Photoemission 1

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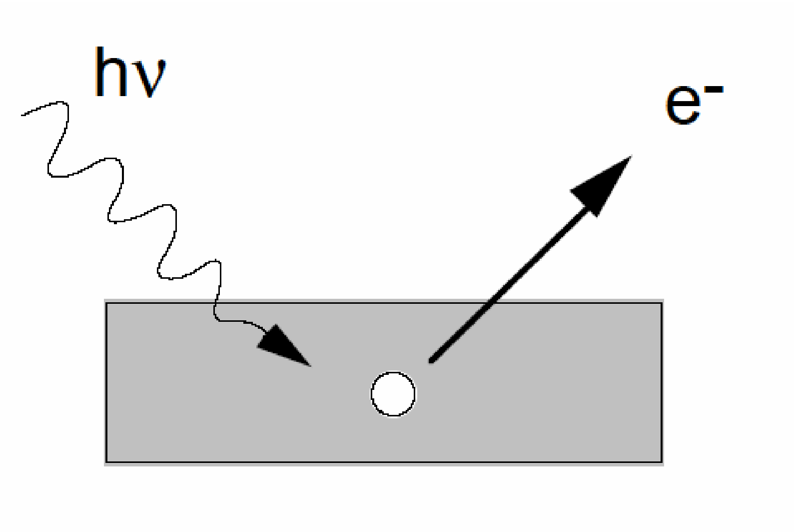
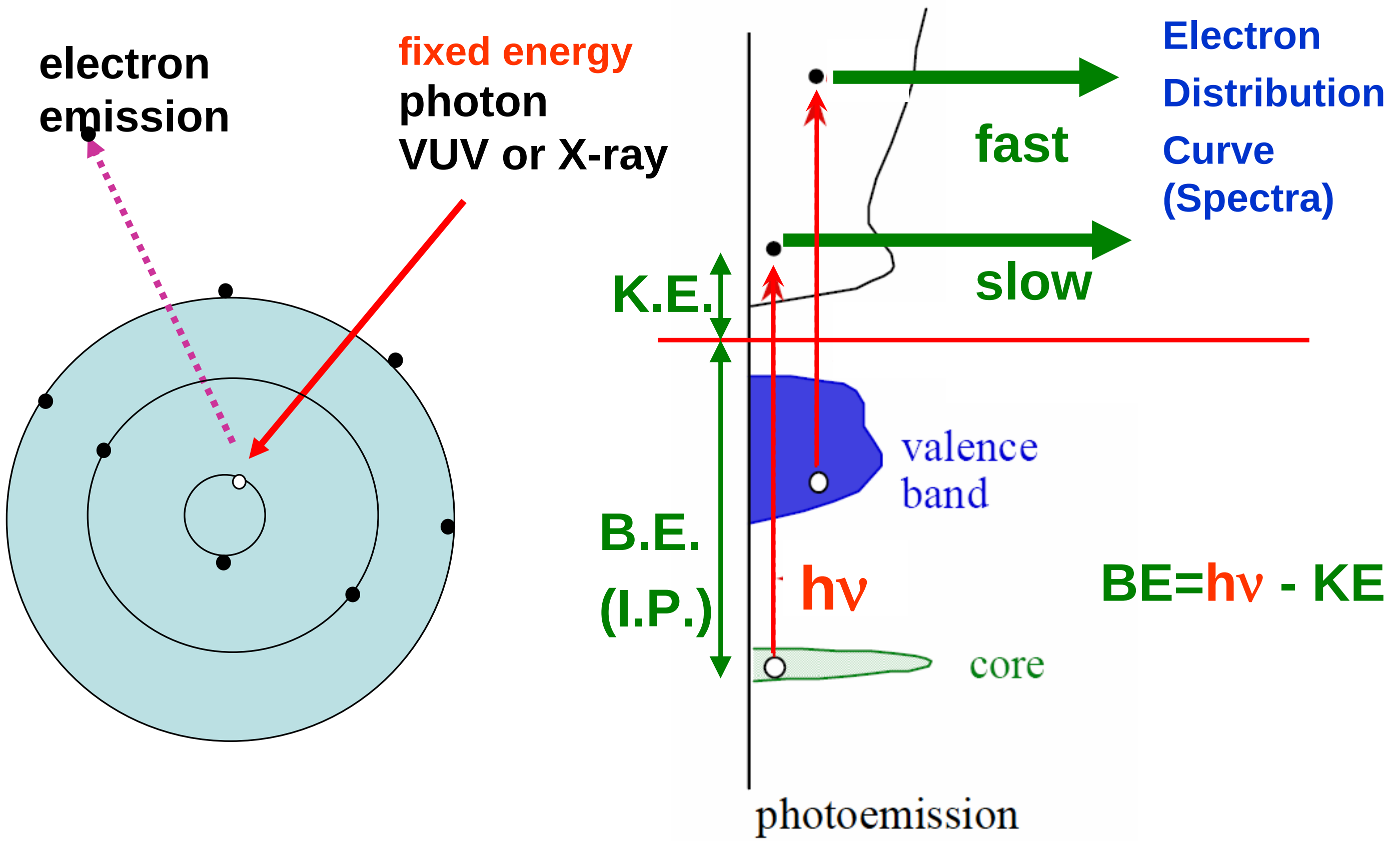
What is photoemision?



