X-ray Science in the 21st Century
KITP Conference August 2 – August 6, 2010

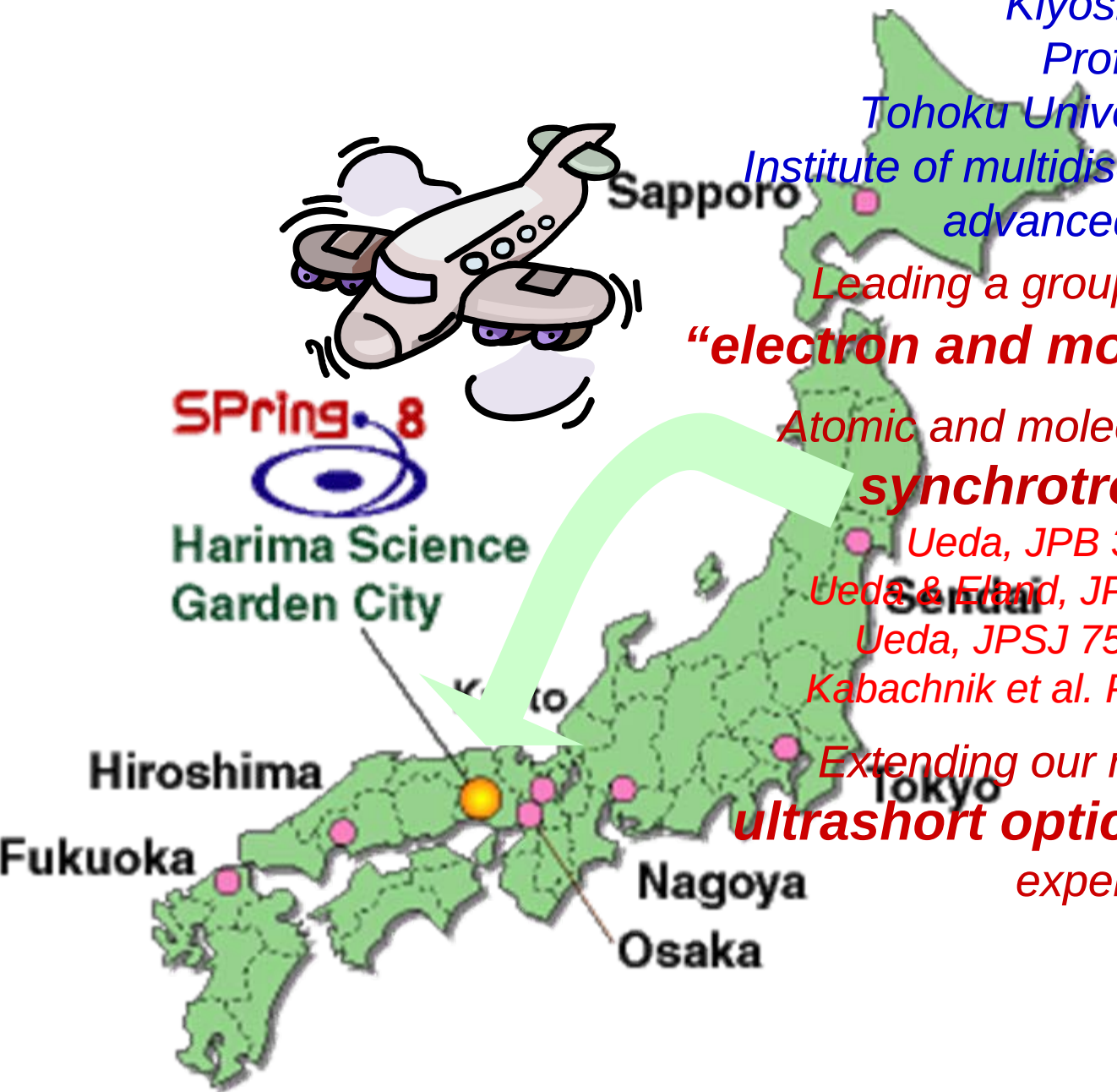
Probing Molecular Structure and Electron Dynamics Using Synchrotron Radiation, IR Laser, and FEL

Kiyoshi Ueda
Tohoku University, Japan

Santa Barbara


AMO meets CDI in Santa Barbara

Introduction….



Kiyoshi Ueda
Professor
Tohoku University（Sendai）
Institute of multidisciplinary research for advanced materials

Leading a group for investigating
"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);
Kabachnik et al. PR 451, 155 (2007).

Extending our research areas to
ultrashort optical laser and FEL
experiments

SPring-8 XFEL

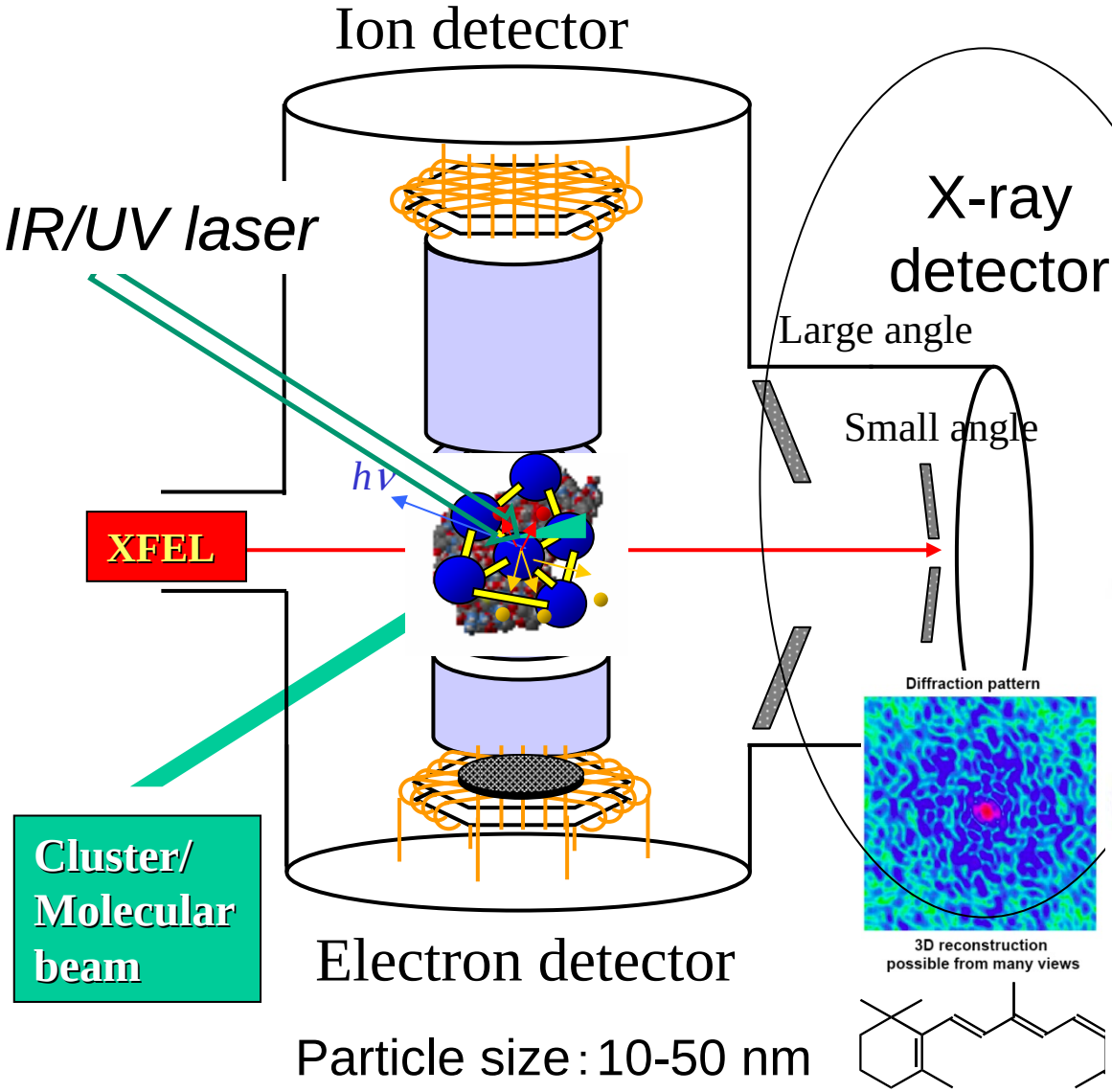
Project Leader: Tetsuya Ishikawa (RIKEN)

Tetsuya Ishikawa
RIKEN

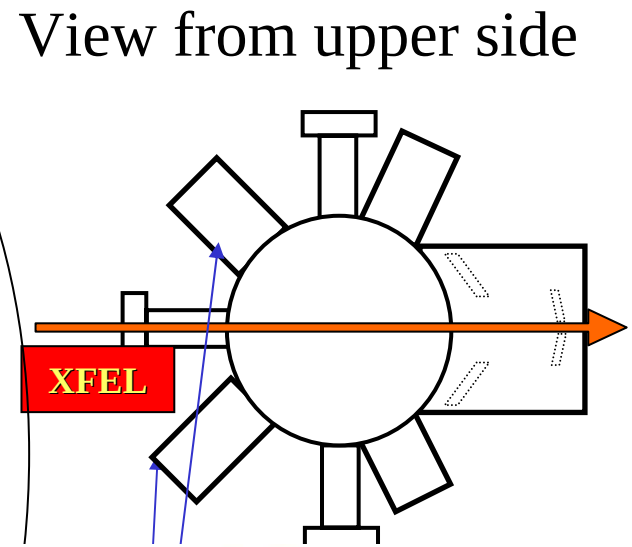
Tsumoru Shintake
RIKEN

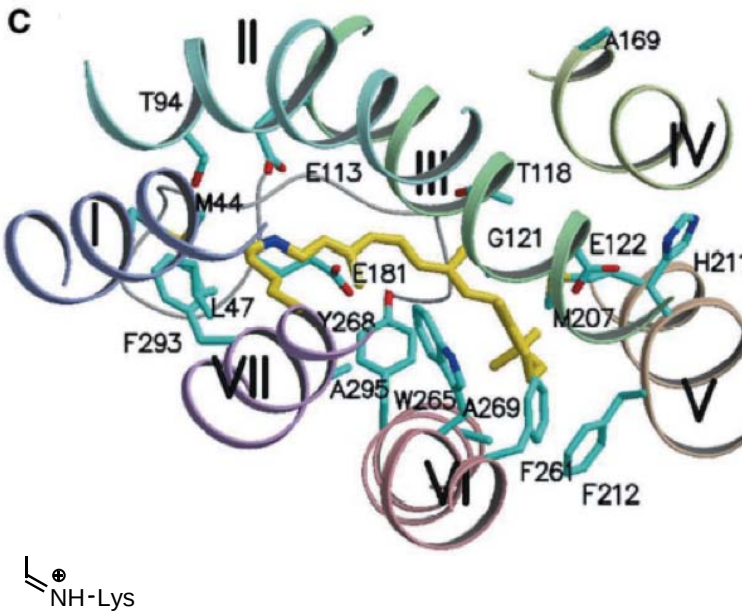
Molecular Movie:

Coherent diffractive imaging of a single particle, undergoing photo-reaction, combined with coulomb explosion ion imaging and photoelectron diffraction



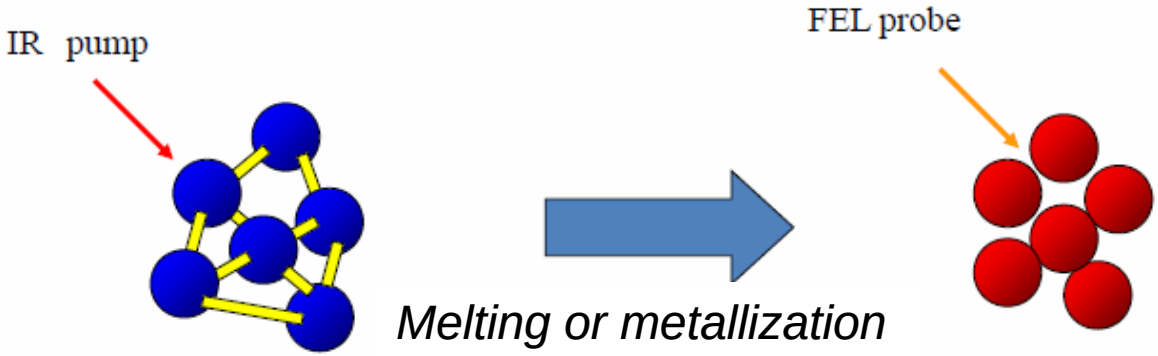
Particle size : 10-50 nm





Phase transition in nano-crystals or nano-clusters

A single nano-cluster or nano-crystal will be "pumped" by IR laser to "heat" them up. Melting or metallization may occur. The atomic displacement will be investigated by x-ray diffraction as a function of time delay of the x-ray pulse.



Conformation change of photo-reactive bio-molecules

A single photo-sensitive giant bio-molecule will be "pumped" by UV laser to trigger photoreaction and time-resolved coherent diffraction image will be recorded. Here, post analysis of simultaneous recording of Coulomb explosion ion momentum spectroscopy may help defining the molecular orientation.

