



With SCSS EUVFEL at SPring-8, **FLASH and LCLS**

- We have been investigating multiple ionization of atoms, molecules and clusters
- We are trying to establish time-resolved spectroscopy

For SACLA XFEL at SPring-8

Targets: biomolecule undergoing structural change We are preparing to make molecular movies nano-crystal undergoing phase change

SACLA XFEL (lased on 7 June!)







RIKEN





SCSS test accelerator : EUV-FEL (20-24 eV)



Multiple ionization of rare gas clusters: with M. Yao's group Electron spectroscopy with VMI: with M. Vrakking's group EUV-pump EUV-probe: with J. Ullrich's group

Outline and summary 1. Introduction
Towards the molecular movie with XFEL
2. Two photon single ionization of He atom Autocorrelation measurements
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3. Multiple ionization of rare gas clusters
Frustration of cluster ionization Electronic decav of multiply excited clusters
Charge transfer
Time dependent Mie plasmon in clusters
4. Double core hole spectroscopy Ab initio study and measurements at LCLS
5. Planned commissioning experiments at SACLA

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C.D. Schroter, J. Ullrich, O. Herrwerth, M.F. Kling, X.-J. Liu, K. Motomura, H. Fukuzawa, A. Yamada, K. Ueda, K. L. Ishikawa, K. Nagaya, H. Iwayama, A. Sugishima, Y. Mizoguchi, S. Yase, Yao, N. Saito, A. Belkacem, M. Nagasono, A. Higashiya, M. Yabashi, T. Ishikawa, R. Moshammer, Th. Pfeifer, A. Rudenko, Y.H. Jiang, L. Foucar, M. Kurka, K.U. Kuhnel, H. Ohashi, H. Kimura, and T. Togashi





accepted for publication in Optics Express.



SCSS Sample Pulse Shapes

 Interence Between the wo-Photon Ionization I. Fukuzawa, A. Yamada, uchi, M. Yao, A. Rouzee, sson, M. Nagasono, K. Tono, bashi, and T. Ishikawa 	FEL Velocity Map Imaging (VMI) spectroscopy (VMI) spectroscopy (MCP + Phosphor camera
Experimental Evidence for Inte Resonant and Non-resonant T R. Ma, K.L. Ishikawa, K. Motomura, H K. Ueda, K. Nagaya, S. Yase, Y. Mizogi A. Hundermark, M. Vrakking, P. John T. Togashi, Y. Senba, H. Ohashi, M. Ya	Photoelectron angular distribution for two-photon single ionization of He Direct numerical simulation of the two-electron time-dependent vs Schrödinger equation (TDSE)



W. F. Chan et al., Phys. Rev. A 44, 186 (1991)



Photoelectron angular distribution for two-photon ionization of He

Ma et al. to be submitted.

1											
	(θ)	and the second					δ (TDSE)	1.6	1.7	1.6	2.8
ion (PAD)	$+ \beta_4 P_4 (cc$					31401(R) (2009).	ð (exper)	1.6	1.7	1.7	2.5
ılar distribut	$_2P_2(\cos heta)$	ers	2			, Phys. Rev. A 79, 0	X (TDSE)	0.3	2.0	1.2	0.6
ectron angu	$\frac{\sigma}{4\pi} \left[1 + \beta\right]$	opy paramet	$= \frac{2/7 - X \cos^2 x}{2}$	$X^{2}/4 + 1/($	$X = c_s/c $	J. L.H. Haber, et al.	X (exper)	0.5	2.0	0.8	1.3
Photoel	$I(\theta) =$	Anisotr	<i>ين</i> ا	1		Ŭ.	hv	20.3	21.3	23.0	24.3

Deviation of wavepacket phase difference from eigen phase shift difference



Photoelectron angular distribution (PAD)

$$I(\theta) = \frac{\sigma}{4\pi} \left[1 + \beta_2 P_2(\cos\theta) + \beta_4 P_4(\cos\theta) \right] \xrightarrow{s} p \frac{d}{4\pi}$$

Anisotropy parameters

$$\beta_2 = \frac{2/7 - X\cos\delta}{X^2/4 + 1/5} \quad \beta_4 = \frac{72}{35} \left(X^2 + \frac{4}{5} \right)^{-1}$$

$$Cf. L.H. Haber, et al., Phys. Rev. A 79, 031401(R) (2009).$$

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$$Cf. L.H. Haber, et al., Phys. Rev. A 79, 031401(R) (2009).$$

$$Cf. L.H. Hab$$

depends on competition between non-resonant and resonant paths, then on pulse width (T)

