Cheiron School, SPring-8, Japan
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Studies on atoms and molecules using synchrotron radiation

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Introduction of myself

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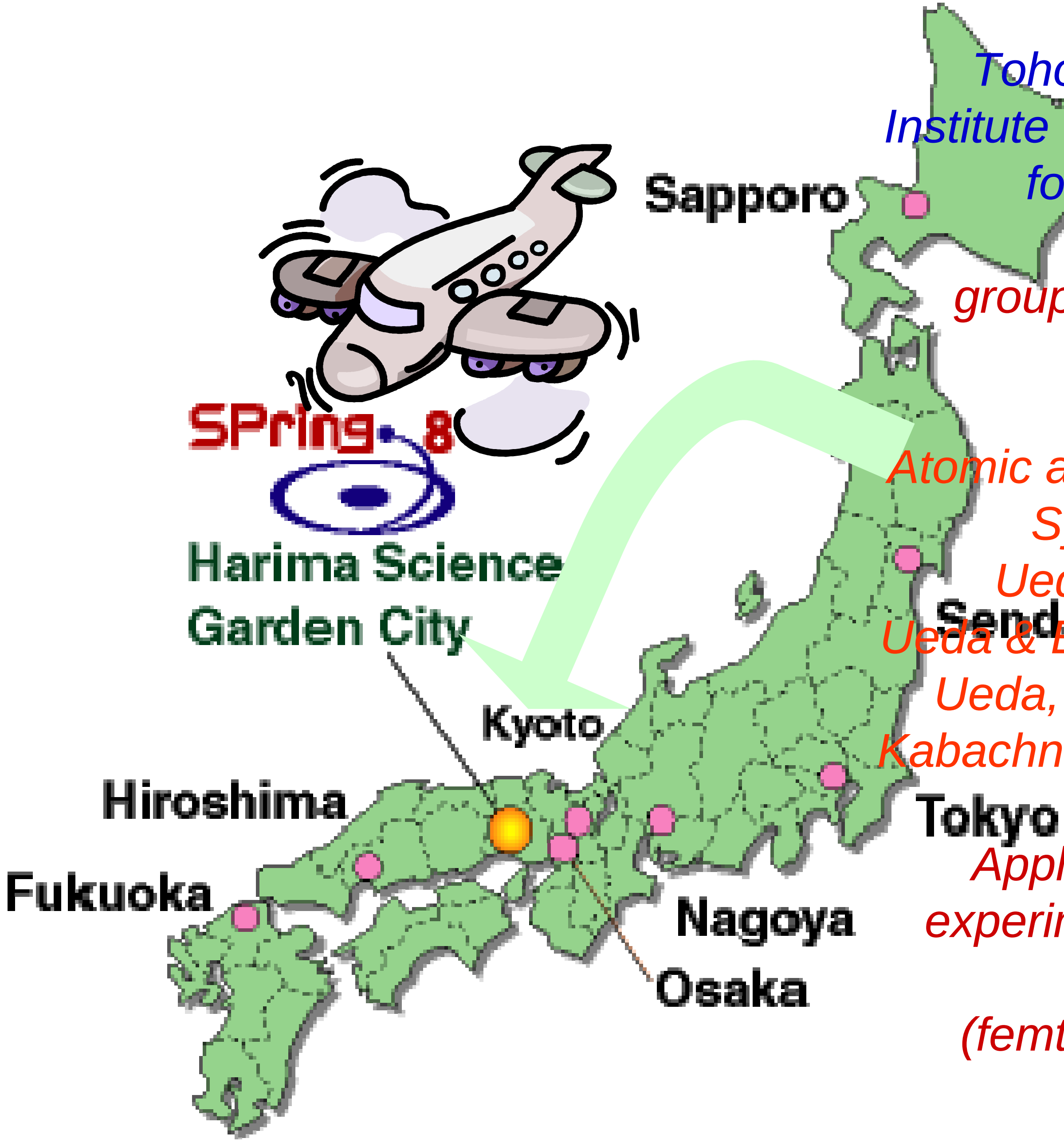
Leading
group for analysis of quantum
processes



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

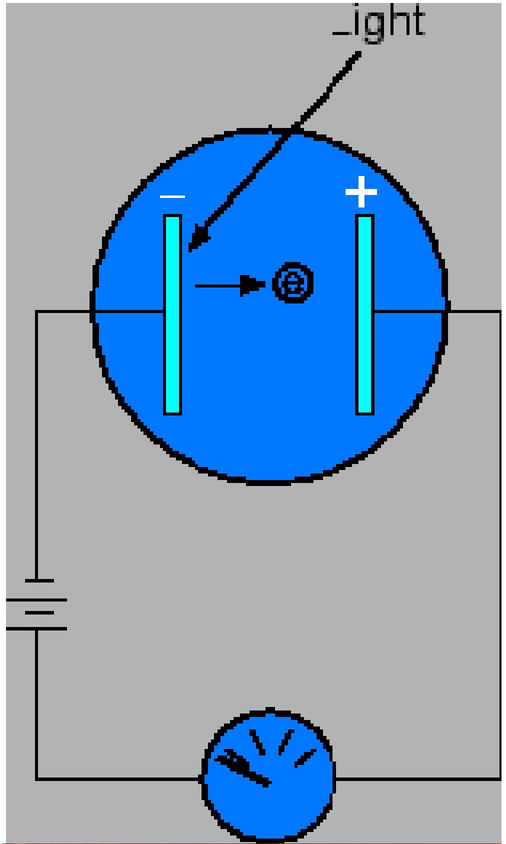
6. Toward future

- FEL experiment

Photoelectric effect

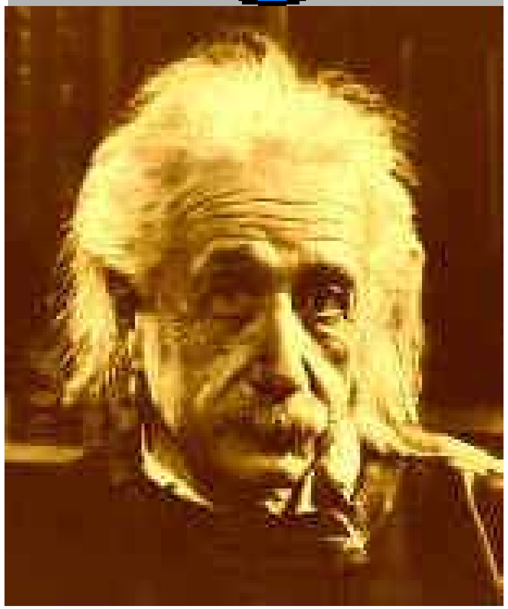
When matter is shined by the light, electron is emitted from the surface.

(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

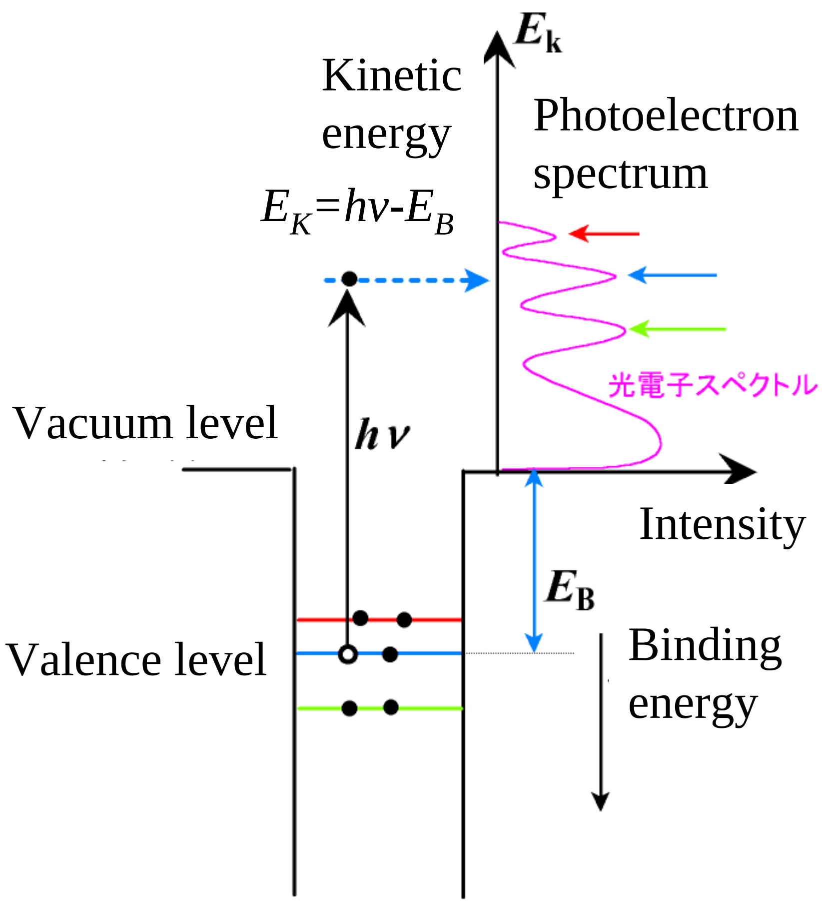
Light at frequency of ν is considered to be a group of particles (photons) and each photon has energy $h\nu$. An electron gets the energy $h\nu$ when it absorb one photon.
The electron in the matter is bound. For the electron to be emitted from the matter, the electron needs to receive the energy more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

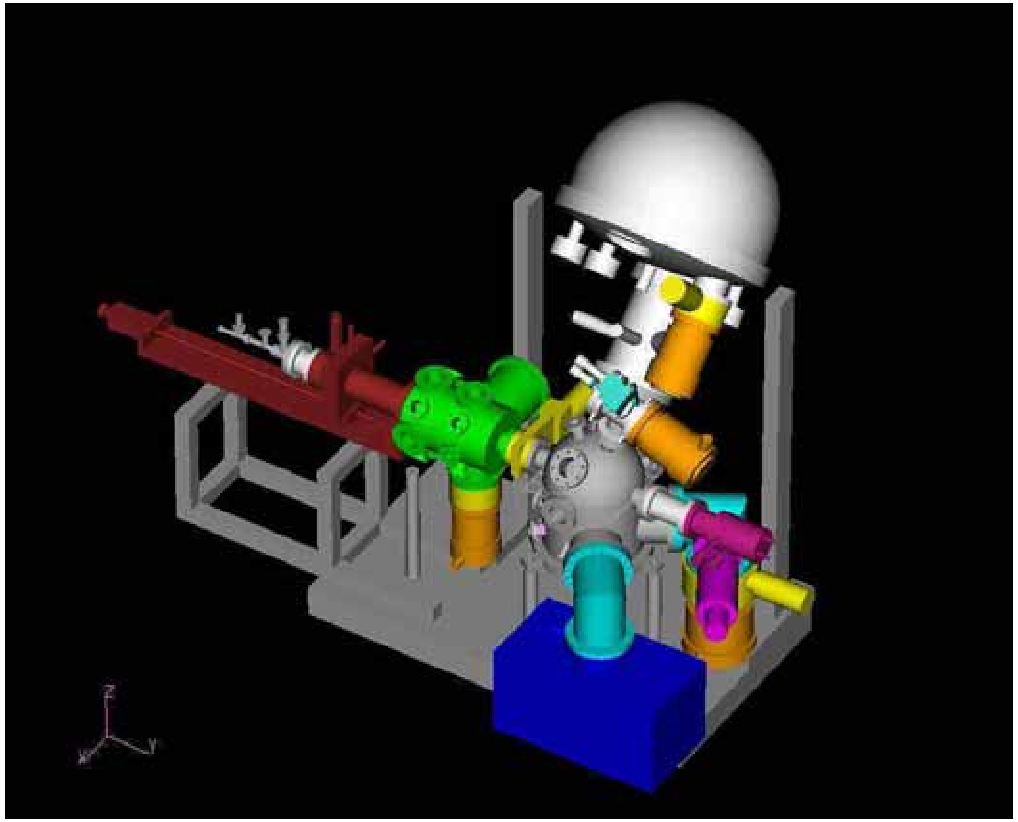


Einstein's miraculous year 1905, Nobel prize in 1912

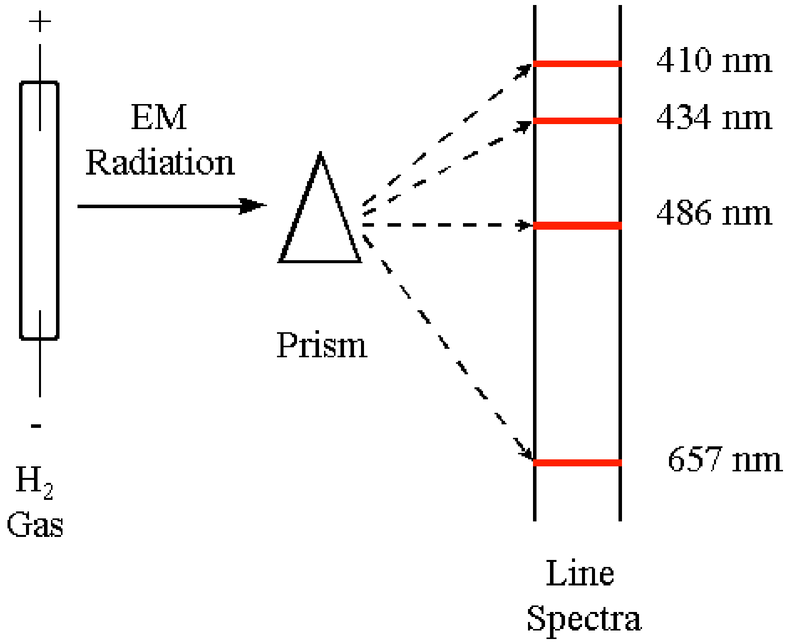
Photoelectron spectroscopy (UPS, XPS)

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

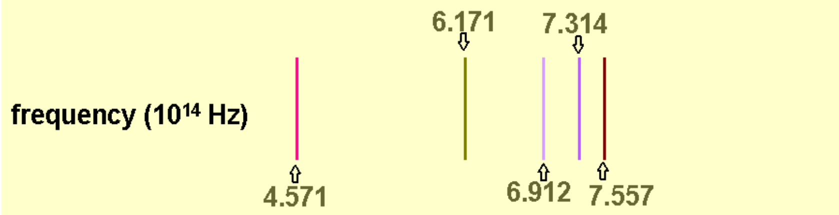




Balmer and Rydberg formulae



Hydrogen Spectrum: Balmer series



Balmer Formula: $\nu = \nu_0 \left((1/n^2) - (1/m^2) \right)$

32.91 (1/4 - 1/9) = 4.571

32.91 (1/4 - 1/16) = 6.171

32.91 (1/4 - 1/25) = 6.911

32.91 (1/4 - 1/36) = 7.313

32.91 (1/4 - 1/49) = 7.556

IT WORKS!

Balmer found beautiful regularity in the H spectrum!

Rydberg formula：

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

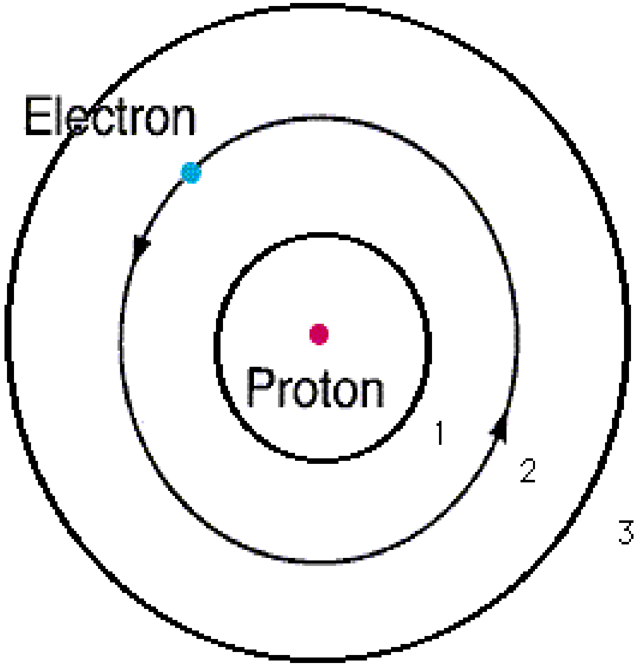
c, **speed of light; λ, wavelength;** ***R***, **Rydberg constant (*R* =109737.309 cm^{-1})**

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 discre

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

Proposed in 1913, Nobel prize in 1922

Schrödinger equation (of H atom in atomic units)

$$H\Psi = E\Psi$$

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

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

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

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

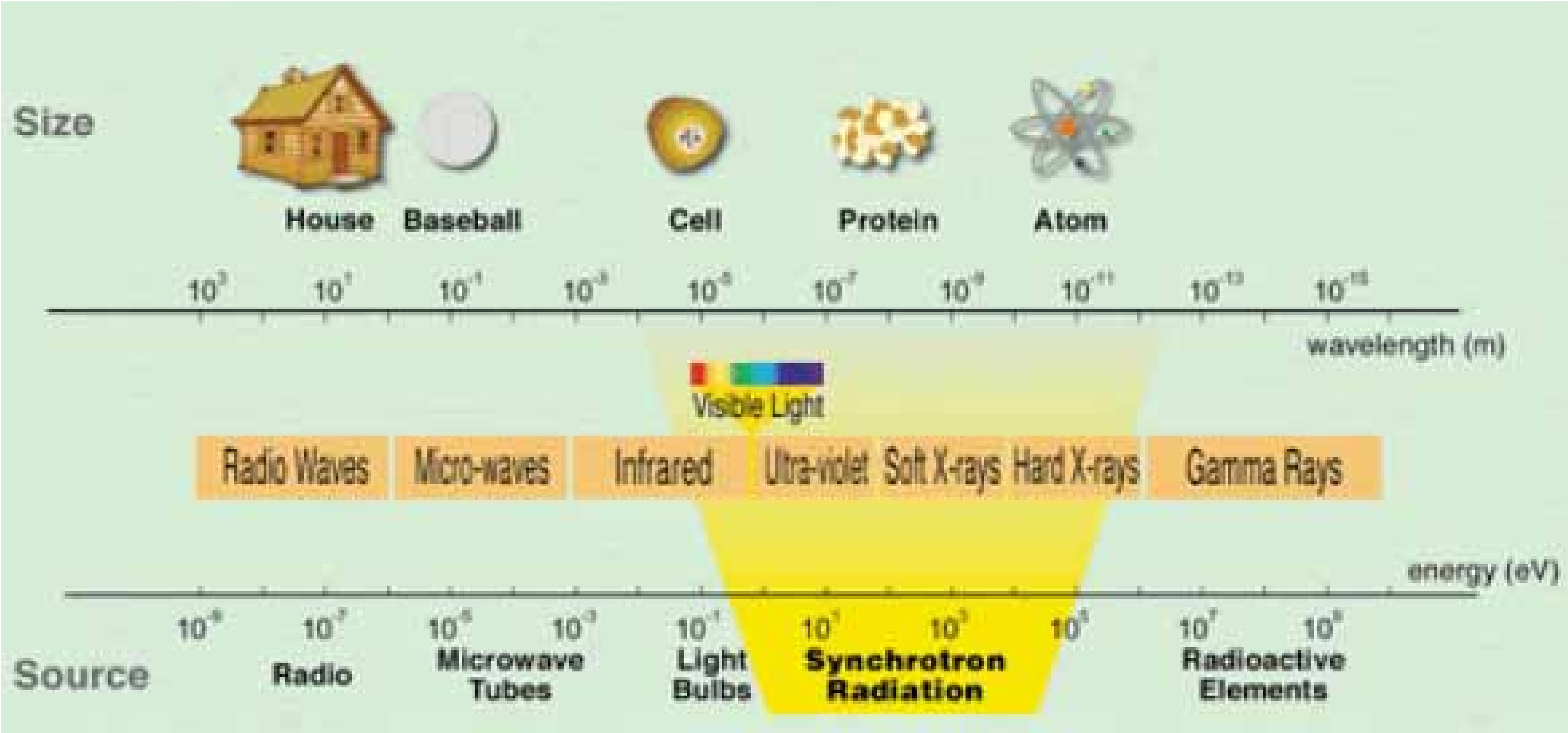
$$E_n = -\frac{1}{2n^2}$$ eigen energy of the H atom

Proposed in 1926,
Nobel prize in 1933

In quantum world, wave function Ψ – which is in general a complex number with a phase! – defines the system!

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.

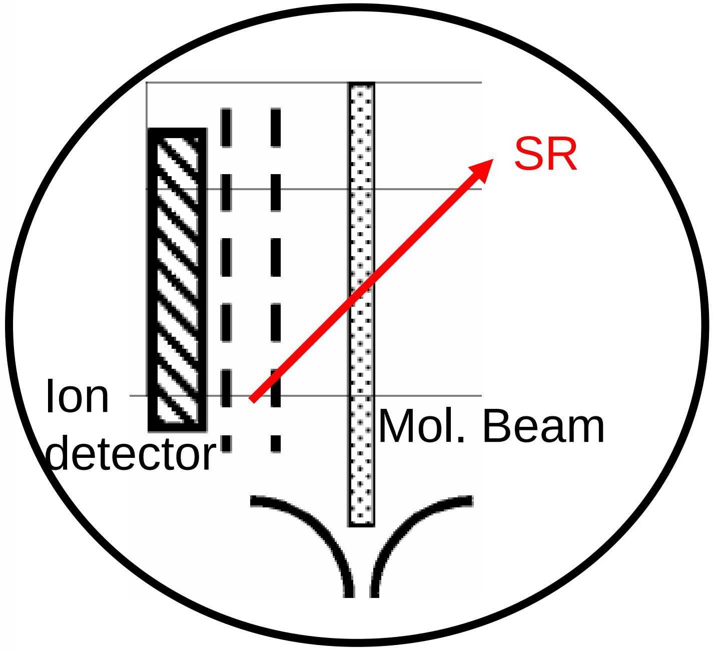
A single photon should be absorbed by a single atom or molecule in the first step!

What photon energies to be used

Electron binding energies (eV) *Vacuum ultraviolet region*

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

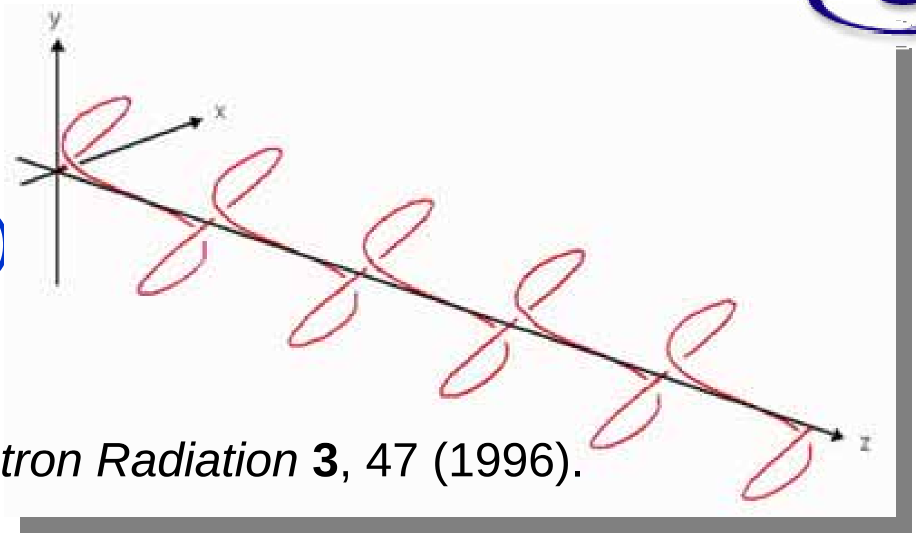
SPring-8 BL27SU

Figure-8 undulator

Linearly polarized light

Horizontal polarization (1st)

Vertical polarization (0.5th)



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

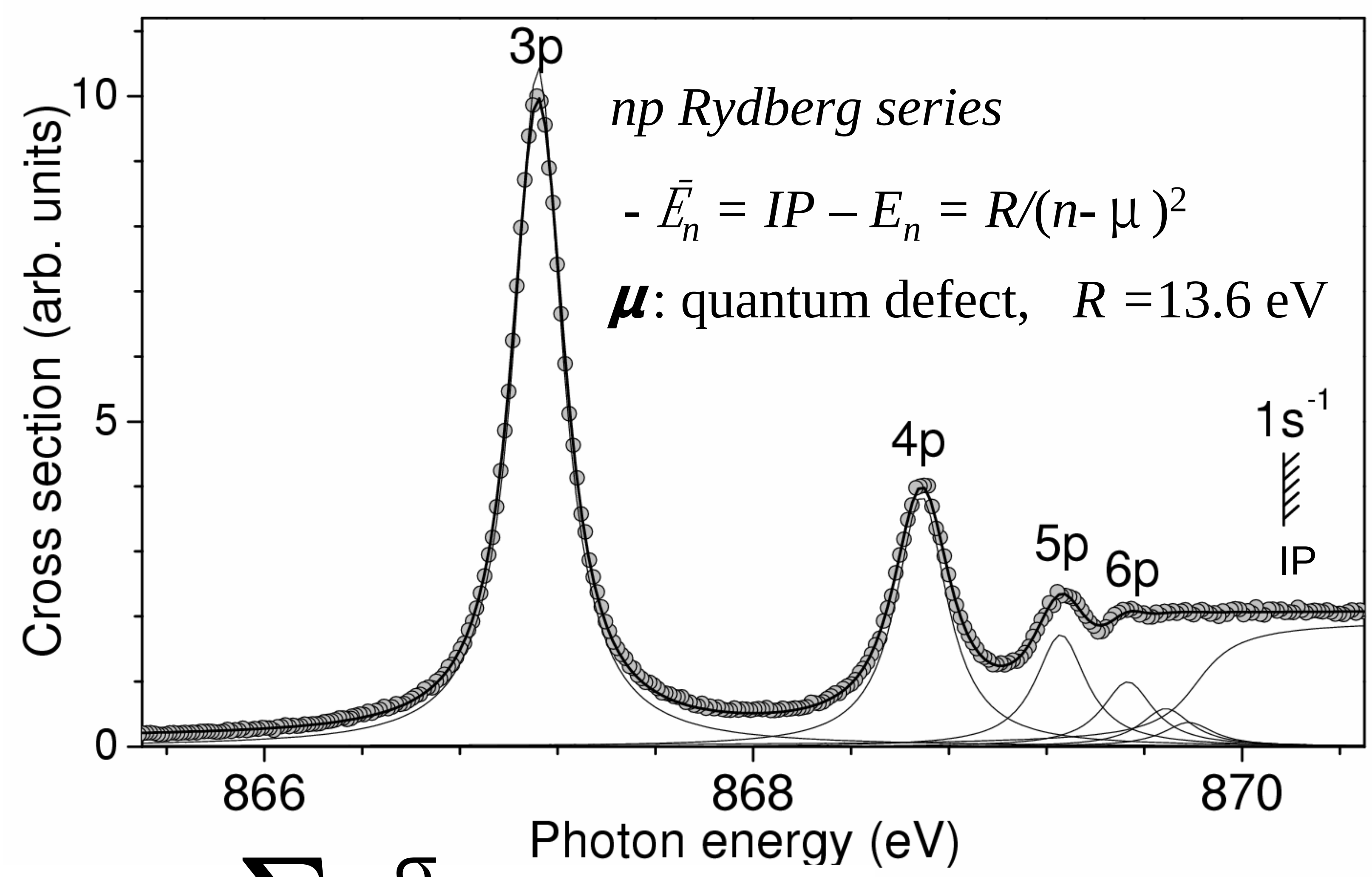
Soft X-ray monochromator

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).