For relatively small bio-molecules, x-ray diffraction may not work because the signals may be embedded in the background. In such a case, ***x-ray core-level photoelectron diffraction*** *using X-FEL would be an alternative approach to extract the structure evolving in time.*

Outline

I. From molecular imaging to molecular movies

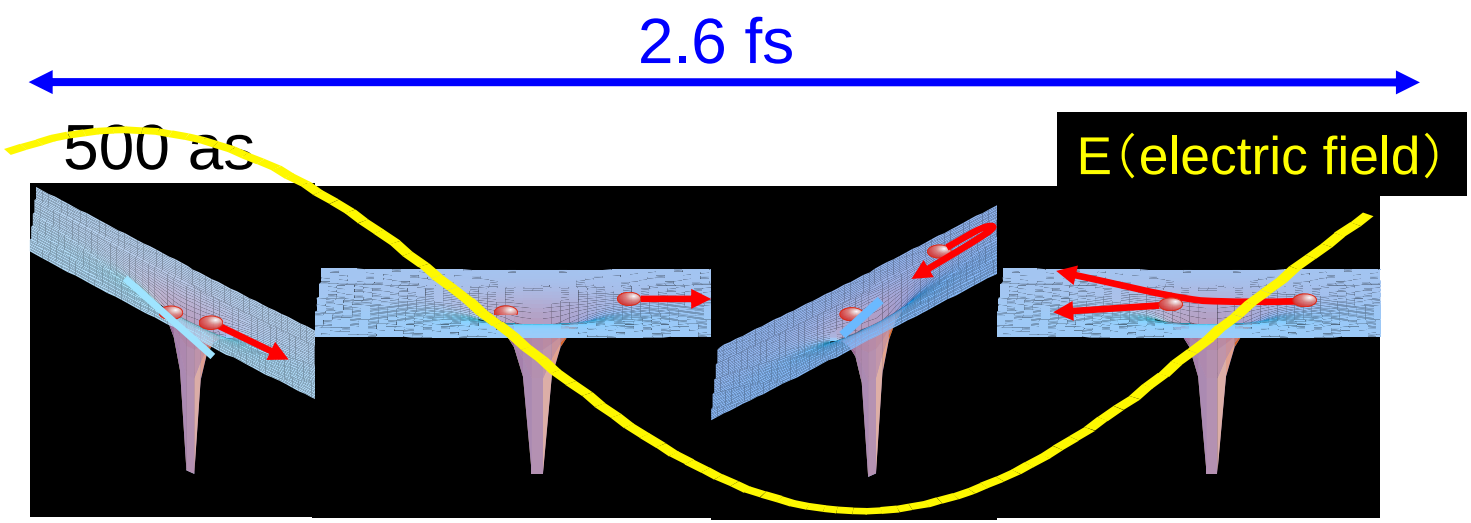
1. **Introduction to molecular movie**
   Time-resolved coherent X-ray diffraction imaging of a single particle, undergoing photoreaction, together with multi-particle momentum imaging
2. **Current status of molecular imaging**
   A. Laser-induced rescattering photoelectron spectroscopy
   B. Core-level photoelectron diffraction using synchrotron radiation

II. Probing electron dynamics, catching electron motion

1. **Introduction to catching electron motion**
   Attosecond X-ray pump-probe spectroscopy for probing charge migration
2. **Current status of electron dynamics study in energy domain**
   A. Interatomic Coulombic decay in rare-gas dimers
   B. Charge migration in clusters

Rescattering Photoelectron Spectroscopy

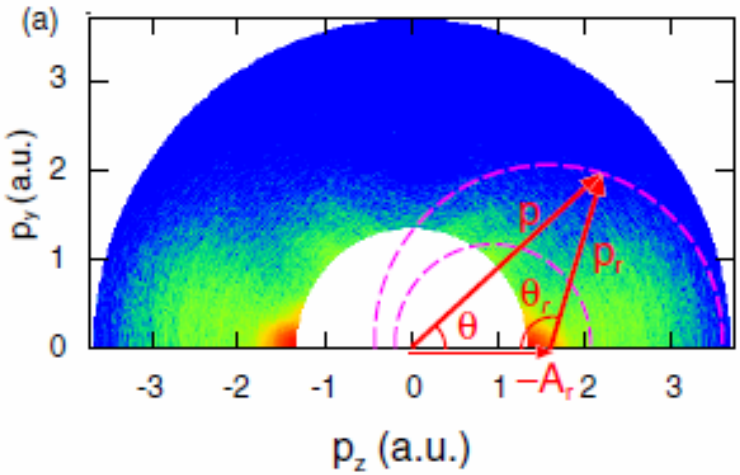
An electron produced by the tunnel ionization may re-collide with the parent ion. Then, spectra of the “rescattering photoelectron” provide the information about the target structure, because this rescattering process is equivalent to the elastic scattering of the free electron by the ion, at the electron momentum at the time of rescattering.



Tunnel ionization Propagation Return Rescattering

resolution：sub fs, sub Å (@ 800 nm)

Extraction of differential electron–ion elastic scattering cross sections from rescattering photoelectron spectra of rare gas atoms



$$D(\mathbf{p}) = W(p_r)\sigma(p_r, \theta_r),$$

$$p_z = p\cos\theta = \pm(p_r/1.26 - p_r\cos\theta_r),$$

$$p_y = p\sin\theta = p_r\sin\theta_r,$$

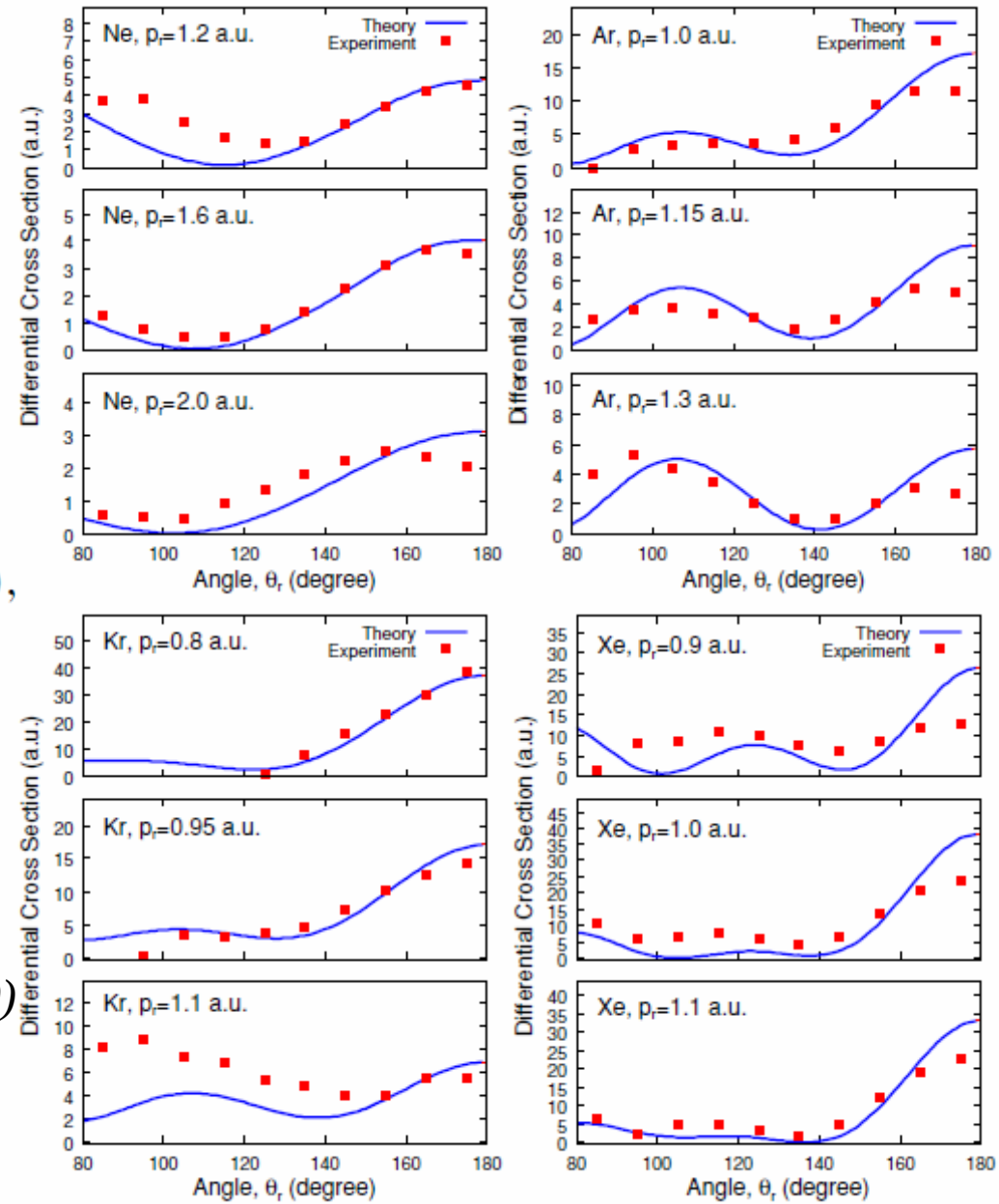
4Up ? < E < 10Up

Lower E depends on samples….

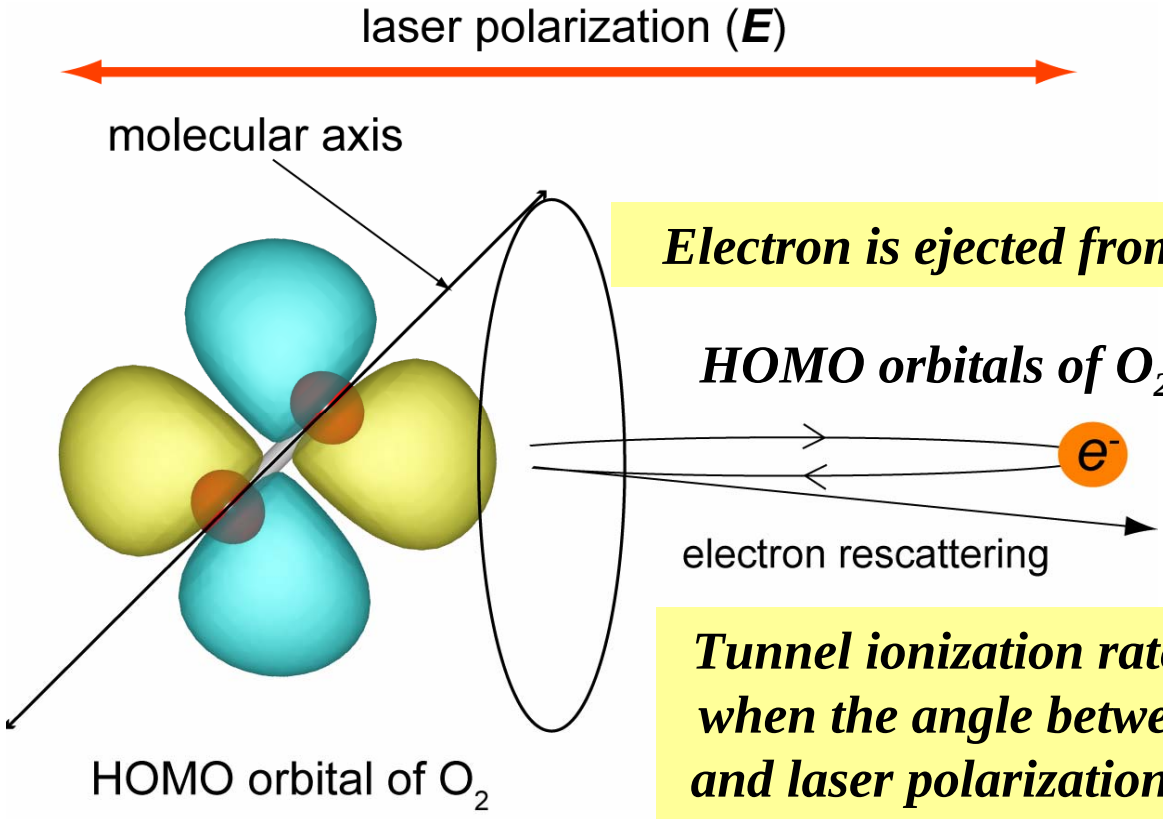
Okunishi et al., PRL 100, 143001 (2008)

Morishita et al. J. Phys. B 42, 105205 (2009)

One can retrieve a potential of the atomic ion!



Photoelectron rescattering for partially aligned O_2 and CO_2 molecules



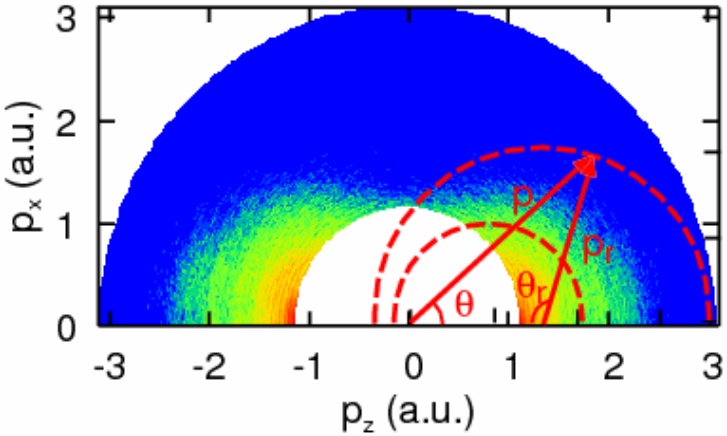
Electron is ejected from the HOMO orbital

HOMO orbitals of O_2 and CO_2 are Π_g

Tunnel ionization rate is strongly enhanced when the angle between the molecular axis and laser polarization is <u>around 45 degrees</u>.

Measurements for partially aligned O_2 and CO_2 molecule

Differential cross sections (DCS) of electron–ion elastic scattering: Comparison between ab initio DCS and DCS extracted from photoelectron rescattering spectra

