Atomic and Molecular Physics at SACLA

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Introduction of myself

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Institute of multidisciplinary research for advanced materials
Leading
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Atomic and molecular science using Synchrotron Radiation
Ueda, JPB 36, R1 (2003);
Ueda & Eland, JPB 38, S839 (2005);
Ueda, JPSJ 75, 032001 (2006);

Application of the SR-based experimental techniques to laser experiments
(femtosecond laser and FEL)
Outline

Introduction to XFEL science

Introduction to SACLA

Atomic and Molecular Physics at SACLA
– Deep inner-shell multi-photon ionization of Ar and Xe atoms
– Photoion-photoion coincidence imaging following deep inner-shell multi-photon ionization of CH3I and 5I-uracil
– Electron spectroscopy on cold nanoplasma formation from argon, krypton and xenon clusters
– Single-shot imaging of xenon nano-clusters
– IR-probe experiment of XFEL-ignited nanoplasma dynamics

Summary and outlook
EUV-X FELs in the world

European XFEL will start operation in 2017
FLASH in operation since 2005
LCLS in operation since 2009
SACLA in operation since March 2012
SCSS+ will start operation in 2016
SCSS test accelerator in operation since 2008; closed down in 2013

FERMI starts operation in December 2012!

Swiss FEL (2017), Korean FEL, Shanghai FEL, etc., are coming!

European XFEL will start operation in 2017
Characteristic properties of FEL pulses

Coherent, intense, and ultra-short pulses at short wavelengths (EUV to X–rays)

Coherent X-ray imaging of non-crystalized samples

Gösta Huldt, Abraham Szöke, Janos Hajdu (J.Struct Biol, 2003 02-ERD-047)

Before

During ~10 fs

After ~50 fs


Single Mimivirus Particles Intercepted and Imaged with an X-ray laser

Coherent X-ray imaging of non-crystalized samples

Three-Dimensional Reconstruction of the Giant Mimivirus Particle with an X-Ray Free-Electron Laser

Can we get 3D image from a single shot data?

In principle, “Yes” but in practice....
Characteristic properties of FEL pulses

Intense and ultra-short pulses at X−rays

Why X-rays? structure determination at atomic resolution


Native structure of photosystem II at 1.95 Å resolution revealed by a femtosecond X-ray laser (SACLA)


"Determination of damage-free crystal structure of an X-ray sensitive protein using an XFEL"
Nature Methods (2014), doi:10.1038/NMETH.2962

SR results (Nature 2011) had radiation damage….
Dynamic behavior of photo-system II

"The Mn₄Ca photosynthetic water-oxidation catalyst studied by simultaneous X-ray spectroscopy and crystallography using an X-ray free-electron laser"
Rosalie Tran et al

"Taking snapshots of photosynthetic water oxidation using femtosecond X-ray diffraction and spectroscopy"
Jan Kern et al
Nature Comm. 5. 4371 (2014)

doi:10.1038/nature13453

"Serial time-resolved crystallography of photosystem II using a femtosecond X-ray laser"
C. Kupitz et al
Nature (2014)
doi:10.1038/nature13991

Towards artificial photosynthesis

Visualizing the non-equilibrium dynamics of photo-induced intramolecular electron transfer with femtosecond X-ray Pulses (SACLA)  Canton et al. Nature Comm. 6, 6359 (2015)

e dissipation  structural change

e transfer (Co IV -> Co III)
Characteristic properties of FEL pulses

**Intense**  $10^{14}$ W/cm$^2$ (EUV) - $10^{20}$ W/cm$^2$ (X)

One LCLS pulse at 2 keV can remove all ten electrons from the neon atom.

The pulse is so intense that it causes electronic damage to the sample.