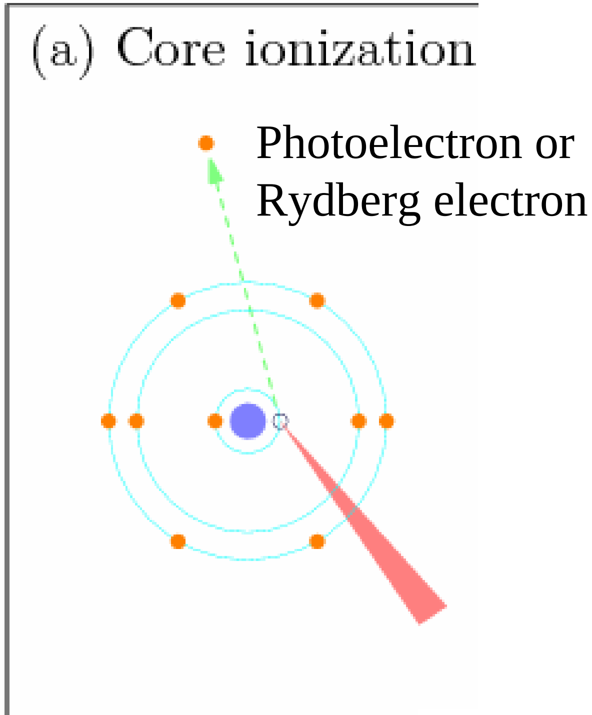
Ne 1s total ion yield spectrum



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

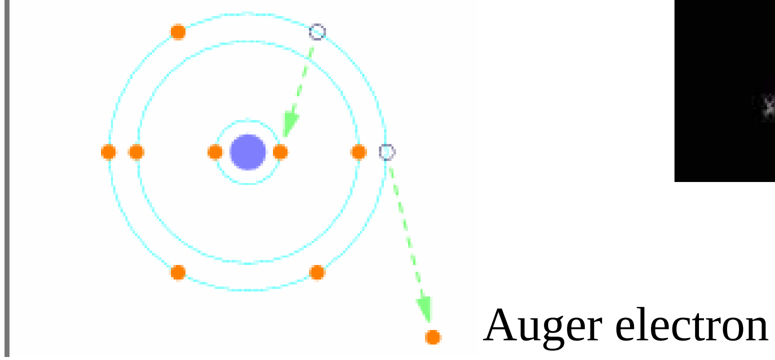
$$\sigma_n \propto 1/(n-\mu)^3 \qquad \Gamma_n = \text{const!}$$

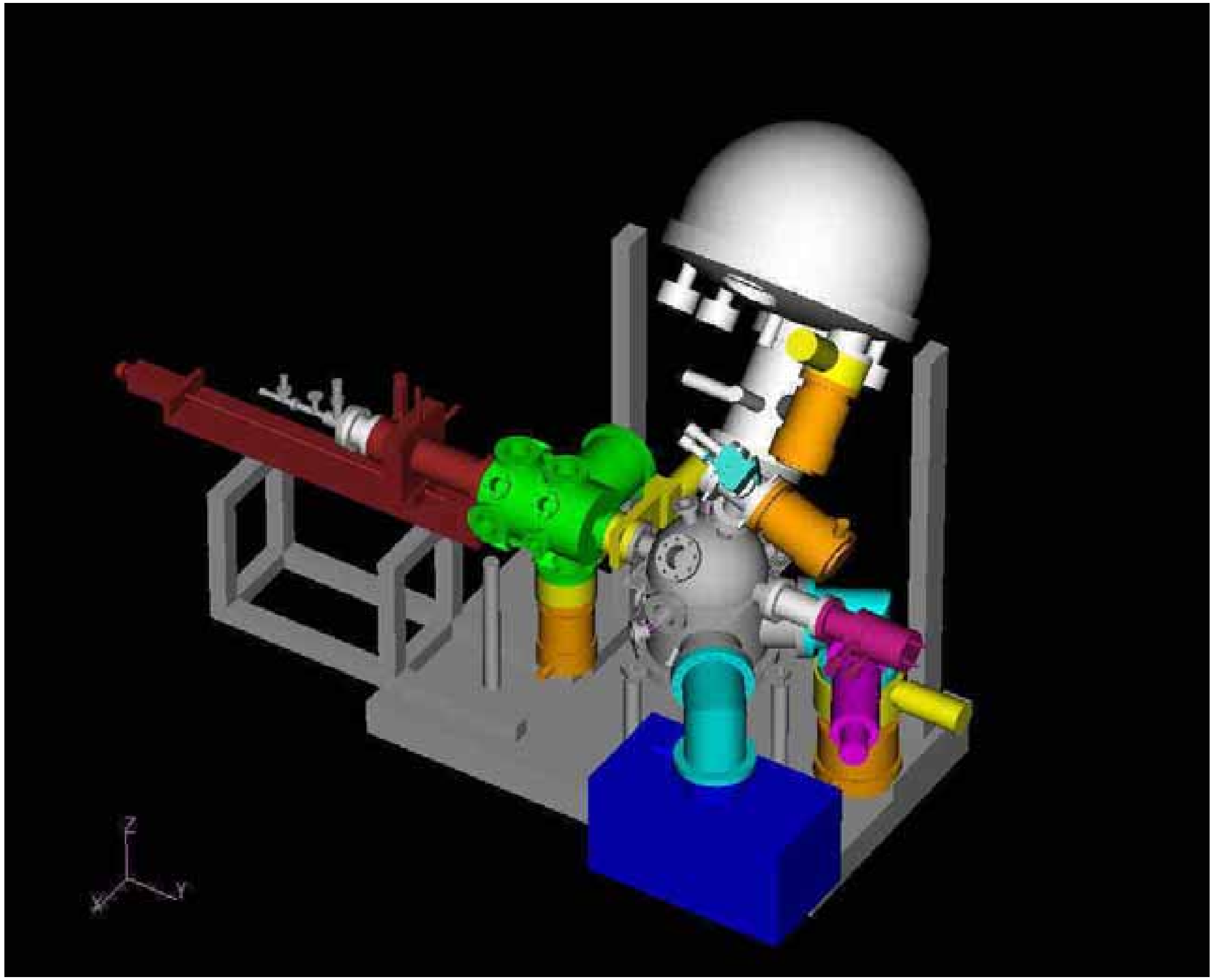
Auger decay and Auger electron spectroscopy



(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

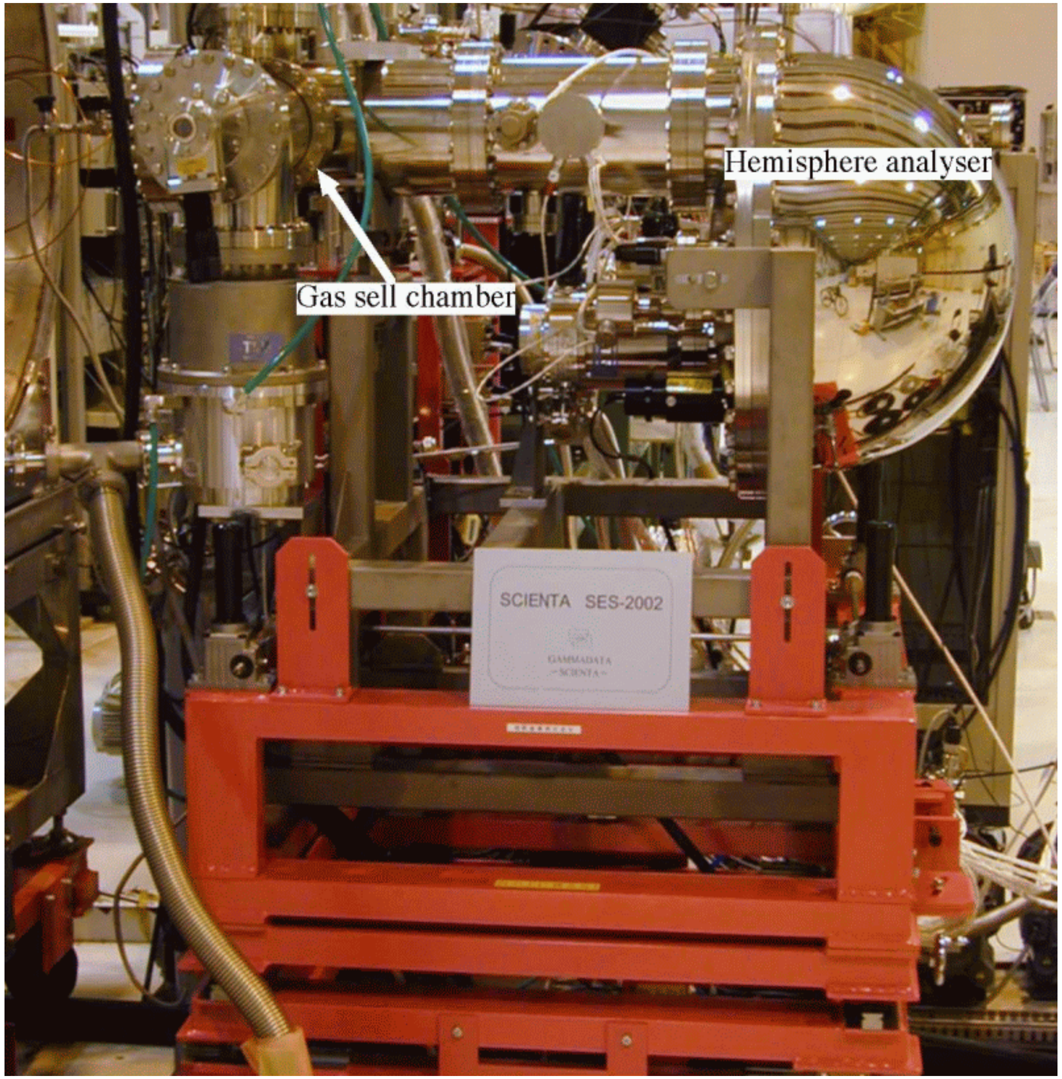
  - **Gas cell system**

  or Doppler-free molecular beam source

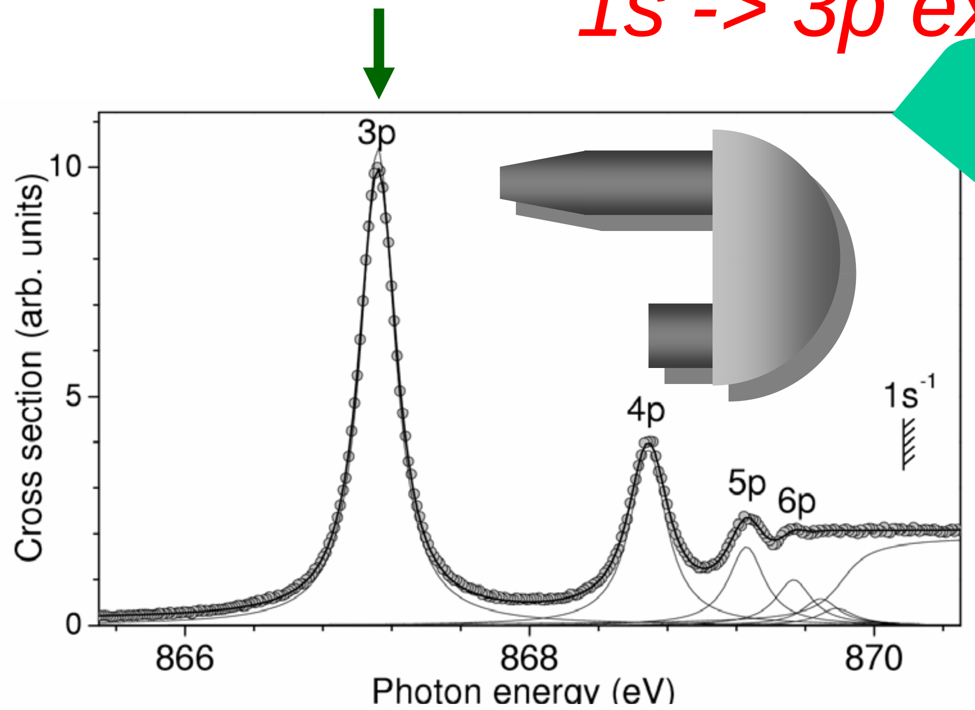
  Ueda *et al. PRL* . **90**, 153005 (2003)

  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

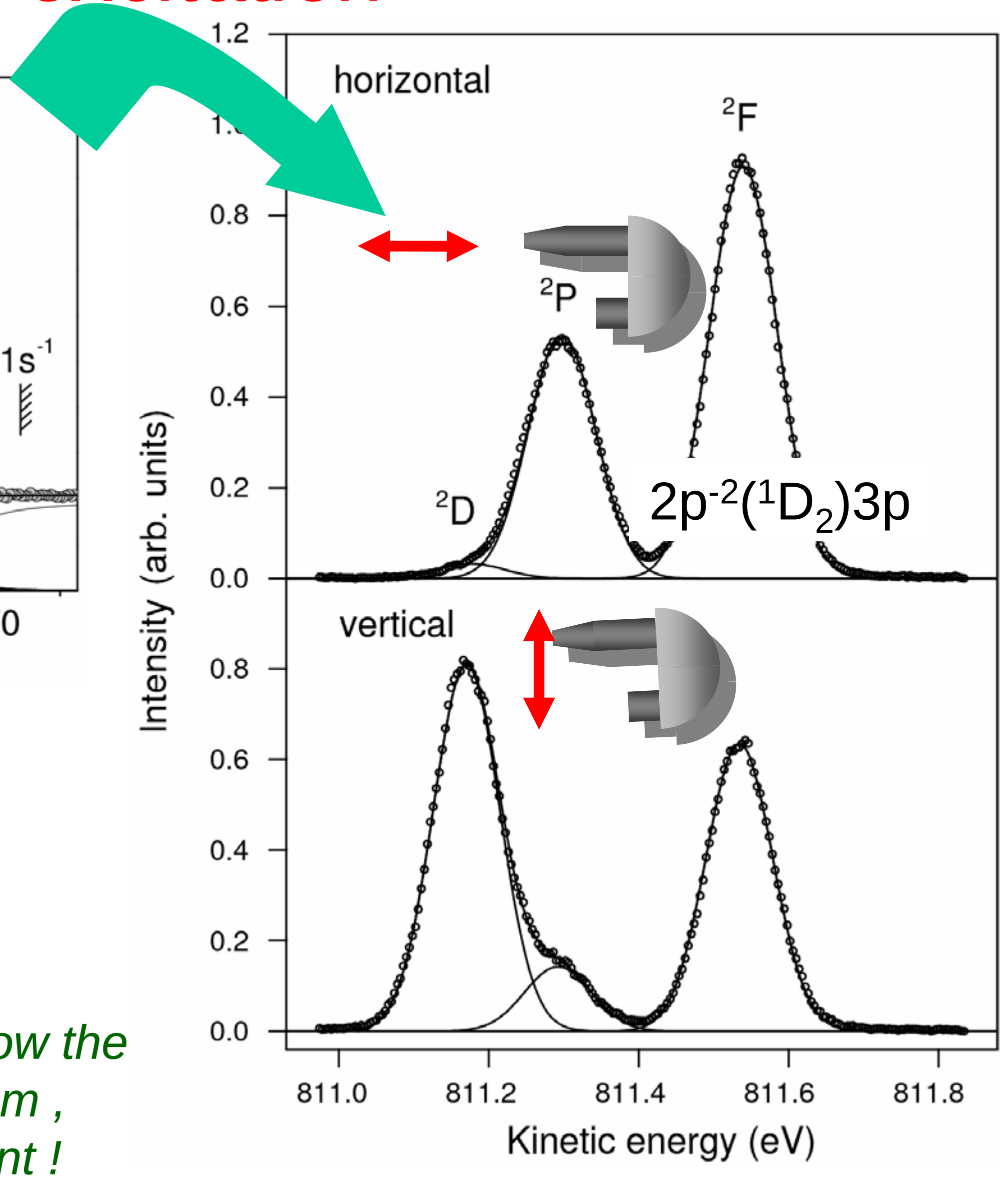


$$\frac{d\sigma}{d\theta} = \frac{\sigma}{4\pi}[1 + \beta P_2(\cos\theta)]$$

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

β: asymmetry parameter

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

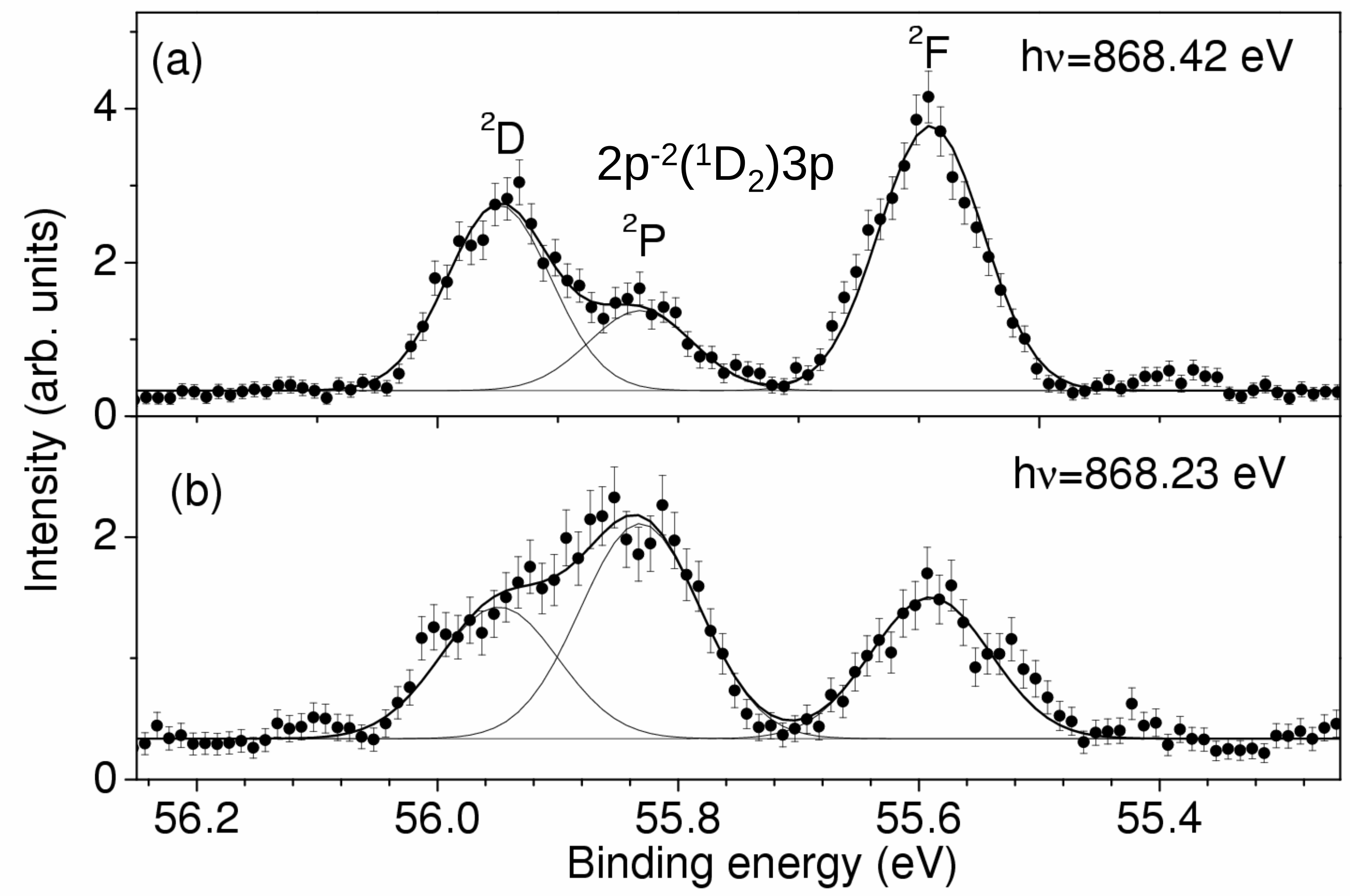


Shimizu *et al*. J. Phys. B **33**, L685 (2000).

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

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

$$\sigma \propto I(0) + 2 \times I(90)$$



Interference effects among difference paths

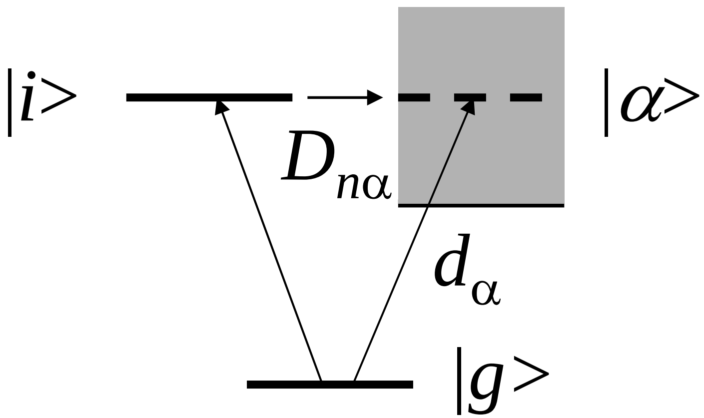
$$A_\alpha = d_\alpha + \sum_n \frac{D_{n\alpha}}{i + \varepsilon_n}$$

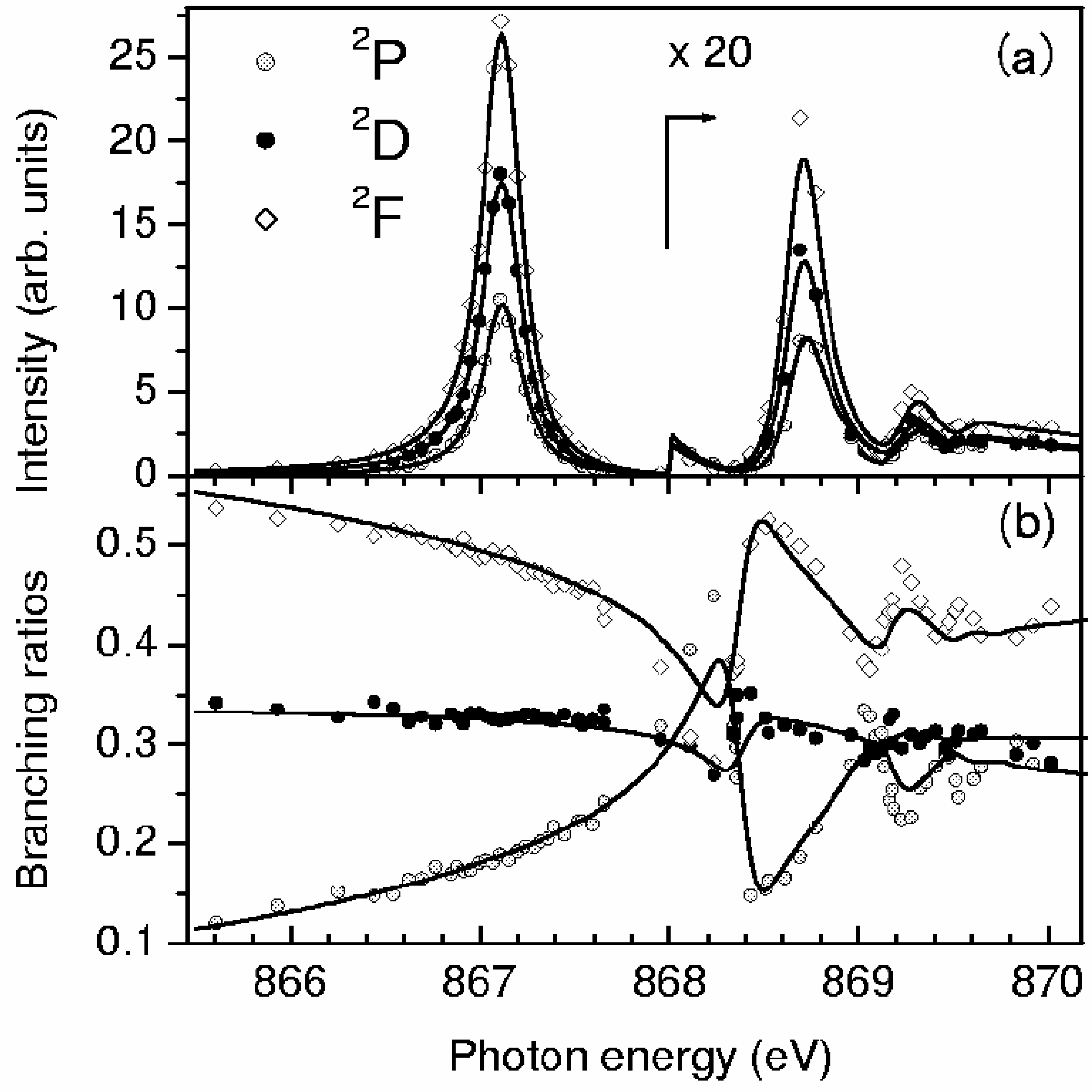
$$\sigma_\alpha = |A_\alpha|^2$$

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

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

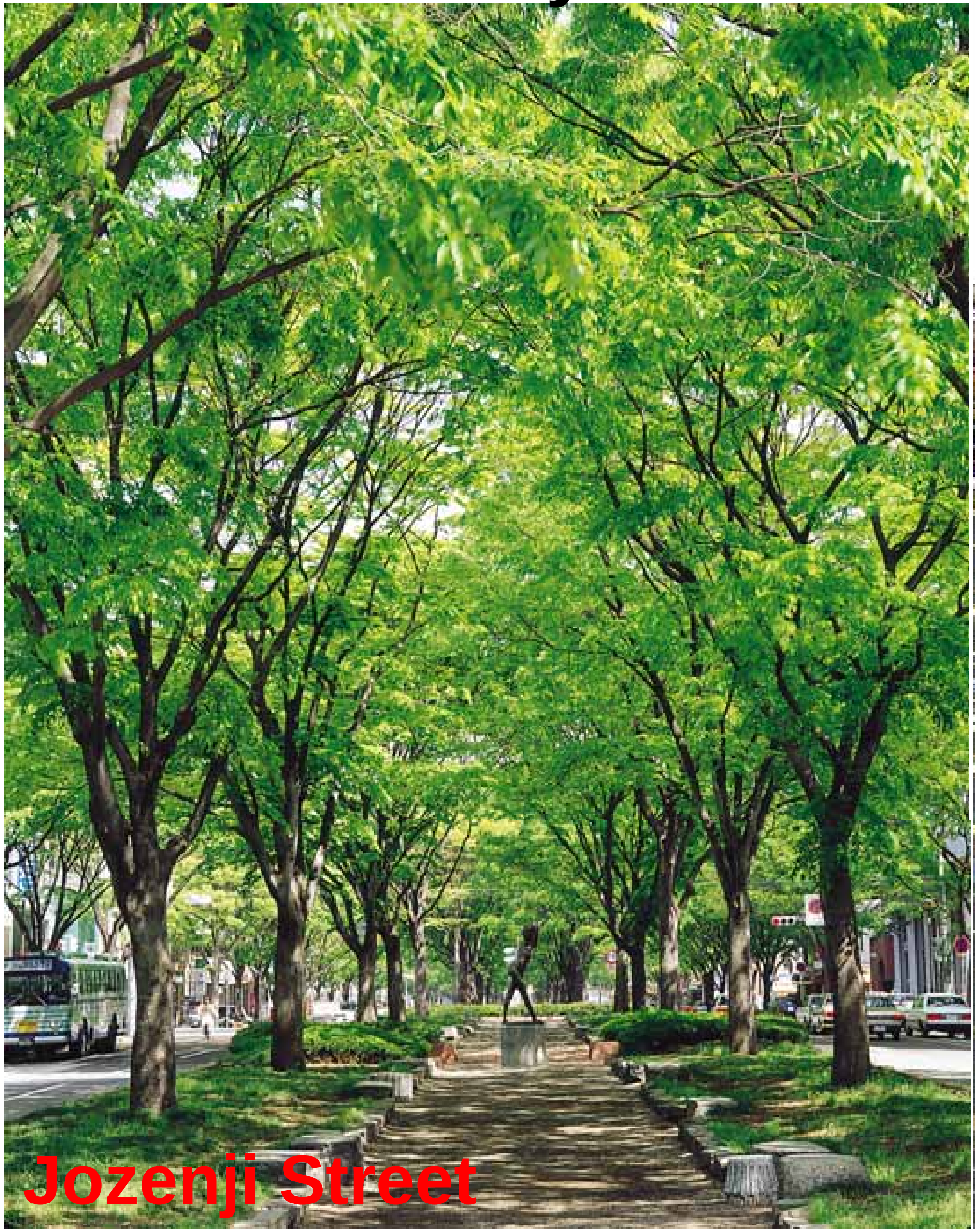
$$D_{n\alpha} = \langle g|r|i_n\rangle\langle i_n|\alpha\rangle$$





