Giant x-ray multiphoton ionization of atoms and molecules.

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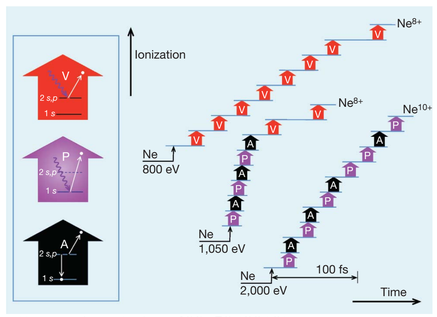
Abstract

Interaction of atoms and molecules with intense x-ray free-electron laser (**XFEL**) pulses is characterized by sequential multiphoton multiple ionization. This sequential ionization model has been verified with a series of gas-phased atomic XFEL experiments. With recent advances of XFELs, we are able to reach extremely high peak intensity in the hard x-ray regime, which gives rise to new multiphoton phenomena that have not been observed with x-ray synchrotron radiation. In this contribution, I will discuss two recent studies of enhancement of x-ray multiphoton ionization: REXMI and CREXIM. First, **REXMI** stands for resonance-enabled or resonance-enhanced x-ray multiple ionization. Due to the broad energy bandwidth of XFEL pulses and multiple resonant excitations followed by Auger-like decays, the system can be further ionized, far beyond the prediction of the straightforward sequential multiphoton ionization model. In our recent experiment with heavy atoms, the charge-state distribution as an outcome of ionization dynamics shows not only a dramatic extension to high charge states but also a characteristic pattern in the extended ion yields, which can be explained only when both relativistic and resonance effects are taken into account in theory. Next, **CREXIM** represents charge-rearrangement-enhanced x-ray ionization of molecules. When a molecule consisting of heavy and light atoms is exposed to high-intensity XFEL pulses, the molecule can be further ionized, far beyond the prediction of the independent-atom model. We propose a mechanism behind molecular x-ray ionization enhancement as the repetition of single-photon absorption on heavy atoms accompanied with electron transfer from light atoms to heavy atoms via chemical bonding. I will present two case studies: Xe atom for REXMI and iodomethane molecule for CREXIM. We employ dedicated theoretical tools, **XATOM** and **XMOLECULE**, and we make a quantitative comparison with our recent experimental results. For both cases, we demonstrate that highly nonlinear behavior is exhibited and the degree of ionization is no longer proportional to photoionization cross section at high x-ray intensity. These two ionization enhancement mechanisms can play an important role for the quantitative understanding of radiation damage dynamics during ultraintense hard x-ray pulses.

X-ray multiphoton ionization

Interaction with *ultraintense* x-ray pulses

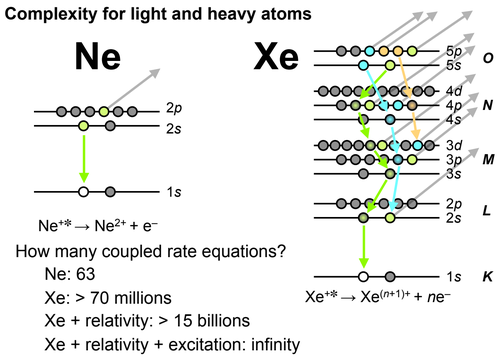


Young *et al.*, *Nature* **466**, 56 (2010).

Interaction of matter with intense XFEL pulses is characterized by sequential multiphoton multiple ionization dynamics.

> First LCLS experiment of Ne: fundamental atomic physics in XFEL
> Sequence of K-shell ionization (P), Auger decay (A), and fluorescence (F)
> Extremely complicated ionization dynamics
> Highly excited electronic structure involved
> No standard quantum chemistry code available

Complexity for light and heavy atoms

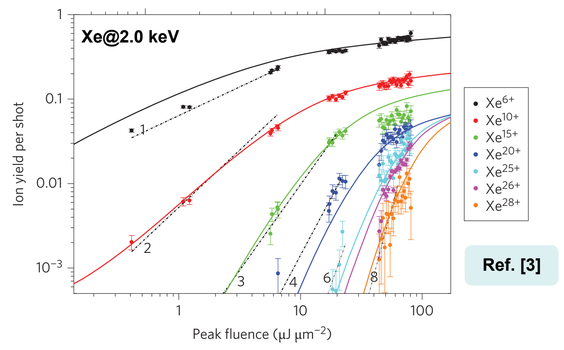


$Ne^{*} \rightarrow Ne^{2+} + e^{-}$

How many coupled rate equations?
Ne: 63
Xe: > 70 millions
Xe + relativity: > 15 billions
Xe + relativity + excitation: infinity

