## **X-ray multiphoton ionization** NATURE | Vol 466, 1910 ARTICLES | V

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# **Abstract**

- > Enabling tools to investigate x-ray multiphoton physics of atoms, molecules, and complex systems exposed to intense XFEL pulses > XATOM: the key player for x-ray-related tools of XMOLECULE and XMDYN (+XPOT)
- > In contrast to frustrated absorption as expected for x-ray multiphoton ionization, the opposite trend is observed when the fluence is extremely high.
- > XREMPI shows a broader, red-shifted, asymmetric resonance profile, in contrast to conventional REMPI.
- > Theory provides the predictive power for x-ray multiphoton ionization.
- > New phenomena to be taken into account for future XFEL applications

#### **Collaboration for XREMPI**

#### **Experimental team**

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#### **Theory team**

**CFEL-DESY Theory Division** Stanislaw Wirok-Stoletow, Daria Kolbasova, Robin Santra

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**System is structural Dynamics in Molecules with an instantaneous Poster 7: Structural Dynamics in Molecules with** X-ray Spectroscopy and Simulations, presented (experiment and simulation), it is evident that the main  $\mathbf{b}$  and simulation), it is evident and simulation  $\mathbf{c}$ part of the emitted protons is distributed at angles around show the absolute momenta of the two protons. Whereas KER for the three fragments. (c) Newton diagrams (experiment and the discoveriment and the discoveriment and t

**X-ray resonance-enhanced multiphoton ionization**

XATOM has been extended to include the resonance and relativistic effects. Recently it has been employed for a joint theoretical and experimental study of multiple-core-hole resonance spectroscopy of Xe atoms irradiated by ultraintense soft-x-ray pulses. With unprecedented wide tunability offered by the variablegap undulators available at the European XFEL, the photon energy is scanned over a wide range of 1 keV, while maintaining a constant 1013 photons on target. The ion yields as a function of photon energy show rich structures. XATOM reveals that they originated from resonance excitations of a broad range of precursor charge states and formation of multiple-core-hole states.

#### $XATOM$  XMOLECULE XMDYN+XPOT Conclusions  $\overline{\phantom{0}}$  $\sqrt{2}$ T. JAHNYE EV VEE AL. PHYS. REV. PHYS. REV.

We develop an x-ray molecular physics toolkit, XMOLECULE. The molecular electronic structure is solved within the HFS model with core-hole-adapted basis functions calculated with 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 with molecular forces, rates, and cross-sections calculated on the fly.

#### **References**

Unprecedentedly intense x-ray pulses, provided by x-ray freeelectron laser (XFEL) facilities, can create unusual, highly excited absorption of states of matter, which have not been conceivable with conventional  $\qquad \big|$ light sources. Interaction of atoms with intense XFEL pulses is  $\vert$  $rac{1}{2}$  characterized by x-ray multiphoton ionization, where complex  $\vert$ ionization dynamics are involved with a sequence of photoionization events and accompanying relaxation processes. We have developed  $\vert$ an integrated toolkit to describe x-ray-induced atomic physics,  $\vert$ XATOM, which has been a key development for interpreting and designing XFEL experiments and advancing XFEL science. In this  $\qquad \qquad \mid$ contribution, we will present an overview of XATOM, highlighting two  $\left| \right|$ recent results: the breakdown of frustrated absorption [10] and x-ray  ${\sf resonance\text{-}enhanced\; multiplication}$  [11].  $\hspace{25pt}$  $p \times q$  maniphoton romadion, where complex mics are involved with a sequence of photoionization  $\begin{bmatrix} \phantom{\alpha} \end{bmatrix}$ at longer wavelengths  $\lambda$  140 nm; reduced atomic priyers,  $\frac{1}{3}$  aluminism targets respectively interpreted the precent  $\frac{1}{3}$ will present an u  $\lceil$  Dicakdown of figure accessible profile the short-with  $\lceil$ ultra-intense, short-wavelength radiation (,10<sup>18</sup> W cm2<sup>2</sup> , ,1 nm)

> XMDYN is a computational tool to simulate dynamics of matter exposed to high intensity x-rays (main developer: Zoltan Jurek). Atomic ions and free electrons are treated as classical particles by molecular dynamics, and electron configurations are tracked using a Monte Carlo algorithm. All atomic data are calculated with XATOM. It has been extended to simulate WDM in combination with the supercell approach and periodic boundary conditions, and the plasma environmental effects such as IPD have been incorporated via XMDYN+XPOT.