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

Sendai City



Introduction of molecular world

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

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

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

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

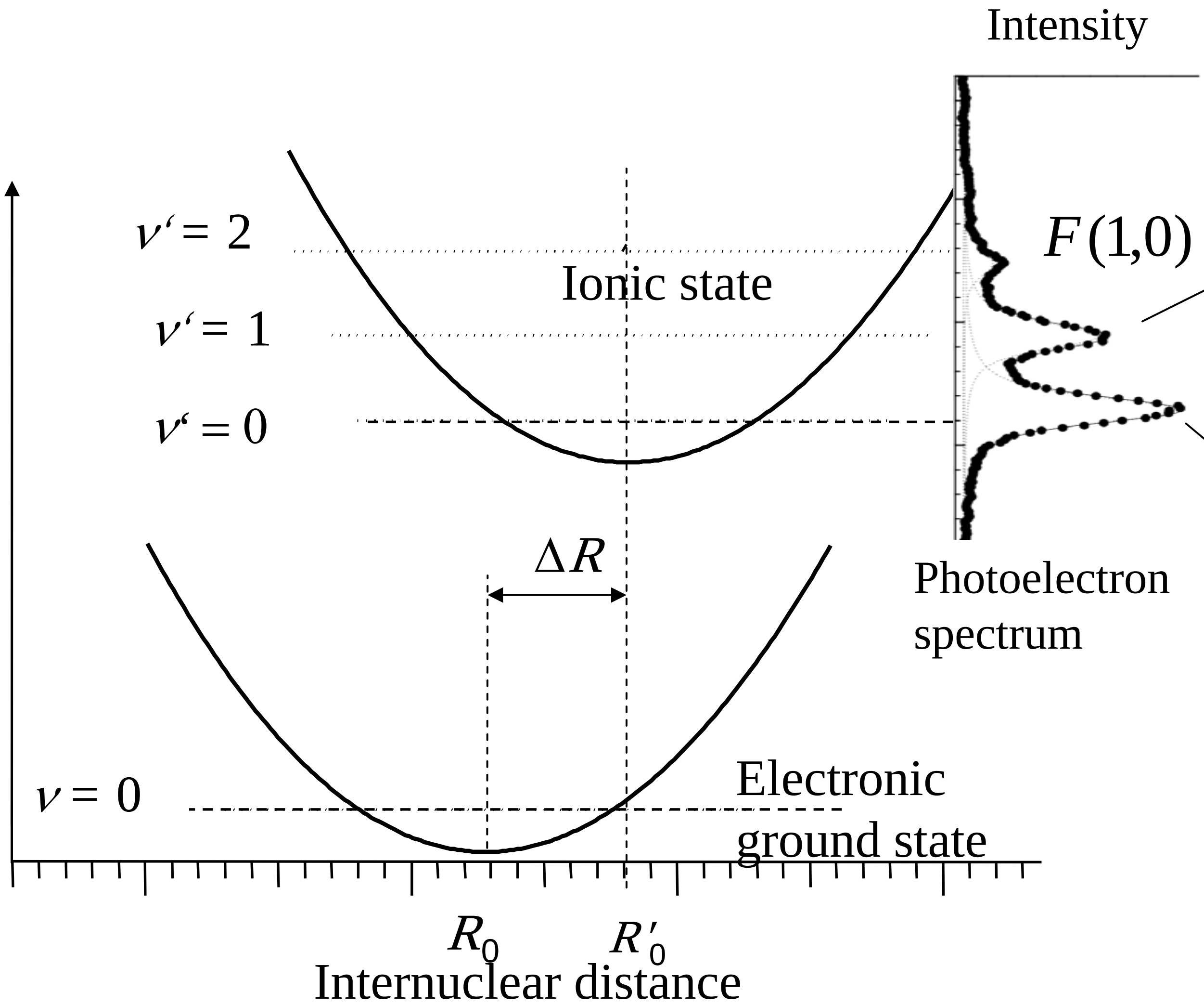
Assume that the dipole moment $D_E(R)$ does not depend on R

$$\sigma^{+}_{iv'}(E) \sim |D_E(R_{\mathrm{e}})|^2\, F(v'0)$$

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



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

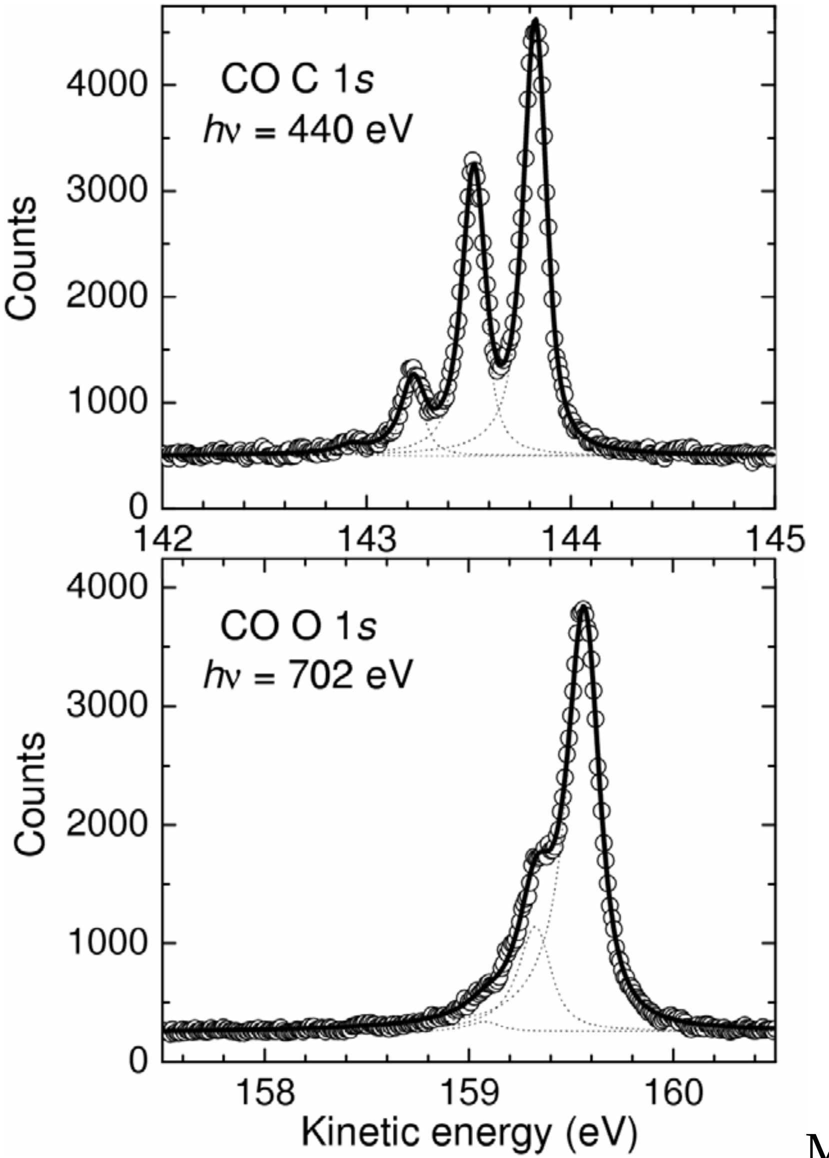
$$\alpha = \mu\omega/\hbar$$

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

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

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

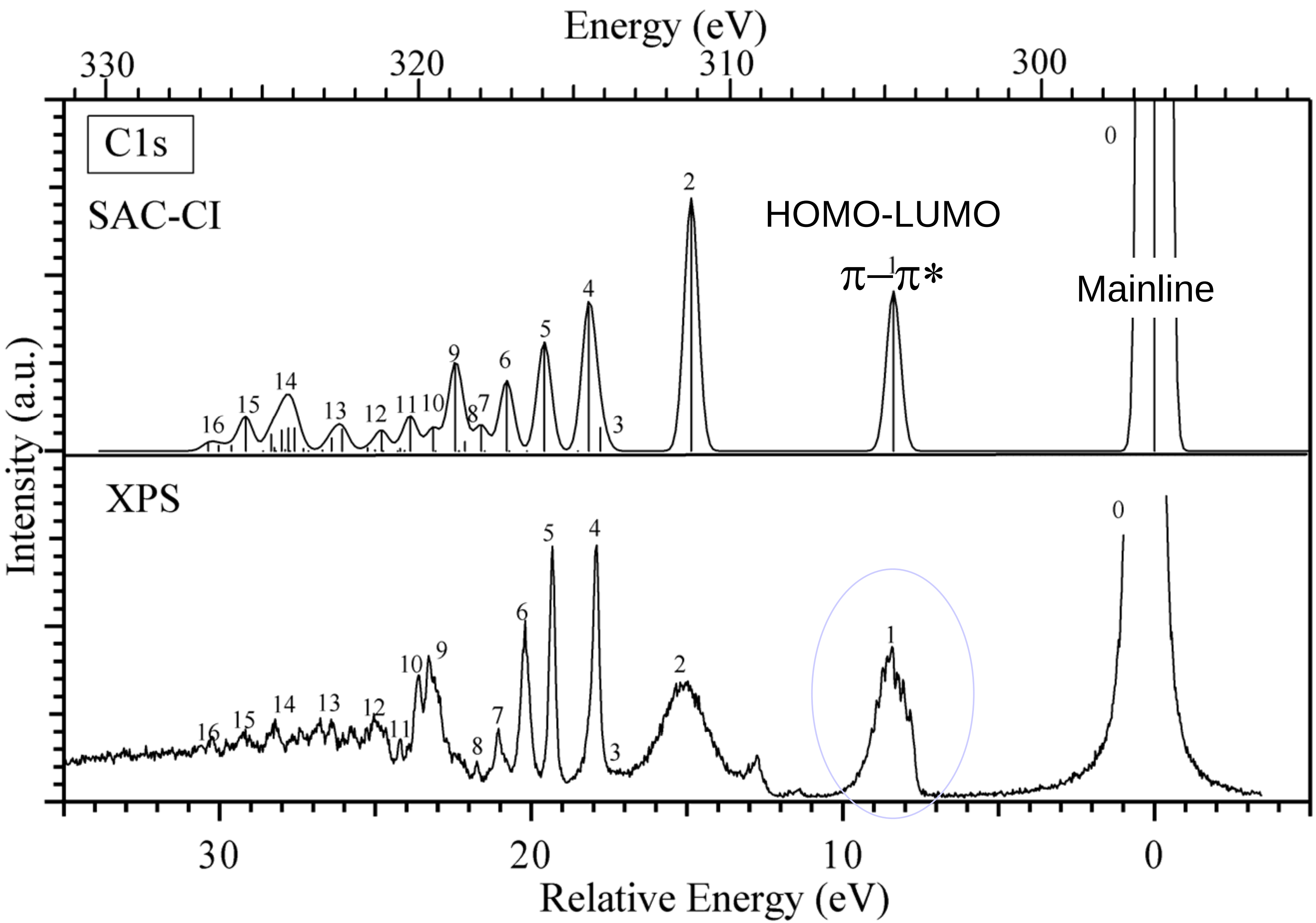
ψ^{+}_{v}: v-th vibrational wave function in the core-ionized state

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

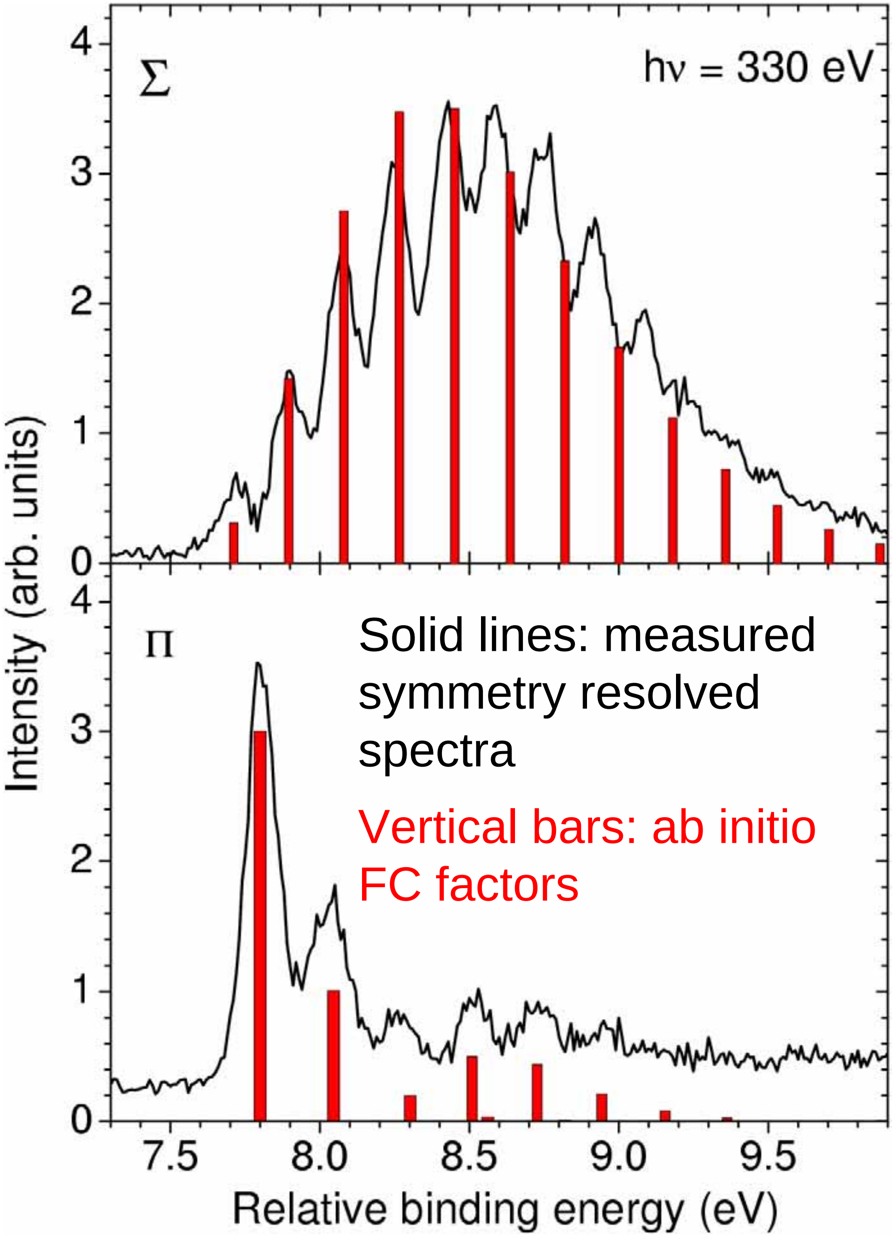
Matsumoto *et al*. Chem. Phys. Lett. **417**, 89-93 (2006).

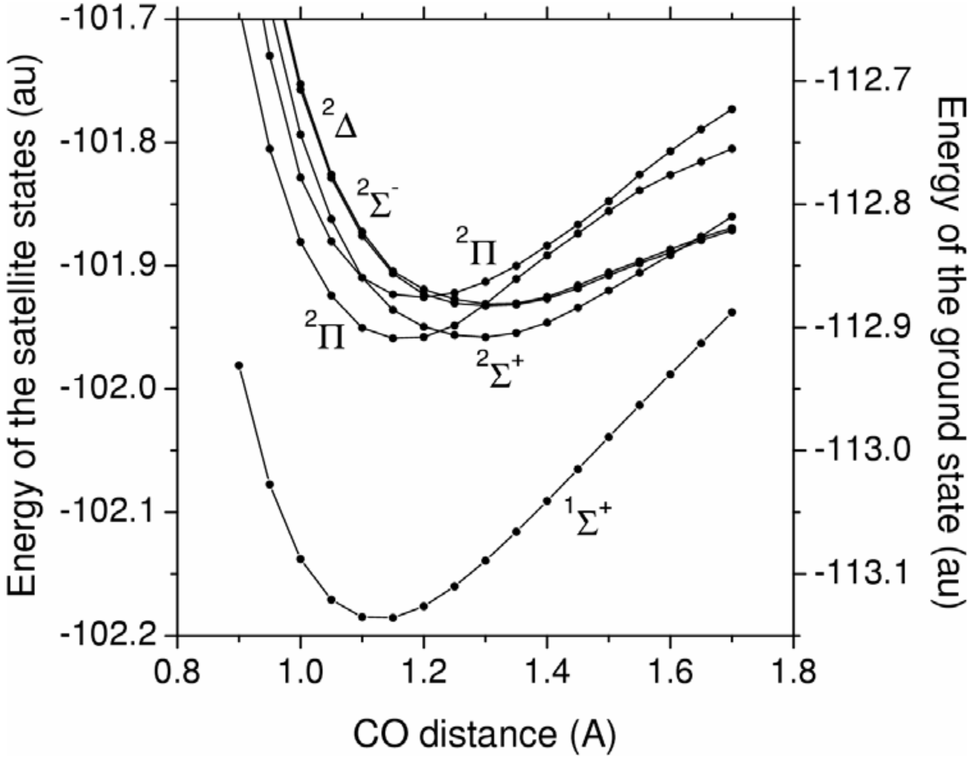
Satellite spectrum in core-level photoemission in CO



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



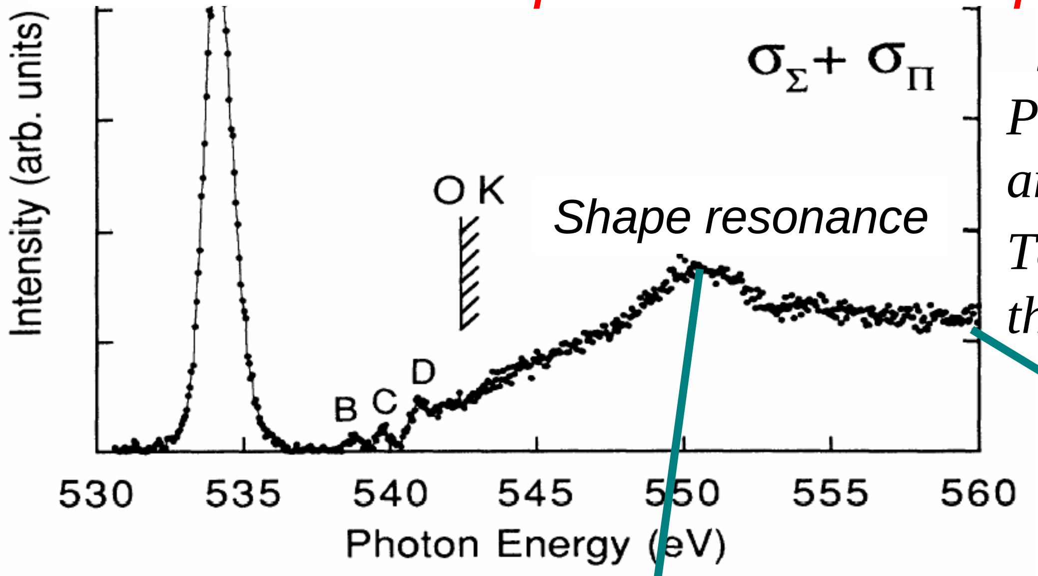


Ab initio potential curves

Ab initio FC factors reproduce the measured vibrational distributions.

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

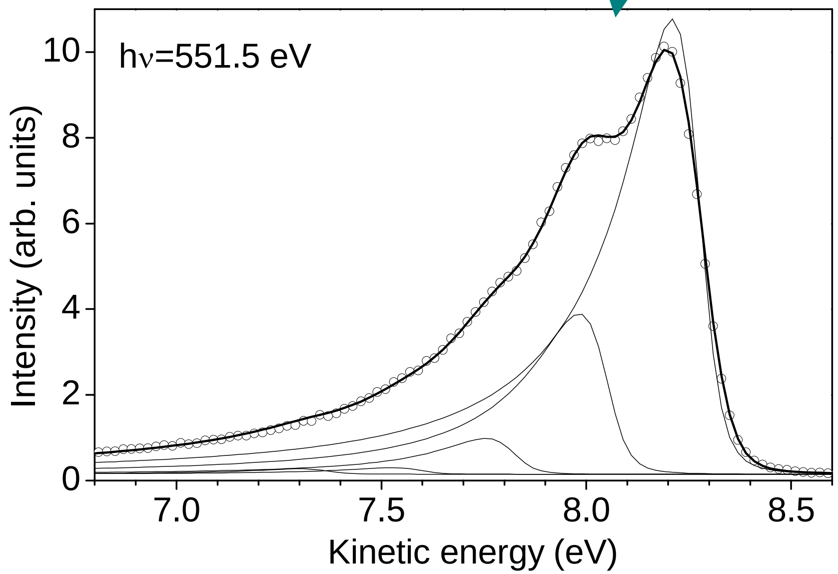
Vibrational effects on the shape resonance energy in the K-shell photoionization spectra of CO

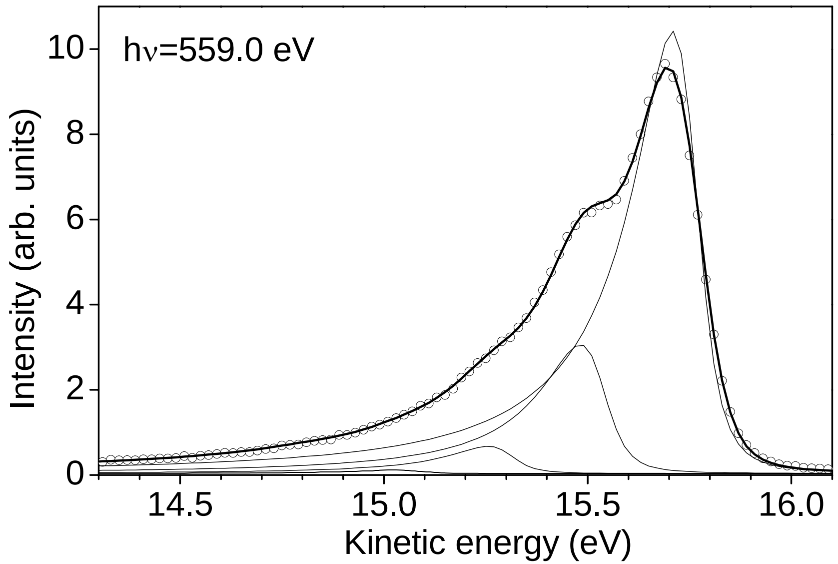


Shape resonance:

Promotion of a core electron to a σ antibonding orbital*

Temporal trapping of a photoelectron by the molecular potential

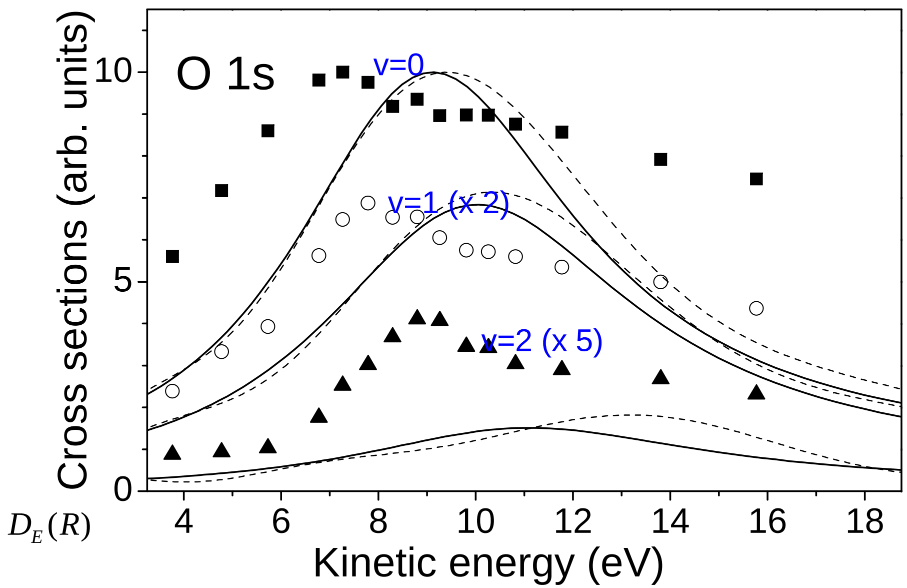




O 1s photoelectron spectra of CO at the shape resonance and far above it.

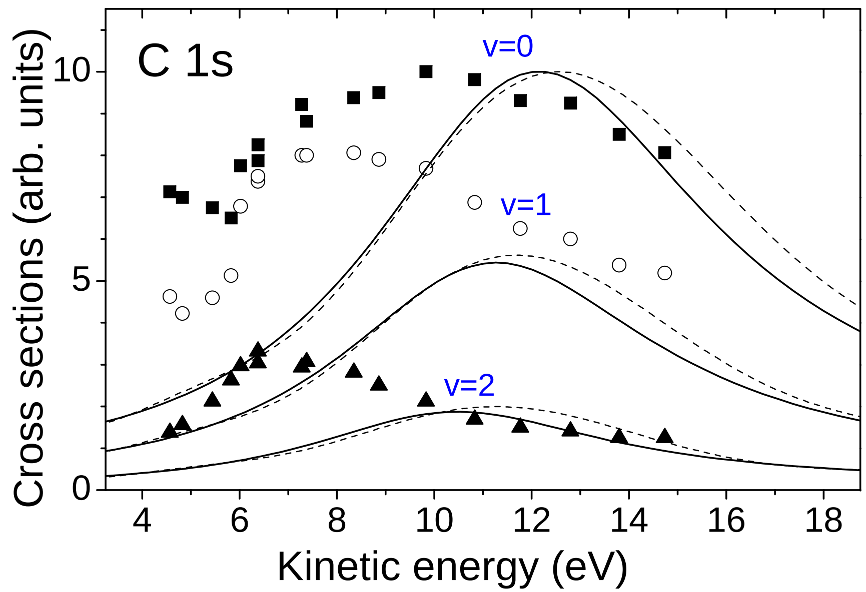
Non-Franck-Condon behavior of vibrational distributions!

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'.