Femtosecond electronic response of atoms to ultra-intense x-rays

L. Young et al., Nature **466**, 56 (2010).
Non-linear X-ray atomic Physics

Ultra-Efficient Ionization of Heavy Atoms by Intense X-Rays

Nature Photonics 6, 858 (2012).
X-ray induced Coulomb explosion

Femtosecond X-ray-induced explosion of \( \text{C}_6\text{O} \) at extreme intensity \( (hv=485 \text{ eV}) \)

Charge state distributions

Kinetic energy distributions

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Summary and outlook
SACLA XFEL (lased on 7 June 2011)
Photon energy range: 4-20 keV
Photon numbers: $\sim 10^{11}$ photons/pulse (5-15 keV)
Repetition rate: 10~30~60 Hz  
Pulse width $\sim 10$ fs
Focusing optics: $\sim 1$ µm (1.5 m) $\rightarrow$ 50 nm (0.5 m)

Commissioning beam time: Nov. 2011-Feb. 2012

7-11 Nov. 2011: Detector test (no real FEL beam...)

......

20-24 Feb. 2012: Serial femtosecond crystallography

User beam time started in March 2012
Phasing of the serial femtosecond x-ray crystallography had been relying on molecular replacements…

If the structure is completely unknown, phasing approaches make use of anomalous dispersion in the scattering signals from specific atoms.

Anomalous signal from S atoms in protein crystallographic data from an X-ray free-electron laser

T.R.M. Barends, L. Foucar, R.L. Shoeman, …. K. Ueda and I. Schlichting


One of the first experiments at SACLA

For phasing with a heavy atom, one has to take account of high x-ray intensity

Multi-wavelength anomalous diffraction at high X-ray intensity


However…..

De novo protein crystal structure determination from X-ray free-electron laser data


Conventional phasing method based on anomalous dispersion worked…..
What should we do with SACLA?

Novel structure determination

- phasing
- radiation damage

understanding dynamic behavior of heavy atoms!

Dynamic structure and light-induced reaction
- Femtosecond electronic and structure changes

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Summary and outlook
Multi-photon, multiple ionization of Atoms, Molecules and Rare-gas clusters

Single-shot imaging of Nano-clusters

Pump-probe experiments for Atoms, Molecules and Rare-gas clusters

Aiming at probing Ultrafast electron and structure dynamics
SACLA atomic & molecular beam times

First two beam times in 2012: Atoms, molecules and atomic clusters

Third beam time in 2013: pump-probe, failed

Fourth beam time in 2014: Single-short imaging of giant xenon clusters

Fifth and sixth beam times in 2014: Pump-probe experiment on clusters

Seventh beam time in 2015: pump-probe, failed
Experimental configuration @ SACLA BL3 EH3

XFEL pulses

**Photon energy**: 5 and 5.5 keV  
(Wavelength: 0.25 and 0.22 nm)

**Band width**: ~60 eV (FWHM)

**Repetition**: 10-30 Hz

**Pulse energy before KB mirror**: ~240 μJ (~3 × 10^{11} photons) @5.5keV

**Fluctuation of pulse energy**: ±25% (50% FWHM)

@Focus point

**Focus size**: ~1.5 μm (FWHM)

**Peak fluence**:  
~47 μJ/μm^2 (atoms, clusters),  
~26 μJ/μm^2 (molecules)

Sample gas was introduced as a pulsed super sonic gas jet to the focus point.
I. Deep inner-shell multiphoton absorption by intense x-ray free-electron laser pulses

Time of Flight spectrum of argon ions

KL_{23}L_{23} \rightarrow 2L_{23}MM

Ar jet

Ar @ 5.5 keV

Intensity (arb. units)

Time-Of-Flight (ns)
In the theory, the pulse shape of Gaussian of 30 fs (FWHM), and Gaussian focal shape of 1 μm (FWHM) × 1 μm (FWHM) are assumed.
By comparison with theory, we obtained peak fluence of 50 μJ/μm² in the experiment!
Time of Flight spectrum of xenon ions

5.5 keV, 50 μJ/μm² at SACLA

High charge states Xe^{n+} with n up to 26 are produced!

2D position resolved TOF improves the resolution!
With help of ab initio calculations, we find that the observed high charge states ($n \geq 24$) are produced via five-photon absorption, evidencing the occurrence of multiphoton absorption involving deep inner shells.
A newly developed theoretical model shows good agreement with the experiment!
A newly developed theoretical model elucidates the complex pathways of sequential electronic decay cascades accessible in heavy atoms, revealing that L shell ionization and sequential electronic decay cycles are repeated multiple times within the XFEL pulse duration of ~10 fs.

