Introduction of myself

Prof. Kiyoshi Ueda

at

Tohoku University (Sendai)
Institute of multidisciplinary research for advanced materials
Leading a research group for electron and molecular dynamics

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

1. Introduction to quantum world
2. Atomic resonant photoemission spectroscopy
   - Introduction to the quantum interference
3. Vibrationally-resolved core-level photoelectron spectroscopy
   - Adiabatic approximation and Franck-Condon analysis
   - Young’s double-slit experiments
4. Multiple-ion momentum imaging
   - Snapshots of molecular deformation within a few fs
5. Electron-ion momentum imaging
   - Molecular-frame photoelectron angular distributions
6. Interatomic Coulombic decay
7. Characteristic properties of free electron lasers
8. Atomic multi-photon processes by FEL: from EUV to X

Photoelectric effect

When matter is shined by the light, electron is emitted from the surface.
(i) Frequency of the light needs to be larger than $\nu_0$.
(ii) Kinetic energy of the electron is determined by the frequency of the light.
(iii) Number of electrons is proportional to the intensity of the light.

Einstein’s explanation

Light at frequency of $\nu$ is considered to be a group of particles (photons) and each photon has energy $h\nu$. An electron gets the energy $h\nu$ when it absorb one photon.

The electron in the matter is bound. For the electron to be emitted from the matter, the electron needs to receive the energy more than the work function $W$.

Then the kinetic energy $KE$ of the emitted electron can be given as $KE = h\nu - W$. 

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(i) Frequency of the light needs to be larger than $\nu_0$.
(ii) Kinetic energy of the electron is determined by the frequency of the light.
(iii) Number of electrons is proportional to the intensity of the light.
Precision measurements for kinetic energies of photoelectrons emitted via Einstein's photoelectric effects on metal surfaces using Photoelectron spectroscopy (UPS, XPS).

- **Balmer and Rydberg formulae**
  - Balmer found beautiful regularity in the H spectrum!
  - Rydberg formula: \( \frac{1}{\lambda} = \frac{R}{n^2} \), where \( \lambda \) is wavelength, \( R \) is Rydberg constant (in m, \( R = 109737 \text{ cm}^{-1} \)).

- **De Broglie's matter wave and Bohr's model**
  - De Broglie's matter wave and Bohr's model
  - Quantization:
    - Bohr's model: \( h = \frac{\phi \phi}{d} \int_{0}^{2\pi} \phi \phi' \phi' \phi' \int_{2}^{0} \phi \phi' \)
  - Bohr's atomic model

- **Quantization**
  - Following condition of quantization:
    - Electron orbits exist only when the classical orbits satisfy the quantization condition:
      -\( n = \frac{nh}{P} = \frac{nh}{mv} \)

- **Precision measurements**
  - Precision measurements for kinetic energies of photoelectrons using Photoelectron spectroscopy (UPS, XPS).
The Schrödinger equation of the H atom (in atomic units):

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \]

**Target:** single atom or molecule; size: \( \sim 1 \) Å (= 0.1 nm = 10\(^{-10}\) m)

We use monochromatic synchrotron radiation to study atoms and molecules because a single photon should be absorbed by a single atom or molecule, as well as excite electrons and study their electronic structures as well.

**How to use synchrotron radiation to study atoms and molecules?**

- **Soft X-ray monochromator**

**Ion yield spectroscopy**

- The easiest experiment:

<table>
<thead>
<tr>
<th>Energy Resolution</th>
<th>&lt; 1.0 eV/atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photon Flux</td>
<td>&gt; ( 10^{11} ) photons/s</td>
</tr>
<tr>
<td>Energy Range</td>
<td>0.15 ~ 2.5 keV</td>
</tr>
</tbody>
</table>

**Figure-8 undulator**

- Linearly polarized light
  - Vertical polarization (0.5th)
  - Horizontal polarization (1th)

