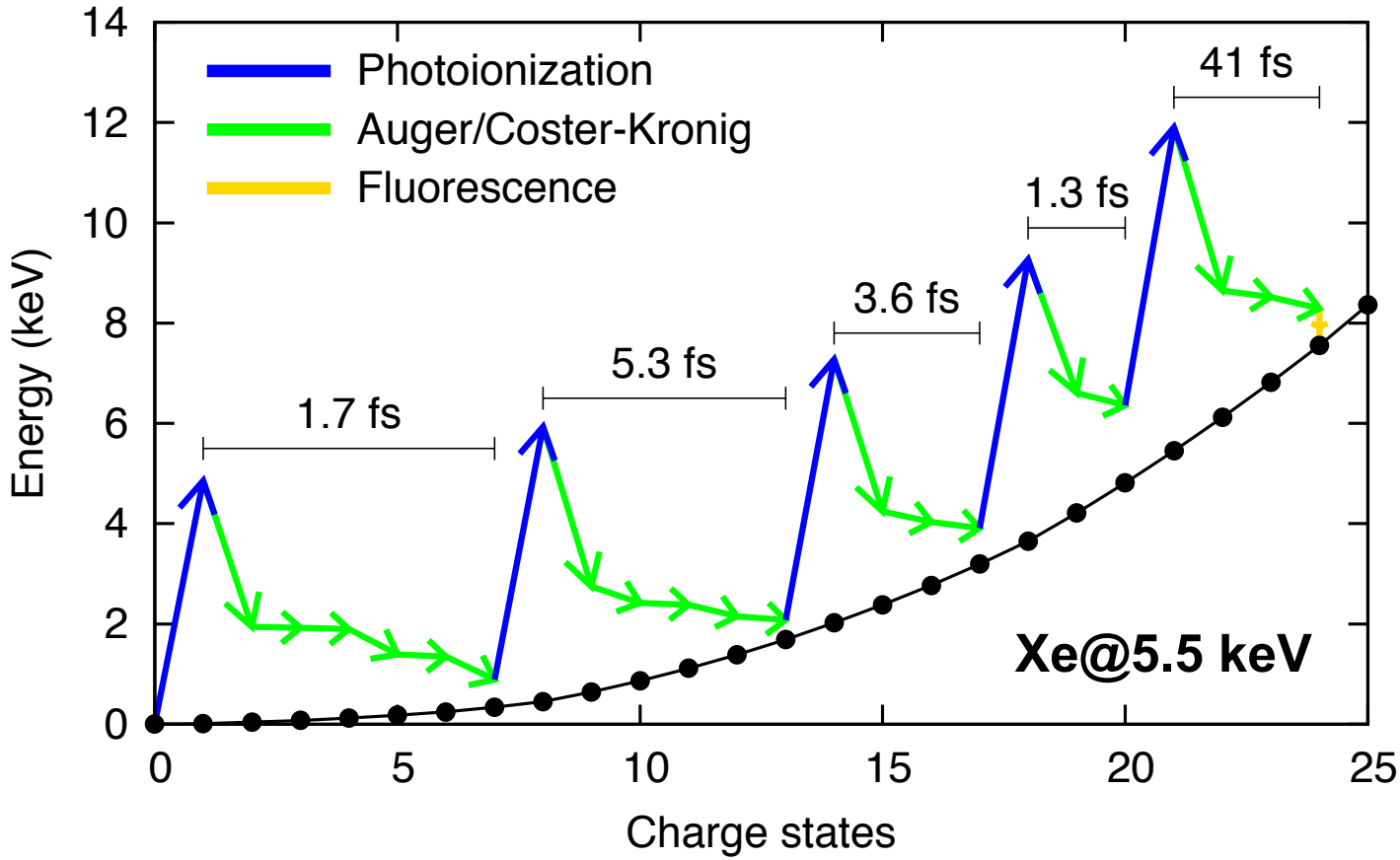
X-ray multiphoton ionization dynamics



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

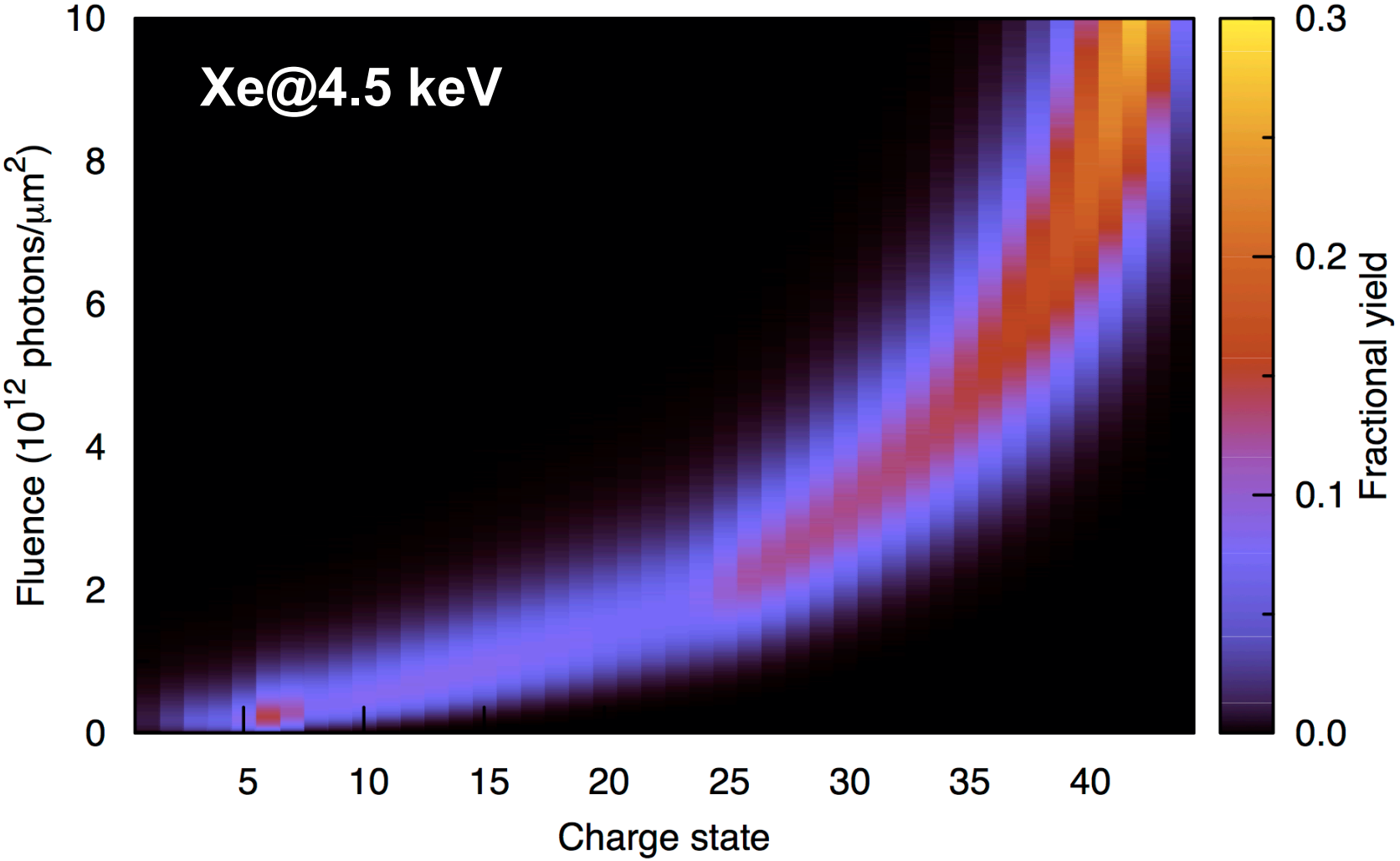
Ionization mechanism described by theory