photon-in electron-out

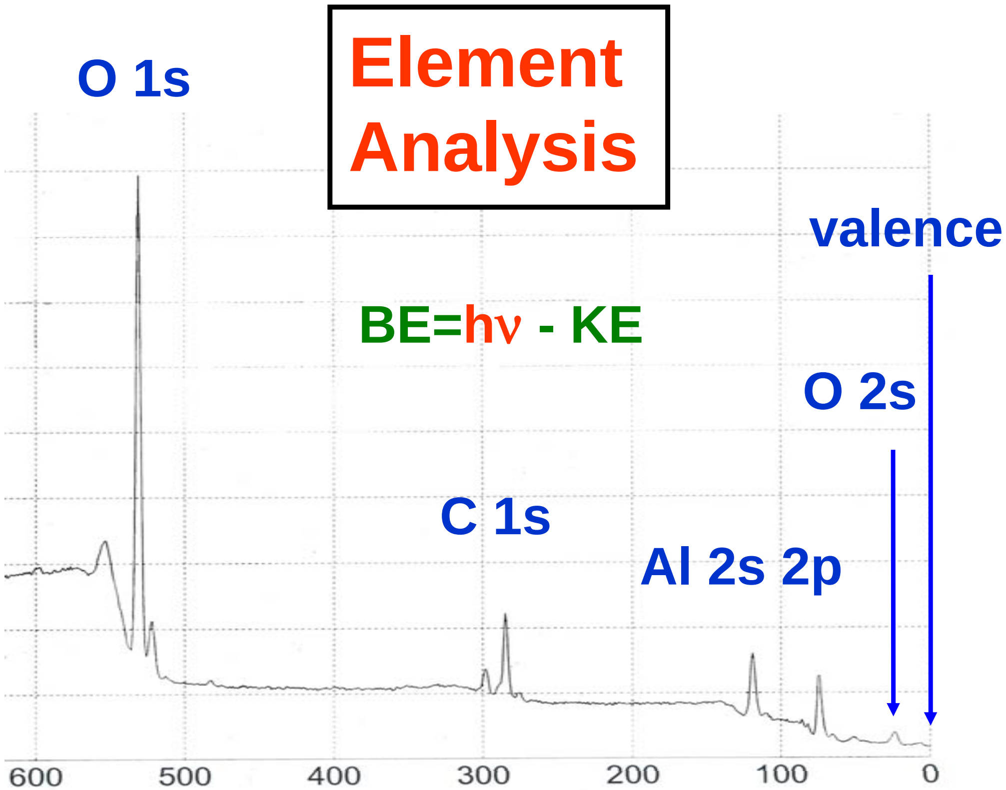
What is photoemission?



ATOM

Molecules/Solids

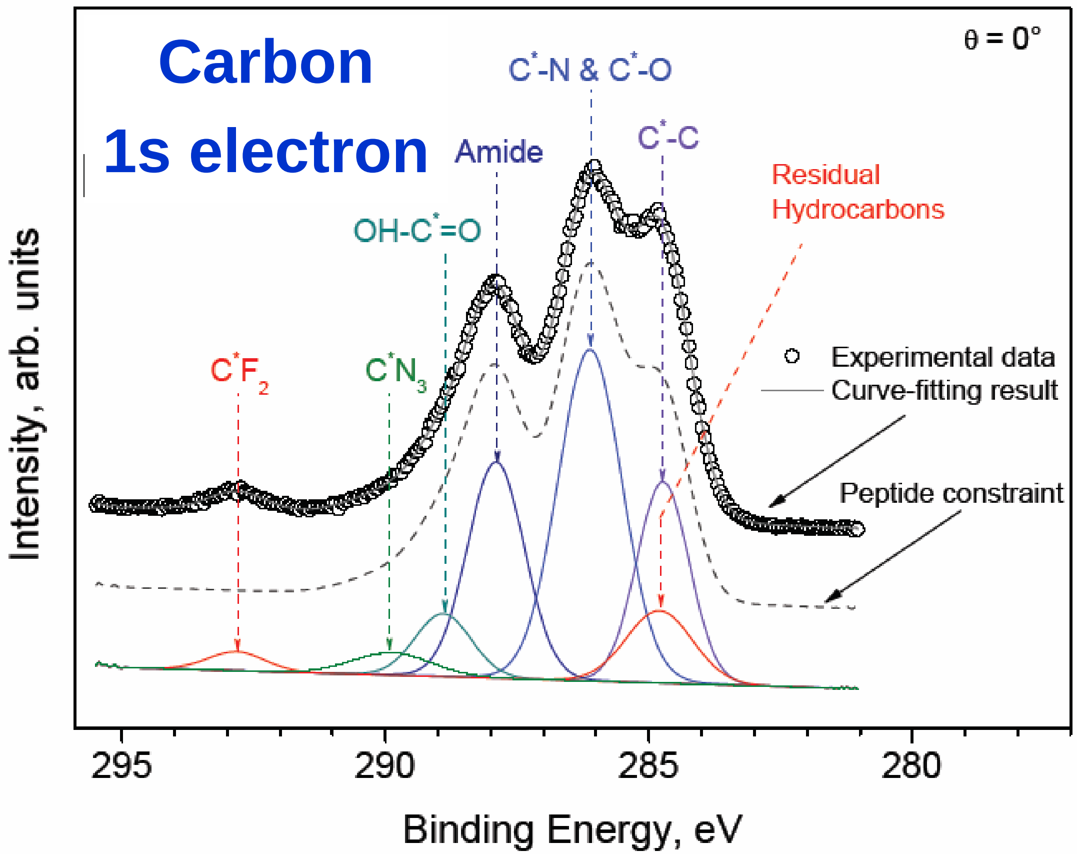
What is photoemision?



