Cheiron School, SPring-8, Japan
October 2, 2008

Studies on atoms and molecules using synchrotron radiation

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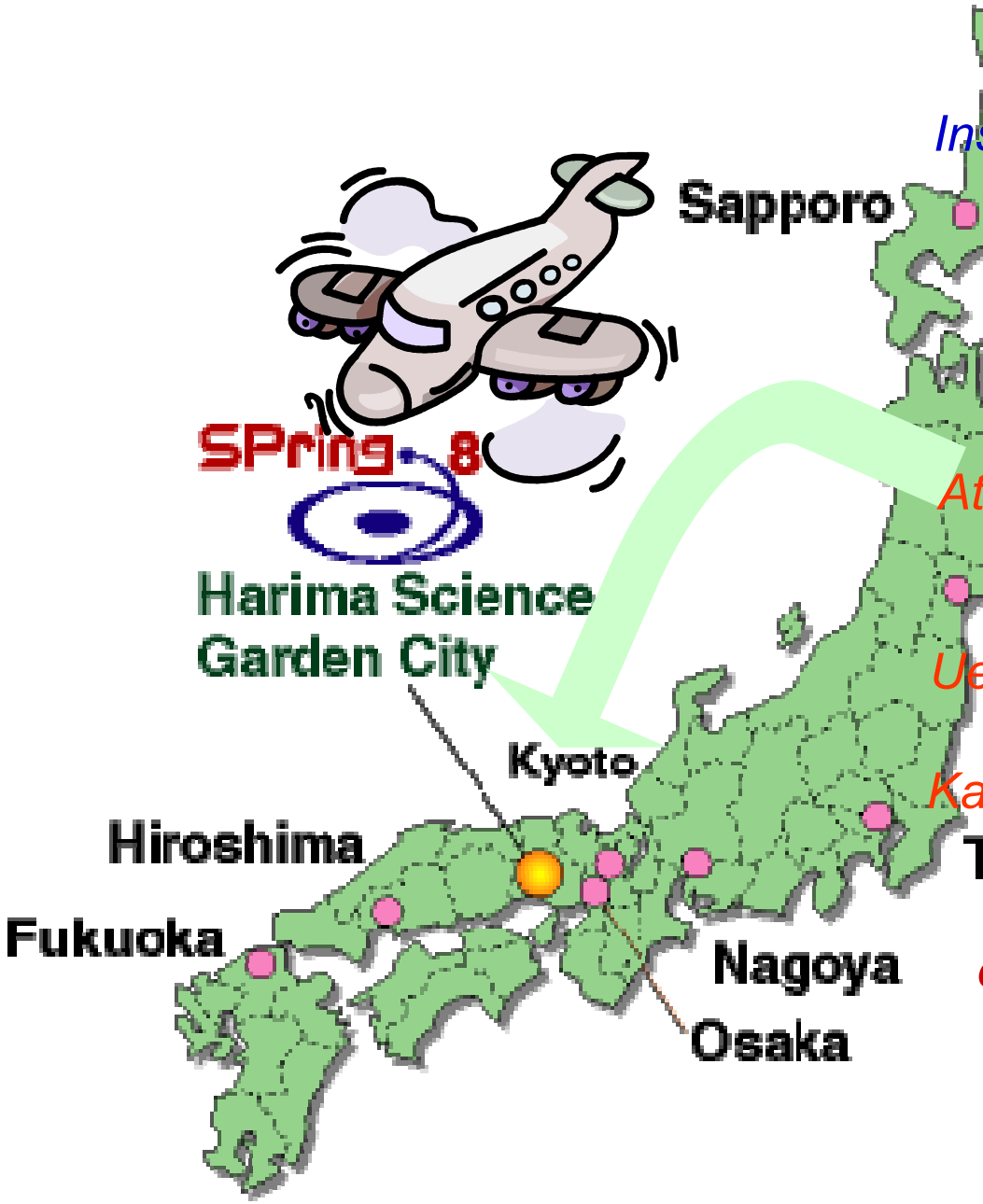
Introduction of myself



Prof. Kiyoshi Ueda
at
Tohoku University（Sendai）
Institute of multidisciplinary research for advanced materials
Leading group for analysis of quantum processes

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).

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

- Franck-Condon analysis and shape resonance effects

- Young's double-slit experiments

- Intermission -

4. Multiple-ion momentum imaging

- Snapshots of molecular deformation within a few fs

5. Electron-ion momentum imaging

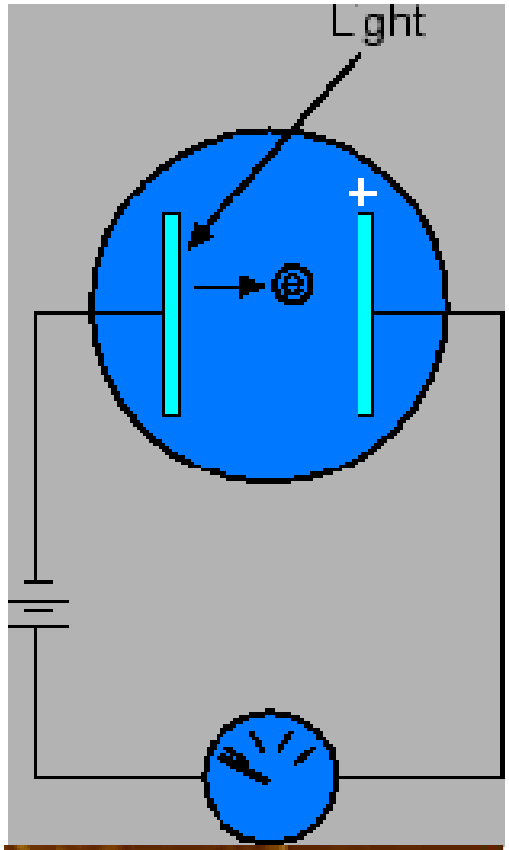
- Molecular frame photoelectron angular distributions

- Interatomic Coulombic decay

Photoelectric effect

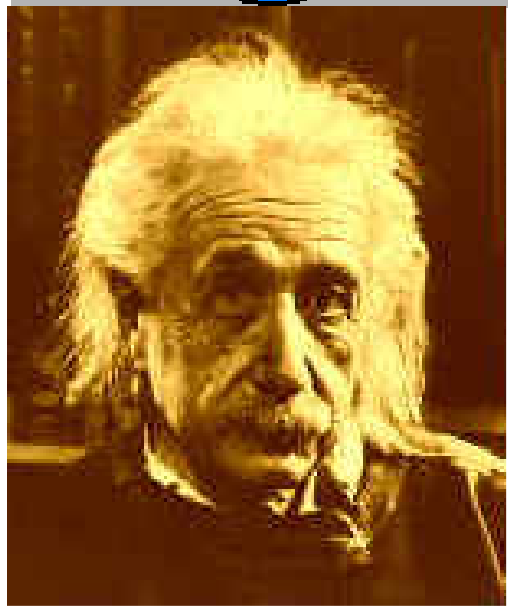
When matter is shined by the light, electron is emitted from the surface.

(i) Frequency of the light needs to be larger than ν_0.
(ii) Kinetic energy of the electron is determined by the frequency of the light.
(iii) Number of electron is proportional to the intensity of the light.



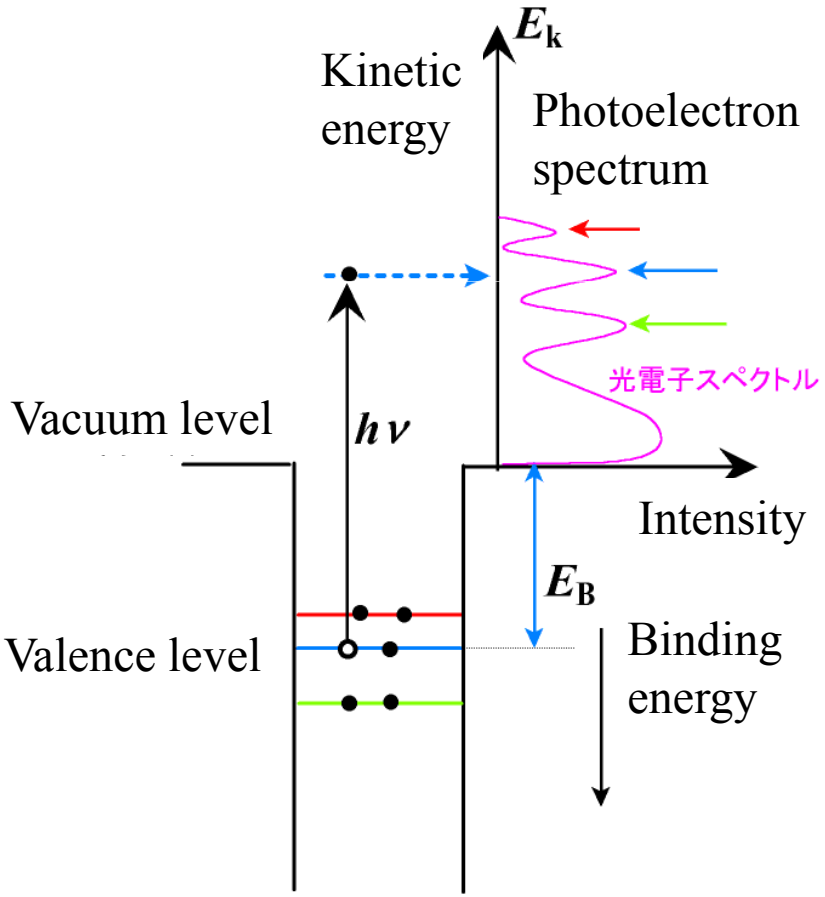
Einstein's explanation

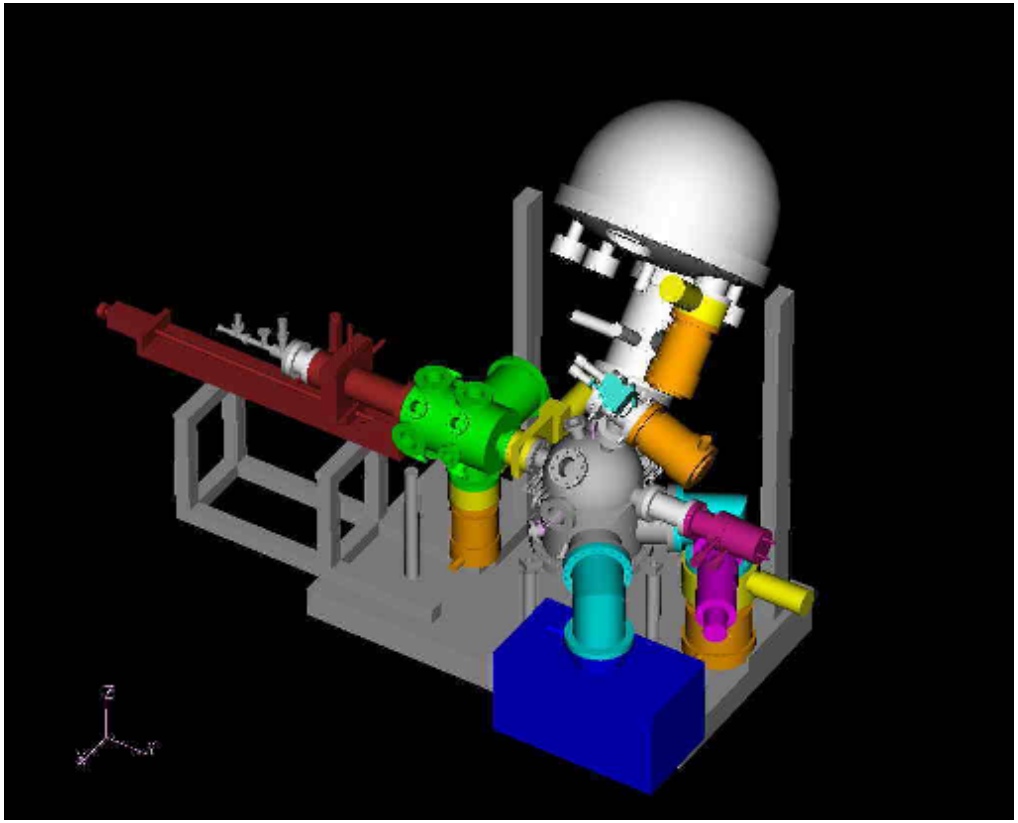
Light at frequency of ν is considered to be a group of particles (photons) and each photon has energy $h\nu$.
An electron gets the energy $h\nu$ when it absorb one photon.
The electron in the matter is bound. For the electron to be emitted from the matter, the electron needs to receive the energy more than the work function *W.*
Then the kinetic energy *KE* of the emitted electron can be given as $KE = h\nu - W$.



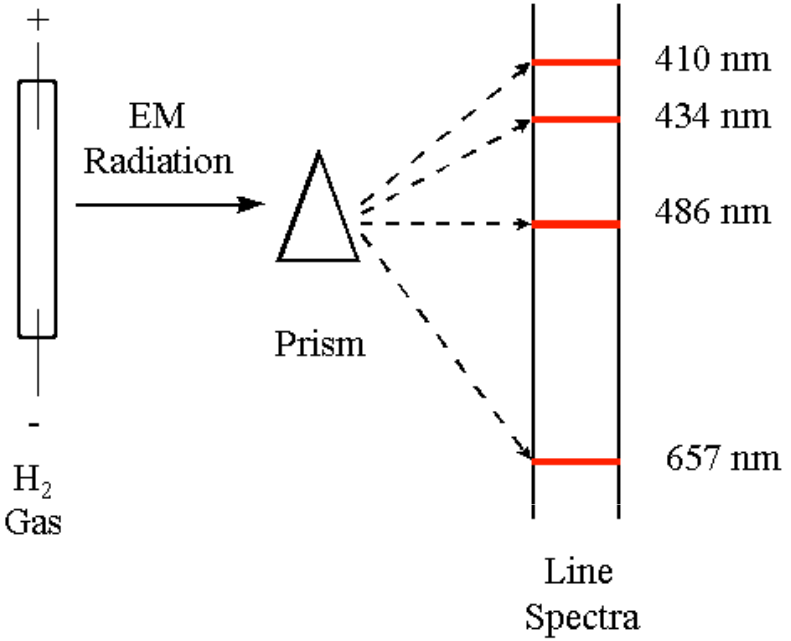
Photoelectron spectroscopy (UPS, XPS)

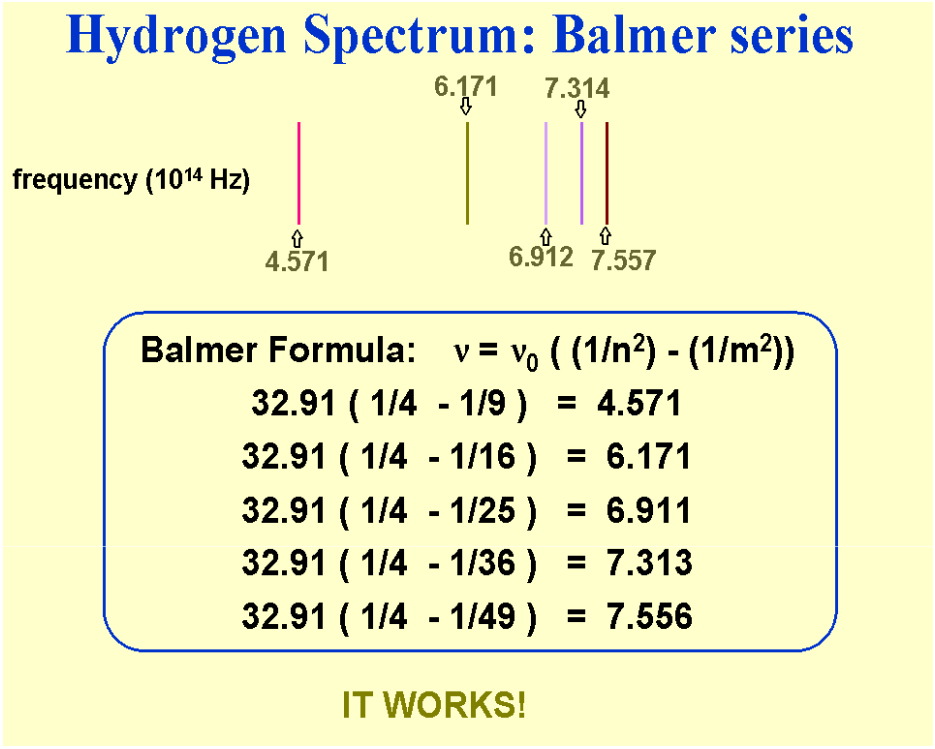
Precision measurements for kinetic energies of photoelectrons emitted via Einstein's photoelectric effects





Balmer and Rydberg formulae





Balmer found beautiful regularity in the H spectrum!

Rydberg formula: $$\frac{\nu}{c} = \frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$$

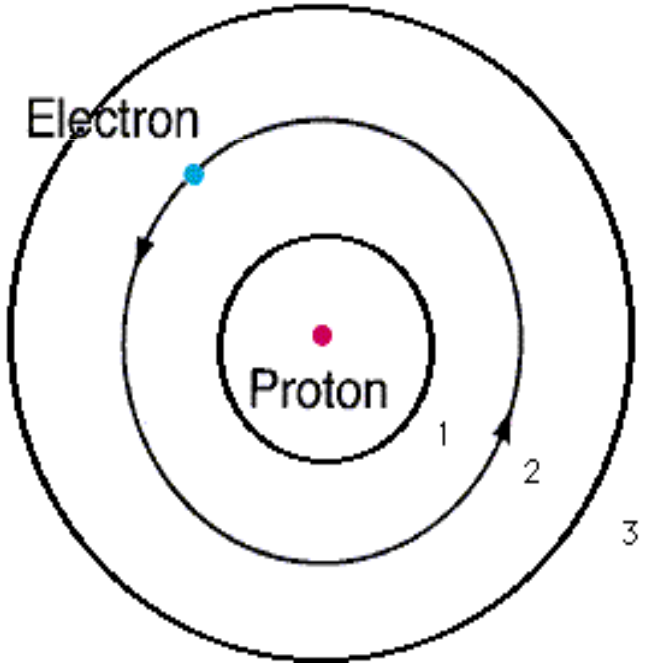
c, speed of light; λ, wavelength; *R*, Rydberg constant (*R* =109737.309 cm^{-1})

Bohr's atomic model

Electron orbits exist only when the classical orbits satisfy the following condition of quantization:

$$\int_0^{2\pi} p_\varphi \, \mathrm{d}\varphi = nh$$

φ, angle of rotation; $p_\varphi = m_e r^2 d\varphi / \mathrm{d}t$, angular momentum; r, radius; m_e, electron mass



The electron binding energies are discrete:

$$\bar{E}_n = -hcR/n^2$$

Schrödinger equation of H atom (in atomic units)

$$H\Psi(r) = E\Psi(r)$$

$$H = T + U(r)$$ Hamiltonian

$$T = \frac{p^2}{2} = -\frac{1}{2}\frac{\partial^2}{\partial r^2}$$ kinetic energy

$$p = i\frac{\partial}{\partial r}$$ momentum

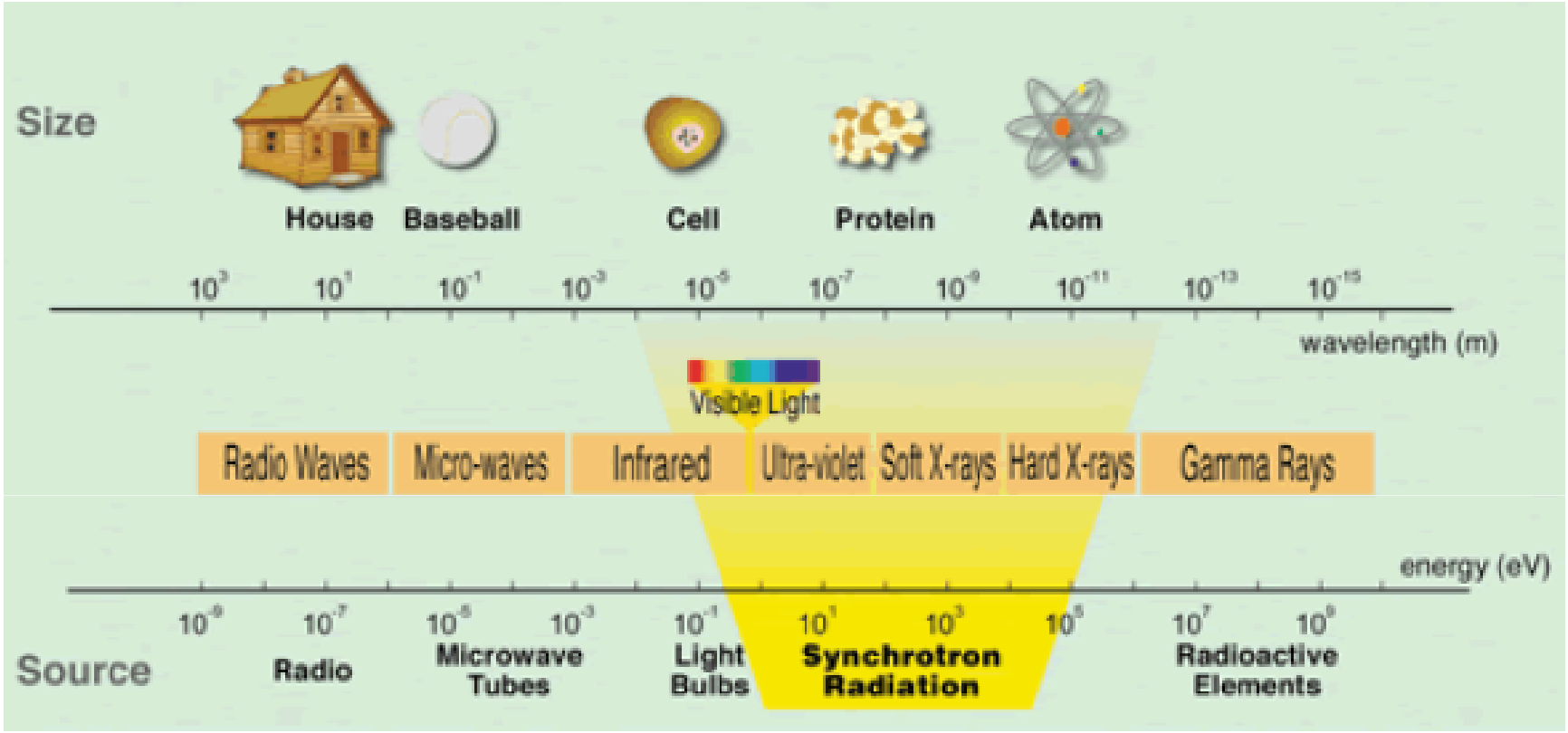
$$U(r) = -\frac{1}{r}$$ potential energy

$$E_n = -\frac{1}{2n^2}$$

Ψ: wave function
complex number (with phase!)

Atomic and molecular science now

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



How to use synchrotron radiation to study atoms and molecules

We use monochromatic synchrotron radiation to excite atoms and molecules and to study their electronic structures as well as electron and nuclear dynamics in the excited states.

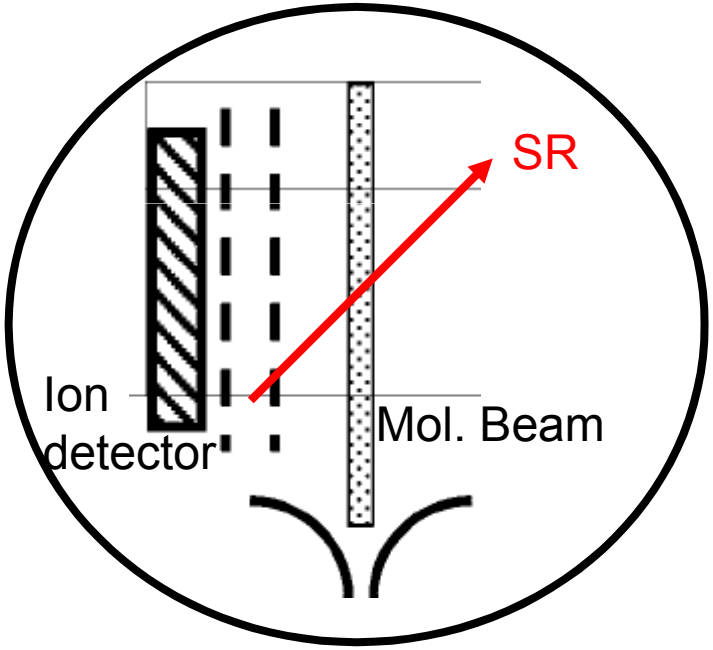
A single photon should be absorbed by a single atom or molecule first!

What photon energies to be used

Electron binding energies (eV) *Vacuum ultraviolet light!*

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$
1 H	13.6			
2 He	24.6*			
3 Li	54.7*			
4 Be	111.5*			
5 B	188*			
6 C	284.2*			
7 N	409.9*	37.3*		
8 O	543.1*	41.6*		
9 F	696.7*			
10 Ne	870.2*	48.5*	21.7*	21.6*

The experiments need to be in the vacuum!