as atoms irradiated by EUV r pulses at 51 nm	il, A. Rudenko, H. Fukuzawa, L. Foucar, J. Kühnel, G. Prümper, P. Labropoulos, ikami, M. Yao , A. Belkacem, R. Feifel, H. Ohashi, and H. Kimura, M. Yabashi, shikawa	hen at 141 def - 30 bills
Multiple ionization of rare ga	 MKurka, K. Motomura, K. Papamihai H. Iwayama, K. Nagaya, XJ. Liu, HU J. Ullrich, K. Ueda, N. Saito, H. Mura M. Nagasono, A. Higashiya, T. Togashi, and T. I. 	Ne th yield

y EUV		Foucar, poulos,	Feifel, Yabashi,				<u>R</u>		80000	
diated b	1 nm	ukuzawa, L. J ver, P. Labro	elkacem, R. J Kimura, M.		Ar Ar	 			60000	ight (ns)
oms irra	ses at 5	idenko, H. Fi el, G. Prümp	M. Yao , A. B ashi, and H.	a	Al ³⁺ At 2+		A 1 1 1 1 1 1 1 1 1 1	Kr st	40000	Time-of-fl
re gas at	laser pul	amihail,A. Ru ı, HU. Kühn	. Murakami, I gashi, H. Oh	id T. Ishika w	$\begin{array}{c} \begin{array}{c} +0\\ 20\\ -20\\ -20\\ \end{array} \end{array} \right) \xrightarrow{4}{} \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \end{array}$	-40 - Ar ⁵⁺ Ar ⁴ -40	20-1 0-1	$-20 - \frac{\mathbf{Kr}^{*}}{-40} + \frac{\mathbf{Kr}^{7+}}{\mathbf{Kr}^{7+}}$	20000	
fra	UO.	Papa J. Lin	to, H T. To	an	ctor (mm)	n at dete	Position			
Multiple ionization of	free-electr	MKurka, K. Motomura, K. H. Iwayama, K. Nagaya, X	J. Ullrich, K. Ueda, N. Sai M. Nagasono, A. Higashiya, ⁷		Ar ⁷⁺ > 434 eV > 18 photons	Kr ⁸⁺ > 508 eV	> 21 photons	Mirror: Mg/Si multilayer	f=250 mm,	made by LBNL

of sequential three-photon double by EUV free-electron laser pulses	ra, A Yamada, K Ueda , A N Grum-Grzhimailo , 1, Y Mizoguchi, H Iwayama, M Yao , N Saito, 50reno, M Nagasono, K Tono, M Yabashi, 1 Kimura, T Togashi, and Y Senba	Ar ²⁺ production by resonant two-photon ionization of Ar ⁺	$Ar^{+}(3p^{4}(^{3}P)6s {}^{2}P_{3/2,1/2}) + hv \rightarrow Ar^{2+}(3p^{4} {}^{3}P_{2,1,0}) + e^{-}(21.2 eV)$	$\int_{-1}^{1} Ar^{+}(3p^{4}({}^{1}D)4d {}^{2}P_{3/2,1/2}) + hv \rightarrow$ $\int_{-1}^{1} Ar^{2+}(3p^{4} {}^{1}D_{2}) + e^{-}(19.5 eV)$	$I(\theta) \sim I + \beta_2 P_2(\cos \theta)$ $\pm R D I \cos \theta + R D I \cos \theta$	$(n \sin^2 \theta)^2 J^2 d_\perp$ (n $\sin^2 \theta)^2 J^2 d_\perp$	JPB 42, 111001 (2009).
Photoelectron spectroscopy ionization of Ar irradiated b	H Fukuzawa, E V Gryzlova, K Motomun S I Strakhova, K Nagaya,A Sugishima P Piseri, T Mazza, M Devetta, M C T Ishikawa , H Ohashi, H	1.0 0° (a)	eso (sin	u. due ou	10- 	0.5	0.0 18 19 20 21 22 23 Electron kinetic energy (eV)







Mechanism of two-photon ionization





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Cold pulsed cluster source



Pulse valve is equipped with liquid He cooling unit. Temperature of cluster source is controlled in the range of 10-300K.

Pulsed cluster beam is coincided with FEL pulses.

K. Nagaya, H. Iwayama, H. Murakami, **M. Yao**, H. Fukuzawa, K. Motomura, K. Ueda et al, J. Electr. Spectrosc. Relat. Phenom. 181, 125-128 (2010).





beam are exposed to

Cold Unit (Oxford Instruments Corp.)

cooled by liq.N₂ or liq.He.

fast electro-magnetic valve (min. pulse width : 0.2ms)

Pulse Valve Series99 (Parker Instrumentation Corp.)