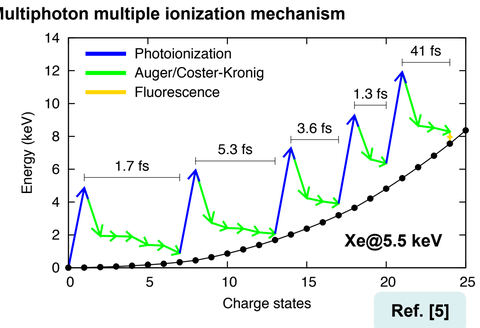
$Xe^{*} \rightarrow Xe^{(n+1)+} + ne^{-}$

Quantitative comparison between theory and experiment



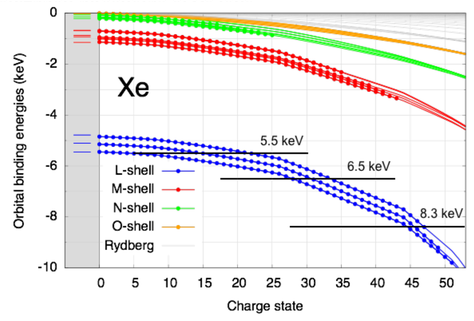
Ref. [3]

Multiphoton multiple ionization mechanism



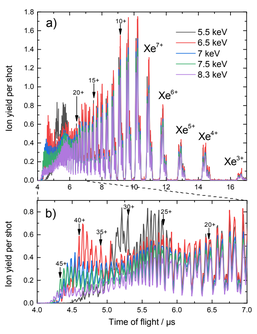
Ref. [5]

Ionization thresholds of Xe ions

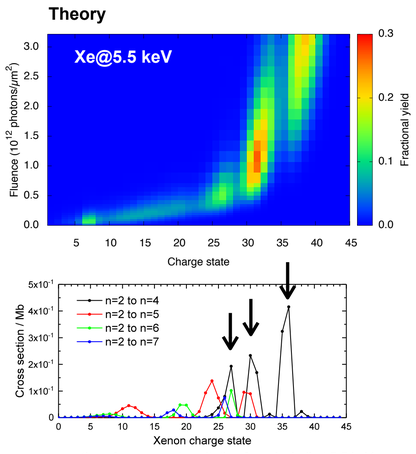


REXMI: Resonance-enabled or -enhanced x-ray multiple ionization, now with relativistic effects

Experiment
Xe atom at three different photon energies at LCLS CXI using nano-focus
➔ new realm of intensity approaching ~2×10¹⁹ W/cm²



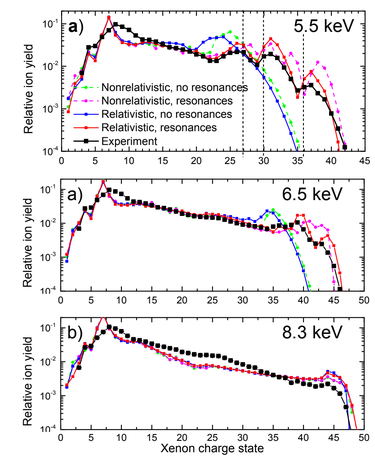
Theory



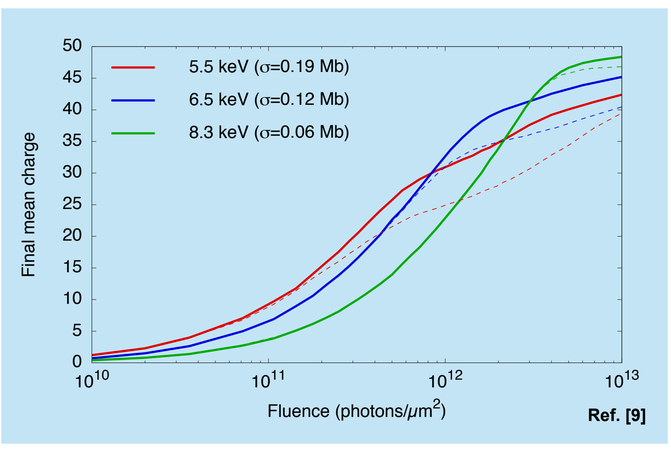
cross sections for resonant excitation from *L*-shell at 5.5 keV

> REXMI dramatically enhances the degree of ionization by multiple resonant excitations and autoionization of multiply excited states with the help of a large bandwidth of XFEL pulses.
> Resonance effect
  > one resonance channel: Xiang *et al.*, *PRA* **86**, 061401 (2012).
  > multiple resonance channels: Ho *et al.*, *PRL* **113**, 253001 (2014); *PRA* **92**, 063430 (2015).
> Relativistic energy correction within first-order perturbation theory
  > open new Coster-Kronig decay channels
  > close photoionization channels earlier
  > the closer to photon energy, the higher cross section
> Both resonance and relativistic effects are implemented in XATOM: Ref. [8].
> Numerical complexity for Xe with n_{max}=30 and l_{max}=7 ➔ 10^{68} electronic configurations to be considered!