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



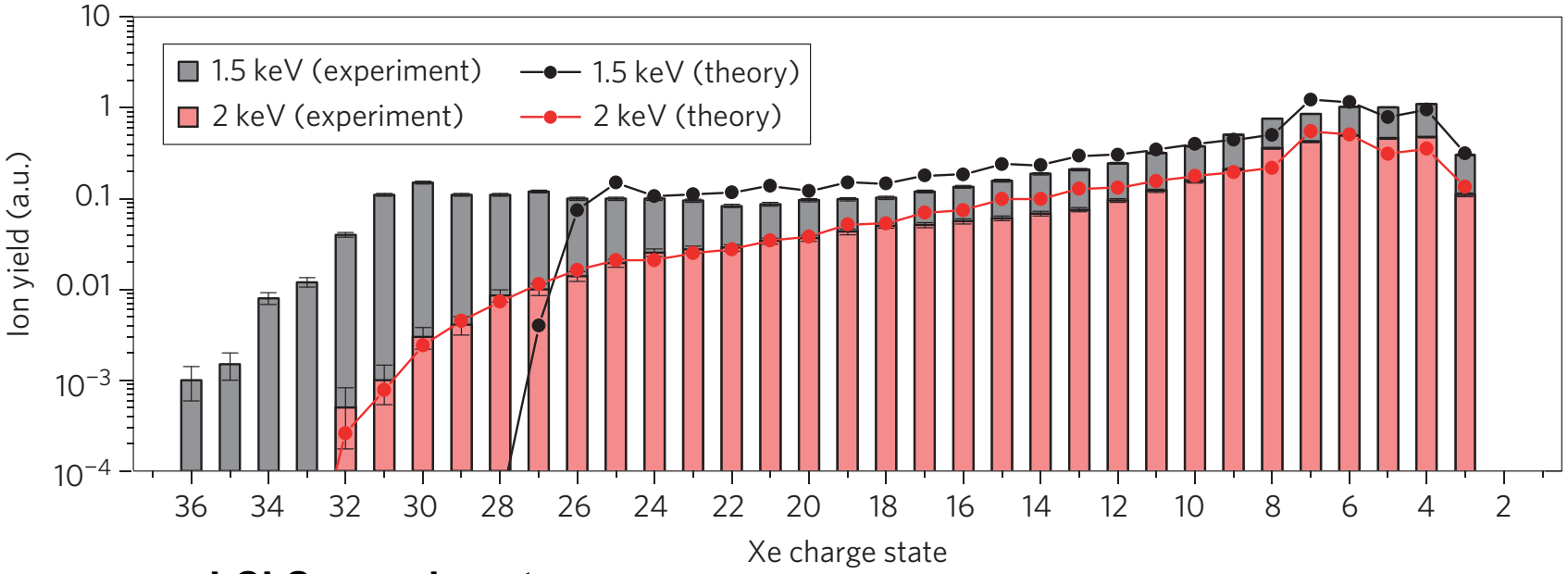
Fukuzawa *et al.*, *Phys. Rev. Lett.* **110**, 173005 (2013).

Charge-state distributions of Xe



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

Comparison with LCLS experiment



LCLS experiment

Daniel Rolles
at KSU

Artem Rudenko
at KSU

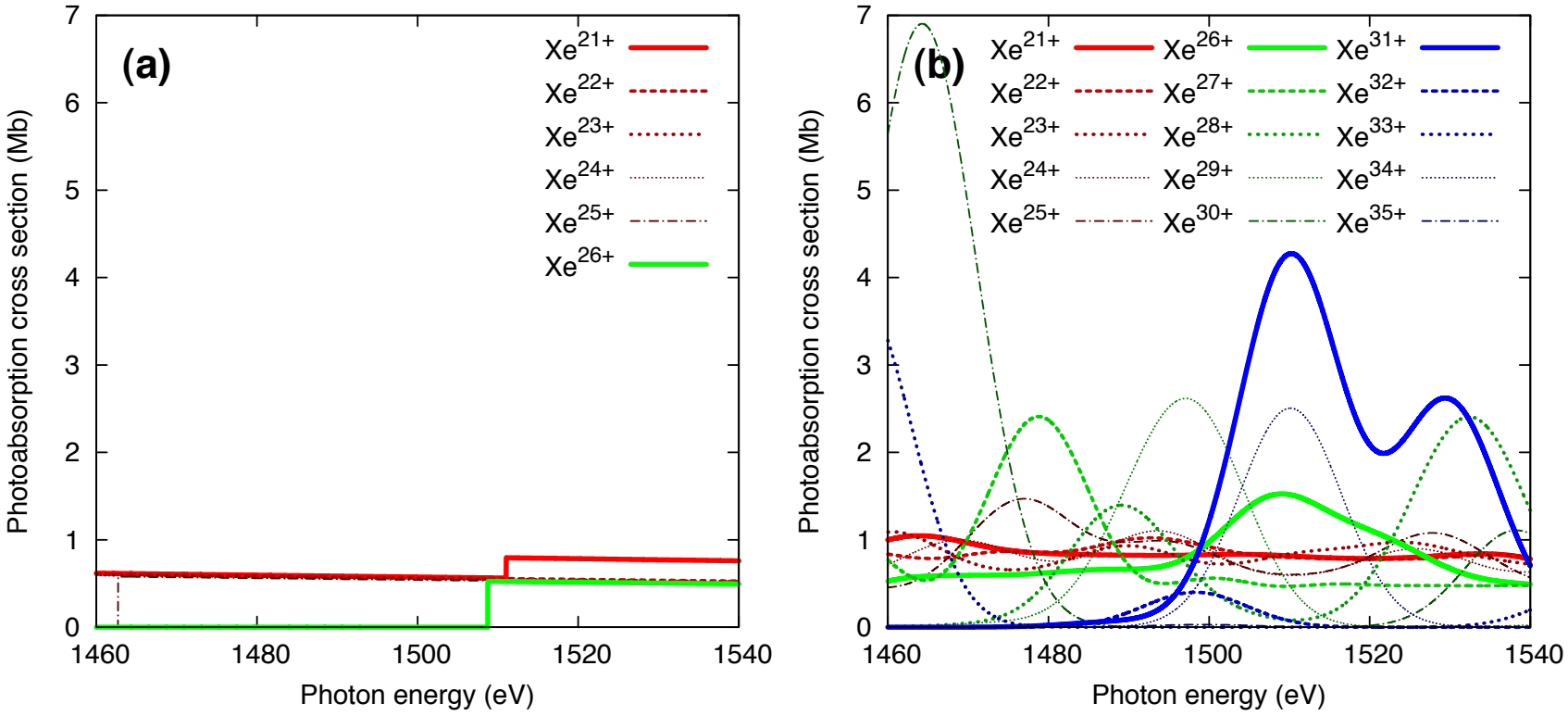
Benedikt Rudek
at PTB

- 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).

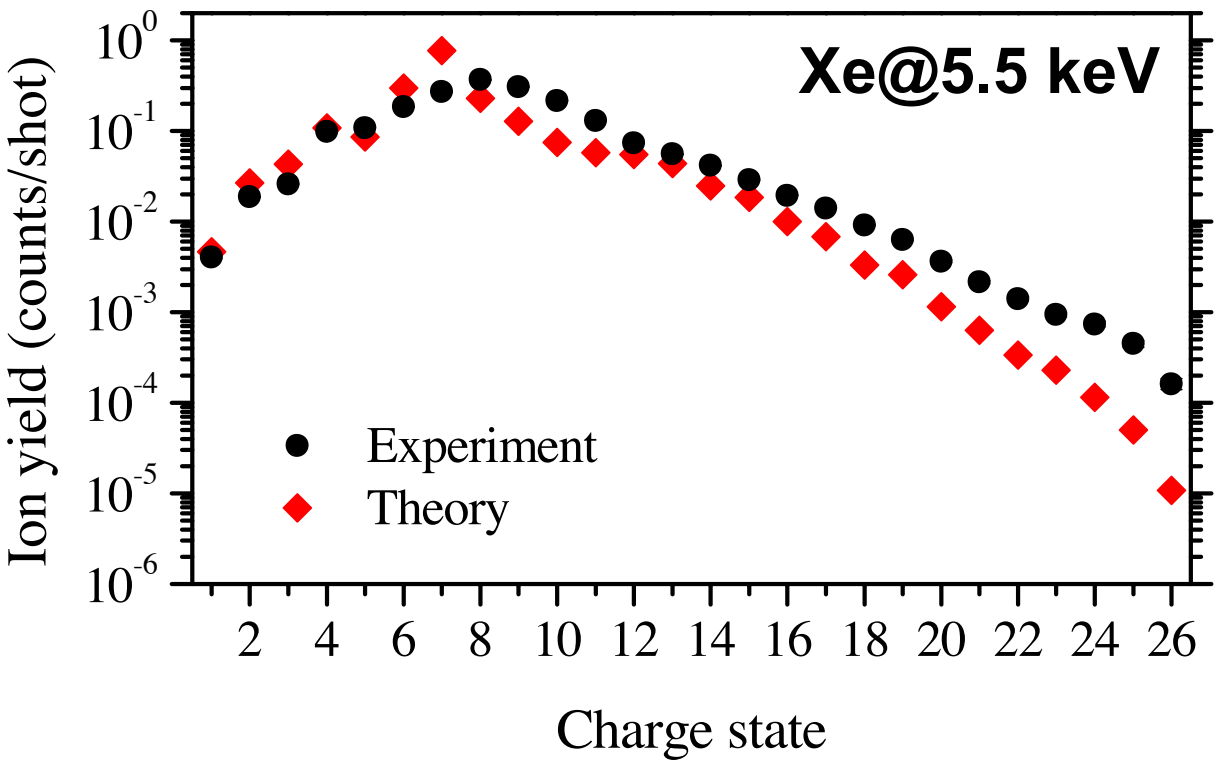
Ultra-efficient ionization by XFEL

- 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

Improving theory

- One resonance channel: Ne@1050 eV
  - Xiang *et al.*, *Phys. Rev. A* **86**, 061401 (2012).
- Multiple resonance channels: Xe@1.5 keV
  - Ho *et al.*, *Phys. Rev. Lett.* **113**, 253001 (2014).
  - Ho, Kanter, and Young, *Phys. Rev. A* **92**, 063430 (2015).
- What about both resonance effect and relativistic effects?
  - resonance effect: Xe *M*-shell ionization at 1.5 keV
  - relativistic effects: Xe *L*-shell ionization at 5.5 keV
  - interplay between resonant excitations and relativistic corrections