Frustration of the cluster ionization

lonization energy of atomic Xe (12.13 eV) < 20 eV







cf: *Bostedt et al.*, *PRL 100*, *133401 (2008)*. Detection efficiencies of electron Continuous electron emission is dependence of beta parameter. N Saito, P Piseri, T Mazza, M Devetta, K Nagaya, A Sugishima, Y Mizoguchi, frustration of cluster ionization! detectors are calibrated using M Yabashi, **T Ishikawa**, H Ohashi, H Kimura,T Togashi, and Y Senba H Iwayama, M Yao, H Fukuzawa, K Motomura, A Yamada, **K Ueda**, M Coreno, M Nagasono, K Tono, decrease in kinetic energy! Beta values decrease with We evaluated the energy observed as evidence of data of atomic xenon. To be submitted.

tion in neon clusters at free electron laser	i, M. Yao , H. Fukuzawa, oucar, A. Rudenko, er, R. Feifel, M. Nagasono, . Kimura, and H. Ohashi	Analvzer	G		<u>5</u>		EUV-FEL	超音速	Cluster beam
Electronic decay following multiple excita exposed to an intense extreme ultraviole	 K. Nagaya, A. Sugishima, H. Iwayama, H. Murakam XJ. Liu, K. Motomura, K. Ueda, N. Saito, L. F. M. Kurka, KU. Kuhnel, J. Ullrich, A. Czasch, R. Dorn, A. Higashiya, M. Yabashi, T. Ishikawa, T. Togashi, H 	(To be submitted)	Target: Ne clusters (<n>=1000)</n>	We have measured FEL power depent Detection of ions on vields	3D momentum imaging:	Time-of-Flight T, 2D detection position (X,Y) $T \propto \sqrt{m/a}$ $D_{X} = m\frac{X}{2}$ $D_{X} = m\frac{Y}{2}$ $D = -aEAT$	"Dead time free" detection with wide	acceptance angle	

Linear FEL power dependence of energetic Ne⁺ yields



We analyzed kinetic energy distributions of energetic atomic ions using spherical uniform cluster analytical model (Islam et al PRA 73, 041201(R) 2006).

We found ~ 100 photons are absorbed and ~ 50 electrons are emitted.



We found linear FEL-power dependence of energetic Ne⁺ yields ejected from clusters (<N>=1000), in sharp contract with quadratic FEL-power dependence of Ne⁺ yields from the atomic beam.

Electronic decay !

с, НМ



charge redistribution in Xe clusters exposed se extreme ultraviolet free electron laser	ishima, K. Nagaya, M. Yao, H. Fukuzawa, K. Motomura, la, C. Wang, K. Ueda, N. Saito, M. Nagasono, K. Tono, 7. Ishikawa, H. Ohashi, H. Kimura, and T. Togashi B: At. Mol. Opt. Phys. 43 , 161001 (2010).	Xe clusters (<n>=2000, 10000, 50000)</n>	red kinetic energy distribution of the daughter r irradiation of the FEL pulse at 52nm.	(c) < N > -2000	V Distribution of Xe ²⁺ has a hollow distribution.
Inhomogeneous to an inten	H. Iwayama, A. Sug XJ. Liu, A. Yama M. Yabashi, J. Phys	Target:	We have measu ions ejected afte	ions per shot	Kinetic Energ



 Charge and Energy Transfers in Ar core-Ne shell clusters irradiated by Free Electron Laser Pulses at 62 nm A. Sugishima, H. Iwayama, S. Yase, H. Murakami, K. Nagaya, M. Yao, H. Fukuzawa, XJ. Liu, K. Motomura, K. Ueda, N. Saito, L. Foucar, A. Rudenko, M. Kurka, KU. Kuhnel, J. Ullrich, A. Czasch, R. Dorner, R. Feifel, M. Nagasono, A. Higashiya, M. Yabashi, T. Ishikawa, T. Togashi, H. Kimura, and H. Ohashi (submitted) 	Target: Ar core- Ne shell clusters (<n>=1000)</n>	We have measured kinetic energy distributions of Ne ⁺ and Ar ⁺ ions ejected from Ar core- Ne shell clusters irradiated by the FEL pulse at 62 nm, i.e., below the Ne ionization threshold and found charge and energy transfer from Ar core to Ne shell.
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X-ray two photon photoelectron spectroscopy



hole electron spectroscop	nical analysis	zawa, K. Ueda, C. Buth, N. V. Kryzhevoi	. S. Cederbaum	's. 132, 184302 (2010).	$\stackrel{16}{=} \frac{16}{i \neq j} (two sites) \stackrel{co}{\bullet}$		$AE2 \begin{pmatrix} e^{\sqrt{-1}} \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\$	6 ² H ⁶ C ₂ H ⁶ C ₂ H ⁴ (C-0)	10 0.2 0.3 0.4 0.5	hotoelectron spectroscopy	Z^{m} step) = $DIF(u,j)$ - $[IF(u)+IF(j)]$	n, we made the LCLS beam time proposal
Molecular double core	for cher	M. Tashiro, M. Ehara, H. Fukuz	and L.	J. Chem. Phy	i=j (one site)	100- C2H ₆ C2H ₆ LiF C2H ₄ N2O ●		50 - LiF • CO 40 - •	30 1 1 1 1 1 1 1 1 1 1 1 1 2 3 4 5 6 7 8 9 4 4 5 6 7 8 9	X-ray two-photon pl	Probing change of electron density	Based on this theoretical prediction

