What happens to atoms and molecules during XFEL pulses?

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Physics Seminar, Dept. of Physics, UNIST
Ulsan, Korea, July 16, 2019

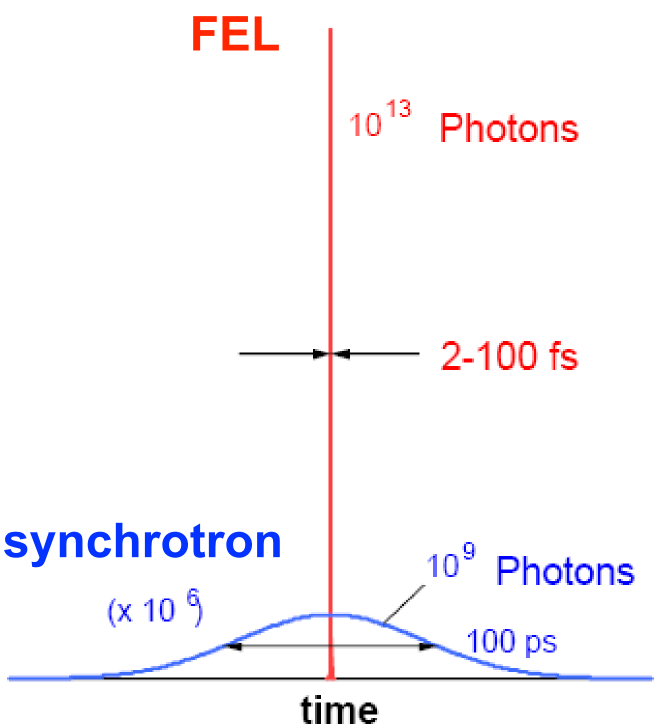
CFEL SCIENCE DESY. HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

Overview

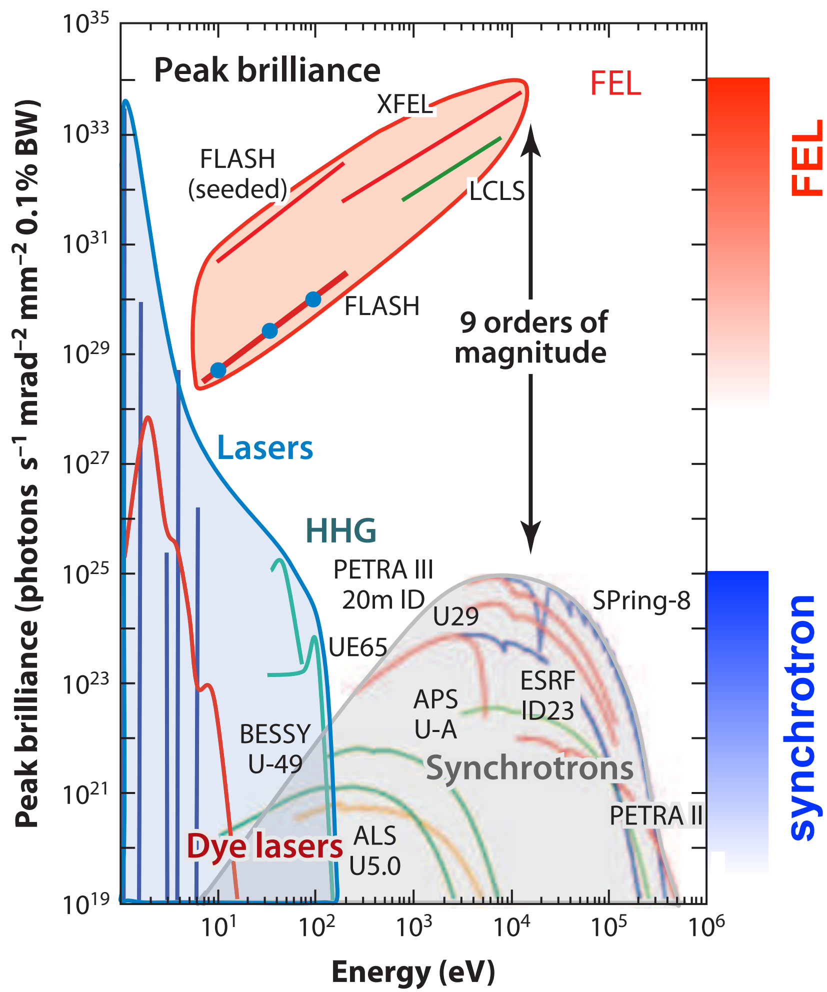
- Introduction to XFEL and XFEL–matter interaction
- XATOM and x-ray multiphoton multiple ionization dynamics of Xe
- XMOLECULE and x-ray-induced ultrafast explosion dynamics of CH_3I
- Toward complex systems
- Summary

XFEL: X-ray free-electron laser

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



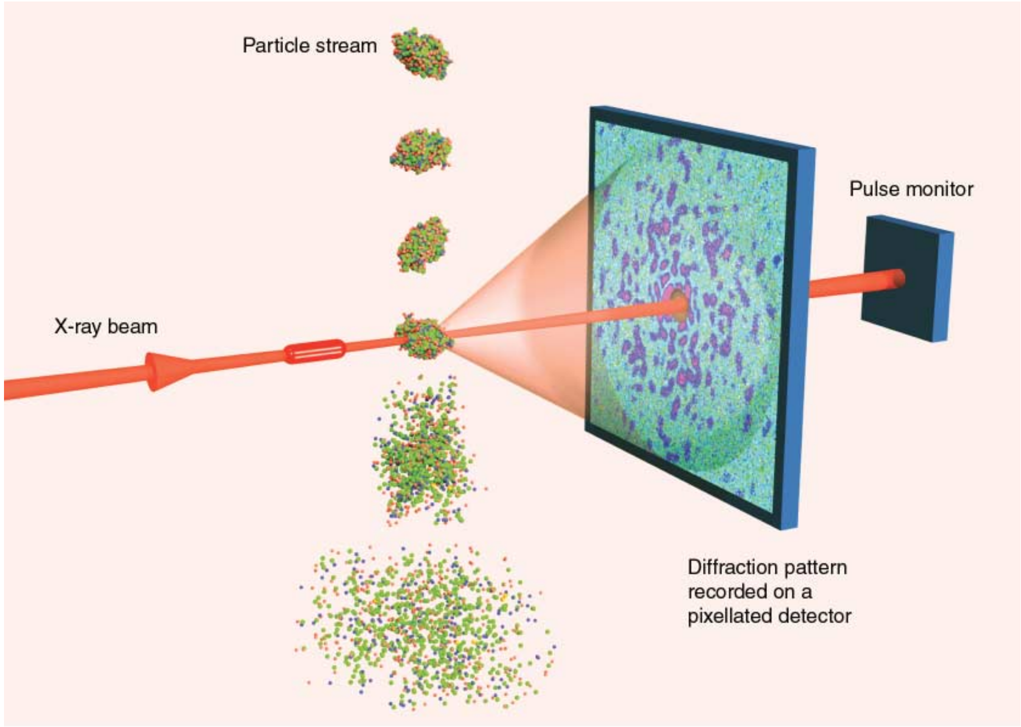
Schneider, *Rev. Accl. Sci. Tech.* **3**, 13 (2010).



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

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?

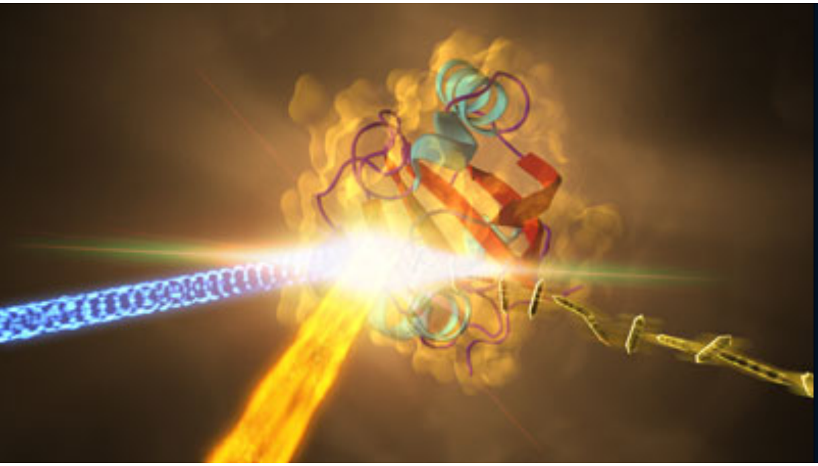
Where are XFELs?