Inclusion of relativistic effects

- Relativistic energy correction within first-order perturbation theory

$$\hat{H} = \hat{H}_0 - \frac{\alpha^2}{8}\hat{p}^4 - \frac{\alpha^2}{4}\frac{dV}{dr}\frac{d}{dr} + \frac{\alpha^2}{2}\frac{1}{r}\frac{dV}{dr}\hat{l}\cdot\hat{s}$$

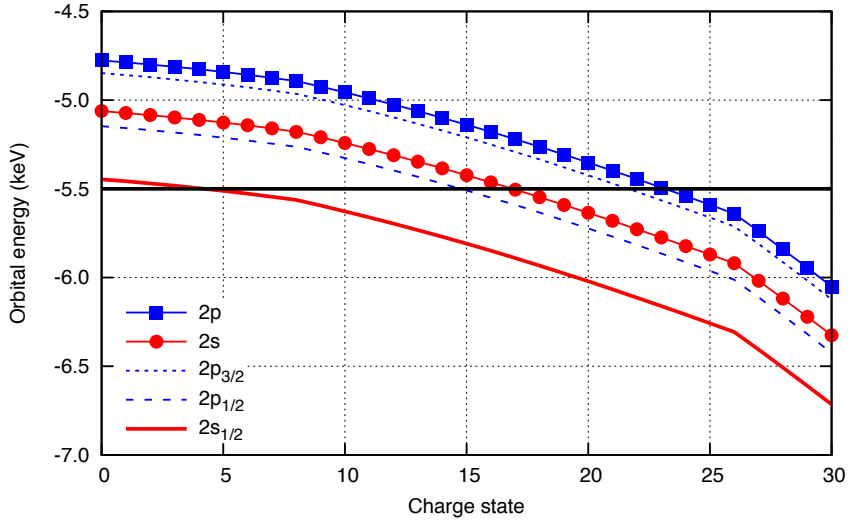
$$E_{nlj} = \varepsilon_{nl} + \Delta\varepsilon_{nl}^{\text{mass}} + \Delta\varepsilon_{nl}^{\text{Darwin}} + \Delta\varepsilon_{nlj}^{\text{so}}$$

Toyota, Son & Santra, *Phys. Rev. A* **95**, 043412 (2017).

- Open new Coster-Kronig decay channels due to spin-orbit splitting

group	non-rel (a.u.)	rel	McGuire [37]
M_2-X	1.61×10^{-4}	2.20×10^{-4}	1.60×10^{-4}
M_3-X		1.75×10^{-4}	1.37×10^{-4}
M_2-XY	2.09×10^{-2}	1.97×10^{-2}	2.27×10^{-2}
M_3-XY		2.06×10^{-2}	2.13×10^{-2}
M_2-M_3X	forbidden	5.38×10^{-3}	5.50×10^{-3}
M_2-$M_{45}X$	2.05×10^{-1}	1.54×10^{-1}	1.50×10^{-1}
M_3-$M_{45}X$		1.88×10^{-1}	1.80×10^{-1}

- Close photoionization earlier due to relativistic energy corrections



- Closer to photon energy due to energy corrections: higher cross sections

Relativistic heavy atom

- Number of all possible electronic configurations

non-relativistic

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

M-shell: 1,120,581

L-shell: 23,532,201

---

relativistic

Xe: $1s_{1/2}^2\ 2s_{1/2}^2\ 2p_{1/2}^2\ 2p_{3/2}^4\ 3s_{1/2}^2\ 3p_{1/2}^2\ 3p_{3/2}^4\ 3d_{3/2}^4\ 3d_{5/2}^6$

$4s_{1/2}^2\ 4p_{1/2}^2\ 4p_{3/2}^4\ 4d_{3/2}^4\ 4d_{5/2}^6\ 5s_{1/2}^2\ 5p_{1/2}^2\ 5p_{3/2}^4$

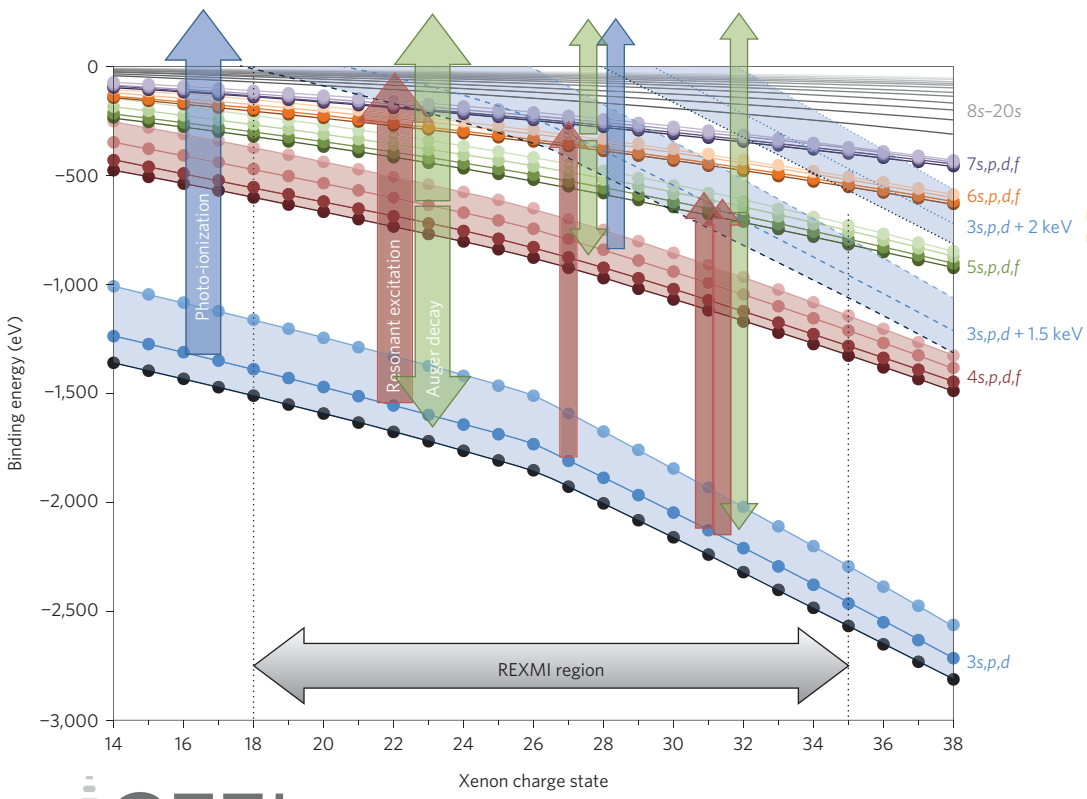
M-shell: 111,628,125

L-shell: 5,023,265,625

Inclusion of resonant excitations

- Resonant photoexcitation cross section

$$\sigma_{\mathrm{R}}(i,f,\omega_{\mathrm{in}}) = \frac{4}{3}\pi^2\alpha\omega_{\mathrm{in}} l_> N_i N_f^H \left\{ \begin{array}{ccc} l_i & s & j_i \\ j_f & 1 & l_f \end{array} \right\}^2 |\langle u_{n_f l_f}(r)|r|u_{n_i l_i}(r)\rangle|^2 \times \delta(E - E_{n_f l_f j_m} + E_{n_i l_i j_i})$$

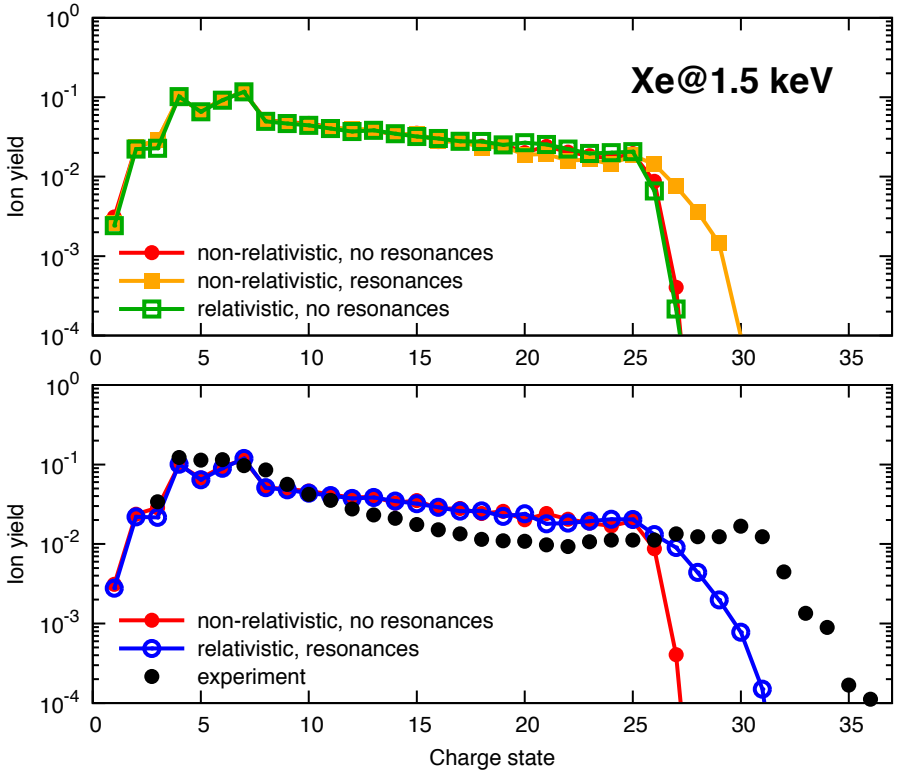


- Number of possible electron configurations explodes depending on n_{max} (=15~20) and l_{max} (=6~7)