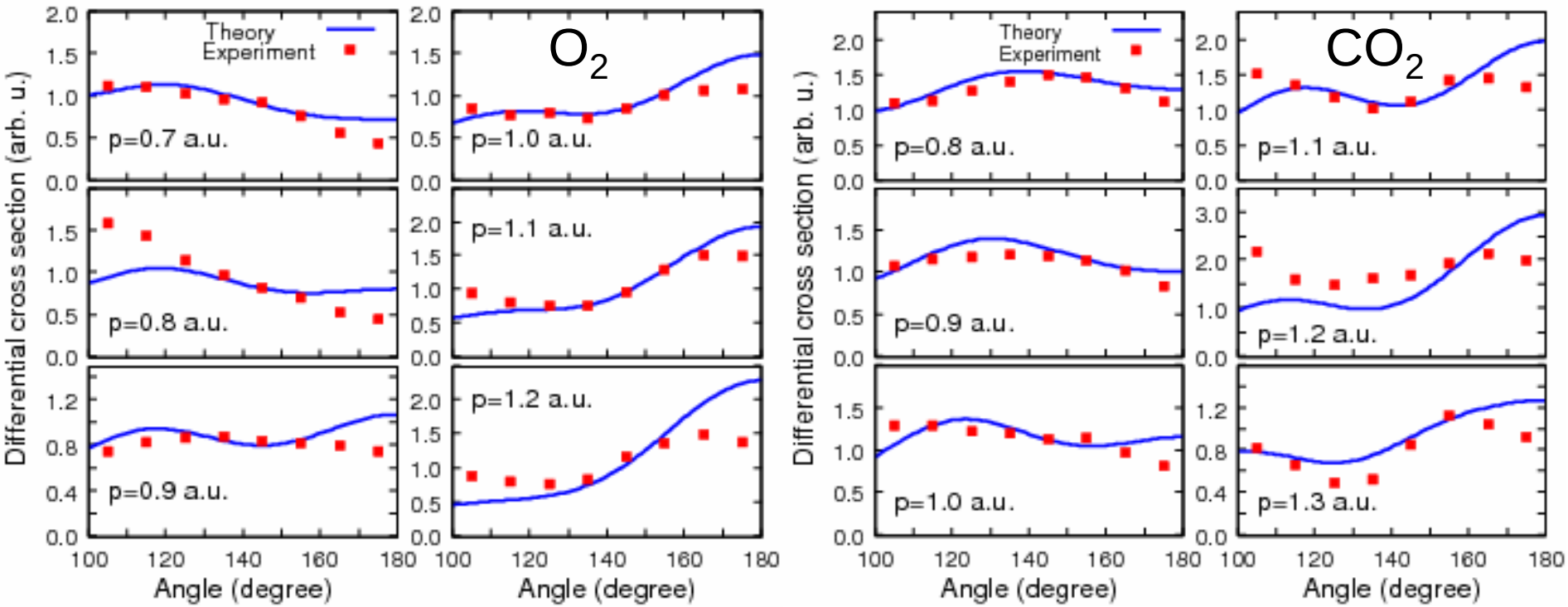


$$D(\mathbf{p}) = W(p_r)\sigma(p_r, \theta_r),$$

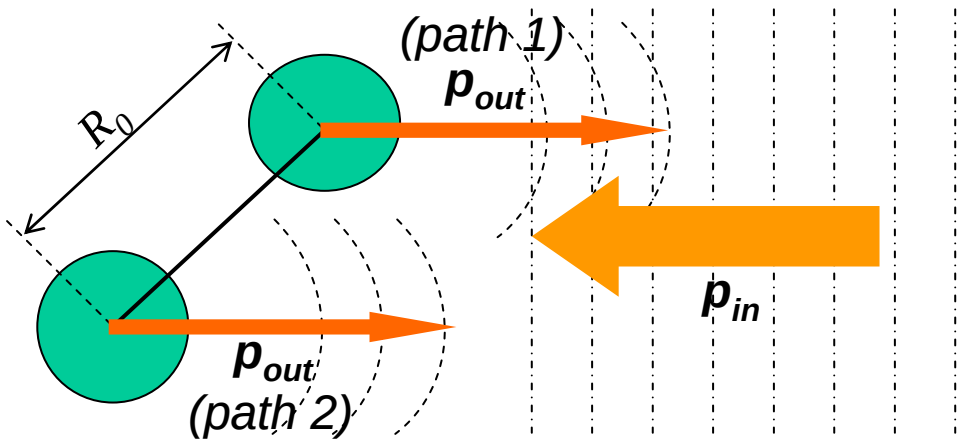
$$p_z = p\cos\theta = \pm(p_r/1.26 - p_r\cos\theta_r),$$

$$p_y = p\sin\theta = p_r\sin\theta_r,$$

Partial alignment effects of molecules are taken into account in theory using angular dependent molecular ADK ionization rates.



Simple estimation of the momentum of backward rescattered electrons



simple plane wave approximation

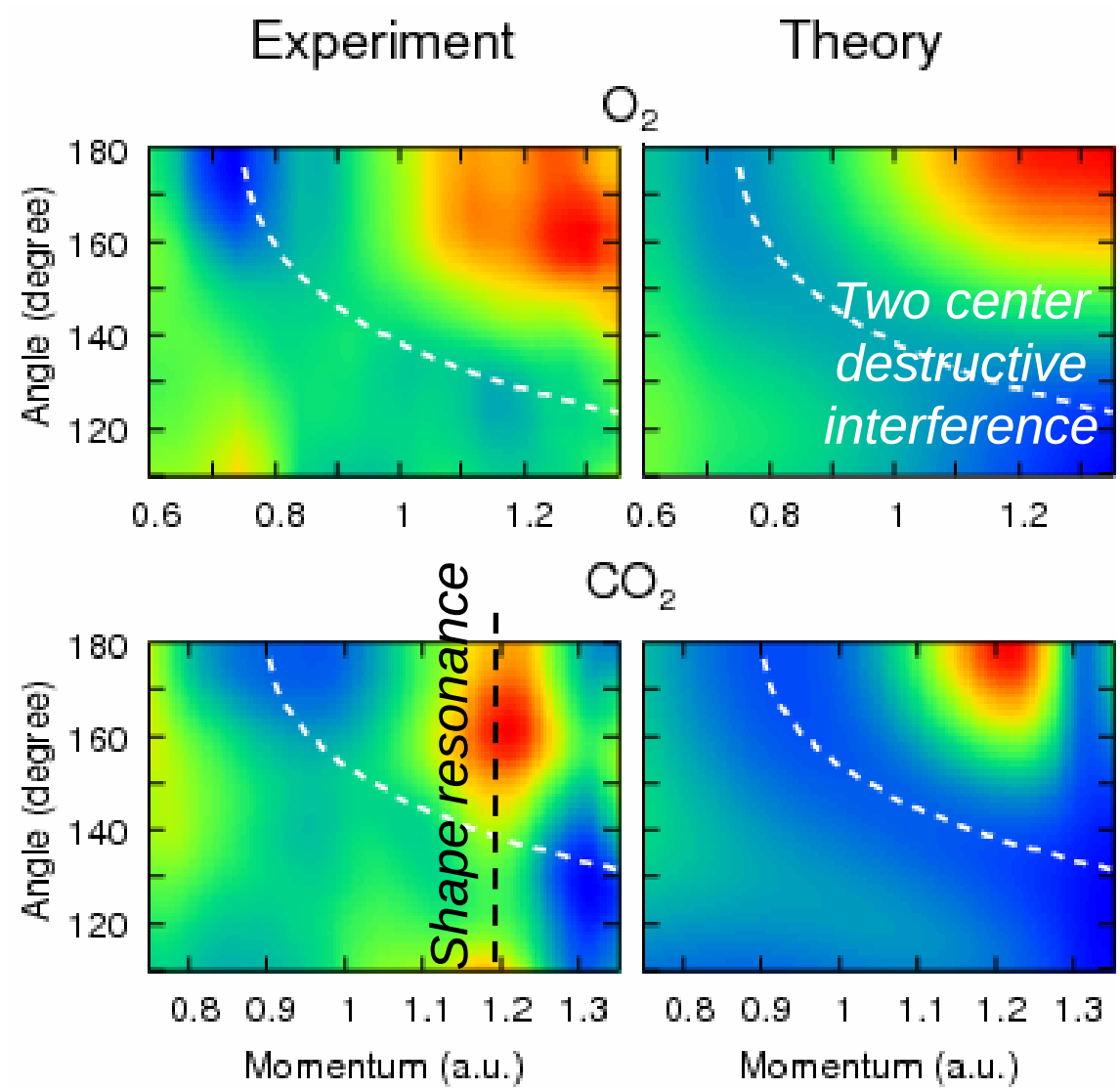
Elastic scattering
$|\boldsymbol{p}_{in}| = |\boldsymbol{p}_{out}| = p$

difference of the path between 1 and 2 = $2 \times R_0 / \sqrt{2} = \sqrt{2} R_0$

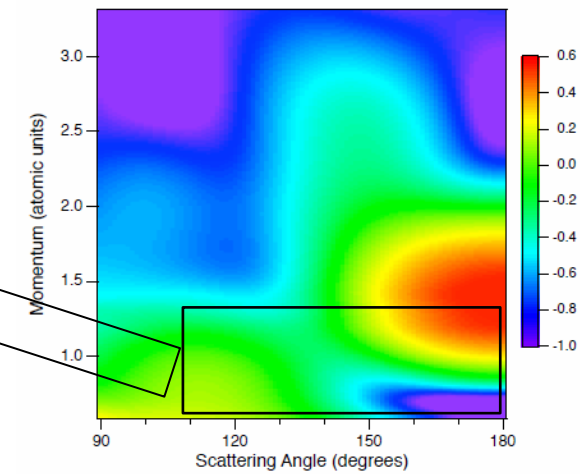
$$\text{destructive interference}: \sqrt{2} R_0 \times p = (2n+1)\pi \quad (\text{n : integer})$$

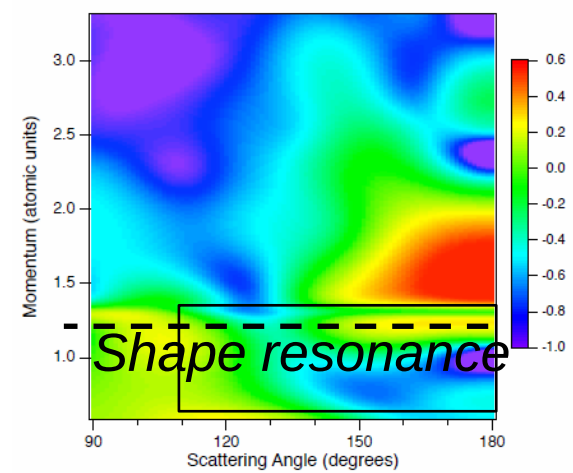
for O_2 R_0=2.28 (a.u.) ⇨ *p= 0.97, 2.91, 4.85, … (a.u)*

How to correlate DCSs with structure information



Theory (wide range) DCS at 45 degs





Both destructive interference and shape resonance include structure information but the plane wave approximation does not work.

Rescattering photoelectron spectroscopy collaborations

Experimental retrieval of target structure information from laser-induced rescattered photoelectron momentum distributions
M. Okunishi, T. Morishita, *G. Prümper, K. Shimada, C. D. Lin, S. Watanabe, and K. Ueda*
Phys. Rev. Lett. 100*, 143001 (2008).*

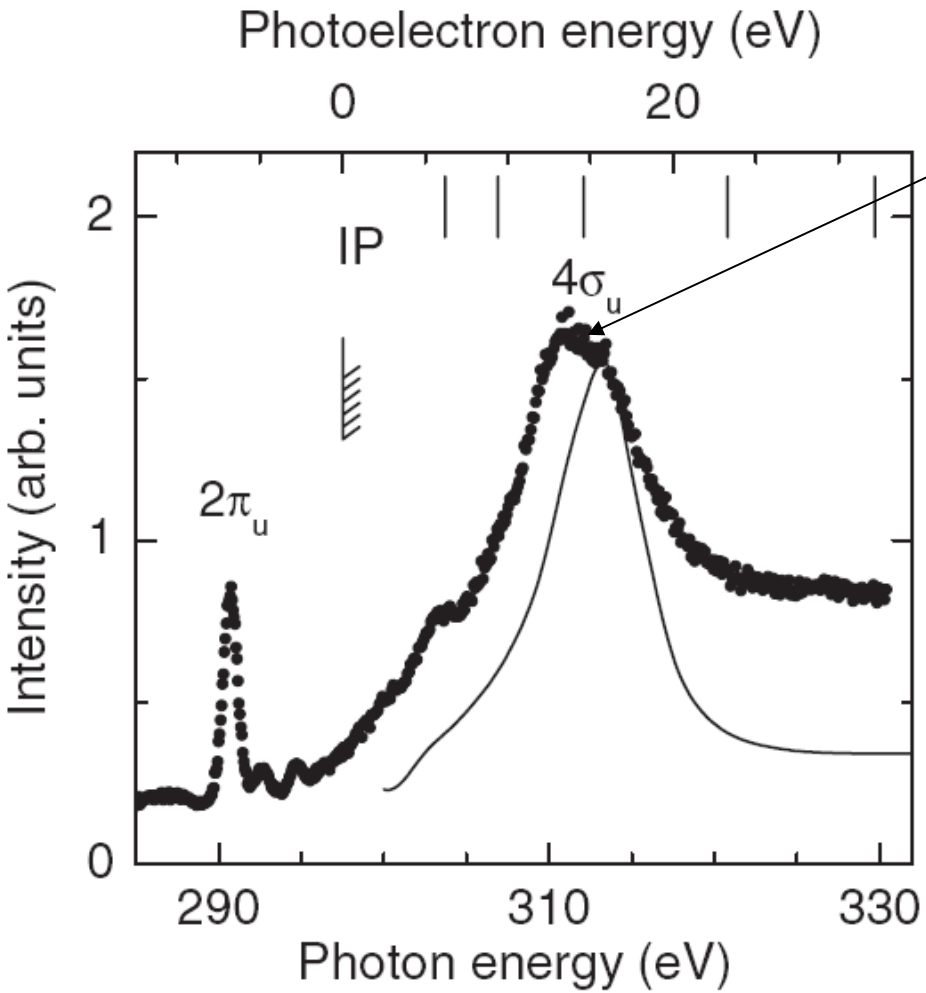
Retrieval of experimental differential electron–ion elastic scattering cross sections from high-energy ATI spectra of rare gas atoms by infrared lasers
T.Morishita, M. Okunishi*, K. Shimada, G.Prümper, Z. Chen, S. Watanabe, K. Ueda, and C. D. Lin*
J. Phys. B: At. Mol. Opt. Phys. ***42****, 105205 (6pp) (2009).*

Two-Source Double-Slit Interference in Angle-Resolved High-Energy Above-Threshold Ionization Spectra of Diatoms
M. Okunishi, *R. Itaya, K. Shimada, G. Prümper, K. Ueda, M. Busuladžić, A. Gazibegović-Busuladžić, D. B. Milošević, and W. Becker*
Phys. Rev. Lett. 103*, 043001 (2009).*

Extracting Electron-Ion Differential Cross Sections of Fixed-in-Space Molecules by Laser-induced Rescattering Photoelectron Spectroscopy
R.R. Lucchese, *M. Okunishi, T. Morishita, and K. Ueda,* ***submitted***

Core-level photoelectron diffraction for fixed-in-space molecules or Molecular Frame Photoelectron Angular Distribution (MFPAD)

Total electron yield spectrum of CO_2 in the C1s ionization region



$4\sigma_u \leftarrow 2\sigma_g$ *shape resonance*

CO_2 ground state configuration:

$$\underbrace{1\sigma_g^2 1\sigma_u^2}_{O1s}\underbrace{2\sigma_g^2}_{C1s}\underbrace{3\sigma_g^2 2\sigma_u^2}_{O2s}\underbrace{4\sigma_g^2}_{C2s}$$