- LCLS at SLAC, USA (2009)
- SACLA at RIKEN Harima, Japan (2011)
- PAL XFEL at Pohang, Korea (2016)
- European XFEL, Germany (2017)
- SwissFEL, Switzerland (2017)

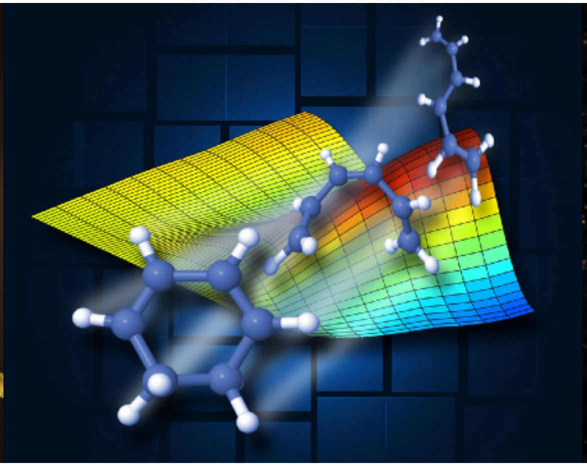
XFEL science

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

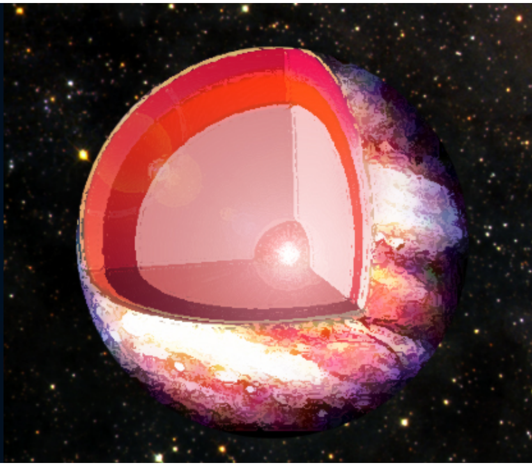
➔ XFEL applications waiting for increased theoretical support



SLAC



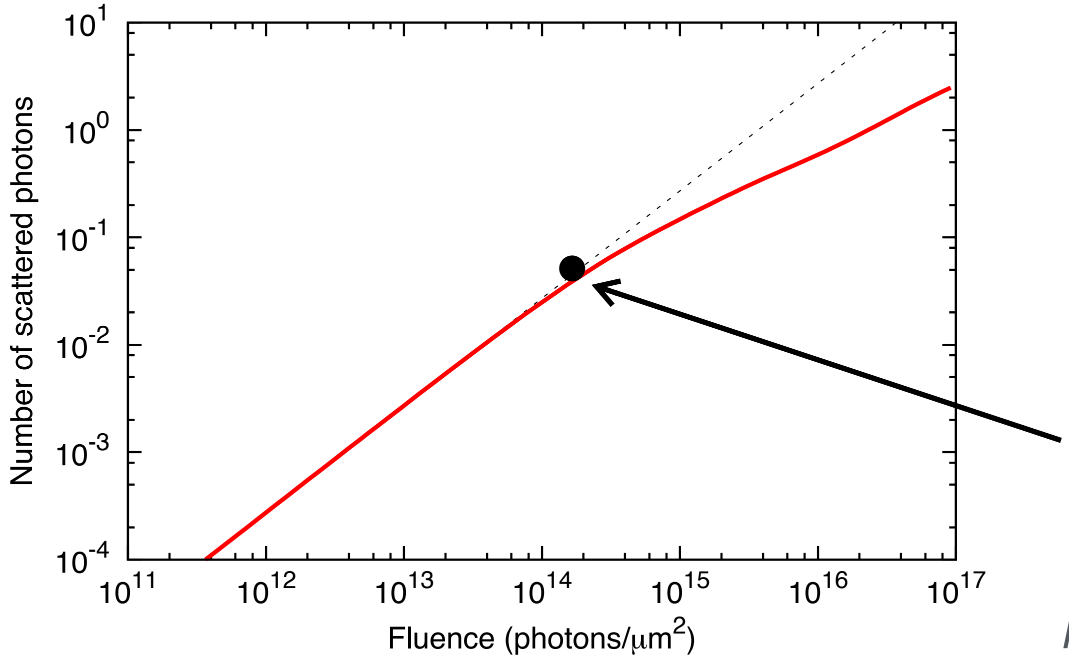
SLAC



LBL

What high x-ray intensity means?

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



Carbon @ 8 keV

σ_{abs} = 0.084 kbarns = 8.4×10^{-15} μm^2

⬇

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

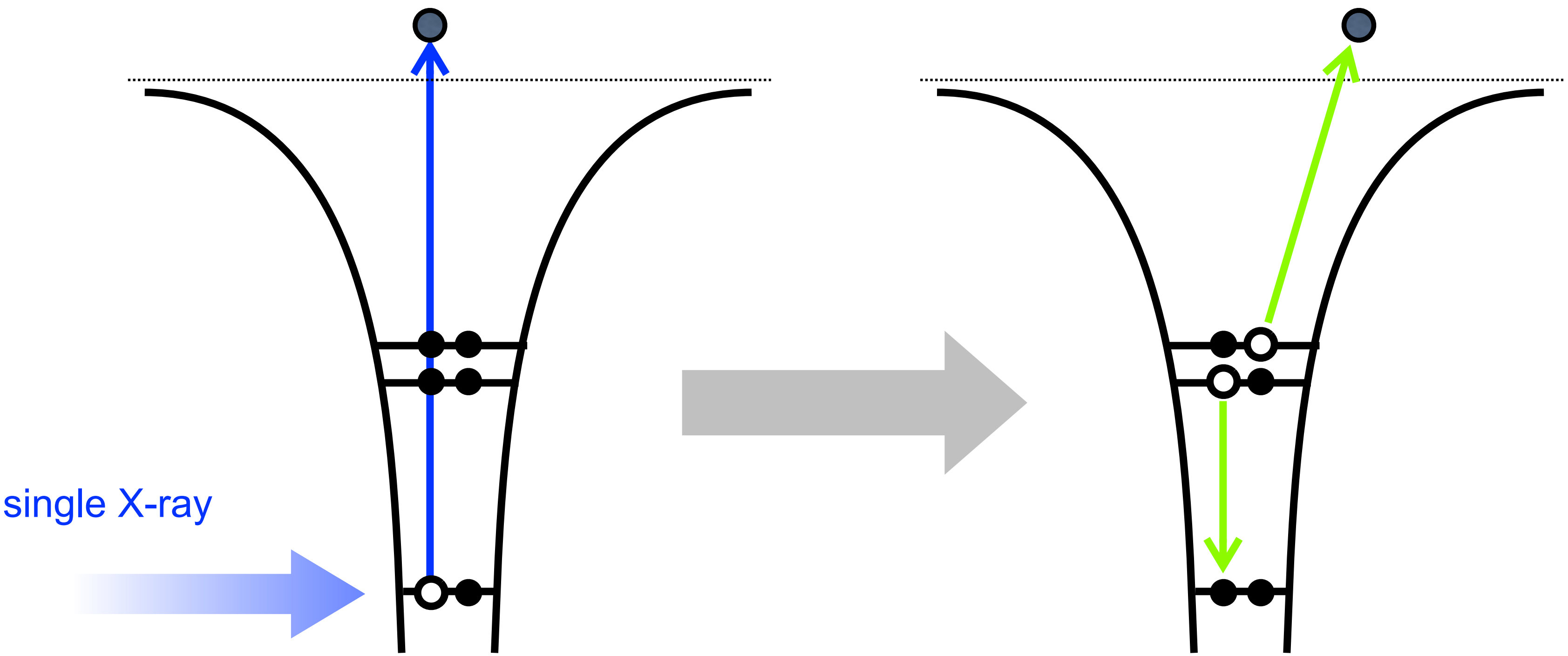
⬇

$F_{sat} = 1.2\times10^{14}$ 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

Fundamental x-ray–matter interaction



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

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

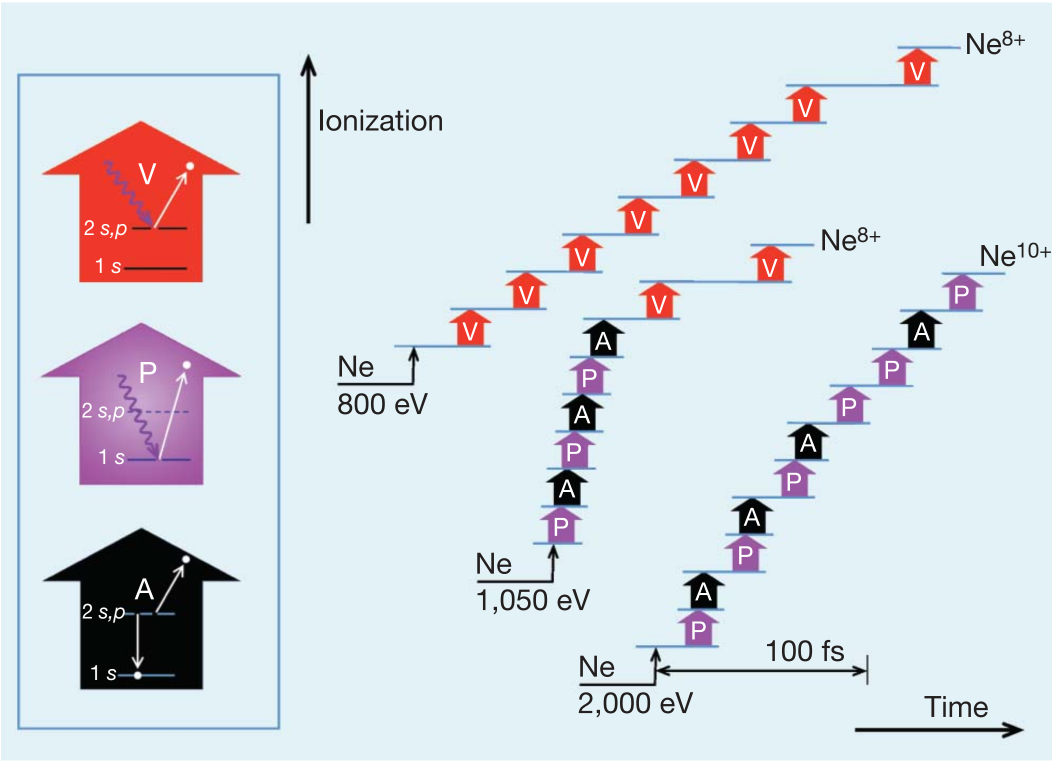
synchrotron: one-photon absorption ➔ **PA** ➔ C^{2+}

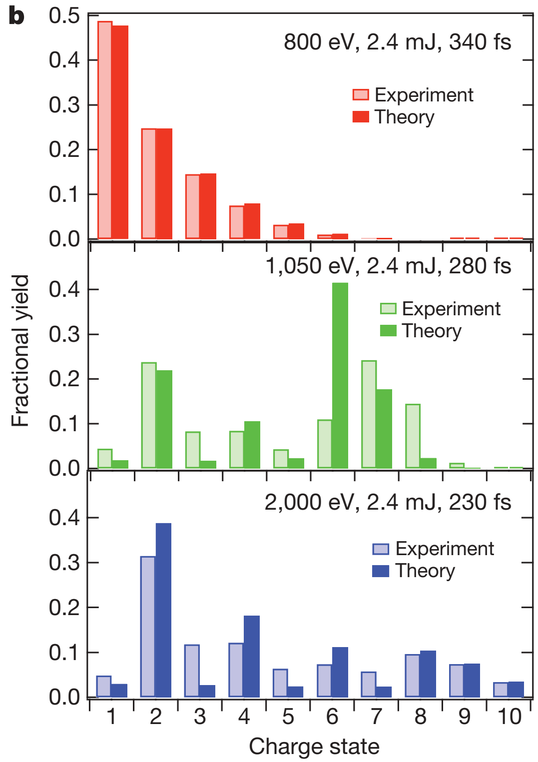
XFEL: many-photon absorption ➔ **PAPAPP** ➔ C^{6+}

CFEL SCIENCE

DESY.