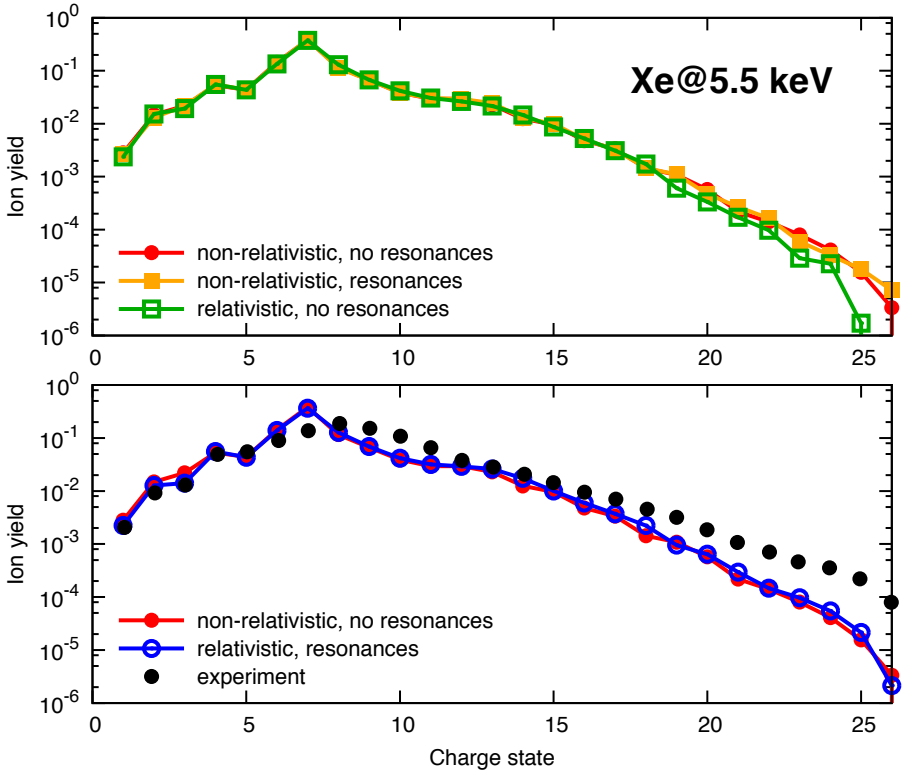
Toyota, Son & Santra, *Phys. Rev. A* **95**, 043412 (2017).

Interplay between resonance and relativity

- Xe@1.5 eV (*M*-shell)
  - strong REXMI expected
  - no relativistic effect expected



- Xe@5.5 keV (*L*-shell)
  - strong relativistic effect expected
  - no REXMI expected



Toyota, Son & Santra, *Phys. Rev. A* **95**, 043412 (2017).

Xe atom at higher x-ray intensity

- New experimental setup:
  LCLS CXI using nano-focus
  ➔ new realm of intensity approaching ~10^{20} W/cm^2
- Various photon energies: 5.5 keV ~ 8.3 keV
  - Trend of REXMI examined
  - Peak structure in the REXMI region
  - *L*-shell initiated ionization ➔ large relativistic effects
- Improved experimental analysis and
  improved calibration procedure with Ar data
  XCALIB: developed by Zoltan Jurek and
  Koudai Toyota

LCLS experiment

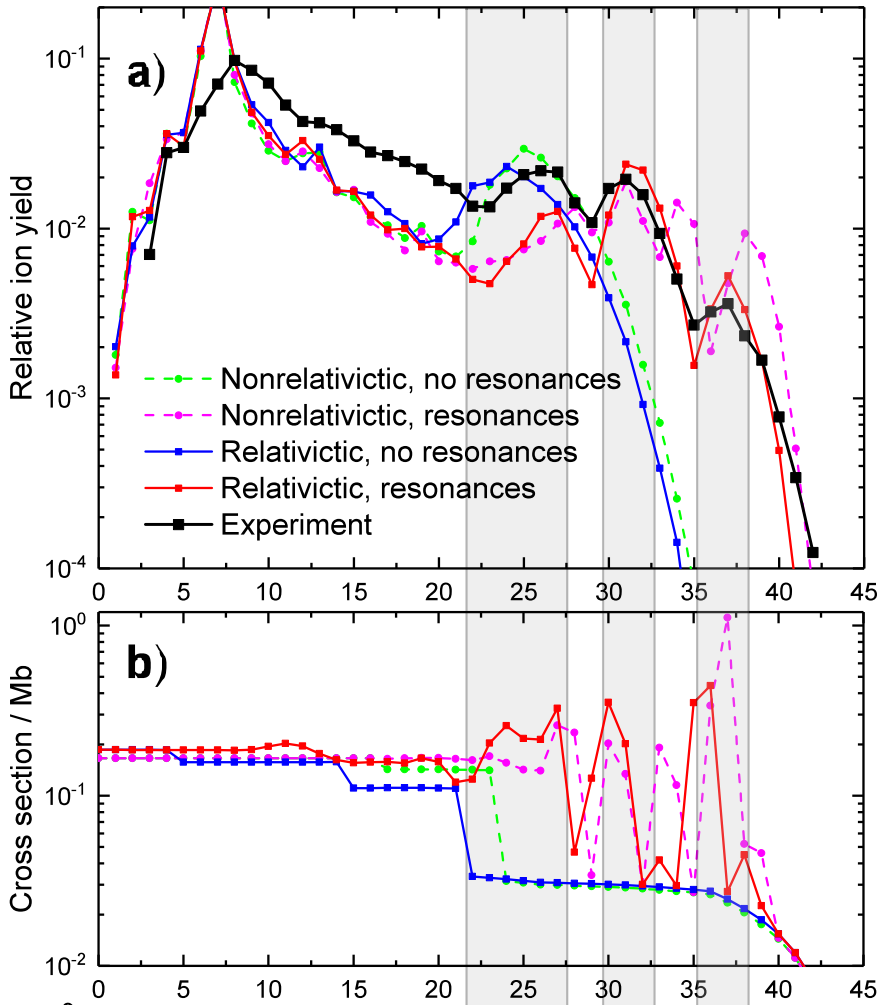
Benedikt Rudek
at PTB

XCALIB development

Koudai Toyota

Zoltan Jurek

New data for Xe at 5.5 keV



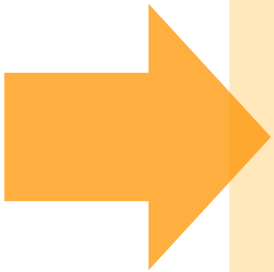
Preliminary results

Rudek, Toyota, *et al.*, (in preparation).

- ~40× higher fluence than before
- REXMI region: accurate electronic structure of bound and Rydberg states
- Only relativistic, resonance calculation reproduces well the peak structure of experiment.
- Importance of interplay between resonance and relativistic effects

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
  - formidable task: e.g. CH_3I ~ 200 trillion rate eqs 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, *PRA* **94**, 023422 (2016).

XMOLECULE: Electronic structure

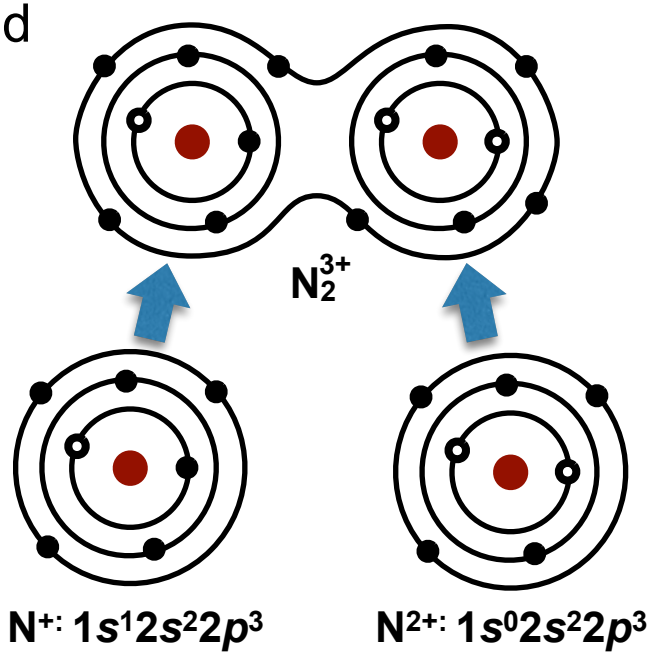
- Efficient electronic structure calculation required
- Hartree-Fock-Slater method
- Bound states: LCAO-MO

$$\psi_i(\mathbf{r}) = \sum_\mu C_{\mu i}\phi_\mu(\mathbf{r})$$

  - Core-hole-adapted NAO
  - Matrix eigenvalue problem of $N_{\text{basis}} \times N_{\text{basis}}$