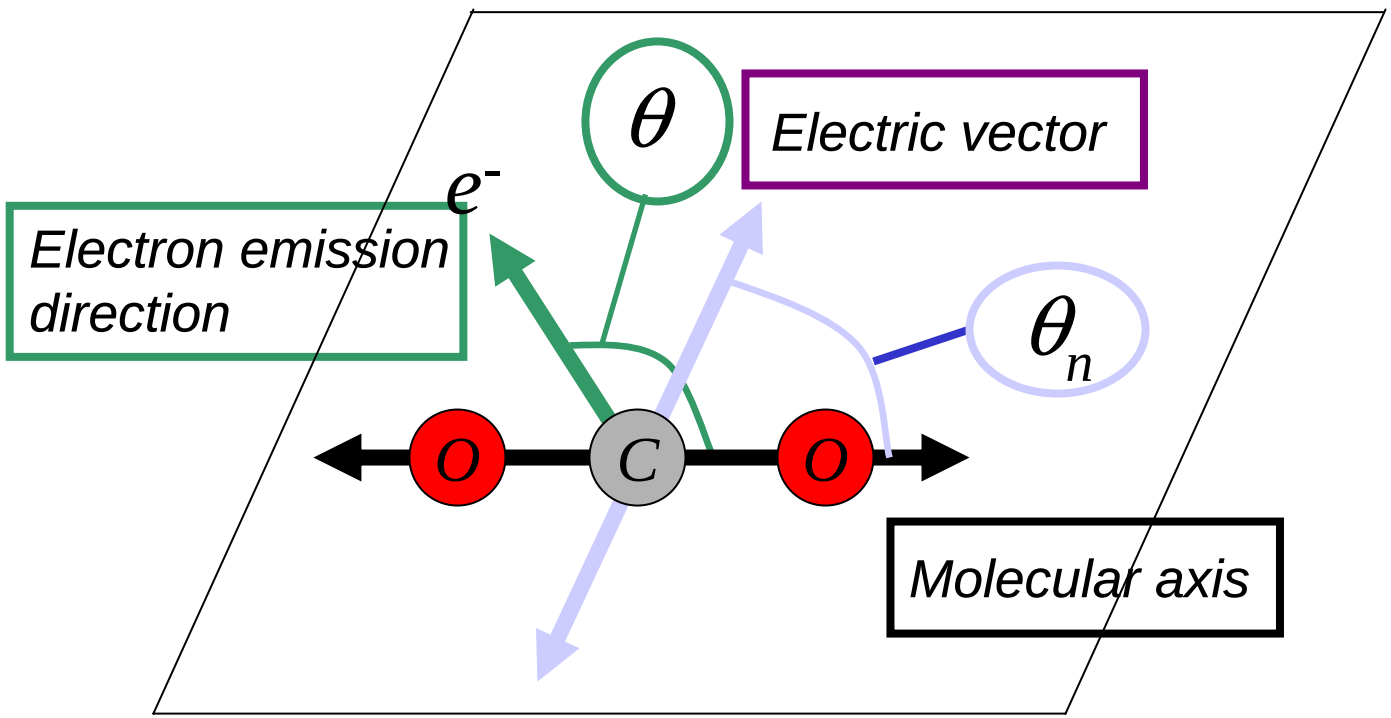
$$3\sigma_u^2 1\pi_u^4 1\pi_g^4 (^1\Sigma_g^+);\ 2\pi_u^0 5\sigma_g^0 4\sigma_u^0$$

C 1s threshold
297.63 eV

*N. Saito et al., J. Phys. B, **36** L25 (2003).*
J. D. Bozek et al., Phys. Rev. A 51, 4563 (1995).

Reaction plane

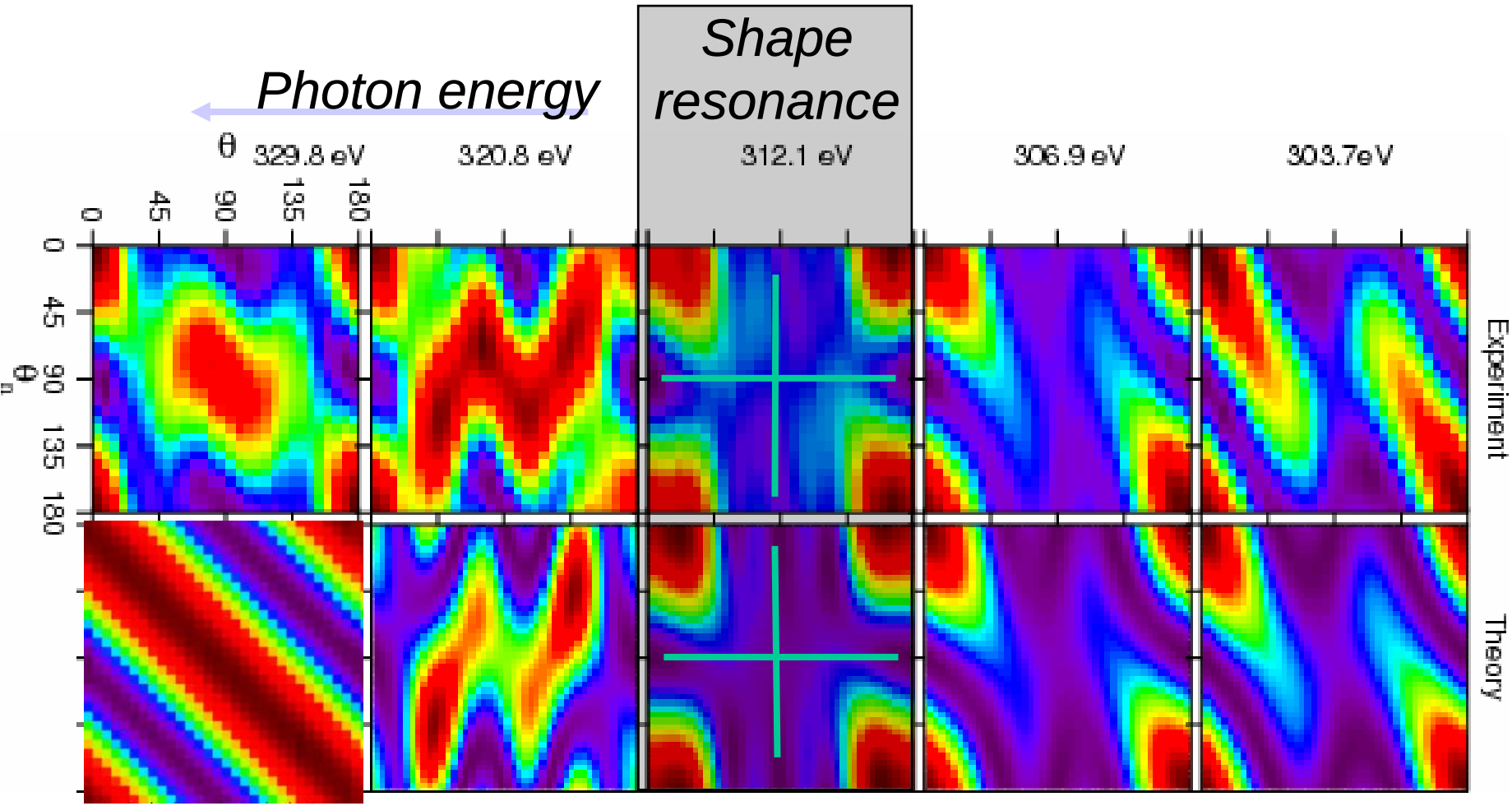
Reaction plane =plane defined by the E vector and molecular axis



We focus on the electron emission within this reaction plane

The molecular axis is defined by the O^+-CO^+ coincidence

C1s photoelectron diffraction (MFPAD) of CO_2: comparison between experiment and theory



The general agreement between experiment and theory is reasonable.

At the shape resonance, the intensity drops at $\theta_n = 90°$ *i.e.* Σ-Σ *parallel transition. The intensity drops at* $\theta = 90°$*, i.e.,* σ_u *photoelectron wave !*

MFPAD collaborations

Carbon K-shell photoelectron angular distribution from fixed-in-apace CO2 molecules
N. Saito, *A. De Fanis, K. Kubozuka, M. Machida, M. Takahashi, H. Yoshida, I.H. Suzuki, A. Cassimi, A. Czasch, L. Schmidt,* ***R. Dörner****, K. Wang, B. Zimmermann,* ***V. McKoy, I****. Koyano, and K. Ueda*
J. Phys. B: At. Mol. Opt. Phys. 36, L25 (2003).

Molecular frame photoelectron angular distribution for oxygen 1s photoemission from CO2 molecules
N. Saito, K. Ueda, A. De Fanis, K. Kubozuka, M. Machida, I. Koyano, R. Doerner, A. Czasch, L. Schmidt, A. Cassimi, K. Wang, B. Zimmermann, and ***V. McKoy****; J. Phys. B: At. Mol. Opt. Phys. 38, L277-L284 (2005).*

Projection methods for the analysis of MFPAD I: Minimal parameterizations in the dipole limit,
R. R. Lucchese, *R. Montuoro, A. N. Grum-Grzhimailo, X.-J. Liu, G. Prümper, Y. Morishita, N. Saito, and K. Ueda,*
J. Electr. Spectrosc. Relat. Phenom. ***155****, 95-99 (2007)*

Projection methods for the analysis of MFPADs II. Nondipole contributions
A. N. Grum-Grzhimailo*, R. R. Lucchese, X.-J. Liu, G. Prümper, Y. Morishita, N. Saito, and K. Ueda,*
J. Electr. Spectrosc. Relat. Phenom. ***155****, 100-103 (2007)*

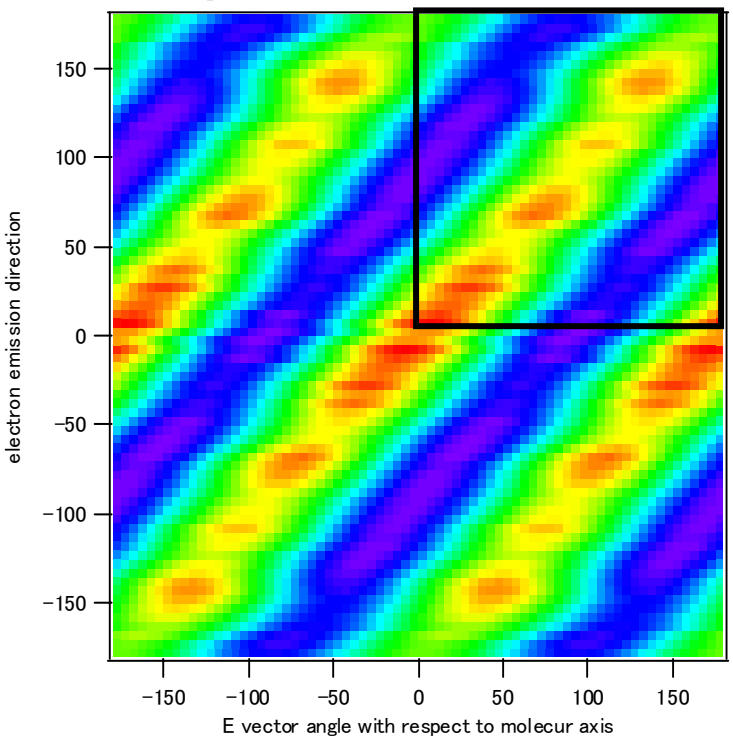
Internal inelastic scattering satellite probed by molecular-frame photoelectron angular distributions from CO_2
X.-J. Liu, H. Fukuzawa, *T. Teranishi, A. De Fanis, M. Takahashi, H. Yoshida, A. Cassimi, A. Czasch, L. Schmidt, R. Dörner, I. Koyano, N. Saito, and K. Ueda;* ***Phys. Rev. Lett. 101,*** *023001 (2008).*

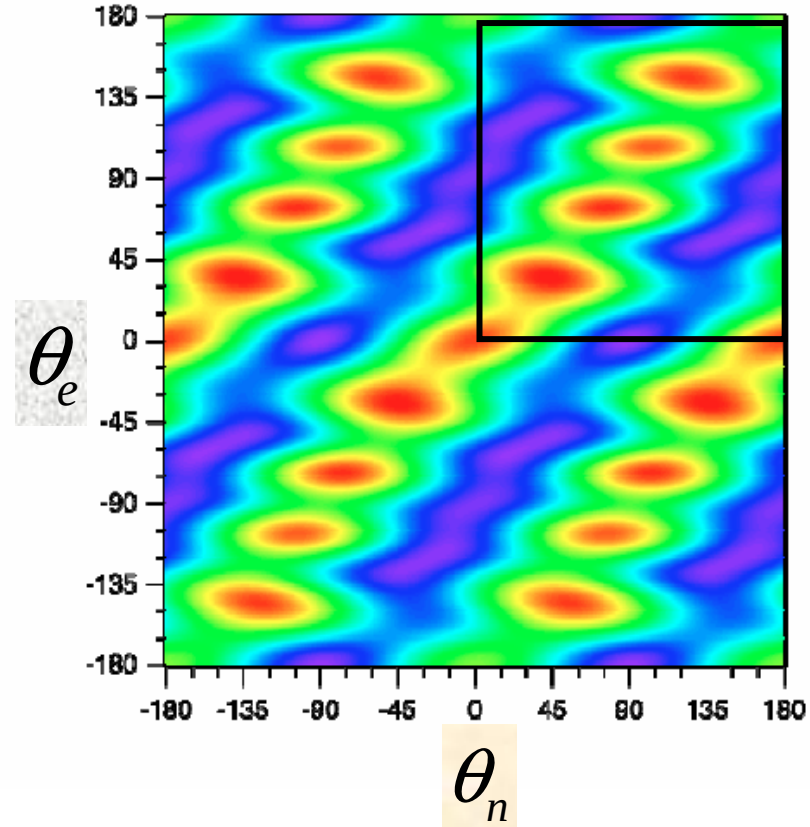
Breakdown of the two-step model in K-shell photoemission and subsequent decay probed by the molecular-frame photoelectron angular distributions of CO_2
X.-J. Liu,1 H. Fukuzawa*, T. Teranishi, A. De Fanis, M. Takahashi, H. Yoshida, A. Cassimi, A. Czasch, L. Schmidt, R. Dörner, K. Wang, B. Zimmermann, V. Mckoy, I. Koyano, N. Saito, and K. Ueda;* ***Phys. Rev. Lett. 101****, 109901 (2008).*

Theoretical study of asymmetric PADs for C 1s photoejection from CO_2
S. Miyabe, C.W. McCurdy, A.E. Orel, and T.N. Rescigno; Phys. Rev. A ***79****, 053401 (2009).*

Photo- and Auger Electron Angular Distributions of Fixed-in-Space CO_2
F.P. Sturm, M. Schoeffler S. Lee, T. Osipov, N. Neumann, H.-K. Kim, S. Kirschner, B. Rudek, J.B. Williams, J.D. Daughhetee, C.L. Cocke, ***K. Ueda,*** *A.L. Landers, Th. Weber, M.H. Prior, A. Belkacem,* ***and R. Doerner***
Phys. Rev. A ***79****, 053401 (2009).*

O1s photoelectron diffraction (MFPAD) of CO_2: comparison between experiment and theory (574 eV)