Fukuzawa, Son et al. PRL 110, 173005 (2013)
Radio-sensitizer  Anomalous X-ray scattering

5Br-Uracil

5I-Uracil

Relevance to other fields: Radiation damage

Multiwavelength anomalous diffraction at high X-ray intensity

II. Charge transfer and molecular dissociation following deep inner-shell multi-photon multiple ionization of CH$_3$I and 5-Uracil molecules by intense x-ray free-electron laser pulses from SACLA


in preparation
We expect that the ionization proceeds with this sequence.

**Selective ionization of iodine L-shell**

**Production of highly charged iodine ion by Auger cascades**

**Charge transfer from iodine**

**XFEL (5.5keV)**

**Coulomb explosion**

**Next photon absorption**

*We tried to understand these processes by measuring momentum of ion fragments.*
Iodomethane: Charge distribution

Momentum conservation: \[ P(H_1) + P(H_2) + P(H_3) + P(C) + P(I) = 0 \]

Ion yields (a.u. unit)

Time of Flight (ns)

Iodine charge state

Yield (counts)

I\textsuperscript{15+} + C\textsuperscript{4+} + 3H\textsuperscript{+} \rightarrow (CH_3I)^{22+}
**Dashed line:** Simulation with instant charge build up and transfer within the intact molecule; the charges are arranged before the Coulomb explosion starts.

The results of the simulation do not agree with the experimental results. Dissociation may compete with the charge buildup and transfer.
We introduced two parameters “τ” and “R”.

**Charge build up in a molecule.**

\[ Q_{\text{total}}(t) = Q \left( 1 - e^{-\frac{t}{\tau}} \right) \]

**Charge transfer from iodine**

\[ \frac{dQ_{\text{CH}_3}(t)}{dt} = R \times Q_I(t) \]

**XFEL**

XFEL ionizes iodine L-shell

**Time constant: τ**

Next photon absorption

**Transfer rate: R**

Coulomb explosion
Comparison with charge build up and transfer model

**Charge state dependence** for the momentum of carbon ions

**Ratio of the momentum of carbon ions and iodine ions**

**Solid line:** Simulation with charge build up and transfer  
**Dashed line:** Simulation with Instant charge buildup and transfer

Using the parameters $\tau = 9 \text{ fs}$ and $R = 0.37 \text{ fs}^{-1}$, the simulations agree with experimental results.  
$\tau$ of 9 fs is consistent with the results of atomic xenon results and roughly the same as the XFEL pulse width ($\sim 10$ fs).
We obtained the experimental data similar to CH$_3$I and analyzed them employing a charge-build up and transfer model. Using the parameters $\tau \sim 10$ fs and $R \sim 0.5$ fs$^{-1}$, the simulations agree with experimental results. These numbers are almost the same as those for CH$_3$I.
III. Efficient Nanoplasma Formation from Argon Clusters Irradiated by the Hard X-ray Free Electron Laser

Nanoplasma formation by intense laser irradiation

Laser irradiation into cluster

Many atoms in the cluster are ionized

Nanoplasma is formed when the electrons ejected from atoms trapped by the Coulomb potential of the multiply charged cluster ion.

Is nanoplasma also formed by intense hard x-ray pulse irradiation?

How is nanoplasma formed?
A plateau in the spectra is produced by the deceleration of the electrons. With the increase of the cluster size, a stronger potential builds up, decelerating the emitted electrons more.

The strong peak at zero kinetic energy is due to the thermal emission from nanoplasma.

During the XFEL pulse, only the plateau is formed. The main peak at 0 eV develops after the XFEL pulse when the ionic system has started to expand and let some of trapped electrons escape from nanoplasma.

Electron spectra of $\text{Ar}_{1000}$ in the whole region

Photon energy: 5 keV
Ar K edge: 3.2 keV

Photo electron
Auger electron

Ejected electrons are decelerated ~500 eV

The majority of trapped electrons are created by impact ionizations caused by low-energy Auger and secondary electrons.