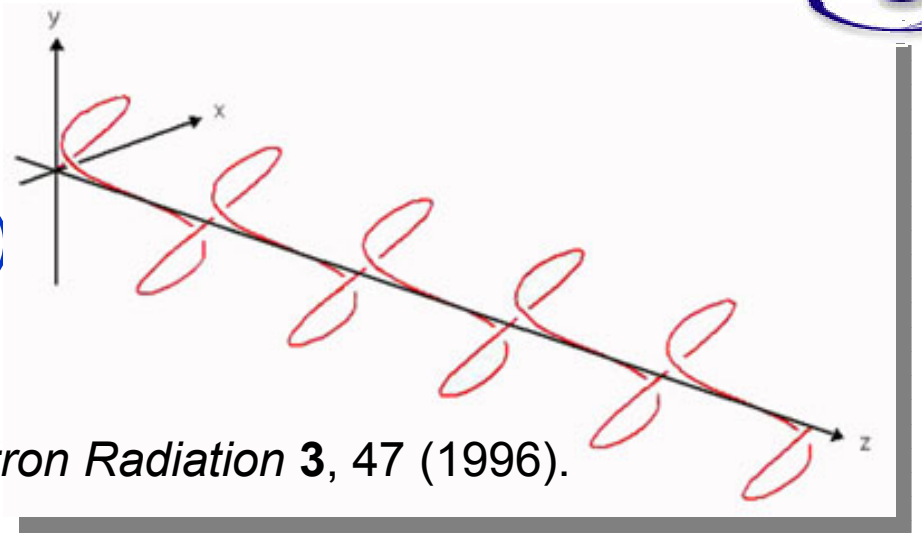


The easiest experiment: ion yield spectroscopy

SPring-8 BL27SU

Figure-8 undulator

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



T. Tanaka and H. Kitamura, *J. Synchrotron Radiation* **3**, 47 (1996).

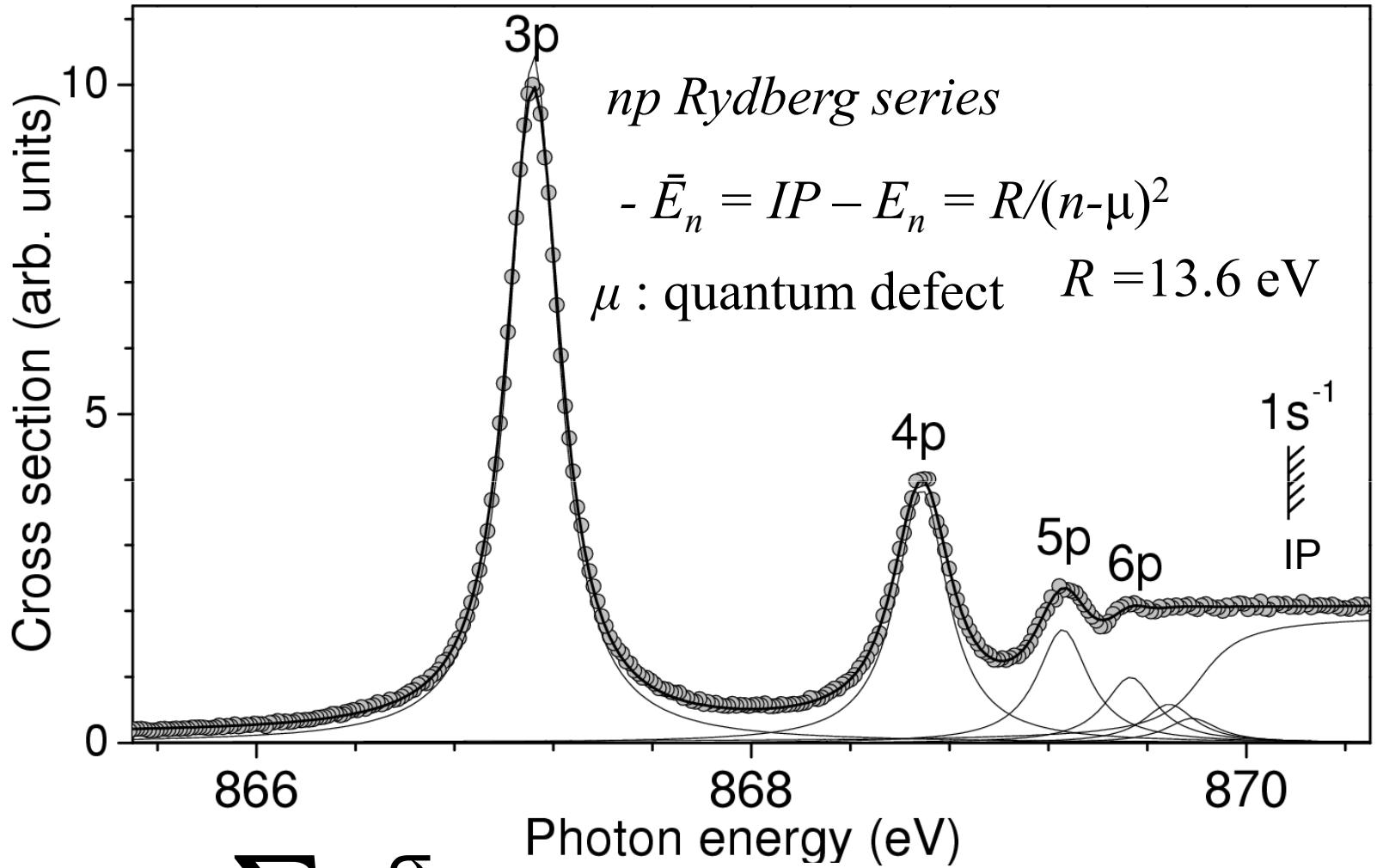
Soft X-ray monochromator

Hettrick type: varied line spacing plane grating

Energy range	0.15 ~ 2.5 keV
Photon Flux	> 10^{11} photon/s
Energy resolution	10000 - 20000

H. Ohashi, Y. Tamenori, E. Ishiguro *et al*. *Nucl. Instr. Methods A* **467**, 533 (2001).

Ne 1s total ion yield spectrum

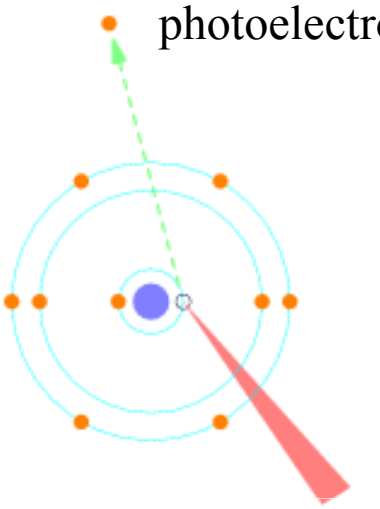


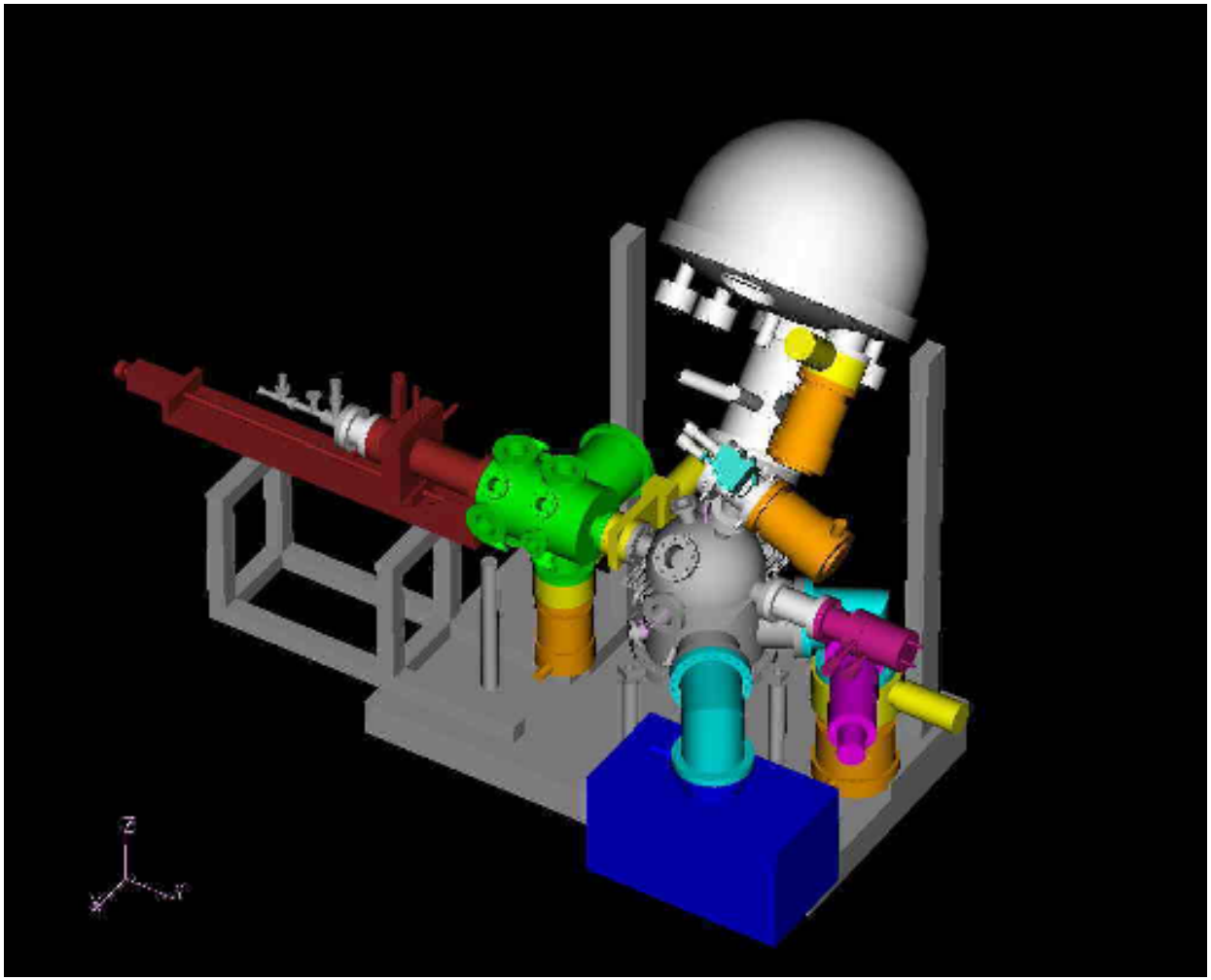
$$\sigma = \sigma_{dir} + \sum_n \frac{\sigma_n}{1+\varepsilon_n^2} + \sigma_{1s} \qquad \varepsilon = (h\nu\text{-}E_n)/(\Gamma_n/2)$$

$$\sigma_n \propto 1/(n-\mu)^3 \qquad \Gamma_n = \text{const!}$$

Auger decay and Auger electron spectroscopy

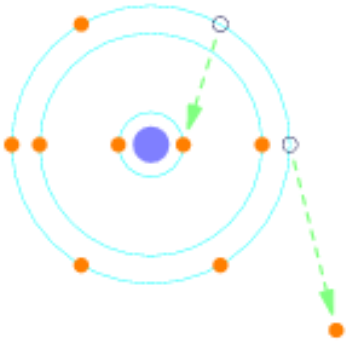
(a) Core ionization





(b) Auger decay:

Core hole lifetime
defines the line width!



SES2002 analyzer

- Electrostatic hemispherical analyzer
  - Mean radius 200 mm
  - ΔE/PE=1/1600

  (66 meV at pass 100 eV)
  - **MCP+CCD camera**

  or MCP+Delay line anode

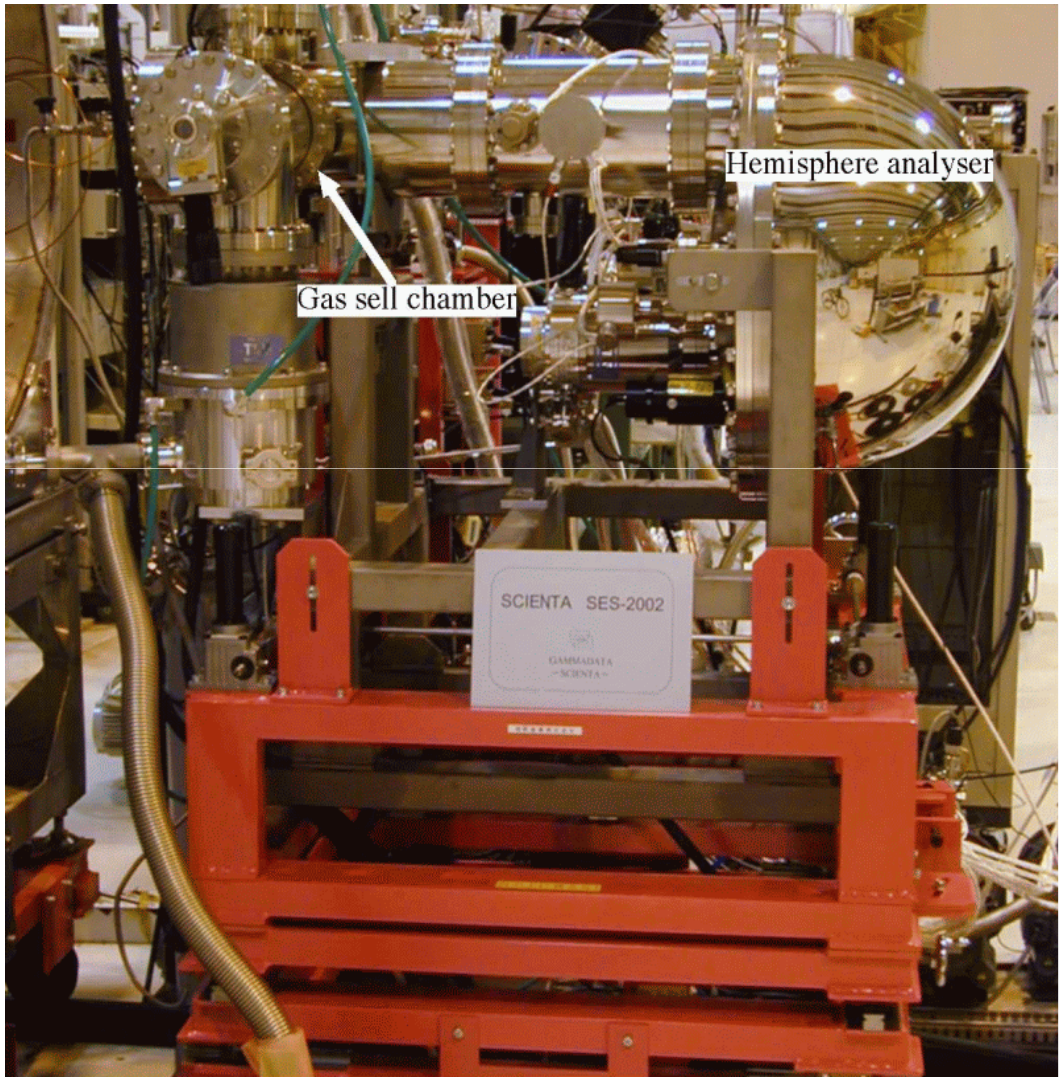
  - **Gas cell system**

  or Doppler-free molecular beam source

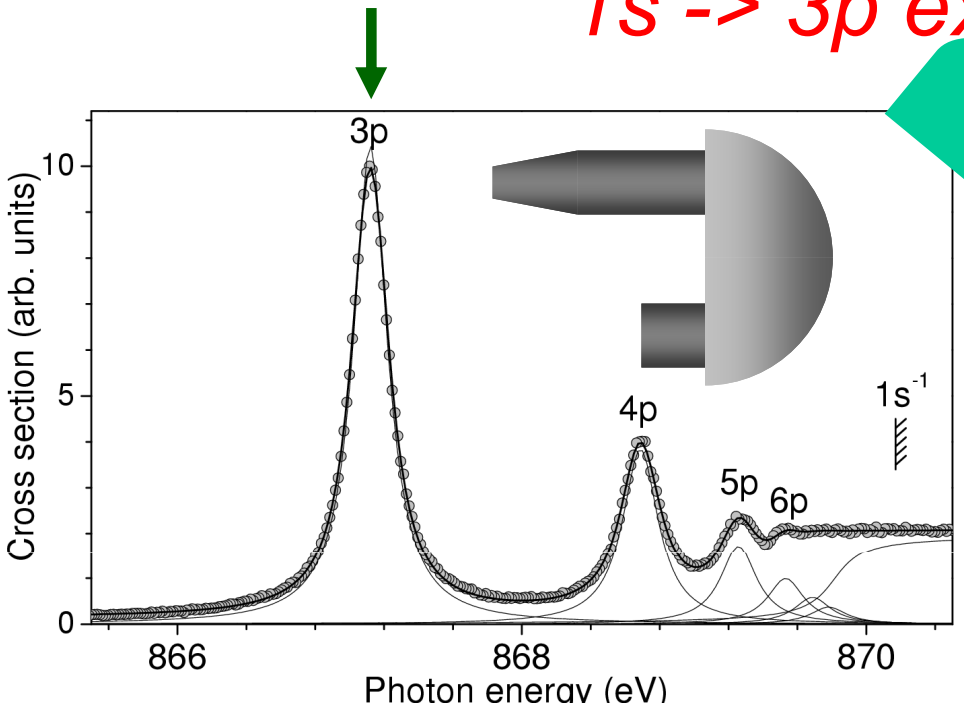
  Ueda *et al. PRL* . **90**, 153005 (2003)

  or effusive beam + momentum resolved ion spectrometer

  Prümper *et al.* PRA **71**, 052704, (2005).



Angle-resolved resonant Auger spectra of Ne at 1s -> 3p excitation

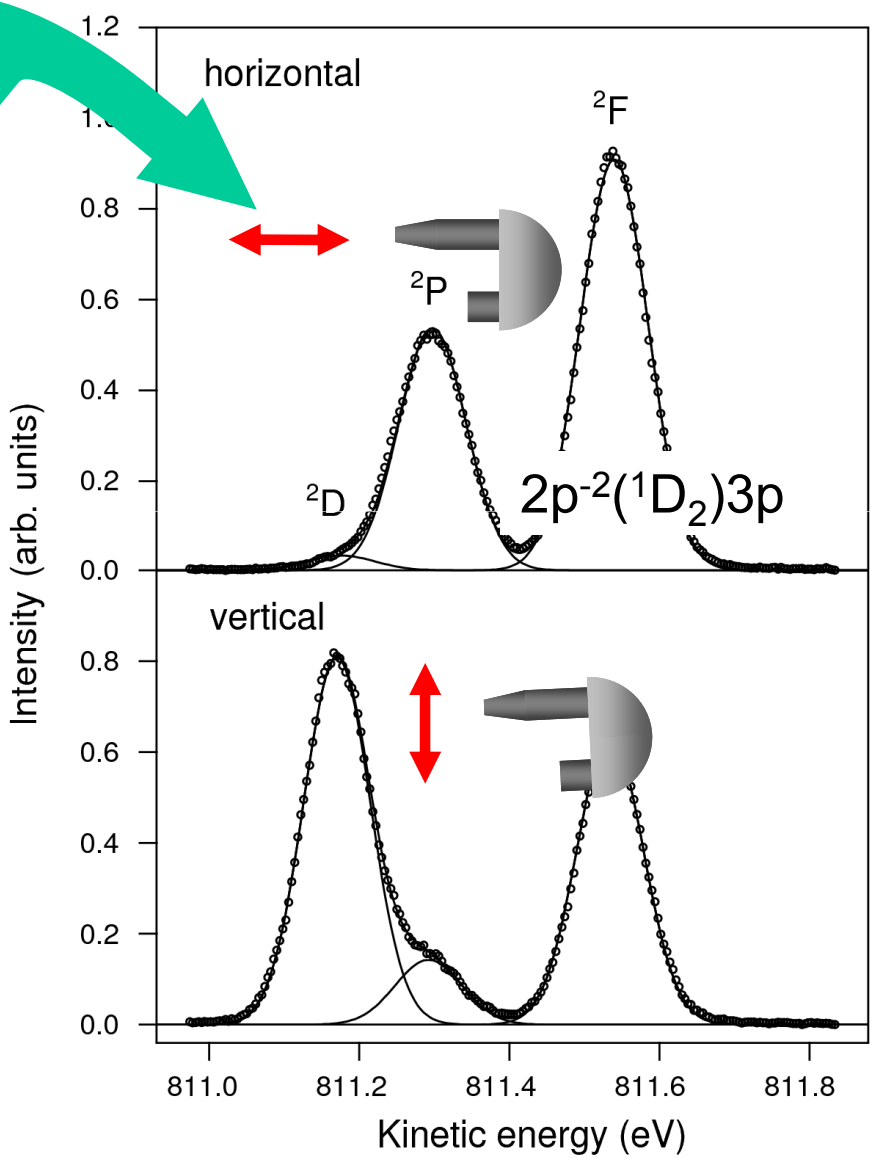


$$\frac{d\sigma}{d\theta} = \frac{\sigma}{4\pi}[1 + \beta P_2(\cos\theta)]$$

$$P_2(\cos\theta) = [3\cos\theta - 1]/2$$

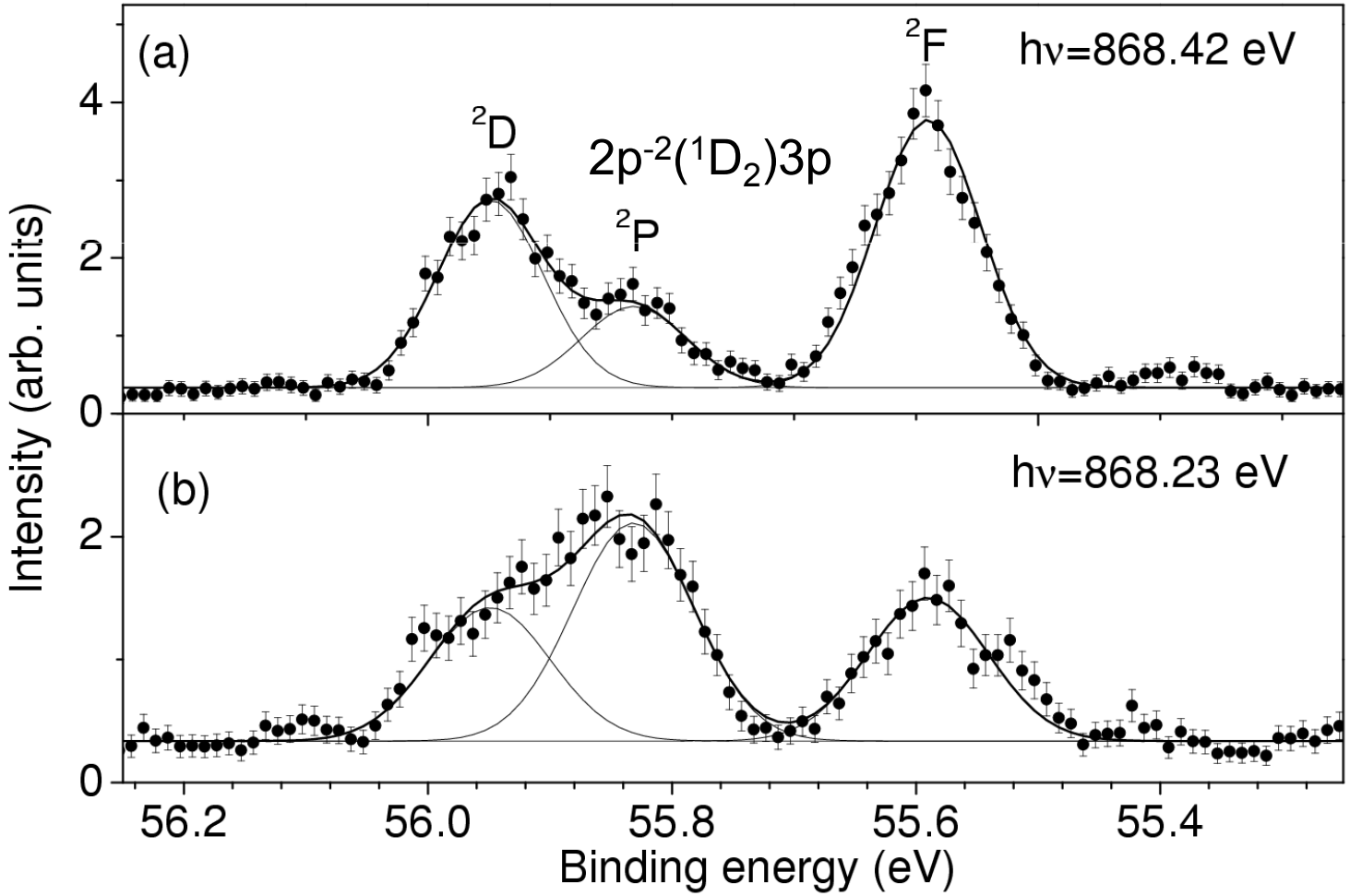
β: asymmetry parameter

Measured angular distributions tell us how the angular momenta are coupled in the atom , allowing us the spectroscopic assignment !



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

$$\frac{d\sigma}{d\theta} = \frac{\sigma}{4\pi}[1 + \beta P_2(\cos\theta)] \qquad \sigma \propto I(0) + 2 \times I(90)$$



Interference effects between the two paths

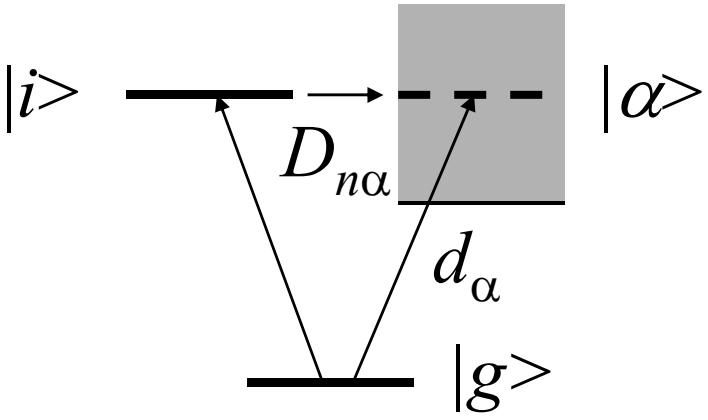
$$A_\alpha = d_\alpha + \sum_n \frac{D_{n\alpha}}{i+\varepsilon_n}$$

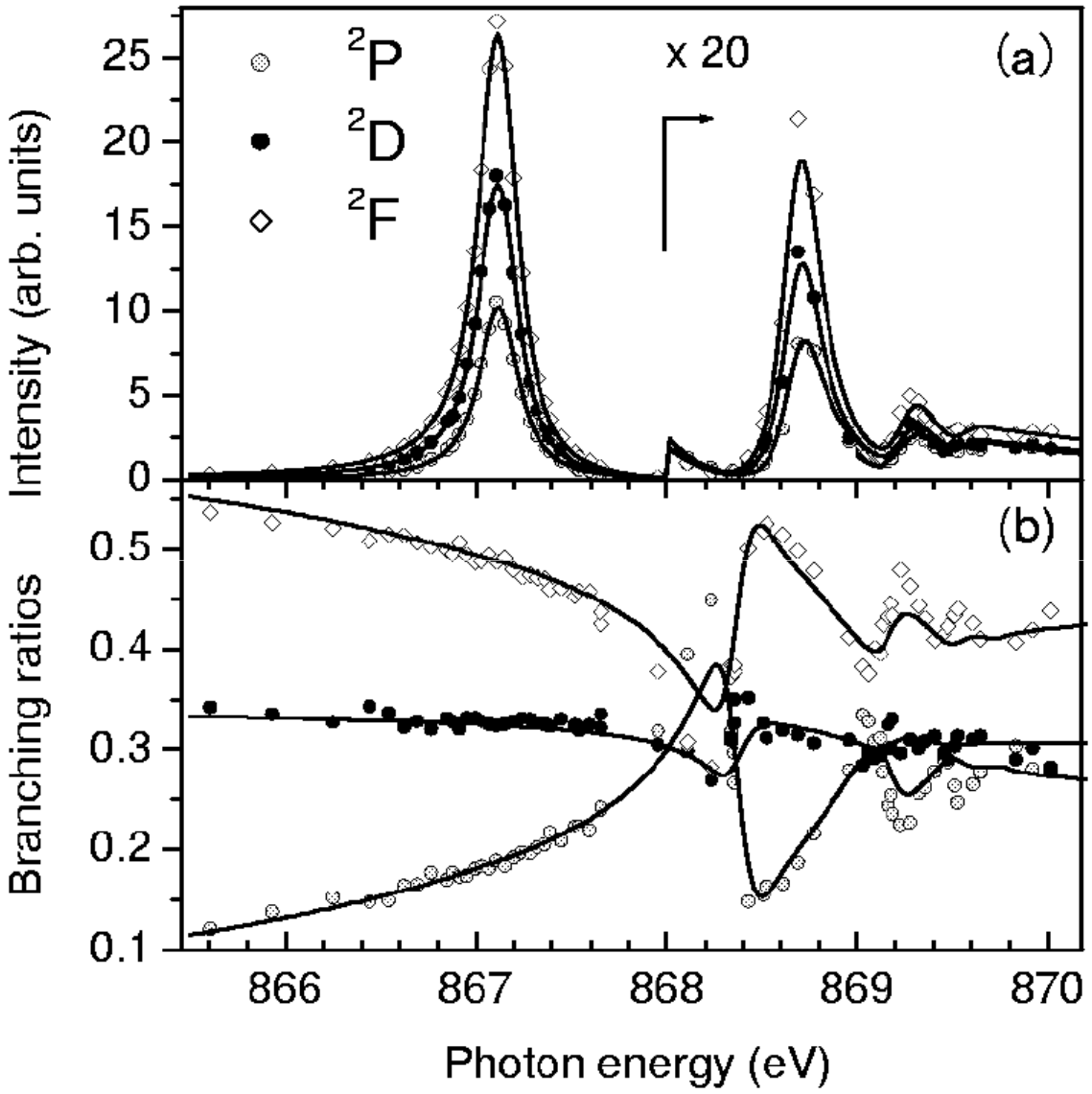
$$\sigma_\alpha = |A_\alpha|^2$$

$$\varepsilon_n = (h\nu - E_n)/(\Gamma_n/2)$$

$$d_\alpha = \langle g|r|\alpha\rangle$$

$$D_{n\alpha} = \langle g|r|i_n\rangle\langle i_n|\alpha\rangle$$





De Fanis *et al.* Phys. Rev. Lett. **89**, 023006 (2002).