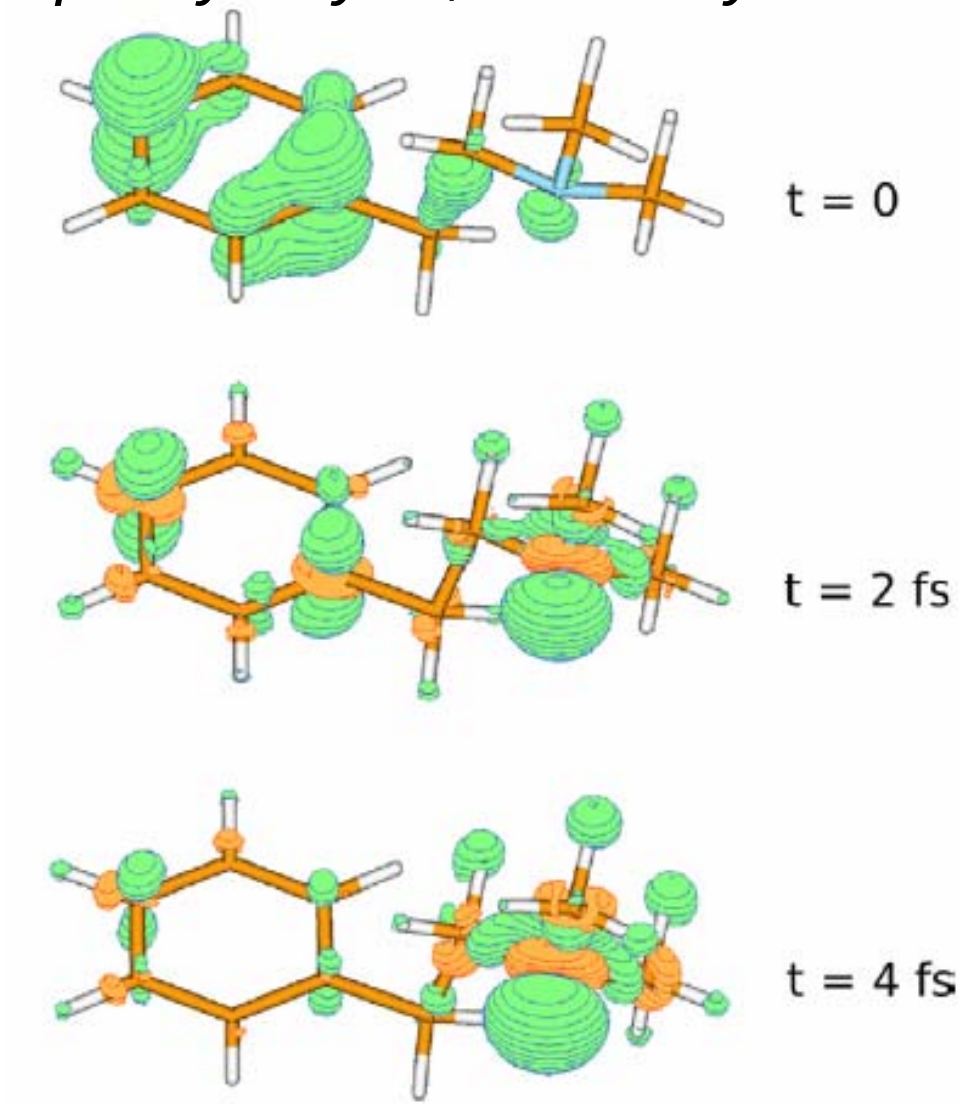


Photoelectron diffraction spectrum includes information about molecular structure. Ab initio calculations well agree with measurements. However, retrieval of the structure information based on the plane wave approximation does not work. ***We need to solve the inverse problem!***

H. Fukuzawa, R. R. Lucchese, X.-J. Liu, T. Teranishi, K. Sakai, G. Prümper, M. Schöffler, K. Kreidi, H. Iwayama, K. Nagaya, M. Yao, Y. Tamenori, N. Saito, and K. Ueda

Probing electron dynamics, catching electron motion

Ultrafast charge migration in 2-phenylethyl-N,N-dimethylamine



Lunnemann et al. CPL 450 (2008) 232–235.

Can you measure it?

Yes, we can!

For that, we need atto-second pulses

Catching Electrons with Light

Julien Bertrand

Paul.Corkum@nrc.ca

Sarah Golin

VUVX Public lecture (Vancouver)

Atto-researchers (2010)

Canada

China

Cuba

England

Germany

Iran

Israel

Italy

Japan *

Korea

Switzerland

* K. Ueda - an honorary member of the Atto-group

uOttawa

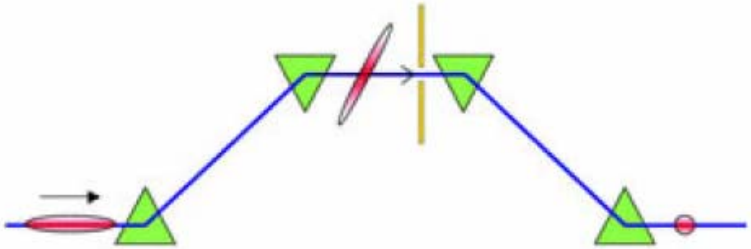
Need Ultra-short X-ray Pulses? Try Aluminum Foil

SLAC Today, July 27, 2010

VOLUME 92, NUMBER 7 PHYSICAL REVIEW LETTERS week ending 20 FEBRUARY 2004

Femtosecond and Subfemtosecond X-Ray Pulses from a Self-Amplified Spontaneous-Emission–Based Free-Electron Laser

P. Emma,* K. Bane, M. Cornacchia, Z. Huang, H. Schlarb,† G. Stupakov, and D. Walz
Stanford Linear Accelerator Center, 2575 Sand Hill Road, Menlo Park, California 94025, USA



The foil (yellow) slices each electron bunch (pink) while it is diverted into an upright shape inside a bunch compressor. The green triangles represent magnets that redirect the electrons' path of travel. (Image courtesy Paul Emma.)

But it wasn't until last week that the idea was tested experimentally. A group of SLAC physicists, including Clive Field, Mark Petree and David Kharakh, built and installed a prototype foil in early June; user experiments led by Reinhard Kienberger from the Technische Universitaet Munich, together with data collected previously by LCLS staff scientists, could determine whether the foil is, in fact, producing one-femtosecond X-ray pulses.

Attosecond X-ray pump-probe is no more a dream!

Can we catch the electron motion? Yes, we can!

Slotted foil: The open "V" (bottom) allows one bunch of electrons through; the double-slot "V"s (middle and top) create two narrow bunches. The width of the V determines the bunch width (single bunch) or timing between bunches (double-slot). (Image courtesy Paul Emma.)

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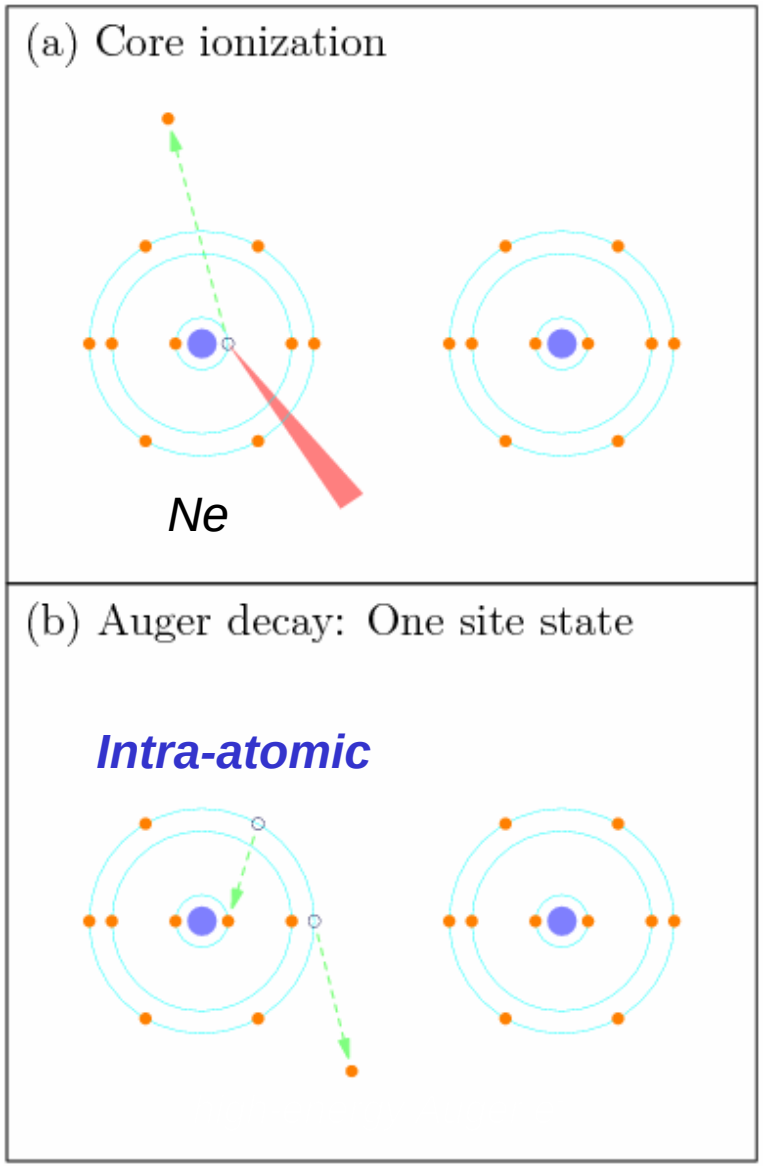
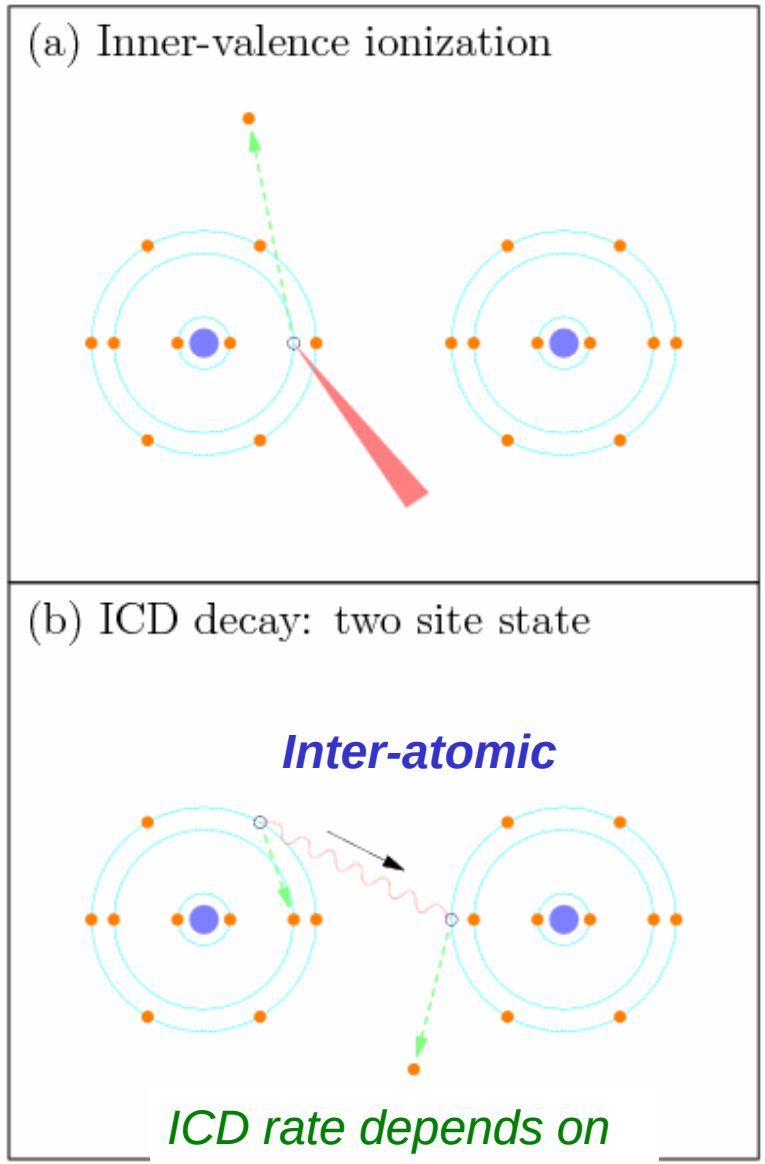
Auger vs Interatomic Coulombic Decay (ICD)





ICD rate depends on inter nuclear distance!

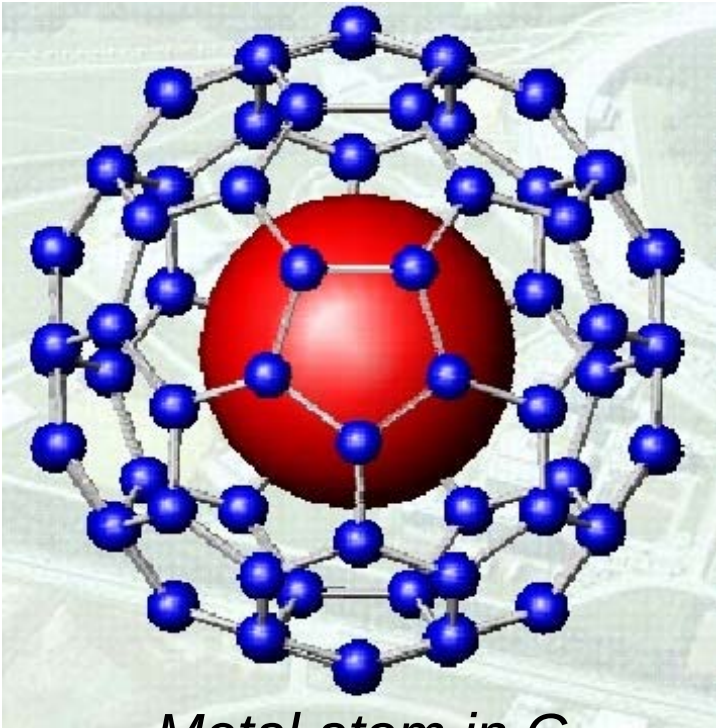
Why is ICD important?

ICD: electronic decay where the environment plays a role!

ICD occurs in van der Waals clusters, in hydrogen bonding clusters, in metallofullerenes, in bio-molecules in the living cell, etc

ICD is everywhere!

ICD is one of the key players in energy and charge transfer in these systems.