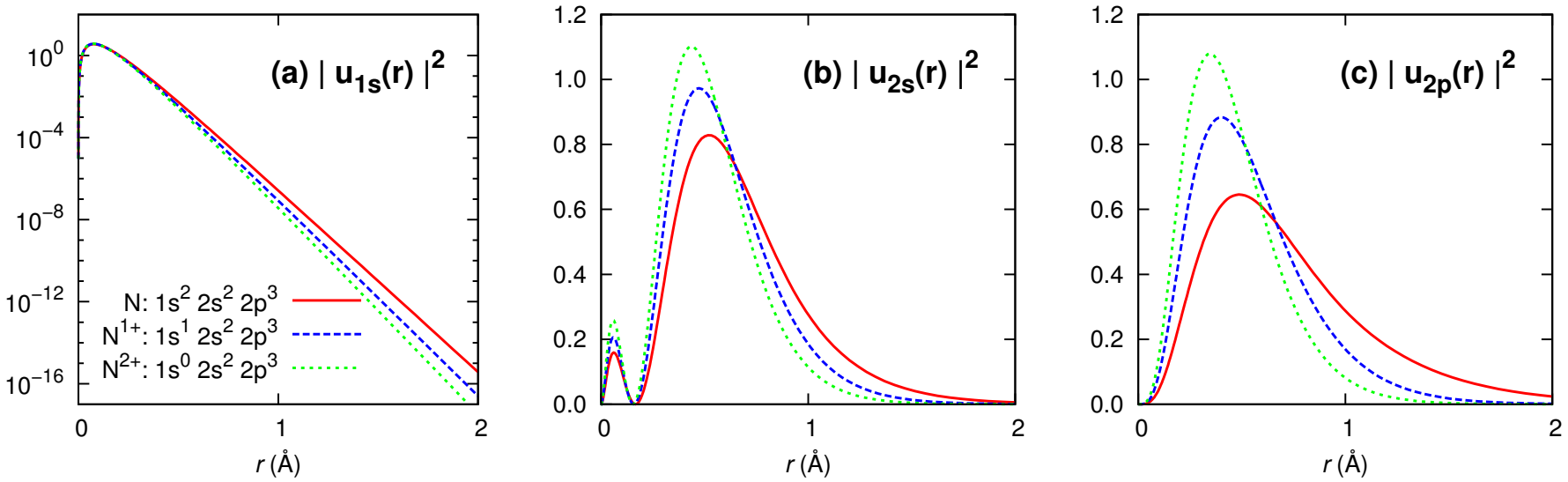
$$\mathbf{HC} = \mathbf{SCE}$$

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



- Cross sections and rates calculated on the fly for given elec. structure
- Gradients calculated on the fly for given electronic structure

XMOLECULE: Core-hole-adapted NAOs



- NAO: numerical atomic orbitals calculated by XATOM

$$\psi_i(\mathbf{r}) = \sum_\mu C_{\mu i}\phi_\mu(\mathbf{r}) \qquad \phi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r}Y_{lm}(\theta,\varphi)$$

- Molecular core-hole states with corresponding atomic core-hole states
- Good treatment for molecular core-hole states with a minimal basis set

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

Molecular cross sections and rates

- Molecular continuum approximated by atomic continuum: $\psi_\varepsilon \to \phi_{A\varepsilon}$
- Photoionization cross section

$$\sigma_{\mathrm{P}} \propto |\langle\psi_i|d|\psi_\varepsilon\rangle|^2 \approx \sum_A \left| \sum_{\mu}^{\text{on atom } A} C_{\mu i}\langle\phi_\mu|d|\phi_{A\varepsilon}\rangle \right|^2$$

- Fluorescence rate $\Gamma_{\mathrm{F}} \propto |\langle\psi_i|d|\psi_j\rangle|^2$ evaluated by multicenter integration
- Auger rate: one-center approximation

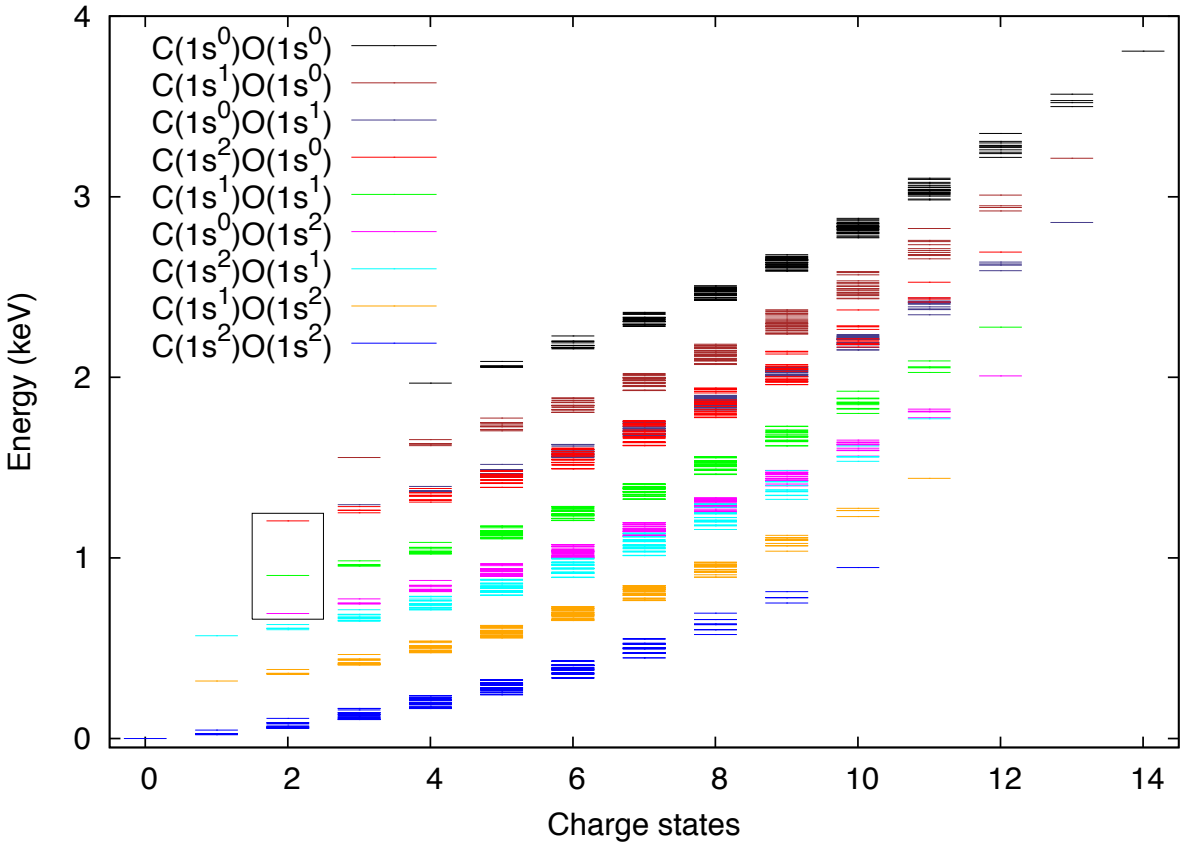
$$\langle jj'|i\varepsilon\rangle = \int d^3r_1 \int d^3r_2\, \psi_j(\mathbf{r}_1)\psi_{j'}(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\psi_i(\mathbf{r}_1)\psi_\varepsilon(\mathbf{r}_2)$$

$$\langle jj'|i\varepsilon\rangle \approx \sum_{\mu,\nu,\lambda}^{\text{on atom } A} C_{\mu j}C_{\nu j'}C_{\lambda i}\langle\mu\nu|\lambda\varepsilon\rangle$$

intra-atomic process included

Inhester, Hanasaki, Hao, Son & Santra, *Phys. Rev. A* **94**, 023422 (2016).