Sequential multiphoton multiple ionization





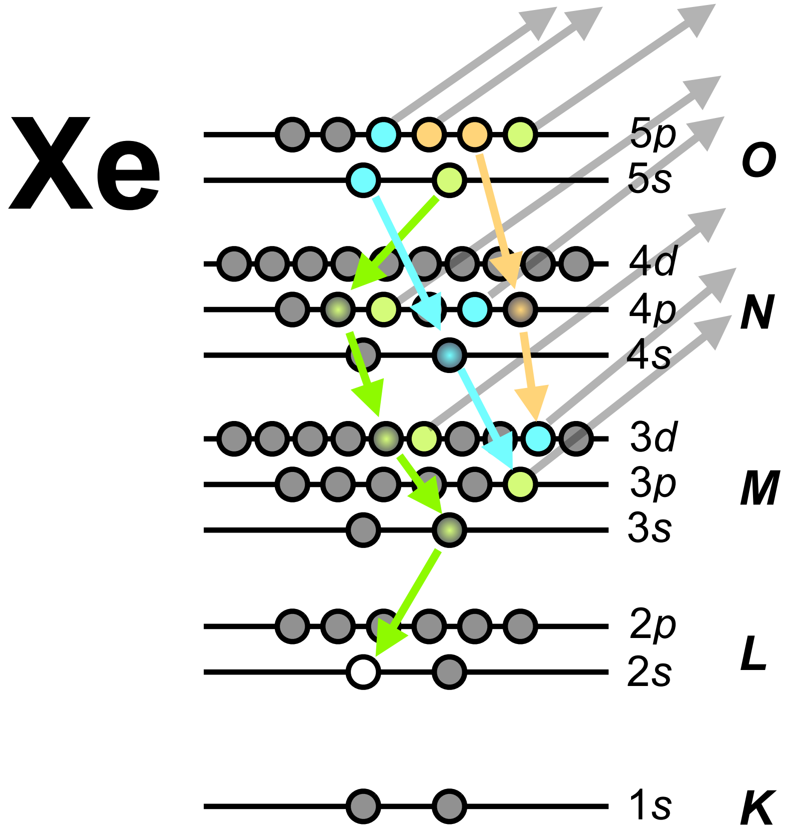
Young *et al.*, *Nature* **466**, 56 (2010).

- First LCLS experiment: fundamental atomic physics in XFEL
- Direct multiphoton absorption cross section is too small

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

Challenges for x-ray multiphoton ionization

- 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
- No standard quantum chemistry code available

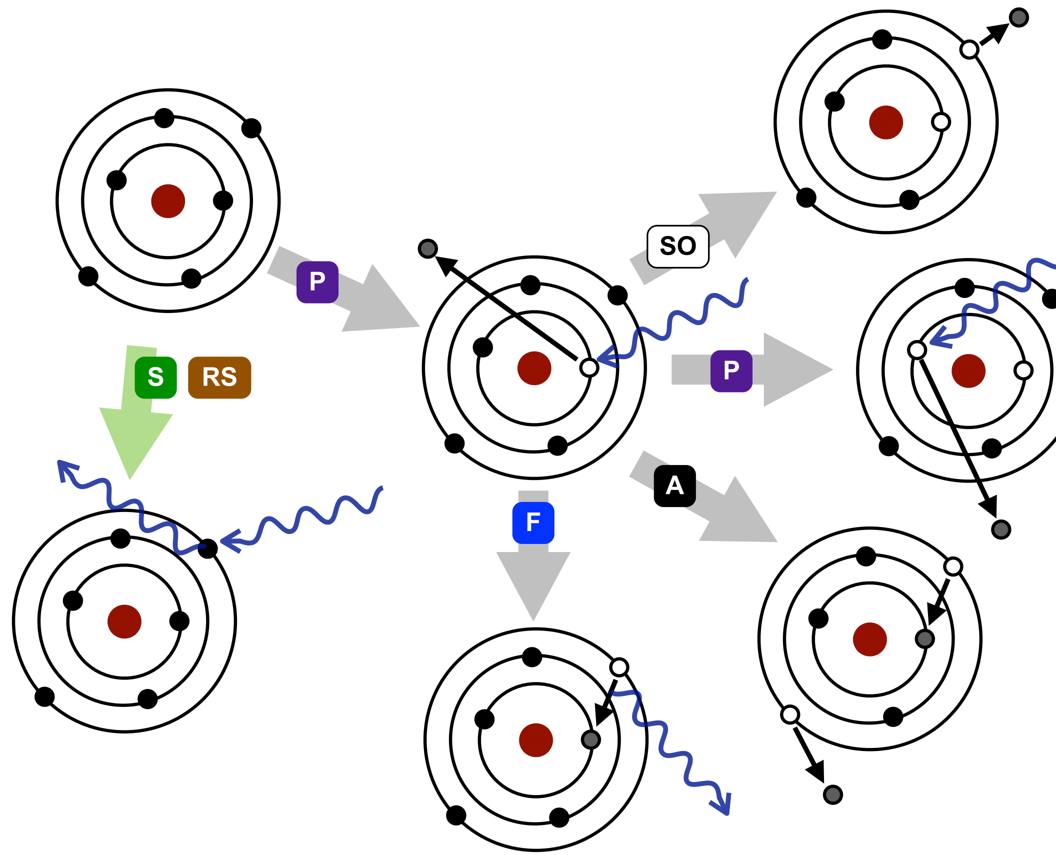


Multiphoton absorption after/during decay cascade creates:

- More than 20*M* multiple-hole config.
- More than 2*B* x-ray-induced processes

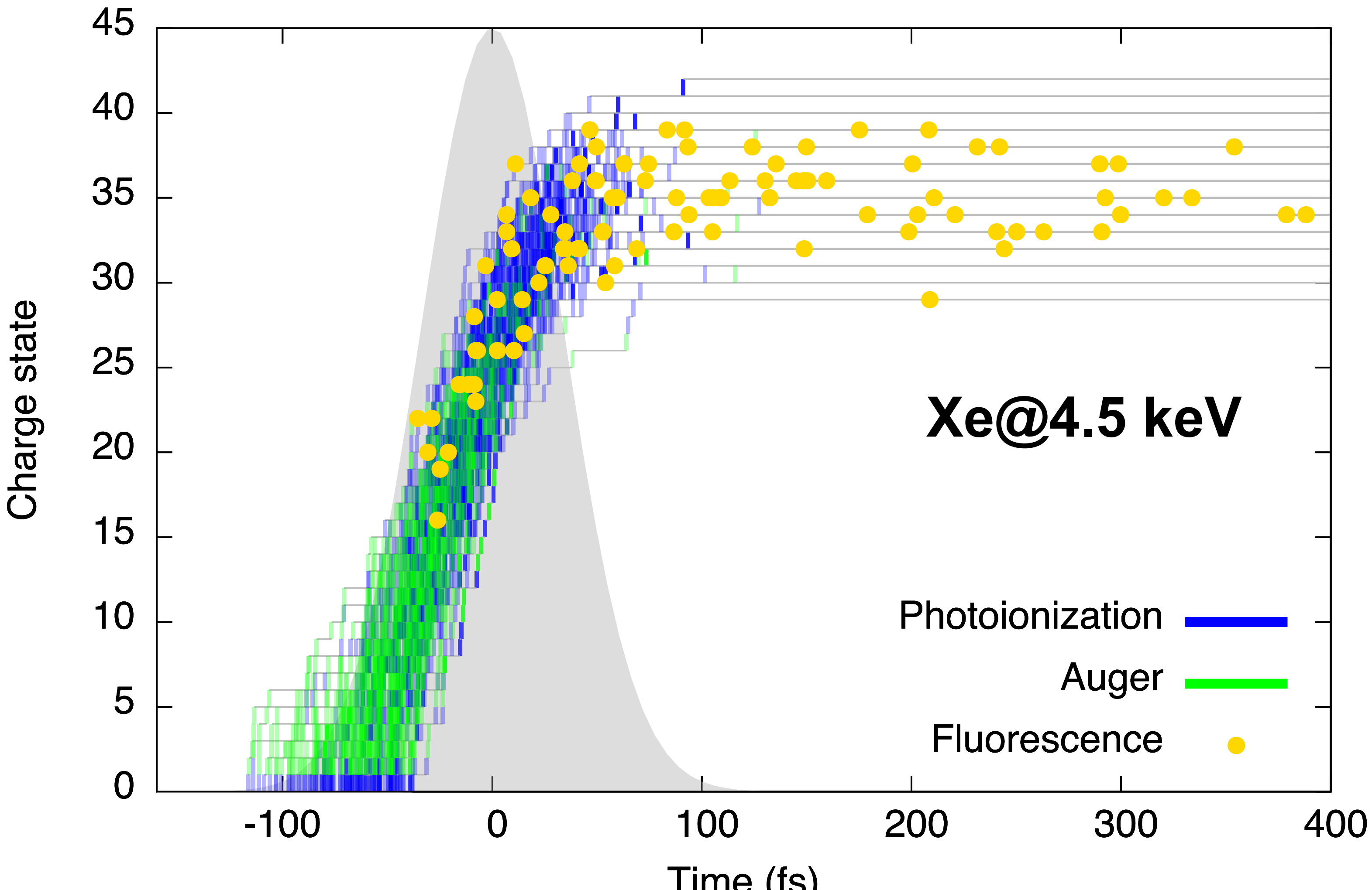
XATOM

- Electronic structure (HFS) for any given element and configuration
- X-ray-induced atomic processes for any given element and configuration
- Solve coupled rate equations to simulate ionization dynamics
- Sequential ionization model tested by a series of atomic XFEL experiments