Metal atom in C_{60}

Benchmark study on Interatomic Coulombic Decay

Theoretical

First prediction - HF clusters:

L.S. Cederbaum, J. Zobeley, and F. Tarantelli, Phys. Rev. Lett. ***79****, 4778 (1997).*

Prediction - Ne dimer (and Ne clusters):

R. Santra, J. Zobeley, L.S. Cederbaum et al., Phys. Rev. Lett. ***85****, 4490 (2000).*

Experimental

First observation - Ne cluster:

U. Hergenhahn and coworkers, Phys.Rev. Lett. ***90****, 203401 (2003).*

Ne_2 e-ion-ion coincidence:

R. Dörner and coworkers, Phys. Rev. Lett. ***93****, 163401 (2004).*

Interatomic Coulombic Decay after Auger decay

Prediction - ICD from Auger final states in Ne dimer

R. Santra and L.S. Cederbaum, Phys. Rev. Lett. ***90****, 153401 (2003).*

Why is ICD after Auger decay important?

It may be relevant to radiation damage in bio-molecules in the living cell

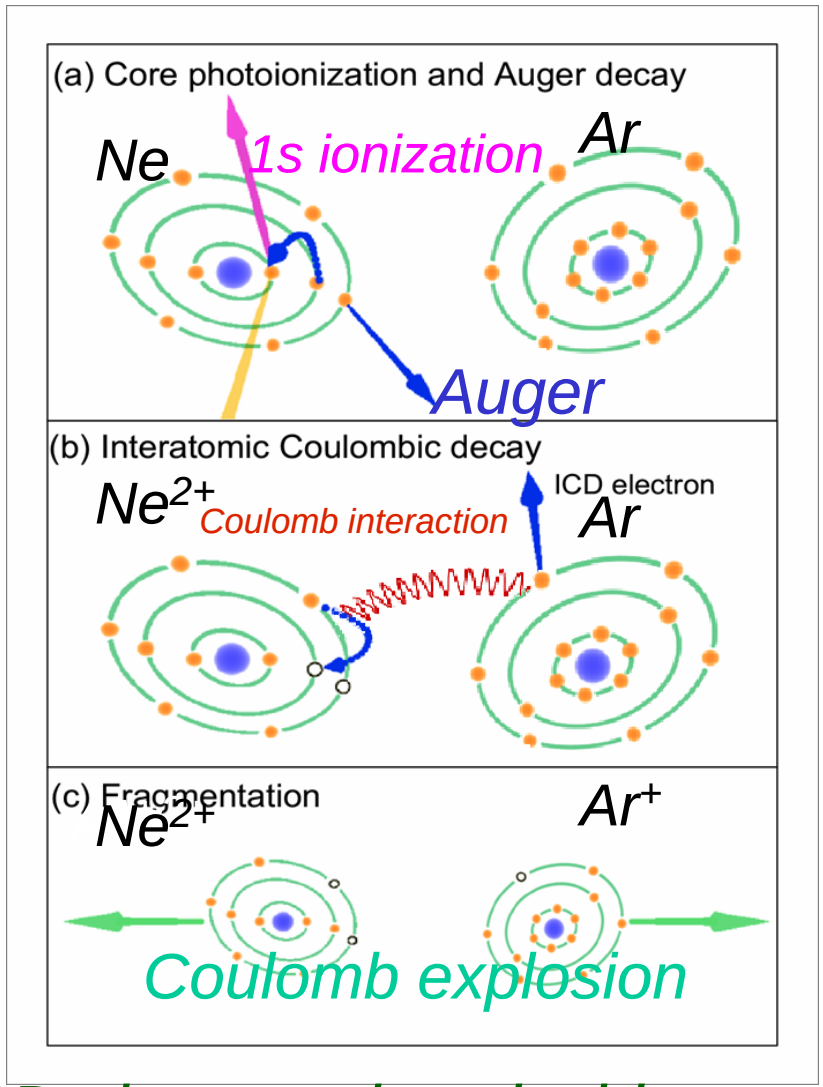
Core ionization by X-ray radiation is first step of radiation damage.

Radiation damage is known to be caused by low energy electron collisions, not high energy Auger electrons.

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

So ICD may be relevant to radiation damage!

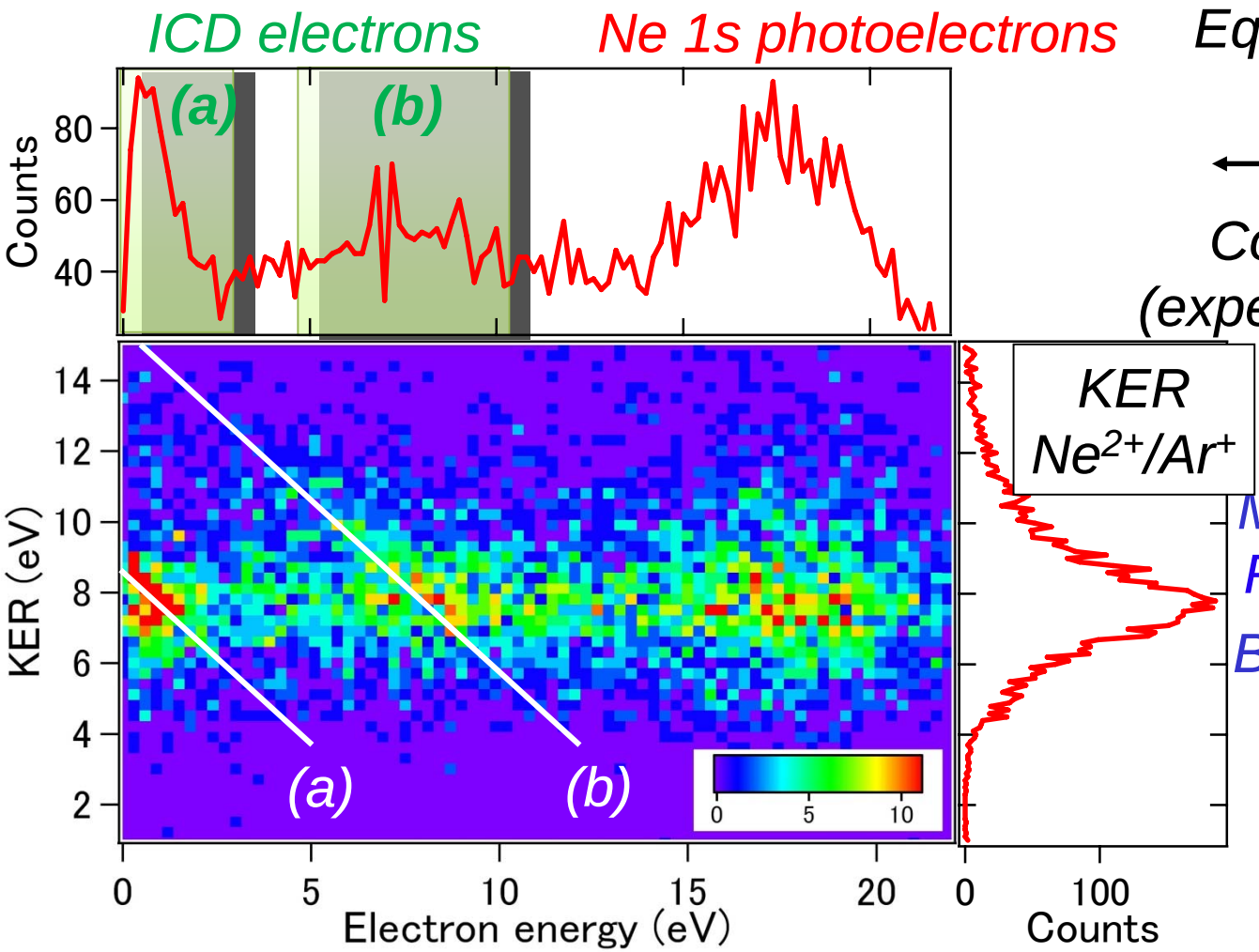
ICD in Ne-Ar after Ne 1s Auger decay



We detect ICD electrons in coincidence with Ne^{2+} and Ar^{+} using e-i-i coincidence momentum imaging

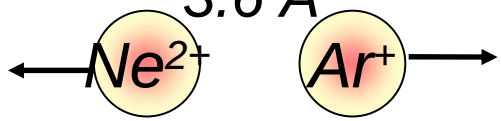
ICD in Ne-Ar after Ne 1s Auger decay

Electron ion coincidence map



Equilibrium distance

3.6 A



Coulomb explosion

(expected KER ~ 8.0 eV)

Measured KER~ 8 eV

R~3.6 A

Breakup following ICD takes place almost instantaneously.

ICD is very fast!

(a) $Ne^{2+}(2s^{-1}2p^{-1}\ {}^{3}P)$–Ar → $Ne^{2+}(2p^{-2}\ {}^{3}P)$–$Ar^{+}(3p^{-1})$

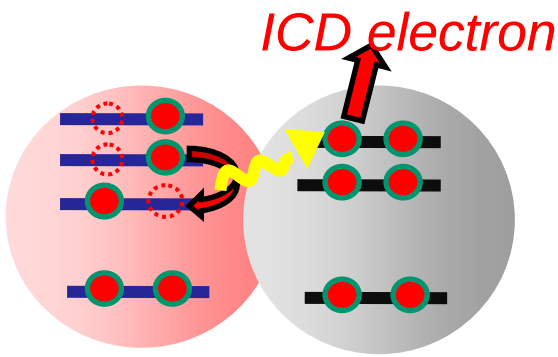
(b) $Ne^{2+}(2s^{-1}2p^{-1}\ {}^{1}P)$–Ar → $Ne^{2+}(2p^{-2}\ {}^{1}D)$–$Ar^{+}(3p^{-1})$

ICD and ETMD after triple ionization

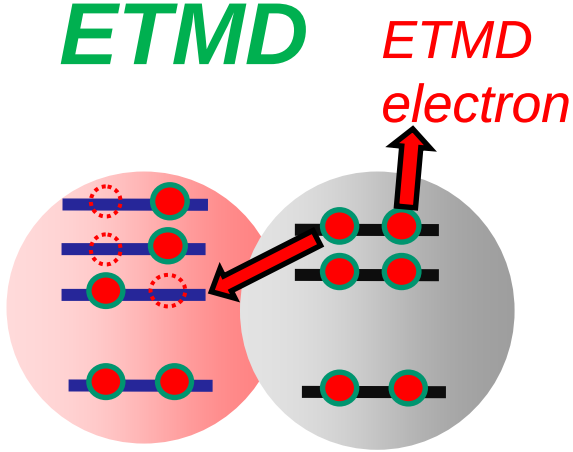
Triple ionization can occur by double Auger decay

interatomic Coulombic decay | **electron-transfer-mediated decay**

ICD



ETMD



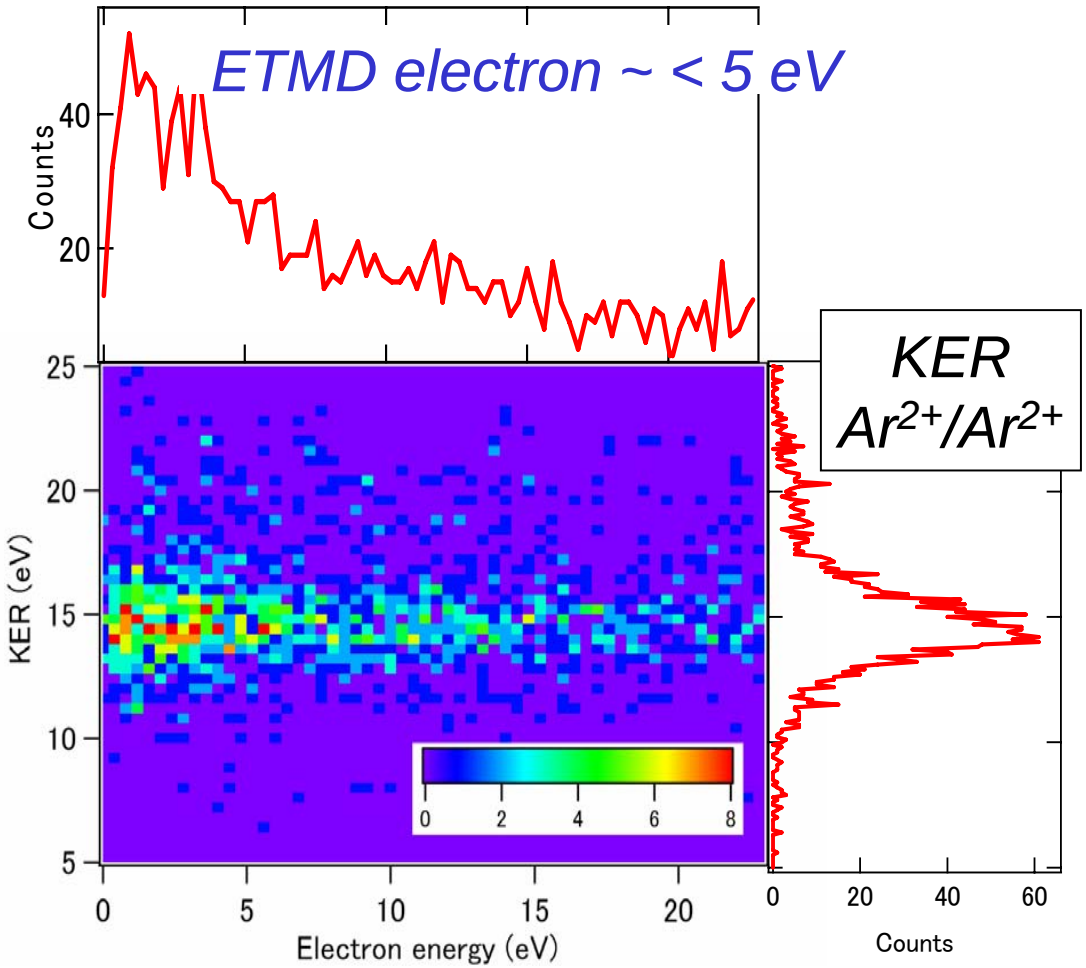
ICD $Ar^{3+} - Ar \rightarrow Ar^{3+} + Ar^{+} + e^{-}_{ICD}$

ETMD $Ar^{3+} - Ar \rightarrow Ar^{2+} + Ar^{2+} + e^{-}_{ETMD}$

We can distinguish ETMD from ICD

J. Zobeley et al., J. Chem. Phys. ***115****, 11(2001)*

ETMD in Ar_2 after triple ionization
Ar^{3+}-Ar → Ar^{2+}-Ar^{2+}



Equilibrium distance

3.8 A

Coulomb explosion

(expected KER ~ 15.2 eV)