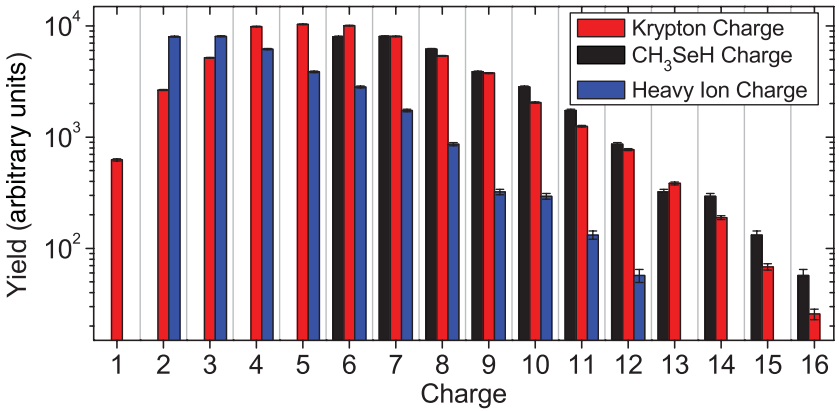
Various multiple-hole states of CO



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

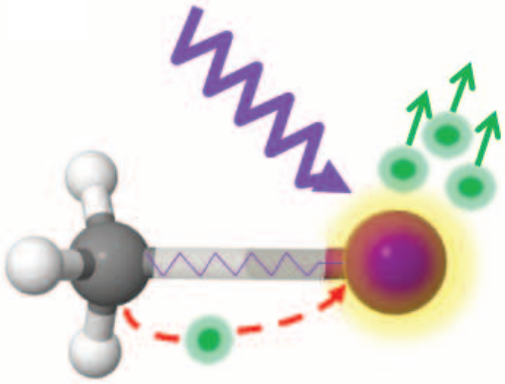
All possible multiple-hole configurations (N=2187)
formed by x-ray multiphoton ionization (at single molecular geometry)

Molecules at low x-ray 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?

Iodomethane at higher x-ray intensity

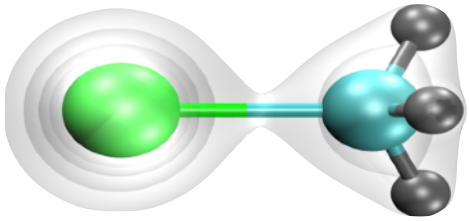
- New experimental setup:
  LCLS CXI using nano-focus
  ➔ new realm of intensity
  approaching ~10^{20} W/cm^2
- Selective ionization on heavy atom

LCLS experiment

Daniel Rolles
at KSU

Artem Rudenko
at KSU

CH_3I @ 8.3 keV



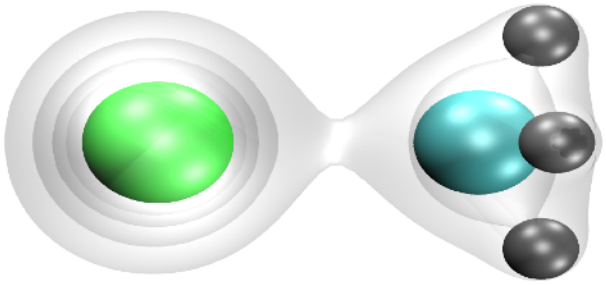
σ(I)~50 kbarn
σ(C)~80 barn
σ(H)~8 mbarn

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

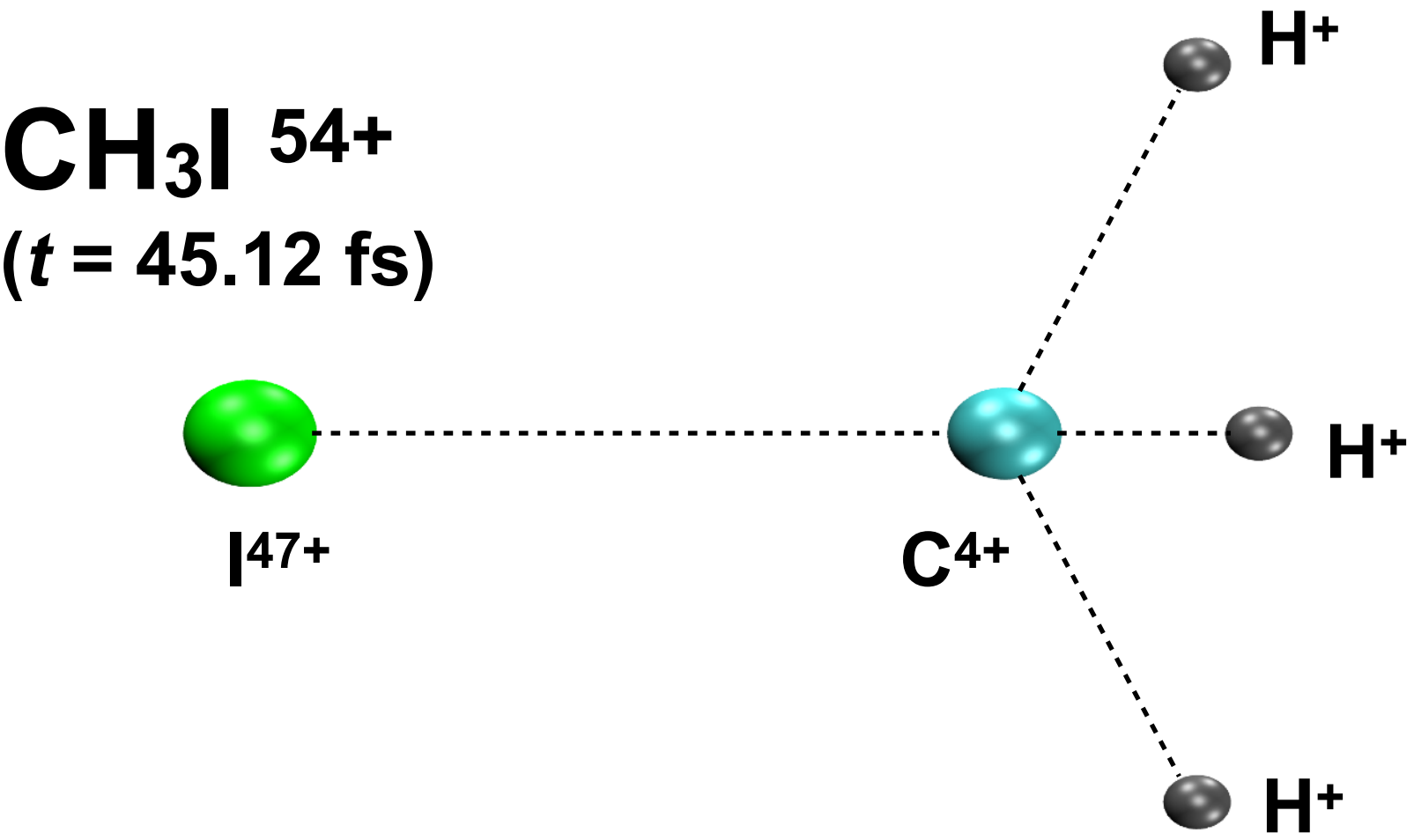
Coulomb explosion of iodomethane

CH_3I

(t = 0 fs)

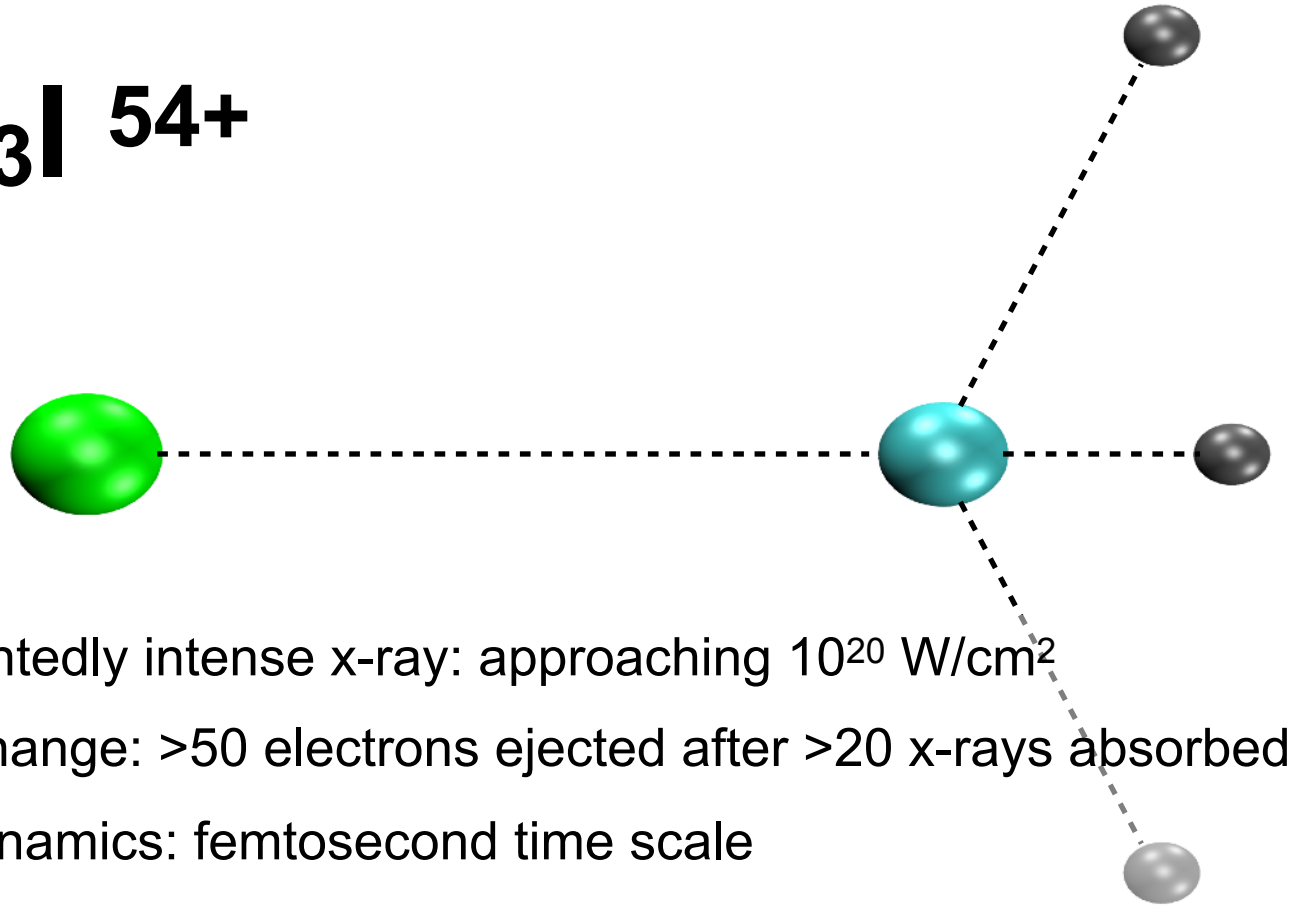


Coulomb explosion of iodomethane



What happened?