Sendai City

Introduction of molecular world

$$H\Psi(R,r) = E\Psi(R,r) \qquad H = T_R + T_r + V(r,R)$$

$$T_R = -\frac{\hbar}{2}\sum_k \frac{\partial^2}{M_k \partial R_k^2} \quad \text{KE of nucleus} \qquad T_r = -\frac{\hbar}{2m}\sum_j \frac{\partial^2}{\partial r_j^2} \quad \text{KE of electrons}$$

$$H = H_0 + T_R \qquad H_0 = T_r + V(r,R)$$

$$[H_0 - \varepsilon_n(R)]\varphi(R,r) = 0$$

$\varepsilon_n(R)$: adiabatic potential energy

$$\Psi(R,r) = \sum_n \Phi_n(R)\varphi_n(R,r)$$

$$\int \varphi^*(R,r)(H-E)\Psi(R,r)dr = 0$$

$$[T_R + \varepsilon_m(R)]\Phi^0_{mv}(R) = E^0_{mv}\Phi^0_{mv}(R)$$

Nuclear motion is within the adiabatic potential energy surface!

Born-Oppenheimer approximation

Franck-Condon approximation for photoionization

$$\sigma^{+}_{iv'}(E) \sim \left| \int X^{*}_{iv'}(R) D_E(R) X_0(R) dR \right|^2$$

$X^{*}_{iv'}(R), X_0(R)$: Vibrational wavefunctions of ionic *iv'* and ground 0 states

$$D_E(R) = \int \varphi^{*}_{E}(r,R)\, r\, \varphi_{\text{core}}(r,R)\, \mathrm{d}r$$

$\varphi_E(r,R), \varphi_{\text{core}}(r,R)$: Electronic wavefunctions of the continuum *E* and core orbitals

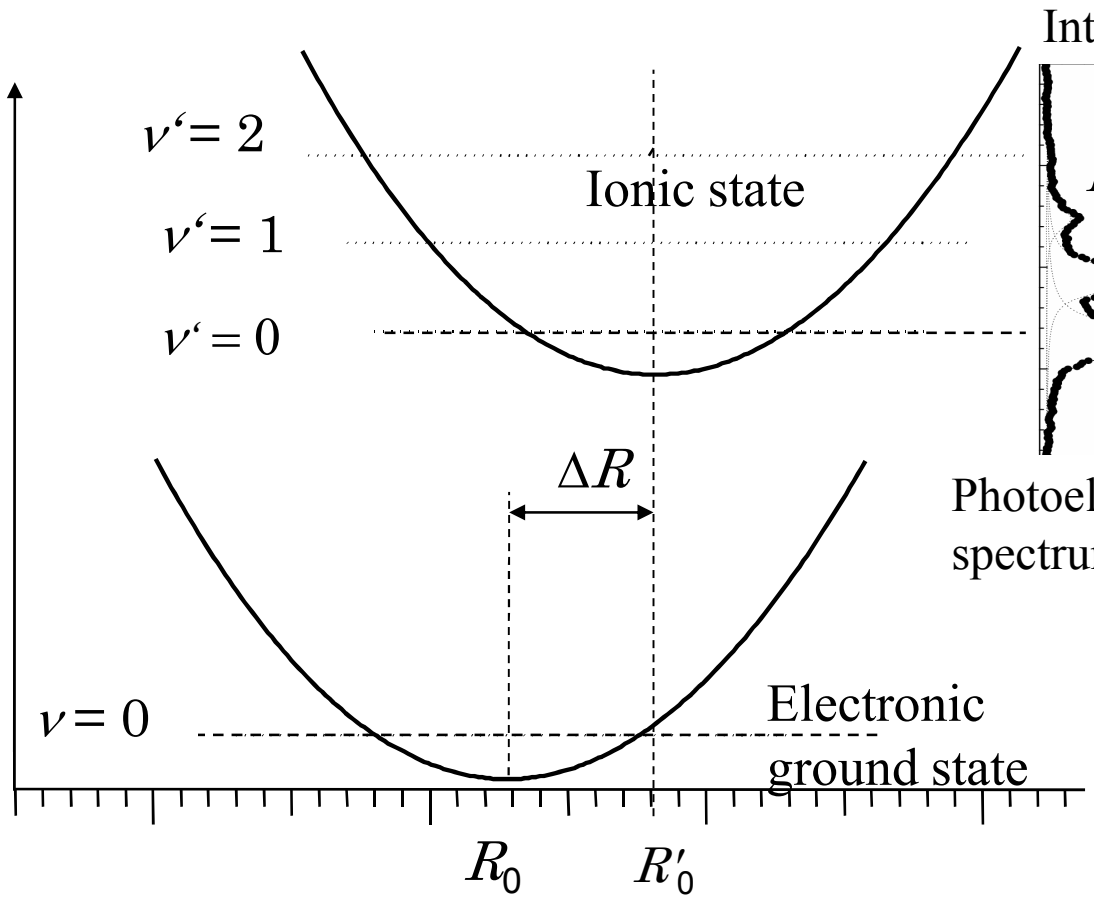
Assume that the dipole moment $D_E(R)$ does not depend on R

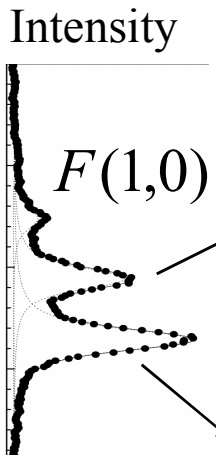
$$\sigma^{+}_{iv'}(E) \sim \left| D_E(R_e) \right|^2 F(v'0)$$

$$F(v'0) = \left| \int X^{*}_{iv'}(R) X_0(R) \mathrm{d}R \right|^2$$ Franck-Condon factor

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

Franck-Condon analysis based on harmonic approximation
Linear coupling model





$$F(1,0) = \frac{\alpha(\Delta R)^2}{2}\exp\left(-\frac{\alpha(\Delta R)^2}{2}\right)$$

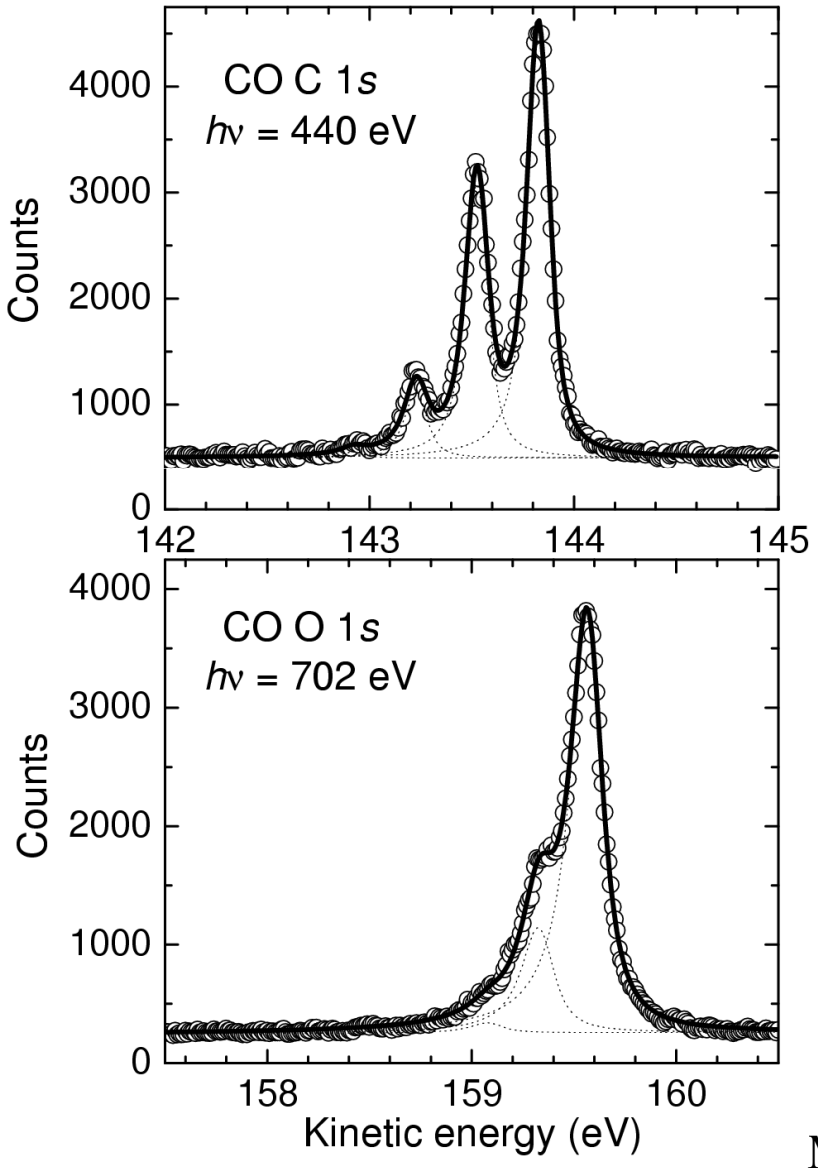
$$\alpha = \mu\omega/\hbar$$

$$F(0,0) = \exp\left(-\frac{\alpha(\Delta R)^2}{2}\right)$$

$$\frac{F(1,0)}{F(0,0)} = \frac{\alpha(\Delta R)^2}{2}$$

One can extract ΔR from photoelectron spectroscopy!

Franck-Condon analysis for the vibrational structure of the C 1s and O 1s mainlines of CO



$I \sim |\langle \psi^{+}_{v} | \psi_0 \rangle|^2$: FC factor

ψ_0: v=0 vibrational wave function in the ground state

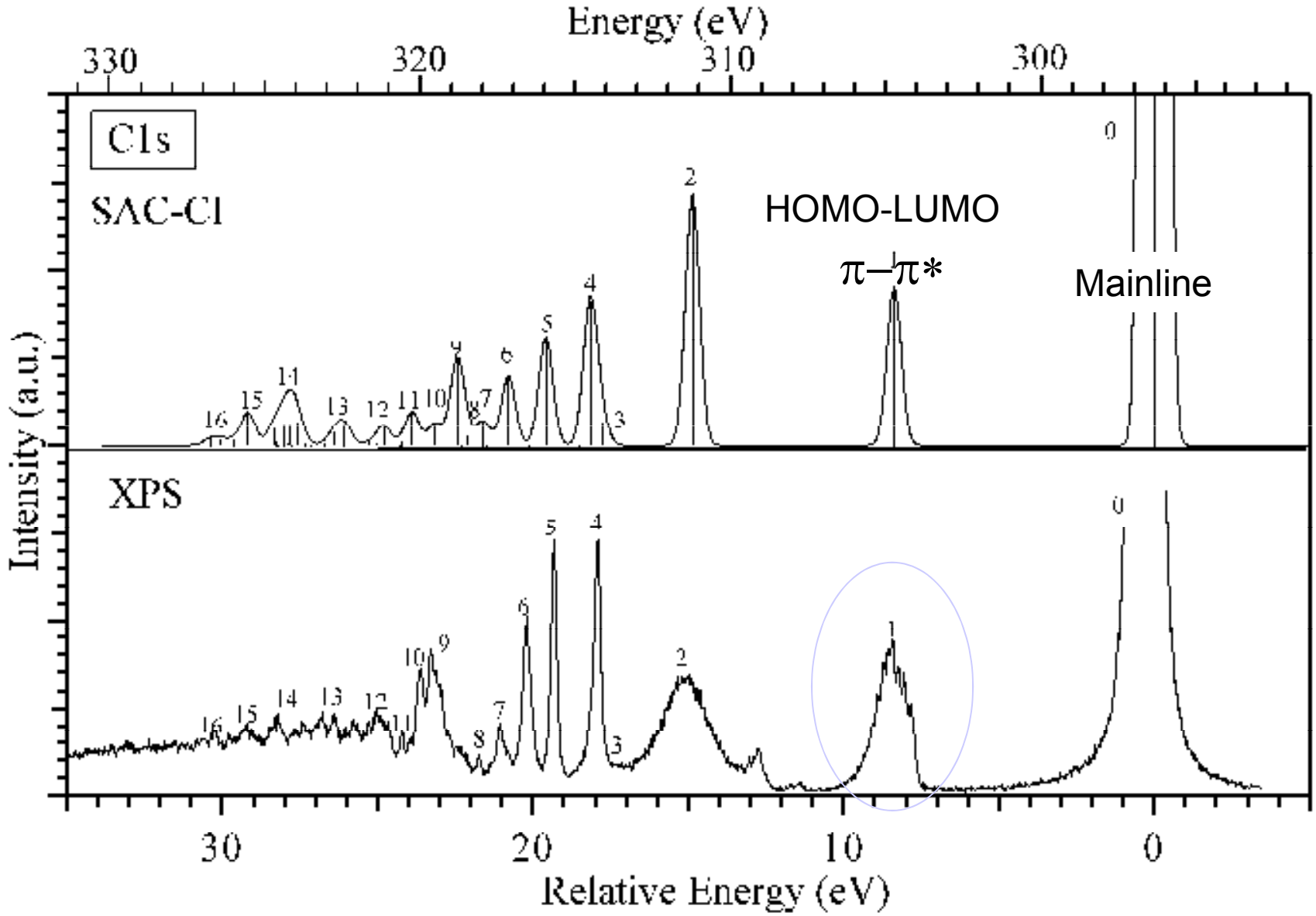
ψ^{+}_{v}: v-th vibrational wave function in the core-ionized state

Stable geometry of the core-ionized state extracted from the vibrational structure

	Exper.	Theory
C $1s^{-1}$		
ΔR_e (Å)	-0.051 (1)	-0.051
O $1s^{-1}$		
ΔR_e (Å)	0.037(2)	0.028

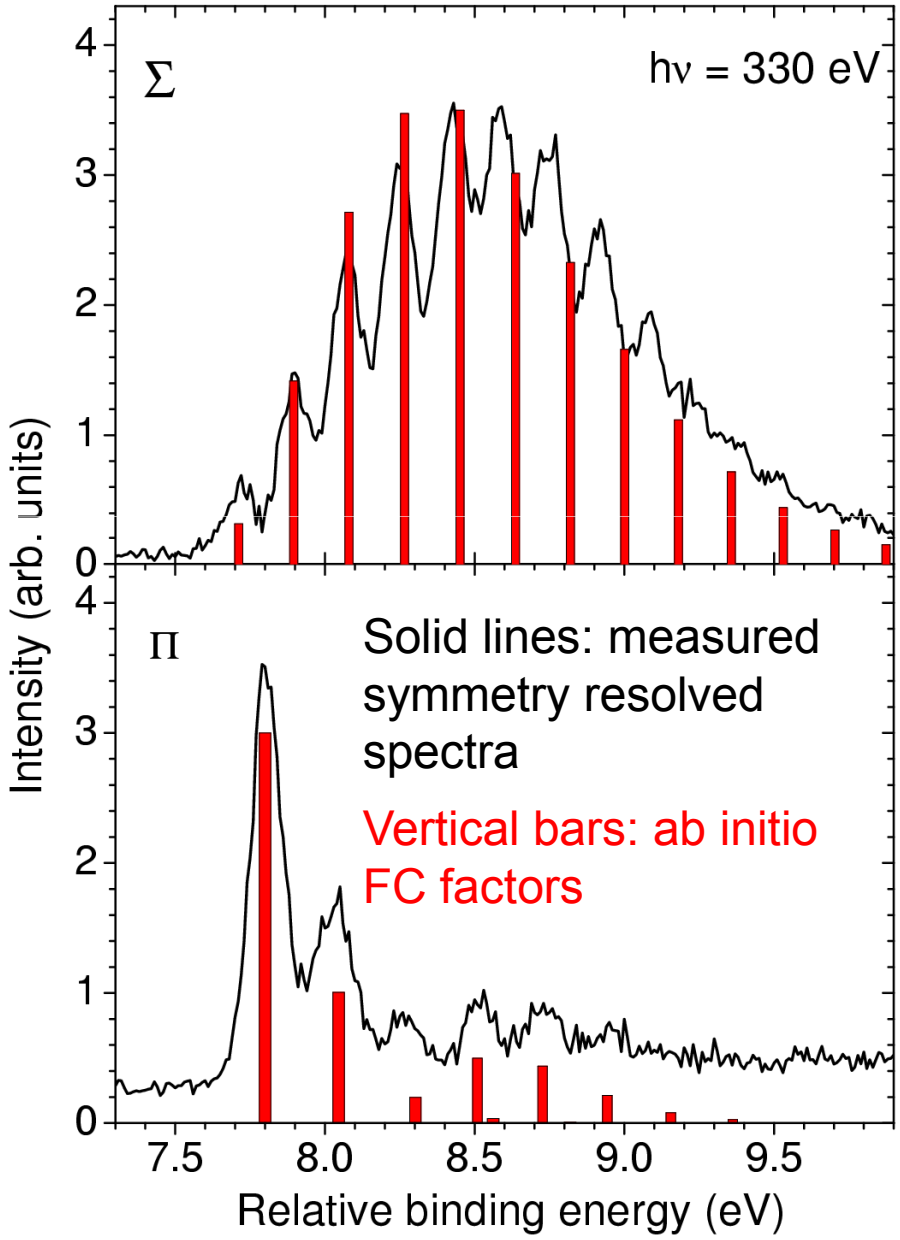
Matsumoto *et al.* Chem. Phys. Lett. **417**, 89-93 (2006).

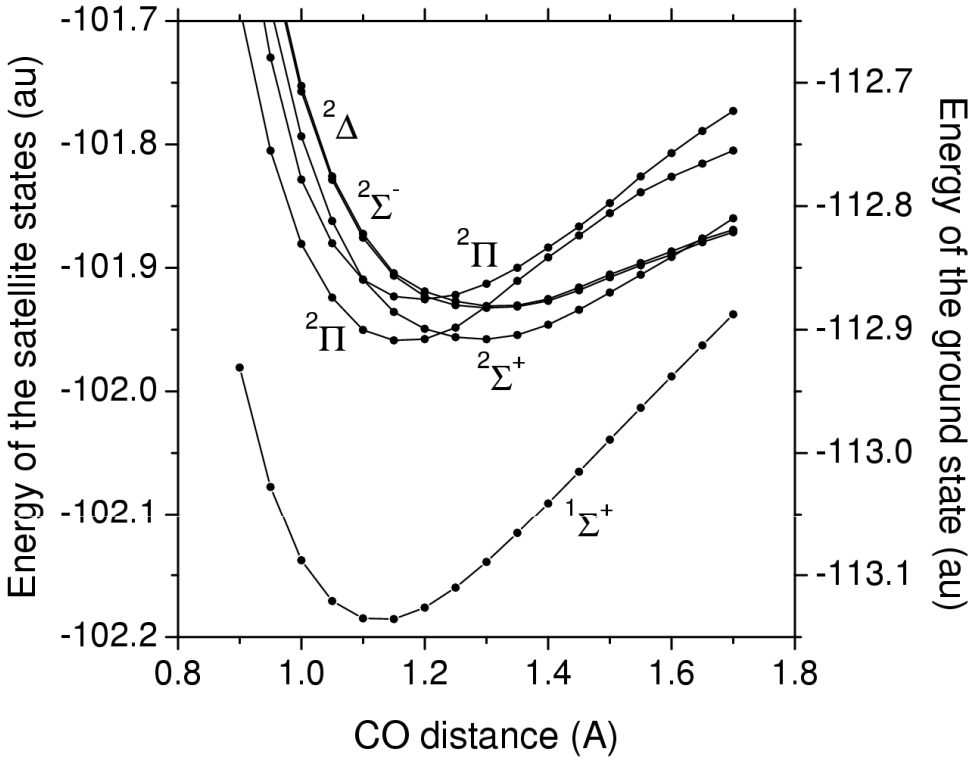
Satellite spectrum in core-level photoemission in CO



Ehara *et al.* J. Chem. Phys. **125**, 114304 (2006).

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



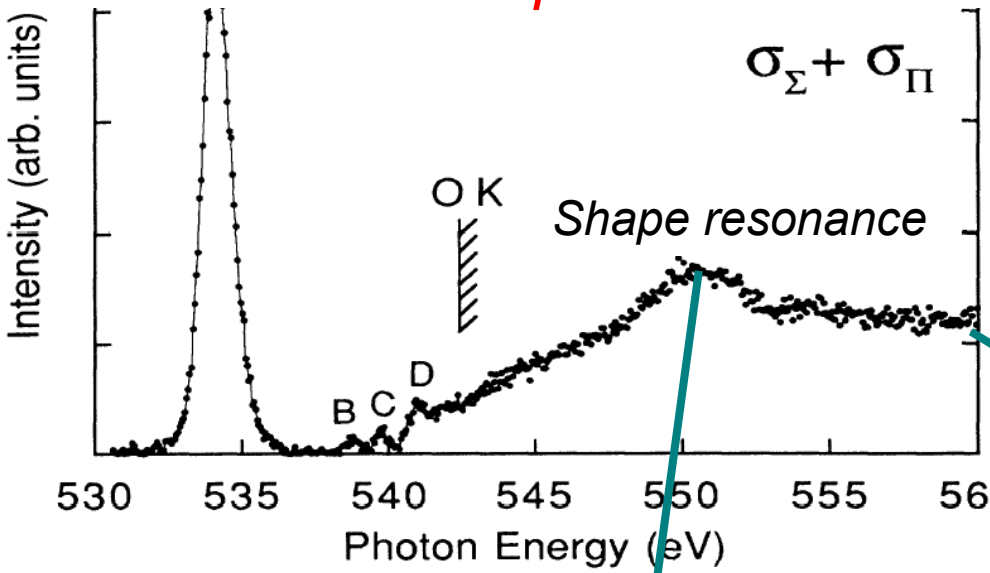


Ab initio potential curves

Ab initio FC factors reproduce the measured vibrational distributions.

Ueda *et al.*, Phys. Rev. Lett. **94**, 243004 (2005).

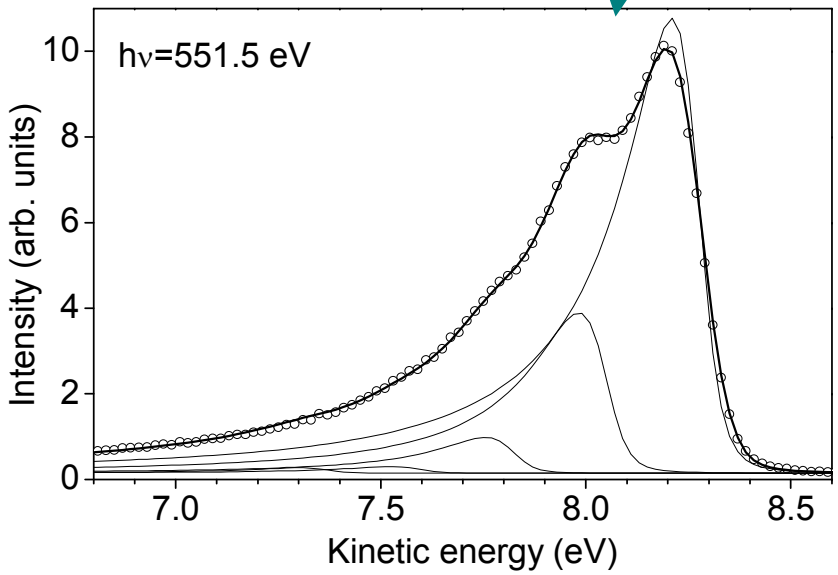
Vibrational effects on the shape resonance energy in the K-shell photoionization spectra of CO

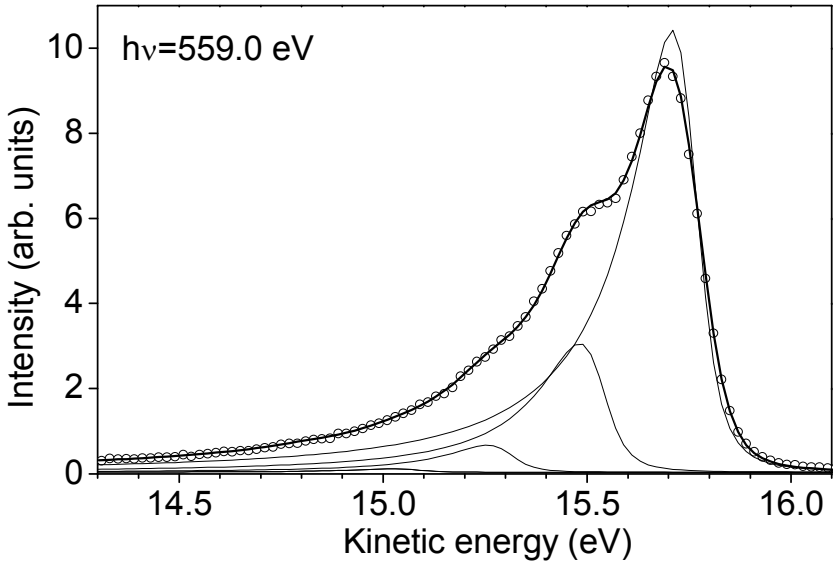


Shape resonance:

Promotion of the core electron to the σ antibonding orbital*

Temporal trapping of a photoelectron by the molecular potential

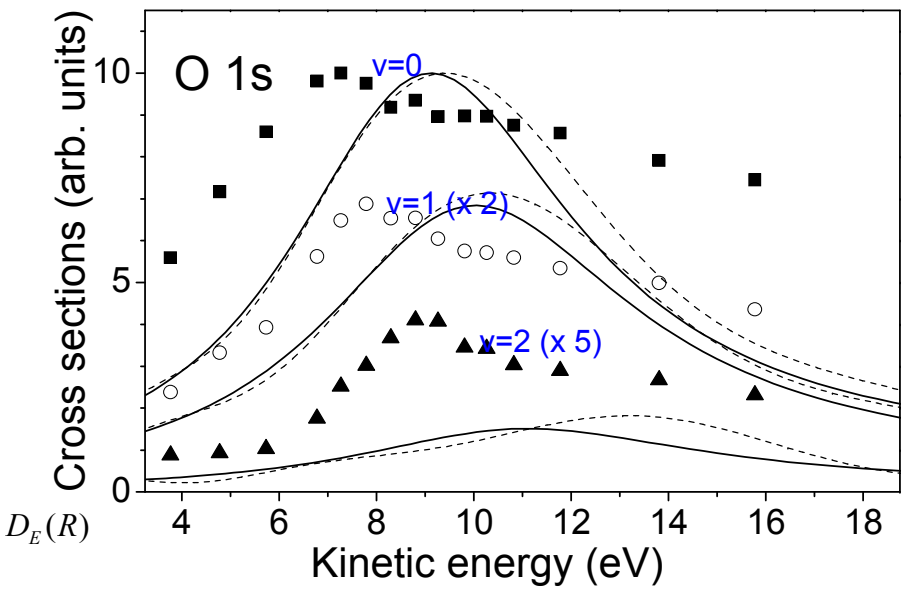


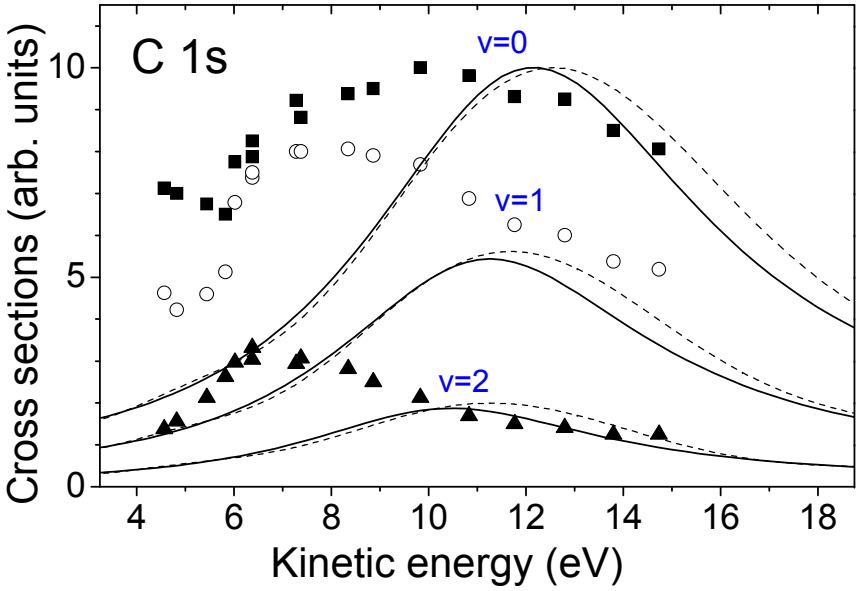


O 1s photoelectron spectra of CO at the shape resonance and far above it.