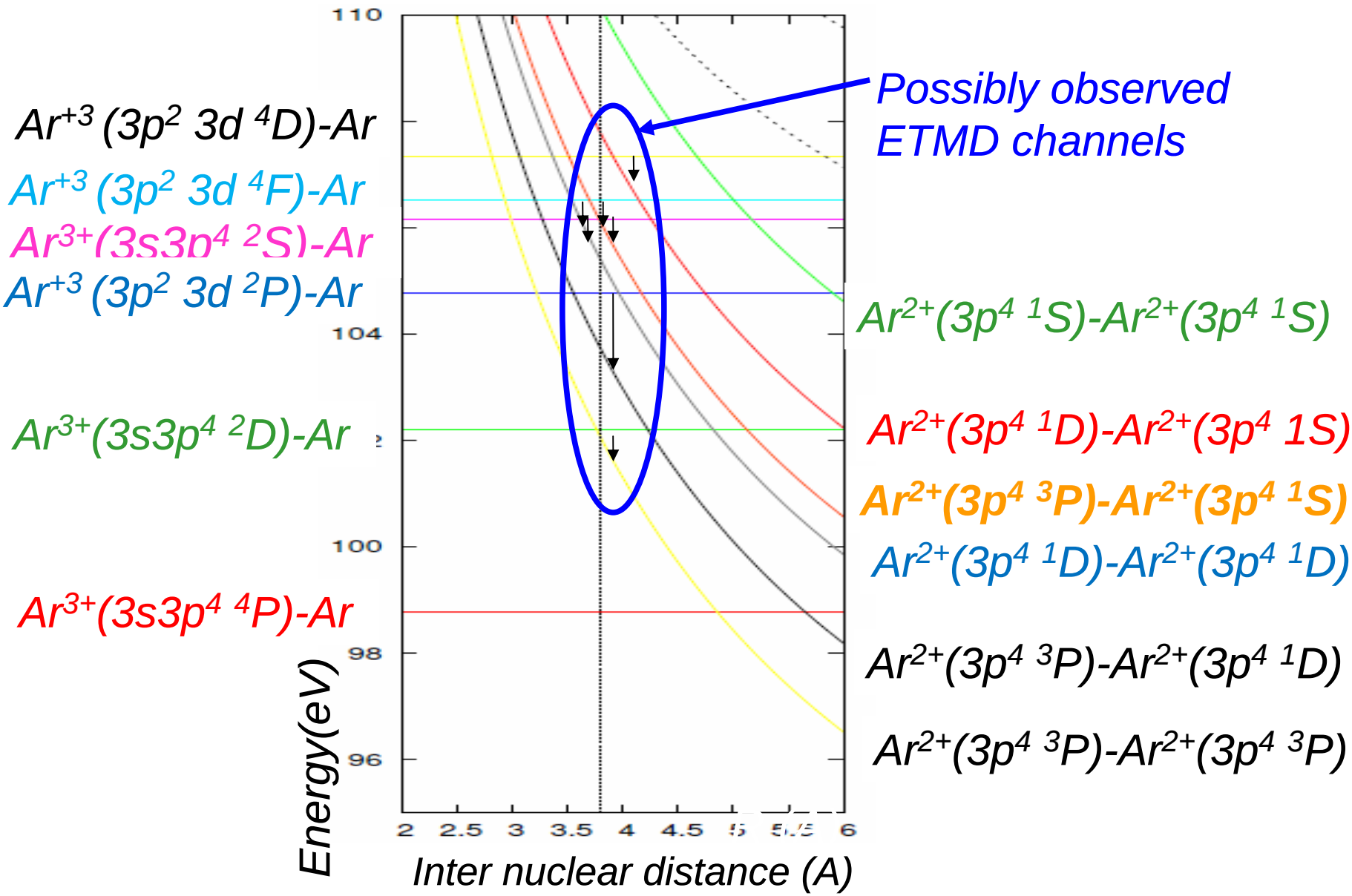
Measured KER ~ 14 eV

R= 4.1 A

Breakup following ETMD takes place almost instantaneously.

first observation of ETMD

ETMD in Ar_2 after triple ionization



ICD collaborations at SPring-8

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K. Ueda (Tohoku U.)

I. Higuchi, Y. Tamenori (JASRI/SPring-8)

H. Iwayama, K. Nagaya, M. Yao (Kyoto U.)

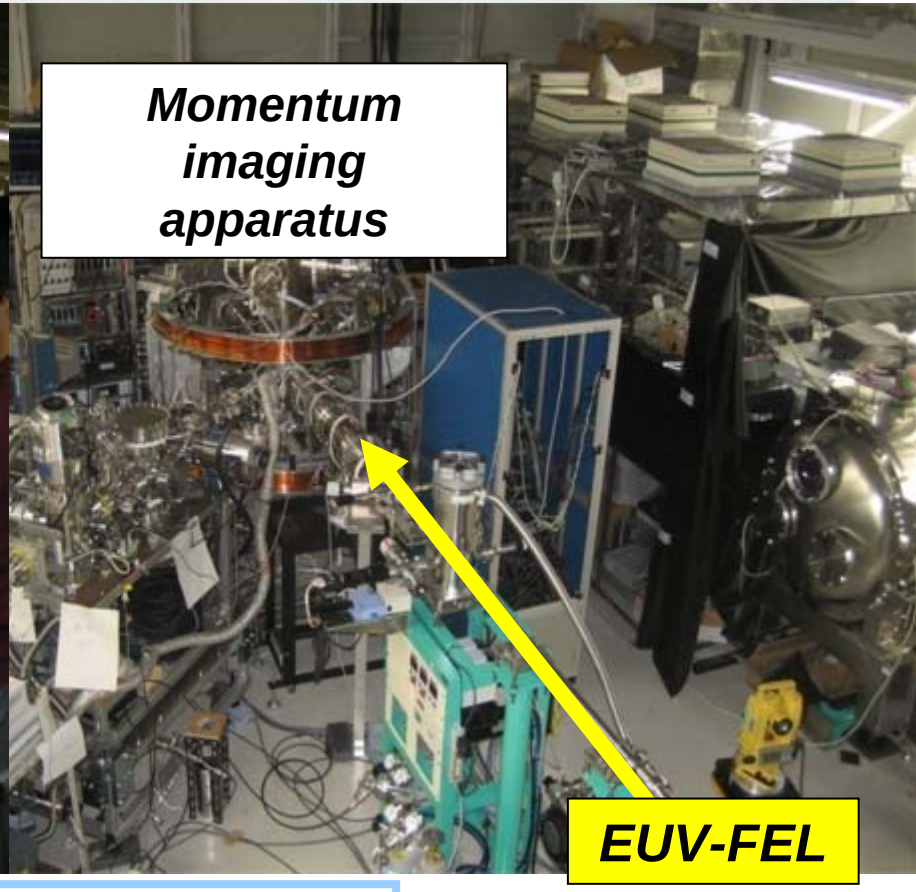
N. Saito (AIST)

D. Zhang, D. Ding (Jilin U.)

M. Schoffler (LBNL)

S.D. Stoychev, A.I. Kuleff, L.S. Cederbaum (Heidelberg U.)

SCSS test accelerator : EUV-FEL



Faciliy : EUV-FEL (SASE), RIKEN, Harima

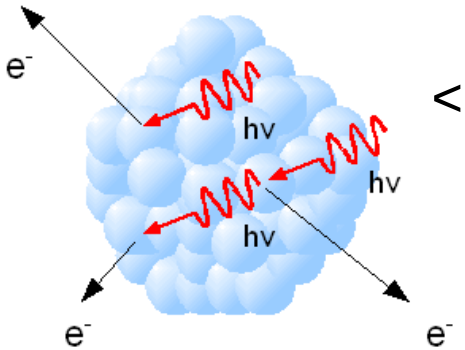
Wavelengths	: 51 ~62nm
pulse energy	: ~ 30 μ J at source point
pulse duration	: ~ 30 fs
focus size	: > 3 ~20 μ m
Laser power	: $\lesssim 10^{14}$ W/cm^2

Frustration of the cluster ionization

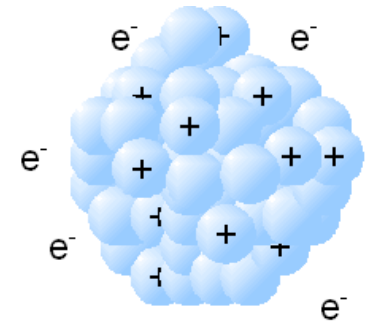
Bostedt et al., PRL 100, 133401 (2008)

Ionization energy of atomic Ar (14.6 eV) < 37.8 eV

Ar_{100}

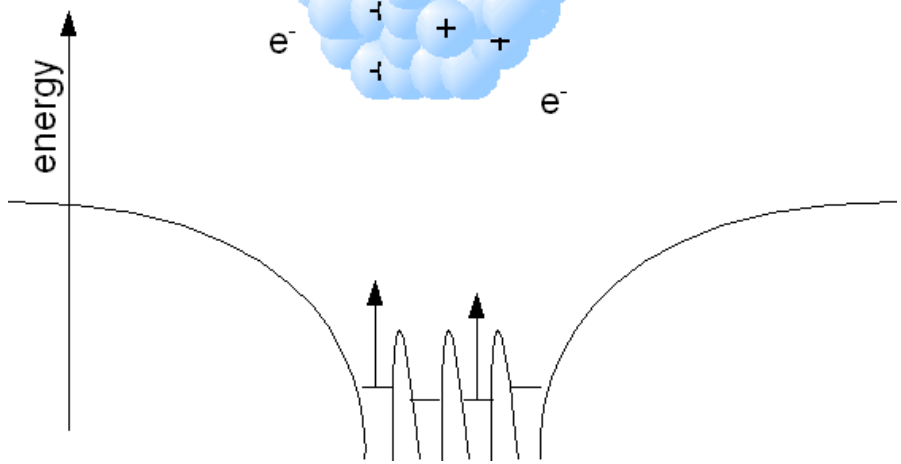


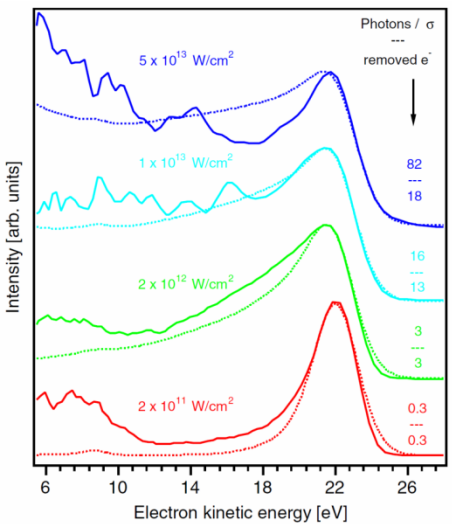
< 5 x10^{13} W/cm^2



Each individual atom will be ionized

Coulomb attractive potential increases with the increase in the charge of the parent cluster.





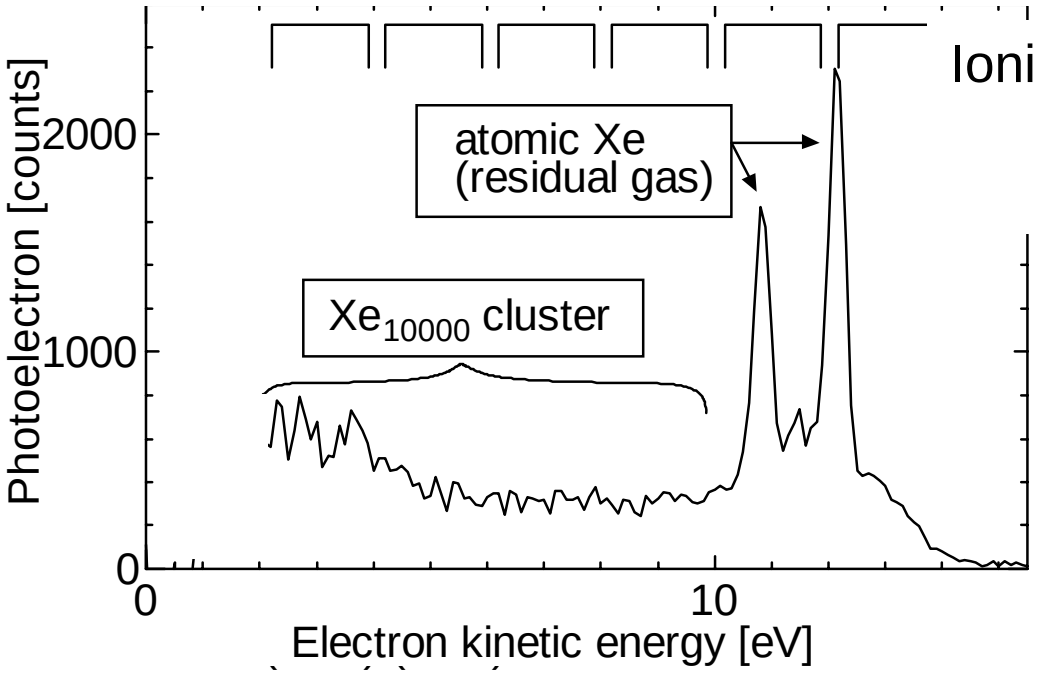
The photoelectron cannot escape from the cluster.
Inner ionization occurs but outer ionization is prohibited.

Frustration of the cluster ionization

Low energy photoelectron emission is due to lowering of the ionization potential with the increase in the charge of the cluster.

***Fukuzawa** et al., PR A 79, 031201 (R) (2009);*
***Iwayama** et al., JPB **42**, 134019 (2009).*

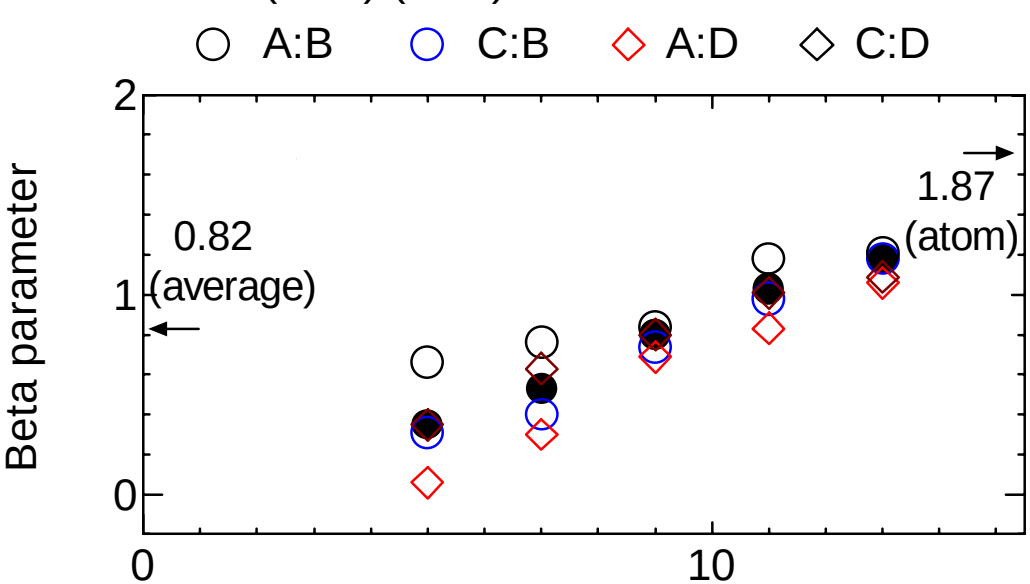
Electron emission from the Xe_{10000} cluster



Ionization energy of atomic Xe 12.13 eV
FEL photon energy 20.3 eV
Power density < 10^{13} W/cm^2

Continuous electron emission is observed as evidence of lowering of the ionization potential of the charged clusters.