**Soft X-ray monochromator**

- Hetrick-type: varied line spacing plane grating

**SR Mol. Beam Ion detector**

**Figure-8 undulator**

**Soft X-ray monochromator**

- Energy range 0.15 ~ 2.5 keV
- Photon Flux: > \( 10^{11} \) photon/s
- Energy resolution: 10,000 ~ 20,000

**SR**

**Linearly polarized light**

- Vertical polarization (0.5th)
- Horizontal polarization (1th)

**Energy range**

<table>
<thead>
<tr>
<th>Element</th>
<th>K (L)</th>
<th>L (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>1.36</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>1.54</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>1.55</td>
</tr>
<tr>
<td>N</td>
<td>1</td>
<td>1.58</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>1.58</td>
</tr>
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</tbody>
</table>

**What photon energies to be used?**

- Electron binding energies (eV)
  - Vacuum ultraviolet light

**Experiments need to be in the vacuum!**

**Target: single atom or molecule; size: \( \sim 1 \) Å (= 0.1 nm = 10\(^{-10}\) m)

**Atomic and molecular science now**

**Schrodinger equation of H atom (in atomic units):**

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \]
Angle-resolved resonant Auger spectra of Ne at

Auger decay and Auger electron spectroscopy

Ne 1s total ion yield spectrum
Resonant Auger spectra of Ne "between" 1s -> 3p and 1s -> 4p excitations

Interference effects between the two paths

Introduction of molecular world

Born-Oppenheimer approximation
Nuclear motion is within the adiabatic potential energy surface

\[(\mathcal{R})^\mu \Phi^\mu \mathcal{F} = (\mathcal{R})^\mu \Phi [ (\mathcal{R})^\mu \mathcal{F} + \mathcal{F}] \]

\[ (\mu, \lambda) \Phi^\mu (\mu, \lambda) \Phi \mathcal{F} = (\mu, \lambda) \Phi \mathcal{F} \]

adiabatic potential energy:

\[ 0 = (\mu, \lambda) \Phi [(\mathcal{R})^\mu \mathcal{F} - \mathcal{F}] \]

\[ \lambda \Phi = 0 \]

\[ (\mu, \lambda) \Phi \mathcal{F} = (\mu, \lambda) \Phi \mathcal{F} \]

\[ H = \lambda \Phi = (\mu, \lambda) \Phi \mathcal{F} \]

Interference of molecular world

DC-10s in the Ps Rev. Lett. 93, 023006 (2002).

Doseyia Street

Statue of Load Date

Sendai City

Interference effects between the two paths

Resonant Auger spectra of Ne "between" 1s -> 3p and 1s -> 4p excitations
Franck-Condon analysis for vibrational structure

One can extract AR from photoelectron spectroscopy. 

\[ \frac{\gamma}{\gamma(R')} = \frac{(0^0)_{R'}}{(0^1)_{R'}} \]

Intensity distribution

Linear coupling model

Franck-Condon analysis based on harmonic approximation

Franck-Condon factors

Vibrational intensity distribution in the photoelectron spectrum is determined by the Franck-Condon factors:

\[ \frac{\gamma(R')}{\gamma(R)} \propto \int |(0^0)_{R'} \langle \phi_{R'}(\lambda) \rangle |^2 d \lambda \]

Assume the dipole moment of the continuum $\lambda$ does not depend on $R$.

Electronic wavefunctions of the continuum $\phi$ and core orbitals:

\[ \langle \phi_{R'}(\lambda) \rangle = \sum \phi_{R'}(\lambda) \phi_{\lambda} \]

Assume that the dipole moment $\mu(R)$ does not depend on $R$.

Franck-Condon approximation for photoionization

Stable geometry of the core-ionized state

Vibrational wavefunction in the ground state

Vibrational wavefunction in the core-ionized state

Franck-Condon factors

FC factor

\[ I < \psi_{R'}, \psi_0 > |^2 \]

Exper. Theory

C 1s-1

Re (Å) -0.051 (1) -0.051

O 1s-1

Re (Å) 0.037 (2) 0.028

Matsumoto et al.