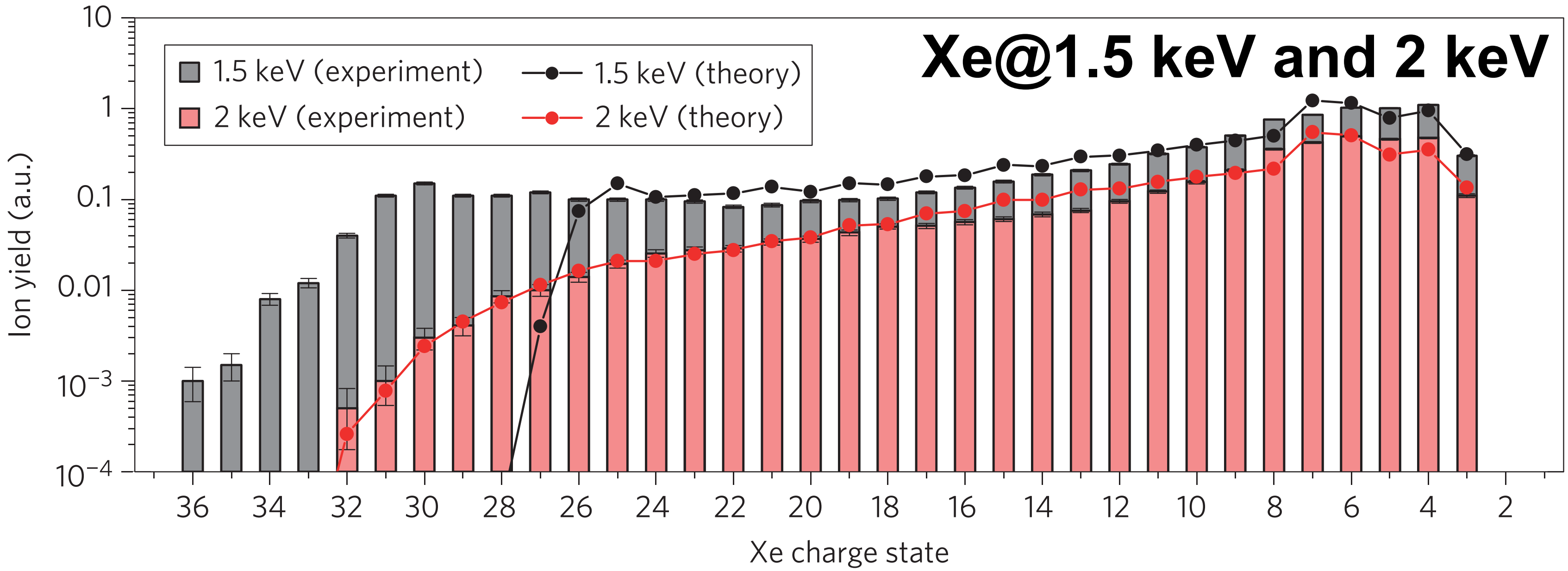
Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).
Jurek, Son, Ziaja & Santra, *J. Appl. Cryst.* **49**, 1048 (2016).
Download executables: http://www.desy.de/~xraypac

X-ray multiphoton ionization dynamics



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

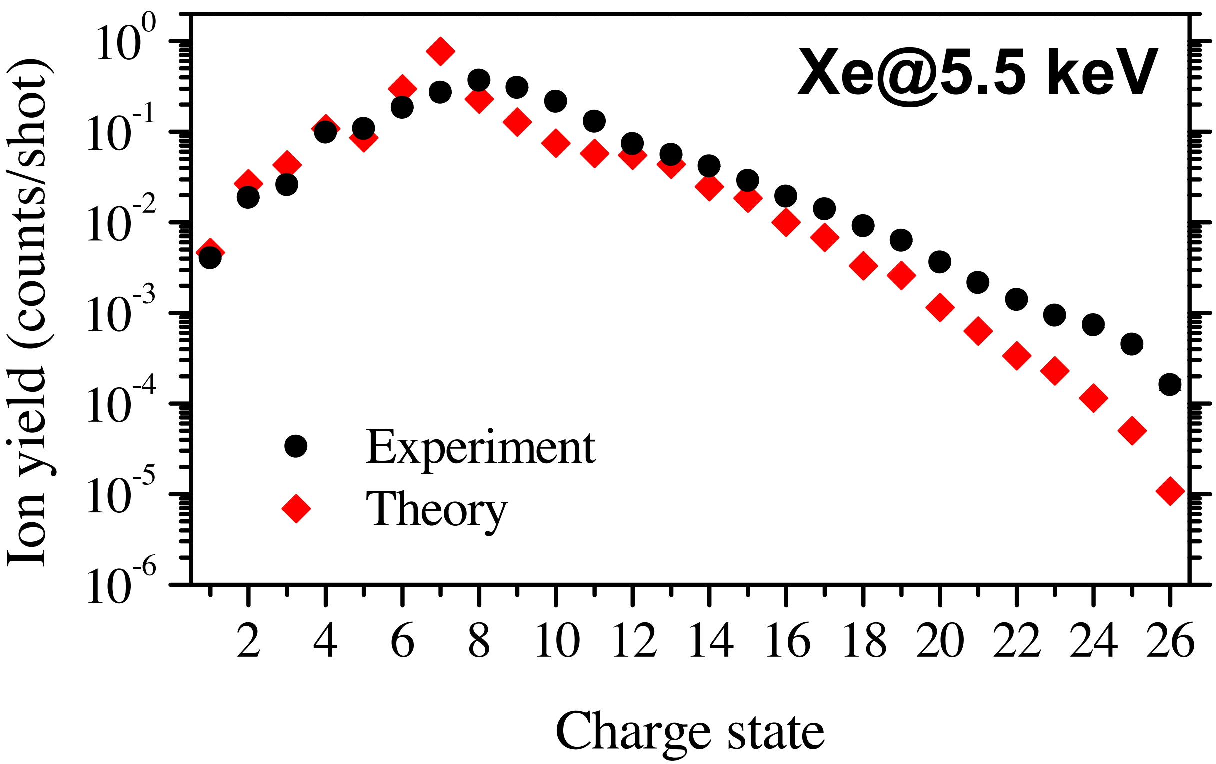
- Xe *M*-shell ionization
- 2 keV: excellent agreement between theory and experiment
- 1.5 keV: further ionization via resonance
- REXMI: Resonance-Enabled X-ray Multiple Ionization

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

CFEL SCIENCE

DESY.

Comparison with SACLA experiment



SACLA experiment

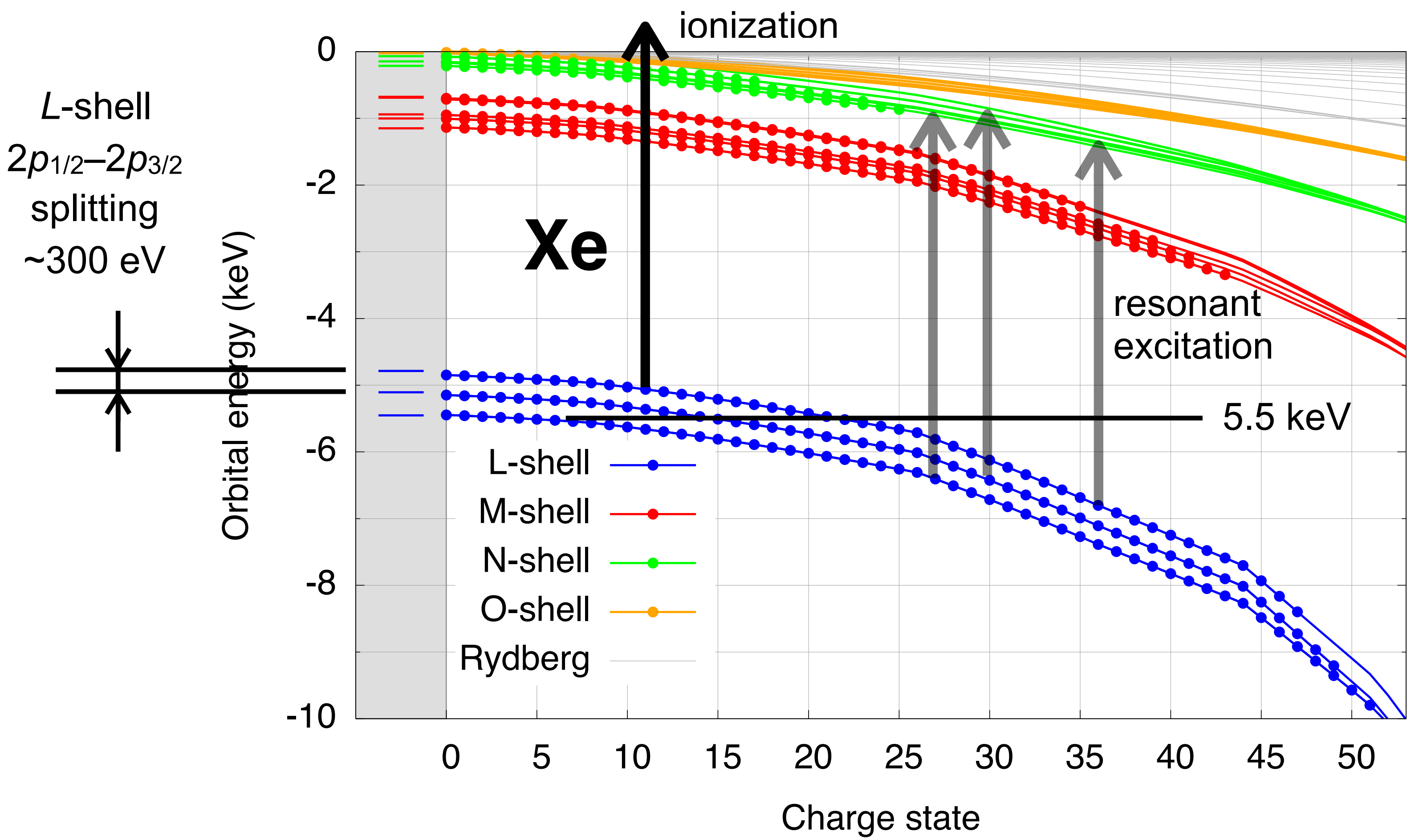
Kiyoshi Ueda
at Tohoku Univ.

