X-ray multiphoton ionization NATURE | VOL 466, 1910 ARTICLES | V

Abstract

- > 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 CH₃I and C₆H₅I:
- 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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[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).

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.

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 **N+: 1***s***12***s***22***p***³ N2+: 1***s***02***s***22***p***³ I47+ H+ H+** $t = 45$ fs

 2 Å

 $\overline{\mathcal{O}}$

 $t = 0$ fs

 $t = 10$ fs

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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).

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.

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 \vert phenomena that have not been observed with x-ray synchrotron $\qquad \qquad \mid$ radiation. In this contribution, I will discuss two recent studies of \vert enhancement of x-ray multiphoton ionization: REXMI and CREXIM. \vert First, **REXMI** stands for resonance-enabled or resonance-enhanced | x-ray multiple ionization. Due to the broad energy bandwidth of XFEL \parallel pulses and multiple resonant excitations followed by Auger-like \vert decays, the system can be further ionized, far beyond the prediction \Box aecays, the system can be funner fonized, far beyond the prediction
of the straightforward sequential multiphoton ionization model. In our of the straighter ward edged than manipheten remeation model. In early 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. \vert Next, CREXIM represents charge-rearrangement-enhanced x-ray \vert ionization of molecules. When a molecule consisting of heavy and \qquad light atoms is exposed to high-intensity XFEL pulses, the molecule \vert can be further ionized, far beyond the prediction of the independentatom model. We propose a mechanism behind molecular x-ray atom. ionization enhancement as the repetition of single-photon absorption on heavy atoms accompanied with electron transfer from light atoms on heavy atoms assempanted with sissilon transier nothingin dising \vert Xe atom for REXMI and iodomethane molecule for CREXIM. We employ dedicated theoretical tools, **XATOM** and **XMOLECULE**, and **i** we make a quantitative comparison with our recent experimental $\qquad \qquad \mid$ results. For both cases, we demonstrate that highly nonlinear \vert behavior is exhibited and the degree of ionization is no longer proportional to photoionization cross section at high x-ray intensity. \vert These two ionization enhancement mechanisms can play an \vert important role for the quantitative understanding of radiation damage \Box dynamics during ultraintense hard x-ray pulses. $\frac{1}{2}$ representation to reach the next higher charge $\frac{1}{2}$ $\frac{1}{\sqrt{2}}$ and $\frac{1}{\sqrt{2}}$ and $\frac{1}{\sqrt{2}}$ are a given as a given of spectral and $\frac{1}{\sqrt{2}}$ $r = 18$, we are able to reach extremely high-peak p_{min} with neavy atoms, the endige-state distribution as \vert onization dynamics shows not only a dramatic
hechanological radiation (,1018 W cm2 , ,1 nm) $\overline{\text{m}}$ charge states but also a characteristic pattern in the $\overline{\text{m}}$ ioenient as the repetition of sing response occur over the initial operating photon energy range of Λ IVII dilu IOUOIII euidile IIIOI eCule IOI UNEAIIVI. VV e $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$ ejected, creating 1s vacancies that are refilled by rapid Auger decay,

References

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).

Giant x-ray multiphoton ionization of atoms and molecules.

dimensional interaction volume defined by a circular Gaussian FEL beam profile \sim 3 μ \sim 3 μ m2 (FWHM) and a gas jet diameter of diame

an estimated beamline transmission of "35% and an X-ray focus size of "3 × 3 mm2 (FWHM) at 2.0 keV. Thus, at a maximum pulse energy of 2.6 mJ as measured energy of 2.6 mJ as measured

Sang-Kil Son,^{1,*} Koudai Toyota,¹ Ludger Inhester,¹ Yajiang Hao,^{1,2} Kota Hanasaki,^{1,3} Robin Santra,^{1,4} Benedikt Rudek,⁵ Artem Rudenko,⁶ Daniel Rolles⁶ — ¹CFEL, DESY, Germany; ²USTB, China; ³Kyoto Univ., Japan; ⁴Univ. of Hamburg, Germany; ⁵PTB, Germany; ⁶Kansas State Univ., USA $3/7$ $3/7$ $3/7$ $1/7$ $1/7$ $1/1$ io
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ion charge state distributions for the photo-ionization of xenon

by multielectron excitation accompanied by electron-correlation-

driven relaxation processes. For certain photon energy ranges,

REXMI results in a strong resonant increase in the X-ray absorption

cross-sections and hence leads to enhanced photo-ionization, which

dramatically increases energy absorption in the target. This effect

 \mathbf{r}_c be used to effect to effect to effect the neutral excited, dense plasmas of plasmas of plasmas of plasmas of \mathbf{r}_c

damage due to enhanced absorption and photo-ionization. This

detrimental effect can be reduced by using a narrower-band X-ray

source (for example, a seeded FEL), because fewer of the densely

spaced resonances can be excited. In addition, REXMI can be

avoided by choosing a photon energy sufficiently above the

nearest inner-shell threshold, where smaller X-ray absorption

cross-sections make it difficult to reach the high charge states

where REXMI commences.