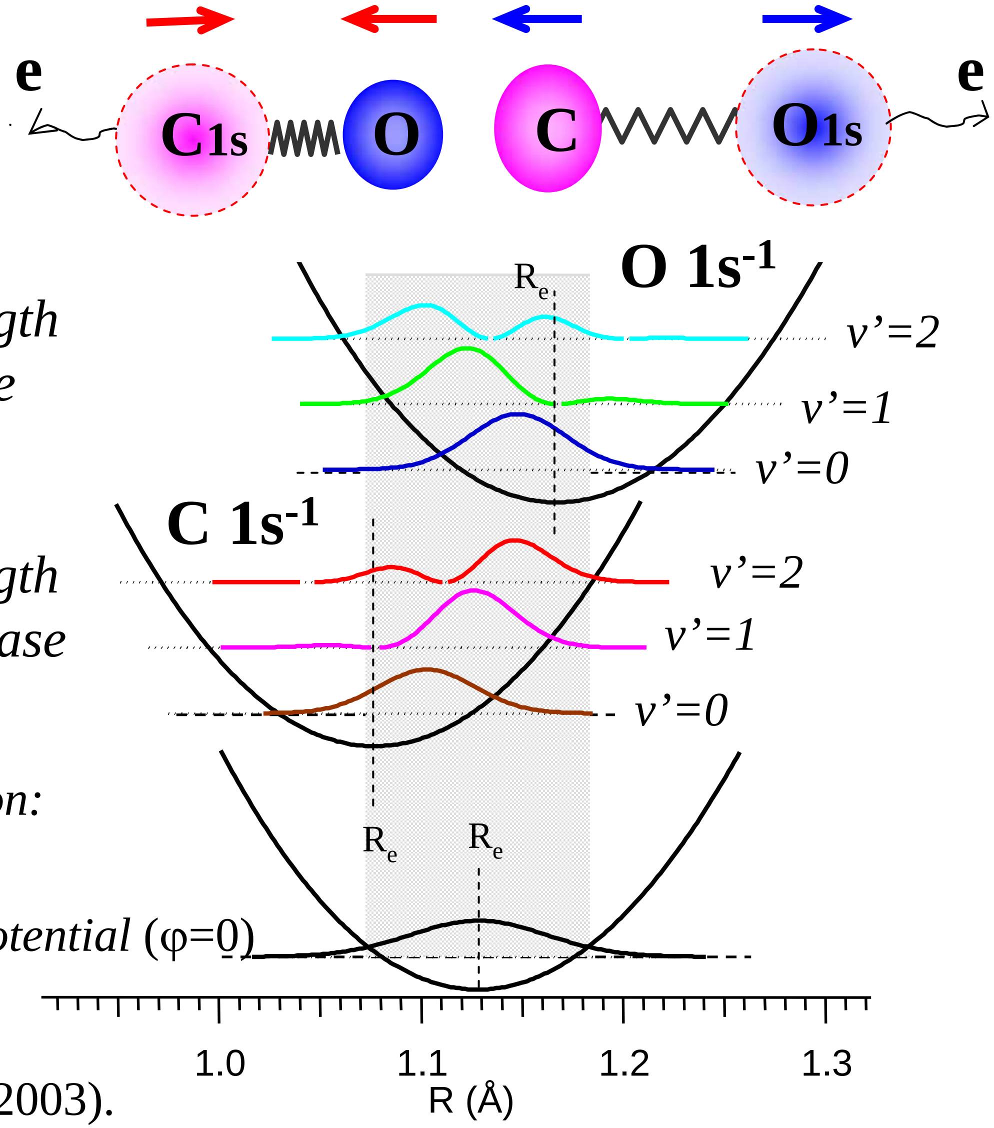
K. J. Randall *et al.*, Phys. Rev. Lett. **71**, 1156 (1993).

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

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.

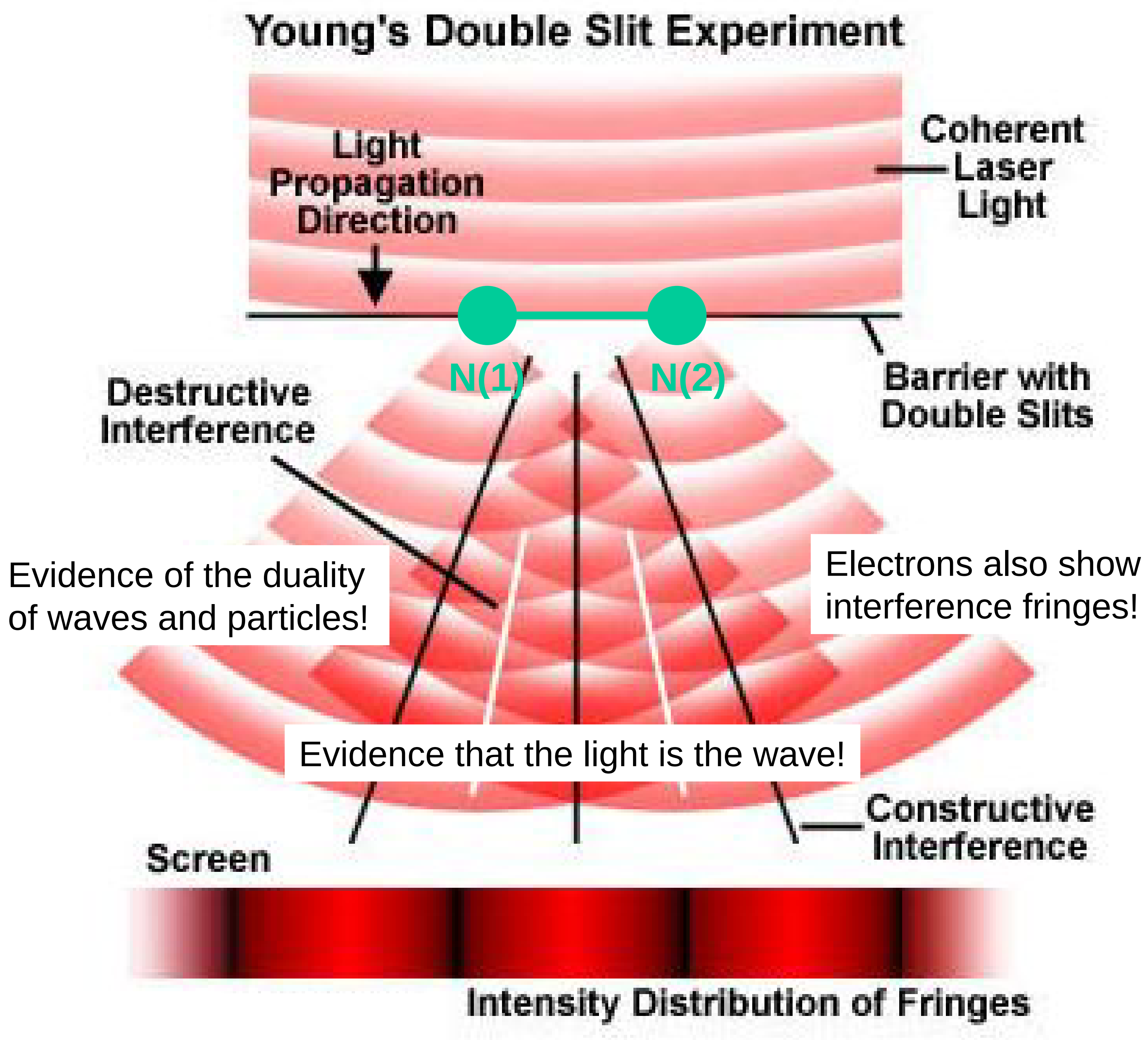
Characteristic bond length elongates with the increase in v' for C1s.

Shape resonance formation:

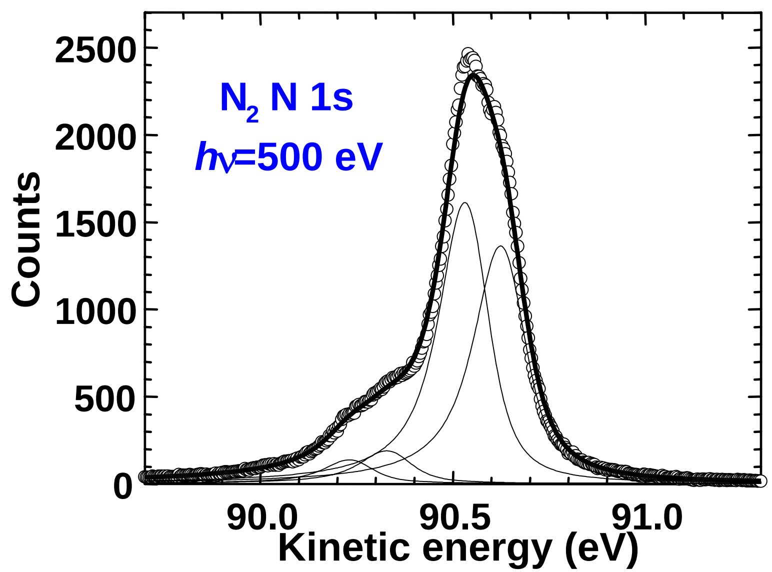
$$kR + \varphi = \pi$$

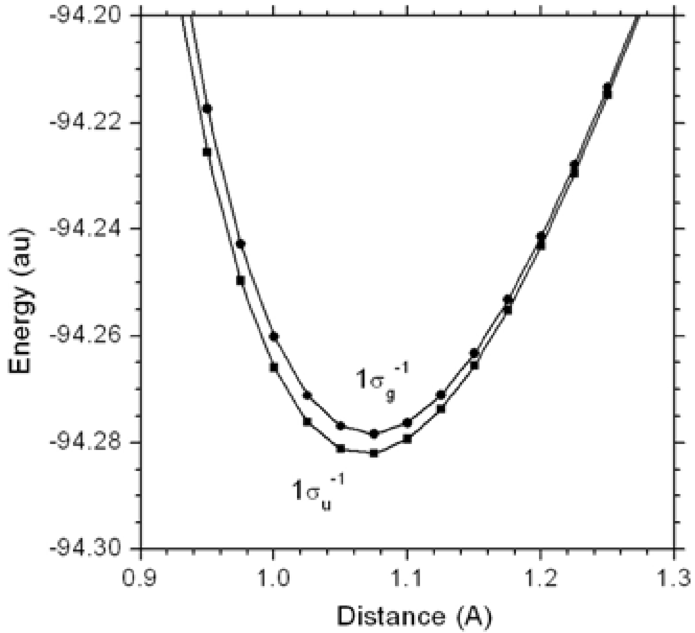
Cf. standing wave in the box potential (φ=0)

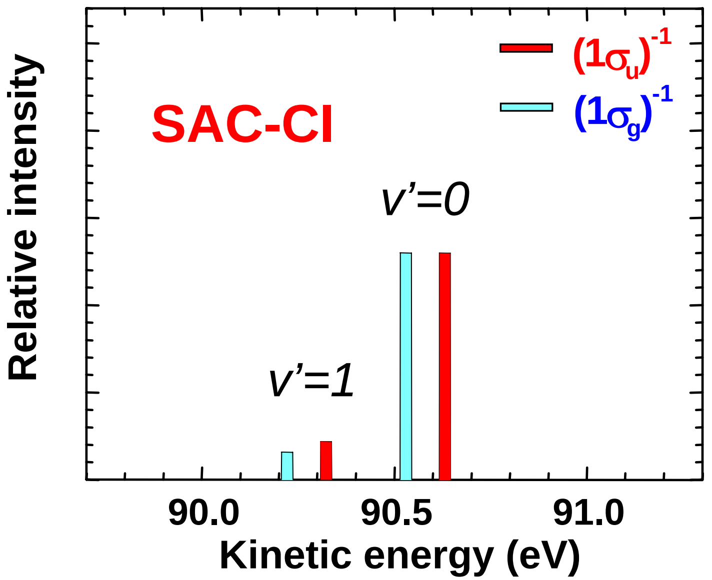
D. A. Mistrov *et al.*
Phys. Rev. A **68**, 022508 (2003).


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: $$1\sigma_{g,u} = \frac{1s_1 \pm 1s_2}{\sqrt{2}} .$$

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)

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

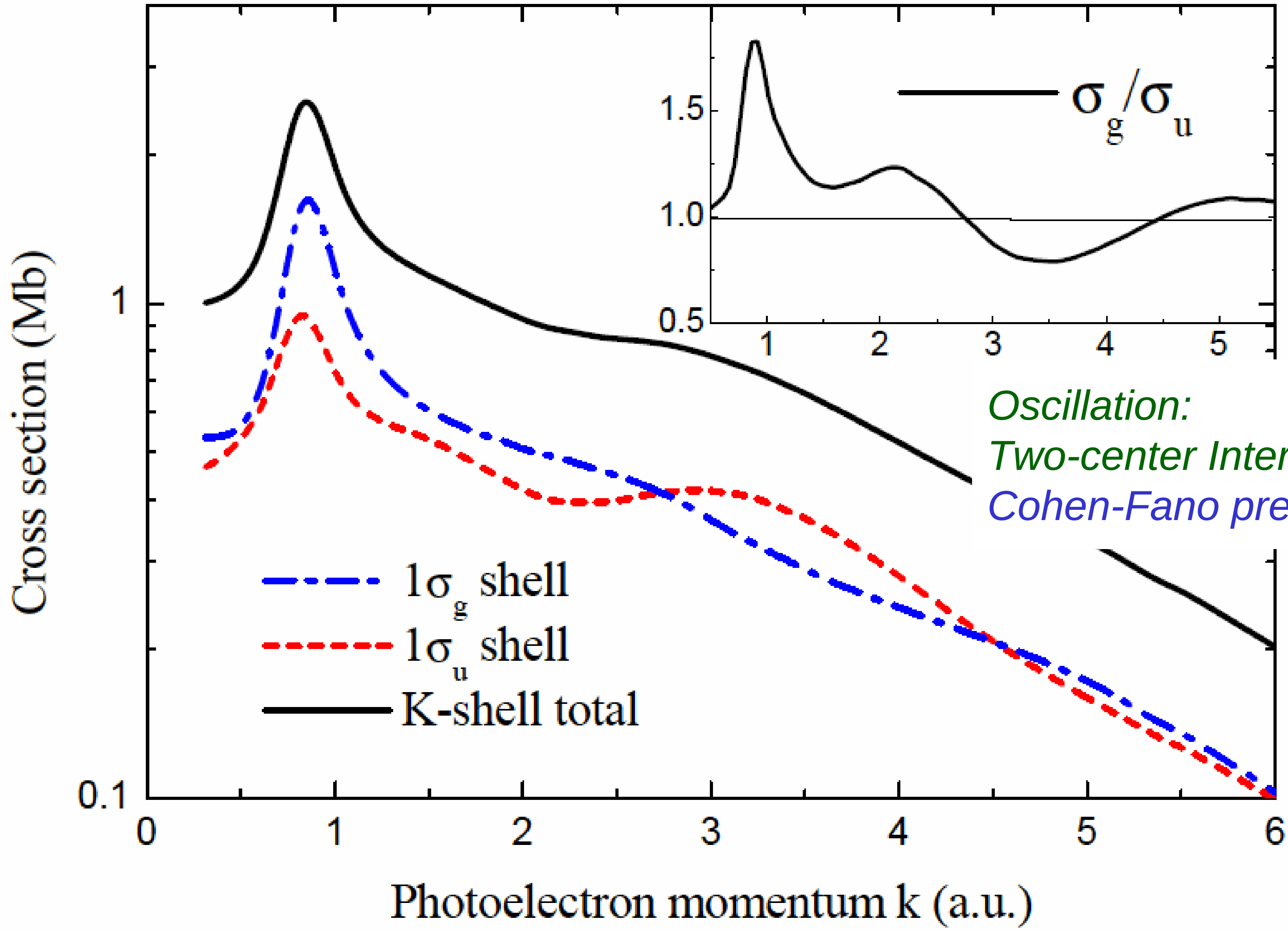
Orientational average: Cohen-Fano formula

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

Interference oscillatory structure becomes much smaller but remains!

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

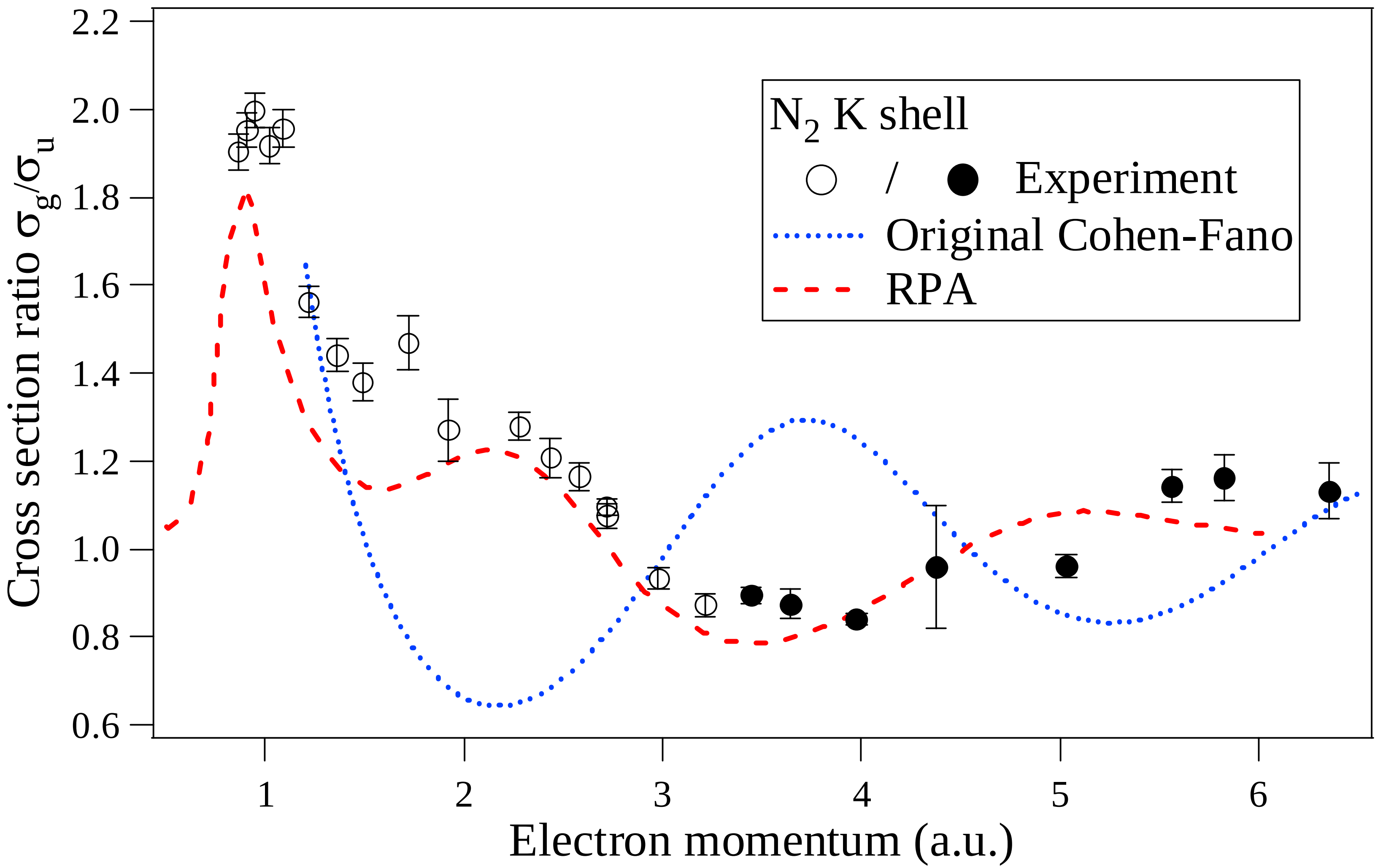
Ab initio N 1s $1\sigma_u$ and $1\sigma_g$ photoionization cross sections of N_2



Oscillation:
Two-center Interference
Cohen-Fano prediction !

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).

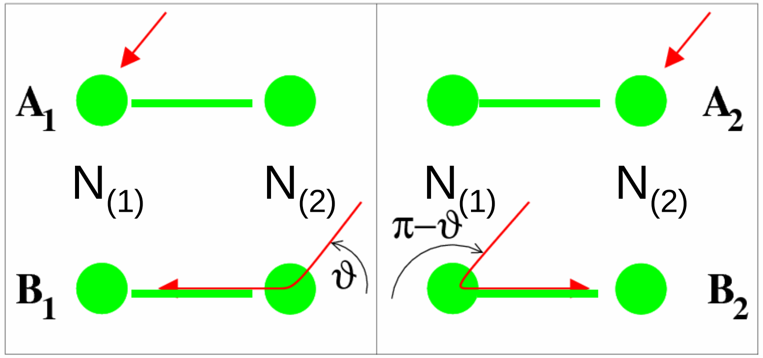
Photoelectron scattering by the neighboring N atom

The amplitude of the photoelectron wave from one center:

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

$$\psi_2 = A_2 + B_2$$

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



Cohen-Fano interference

A_1A_2 interference term

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

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

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

0

A_1B_1 and A_2B_2 one-center interference terms

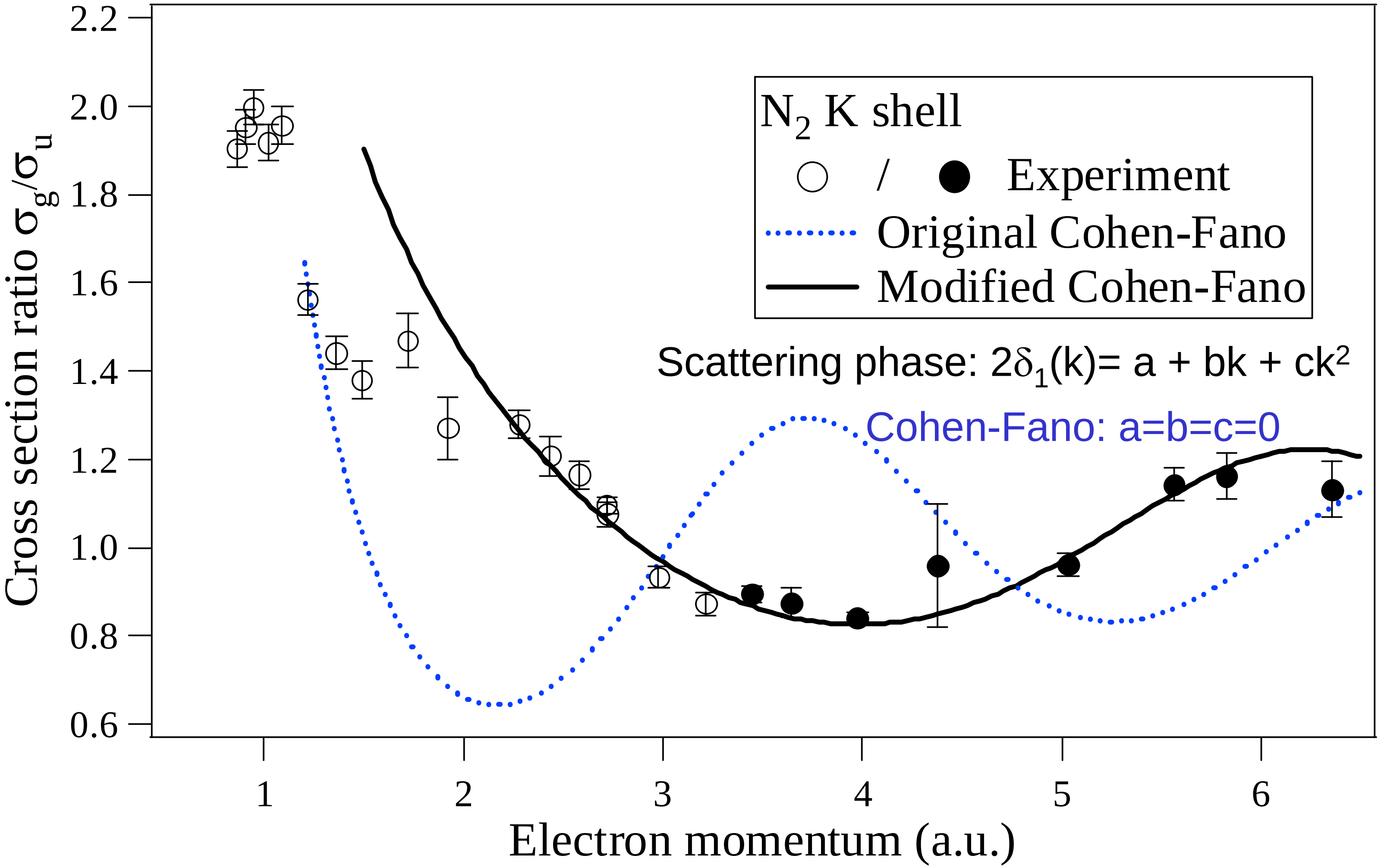
$$\chi(k) = \frac{1}{kR} \sin\left[kR + 2\delta_1(k)\right]$$

$\delta_1(k)$: 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



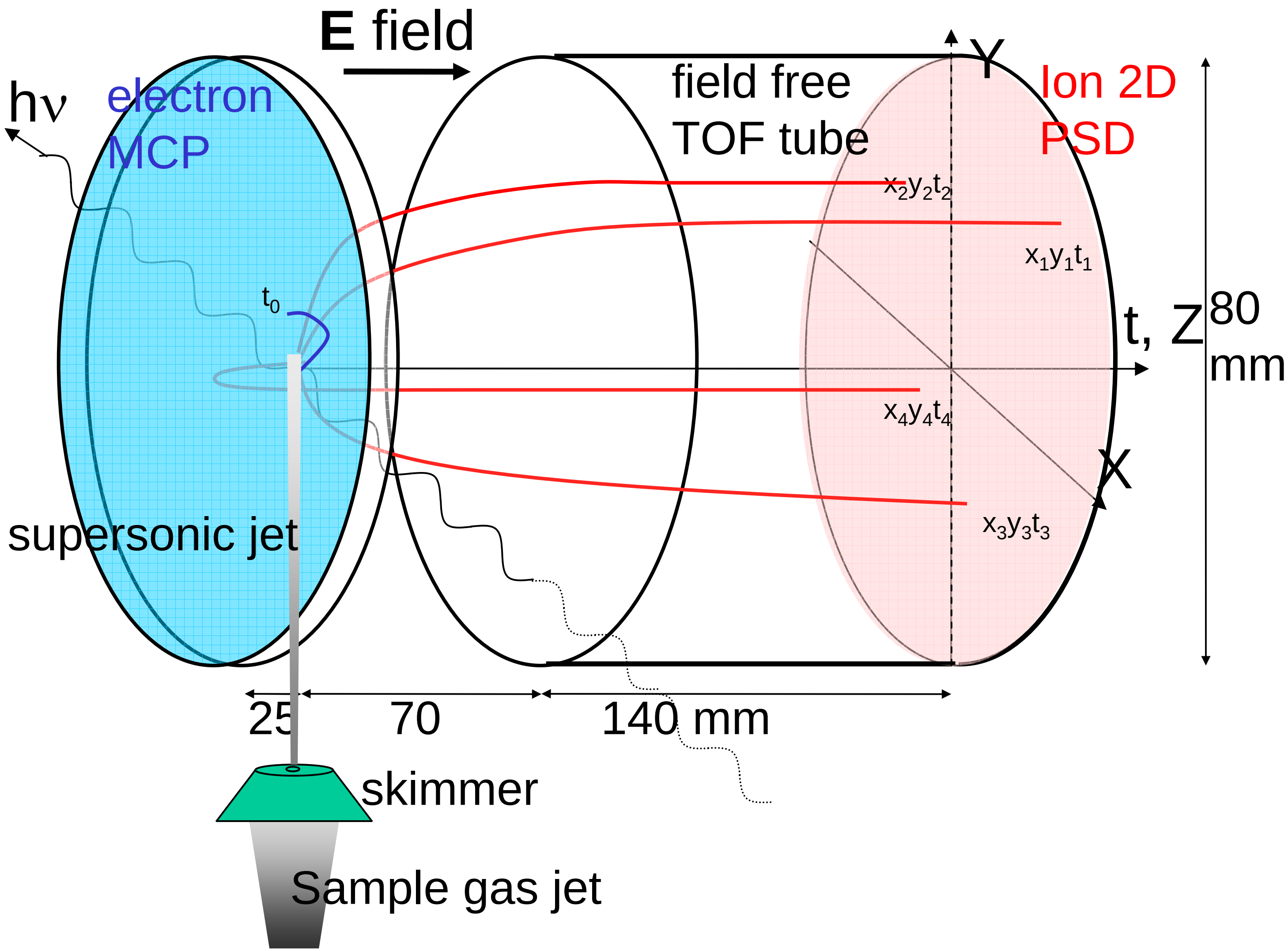
Fitted results: a = −5.2±0.6, b = −1.6±0.4, c = 0.09 ± 0.05 a.u.