- 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

Both resonance and relativity matter



- REXMI: multiple resonant excitation and Auger-like decay
- *N* of rate eqs: ~20*M* (non-rel) ➔ ~5*B* (rel) ➔ ~2.6×10^{68} (resonance+rel)

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
  - *L*-shell initiated ionization ➔ large relativistic effects
- XATOM extended to include both relativistic energy corrections and resonant excitations

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

LCLS experiment

Daniel Rolles
at KSU

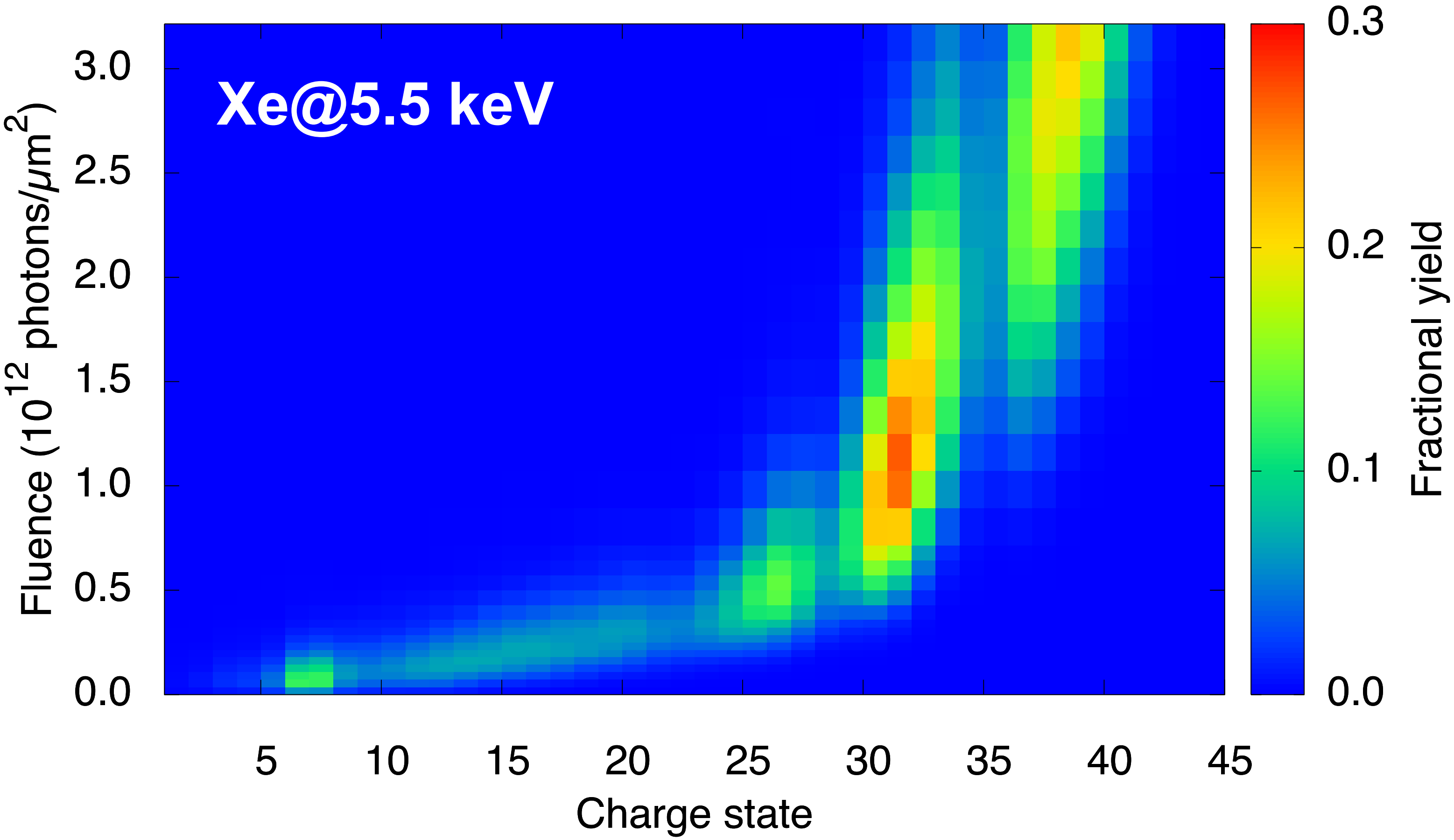
Artem Rudenko
at KSU

& Benedikt Rudek

XATOM extension

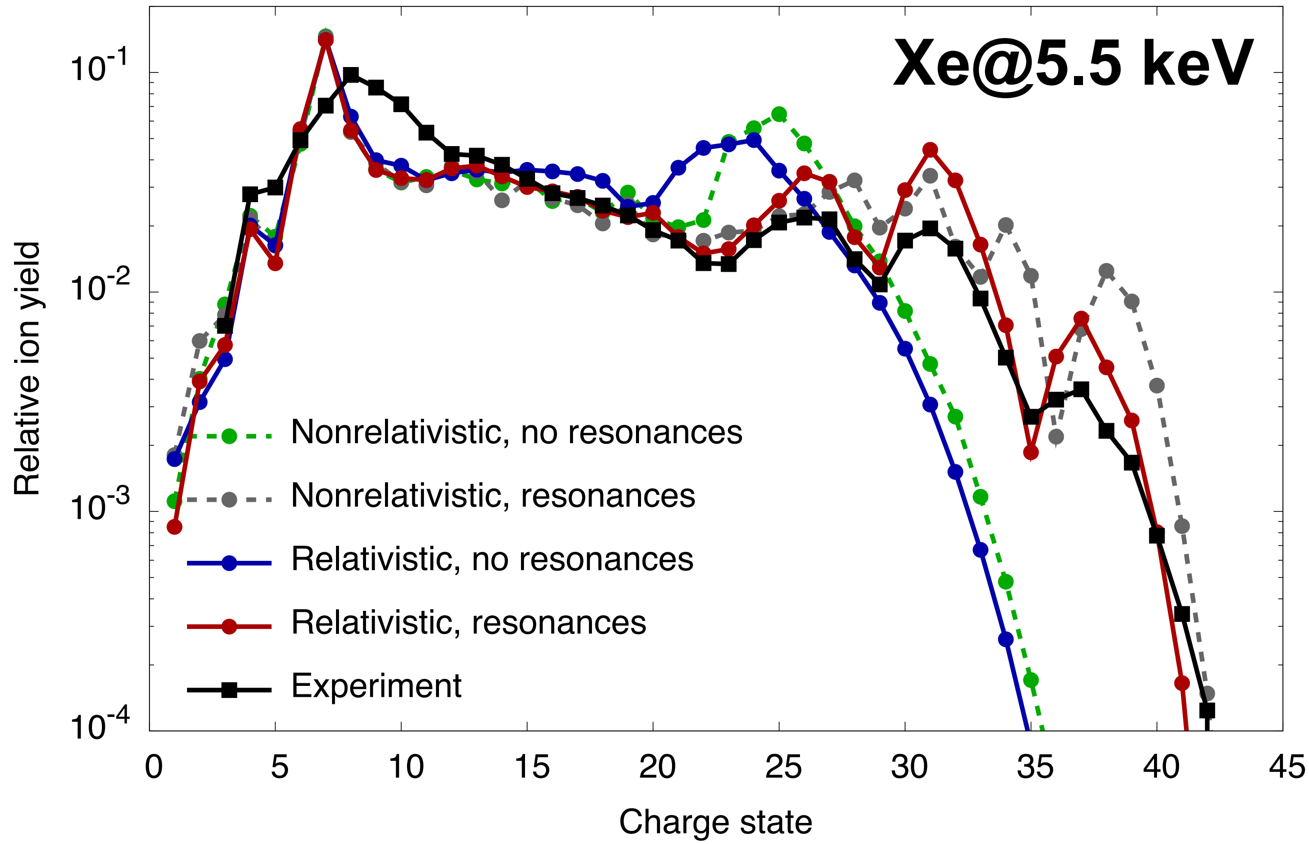
Koudai Toyota

CSD with resonance & relativity



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

Comparison with new LCLS data



- ~50 times higher fluence than the SACLA experiment
- Highlighting the interplay between resonance and relativistic effects