IV. Single-shot imaging of giant Xe clusters with X-ray free-electron laser (5.5 keV)


Diameter: 250nm ~1.1 \times 10^8 \text{ atoms}

FEL fluence: \sim 10 \mu J/\mu m^2
V. Real-time study on the ultrafast plasmon resonance heating of nanoplasma produced by the XFEL irradiation to rare gas clusters at SACLA

(in preparation)
Dynamics of nanoplasma produced by XFEL

- Photoionization
- Auger cascades
- Nanoplasma formation

XFEL pulse

Coulomb potential of the charged cluster

Electrons

Xe clusters

\(<N> \sim 5000 \text{ at SACLA}

XFEL: 5.5 keV, 16 \mu J/\mu m^2

Thermal emission from nanoplasma

Intensity (arb. units)

Electron Kinetic Energy (eV)
To search the plasmon resonance heating

**Photoionization Auger cascades**

**Nanoplasma formation**

**Coulomb explosion**

Surface-plasma frequency

\[ \Omega_t \propto \sqrt{\frac{N_t Z_t}{R_t^3}} = \frac{\omega_{pl}}{\sqrt{3}} \]

Plasmon Resonance Heating

Laser frequency

Time \( t \) \( t_c \)
**Experimental setups**

- **XFEL @ SACLA**
  - Photon energy: 5.5 keV
  - Spectral width: ~33 eV (FWHM)
  - Repetition rate: 30 Hz
  - Pulse duration: <10 fs
  - Focused beam size: ~1 μm
  - Peak intensity: ~3.28 / 3.38 x 10^{16} W/cm^2

- **NIR laser**
  - Wavelength: 800 nm
  - Repetition rate: 30 Hz
  - Pulse duration: 80 fs
  - Focused beam size: ~200 μm
  - Intensity: ~2.7 / 5.1 x 10^{12} W/cm^2

- **Clusters**
  - Size of Xe clusters: ~5000 atoms
  - Nozzle diameter: ~250 μm

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Time-resolved TOF spectra of Xe clusters

XFEL: 16 μJ/μm²; NIR: 4.1 nJ/μm²

XFEL + NIR @ 1 ps delay

Xe\textsuperscript{+} (from cluster)

Xe\textsuperscript{2+}

Xe\textsuperscript{3+}

Xe\textsuperscript{4+}

Xe\textsuperscript{n+} (from atom)

Xe\textsuperscript{2+}

Xe\textsuperscript{3+}

Xe\textsuperscript{4+}

XFEL: 16 μJ/μm²; NIR: 4.1 nJ/μm²

XFEL-only

Xe\textsuperscript{2+}

Xe\textsuperscript{3+}

Xe\textsuperscript{4+}

Xe\textsuperscript{n+} (from atom)
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Summary and outlook
Summary

- Deep inner-shell multi-photon absorption of Ar and Xe atoms by SACLA XFEL pulses – Electronic damage

- Photoion-photoion coincidence imaging following deep inner-shell multi-photon absorption by SACLA XFEL pulses (CH$_3$I, 5I-uracil) – Radiation damage in the atomic level

- Electron spectroscopy of argon and xenon clusters heated by SACLA XFEL pulses – Nanoplasma formation

- Single-shot imaging of xenon nano-clusters – Influence of the electronic damage to the imaging

- IR-probe experiment of XFEL induced nanoplasma formation – Nanoplasma dynamics
What’s next…

● IR/XFEL pump – XFEL probe for I-contained molecules
  Intra-molecular charge transfer via ionic fragmentation

● X-ray imaging for UV/XFEL induced nanoplasma from giant clusters
  Influence of nanoplasma formation to X-ray imaging….

● UV pump – XFEL probe for photocatalytic molecules
  Intra-molecular charge transfer via TR X-ray spectroscopy

● Serial femtosecond X-ray crystallography
  Phasing vs radiation damage
The end

Thank you very much for your attention!