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

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

Intermission

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

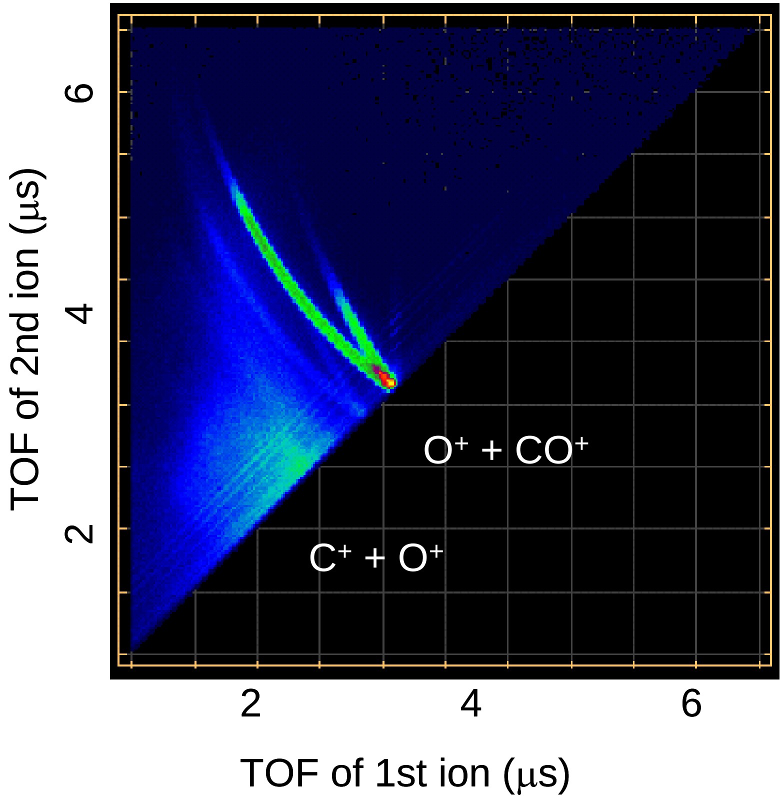
x, *y*: arrival position on the detector.

x_0, y_0 : initial position of the ion

m : ion mass

q: ion charge

E: electric field in the acceleration region



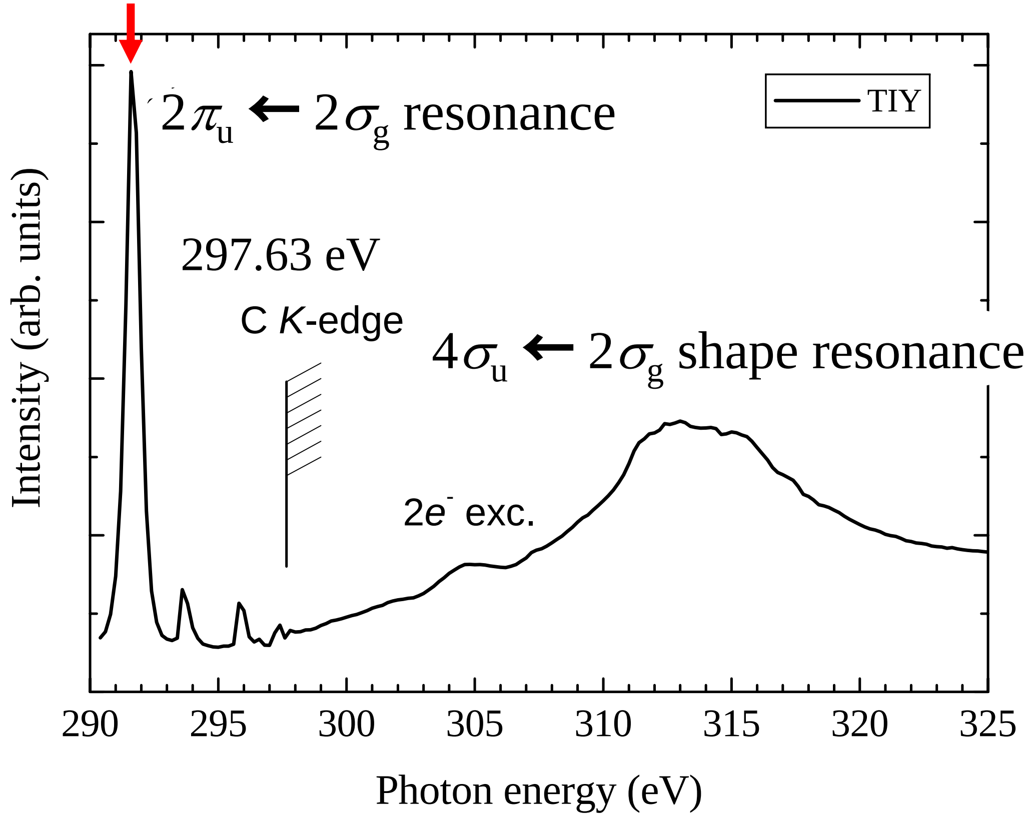
To be exact Pz becomes nonlinear → Iterative procedure

Total ion yield spectrum of CO_2 in the C1s ionization region

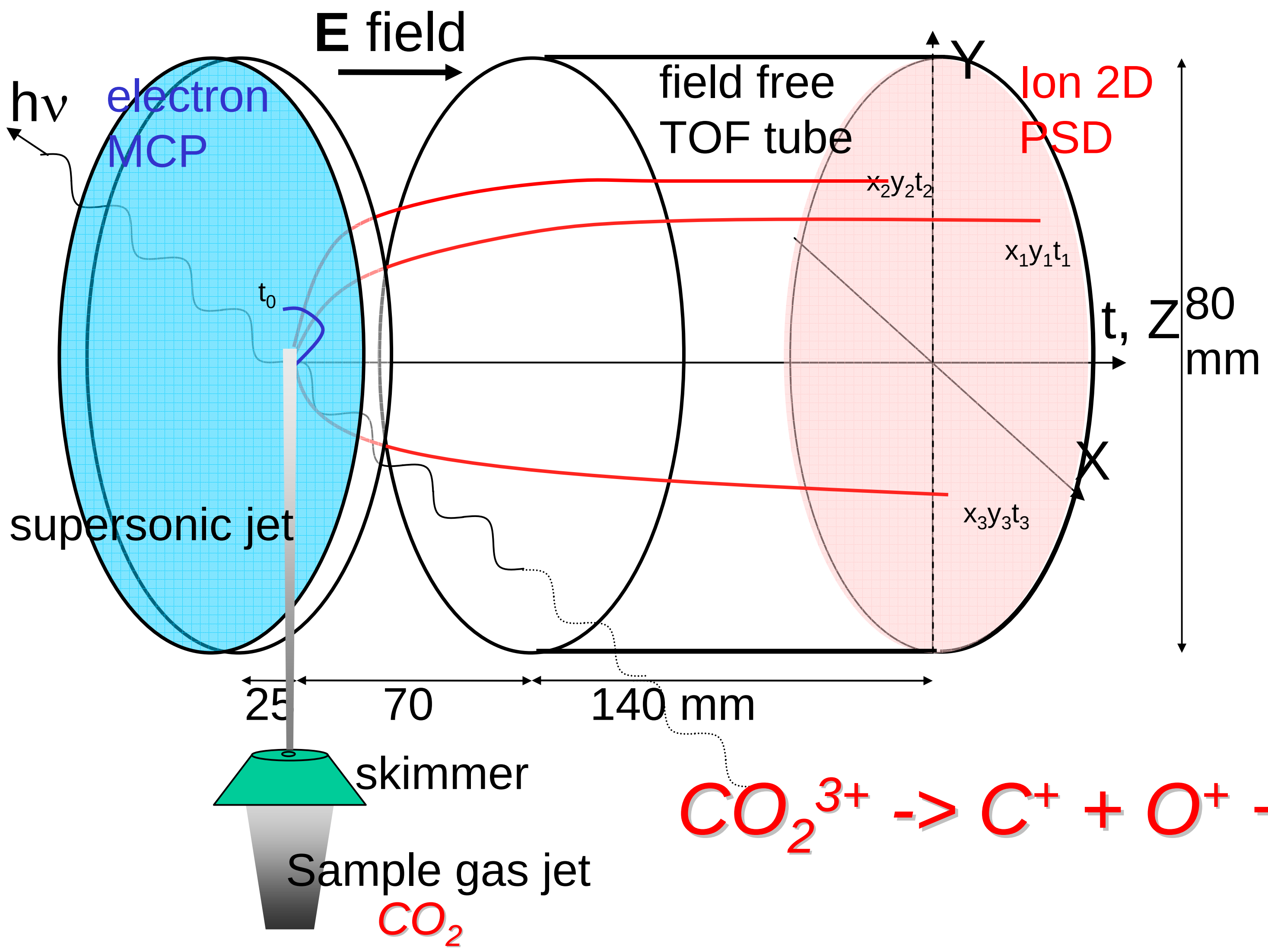
CO_2 ground state configuration:

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

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



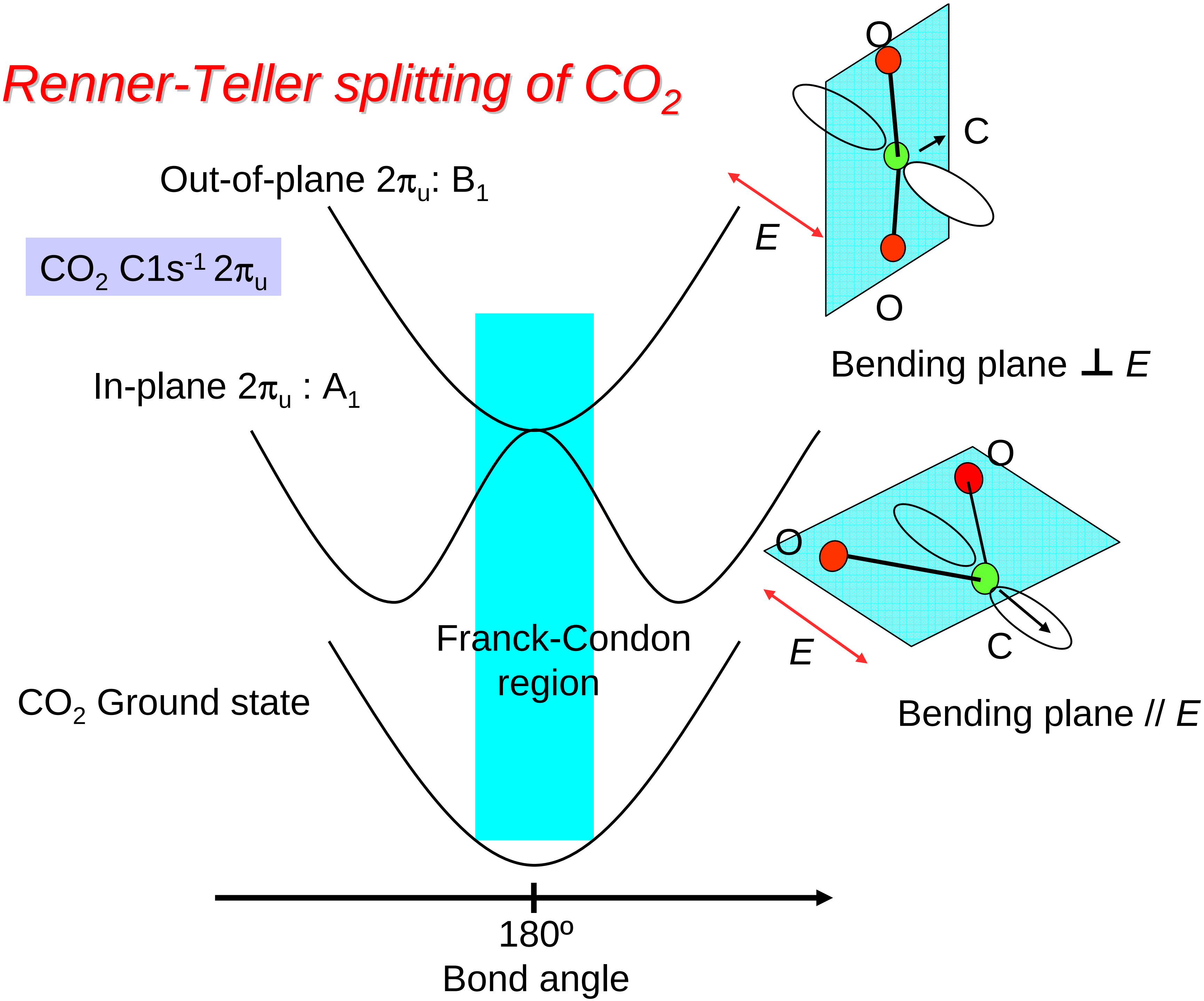
SR experiments with multiple-ion coincidence



CO_2^{3+} -> $C^+ + O^+ + O^+$

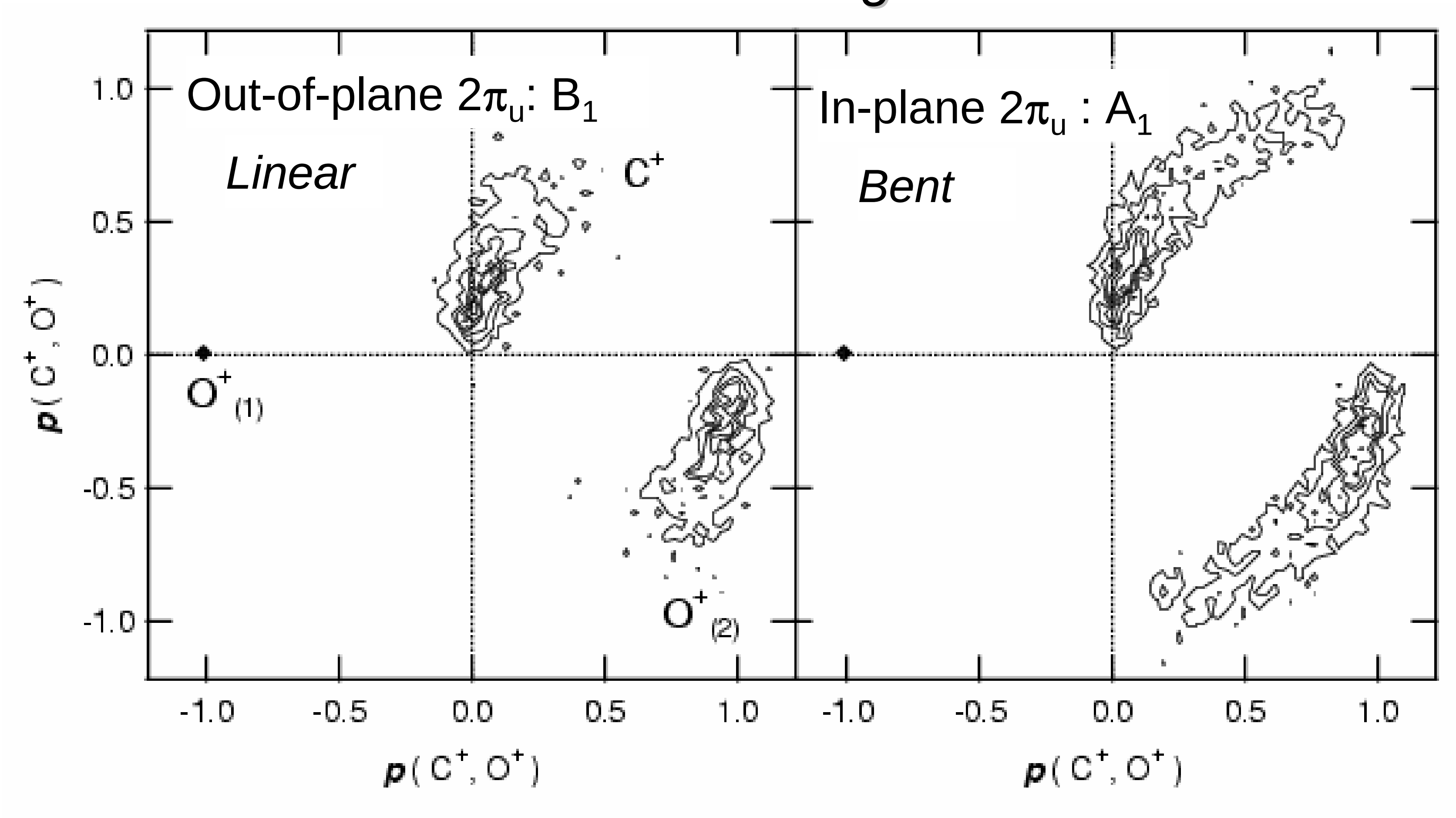
position & time of flight (x,y,t) → *3D momentum of each ion*

Renner-Teller splitting of CO_2



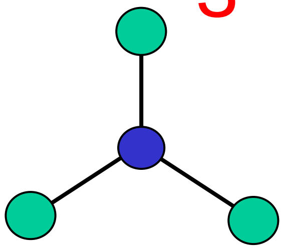
Snapshot of the bending motion in the core-exited state with a liftetime ~7 fs

Newton Diagram



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

BF_3



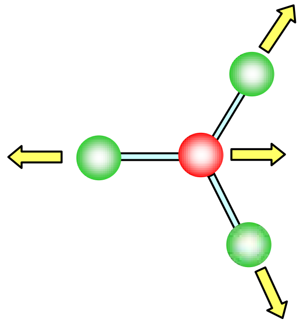
D_{3h} planar

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

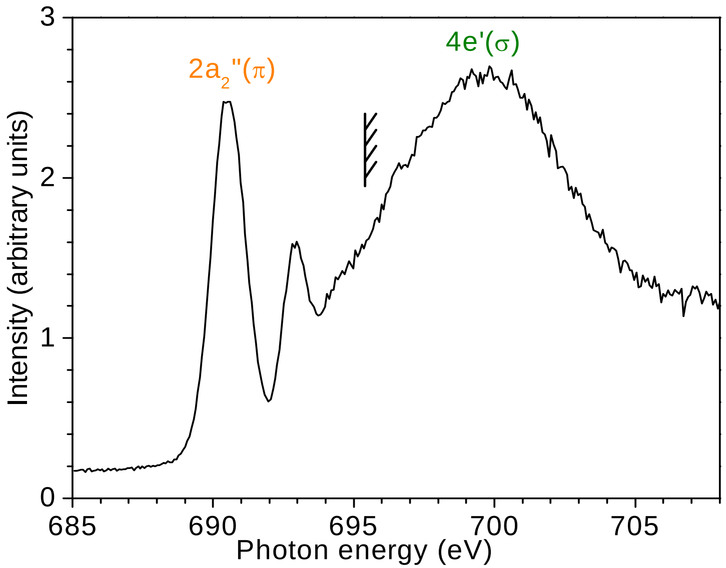
F, B 1s

Asymmetric stretching?

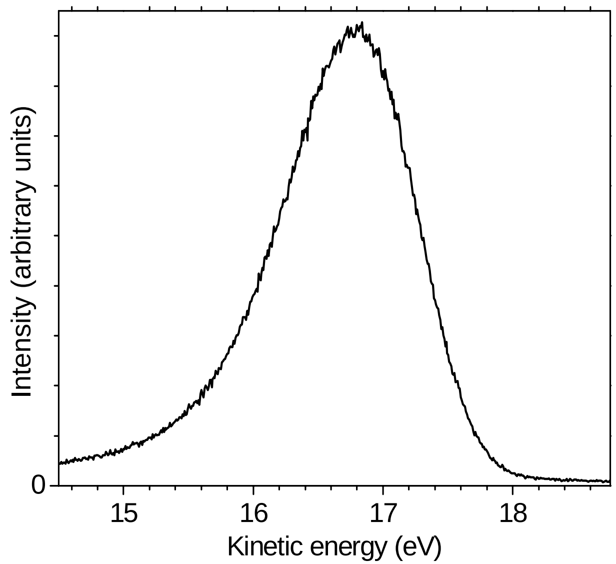


F 1s excitation/ionization

Symmetry breaking (due to vibronic coupling)

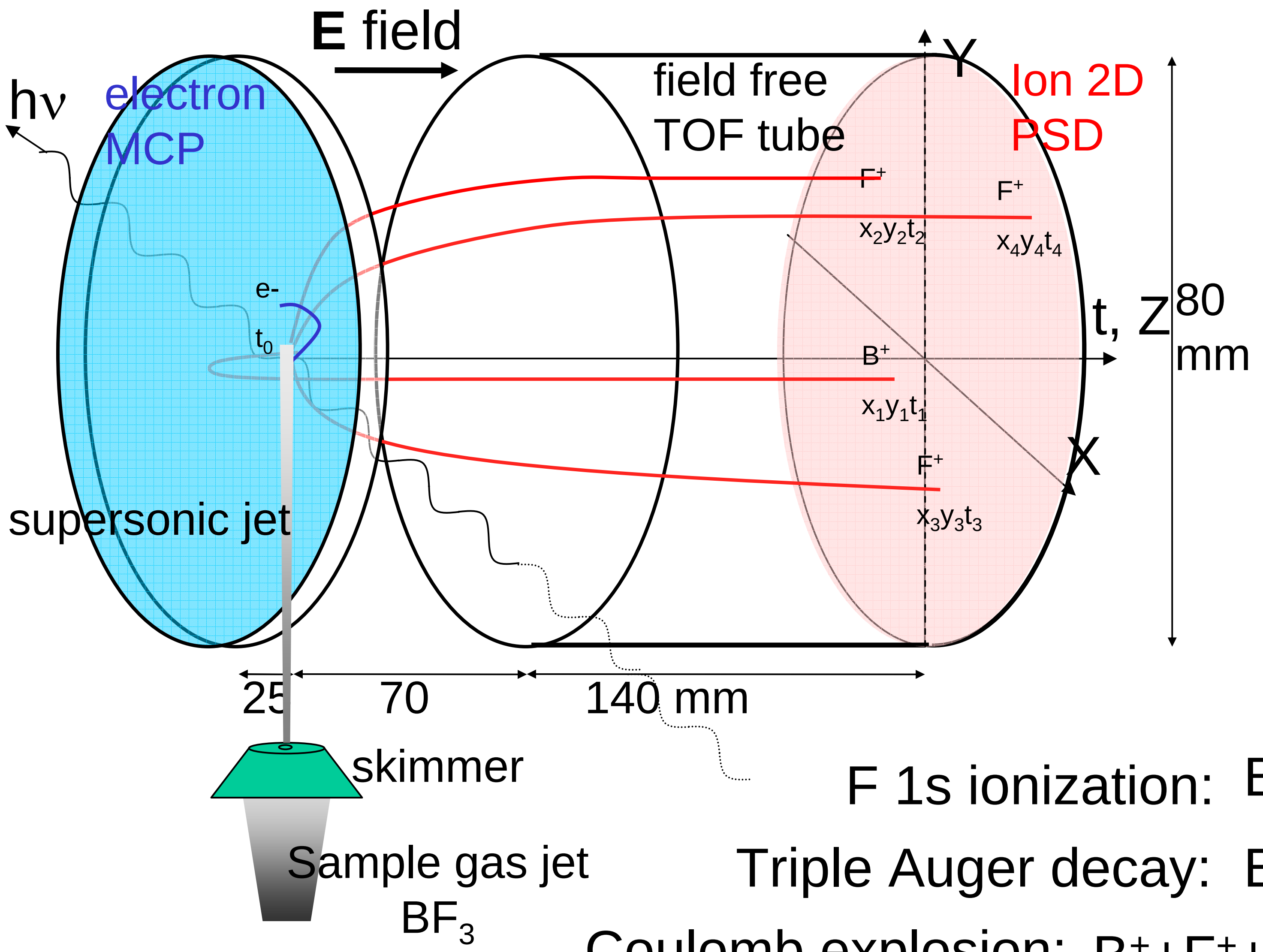


F1s excitation spectrum



F1s photoelectron spectrum

Multiple ion coincidence momentum imaging



F 1s ionization: BF_3^{+}

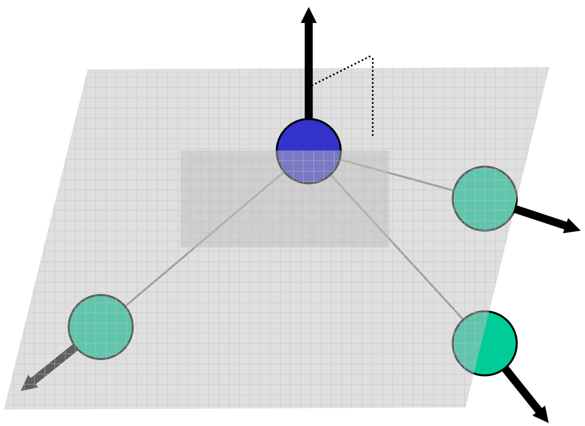
Triple Auger decay: BF_3^{4+}

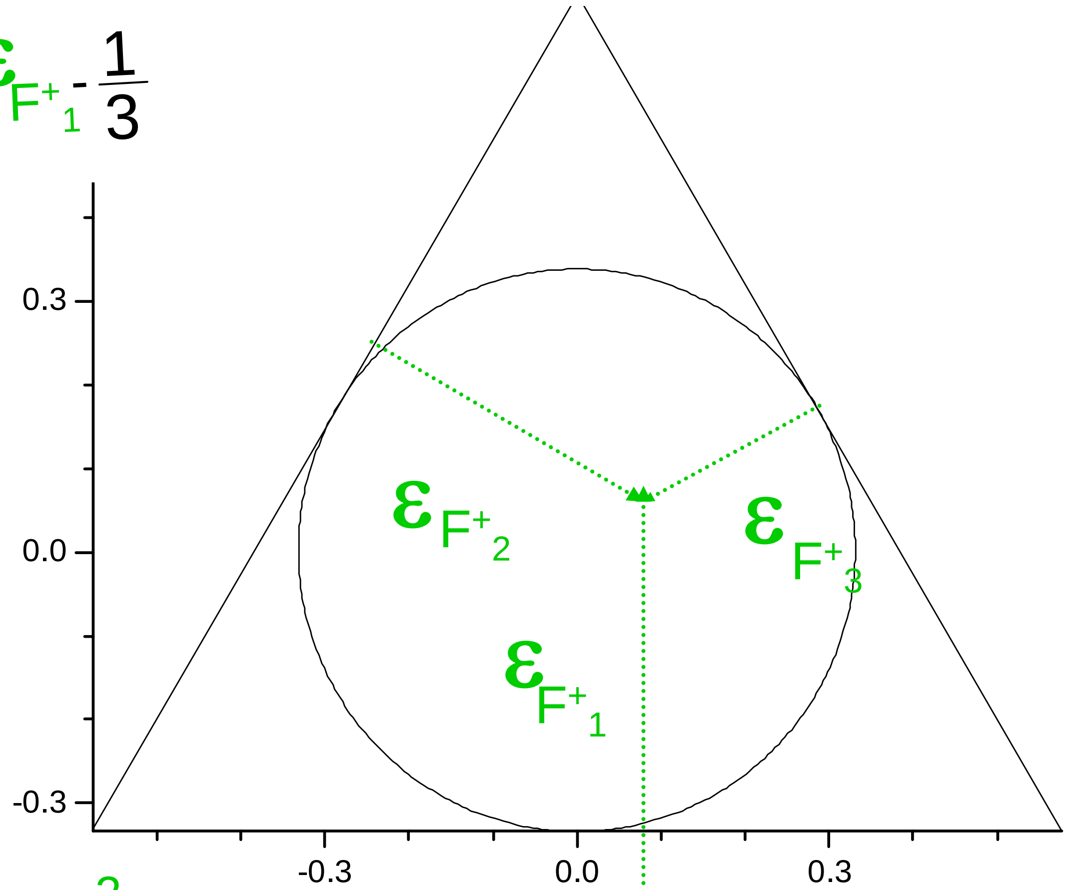
Coulomb explosion: $B^{+} + F^{+} + F^{+} + F^{+}$

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^+





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

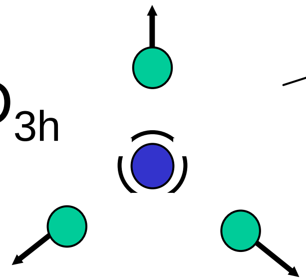
$$X_D = \frac{\varepsilon_{F^+_3} - \varepsilon_{F^+_2}}{3^{1/2}}$$