Non-Franck-Condon behavior of vibrational distributions!

Vibration-dependent shape resonances





Shape resonance energy increases with v'.

D. A. Mistrov *et al.* Phys. Rev. A **68**, 022508 (2003).

Shape resonance energy decreases with v'.

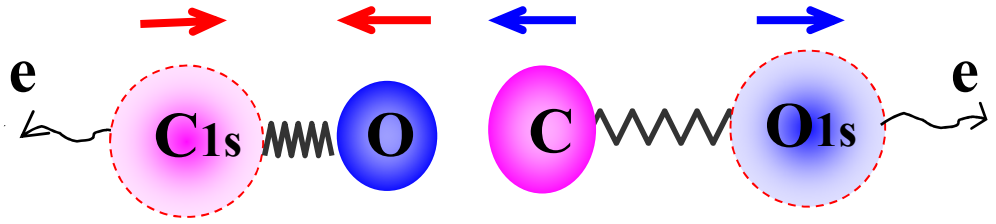
K. J. Randall *et al.*, Phys. Rev. Lett. **71**, 1156 (1993).

$$\sigma^{+}_{iv'}(E) \sim \left| \int X^{*}_{iv'}(R) D_E(R) X_0(R) dR \right|^2 , \quad D_E(R) = \int \varphi^{*}_{E}(r,R) r \varphi_{\text{core}}(r,R) \mathrm{d}r$$

$D_E(R)$ strongly depends on R in the shape resonance region!

J. L. Dehmer, D. Dill, and S. Wallace, *Phys. Rev. Lett.* **43,** 1005 (1979).

Origin of the vibrational energy on the shape resonance energy



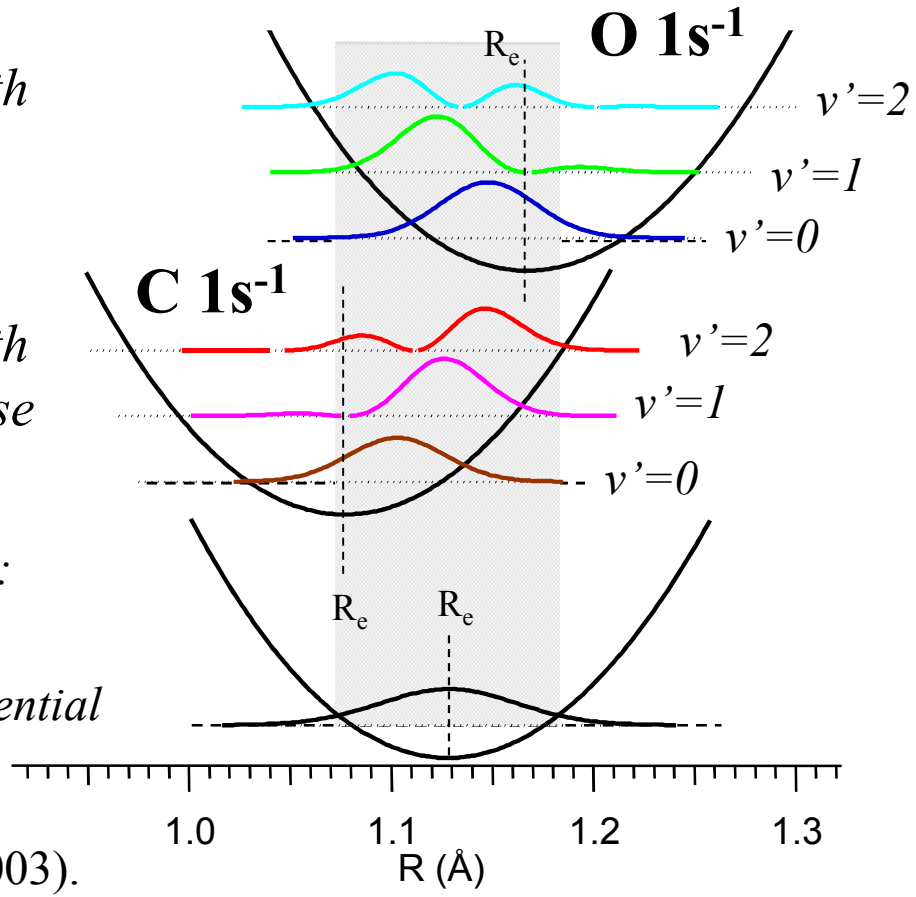
Characteristic bond length shrinks with the increase in v'for O 1s.

Characteristic bond length elongates with the increase in v'for C1s.

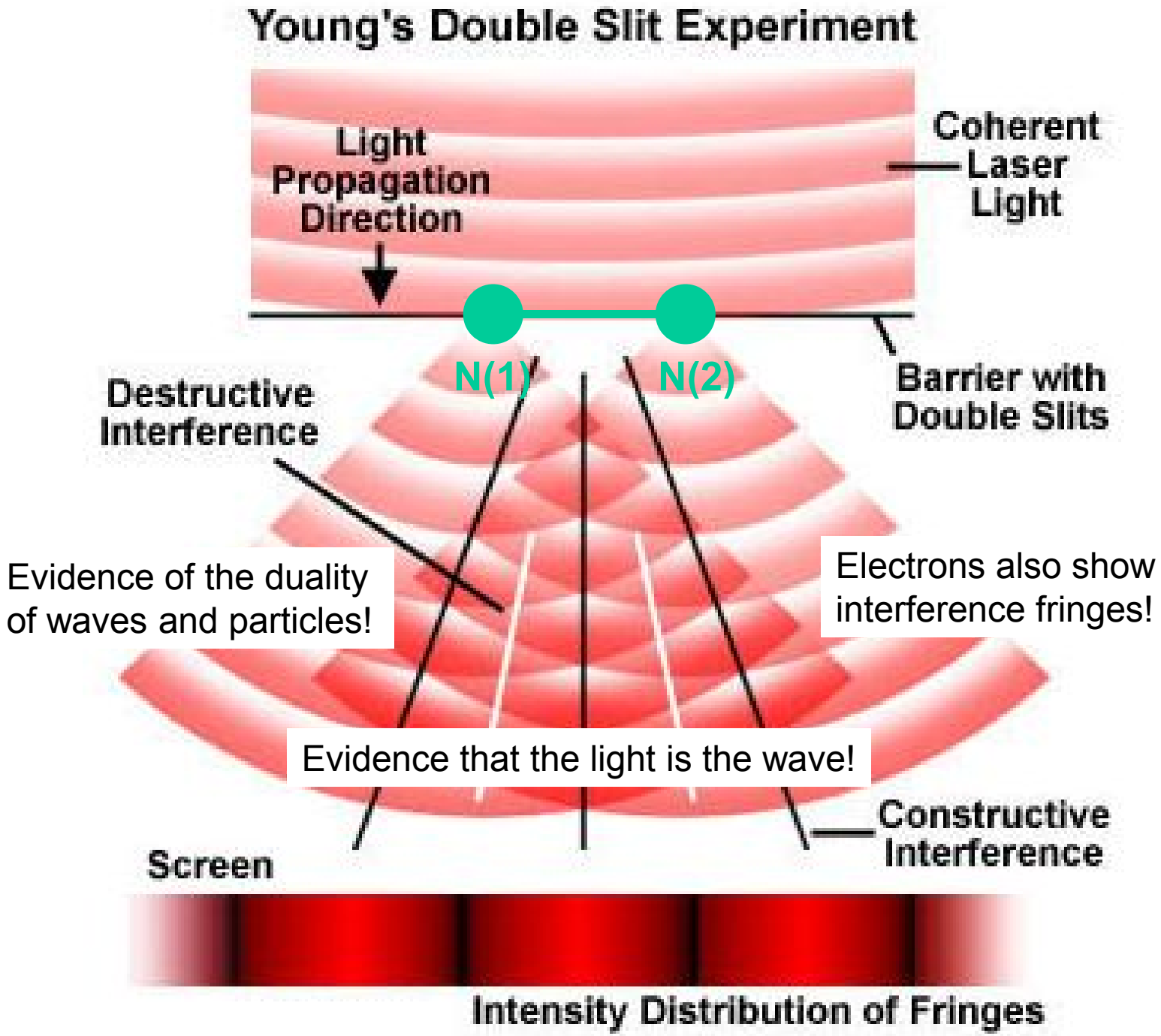
Shape resonance formation:

$kR + \varphi = \pi$

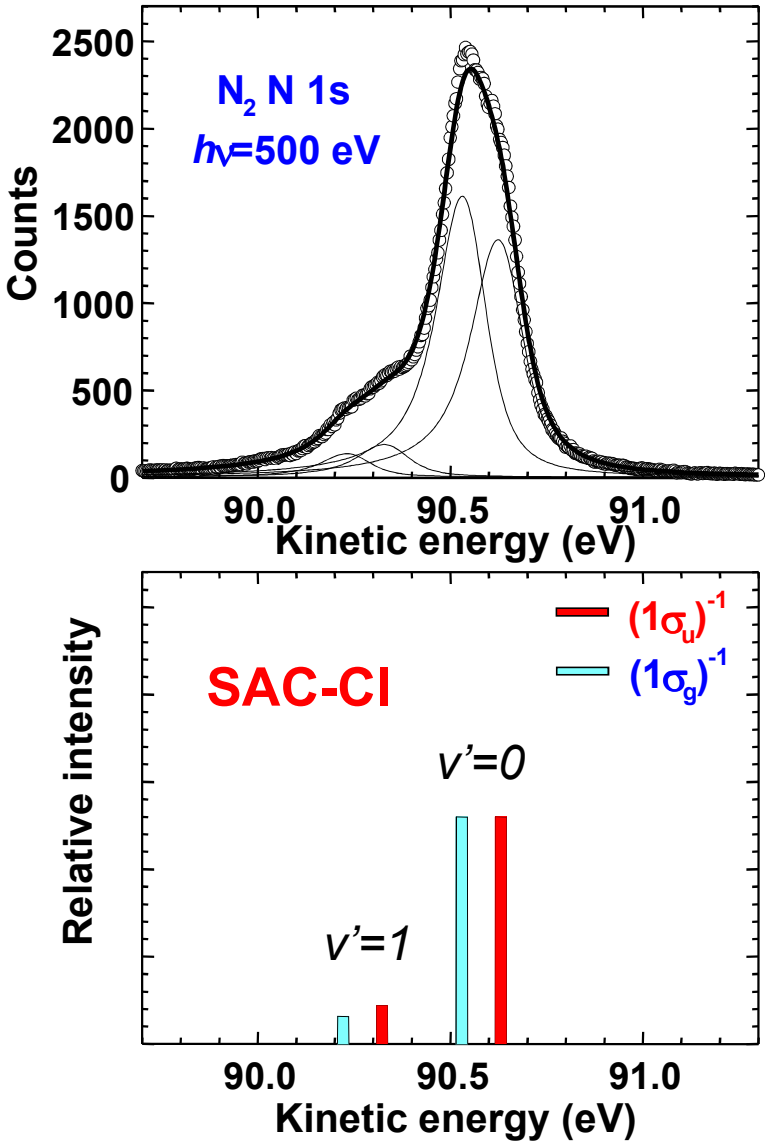
Cf. standing wave in the box potential

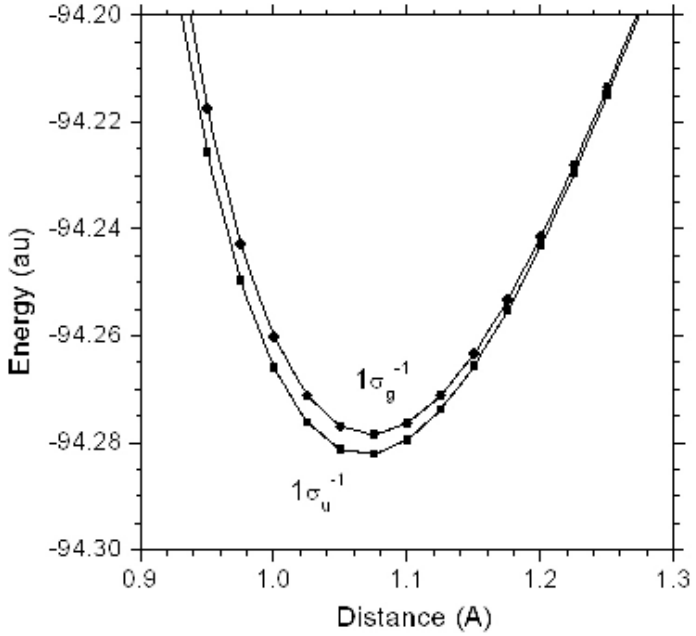


D. A. Mistrov *et al.*
Phys. Rev. A **68**, 022508 (2003).


Young's Double Slit Experiment
Light Propagation Direction
Coherent Laser Light
N(1)
N(2)
Barrier with Double Slits
Destructive Interference
Evidence of the duality of waves and particles!
Electrons also show interference fringes!
Evidence that the light is the wave!
Constructive Interference
Screen
Intensity Distribution of Fringes

Franck-Condon analysis for the vibrational structure of the N 1s $1\sigma_u$ and $1\sigma_g$ mainlines of N_2





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

	Exper.	Theory
N $1\sigma_u^{-1}$		
ΔR_e (Å)	-0.023(1)	-0.021
N $1\sigma_g^{-1}$		
ΔR_e (Å)	-0.018(1)	-0.017

Ehara *et al.* JCP **124**, 124311 (2006)

Cohen-Fano two-center interference

Two 1s ortibals in N_2 correspond to Young's double slits.

Molecular core-level ortibals: $1\sigma_{g,u} = \dfrac{1s_1 \pm 1s_2}{\sqrt{2}}$.

Core-level photoemission from fixed-in-space N_2:

$$\sigma_{g,u}(\omega) \propto \frac{1}{2}\left|e^{i\mathbf{k}\cdot\mathbf{R}_1} \pm e^{i\mathbf{k}\cdot\mathbf{R}_2}\right|^2 = 1 \pm \cos(\mathbf{k}\cdot\mathbf{R}) \ ,$$

Two center photoelectron wave — *Interference fringe*

where k: photoelectron momentum; R_1,R_2: position vectors of N (1) and N(2)

$\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2.$

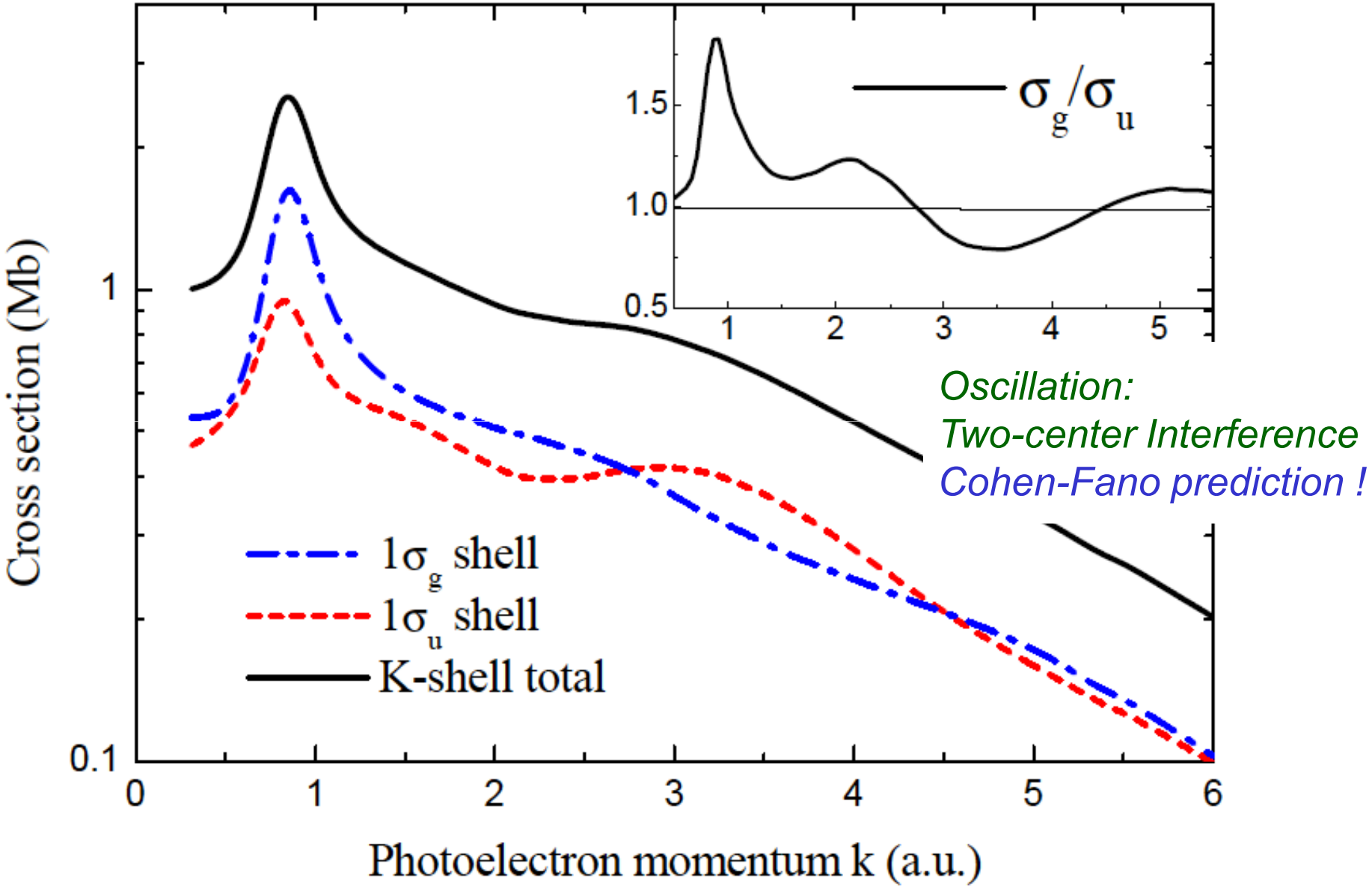
Orientational average: Cohen-Fano formula

$$\sigma_{g,u}(\omega) = \sigma_0(\omega)\left[1 \pm \chi_{\mathrm{CF}}(k)\right] \ , \quad \chi_{\mathrm{CF}}(k) = \frac{\sin kR}{kR}$$

Interference oscillatory structure becomes much smaller but remains!

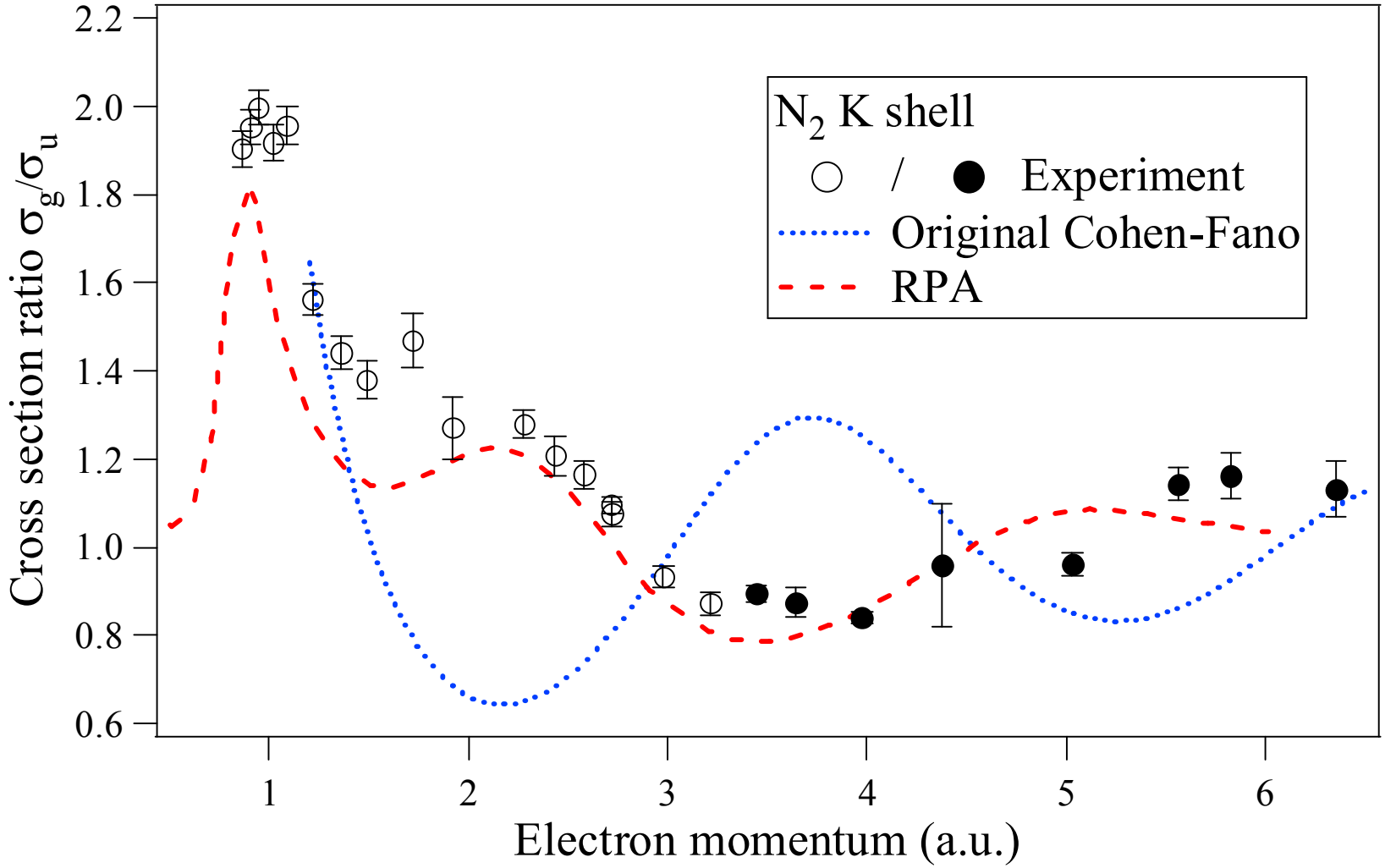
H.D. Cohen and U. Fano, Phys. Rev. **150**, 30 (1966).

Ab initio N 1s $1\sigma_u$ and $1\sigma_g$ photoionization cross sections of N_2



Semenov *et al*., J. Phys. B: At. Mol. Opt. Phys. 39, L261 (2006)

σ_g/σ_u ratio: experiment vs ab initio and Cohen-Fano



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

Liu *et al.,* J. Phys. B. **39,** 4801-4817 (2006); JESRP **156-158**, 73-77 (2007).