#### **References**

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# **Unusual phenomena in x-ray multiphoton ionization of atoms.**

consequent Auger decay the 1s-shell vacancy is filled by a 2s,p-shell electron > First experiment of Ne: fundamental atomic physics in XFEL > Sequence of K-shell ionization (P), Auger decay (A), and fluorescence (F)

- $\frac{1}{2}$  multiplot absorption stripping the neutrinon stripping the neutrinon atom. The horizontal direction of  $\frac{1}{2}$ > Extremely complicated ionization dynamics
- $\epsilon$  Highly everted electronic structure involved > Highly excited electronic structure involved
- > No standard quantum chemistry code available



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

induced by untersection  $\mathbf{x}$  and  $\mathbf{x}$  intense below  $\mathbf{x}$ Interaction of matter with intense XFEL pulses is characterized by sequential multiphoton multiple ionization dynamics.

> dimensional interaction volume defined by a circular Gaussian FEL beam profile of 3  $\times$  3  $\times$  3  $\times$  3  $\times$  3  $\times$

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

multiphoton ionization dynamics, based on rate-equation approach, within a consistent theoretical framework of on B4C mirrors (for details, see Methods). The focal spot size was nonrelativistic quantum electrodynamics, perturbation theory, and the Hartree–Fock–Slater model. We implement an integrated toolkit, XATOM, to treat x-ray

- > **Broad, red-shifted, asymmetric** resonance profile in stark contrast to the conventional REMPI
- > It can be explained by the **various ionization pathways at lower charges** and associated decay lifetimes, rather than the bandwidth → potentially applicable to characterize FEL beam parameters.

ion charge state distributions for the photo-ionization of xenon

atoms with intense FEL pulses at photon energies of 1.5 and

1 multiphoton ionization

#### **Breakdown of frustrated absorption** if the photoionization rate exceeds that of Auger decay. For energies surements is corroborated by in situ ion-charge-state measurements, both at 800 eV, where is dependent only on fluence and fluence and fluence and fluence and fluence and fluence  $\sim$  on persont  $\sim$

 $\overline{\mathbf{p}}$  5 **Frustrated absorption or suppression of ionization** > At extremely high fluence → anti-frustrated absorption > At intermediate or high fluence ➔ frustrated absorption

 $\theta$  of a representation in  $\theta$  as a function of selected charge states  $\theta$  as a function of  $\theta$ **References**



#### Budewig *et al., Priys. Rev. A* **105**, 055 FT (2022).  $\frac{1}{2}$  Constructs for photon for  $\frac{1}{2}$ . Measurements for  $\frac{1}{2}$  $2.0$  keV ( $2.0$  keV  $R_{\text{max}}$   $R_{\text{max}}$   $R_{\text{max}}$   $R_{\text{max}}$   $R_{\text{max}}$   $R_{\text{max}}$  (80 for  $(0.040)$ )  $\mathcal{L}_1$  con  $\alpha$  called,  $\mathcal{L}_1$  hyd. Nov. A co,  $\cos \theta$  (2012). [3] Rudek *et al., Nature Photon.* **6**, 858 (2012).<br>[4] Rudek et al., *Phys. Rey. A* 87, 023413 (2013). [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] Son, Boll & Santra, *Phys. Rev. Res.* **2**, 023053 (2020). [1] Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011). [2] Son & Santra, *Phys. Rev. A* **85**, 063415 (2012). [11] LaForge *et al.*, *Phys. Rev. Lett.* **127**, 213202 (2021).

#### ation of precedented in the state states at 1.5 keV is  $\epsilon$  and  $\epsilon$  are to a transient resonance-enhanced absorption  $\epsilon$ Comparison b/w theory and experiment Refield **Ref. [11]**

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

 $\times$  Xe<sup>6+</sup>  $Xe^{10+}$  $Xe^{15+}$  $\times e^{20+}$ •  $Xe^{25+}$ •  $Xe^{26+}$ •  $Xe^{28+}$ 

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

by the LCLS Free-Electron Laser1

mirrors to an estimated 3 <sup>×</sup> <sup>3</sup> <sup>m</sup>m2 (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.