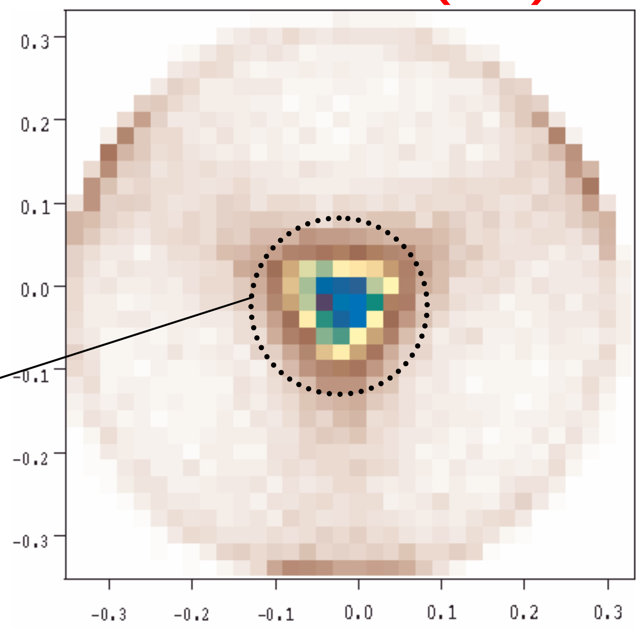
Motion of F^+ F^+ F^+ in the plane perpendicular to **P**(B^+)

B1s ionization

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

D_{3h}

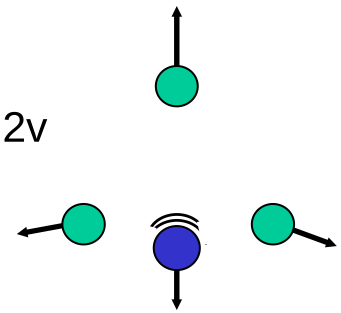


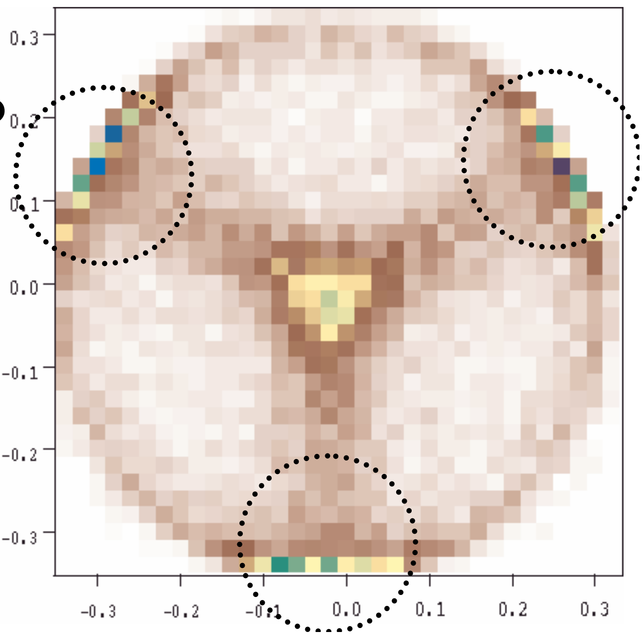


F1s ionization

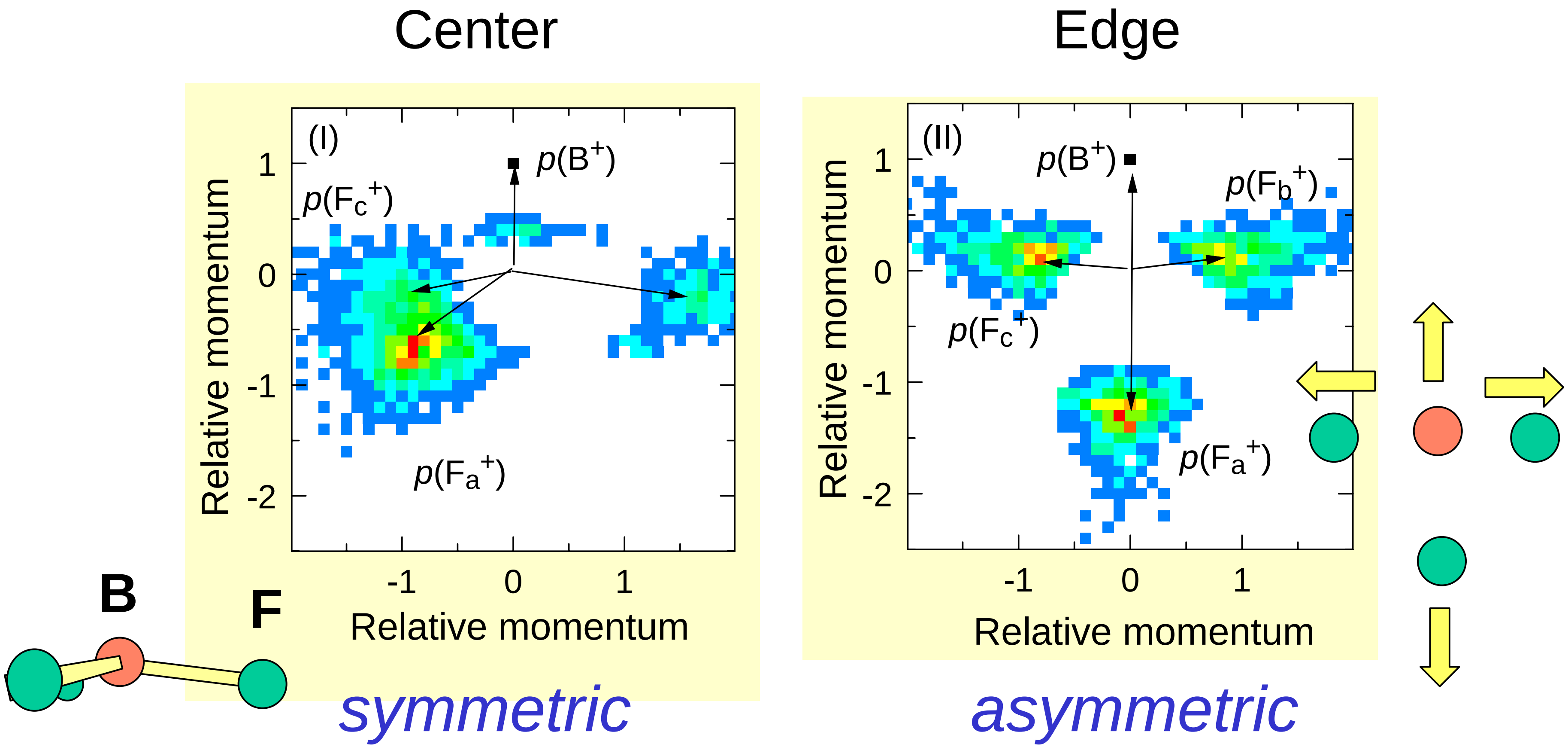
asymmetric sharing of momenta $\mathbf{P}^{\perp}$ ⇒ asymmetric stretching ?

C_{2v}



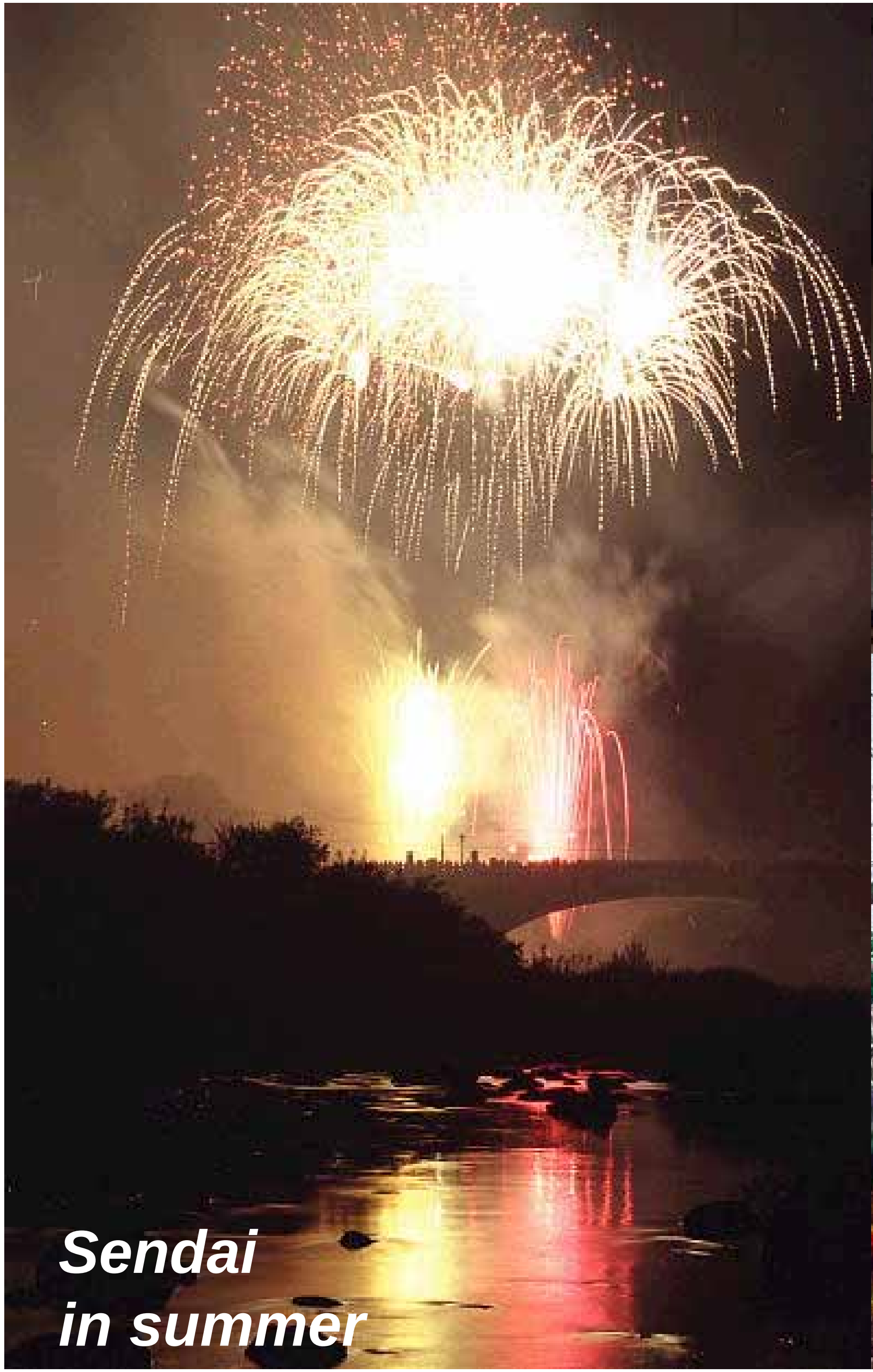


Newton diagrams for symmetric and asymmetric nuclear motion probed by quadruple ion momentum imaging



Asymmetric nuclear motion as result of symmetry breaking by F 1s ionization can be detected only via *quadruple ion momentum imaging.*

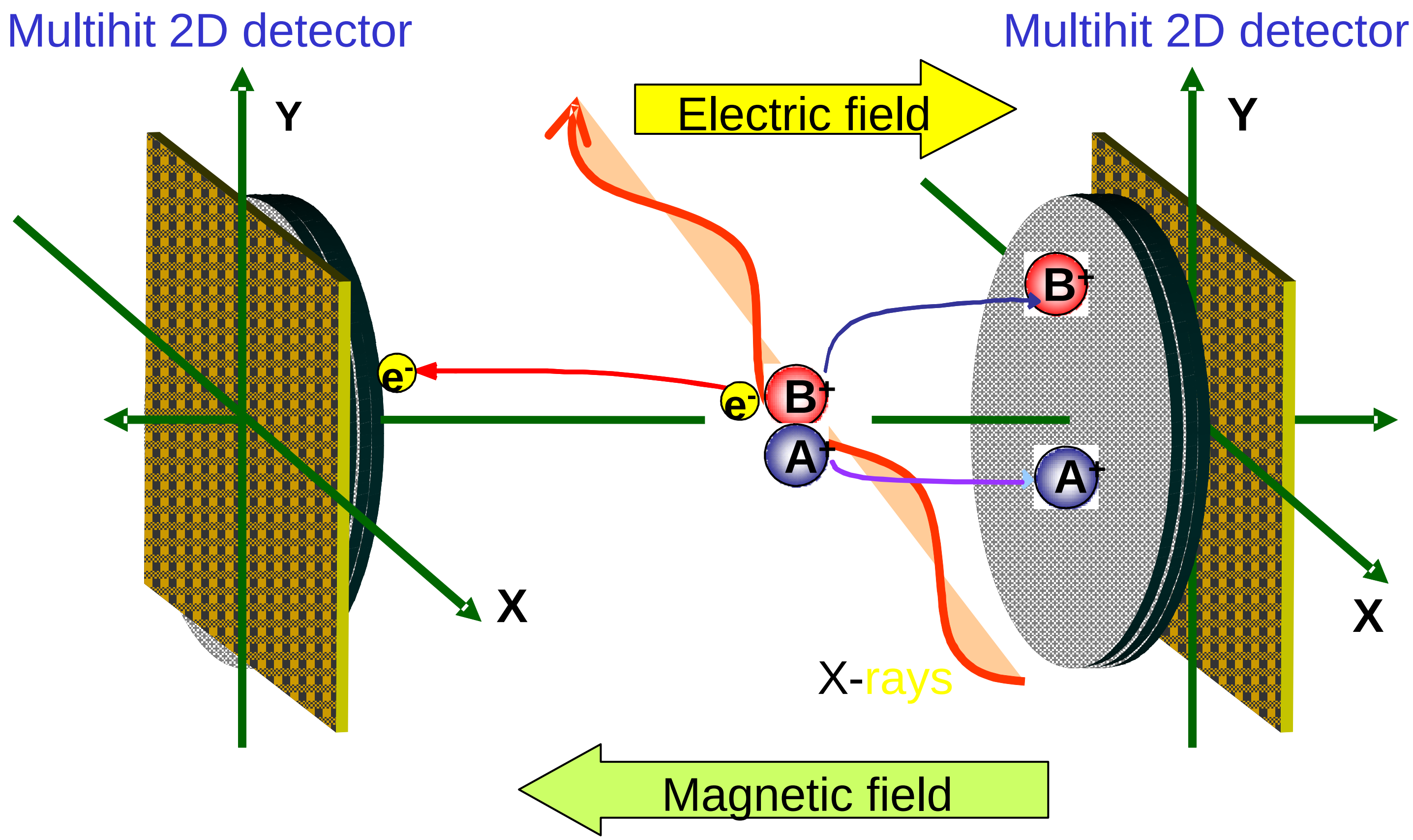
De Fanis *et al.* Phys. Rev. A **69**, 022506 (2004).



Sendai
in summer

Tanabata festival

Electron-ion coincidence momentum imaging



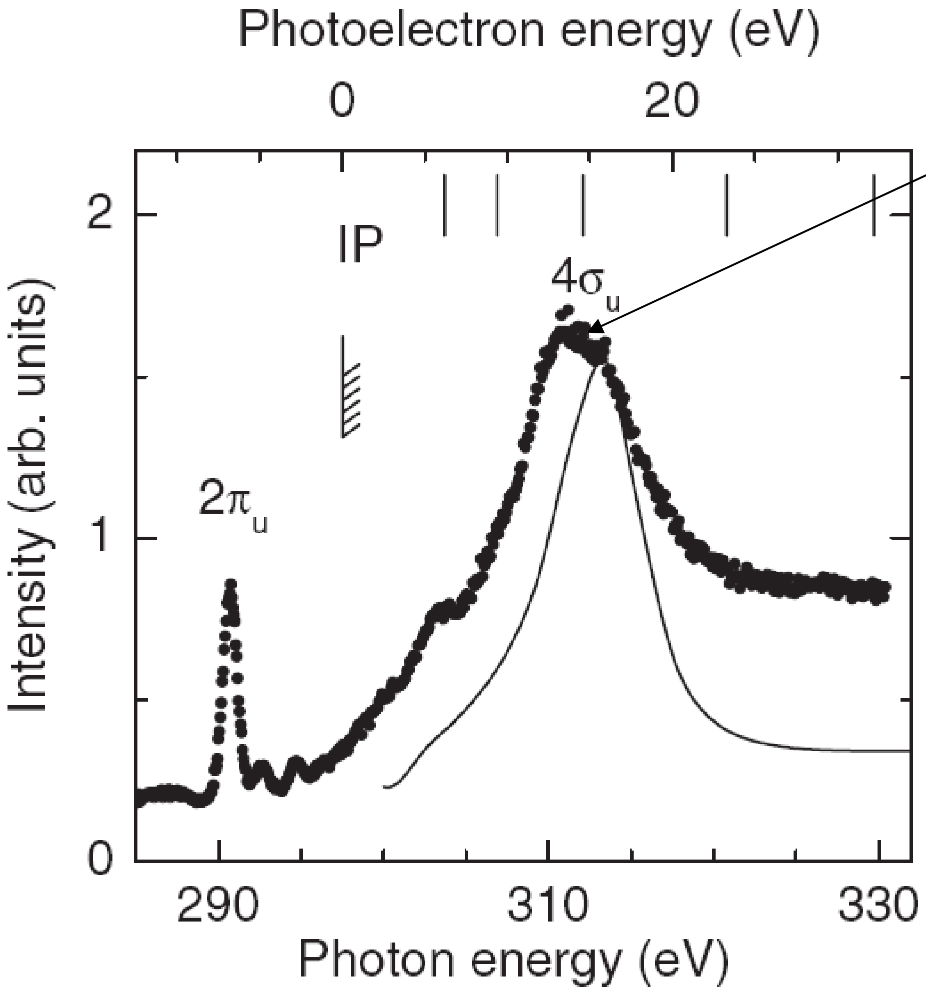
Ion-ion coincidence → *Molecular axis*

Ion momentum conservation → *Retrieval of the source point*

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

Towards photoelectron diffraction measurement

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:

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

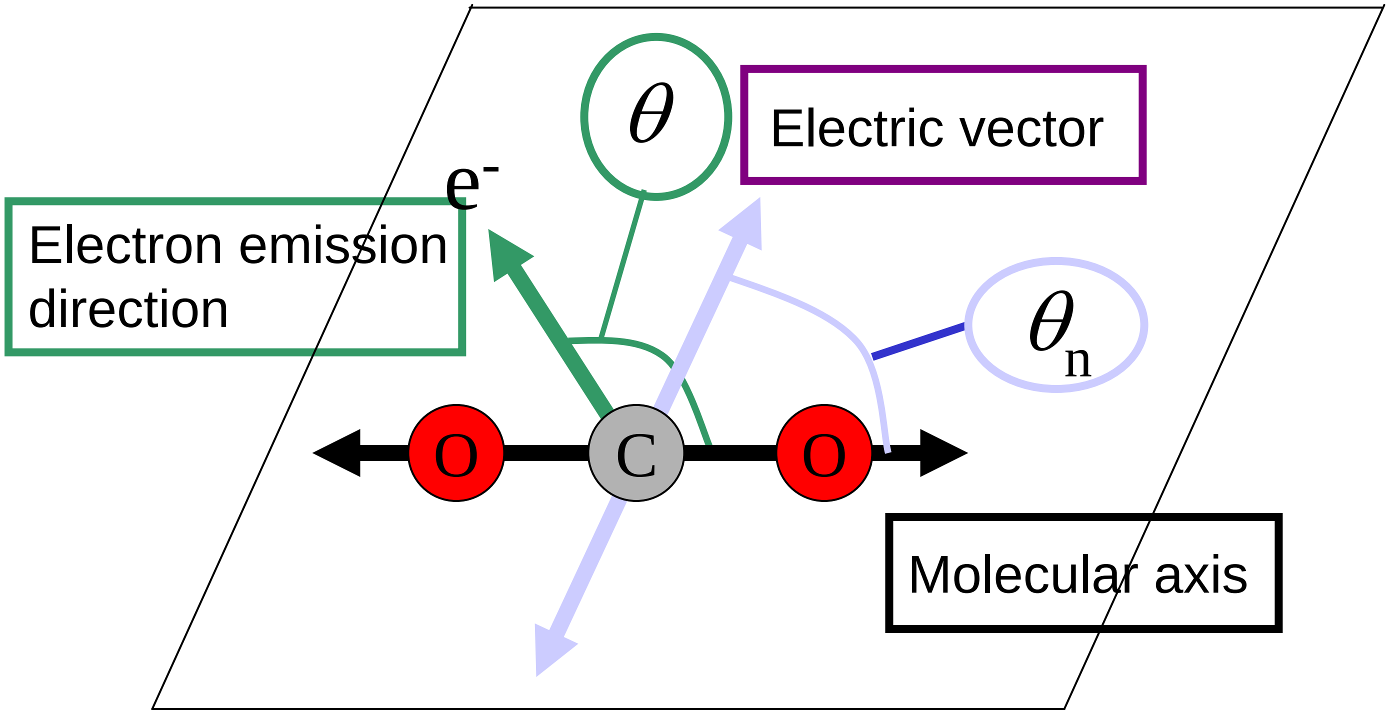
$$3\sigma_u^{\,2}1\pi_u^{\,4}1\pi_g^{\,4}(^1\Sigma_g^{\,+});\ 2\pi_u^{\,0}5\sigma_g^{\,0}4\sigma_u^{\,0}$$

C 1s threshold
297.63 eV

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

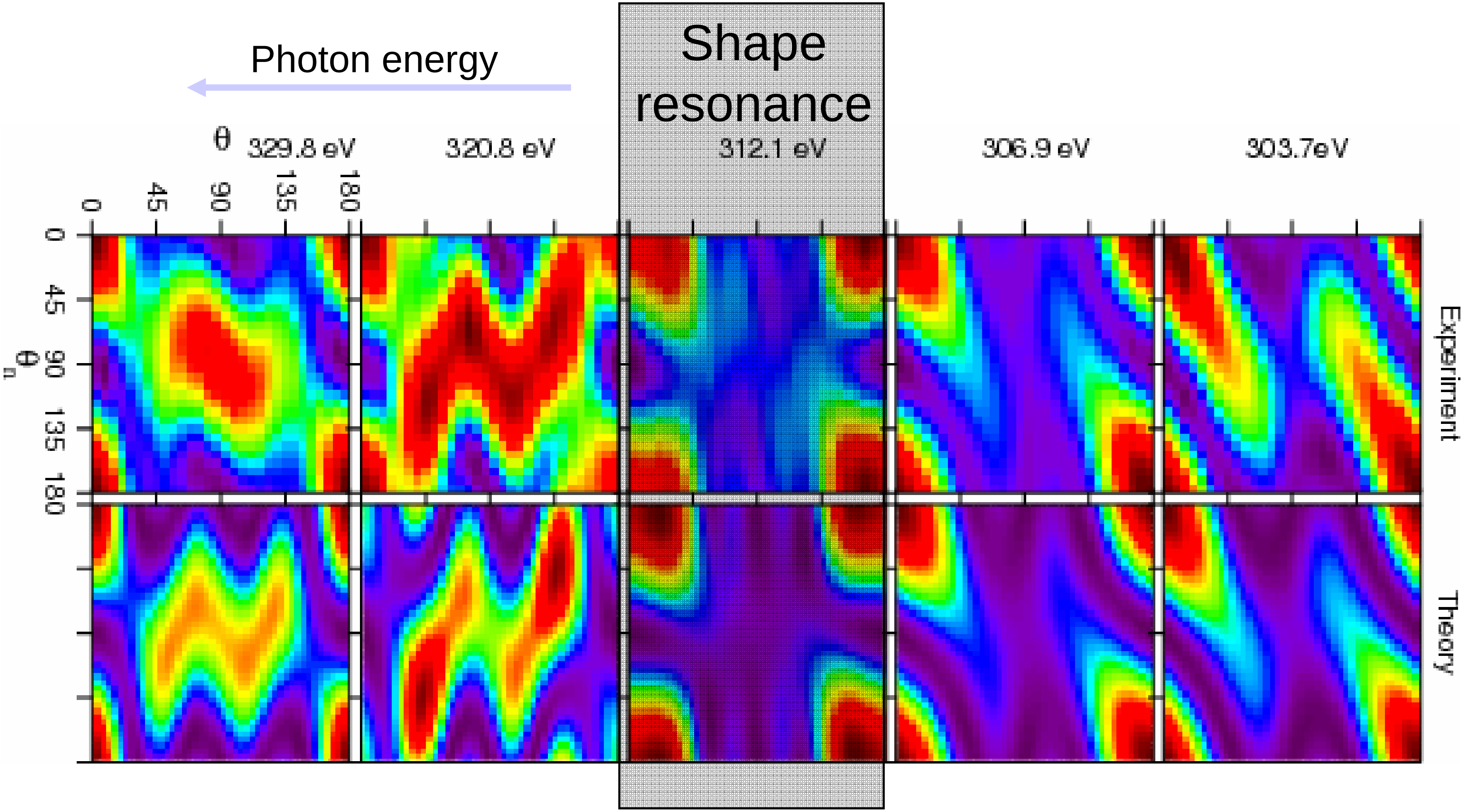
Reaction plane

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



We focus on the electron emission within this reaction plane

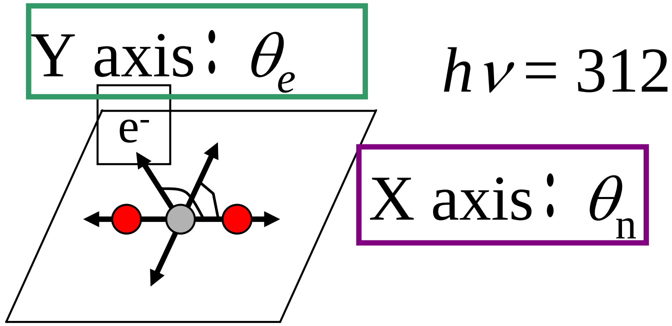
MFPADs for C1s emission from CO_2: comparison between experiment and theory



The general agreement between experiment and theory is reasonable.

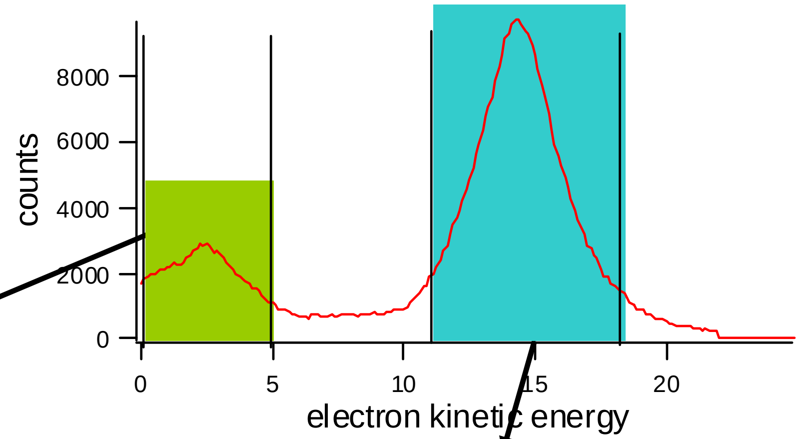
Liu *et al*. Phys. Rev. Lett. **101**,083001(2008).