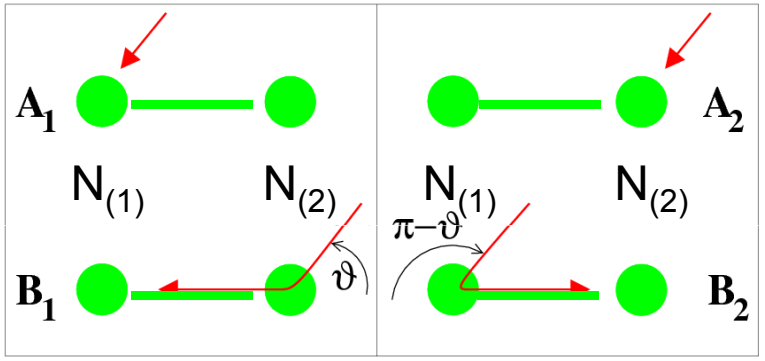
Photoelectron scattering by the neighboring N atom

The amplitude of the photoelectron wave from one center:

$$\psi_1 = \underbrace{\hat{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_1}}_{A_1} + \underbrace{\hat{\mathbf{R}} \frac{e^{ikR}}{R} f(\vartheta) e^{i\mathbf{k}\cdot\mathbf{R}_2}}_{B_1} .$$

$$\psi_2 = A_2 + B_2$$

The amplitude of the photoelectron wave from two centers: $\psi_1 \pm \psi_2$



Cohen-Fano interference
A_1A_2 interference term

$$\chi_{CF}(k) = \frac{\sin kR}{kR}$$

The cross section~ $|\psi_1 \pm \psi_2|^2 = |(A_1+B_1) \pm (A_2+B_2)|^2$

$$\frac{\sigma_{g,u}(\omega)}{\sigma_0(\omega)} = 1 - \frac{1}{kR^2} \mathrm{Im}\left\{ f(\pi) e^{2i[kR+\delta_1(k)]} \right\} \pm \chi(k) ,$$

0

A_1B_1 and A_2B_2 one-center interference terms

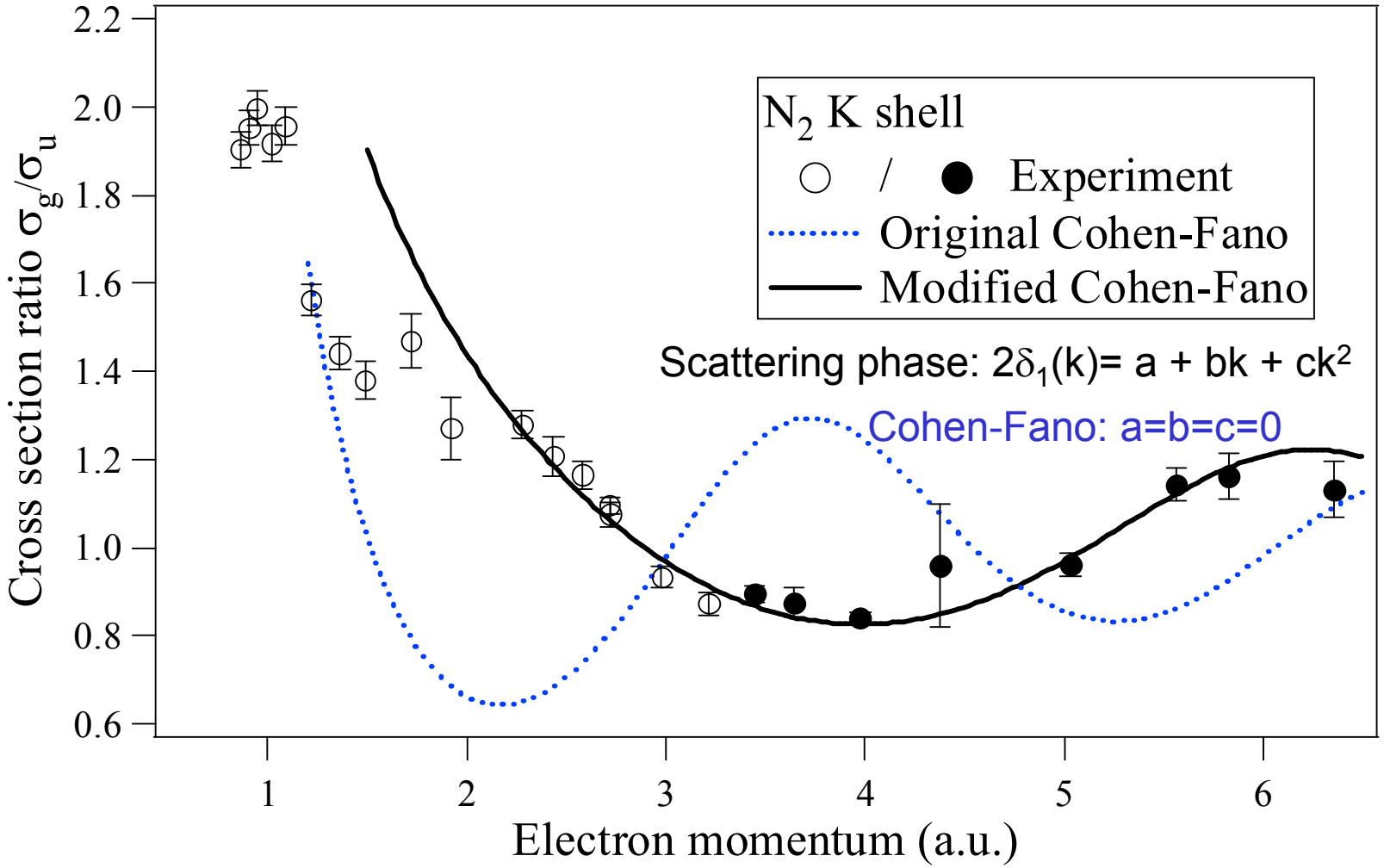
$$\chi(k) = \frac{1}{kR} \sin\left[kR + 2\delta_1(k)\right]$$

δ_1(k): scattering phase

CF A_1A_2 interference term

A_1B_2 and A_2B_1 two-center interference terms !

σ_g/σ_u ratio fitted by modified Choen-Fano



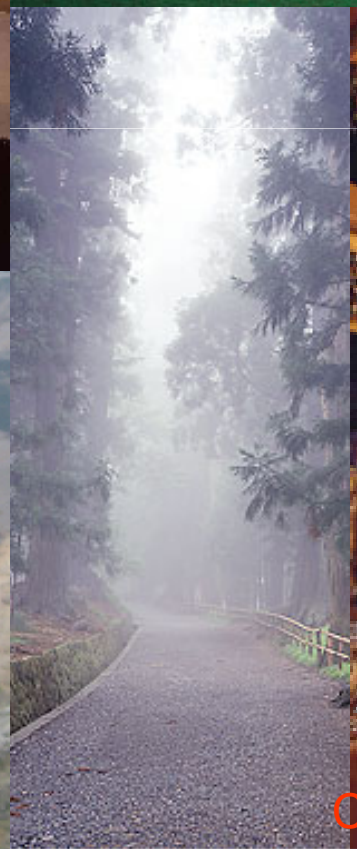
Fitted results: a = −5.2±0.6, b = −1.6±0.4, c = 0.09 ± 0.05 a.u.

Ab initio results: a = −4.8, b = −1.15, c = 0.069 a.u.

(Teo and Lee, J. Am. Chem. Soc. **101**, 2815 (1979))

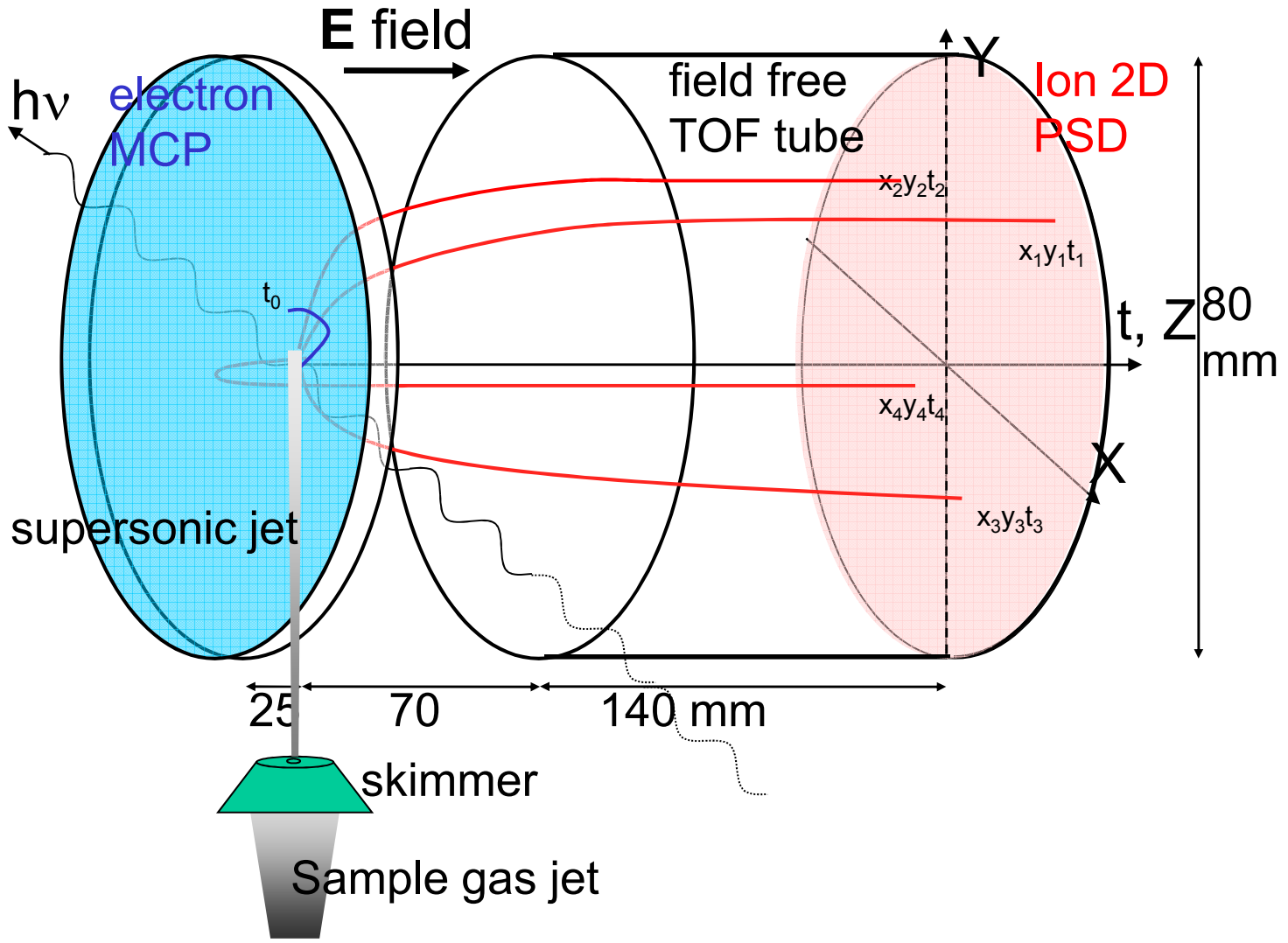
Near Sendai

Motsu-ji



Chuson-ji

Multiple-ion coincidence imaging setup



position & time of flight (x,y,t) → *3D momentum of each particle*

How to obtain 3D momentum

$$p_x = \frac{m(x - x_0)}{t}, \quad p_y = \frac{m(y - y_0)}{t}, \quad p_z = qE(t - t_0)$$

t: ion time-of-flight

t_o: ion TOF at rest

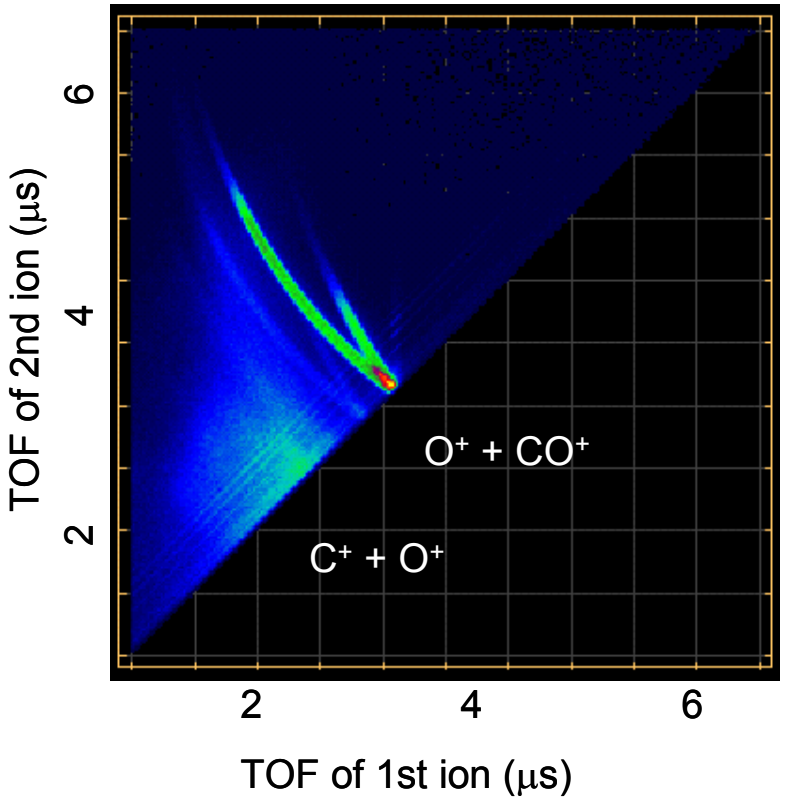
x, y: arrival position on the detector.

x_0, y_0 : initial position of the ion

m : ion mass

q: ion charge

E: electric field in the acceleration region



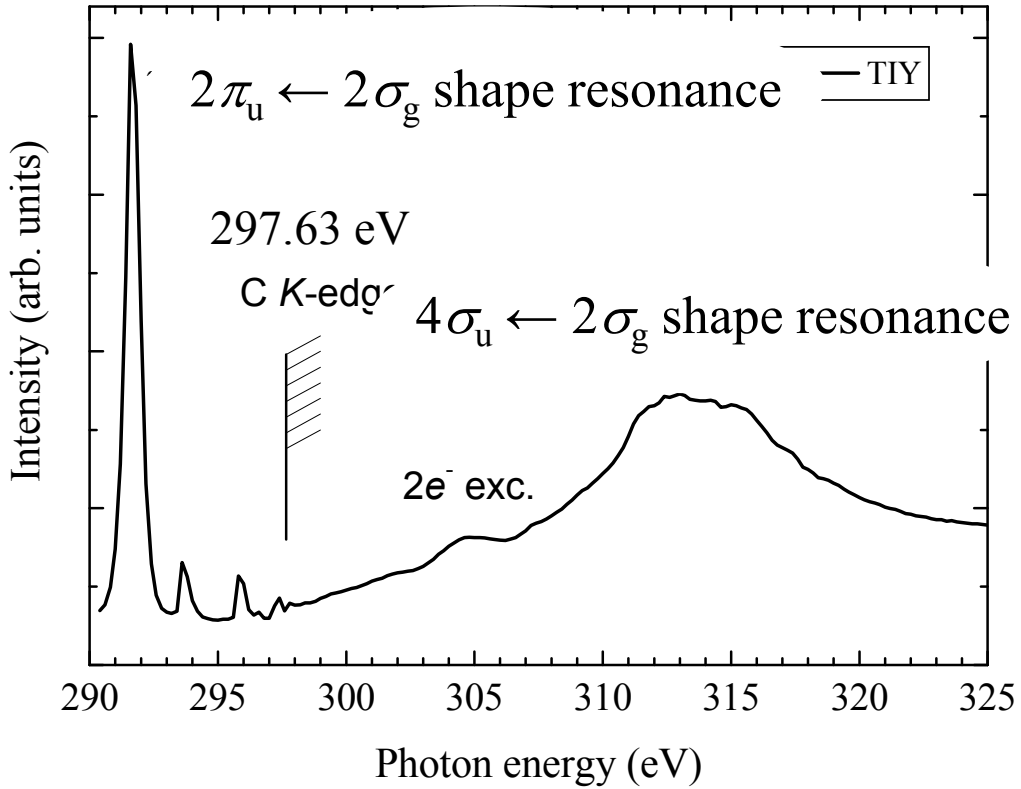
To be exact Pz becomes nonlinear → Iterative procedure

Total electron yield spectrum of CO_2 in the C1s ionization region

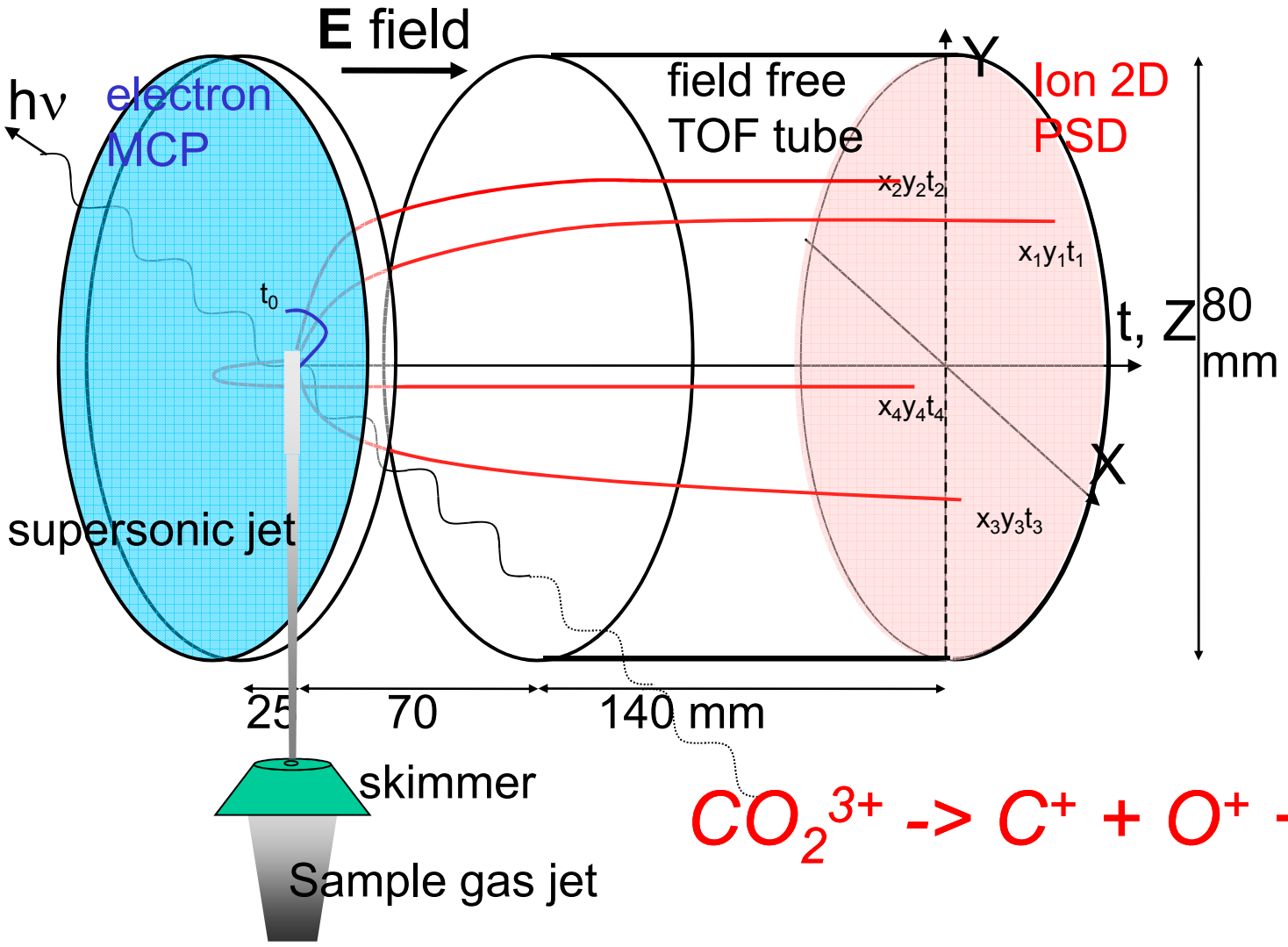
CO_2 ground state configuration:

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

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

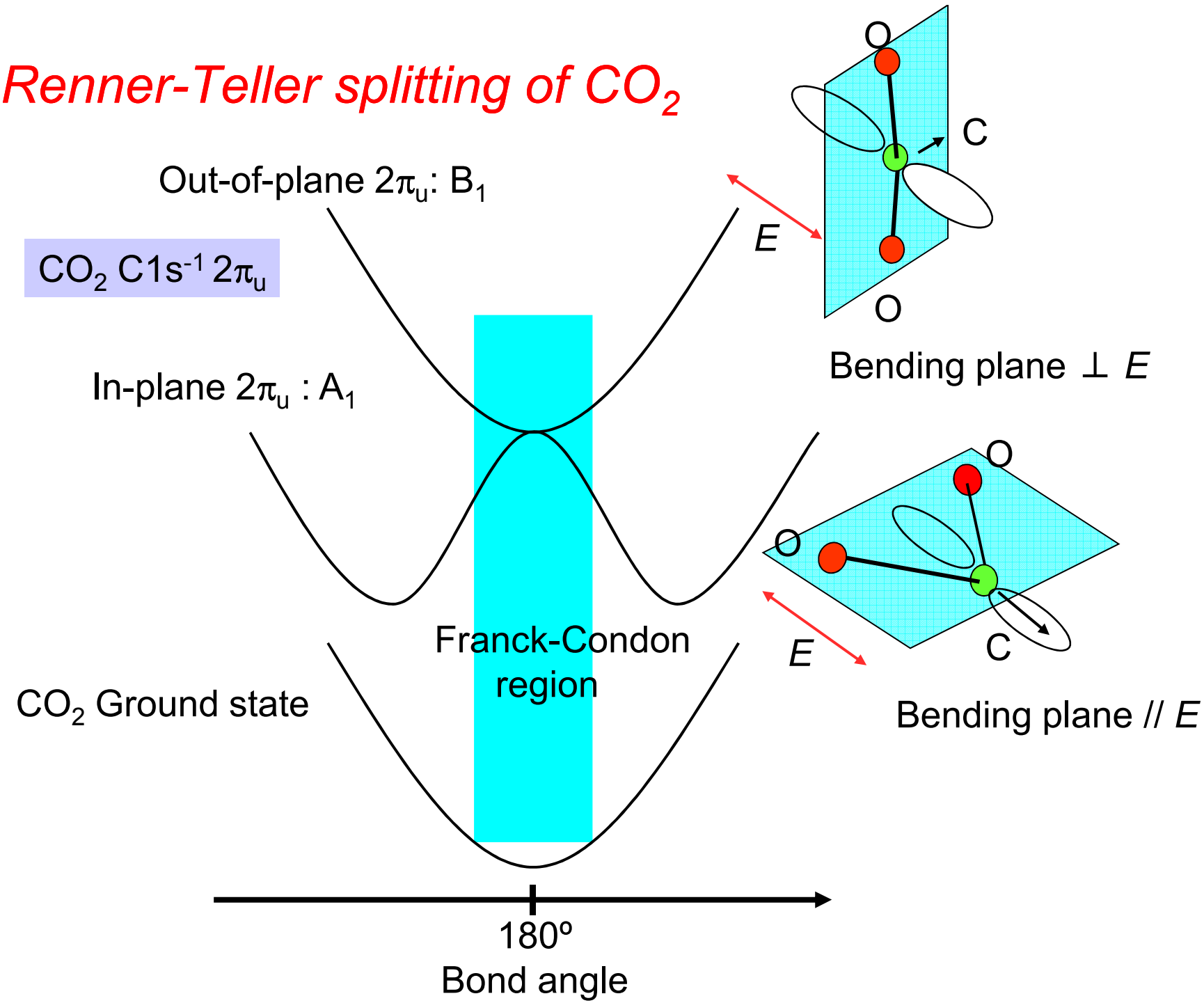


SR experiments with multiple-ion coincidence



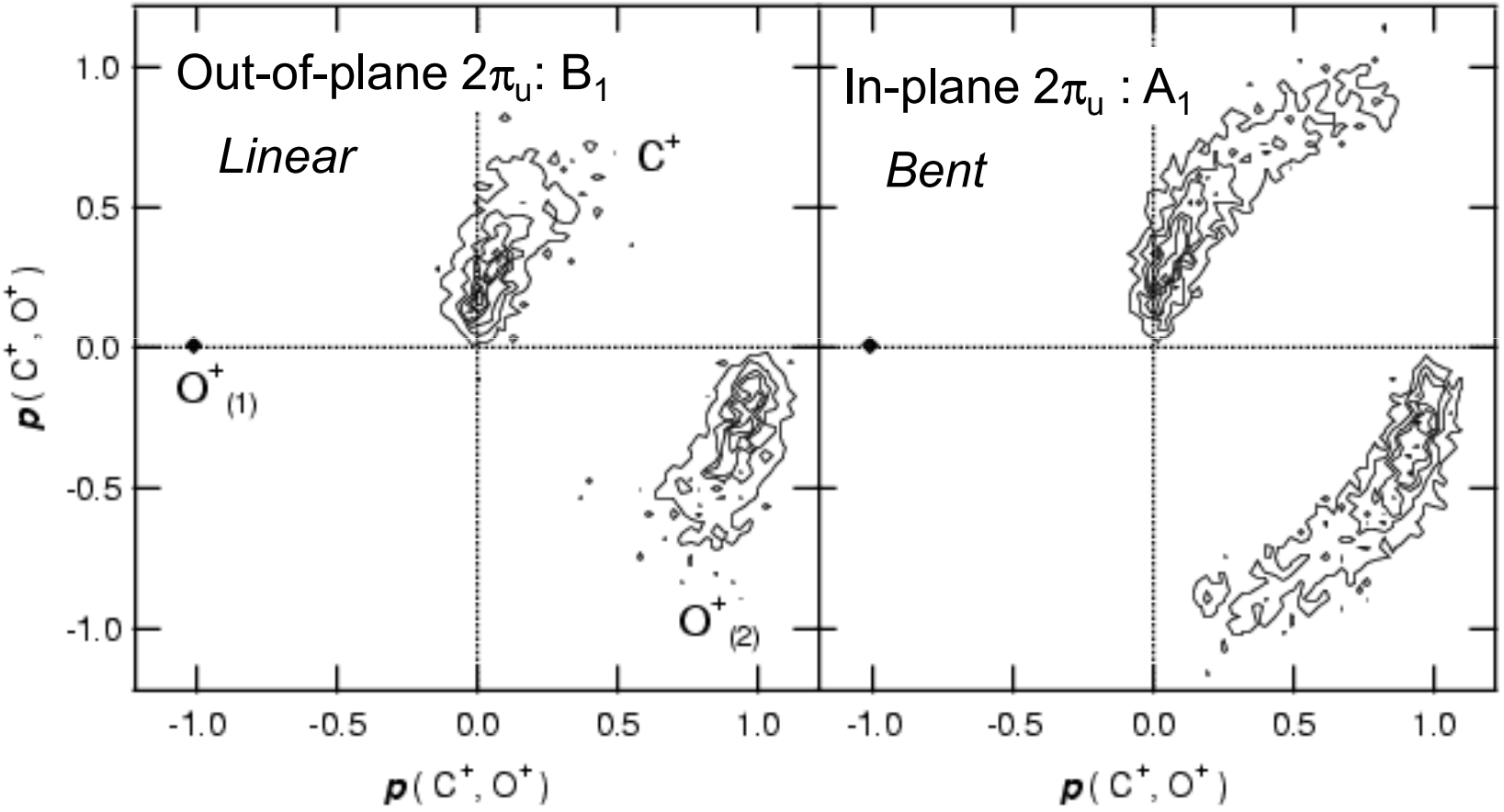
position & time of flight (x,y,t) → *3D momentum of each particle*

Renner-Teller splitting of CO_2



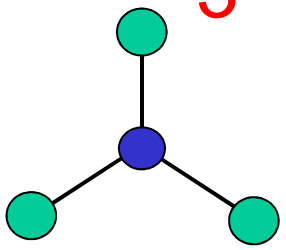
Snapshot of the bending motion in the core-exited state with a liftetime ~7 fs

Newton Diagram



Muramatsu et al. Phys. Rev. Lett. 88, 133002 (2002).