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

Challenges for molecular dynamics at XFEL

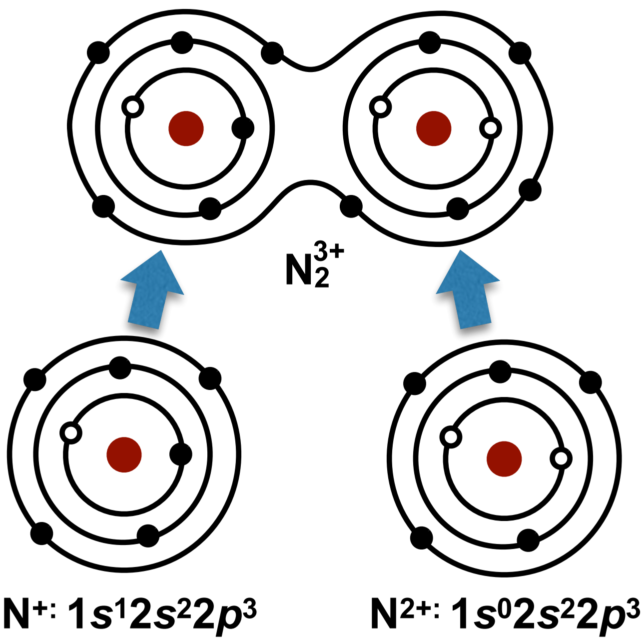
- No *ab initio* theoretical tools available for high x-ray intensity
  - Coupled ionization and nuclear dynamics in the same time scales
  - Extremely complicated dynamics:
    e.g. CH_3I ~ 200 trillion rate equations at single geometry
  - Highly excited molecular electronic structure

XMOLECULE

- Quantum electrons, classical nuclei
- Efficient electronic structure calculation: core-hole adapted basis functions calculated by XATOM
- Monte Carlo on the fly

XMOLECULE: Elec. structure & dynamics

- Hartree-Fock-Slater method
- Bound states: LCAO-MO with core-hole-adapted numerical atomic orbitals calculated by XATOM



XMOLECULE development

Yajiang Hao
Now at USTB (Beijing)

Kota Hanasaki
Now at Kyoto Univ.

Ludger Inhester

- Continuum states: approximated by atomic continuum calculated by XATOM
- Cross sections, rates, and gradients calculated on the fly for given electronic and nuclear configuration

Hao *et al.*, *Struct. Dyn.* **2**, 041707 (2015).
Inhester *et al.*, *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

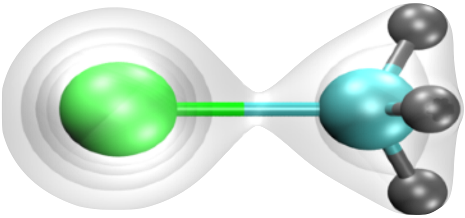
LCLS experiment

Daniel Rolles at KSU

Artem Rudenko at KSU

- Selective ionization on heavy atom

CH_3I @ 8.3 keV



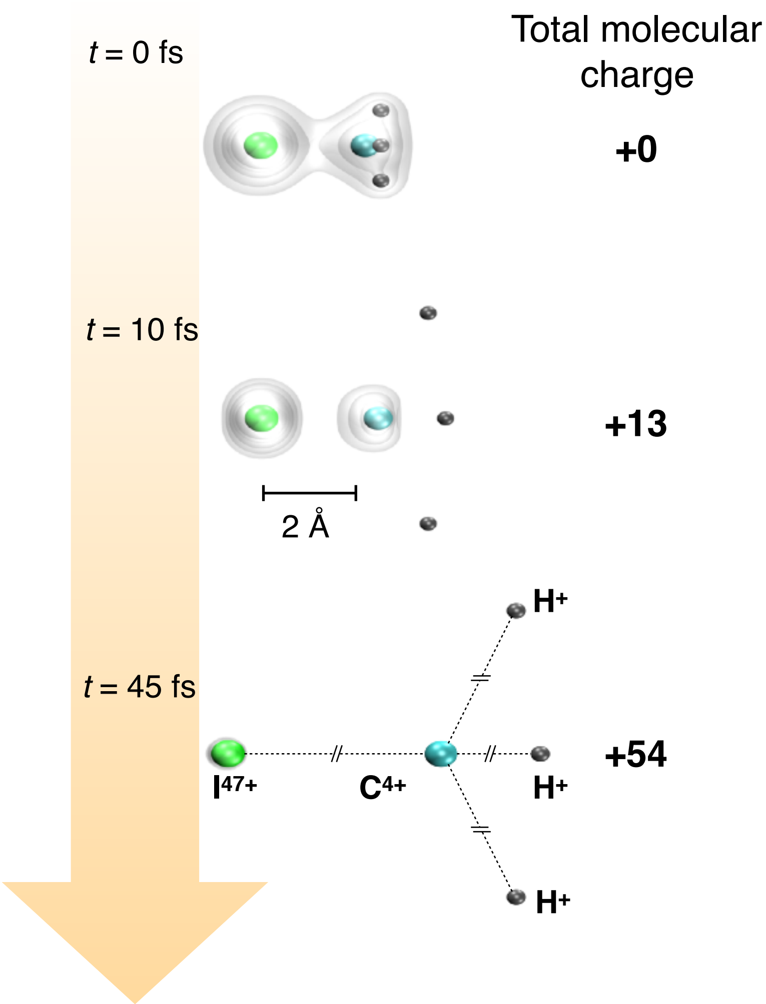
σ(I)~50 kbarn

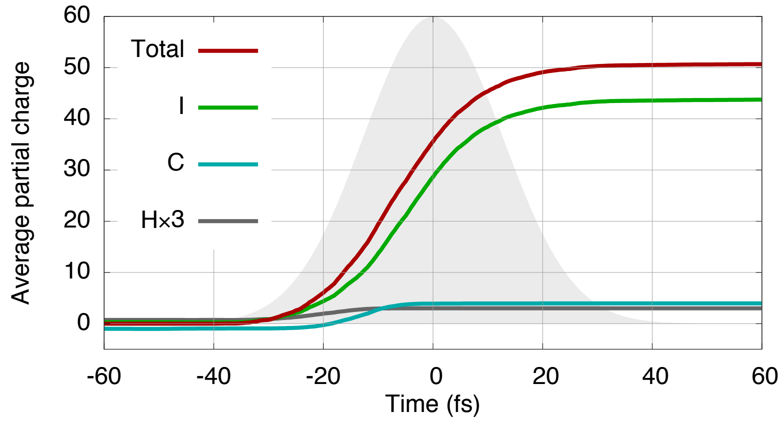
σ(C)~80 barn

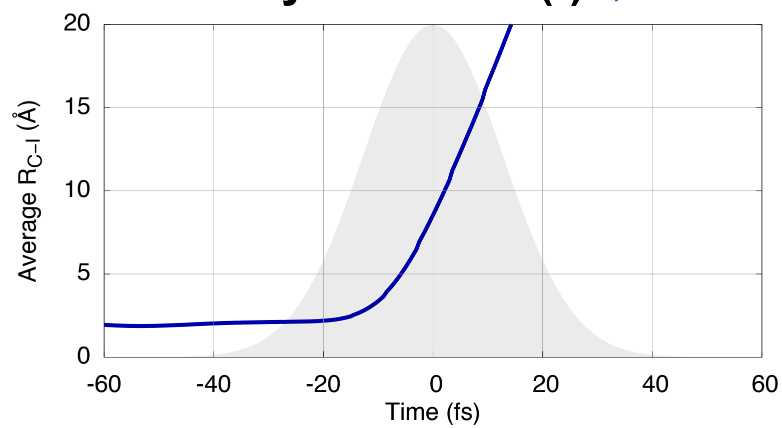
σ(H)~8 mbarn

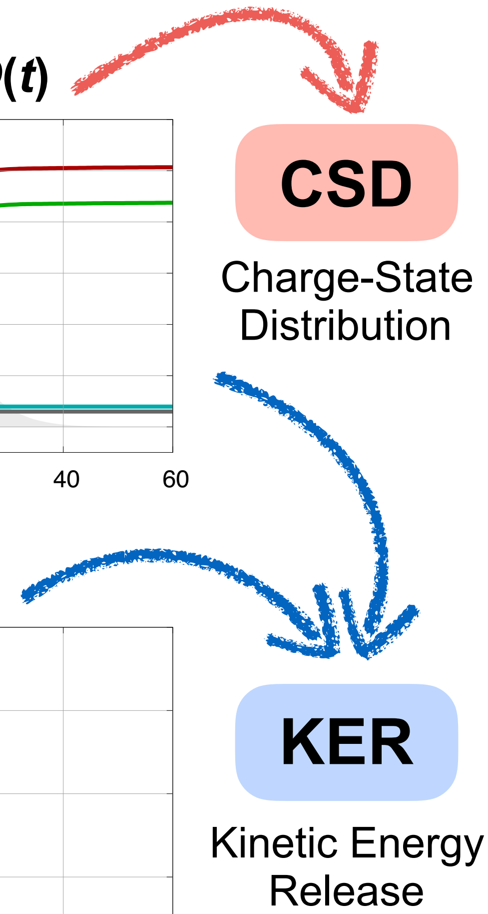
- X-ray multiphoton ionization occurs at high intensity
- Charge imbalance induces charge rearrangement
- Coulomb explosion after/during ionization & charge rearrangement