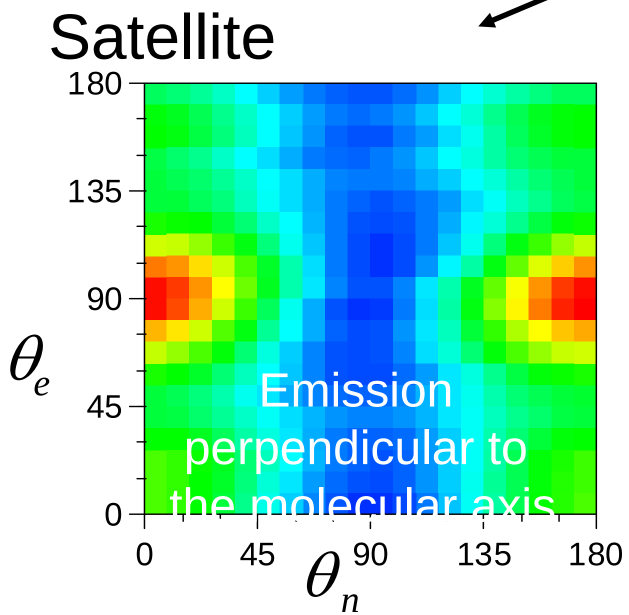
Satellite line vs Main line

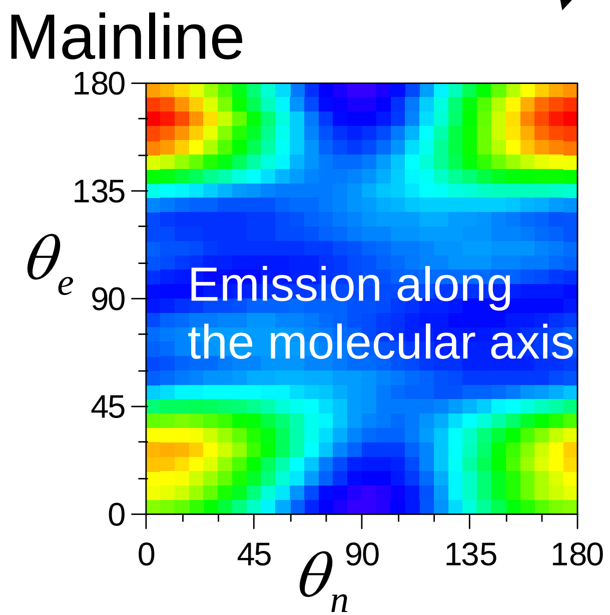


$h\nu = 312.2$ eV

Photoelectron spectrum



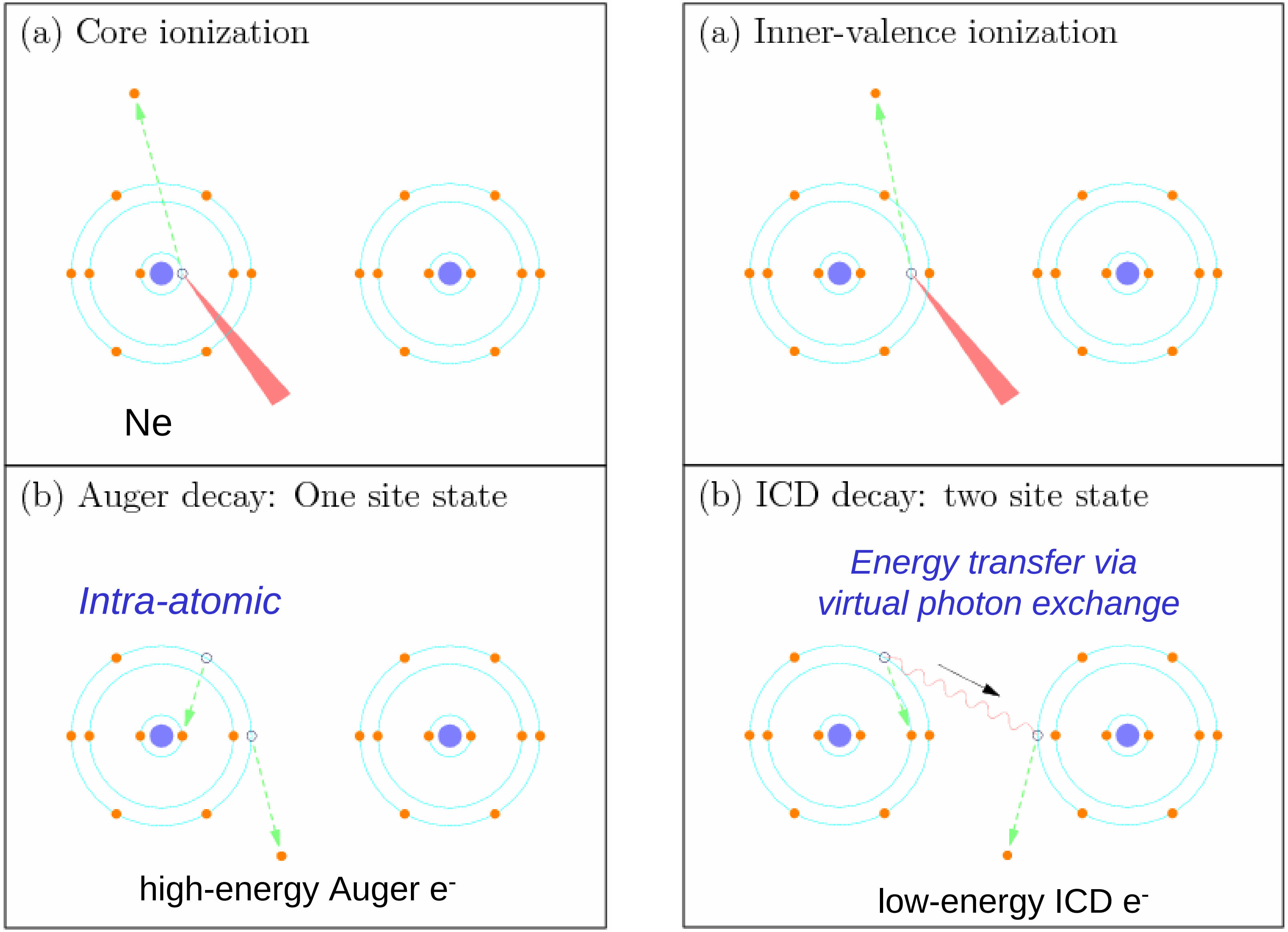




In both cases, the intensity drop at $\theta_n = 90°$ i.e. Σ–Σ parallel transition.
The electron emission directions are completely different.

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).

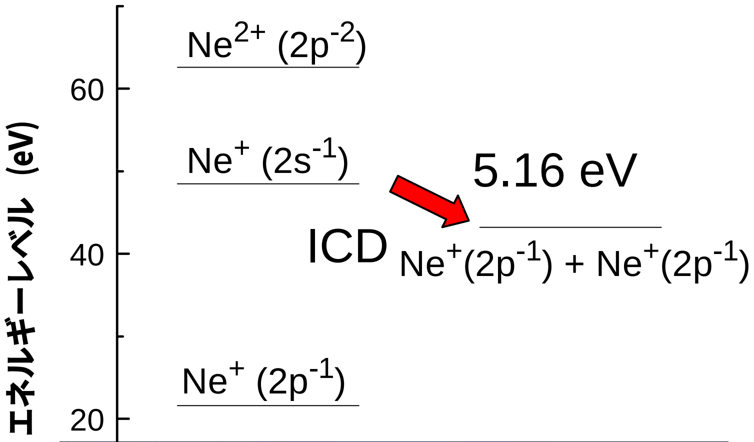
Experimental

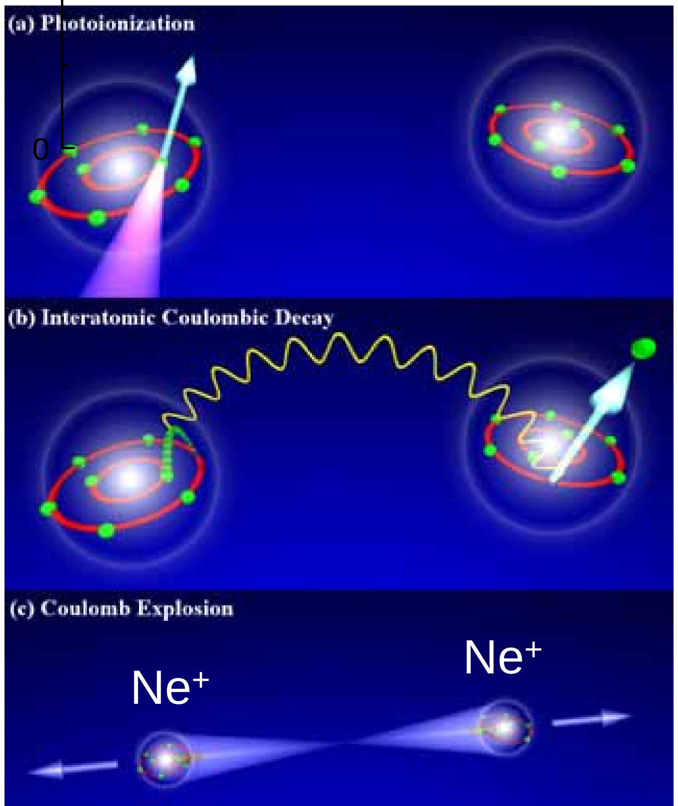
First observation - Ne cluster:
U. Hergenhahn and coworkers, Phys.Rev. Lett. 90, 203401 (2003).

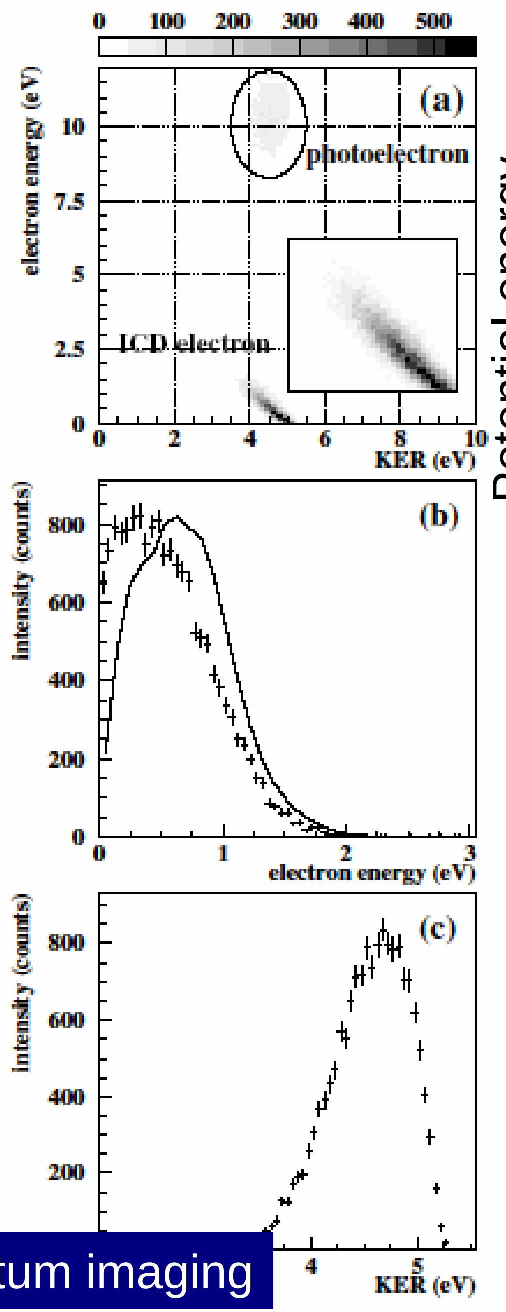
Cluster-size-dependent lifetime:
G. Öhrwall *et al*., Phys. Rev. Lett. 93, 173401 (2004).

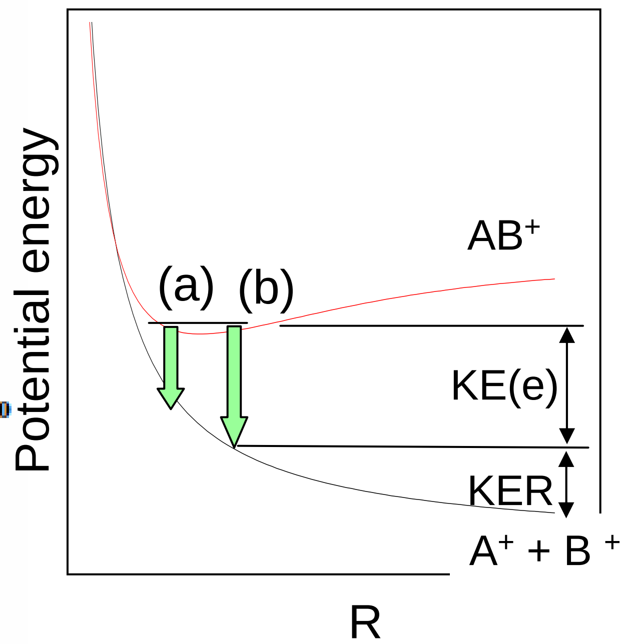
Ne_2 e-ion-ion coincidence:
R. Dörner and coworkers, Phys. Rev. Lett. 93, 163401 (2004).

Observation of ICD in Ne_2 by Frankfurt group







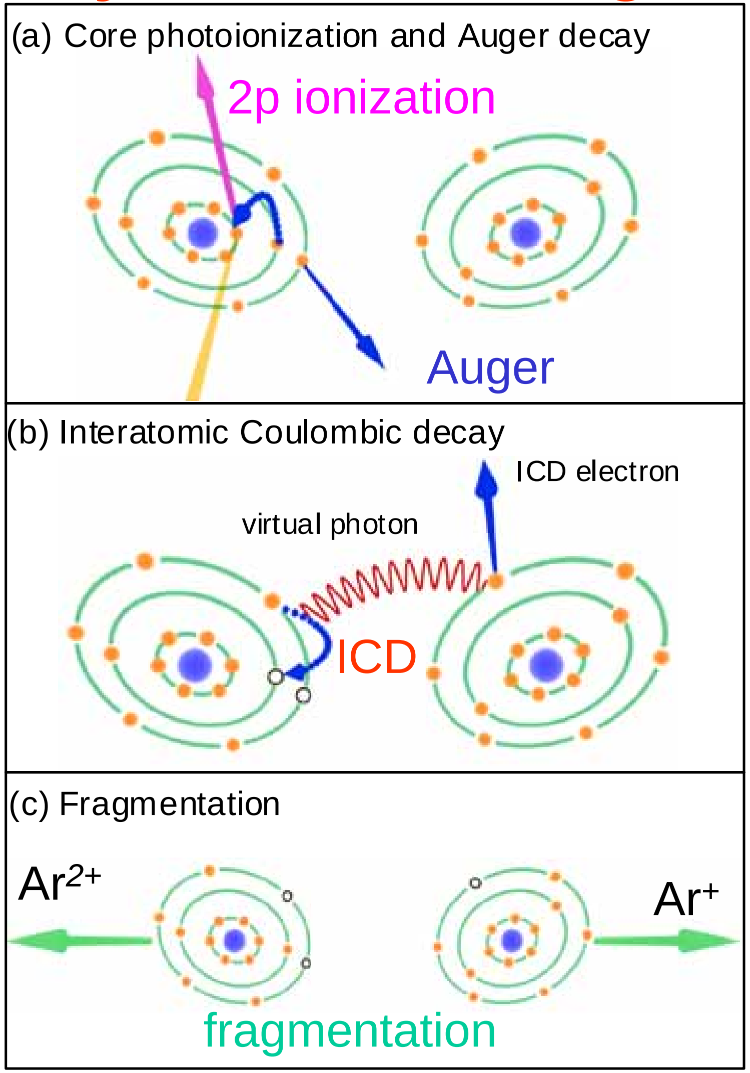


KE(e)+KER = 5.16 eV

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

Electron-ion-ion coincidence momentum imaging

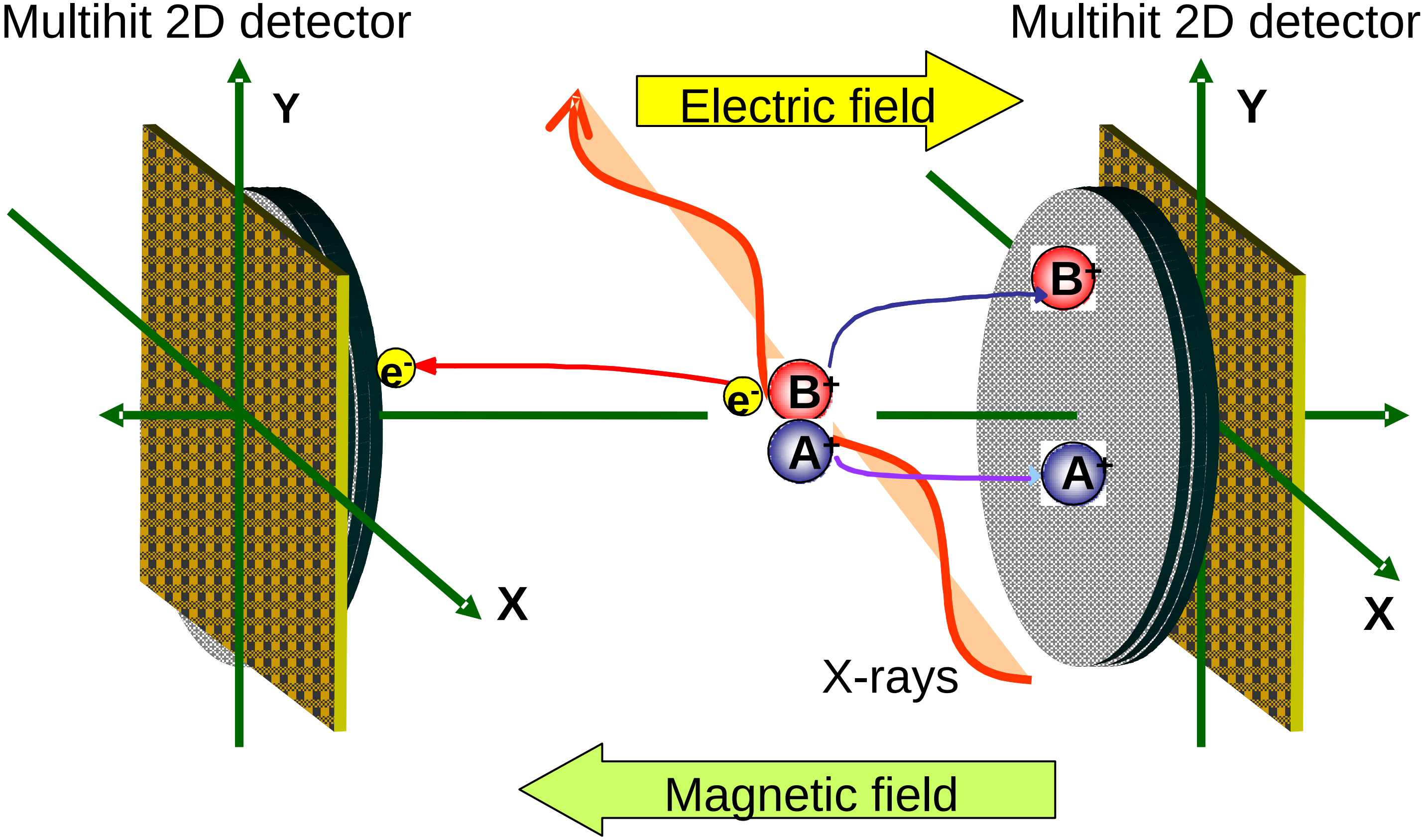
Experimental evidence of interatomic Coulombic decay from the Auger final states in argon dimers



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

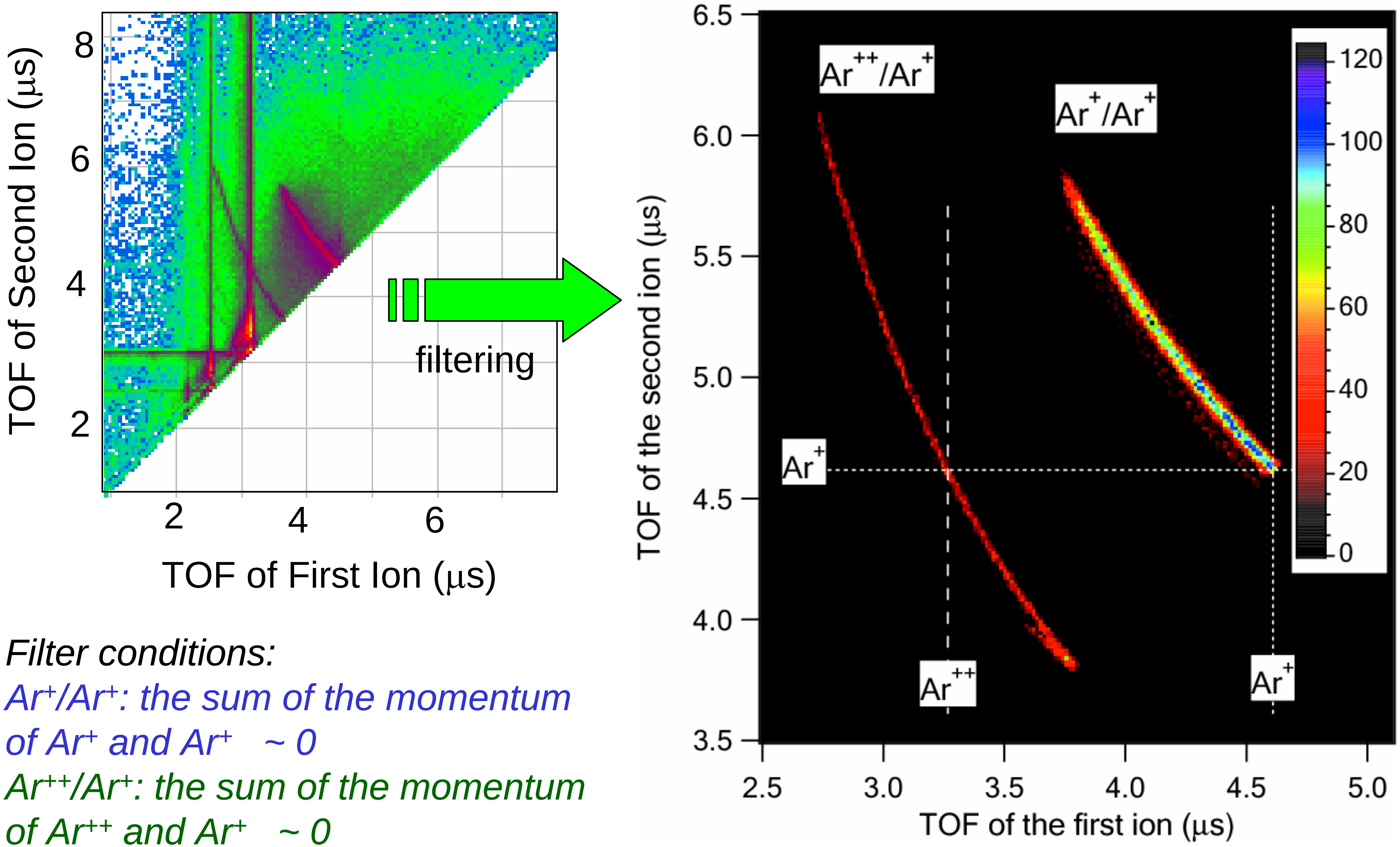


position & time of flight (x,y,t) → *3D momentum of each particle*

Multiple coincidence → *Momentum correlation among the particles*

Momentum conservation → *Selection of Dimer from others !*

Ar_2 PIPICO spectrum



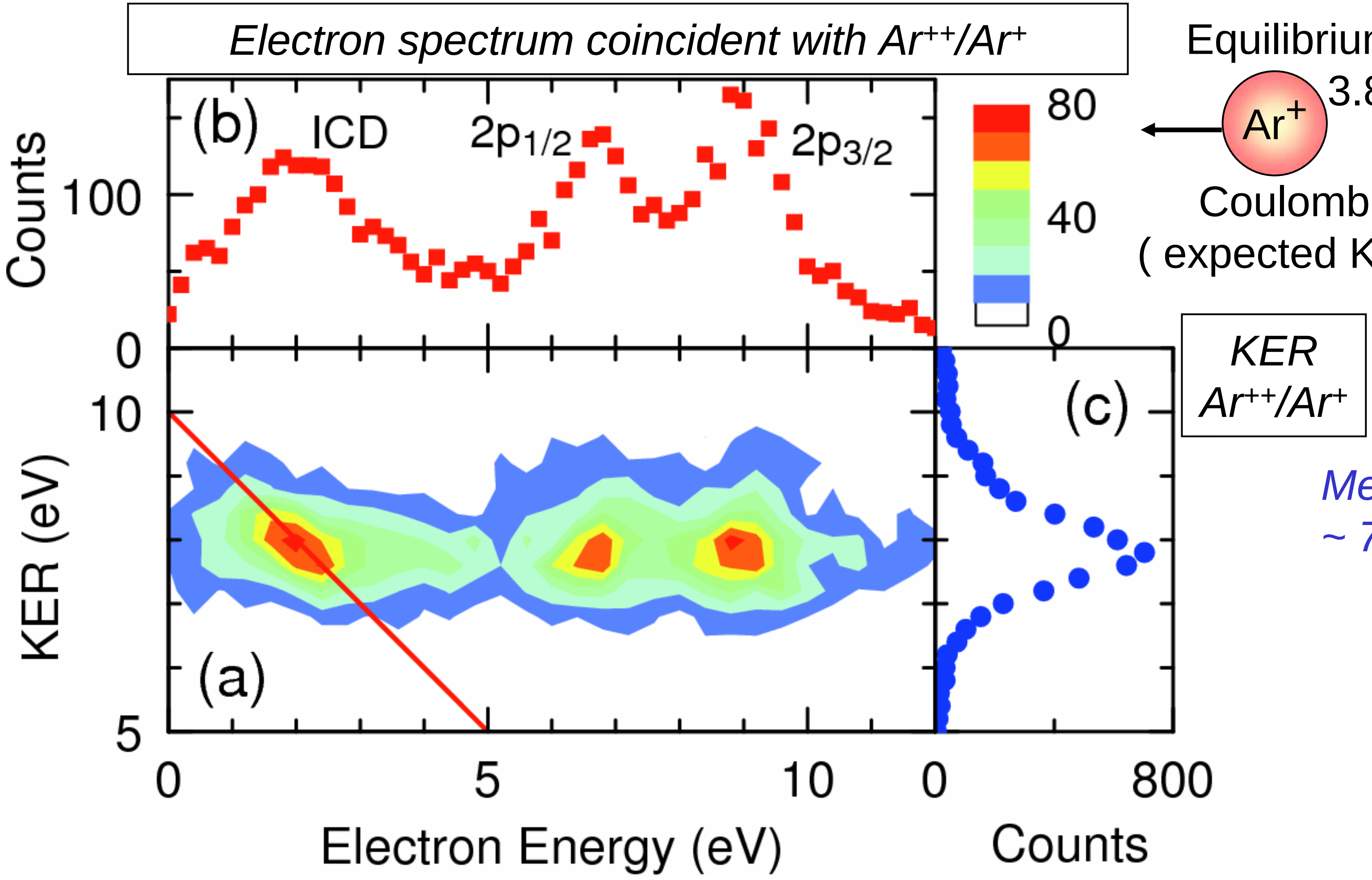
Filter conditions:

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

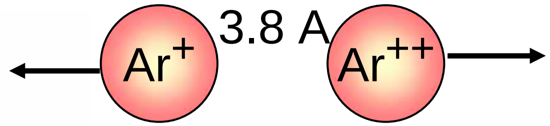
Ar^{++}/Ar^+: the sum of the momentum of Ar^{++} and Ar^+ ~ 0

Ar^{++}/Ar^+ comes from ICD !?