BF_3



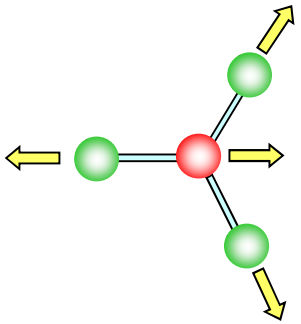
D_{3h} planar

KK $(1a_1')^2(1e')^4(2a_1')^2(2e')^4(1a_2'')^2(3e')^4(1e'')^4(1a_2')^2$; $(2a_2'')^0(4e')^0$

inner valence — outer valence — empty

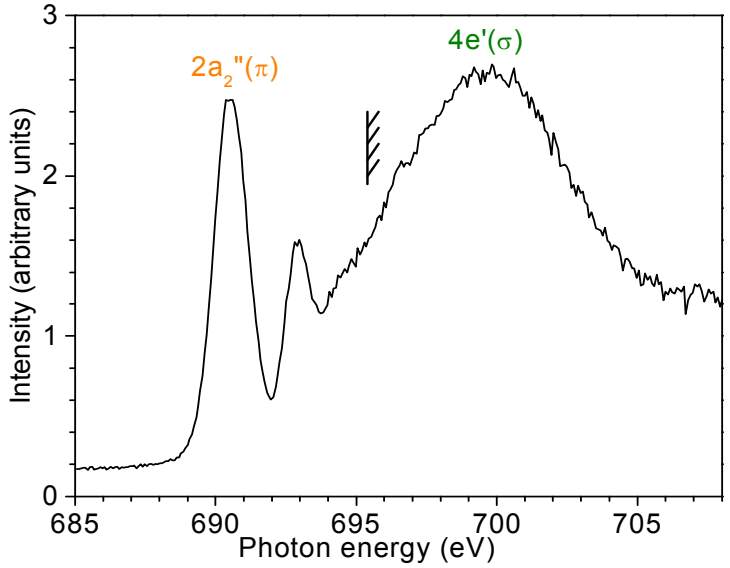
F, B 1s

Asymmetric stretching?

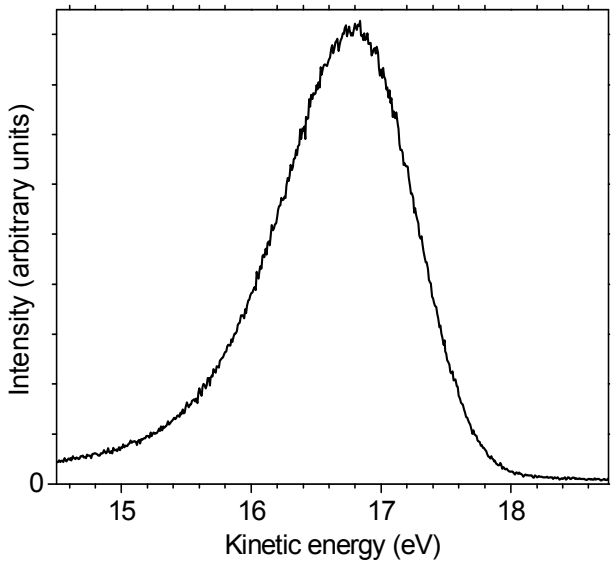


F 1s excitation/ionization

Symmetry breaking (due to vibronic coupling)

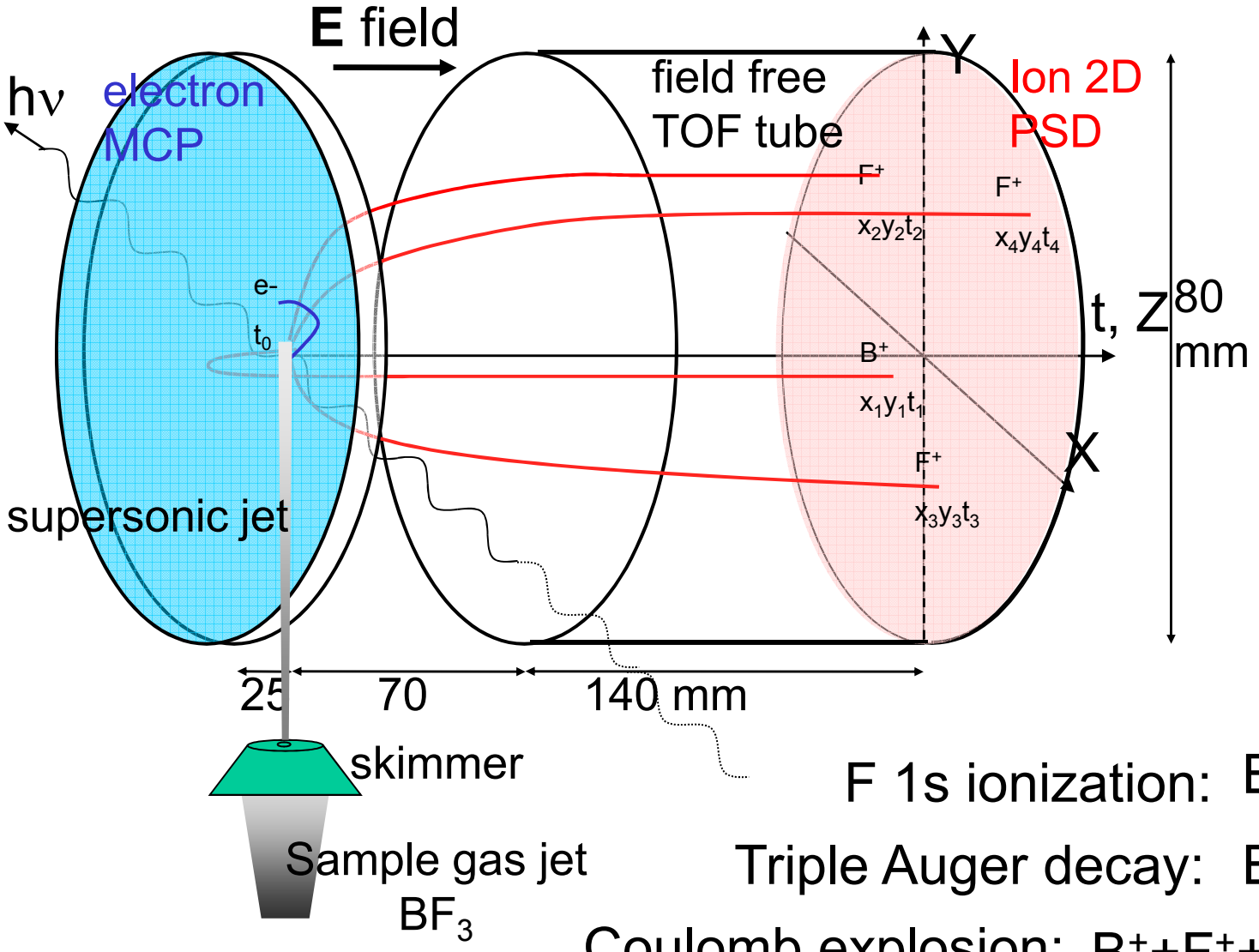


F1s excitation spectrum



F1s photoelectron spectrum

Multiple ion coincidence momentum imaging



F 1s ionization: BF_3^+

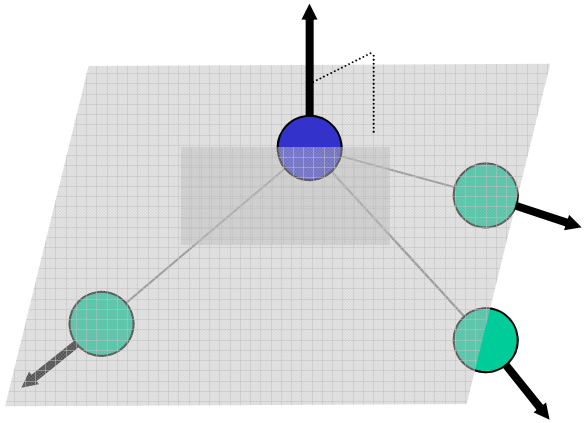
Triple Auger decay: BF_3^{4+}

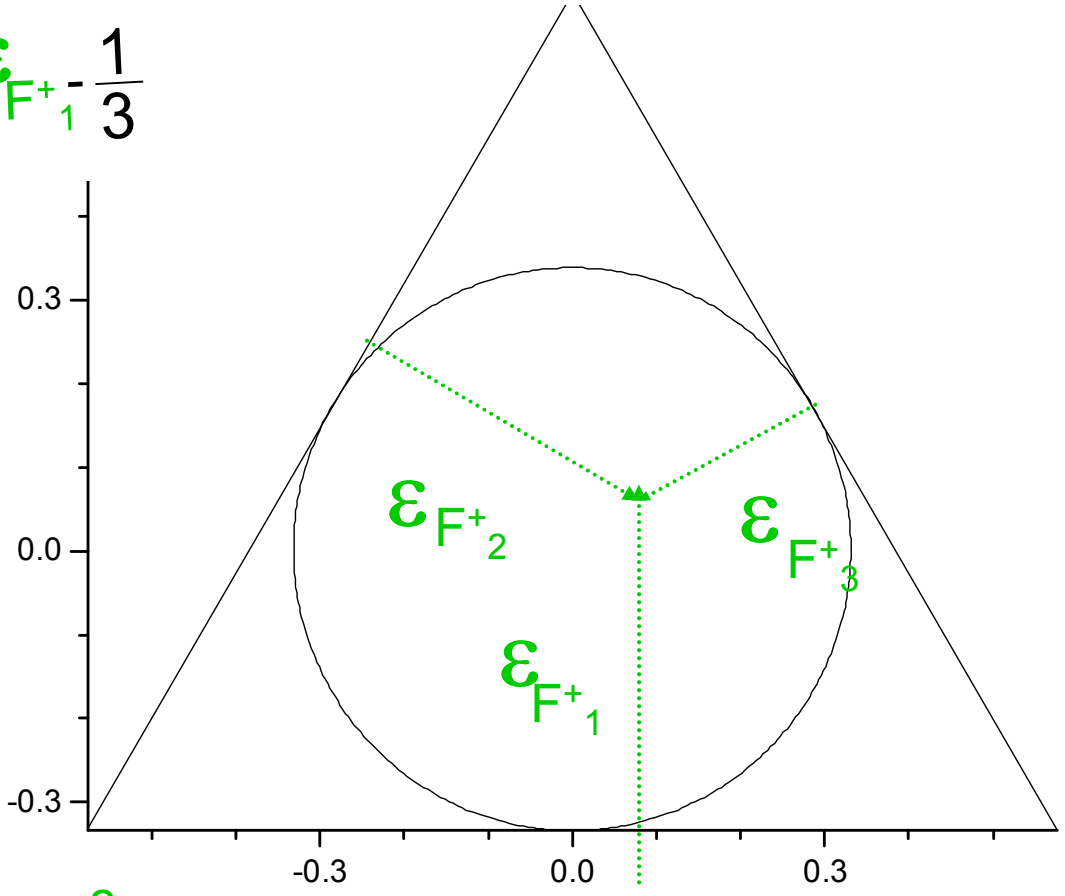
Coulomb explosion: $B^+ + F^+ + F^+ + F^+$

Construction of Dalitz plots for F^+ F^+ F^+ in the plane perpendicular to **P**(B^+)

$$Y_D = \varepsilon_{F^+_1} - \frac{1}{3}$$

$P_{\perp F^+_i}$ are the projections of momenta on the plane perpendicular to the emission of B^+





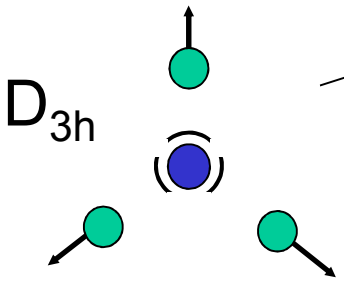
$$\varepsilon_{F^+_i} = \frac{P^2_{\perp F^+_i}}{\sum P^2_{\perp F^+_i}}$$

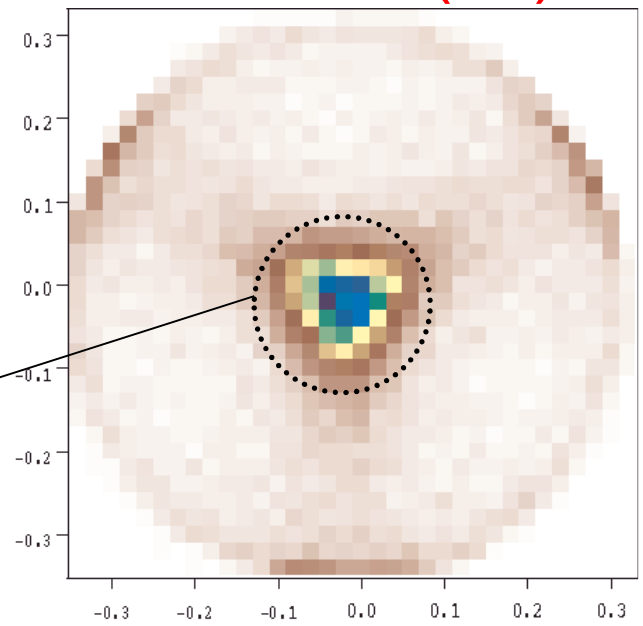
$$X_D = \frac{\varepsilon_{F^+_3} - \varepsilon_{F^+_2}}{3^{1/2}}$$

Motion of F^+ F^+ F^+ in the plane perpendicular to **P**(B^+)

B1s ionization

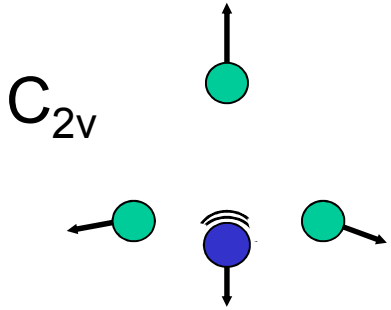
F^+ have similar momenta $\mathbf{P}^\perp$ $\Rightarrow$ symmetric stretching

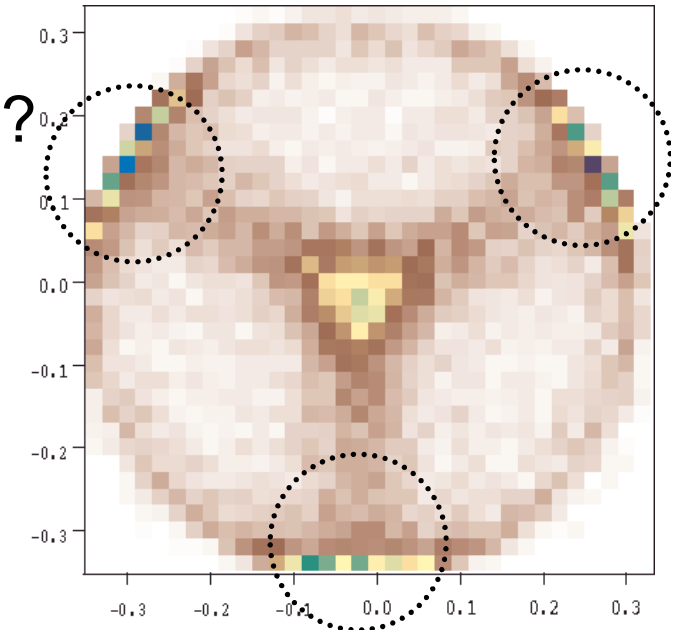




F1s ionization

asymmetric sharing of momenta $\mathbf{P}^\perp$ $\Rightarrow$ asymmetric stretching ?

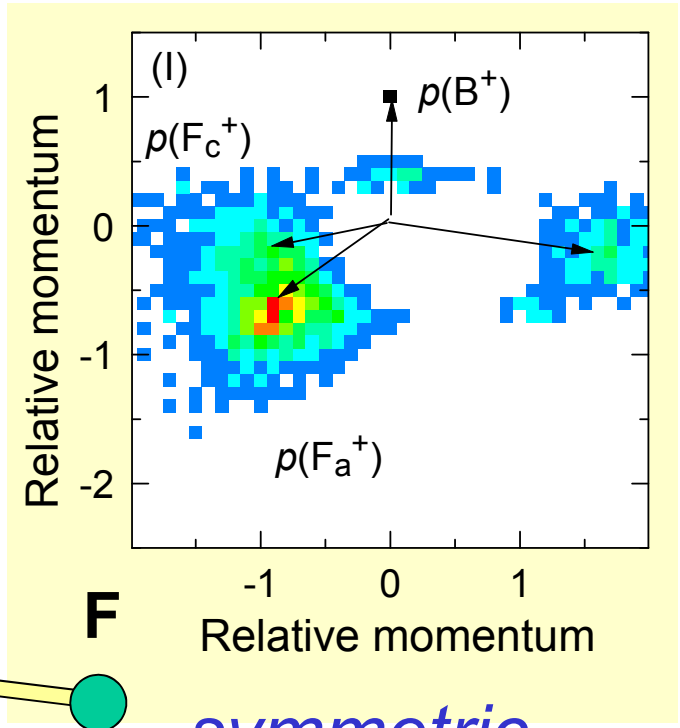


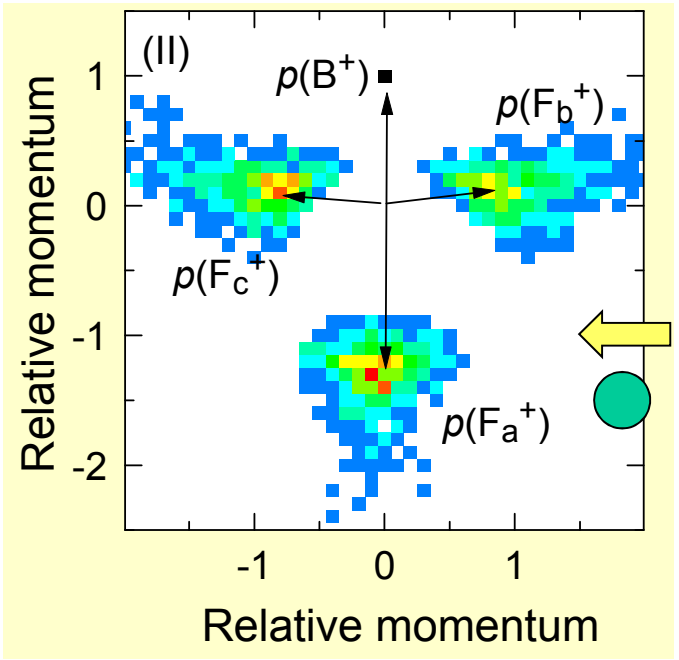


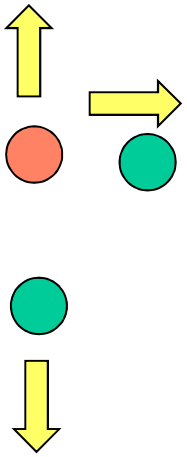
Newton diagrams for symmetric and asymmetric nuclear motion probed by quadruple ion momentum imaging

Center

Edge







symmetric

asymmetric

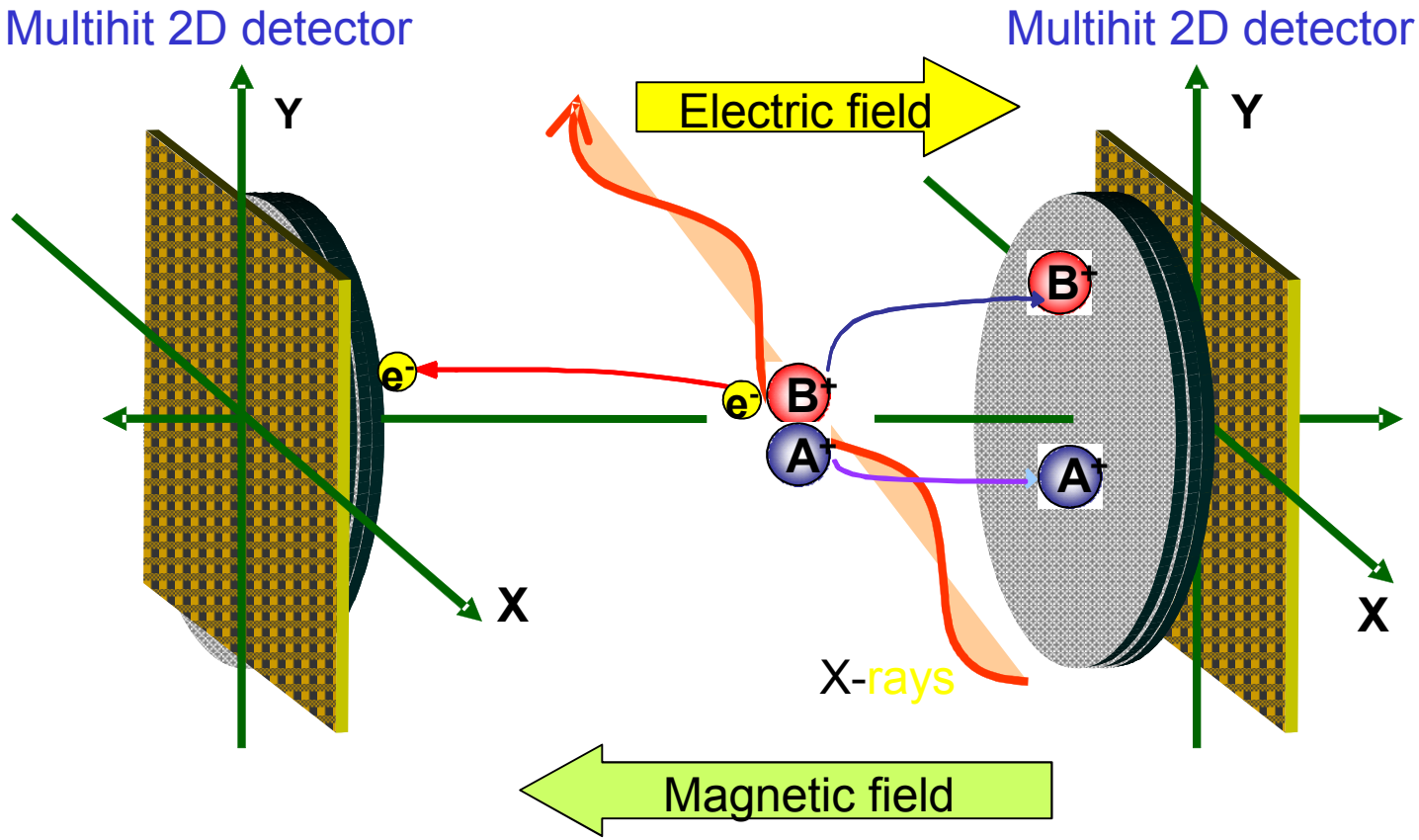
Asymmetric nuclear motion as result of symmetry breaking by F 1s ionization has been detected for the first time via *quadruple ion momentum imaging.*

De Fanis *et al.* Phys. Rev. A **69**, 022506 (2004).


Sendai
in summer


七夕まつり
Tanabata festival

Electron-ion coincidence momentum imaging



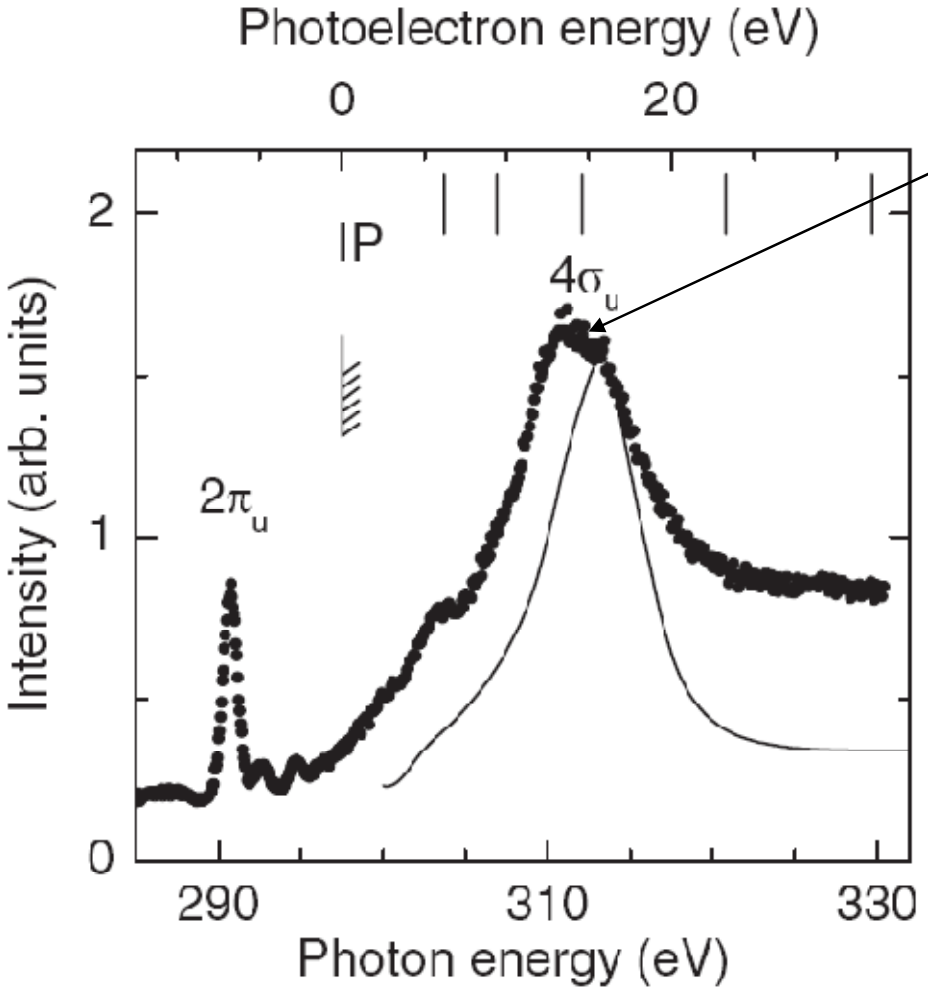
Ion-ion coincidence → *Molecular axis*

Ion momentum conservation → *Retrieval of the source point*

Electron-ion-ion coincidence → *Molecular-frame e^- angular distribution*

Towards photoelectron diffraction measurement

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:

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

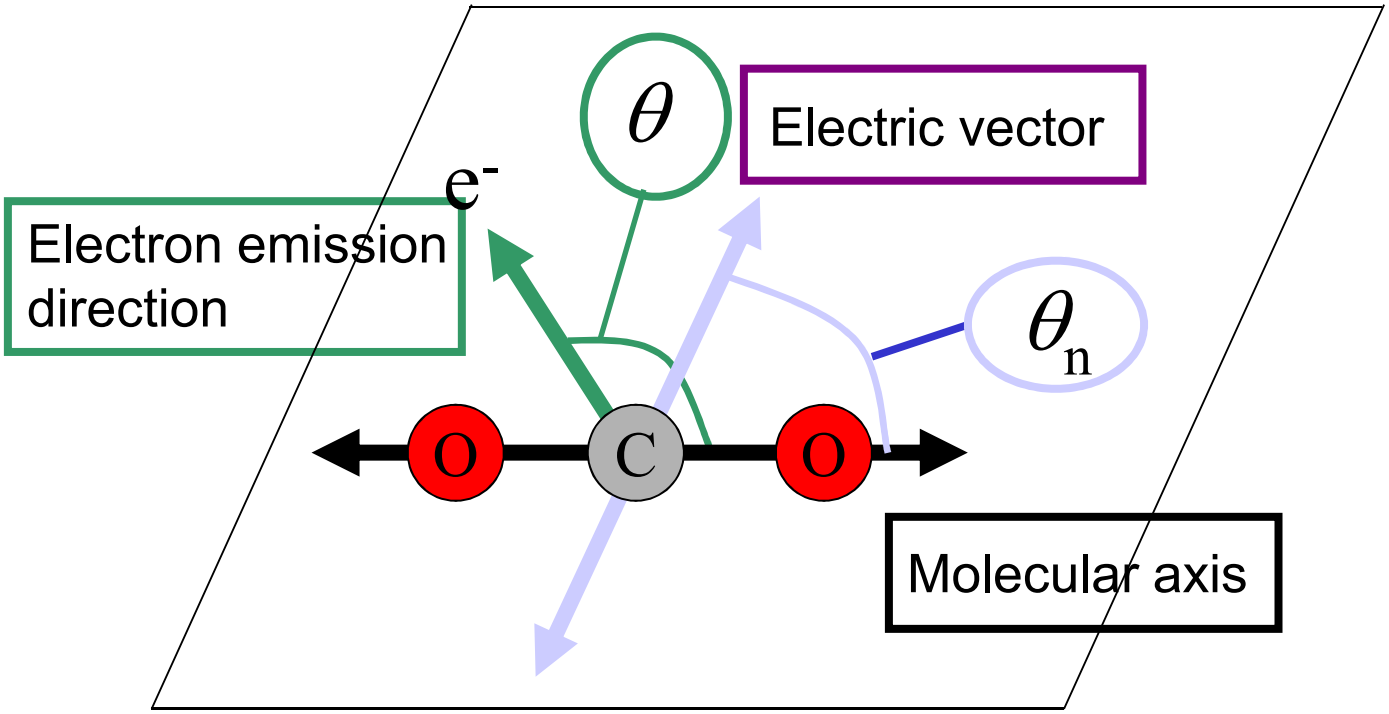
$$3\sigma_u^{\,2}1\pi_u^{\,4}1\pi_g^{\,4}(^1\Sigma_g^{\,+});\ 2\pi_u^{\,0}5\sigma_g^{\,0}4\sigma_u^{\,0}$$

C 1s threshold
297.63 eV

N. Saito *et al.*, J. Phys. B, **36** L25 (2003).

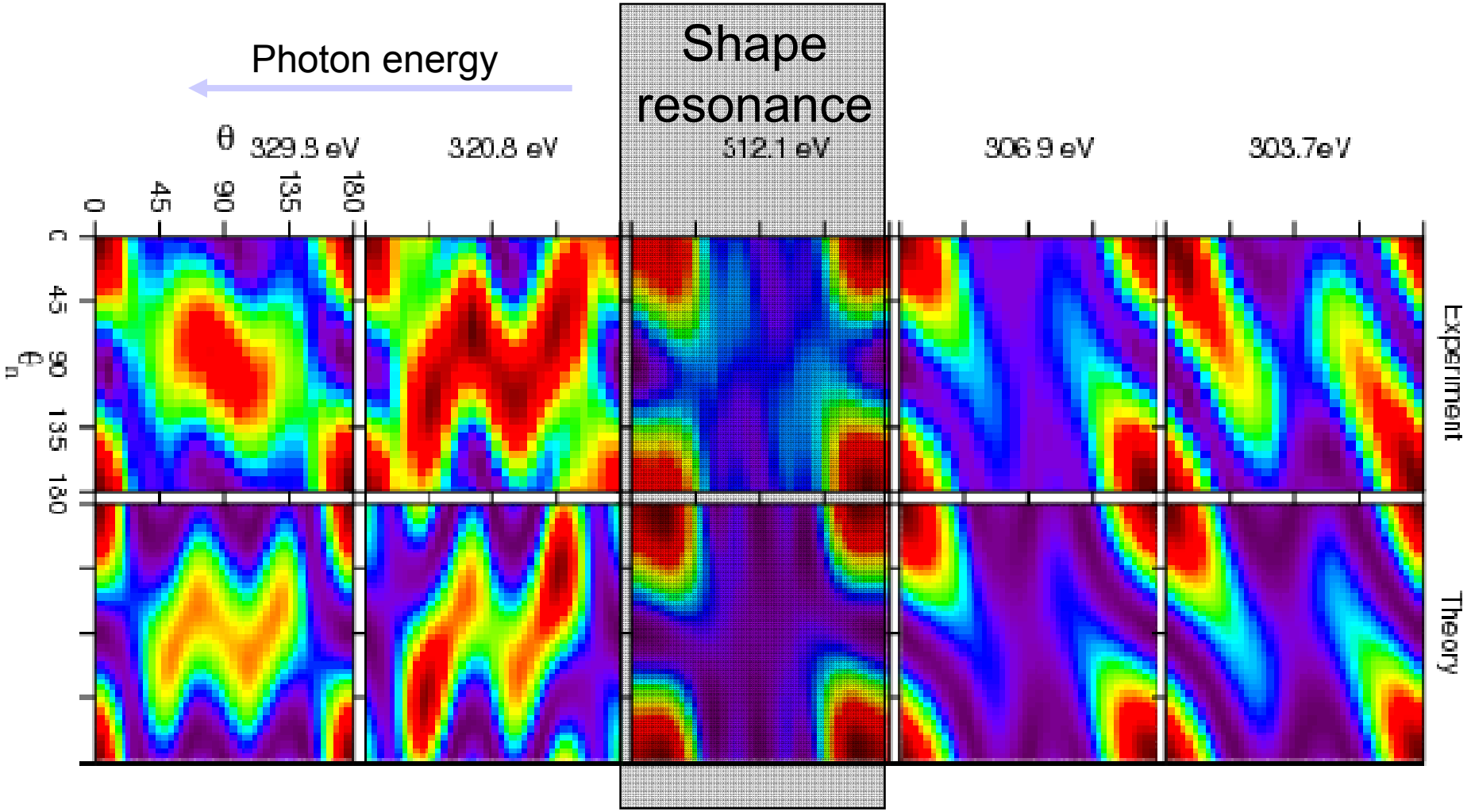
Reaction plane

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



We focus on the electron emission within this reaction plane

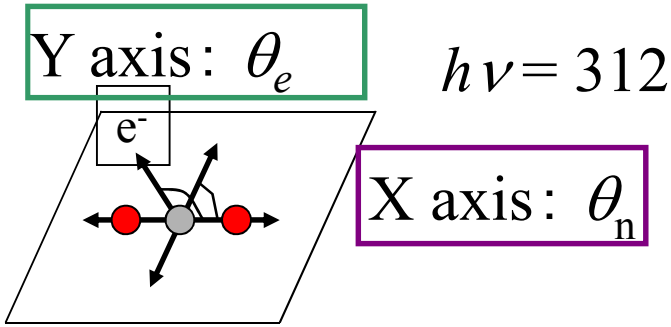
MFPADs for C1s emission from CO_2: comparison between experiment and theory



The general agreement between experiment and theory is reasonable.

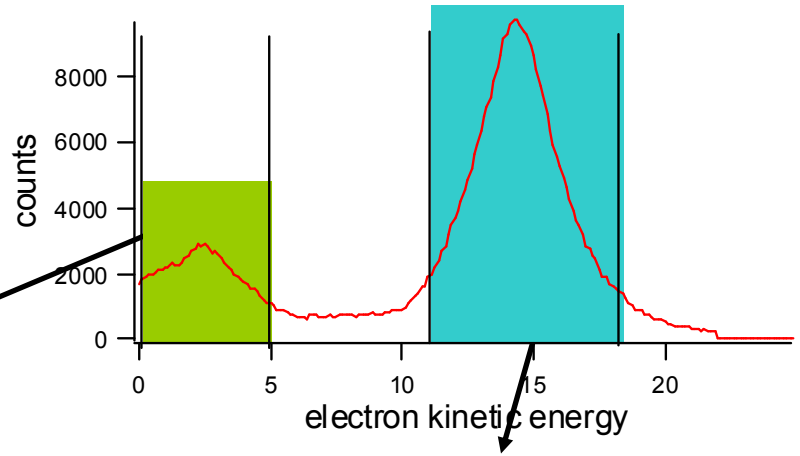
Liu *et al.* Phys. Rev. Lett. **101**,083001(2008).

Satellite line vs Main line

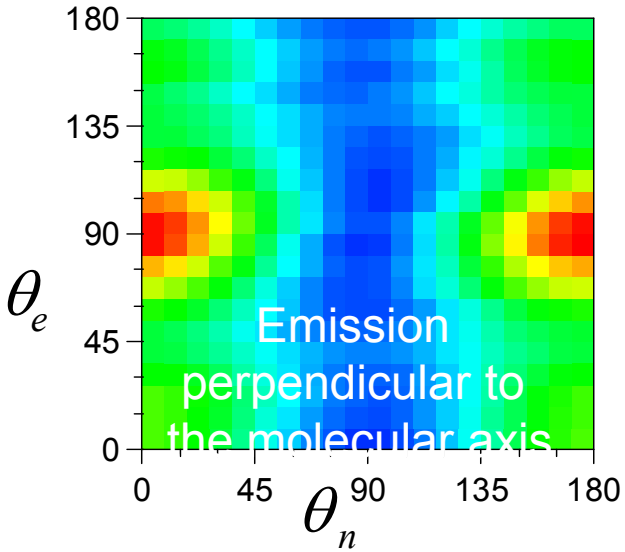


$h\nu = 312.2$ eV

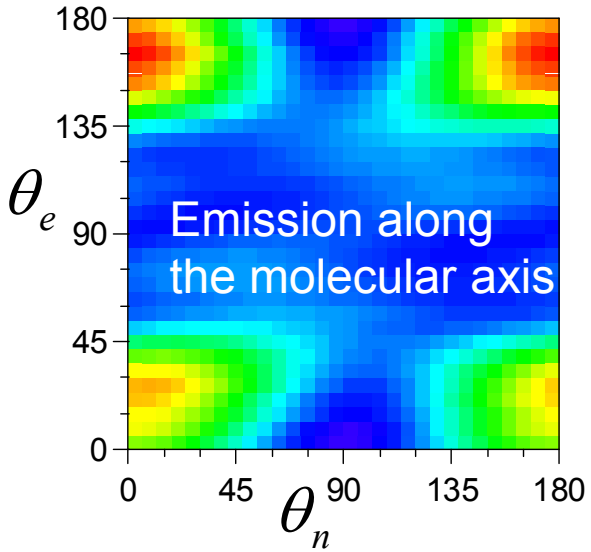
Photoelectron spectrum



Satellite



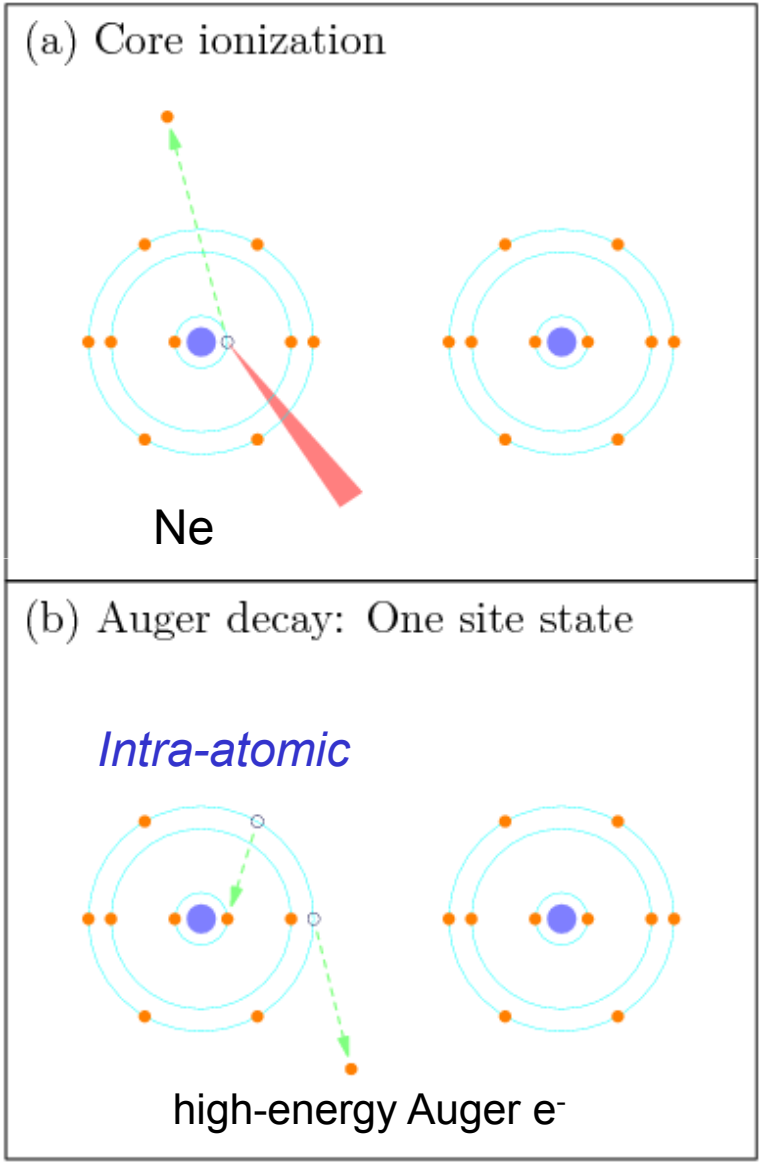
Mainline

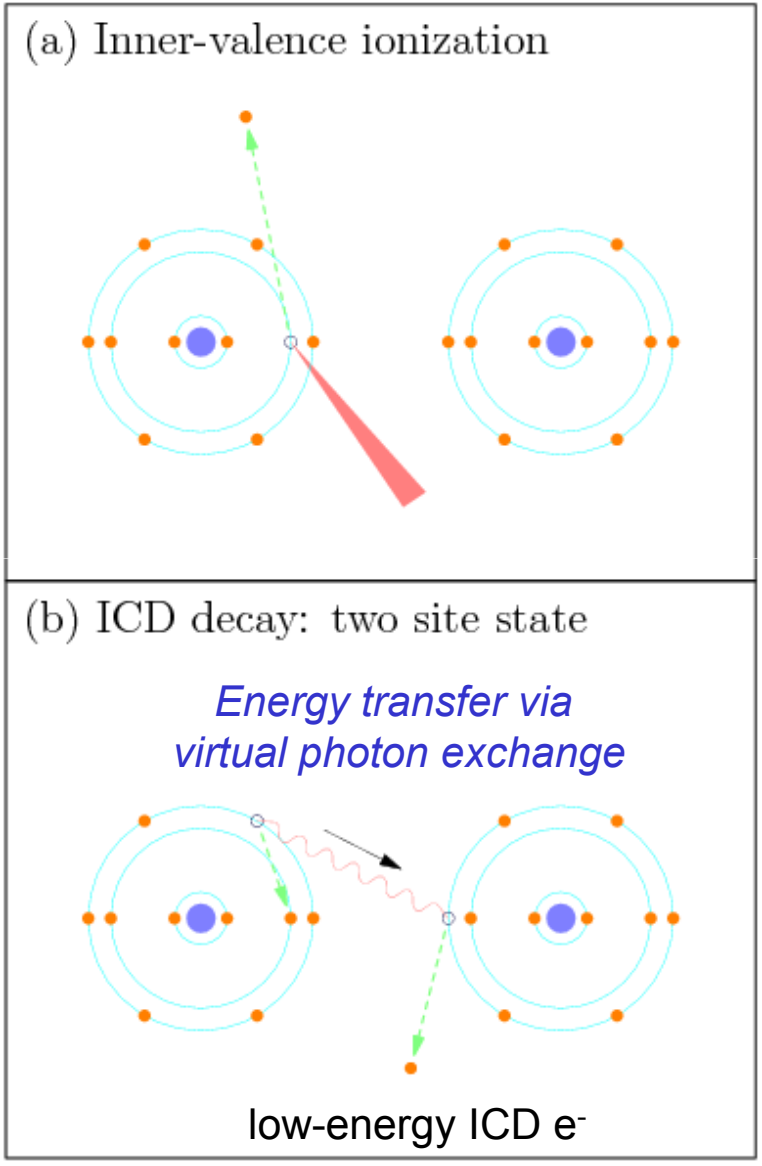


In both cases, the intensity drop at θ_n=90° i.e. Σ–Σ parallel transition.
The electron emission directions are completely different.

Liu *et al.* Phys. Rev. Lett. **101**, 023001 (2008).

Auger vs Interatomic Coulombic Decay (ICD)





ICD rate is R dependent!

Interatomic Coulombic Decay (ICD)

Theoretical

First prediction - HF cluster:
L.S. Cederbaum, J. Zobeley, and F. Tarantelli, Phys. Rev. Lett. 79, 4778 (1997).

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

Prediction - ICD from Auger final states in Ne dimer:
R. Santra and L.S. Cederbaum, Phys. Rev. Lett. 90, 153401 (2003).

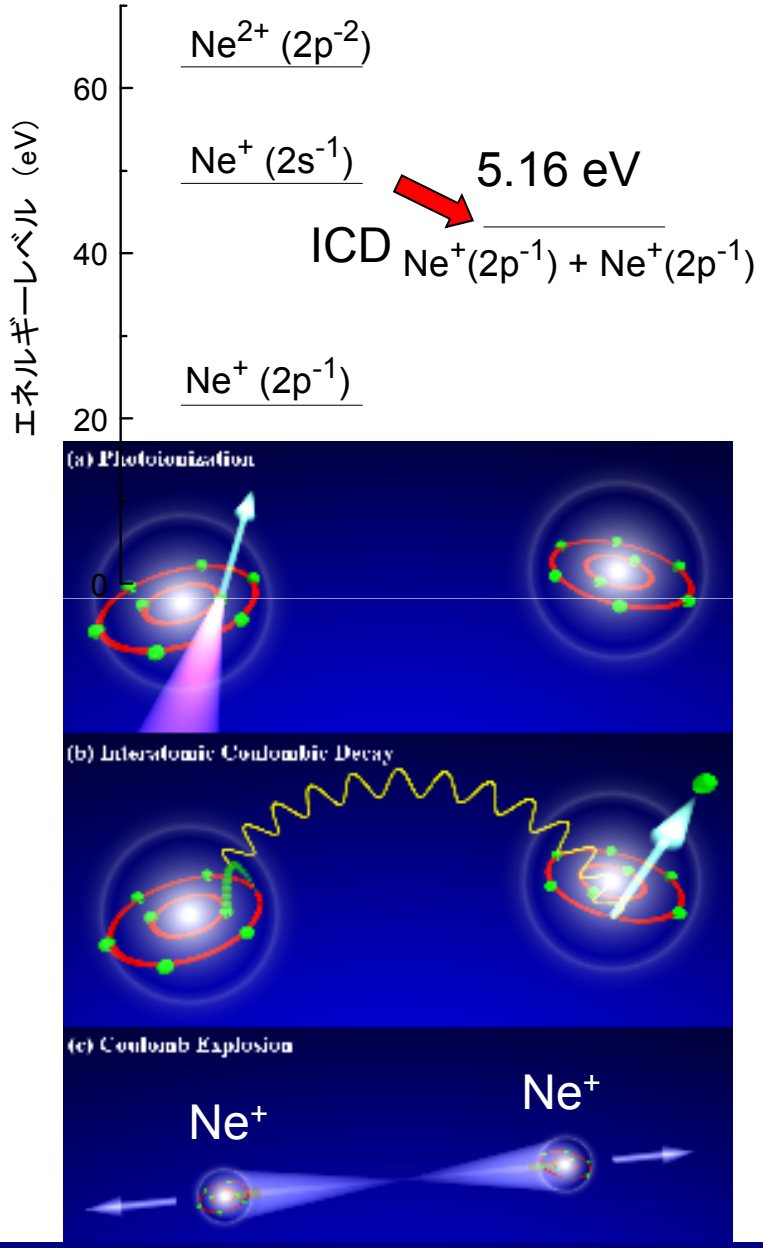
Experimental

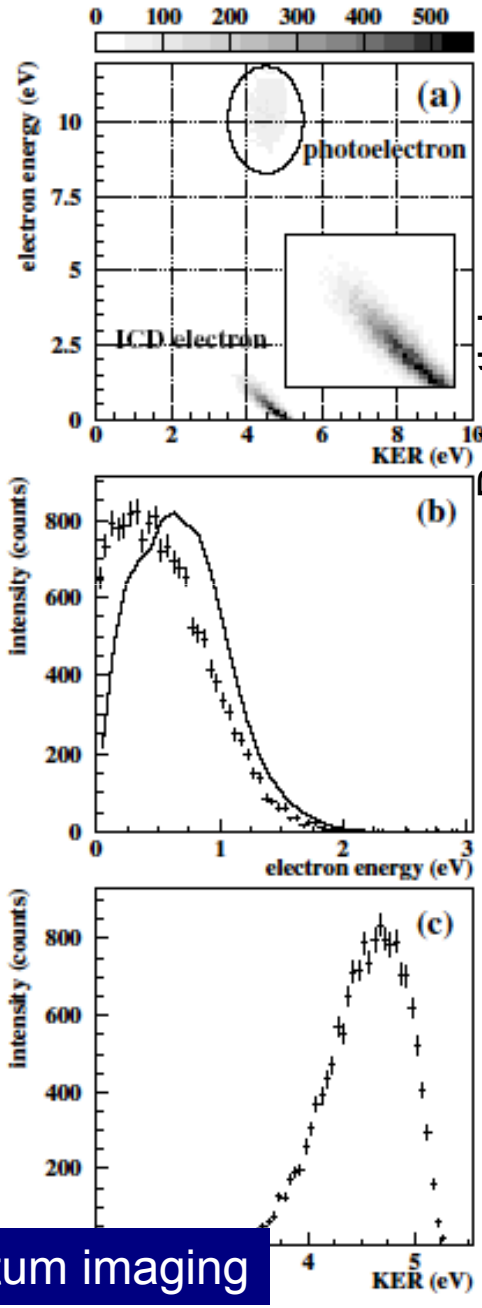
First observation - Ne cluster:
U. Hergenhahn and coworkers, Phys.Rev. Lett. 90, 203401 (2003).

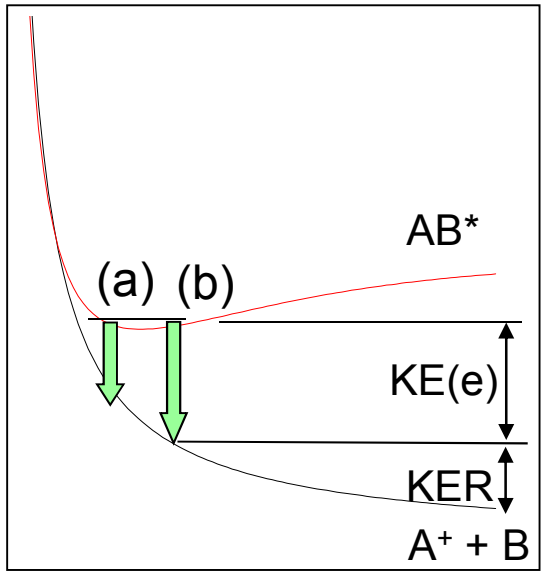
Cluster-size-dependent lifetime:
G. Öhrwall *et al*., Phys. Rev. Lett. 93, 173401 (2004).

Ne_2 e-ion-ion coincidence:
R. Dörner and coworkers, Phys. Rev. Lett. 93, 163401 (2004).

Observation of ICD in Ne_2 by Frankfurt group





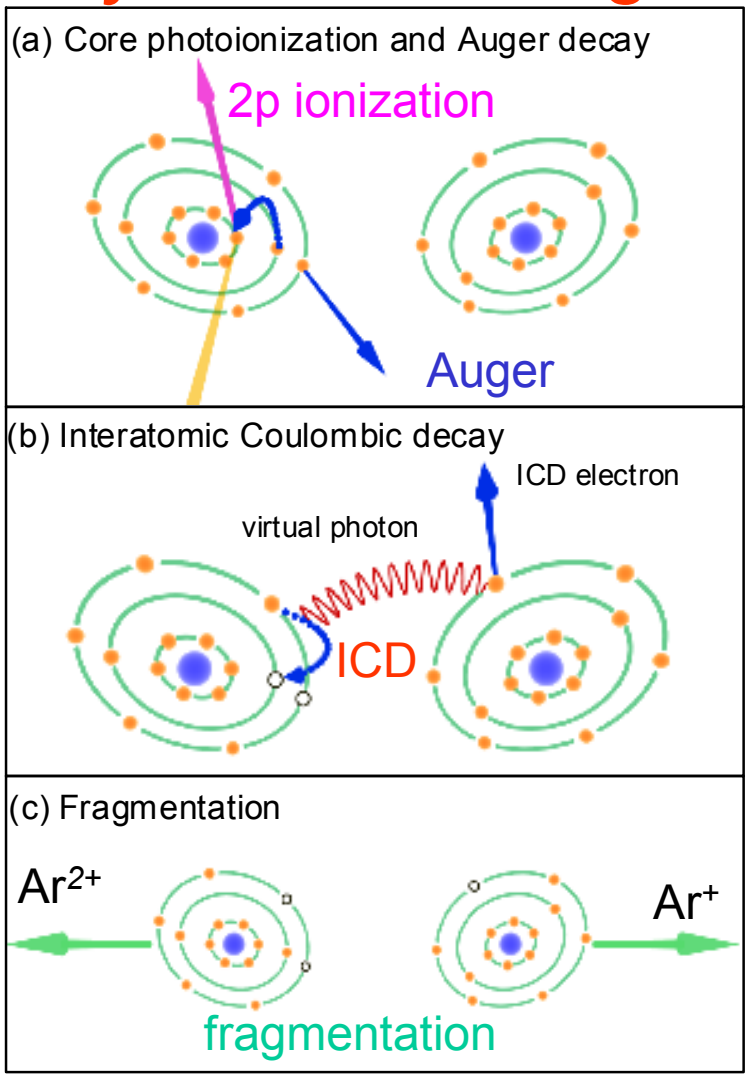


KE(e)+KER = 5.16 eV

T. Jahnke *et al.*
Phys. Rev. Lett.
93, 163401 (2004)

Electron-ion-ion coincidence momentum imaging

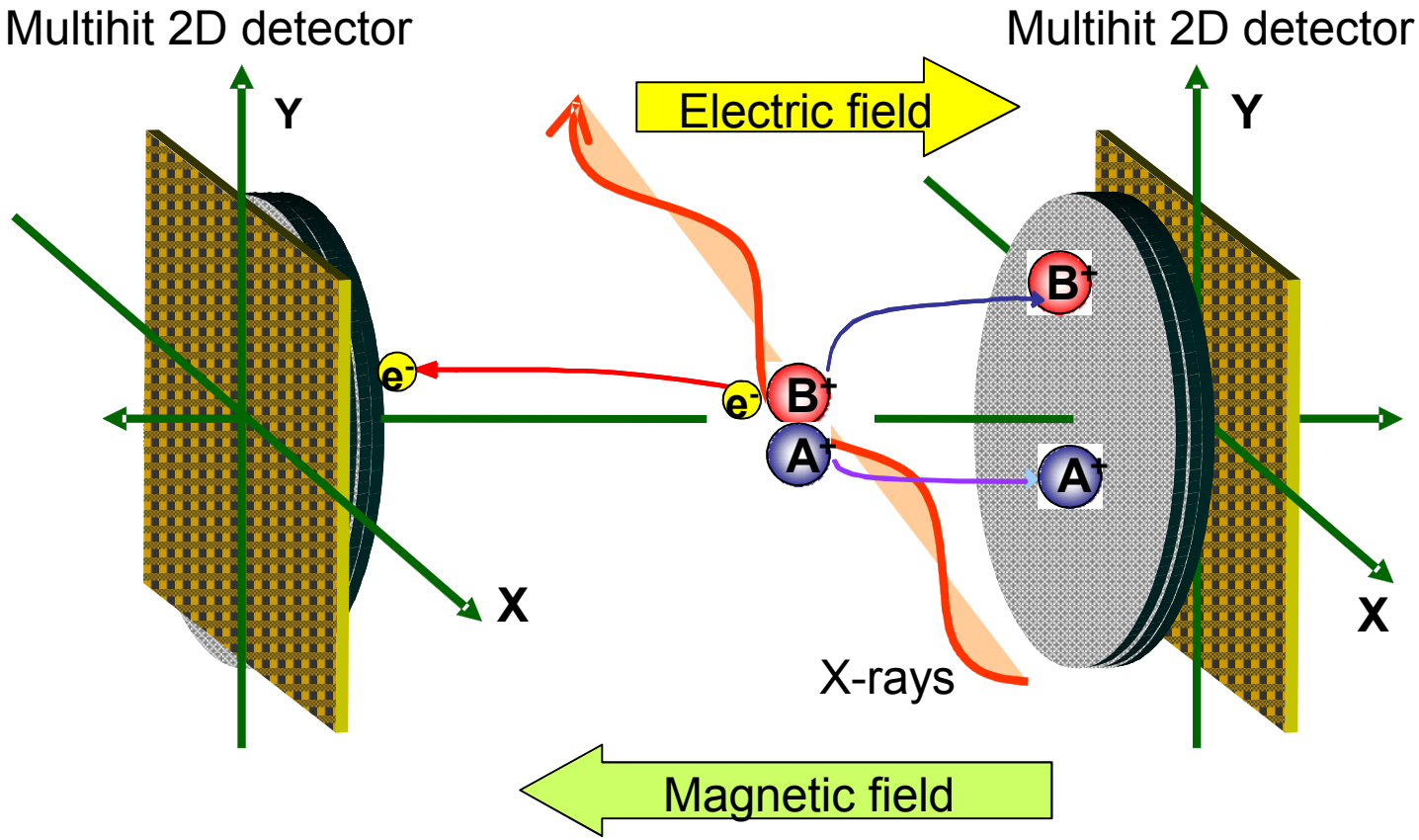
Experimental evidence of interatomic Coulombic decay from the Auger final states in argon dimers



Morishita *et al.* Phys. Rev. Lett. **96**, 243402 (2006).