Comparison between theory and experiment



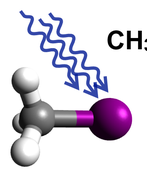
Predictive power of the ionization degree for various photon energies



Ref. [9]

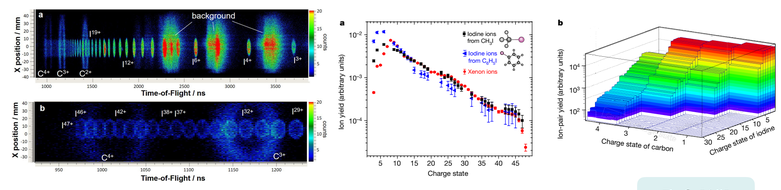
CREXIM: Charge-rearrangement-enhanced x-ray ionization of molecules

Selective ionization on heavy atom



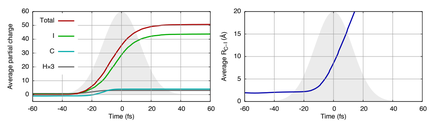
σ(I)~50 kbarn
σ(C)~80 barn
σ(H)~8 mbarn

Experiment: Xe, CH_3I, and C_6H_5I at LCLS CXI using nano-focus ~2×10¹⁹ W/cm²

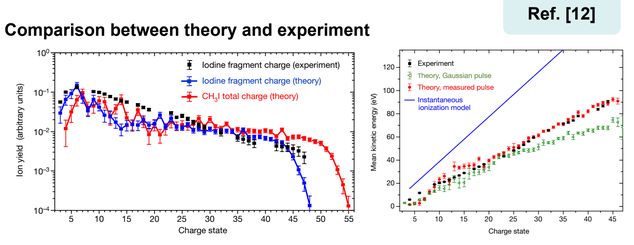


Ref. [12]

Ultrafast ionization and fragmentation dynamics

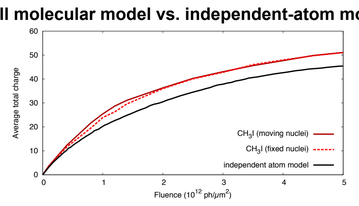


Comparison between theory and experiment

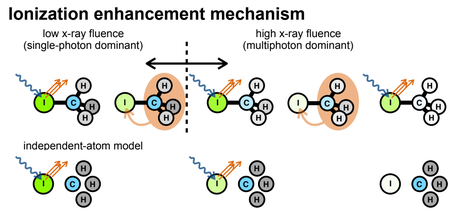


CSD (charge state distribution) and KER (kinetic energy release) of iodine ion fragments

Full molecular model vs. independent-atom model

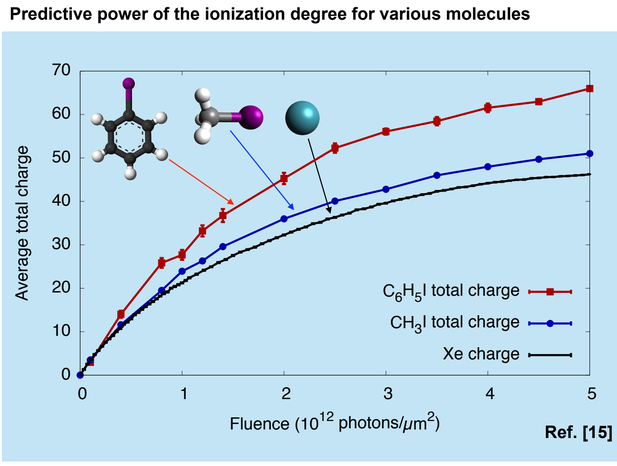


Ionization enhancement mechanism



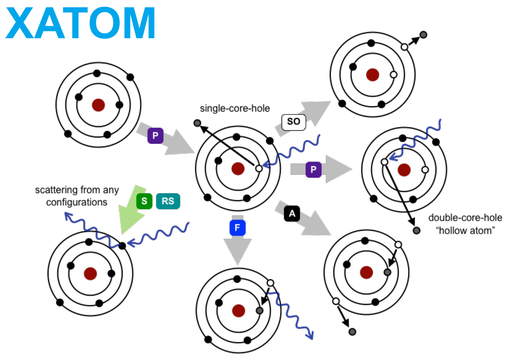
> CREXIM dramatically enhances the degree of ionization via intramolecular charge transfer and repeated photoionization.
> Selective ionization induces charge imbalance.
> Refueling by charge transfer and further ionization at the heavy atomic site
> The bigger molecule, the larger CREXIM effect