HOMO-LUMO

Mainline

Satellite spectrum in core-level photoemission in CO

Franck-Condon analysis for the vibrational structure of the C 1s and O 1s mainlines of CO
Franck-Condon analysis of the vibrational structure in the symmetry-resolved C 1s satellite bands of CO


Ab initio potential curves
Vertical bars: ab initio FC factors
Solid lines: measured symmetry resolved spectra
Ab initio FC factors reproduce the measured vibrational distributions.

Evidence that the light is the wave!
Electrons also show interference fringes!
Evidence of the duality of waves and particles!

N(1) N(2)
Two 1s orbitals in N\(^2\) correspond to Young's double slits.

Cohen-Fano two-center interference

Two-center photoelectron wave
k: photoelectron momentum; R\(_1\), R\(_2\): position vectors of N(1) and N(2)

Interference average: Cohen-Fano formula,
\[
\frac{\gamma}{\sin \gamma} = (\gamma)_{xCP} \propto [\gamma]_{xCP} = (\gamma)^{n_{xCP}} = (\gamma)^{n_{xCP}}
\]

Two-center photoemission from fixed-in-space N\(^2\)
Molecular core-level orbitals:

Cohen-Fano two-center interference

Intensity Distribution of Fringes
Screen
Evidence that the light is the wave
Intensity Interference
Two slits with interference fringes
Electrons also show double slits

Young's Double Slit Experiment
Light Source
Coherent Light Propagation

The symmetric-resolved C 1s satellite bands of CO

Franck-Condon analysis of the vibrational structure in CO

Franck-Condon analysis of the vibrational structure in CO

Equilibrium geometries of the core-ionized states extracted from the vibrational structure

Franck-Condon analysis for the vibrational structure of the N 1s 1\(^{1}S\(^0\) and 1\(^{3}S\(^0\) mainlines of N\(_2\)

90.0 90.5 91.0
0
500
1000 1500
2000
2500
Counts
Kinetic energy (eV)

SAC-CI
Exper.
Theory

N 1\(^{1}S\(^0\)
N 1\(^{3}S\(^0\)
Re
Å
-0.023(1)
-0.021
-0.018(1)
-0.017

Ehara et al. JCP 124, 124311 (2006)

Equilibrium geometries of the core-ionized states extracted from the vibrational structure

Relative intensity
Kinetic energy (eV)

N\(^1\) SS
h
\(\gamma\) = 500 eV

\(v' = 1\)
\(v' = 0\)

Relative binding energy (eV)
Intensity (arb. units)

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Core-level photoemission from fixed-in-space N\(^2\)
Molecular core-level orbitals:
Ab initio N 1s 1/g86 and 1/g86 photoionization cross sections of N2

Oscillation: Two-center Interference Cohen-Fano prediction


Both experimental and ab initio interference fringes shift from the prediction by Cohen-Fano formula!

Cross section ratio

Electron momentum (a.u.)

N2 K shell

Photoelectron scattering by the neighboring N atom

The amplitude of the photoelectron wave from one center:

\[ \psi_1 = \frac{\psi_0}{\sin \theta} \]

The amplitude of the photoelectron wave from two centers:

\[ \psi_2 = \frac{\psi_0}{\sin \theta} \]

A1B1 and A2B2 one-center interference terms

A1B2 and A2B1 two-center interference terms

Cohen-Fano interference

A1A2 interference term

By Cohen-Fano formula:

Both experimental and ab initio interference fringes shift from the prediction

\[ \frac{\sigma}{\sigma_0} \text{Ratio: experiment vs ab initio and Cohen-Fano} \]

\[ \sigma_0 \text{ vs } \sigma \text{} \]

\[ \text{Cross section} \]

\[ \text{Electron momentum (a.u.)} \]

\[ \text{N}^2 \text{ K shell} \]

\[ \text{Photoelectron scattering by the neighboring N atom} \]

\[ \text{CF A1A2 interference term} \]

\[ \text{Cohen-Fano interference} \]

\[ \text{A1B1 and A2B2 interference terms} \]

\[ \text{A1B2 and A2B1 interference terms} \]

\[ \text{Cohen-Fano interference} \]

\[ \text{A1A2 interference term} \]
Multiple-Ion Coincidence Imaging Setup

To obtain 3D momentum:

\[ p_x = \frac{m}{E} (y_t - y_0) \]
\[ p_y = \frac{m}{E} (x_t - x_0) \]
\[ p_z = m \cdot t_0 \]

To be exact, \( P_z \) becomes nonlinear.