Ionization and fragmentation dynamics



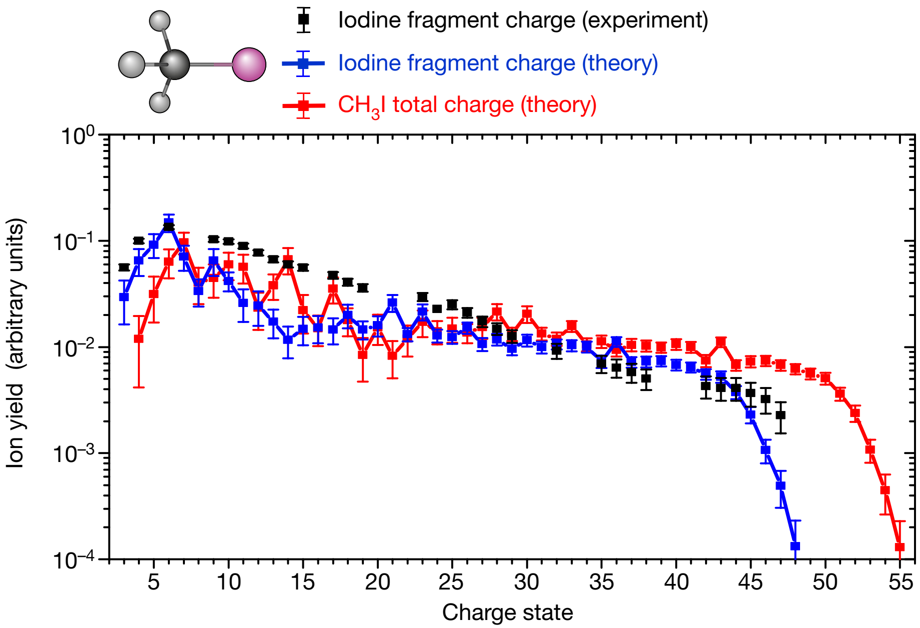




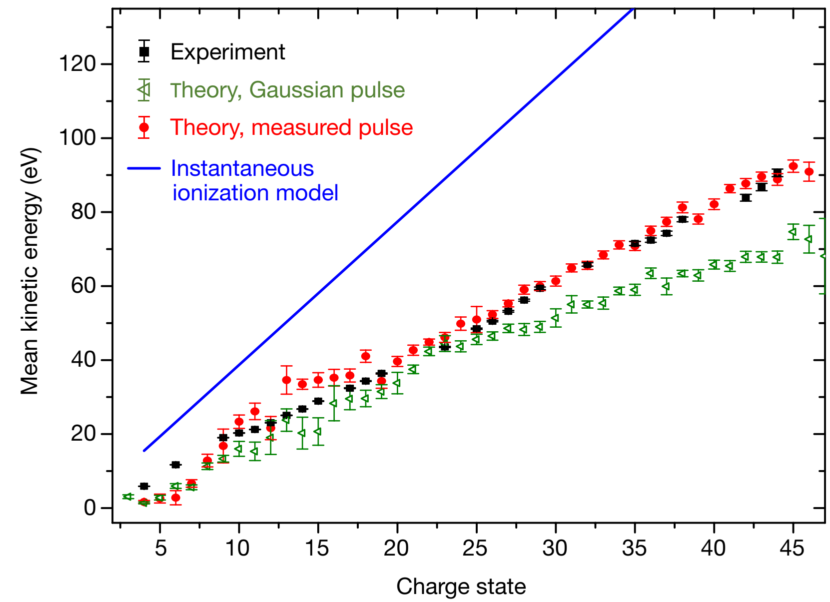


Comparison of CSD and KER

CSD of I and CH_3I



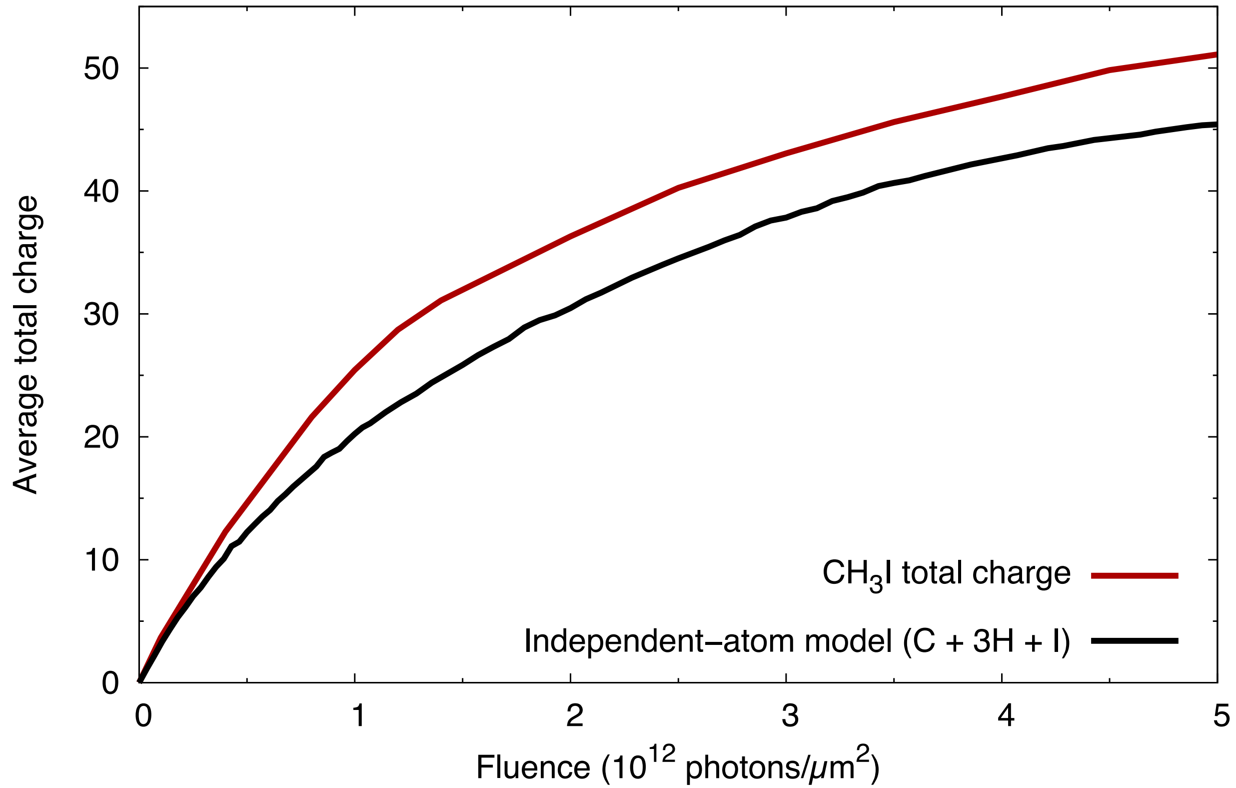
KER of I fragment



- CSD & KER: Capturing detailed ionization and fragmentation dynamics
- First quantitative comparison for the behaviors of polyatomic molecules under XFEL irradiation

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

Molecular ionization enhancement

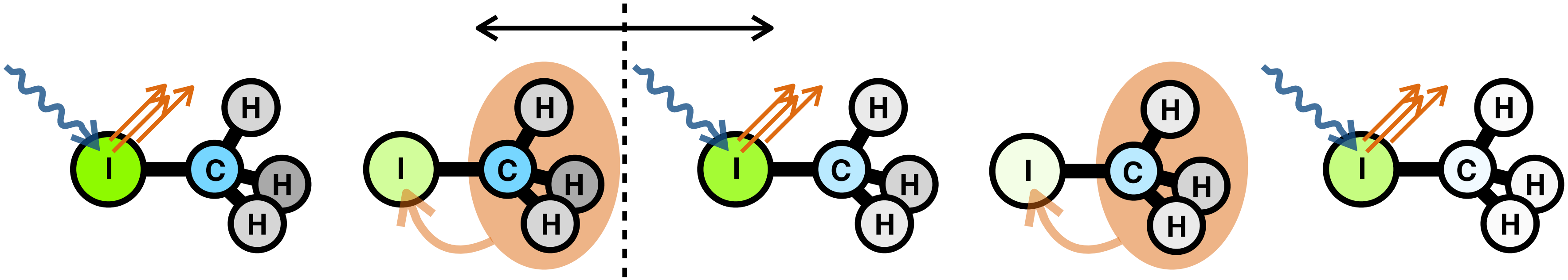


- At low fluence, molecular total charge = sum of individual atomic charges
- At high fluence, molecular total charge > sum of individual atomic charges

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

Ionization enhanced by charge rearrangement

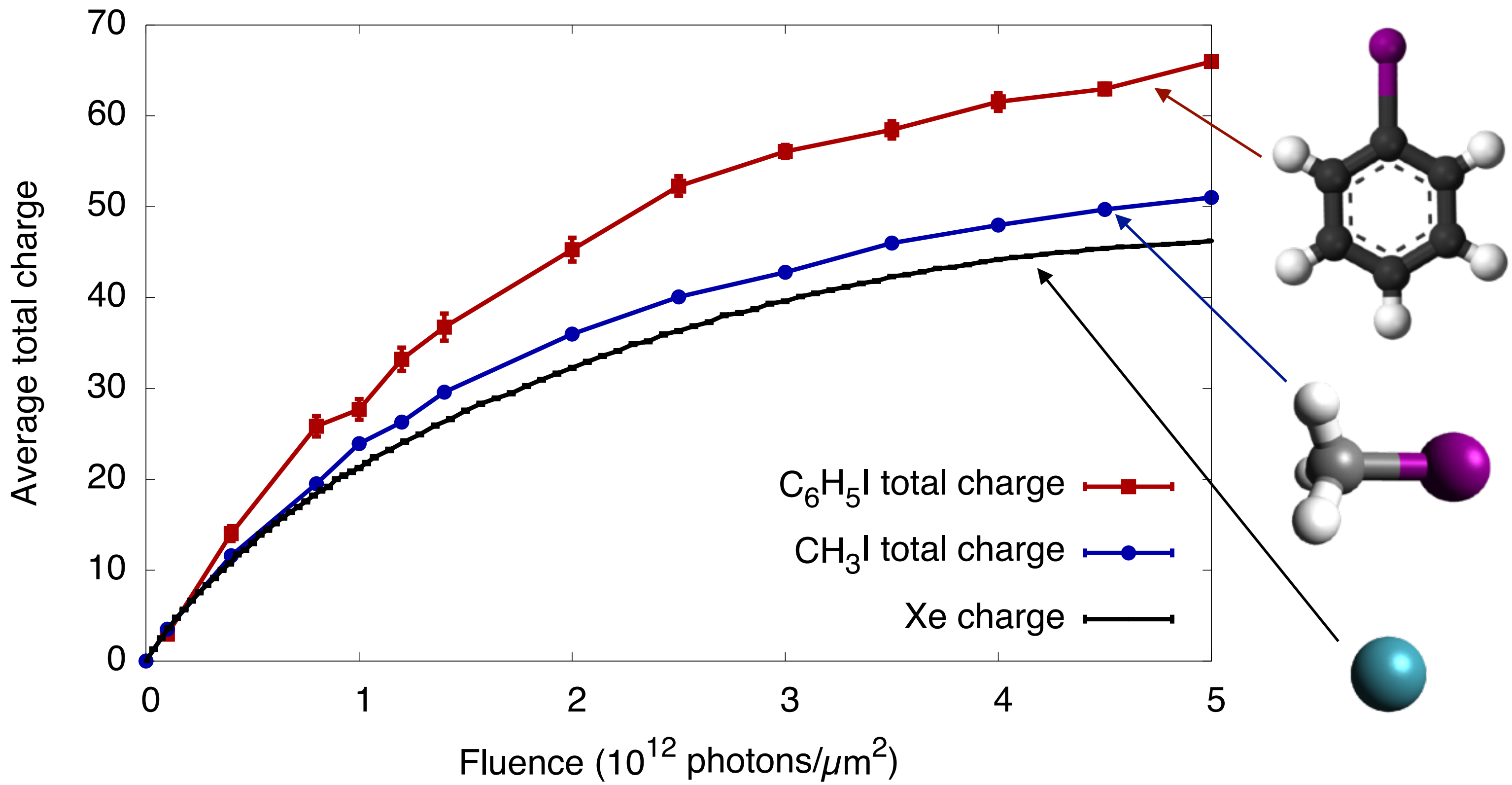
low x-ray fluence (single-photon dominant) | high x-ray fluence (multiphoton dominant)