Methods

 \boldsymbol{V} \mathbf{H} Xe15+ \mathcal{L}

Summary. Experiments were performed with intense, short-pulse X-rays produced

by the LCLS Free-Electron Laser1

mirrors to an estimated 3 [×] ³ ^mm2 (full-width at half-maximum, FWHM),

intersecting with an atomic xenon gas jet inside the Center for Free-Electron Laser Science-Advanced Study Group (CFEL-ASG) Multi-Purpose (CAMP) instrument41 installed at the LCLS Atomic Molecular and Optical (AMO) beamline42. Ion charge state spectra were recorded by an ion TOF mass spectrometer that accepted all ions produced in the interaction region within the 80 mm diameter of the spectrometer electrodes. Simultaneously, X-ray fluorescence was detected with a solid angle of 1.0 sr by a pair of high-speed, single-photon-counting X-ray p-n junction chargecoupled device (pnCCD) detectors41 with an intrinsic spectral resolution of the

pnCCD detectors of "100 eV at 1.5 keV for the chosen operation parameters.

ionize 2s, p-shell valence electrons (V, red arrow). Higher energy α Interaction of matter with intense XFEL pulses is characterized by sequential multiphoton multiple ionization dynamics and another 2s, p electron is emitted (A, black arrow). The V, P and A, black arrow α by sequential multiphoton multiple ionization dynamics.

- > First LCLS experiment of Ne: fundamental atomic physics in OPT absorption stripping the neutrinon stripping the neutrinon stripping the neutrinon stripping the horizontal direction OPT λ indicates the time for which atoms are exposed to the high-intensity λ -ray exposed to the high-in XFEL
- > Sequence of K-shell ionization (P), Auger decay (A), and $f_{\text{U} \cap \text{C} \cap \text{C} \cap \text{C} \cap \text{C} \cap \text{C}}$ (F) fluorescence (F) and indicate the means per extension per and indicate the means \mathbb{R} per formation \mathbb{R} per set \mathbb{R} per set
- > Extremely complicated ionization dynamics
- > Highly excited electronic structure involved
- paper were measured in a gas detector were measured in a gas detector of the second the theorem of the theorem of the theorem of the top of the t the claim and qualitant chonnelity code available > No standard quantum chemistry code available

the model described in refs 2 and 8. Using the Hartree–Fock–Slater method, we calculated photo-ionization cross-sections, Auger and Coster–Kronig rates, and fluorescence rates for all possible q-hole configurations of Xeqþ. The calculated

Figure 5 ion ion ion ion ion ion ion ion selected charge states ions $\mathcal{L}=\left\{ \begin{array}{ll} \mathcal{L}_{\mathcal{A}}\left(\mathcal{L}_{\mathcal{A}}\right) & \mathcal{L}_{\mathcal{A}}\left(\math$ α and a non-independent of 80 fs. The fluence at 2.0 keV α . 3.6 fs 1.3 fs **EXECUTE:** Photoionization **41** fs **Multiphoton multiple ionization mechanism**

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cross-sections and rates serve as input parameters for a set of rate equations for the time-dependent populations of the configurations. For xenon in the photon energy range 1.5–2.0 keV, we had more than one million coupled rate equations, which were solved using a Monte Carlo method. We calculated the charge state distribution and fluorescence spectrum for each set of X-ray pulse parameters, assuming a Gaussian

temporal profile. The charge state distribution was integrated over the three-

4 mm (FWHM).

Experiments. Measurements were performed in the CAMP instrument41 downstream of the LCLS AMO 'high-field physics' endstation42 during two

beamtimes in November 2009 and January 2011, respectively. On its way to the interaction point in the CAMP chamber, the X-ray beam produced by the LCLS undulators was reflected on three steering and two KB-focusing mirrors, resulting in

by the LCLS gas detectors43 upstream of the beamline optics, the estimated

maximum pulse intensity in the interaction zone was "¹ [×] ¹⁰¹⁷ W cm2² and the

maximum fluence "⁹⁰ ^m^J ^mm2²

measurements, the X-ray intensity was reduced by introducing nitrogen gas with variable pressure into an attenuator chamber located between the two pairs of

 A the position of the X -ray focus inside the CAMP chamber, which had a base

gas detectors.