Iterative procedure

Total electron yield spectrum of CO\(_2\) in the C\(_1\)s excitation region

CO\(_2\) ground state configuration:

\[ \begin{align*}
  &1^2 \text{g} 21 \text{u} \\
  &2^2 \text{g} 23 \text{g} 22 \text{u} 24 \text{g} 2 \\
  &3^2 \text{u} 21 \text{u} 41 \text{g} 4(1 + ) 2 \text{u} 05 \text{g} 04 \text{u} 03 \text{g}
\end{align*} \]
We focus on the electron emission within this reaction plane.

Reaction plane = plane defined by the E vector and molecular axes.

Towards photoelectron diffraction measurement

Total electron yield spectrum of CO$_2$ in the C1s ionization region.

Snapshots of the bending motion in the core-excited state with a lifetime ~7 fs.
Comparison between experiment and theory: C1s photoelectron diffraction (MFPAD) of CO2.
Interatomic Coulombic Decay (ICD)

Theoretical
First prediction - HF cluster:
Prediction - Ne dimer:

Experimental
First observation - Ne cluster:
Cluster-size-dependent lifetime:
Ne$_2$ e-ion-ion coincidence:

Observation of ICD in Ne$_2$ by Frankfurt group

Interatomic Coulombic Decay after Auger decay

Prediction - ICD from Auger final states in Ne dimer:

Radiation damage caused in bio-molecules in the living cell

Labeling electron emission site via the ionic charge state

ICD is one of the important mechanisms to produce low energy electrons after Auger decay.

Radiation damage is known to be caused by low-energy electron collisions in the living cell.

Why is ICD after Auger decay interesting and important?


Experimental evidence of Inertial Coulombic Decay

We detect ICD electrons in coincidence with Ar$^+$ and Ar$_2$$^+$

We detect ICD electrons in coincidence with Ar$^+$ and Ar$_2$$^+$ using e-i-i coincidence momentum spectroscopy
The ICD process in Ar₂

Energy diagram of the ICD process in Ar₂

Electron spectrum, KER, and their correlation

Electron spectrum coincident with Ar++/Ar+

KER

Ar++/Ar+

Coulomb explosion (expected KER ~ 7.6 eV)

Equilibrium distance 3.8 Å

Measured KER ~ 7.7 eV

ICD is very fast!

Islands of slope -1 are ICDs!

Ar+

Ar++

hv=262 eV

2p-1

Photoionization

Photoelectron ejection (13.4 and 11.3 eV)

Ar2+

Ar3+

ICD & fragmentation

10eV 3p-1 & 3p-2

Auger decay

Energy diagram of the ICD process in Ar₂

---

Position & time of flight (x,y,t)

3D momentum of each particle

Multiple coincidence

Momentum correlation among the particles

Electric field e-

X

O

A+

N

B+

X-rays

Magnetic field

Multihit 2D detector

Multiple coincidence momentum imaging

PIPCICO spectrum

Ar₂

TOF of First Ion (ns)

2

4

6

8

Filter conditions:

Ar+/Ar+: the sum of the momentum of Ar+ and Ar+ ~ 0

Ar++/Ar+: the sum of the momentum of Ar++ and Ar+ ~ 0

Ar++/Ar+ comes from ICD!

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Photoelectron ejection (13.4 and 11.3 eV)
We detect ICD electrons in coincidence with Ne+ and Ne2+ using e-i-i coincidence momentum spectroscopy. ICD from the Auger final states in Ne dimer.