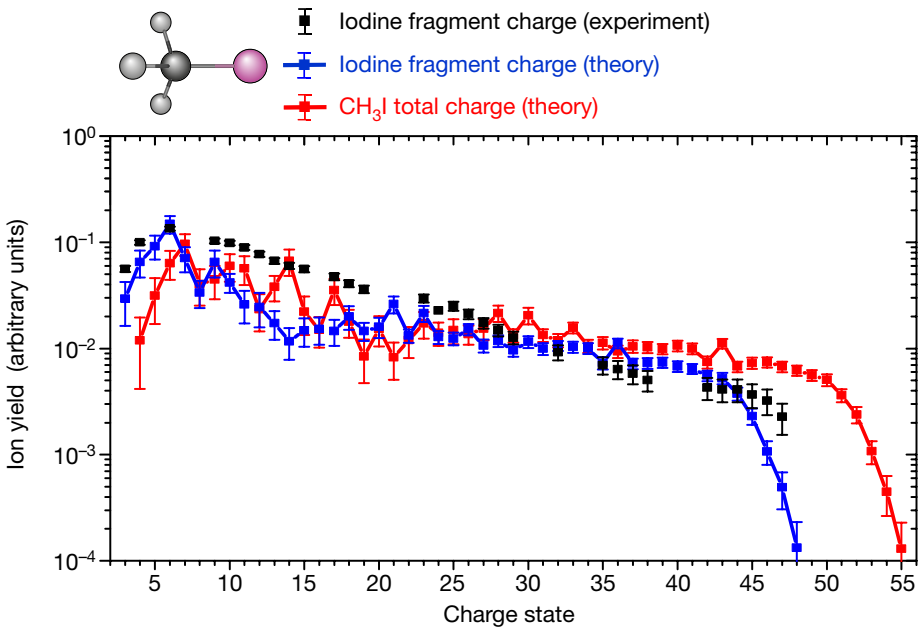
CH_3I^{54+}



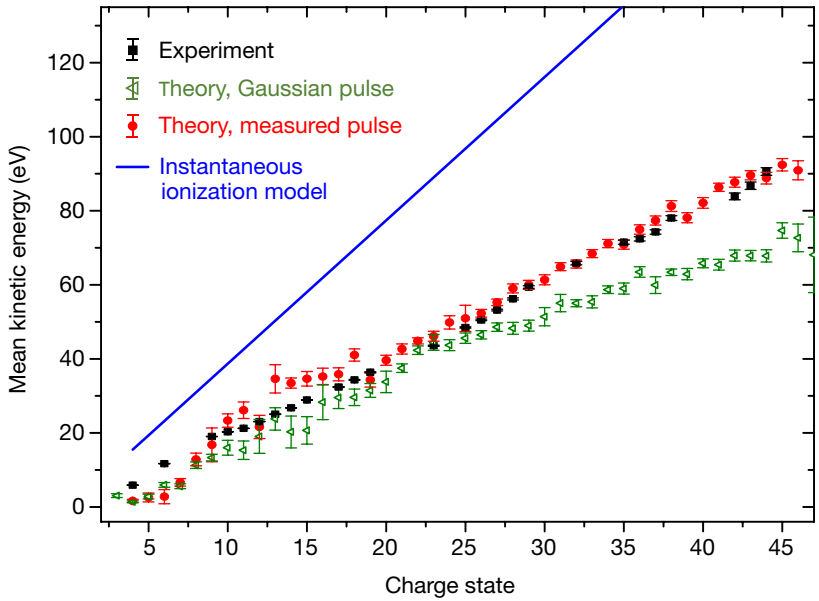
- Unprecedentedly intense x-ray: approaching 10^{20} W/cm^2
- Dramatic change: >50 electrons ejected after >20 x-rays absorbed
- Ultrafast dynamics: femtosecond time scale

Comparison of CSD and KER

CSD of I and CH_3I



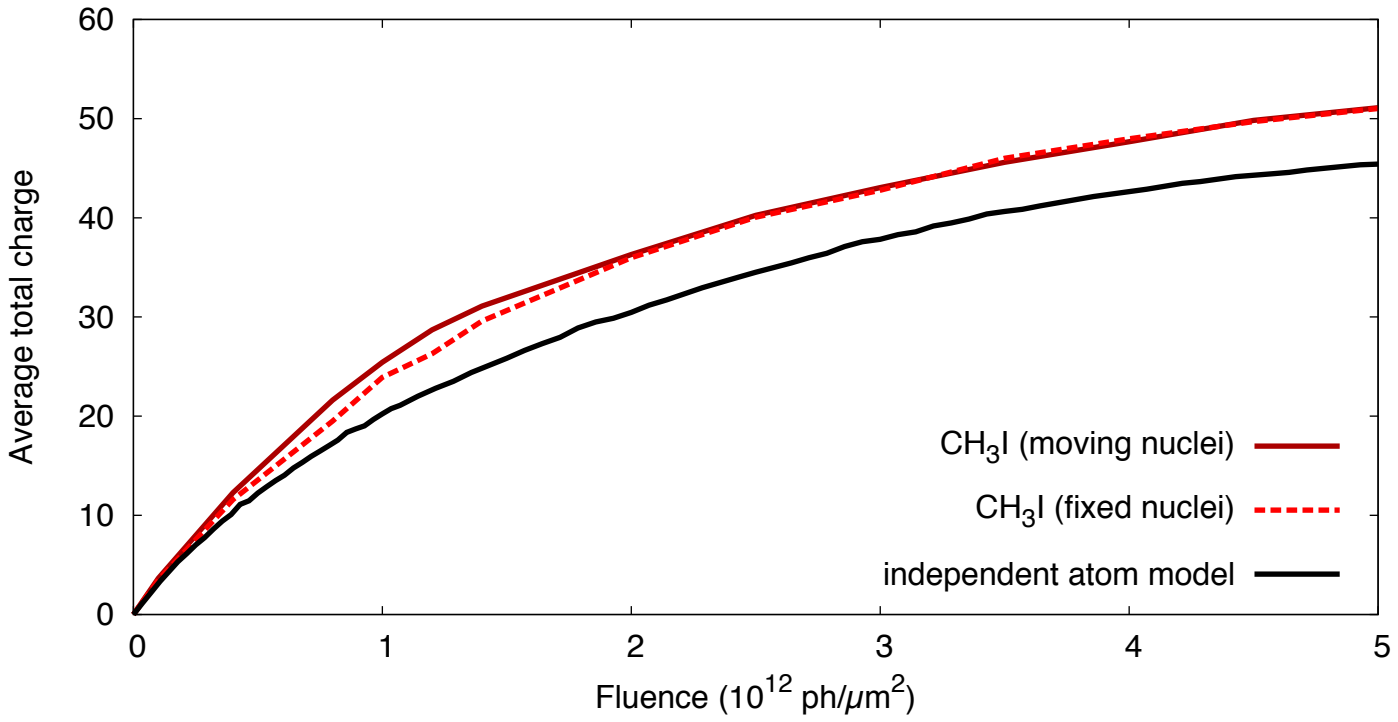
KER of I fragment



- Capturing ultrafast ionization and fragmentation dynamics
  - CSD (charge-state distribution): direct outcome of ionization dynamics
  - KER (kinetic energy release): molecular information when it breaks apart, influenced by detailed dynamical behaviors