Double core hole creation and subsequent Auger
decay in NH ₃ and CH ₄ molecules
J. H. D. Eland, M. Tashiro, P. Linusson, M. Ehara, K. Ueda, and R. Feifel
Phys. Rev. Lett. 132, 184302 (2010).
The measured energies of double core hole states in NH ₃ and CH ₄
nave peen reproduced accurately by the CASSUF calculations.
^(a) CH ₄ C 1S ⁻² CV
Doincide
850 870 890 910 930 950 10 10 10 10 10 10 10 10 10 10 10 10 10
Ionization energy hv- (E1+E2+E3) (eV)
The measured Auger spectrum in NH ₃ has been reproduced well by the
calculations in which Auger rates are evaluated by the overlap integral.
M. Tashiro, K. Ueda, and M. Ehara, submitted

Molecular double core hole spectroscopy at LCLS
M. Larsson , P. van der Meulen, P. Salen, H. T. Schmidt, R.D. Thomas, R. Feifel, M.N. Piancastelli (Sweden)
K.C. Prince, R. Richter, F. Tarantelli (Italy)
K. Ueda, M. Tashiro, M. Ehara (Japan)
N. Berrah, Li Fang, T. Osipov, B. Murphy, P. Juranic, E. Kukk (USA)
J. D. Bozek, C. Bostedt, S. Wada (LCLS)
We have measured double core hole photo-electron spectra and Auger electron spectra of N ₂ , CO, N ₂ O, and CO ₂ . We have calculated Auger spectra of these molecules as well. The first paper on CO (Berrah et al) PNAS printed on line. The second paper on all other molecules submitted to PRL.

X-ray two photon photoelectron spectroscopy on CO

Electron spectra were recorded at focusing and defocusing conditions and the difference spectrum was obtained.



Both one-site and two-site double core hole states are identified at energies closed to predictions by ab initio calculations.





nce ionized Double core hole Auger spectroscopy 480 e **e**⊜⁶ Auger electron kinetic energy (eV) 440 400 360 Éxpt. DCH→CVV CVV→VVVV SCH→VV 320 Example: NH₃ DCH decay 280 0 0.4 0.3 <u>א</u> 0 0.1 Intensity (arb. unit) 3a₁ 1e 2a₁(2s $1a_{\eta}(1s$

M. Tashiro, K. ueda, and M. Ehara, JCP accepted



Auger spectra of CO DCH decays



N. Berrah, L. Fang, T. Osipov, B. Murphy, K. Ueda, E. Kukk, R. Feifel, P. van der Meulen, P. Salen, H. Schmidt, R. Thomas, M. Larsson, R. Richter, K. C. Prince, J. D. Bozek, C. Bostedt, S. Wada, M. Piancastelli, M. Tashiro, M. Ehara, PNAS . 108, 16912 (2011).

M. Tashiro, K. ueda, and M. Ehara, JCP accepted

Disentangling formation and decay of molecular two-site double-core-hole states
Feifel et al: Proposal for use of a new magnetic bottle electron spectrometer and a covariance technique
Two-core-hole spectroscopy of biomolecules
Prince et al: Proposal for applying the above DCH electron spectroscopy to biomolecules (formamide and uracil)
Aug. 25- Sep. 6, 2011
R. Feifel et al.(Sweden), J.H.D. Eland and L. Frasinski (UK) K.C. Prince, L. Avaldi, F. Tarantelli et al(Italy)
K. Ueda, S. Wada, O. Takahashi, M. Tashiro, M. Ehara et al (Japan)
J. Ullrich, L. Faucar et al (Germany)
N. Berrah et al (USA)
J.D. Bozek, C. Bostedt et al (LCLS) , and more

Theoretical double core hole spectroscopy on DNA base





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Molecular Movie:

Coherent diffractive imaging of a single particle combined with coulomb explosion imaging and electron diffraction imaging Ion detector





Rare gas clusters will meet the intense x-ray pulses for the first time!





We found it for EUVFEL pulses

What will happen for

XFEL pulses?

Single shot imaging of micro-clusters....

SACLA commissioning experiments in February 2012

Single shot imaging of protein nano-crystals



Radiation damage for hard x-rays