Predictive power of the ionization degree for various molecules



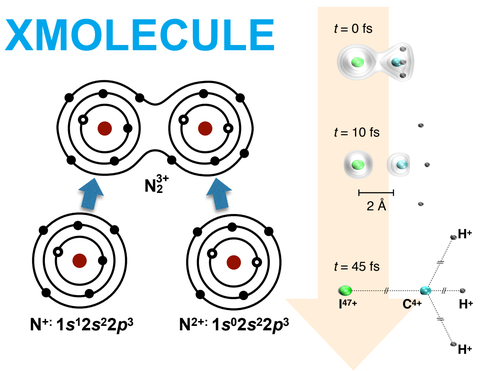
Ref. [15]

XATOM



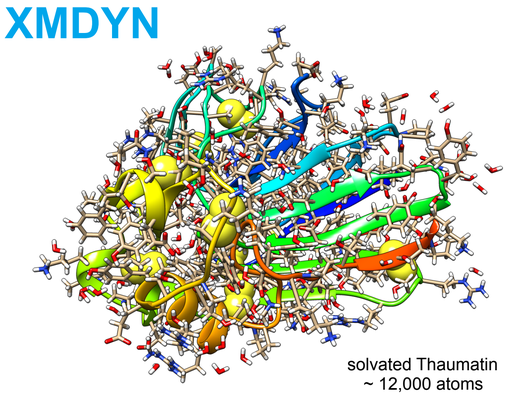
We implement an integrated toolkit, XATOM, to treat x-ray-induced processes based on nonrelativistic quantum electrodynamics and perturbation theory within the Hartree–Fock–Slater model. To simulate ionization dynamics in intense x-ray pulses, we employ the rate equation approach with photoionization cross sections, Auger rates, and fluorescence rates, for all possible *n*-hole electronic configurations for all possible +*n* charge states.

XMOLECULE



We develop an x-ray molecular physics toolkit, XMOLECULE. The molecular electronic structure is solved within the Hartree–Fock–Slater model with core-hole-adapted basis functions calculated by XATOM. To describe ionization dynamics, coupled rate equations are solved with a Monte Carlo approach. To describe fragmentation dynamics, the nuclear motions are propagated classically during each kinetic Monte Carlo trajectory, with molecular forces, rates and cross-sections calculated on the fly from a given electronic configuration and molecular geometry.

XMDYN



solvated Thaumatin
~ 12,000 atoms

Main developers: **Zoltan Jurek**, **Malik M. Abdullah**, and **Beata Ziaja**

> XMDYN: X-ray molecular dynamics
  > classical dynamics for ions and free electrons
  > quantum treatment for bound electrons ➔ combined with XATOM
> 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).
> Chemical dynamics (oligomer formation) in Ar clusters
  > Kumagai *et al.*, *Phys. Rev. Lett.* **120**, 223201 (2018).

Conclusions

> Enabling tools to investigate x-ray multiphoton physics of atoms and molecules exposed to intense XFEL pulses
> Nonlinear behavior of atomic and molecular responses to intense x-rays
> Dramatic enhancement of x-ray multiphoton ionization via resonance and molecular environment
> Interplay of resonance and relativistic effects for Xe: First quantitative comparison for REXMI in atoms at high x-ray intensity
> Molecular ionization enhancement (CREXIM) for CH_3I and C_6H_5I: First quantitative comparison for molecular ionization at high x-ray intensity
> New phenomena to be taken into account for future XFEL applications

Collaboration

Experimental team

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Theory team

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References

[1] Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).
[2] Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).
[3] Rudek *et al.*, *Nature Photon.* **6**, 858 (2012).
[4] Rudek *et al.*, *Phys. Rev. A* **87**, 023413 (2013).
[5] Fukuzawa *et al.*, *Phys. Rev. Lett.* **110**, 173005 (2013).
[6] Motomura *et al.*, *J. Phys. B* **46**, 164024 (2013).
[7] Jurek, Son, Ziaja & Santra, *J. Appl. Cryst.* **49**, 1048 (2016).
[8] Toyota, Son & Santra, *Phys. Rev. A* **95**, 043412 (2017).
[9] Rudek, Toyota, *et al.*, *Nat. Commun.* **9**, 4200 (2018).
[10] Hao *et al.*, *Struct. Dyn.* **2**, 041707 (2015).
[11] Inhester *et al.*, *Phys. Rev. A* **94**, 023422 (2016).
[12] Rudenko *et al.*, *Nature* **546**, 129 (2017).
[13] Inhester *et al.*, *J. Phys. Chem. Lett.* **9**, 1156 (2018).
[14] Schäfer *et al.*, *Phys. Rev. A* **97**, 053415 (2018).
[15] Hao, Inhester, Son & Santra (submitted).

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