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

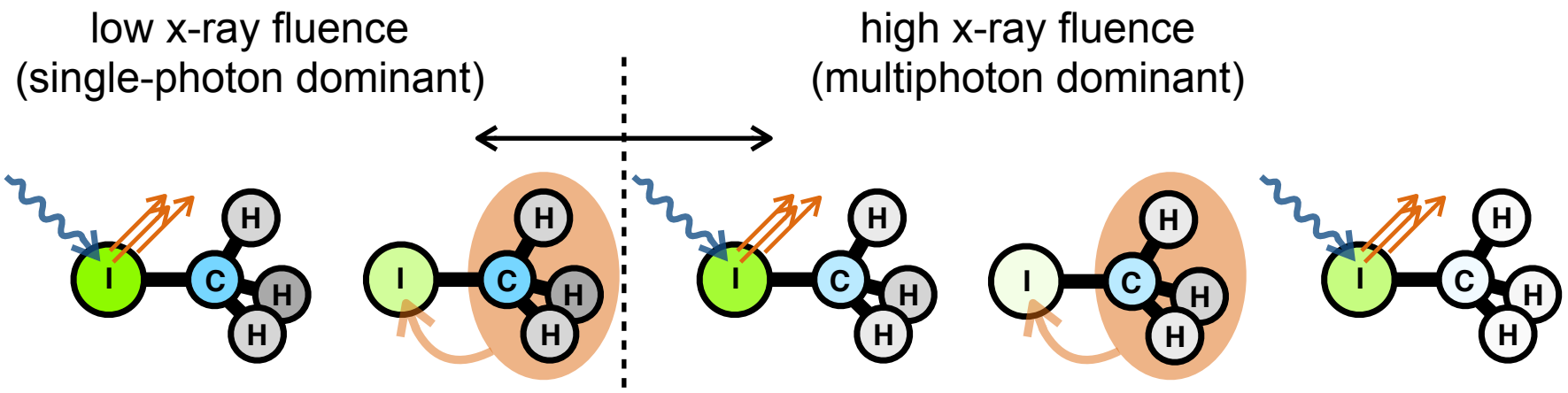
Molecular ionization enhancement



molecular charge > ∑(atomic charges)
theoretically predicted and experimentally confirmed

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

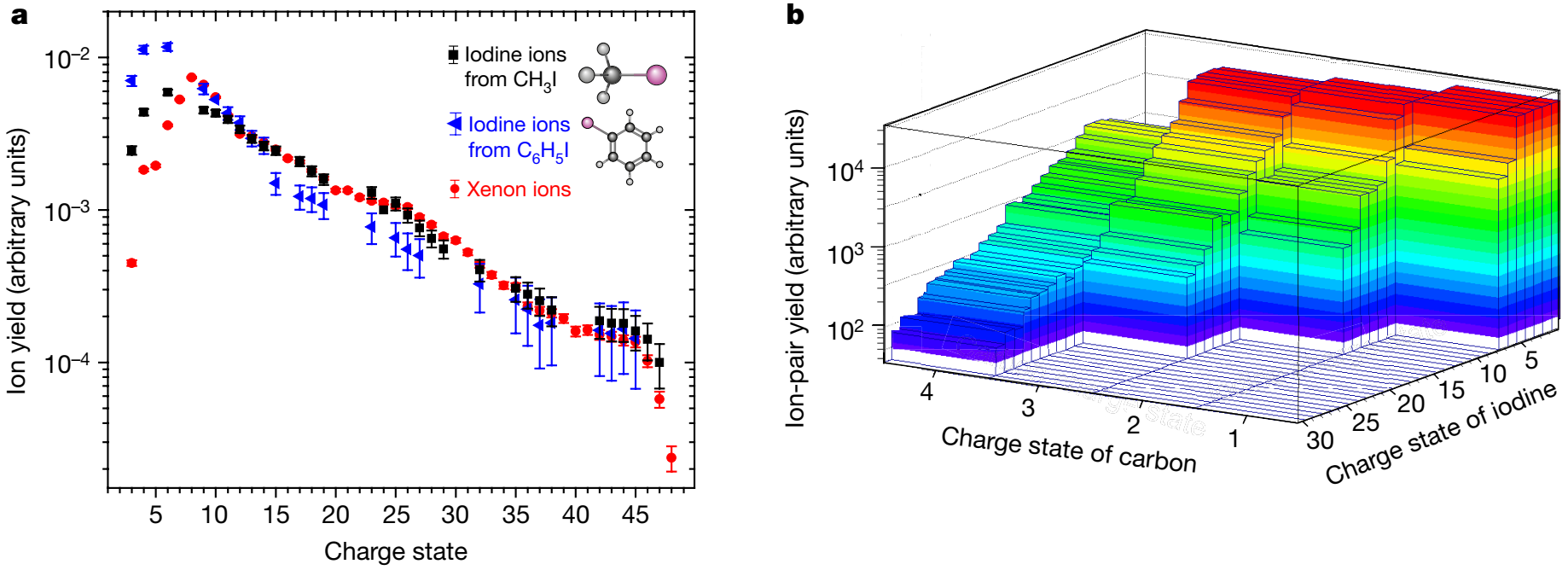
Ionization enhanced by charge rearrangement



- Electrons from light atoms become available for further ionization on heavy atoms after charge rearrangement.
- CREXIM: Charge-Rearrangement-Enhanced X-ray Ionization of Molecules
- Impact on molecular imaging: not reducing partial charges of heavy atoms due to charge rearrangement, but inducing more ionization overall

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

The bigger molecule, the larger effect



- Coincidence measurement at intermediate intensity: higher iodine charge always along with highest carbon charge
- Estimated molecular charge: Xe^{48+}, CH_3I^{54+}, and $C_6H_5I^{>54+}$

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

Molecular black hole

DESY news:
http://www.desy.de/news/news_search/index_eng.html?openDirectAnchor=1232

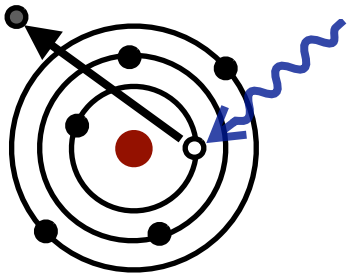
The extremely intense X-ray flash knocks so many electrons out of the iodine atom (right) such that it pulls in the electrons of the methyl group (left) like an electromagnetic version of a black hole, before finally spitting them out.


Credit: DESY/Science Communication Lab

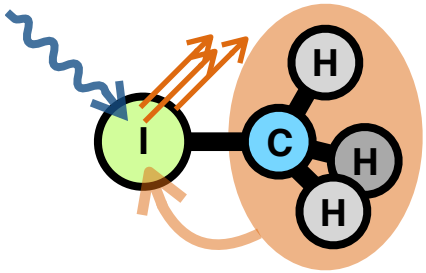
"Femtosecond response of polyatomic molecules to ultra-intense hard X-rays,"

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

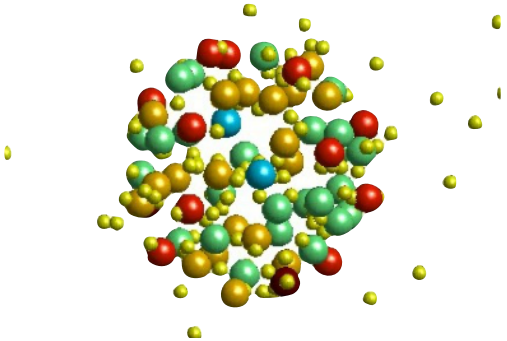
Summary



XATOM



XMOLECULE



XMDYN
(Talk by Zoltan last week)

- Enabling tools to investigate x-ray multiphoton physics of atoms, molecules, and clusters exposed to high intensity x-ray pulses
- X-ray multiphoton ionization dynamics of Xe
  - interplay between resonance and relativistic effects
- X-ray-induced ultrafast explosion dynamics of CH_3I
  - first quantitative comparison for molecules under XFEL irradiation
  - molecular ionization enhancement via CREXIM

CFEL-DESY Theory Division

Prof. Dr. Robin Santra
Dr. Zoltan Jurek
Dr. Sang-Kil Son
Dr. Ralph Welsch
Prof. Dr. Beata Ziaja-Motyka
Dr. Daria Gorelova
Dr. Ludger Inhester
Dr. Antonia Karamatskou
Dr. Zheng Li
Dr. Vladimir Lipp
Dr. Koudai Toyota
Malik M. Abdullah
Caroline Arnold
Sophia Bazzi
John Bekx
Yi-Jen Chen
Athiya M. Hanna
Murali Krishna
Victor Tkachenko
Sevinc Kayadaleren
Dietrich Krebs
Julia Schäfer

CFEL SCIENCE

DESY

Collaboration of CH_3I LCLS experiment

Experiment team

Kansas State University S. J. Robatjazi, X. Li, D. Rolles, A. Rudenko

DESY, Hamburg B. Erk, R. Boll, C. Bomme, E. Savelyev

PTB, Braunschweig B. Rudek

MPI for Medical Research, Heidelberg L. Foucar

Argonne National Lab. Ch. Bostedt, S. Southworth, C. S. Lehmann, B. Kraessig, L. Young

UPMC, Paris T. Marchenko, M. Simon

Tohoku University, Sendai K. Ueda

LCLS, SLAC National Accelerator Laboratory K. R. Ferguson, M. Bucher, T. Gorkhover, S. Carron, R. Alonso-Mori, G. Williams, S. Boutet

Theory team

CFEL, DESY L. Inhester, K. Hanasaki, K. Toyota, Y. Hao, O. Vendrell, S.-K. Son, R. Santra

CFEL SCIENCE

DESY

Thank you for your attention!

CFEL SCIENCE

DESY