Electron spectrum, KER, and their correlation



Equilibrium distance



Coulomb explosion

(expected KER ~ 7.6 eV)

Measured KER ~ 7.7 eV

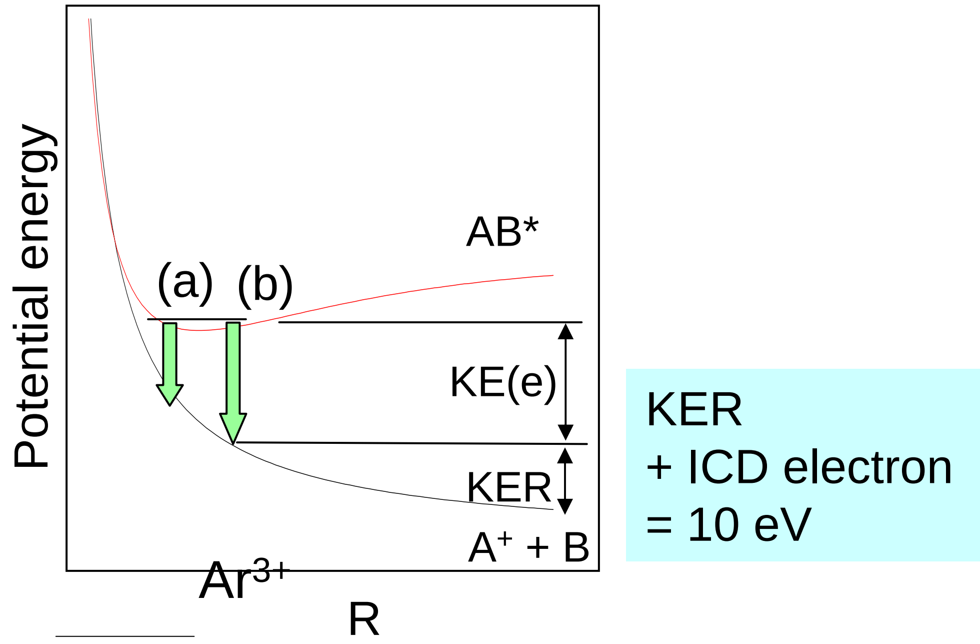
ICD: KER + KE(ICD electron) ~ constant

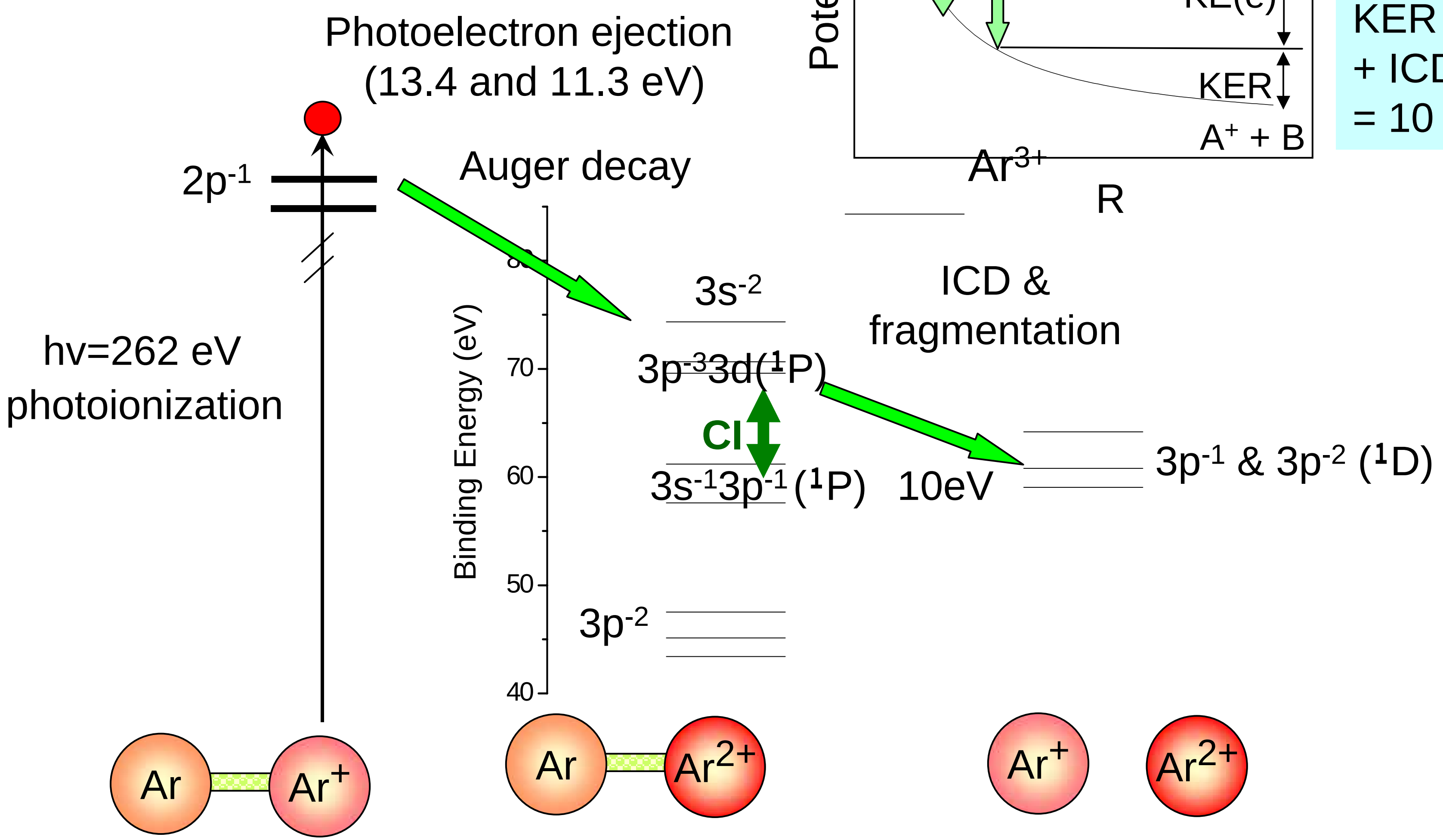
Islands of slope -1 are ICDs !

Breakup following ICD takes place almost instantaneously.

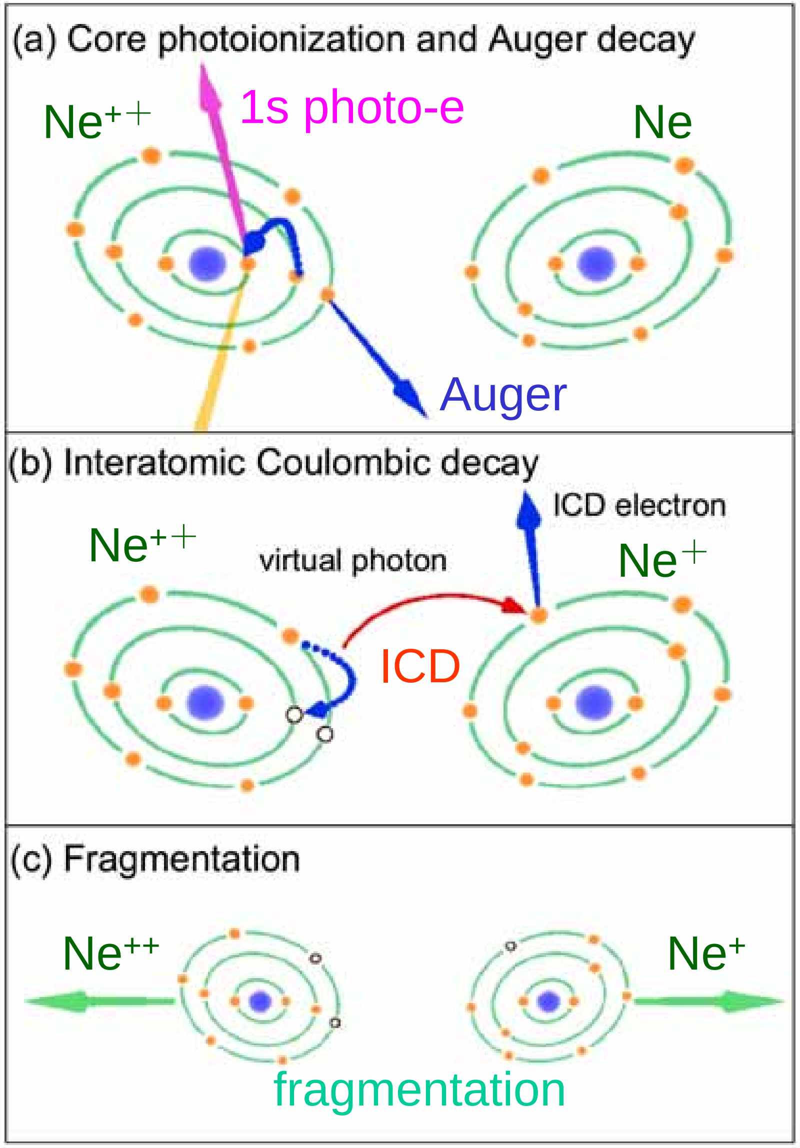
ICD is very fast!

Energy diagram of the ICD process in Ar_2





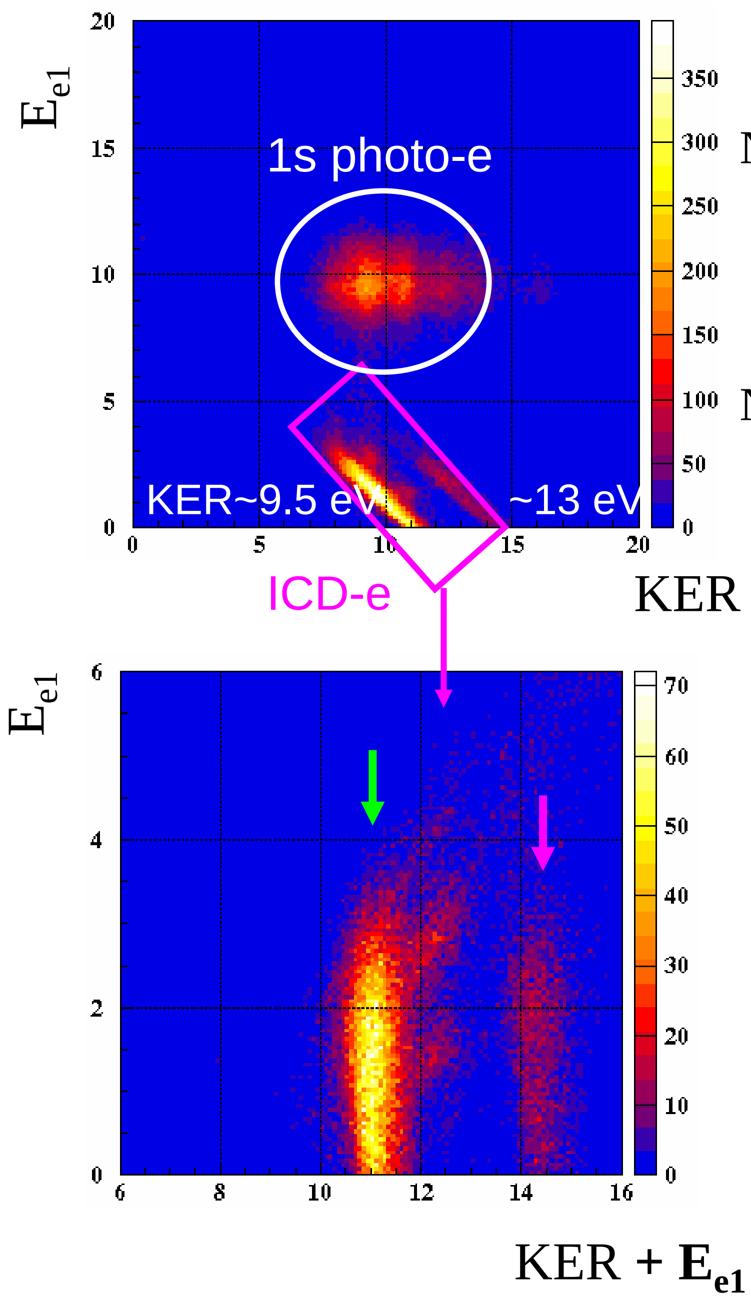
*ICD from the Auger final states in **Ne** dimer*



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



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

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

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

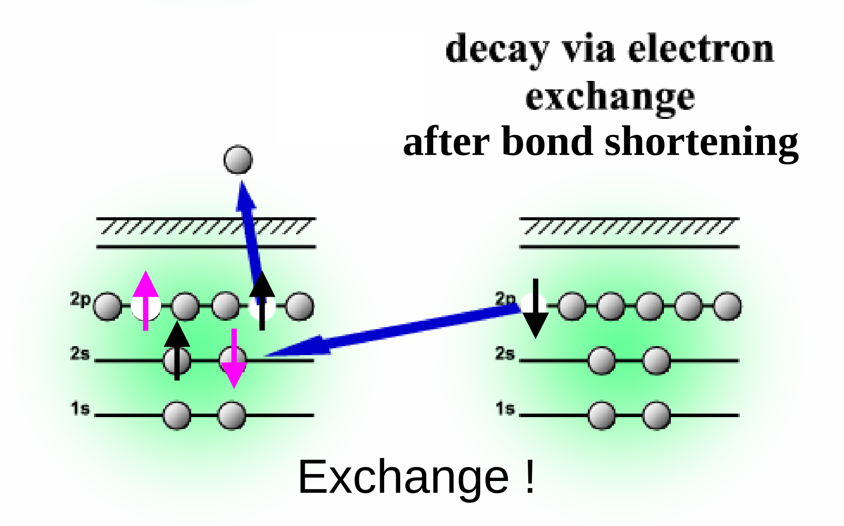
$$E_{e1} + KER = 14.4\ \text{eV}$$

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

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

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

Spin flip!

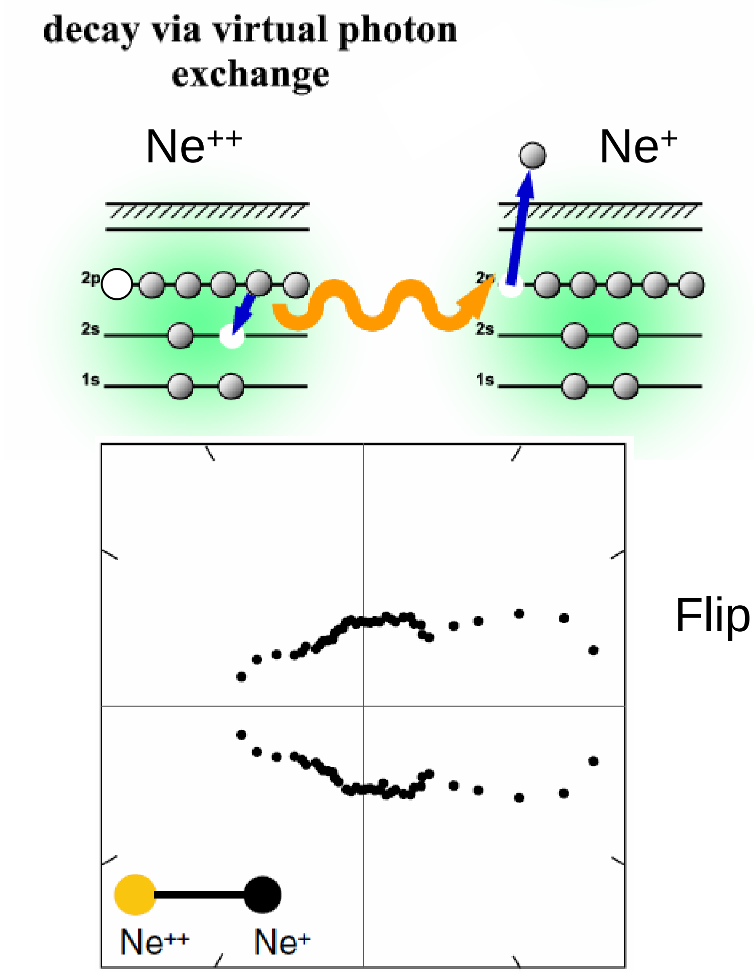


$R\sim 2.2$ A $< R_0 = 3.2$ A

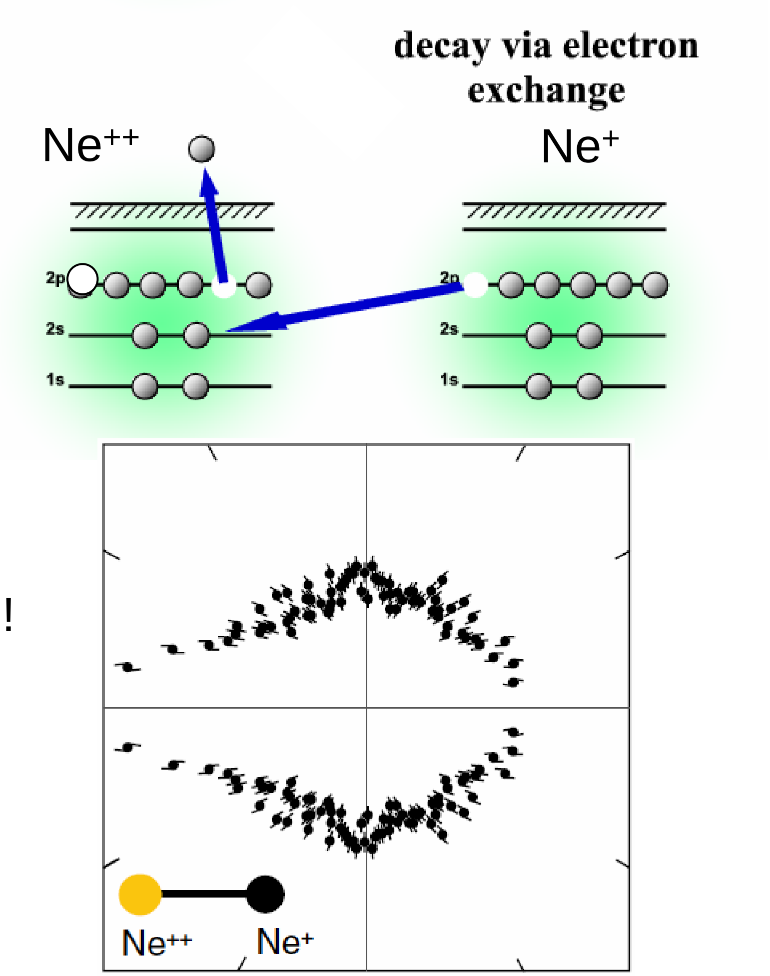
Molecular frame electron angular distributions emitted via ICD

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

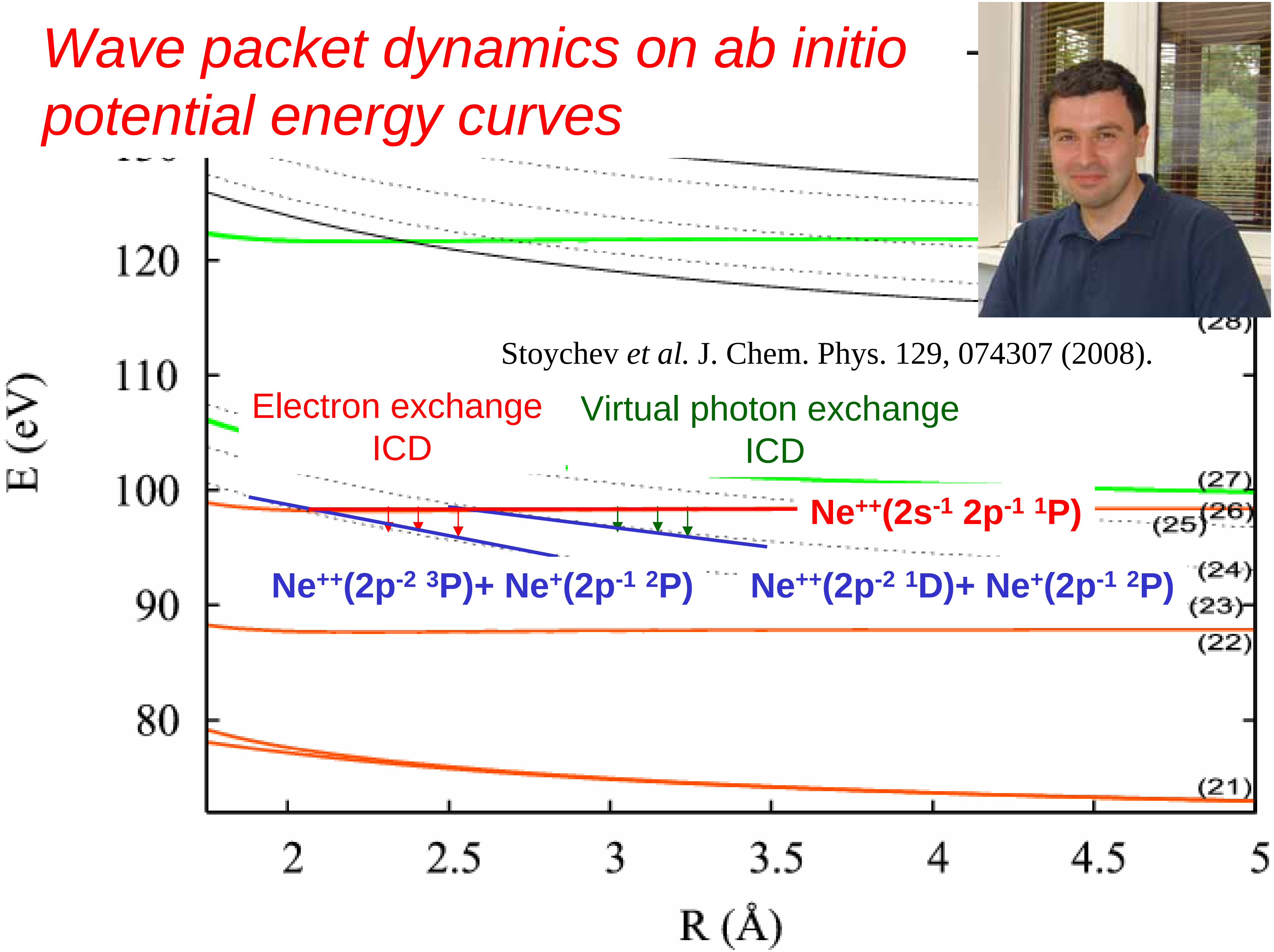
ICD by electron transfer
(exchange integral)
ICD electron is emitted from Ne^{++} site



Flipped!



Wave packet dynamics on ab initio potential energy curves



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

Importance of ICD

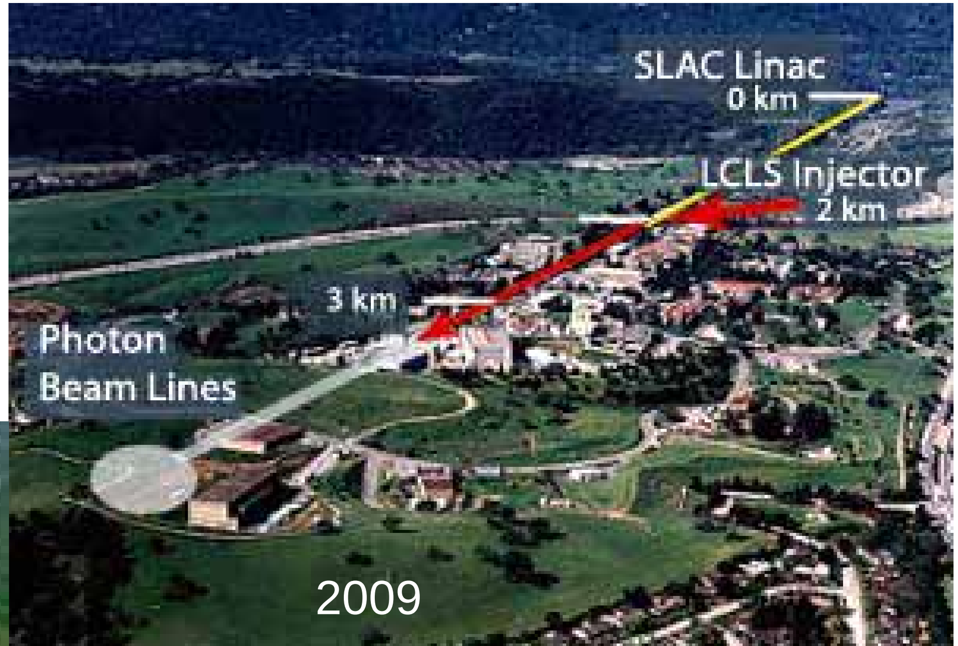
1. *ICD takes place as a result of the interaction between the molecule and the environments*

2. *ICD takes place in any van der waals molecules and clusters, any hydrogen-bonding clusters, any atoms in the C_{60} cage, any bio-molecules in the living cell, etc.*

3. *ICD takes place after inner-valence ionization, after shakeup ionization, and after Auger decay.*

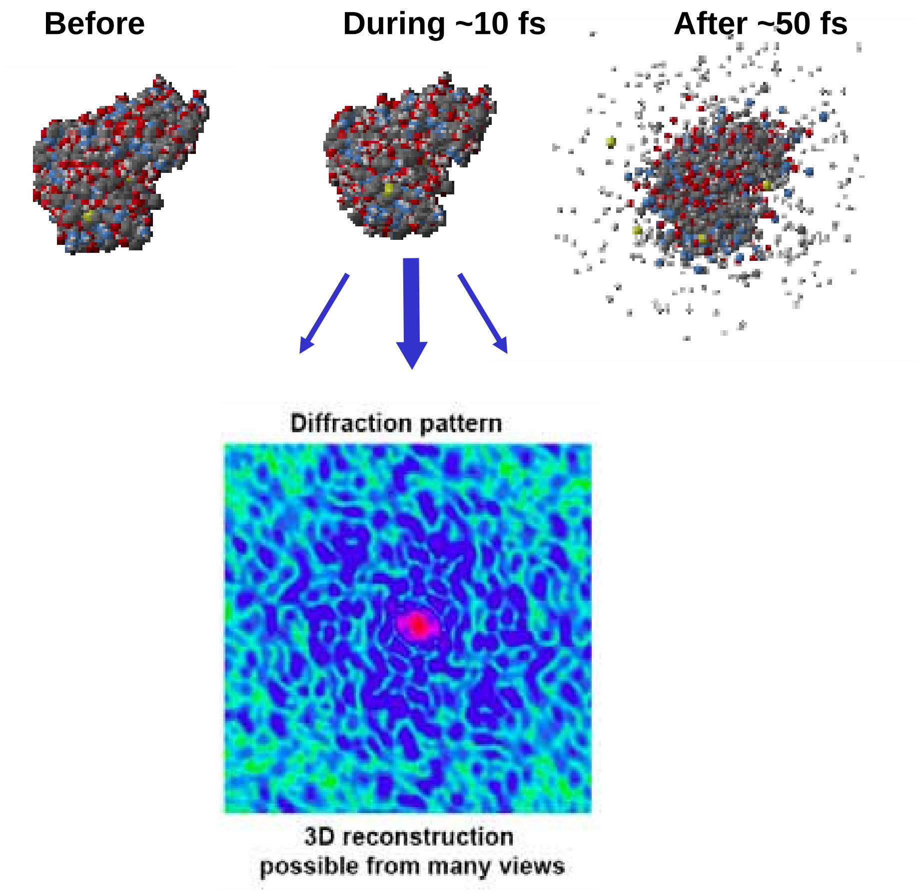
4. *ICD is the important mechanism to produce the low-energy electron after hard X-ray radiation and may be one of the source of radiation damage.*

Ultrafast imaging of a single molecule using XFEL



Structure analysis for a single biomolecule

Neutze, Wouts, van der Spoel, Weckert, Hajdu   Nature 406, 752 (2000)



Should record the X-ray diffraction pattern before Coulomb explosion….
Change of the electron density may be even faster….
Developing the X-ray detectors is the most important issue….

EUV-FEL Facility

X-FEL (will be in operation in 2010)

EUV-FEL
(in operation)

SPring-8

Characteristics of EUV-FEL

Energy range	**51 - 61 nm (20 - 24 eV)**
Band width	< 1 %
Pulse Energy	> 10 μJ at 61 nm
Stability of pulse energy	< 20 %
Pulse width	~ 100 fs
Period of Bunch	10 Hz (60 Hz in future)
Polarization	Horizontal (> 99 %)
Higher harmonics at 54 nm	Second < 0.1 % Third < 1 %

A lot of new opportunities for atomic and molecular science!


The end
Thank you very much for your attention!