- Electrons from light atoms become available for further ionization on heavy atoms after charge rearrangement.
- CREXIM: <u>C</u>harge-<u>R</u>earrangement-<u>E</u>nhanced <u>X</u>-ray <u>I</u>onization of <u>M</u>olecules
- 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).

Bigger molecule, larger enhancement



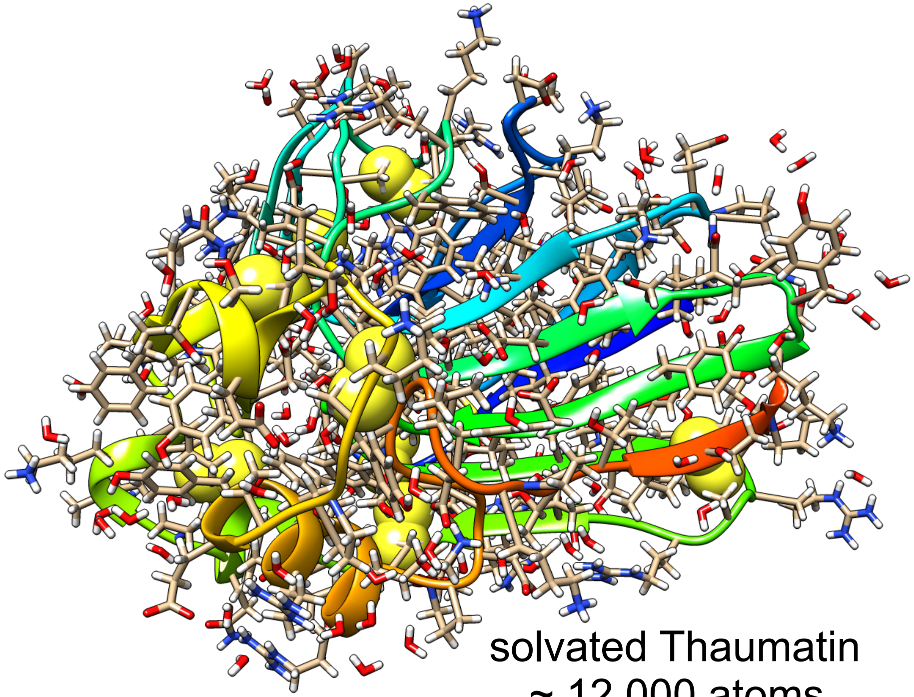
- Xe, iodomethane, iodobenzene: similar cross section at 8.3 keV
- The stronger ionization for the larger molecule

Hao, Inhester, Son & Santra, *PRA* **100**, 013402 (2019).

Toward complex systems

XMDYN development

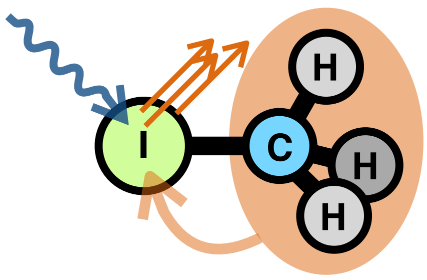
Zoltan Jurek Malik M. Abdullah

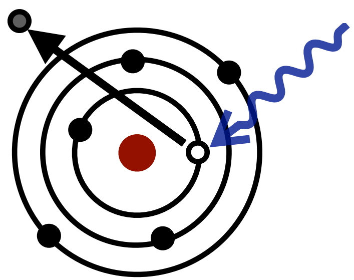


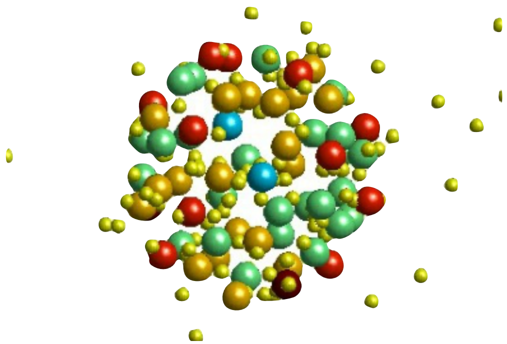
solvated Thaumatin
~ 12,000 atoms

- **XMDYN**: X-ray molecular dynamics
  - Classical dynamics for ions and free electrons
  - Quantum treatment for bound electrons ➔ combined with XATOM
  - *Ab initio* treatment of molecular effects ➔ to be combined with XMOLECULE
- First validation with LCLS (C_{60}) and SACLA (Ar/Xe clusters) experiments
  - Murphy *et al.*, *Nat. Commun.* **5**, 4281 (2014).
  - Tachibana *et al.*, *Sci. Rep.* **5**, 10977 (2015).
- Start-to-end simulation for single-particle imaging at European XFEL
  - Yoon *et al.*, *Sci. Rep.* **6**, 24791 (2016).
  - Fortmann-Grote *et al.*, *IUCrJ* **4**, 560 (2017).

Conclusion







XATOM

XMOLECULE

XMDYN
(Zoltan Jurek)

- Enabling tools to investigate x-ray multiphoton physics of atoms, molecules, and clusters exposed to high-intensity x-ray pulses
- XFEL–matter interaction: sequential multiphoton multiple ionization
- Intriguing phenomena of atoms and molecules with intense XFEL pulses
  - Xe: ionization enhanced via REXMI and modulated by relativity
  - CH_3I: molecular ionization enhancement via CREXIM
- Theory provides crucial insights of the XFEL–matter interaction

Collaboration of CH_3I LCLS experiment

Experiment team

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PTB, Braunschweig B. Rudek

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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

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Koudai Toyota

Yajiang Hao
Now at USTB (Beijing)

Oriol Vendrell
Now at Heidelberg Univ.

Robin Santra

CFEL SCIENCE

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Dr. Rui Jin
Dr. Vladimir Lipp
Dr. Victor Tkachenko
Caroline Arnold
Niels Breckwoldt
John Bekx
Athiya M. Hanna
Daria Kolbasova
Murali Krishna
Adrien Marjollet
Julia Schäfer
Yashoj Shakya
Michael Obermeyer

Molecular black hole

X-ray pulses create “molecular black hole” — *DESY News*

‘Black hole’ created by strongest ever x-ray laser — *Newsweek*

X-rays induce electron-gobbling ‘black holes’ — *C&EN*

X-ray lasers make atoms act like “black holes” in molecules — *Scientific American*

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

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

아름다운 빛의 춤사위, ‘분자 블랙홀’

빛의 춤 선이 동그랗고 납작한 원반을 그려냈다. 넘쳐흐른 빛이 채 뻗어 나가지 못하고 중앙에 붙잡혔다. 그마저 아름다운 춤사위 같다. 이를 자세히 보여주려는 듯, 마치 무대의 핀 조명 같은 강렬한 빛이 그 뒤로 쏟아지고 있다. 새로운 블랙홀이라도 발견한 걸까. 그런데 자세히 보니 중심에 우둘투둘한 표면의 검은 구가 있다.

미묘해 보이는 이 그림은 독일전자가속기연구소(DESY) 연구진이 최근 미국 에너지부 스탠퍼드 선형가속기센터(SLAC) 국립가속기연구소 등과의 공동연구를 통해 발견한 ‘분자 블랙홀’ 현상을 상상해서 그린 것이다. 연구팀은 엑스선 레이저를 가능한 가장 높은 에너지로 작은 분자에 쪼였다가 놀라운 현상을 발견했다. 레이저가 분자를 구성하는 가장 큰 원자의 전자를 대부분 제거했는데, 그 결과로 생긴 빈 공간이 마치 블랙홀처럼 분자의 나머지 원자들로부터 전자를 끌어당기기 시작한 것이다.

연구를 이끈 미국 캔자스주립대 다니엘 롤스 교수는 “강력한 엑스선을 쪼이는 모든 실험은 샘플이 엑스선에 어떻게 반응하는지 보려는 것”이라며 “이번 연구로 엑스선을 쪼인 작은 분자가 어떤 손상을 입는지 예측할 수 있게 됐다”고 말했다. 연구 결과는 학술지 ‘네이처’ 5월 31일자 온라인판에 게재됐다.

우아영 기자 doi:10.1038/nature22373

Credit: DESY/Science Communication Lab