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pressure of 2 [×] ¹⁰2¹⁰ mbar, a thin supersonic jet of xenon atoms with an

 T ocalculate the response of the \mathcal{L}_L

approximate diameter of 4 mm (FWHM) was intersected with the X-ray beam from LCLS (operated at 30 and 120 Hz, respectively) in the extraction region of a TOF mass spectrometer41, which had an acceptance of 80 μ A flight distance of 21 cm from the interaction point, the ions produced by the ions produced interaction of the FEL pulse with the gas target with the gas target were (post-)accelerated to 2.45 keV and for the detection on a V-stack microchannel plate (MCP) detector. The MCP signal trace was recorded for each FEL shot with an Ac $\frac{1}{2}$ hit was identified in post-analysis using a software constant fraction discriminator \mathbf{r} such that the effect of pulse height variations due to varying MCP efficiency for

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Pulse energy (mJ)

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

NATURE PHOTONICS DOI: 10.1038/NPHOTON.2012.261 ARTICLES

 X^2 \mathcal{L} $\overline{}$ \mathbb{Z}

 \times Xe⁶⁺ Xe^{10+} Xe^{15+} $\times e^{20+}$ Xe^{25+} $\times e^{26+}$ Xe^{28+}

N2 3+

CREXIM: Charge-rearrangement-enhanced x-ray ionization of molecules atoms with intense FEL pulses at photon energies of 1.5 and 2.0 keV. Based on detailed calculations, we conclude that the creation of unprecedent charge states at 1.5 keV is 1.5 keV due to a transient resonance-enhance-enhance-enhance-enhance-enhance-enhance-enhance-enhance-enhance-enhance-e dubbed REXMI which is further corresponding to $\mathcal{L}_\mathcal{R}$ which is further corresponding by experimental $\mathcal{L}_\mathcal{R}$ $\frac{1}{2}$ Ion-pair yield (arbitrary units) ant-emilianced Ion yield (arbitrary units) from C6H5I

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> REXMI dramatically enhances the degree of $\frac{1}{\sqrt{1-\frac{1$ $\begin{array}{|c|c|c|c|c|}\n\hline\n\textbf{F} & \textbf{F} & \text$ **Also the absolute values of the fractional charge-state with the states with the help of a large bandwidth of XFEL pulses.** At 2,000 eV, the calculations of \blacksquare

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- $\begin{array}{|c|c|c|c|c|}\n\hline \quad\quad & \ddots & \quad\quad & \end{array}$ and reconomed channel: Viena of **odde–even channel:** Xiang *et al.*, *PRA* 86,
- $\begin{bmatrix} 1 & 0 \end{bmatrix}^{\alpha_1}$ $\stackrel{\alpha_2}{\longrightarrow}$ multiple resonance channels: Ho *et al.*, *PRL* **predicts that 1s one-photon increases that 1s one-photon is one-photon increases up to the state states up to t** Ne2¹ only. Experimentally, one observes a yield of ,75% Ne2¹ and **113**, 253001 (2014); *PRA* **92**, 063430 (2015).
- $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{0.0}$ > Relativistic energy correction within first-order 40 45 **perturbation theory**
- $\frac{1}{\sqrt{1-\frac{1}{$ ping, and in excellent agreement with the observed channels earlier > open new Coster-Kronig decay channels
- \diamond \rightarrow the closer to photon energy, the higher cross
- | > Both resonance and relativistic effects are implemented in XATOM: Ref. [8]. > Numerical complexity for Xe with n_{max} =30 and
	- l_{max} =7 \rightarrow 10⁶⁸ electronic configurations to be

Energy (keV)

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 \subset (ke)

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REXMI: Resonance-enabled or -enhanced x-ray multiple ionization, now with relativistic effects if the photoionization rate exceeds that of Auger decay. For energies above 1.36 keV, it is possible to fully strip neon, as shown at the Ig Ionization, Now Wi ferent photon energies, 800 eV, 1,050 eV and 2,000 eV. These photon surements is controlled by insitu both emilianced x-ray on on internet of A 2,000 a relativictie effects <u>i i gialivistic ellects</u>

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Charge state of carbon Charge state of iodine

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absorption by single electrons in R

from CH3I

Ref. [3]

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H+