We evaluated the energy dependence of beta parameter.



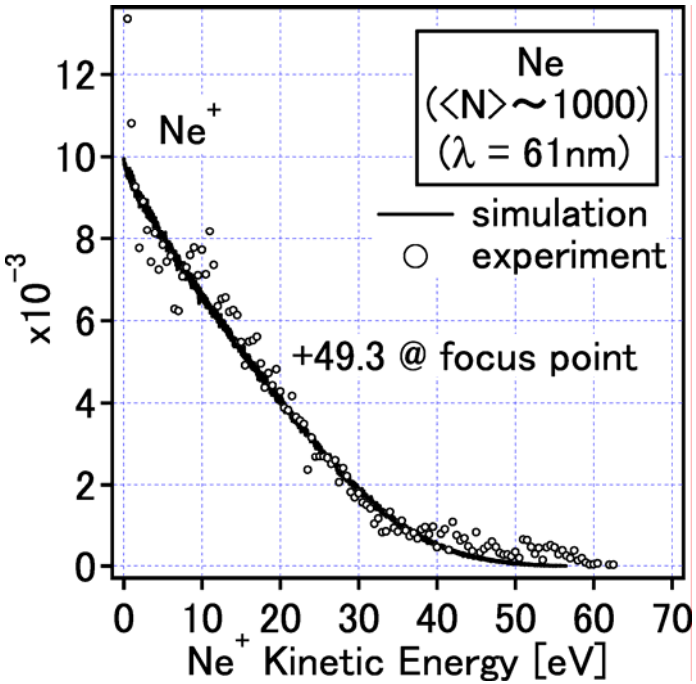
Beta value decreases with decrease in kinetic energy!

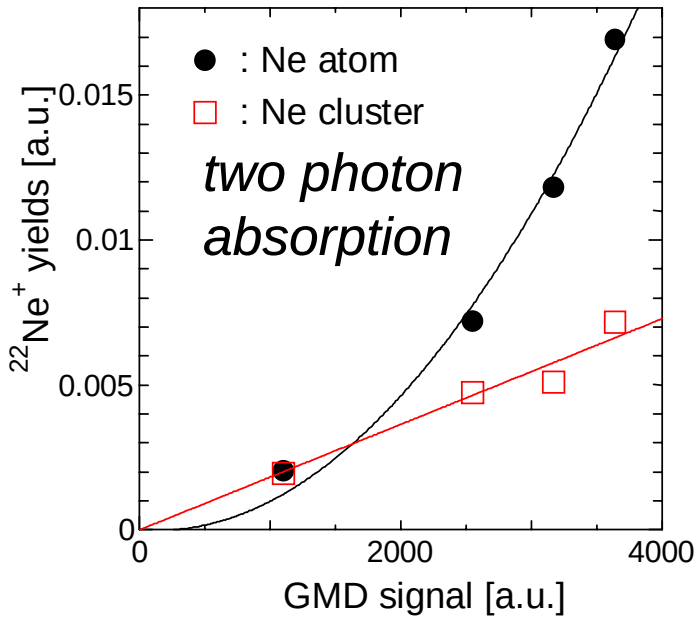
What happens with the trapped electrons?

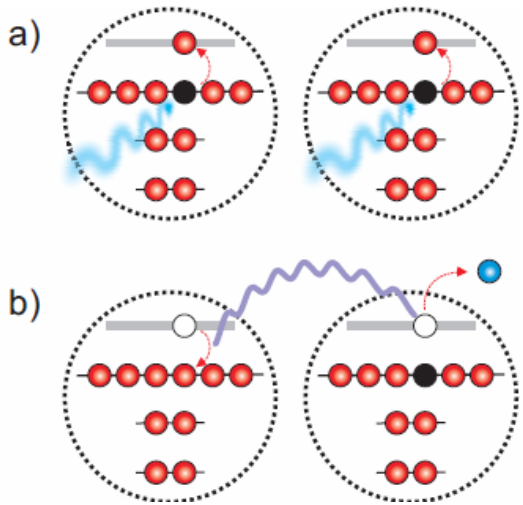
***Nagaya** et al, to be published*

Electronic decay of multiply excited Ne clusters (<N>=1000)

62 nm (Ne 2p->3d excitation)







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.

How will the charge be distributed?

***Nagaya** et al, to be published*

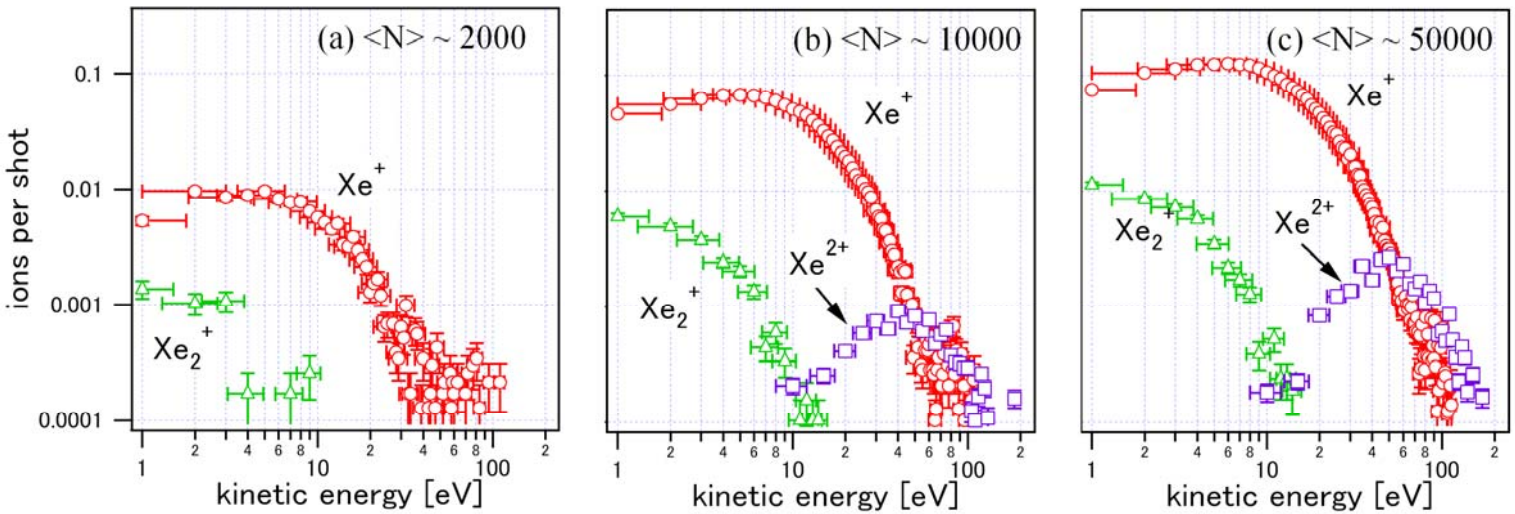
Ultrafast interatomic Coulombic decay in multiply excited clusters (Kuleff et al)

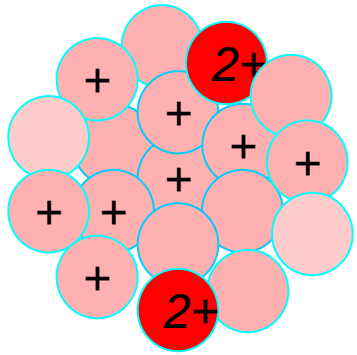
Xe clusters (<N>=2000, 10000, 50000) at 52nm

Kinetic Energy Distribution of the daughter ions

Kinetic Energy of Xe_2^+ : ~ 1 eV
Xe^+ : ~ 10 eV
Xe^{2+} : ~ 50 eV

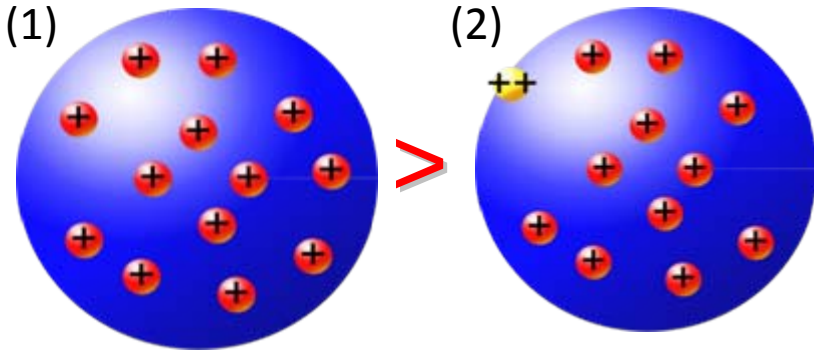
Kinetic Energy Distribution of Xe^{2+} has a hollow distribution.





The FEL power is sufficiently high to ionize the Xe atom up to +4, but for the clusters, multiply charged ions emerge only from giant clusters.

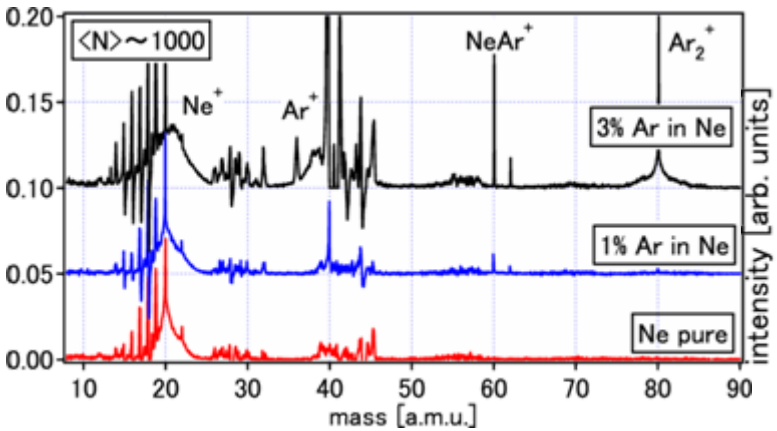
charge redistribution!



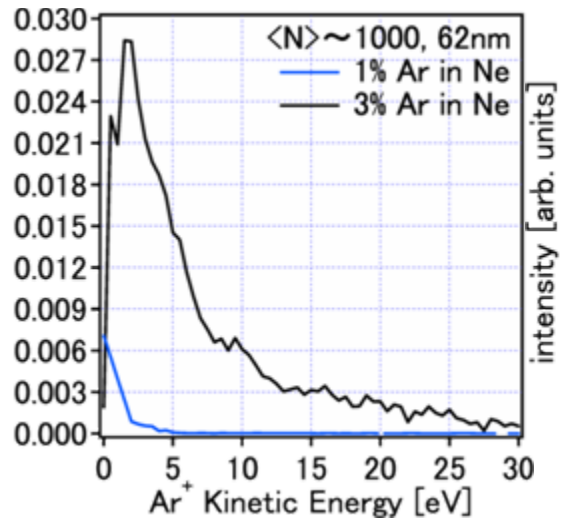
***Iwayama** et al., to be published.*

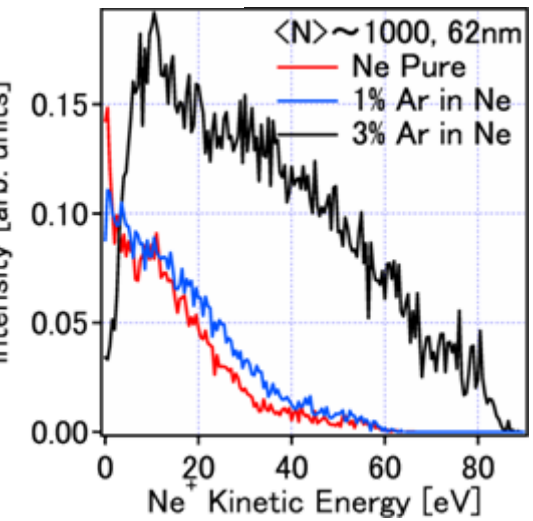
Ar core/Ne shell clusters (<N>=1000) at 62nm

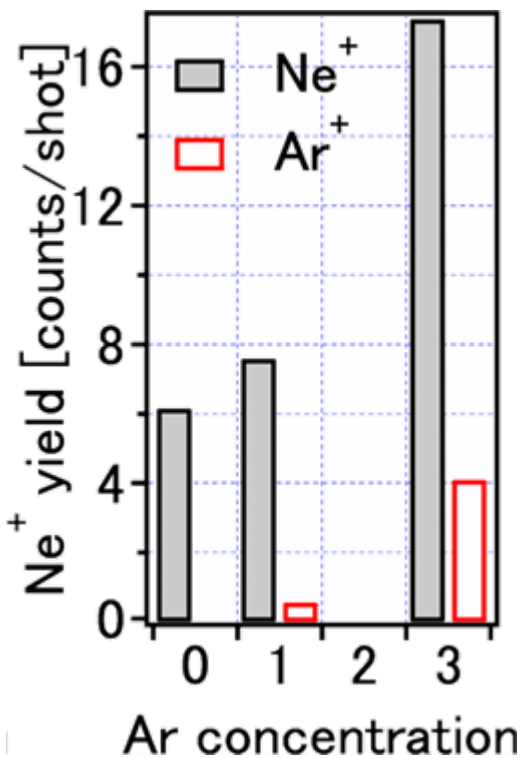
Ion TOF spectra



Ion kinetic energy distributions







The kinetic energy of Ar^+ is much smaller than Ne^+.

The Ar core-Ne shell structure of Ne-Ar cluster is confirmed.

With increasing Ar mixing ratio, the average kinetic energy and the yield of Ne^+ become large.

Evidence that charges produced at the Ar core migrate to the Ne shell.

***Sugishima** et al., to be published.*

Summary of the EUVFEL Cluster experiments

We have investigated multiple ionization of rare-gas nano-clusters

We found frustration of the cluster ionization and absorption

We found interatomic Coulombic decay in multiply excited neon clusters

We found self charge redistributions to minimize the energy in highly charged argon and xenon nano-clusters

We found charge transfer from Ar-core to Ne-shell

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Moscow U.
E. Gryzlova
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Thank you very much for your attention!
Santa Barbara