Variants of ICD

'Structural FeL etc., are coming?

Swiss FEL etc., are coming?

Shanghai FEL etc., are coming?

SACLA in operation since June 2012.

FERMI in operation since March 2012.

ETMD, ICD, direct, exchange, ICD...
(molecular movie)

Catching atomic motion in reaction

Characteristic properties of FEL pulses

Ultra-short (100 – 10 fs)

Femtosecond dynamics

Millisecond mechanics

Attosecond dynamics

0 – 10 ps

0 – 100 fs

0 – 200 ms

0 – 0.5 fs

Why X-rays? Structure determination at atomic resolution

High-Resolution Protein Structure Determination by Serial Femtosecond


Single Photon Pair Production and Imaging with an X-ray Laser. Iván de la Torre 


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Single Photon Pair Production and Imaging with an X-ray Laser. Iván de la Torre 

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

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

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.

SACLA X-FEL

Project Leader: Tetsuya Ishikawa (RIKEN)

Photon energy range: 4-20 keV

Photon numbers: \(10^{11}\) photon/pulse (5-15 keV)

Repetition rate: 10~60 Hz

Focusing optics: ~1 µm (1.5 m)

First round user beam time: March - July 2012

Intense 10^14 W/cm^2 (EUV) - 10^20 W/cm^2 (X)

Light matter interaction

Non-linear response

Electronic damage

Second round beam time: September 2012-March 2013

My second beam time: 2–5 December 2012

Molecules

Characteristic properties of FEL pulses

Short wavelength: toward Hard X-rays

Structure determination of atomic resolution

Coherent X-ray imaging of non-crystallized samples

Electronic damage

Light matter interaction

Non-linear response

Continuous electron detection from the beam

Can remove all ten electrons from the neon atom.

In the sample, it causes electronic damage.

The pulse is so intense that

\(10^4 \text{ W/cm}^2 (\text{EUV}) \rightarrow 10^9 \text{ W/cm}^2 (X)\)

\(> 2 \times 10^9 \text{ as} \): Resolving electron wave-packet motion

\(1 \text{ fs} \rightarrow 100 \text{ fs} \): Resolving atomic motion

\(10^{-13} \text{ fs} \): Resolving electronic motion

\(10^{-15} \text{ fs} \): Resolving atomic motion
**SCSS test accelerator : EUV-FEL (20-24 eV)**

- Momentum or velocity imaging apparatus
- EUV-FEL

**Autocorrelation**
- with J. Ullrich’s group
- Multiple ionization of rare gas atoms and clusters: with M. Yao’s group
- VMI: with help of M. Vrakking’s group

**Photoelectron angular distributions for two-photon Ionization of He atoms by SCSS EUVFEL pulses**

- Potential of coherent control via seeded FEL

**Deep inner-shell multi-photon absorption of Ar and Xe atoms by SACLA XFEL pulses**
- Potential of coherent control via seeded FEL

**Multi-photon ionization of atoms**
- Resolved two-photon single ionization of He atoms by SCSS EUVFEL pulses via IA.

**Second-order autocorrelation of EUV FEL pulses via**

- Split mirror assembly: MIR: ASG: CFEL: MIR

**MPI-K, ASG-CFEL, MPQ Split mirror assembly:**
- Mirror: Mg/Si multilayer (f=600 mm, LBNL)

**Measuring electron yield**
- Ion yield (counts/shot)
- Intensity (arb. units)

**Autocorrelation measurement with He two photon ionization**

**Second-order autocorrelation**
- of EUV FEL pulses via time resolved two-photon single ionization of He

**Autocorrelation measurement with J. Ullrich’s group**

**Optics Express** 19, 21698 (2011).

Experimental evidence for competition between the resonant and non-resonant two-photon ionization of He

- Resonant
- Non-resonant

Coherent excitation of Rydberg manifold

Photon energy range available at SCSS test accelerator

Excitation energies for two-photon ionization of He

20.3 eV
21.3 eV
23.0 eV
24.3 eV

Red lines: Measured PADs
Blue lines: Results of the TDSE calculations

Photoelectron angular distribution for two-photon ionization of He
Anisotropy parameters