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

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 "<sup>1</sup> <sup>×</sup> <sup>10</sup><sup>17</sup> W cm2<sup>2</sup> and the

maximum fluence "<sup>90</sup> <sup>m</sup><sup>J</sup> <sup>m</sup>m2<sup>2</sup>

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.

pressure of 2 <sup>×</sup> <sup>10</sup>2<sup>10</sup> mbar, a thin supersonic jet of xenon atoms with an

 $T$ ocalculate the response of the  $\mathcal{L}_\text{L}$ 

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 mm along the beam direction. After a flight distance of 21 cm from the interaction point, the ions produced by the interaction of the FEL pulse with the gas target were (post-)accelerated to 2.45 keV for the detection on a V-stack microchannel plate (MCP) detector. The MCP signal trace was recorded for each FEL shot with an Acqiris DC282 digitizer, and each ion hit was identified in post-analysis using a software constant fraction discriminator such that the effect of pulse height variations due to varying MCP efficiency for



1 10

 $\overline{1}$  |  $\overline{1}$ 





**Multiphoton multiple ionization mechanism**



- > Calculation with 10-fs matches well with experimental data.
- > The predicted pulse-length dependence cannot be explained by ordinary REMPI, because the same bandwidth is applied and AC Stark shift is negligible in the x-ray regime.
- 

**Ref. [3]**

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**Poster 27**: Multiple-core-hole resonance spectroscopy with ultraintense X-ray pulses, presented by **Aljoscha Rörig**

about 115°, which is close to what one would expect from what one would expect from an immediate Coulomb explosion taking place in almost place in almost place in almost place in almost place in<br>The coulomb explosion taking place in almost place in almost place in almost place in all the coulomb explosion

**Talk in Session 5 (Wed. at 11:20)**: Plasma environmental effects in the atomic structure for simulating XFEL-heated solid-density matter, presented by **Rui Jin**

-5

-4

-3

-2

-1

0

Orbital energy (keV)

## **Ionization pathways of Ar**



## **Experiment: European XFEL**

> Small Quantum System (SQS) scientific instrument > Pulse length: 25 fs FWHM (nominal) / focal size: approx. 1.5×1.5 µm2 (FWHM) / pulse energy: 2~6 mJ

> Photon energy: 1450~1583 eV / energy bandwidth: approx. 1% (FWHM) / second harmonic contrib.: est. 0.2~0.6%





### **Analyzing resonant processes**

- > Add and subtract processes in calculations
- > Dominant process: resonant excitation by 2nd harmonic at Ar14+ (more precisely, *K*2*L*2*Mm* for 0≤*m*≤8)

# $\blacksquare$

 $10^{-3}$ 

de xield<br>5<br>10<sup>-2</sup>

 $10^{-1}$ 





0.2 1 10 100 1000 10000 100 000

Pulse duration (fs)

10-3

0 5 10 15 20 25 30 35 40 45

Charge state

(b) peak fluence=2 $\times$ 10<sup>12</sup> ph/ $\mu$ m<sup>2</sup>

 $\frac{1}{2}$ 

1 fs  $\rightarrow$ 10 fs  $\overline{\phantom{0}}$ 100 fs  $-$ 

 $\frac{1}{2}$ 

(a) peak fluence= $1 \times 10^{11}$  ph/ $\mu$ m<sup>2</sup>

**Ionization pathway at different pulse lengths** cession with a well-known cross-section calibration as a reliable calibration of the second serves as a reliable calibration of the second serves as a reliable calibration of the second serves as a reliable calibration of > A short pulse facilitates multiple-core-hole formation > Detour of ionization barrier makes a higher charge state

> most of the proton momenta are clearly correlated, i.e., they show similar absolute values, a significant fraction of proton



coincidence, where the oxygen momentum defines the x axis, for the full KER range. On the left, the employed momentum coordinate

color shadings.



#### Dissociation dynamics of H<sub>2</sub>O imaged in coincident ion momenta



0 5 10 15 20 25 30 35 40 45

Charge state



# **Ref. [10]**

Figure 20 of 2a shows the distribution of Xe at 1200 eV **Charge-state distribution of Xe at 1200 eV.** 



#### **Photon-energy-dependent Xe charge-state distribution**