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

Multiple coincidence momentum imaging

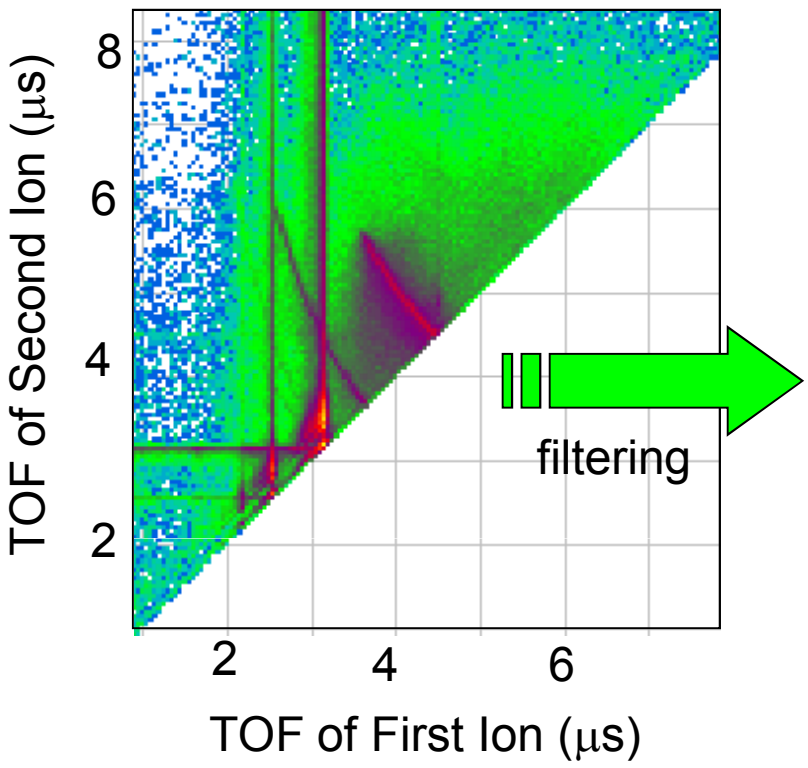


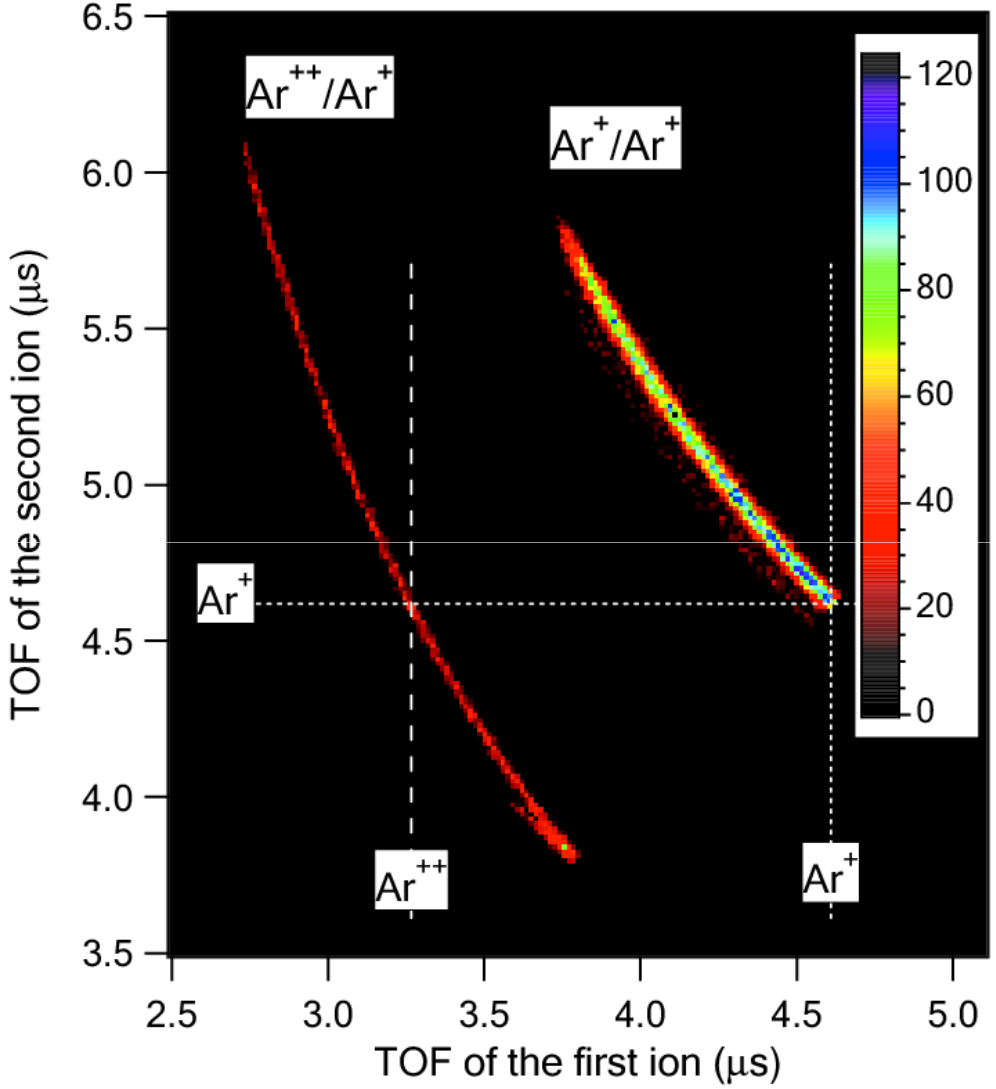
position & time of flight (x,y,t) → *3D momentum of each particle*

Multiple coincidence → *Momentum correlation among the particles*

Momentum conservation → *Selection of Dimer from others !*

Ar_2 PIPICO spectrum





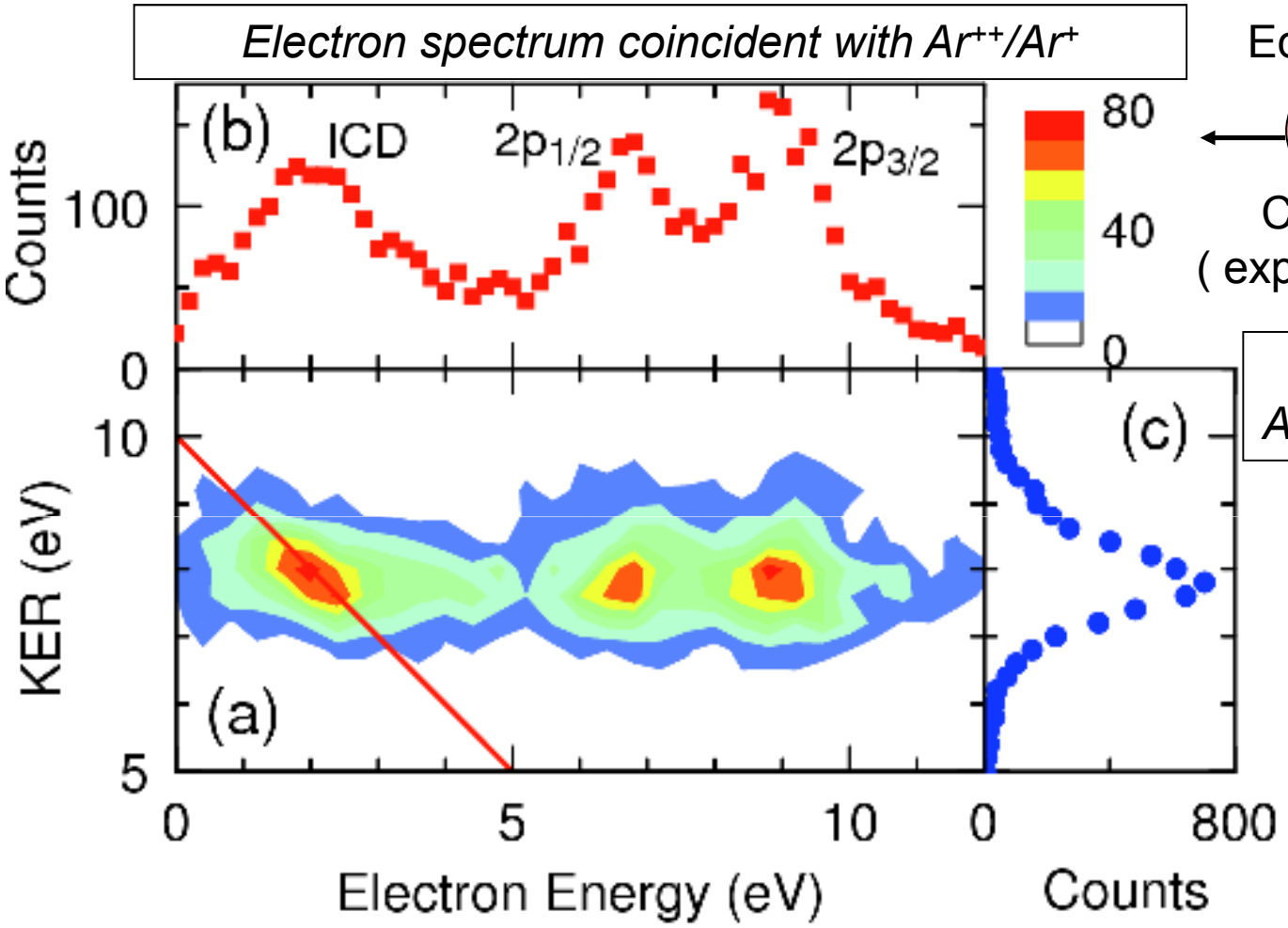
Filter conditions:

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 !?

Electron spectrum, KER, and their correlation



Equilibrium distance

Ar^+ 3.8 A Ar^{++}

Coulomb explosion

(expected KER ~ 7.6 eV)

KER
Ar^{++}/Ar^+

Measured KER
~ 7.7 eV

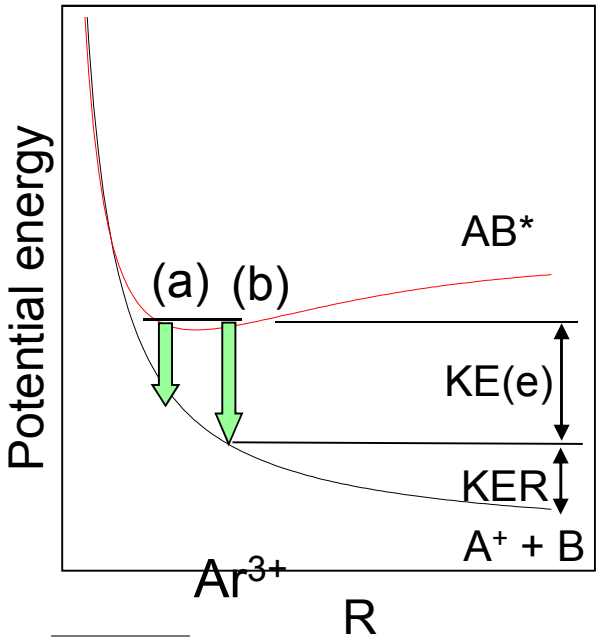
ICD: KER + KE(ICD electron) ~ constant

Islands of slope -1 are ICDs !

Breakup following ICD takes place almost instantaneously.

ICD is very fast!

Energy diagram of the ICD process in Ar_2



KER
+ ICD electron
= 10 eV

Photoelectron ejection
(13.4 and 11.3 eV)

$2p^{-1}$

Auger decay

hv=262 eV
photoionization

Binding Energy (eV)
70
60
50
40

$3s^{-2}$

$3p^{-3}3d(^1P)$

CI

$3s^{-1}3p^{-1}(^1P)$

ICD &
fragmentation

10eV

$3p^{-1}$ & $3p^{-2}$ (^1D)

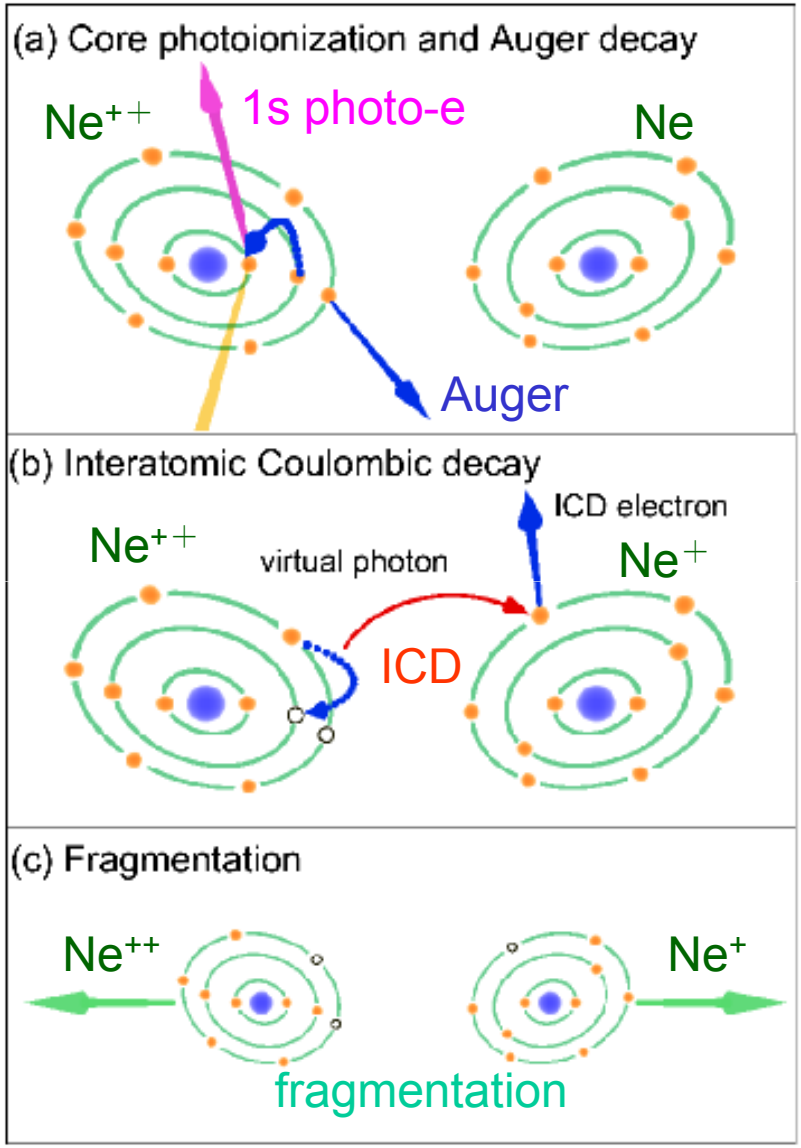
$3p^{-2}$

Ar Ar^+

Ar Ar^{2+}

Ar^+ Ar^{2+}

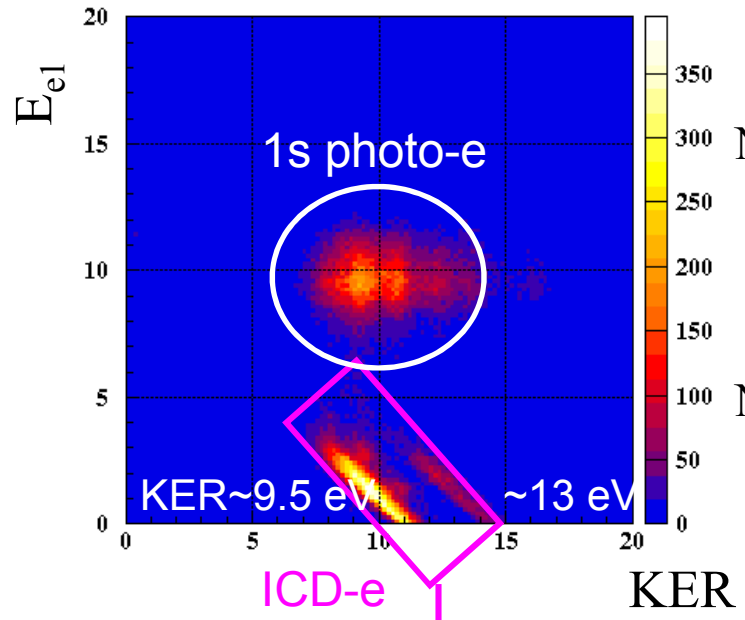
*ICD from the Auger final states in **Ne** dimer*

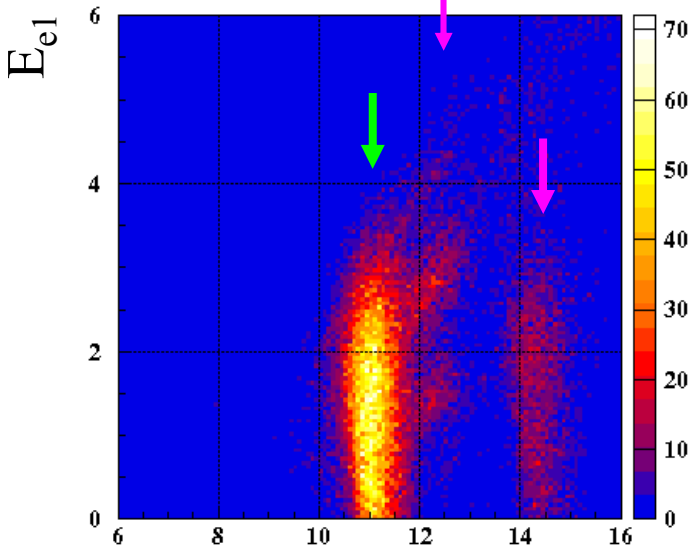


*Kreidi et al. J. Phys. B. **41**, 101002 (2008).*

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

ICD channels in Ne_2 after KL_1L_{23} Auger





$$\rightarrow \quad E_{e1} + KER = 11.2\ \text{eV} \qquad R \sim R_0$$

$$Ne^{++}(2s^{-1}2p^{-1^1}P) - Ne \;->\; Ne^{++}(2p^{-1}2p^{-1^1}D) - Ne^{+}(2p^{-1^2}P)$$

$$98.5\ \text{eV} - (65.7 + 21.6)\ \text{eV} = 11.2\ \text{eV}$$

$$\rightarrow \quad E_{e1} + KER = 14.4\ \text{eV}$$

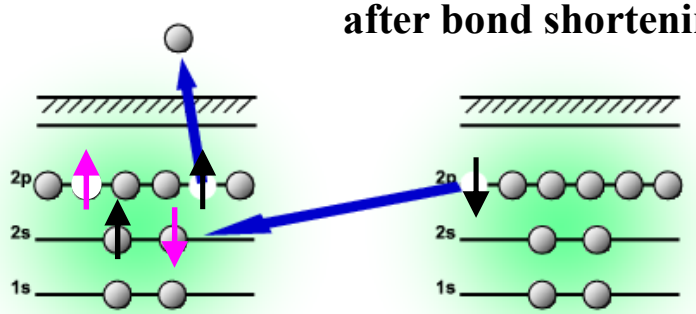
$$Ne^{++}(2s^{-1}2p^{-1^1}P) - Ne \;->\; Ne^{++}(2p^{-1}2p^{-1^3}P) - Ne^{+}(2p^{-1^2}P)$$

$$98.5\ \text{eV} - (63.5 + 21.6)\ \text{eV} = 14.4\ \text{eV}$$

$$Ne^{++}(2s^{-1}2p^{-1^1}P) \rightarrow Ne^{++}(2p^{-1}2p^{-1^3}P)$$

Spin flip!

decay via electron exchange after bond shortening

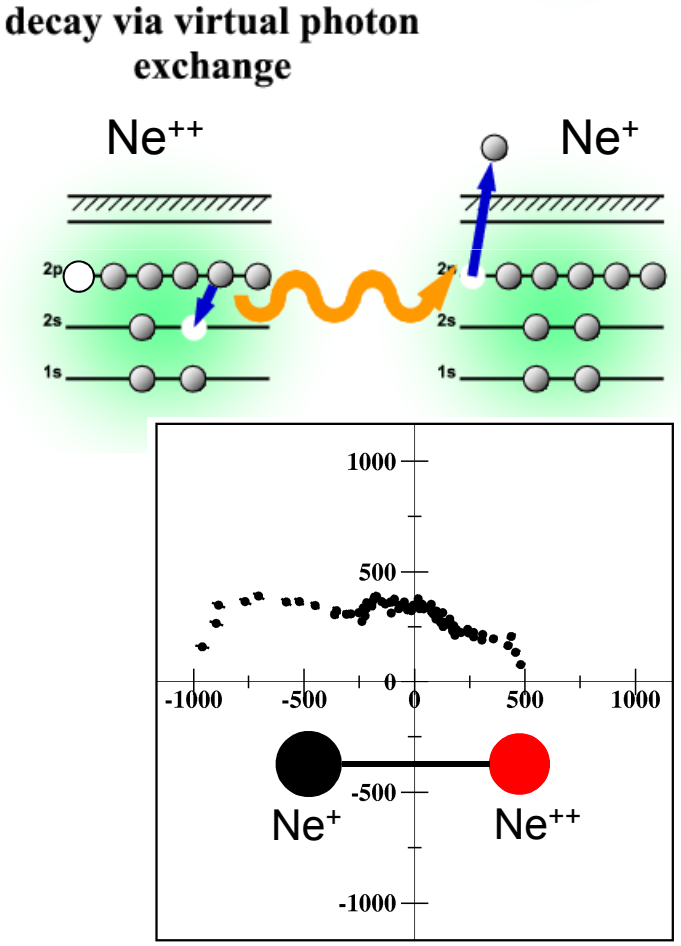


Exchange !

$R \sim 2.2\ \text{A} < R_0 = 3.2\ \text{A}$

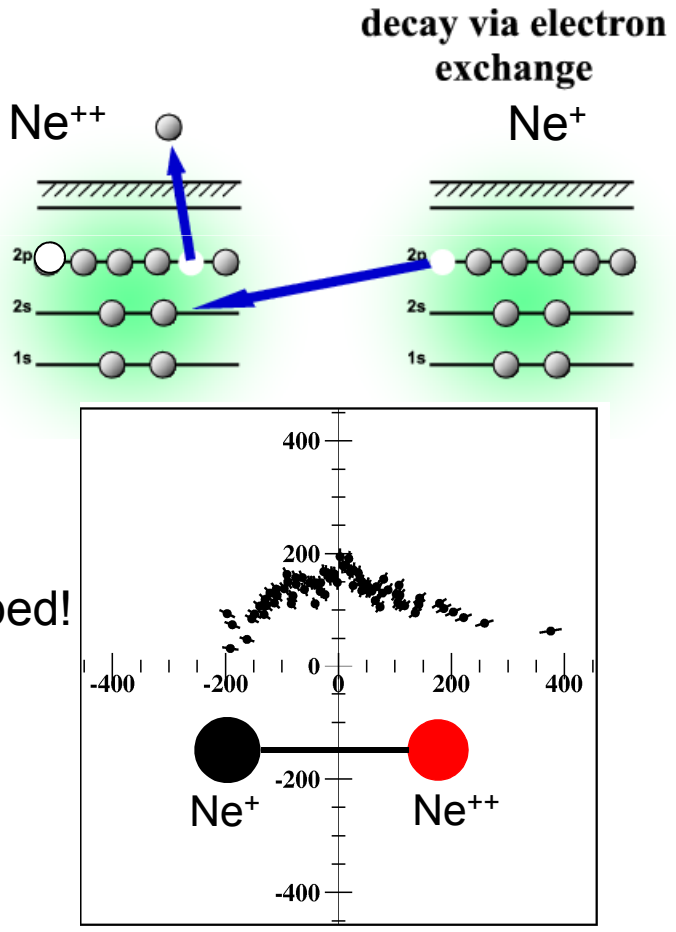
Molecular frame electron angular distributions emitted via ICD

ICD by virtual photon exchange
(direct integral)
ICD electron is emitted from Ne^+ site



ICD by electron transfer
(exchange integral)
ICD electron is emitted from Ne^{++} site

Flipped!



Wave packet dynamics on ab initio potential energy curves

Stoychev *et al.* J. Chem. Phys. 129, 074307 (2008).

The end

Thank you very much for your attention!