Photoelectron angular distribution for two-photon ionization of He

\[ \frac{1}{2} \cos \theta \cos \phi \]

\[ \frac{1}{2} \cos \theta \sin \phi \]

\[ \frac{1}{2} \sin \theta \cos \phi \]

\[ \frac{1}{2} \sin \theta \sin \phi \]

\[ \frac{1}{2} \cos \phi \]

PPI

\[ \frac{1}{2} \cos \phi \]

\[ \frac{1}{2} \sin \phi \]

\[ \frac{1}{2} \cos \theta \cos \phi \]

\[ \frac{1}{2} \cos \theta \sin \phi \]

\[ \frac{1}{2} \sin \theta \cos \phi \]

\[ \frac{1}{2} \sin \theta \sin \phi \]

\[ \frac{1}{2} \cos \phi \]

\[ \frac{1}{2} \cos \phi \]

\[ \frac{1}{2} \sin \phi \]

Deviation from scattering phase shift difference

\[ \Delta \phi \]

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Deep inner-shell multiphoton absorption of Ar and Xe by SACLA XFEL pulses

Theorists

Experimentalists

Time of Flight spectrum of argon ions

Ar jet

XFEL

KLL→2LMM

XFEL fluence dependence for Ar

\[ n^+ \text{ yields} \]

\[ 10^{-3} \]

\[ 10^{-2} \]

\[ 10^{-1} \]

\[ 10^0 \]

\[ 10^1 \]

\[ 10^2 \]

\[ 10^3 \]

\[ 10^4 \]

\[ 10^5 \]

\[ 10^6 \]

\[ 10^7 \]

\[ 10^8 \]

\[ 10^9 \]

\[ 10^{10} \]

\[ 10^{11} \]

\[ 10^{12} \]

\[ 10^{13} \]

\[ 10^{14} \]

Charge state distribution of Ar: experiment and theory

In the theory, the pulse shape of Gaussian of 30 fs (FWHM) and Gaussian focal shape of 1 mm (FWHM) are assumed.

By comparison with theory, we obtained peak fluence of 70 J/mm² in the experiment.

In the experiment, the pulse shape is Gaussian of 30 fs (FWHM) × 1 mm (FWHM). The fluence depends on the pulse shape.

Peak fluence (J/mm²)

Ion yield (counts/shot)

Charge state

Experiment

Theory (40 J/mm²)

Theory (70 J/mm²)

Theory (100 J/mm²)

Theory (150 J/mm²)

Comparison with experiment

Time of Flight spectrum of argon ions

Depth Inner-shell Multiphoton Absorption of Ar and Xe by SACLA XFEL Pulses
Xenon ion charge distributions (exp. vs theo.)

Experiment done at 5.5 keV, at SACLA!

Xe atoms can absorb more than one x-ray photon!

Ion yield (counts/shot) vs XFEL fluence dependence for Xe ions

Time of flight spectrum of xenon ions

One photon absorption
Two photon absorption
Three photon absorption
Four photon absorption
Radio-sensitizer

5I-Uracil

Relevance to other fields:
- Radiation damage
- Anomalous X-ray scattering

S.-K. Son, H. N. Chapman, and R. Santra,

Multiwavelength anomalous diffraction at high X-ray intensity

H. Fukuzawa, S.-K. Son, K. Motomura, S. Mondal, K. Nagaya,
S. Wada, X.-J. Liu, R. Feifel, T. Tachibana, Y. Ito,
M. Kimura, T. Saika, K. Matsunami, H. Hayashita,
J. Kajiwara, P. Johnsson, M. Siano, E. Kukka,
B. Rudek, L. Foucar, E. Robert,
C. Miron, K. Tono, T. Togashi, and K. Ueda
(submitted)

The end

A couple postdoc positions are open at Tohoku University for SACLA project!