Electron Binding Energy (BE)

Ionization Potential (IP) in eV

What is photoemission?



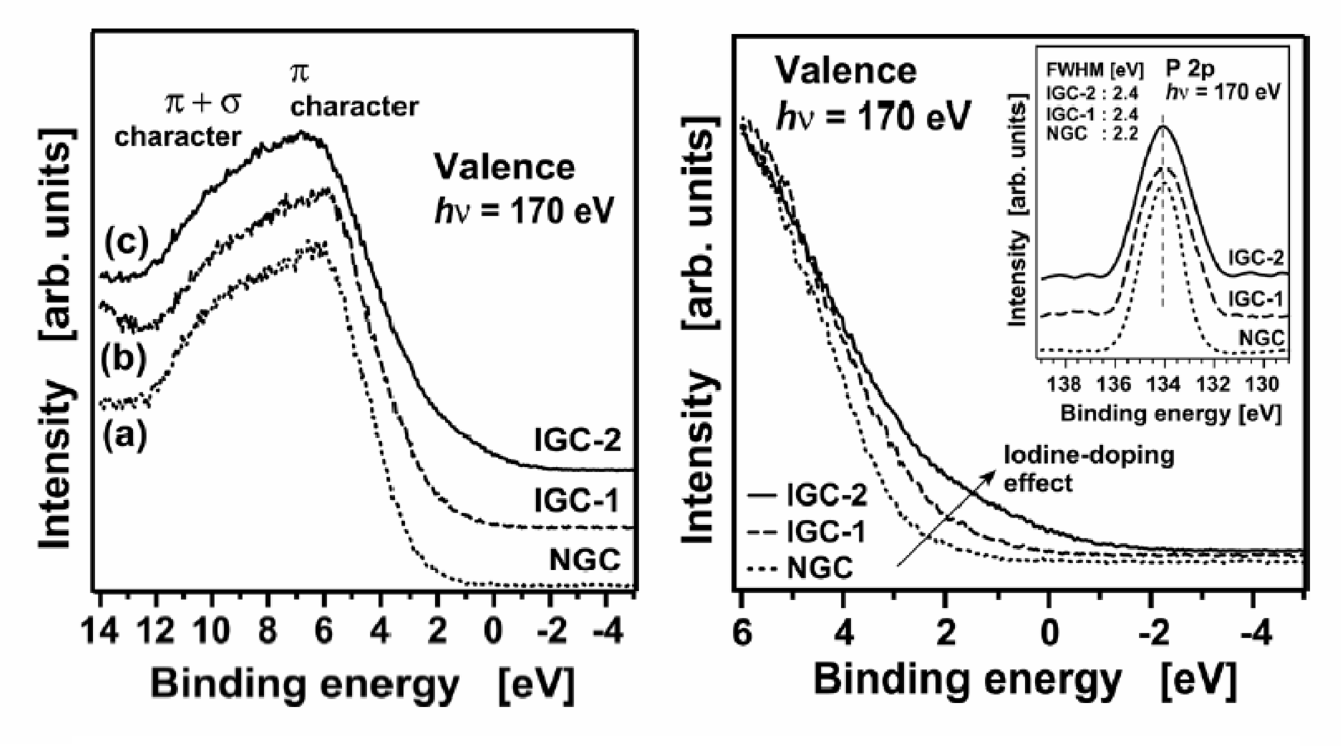
ESCA **(Kai Siegbahn 1918-2007.7.20)**

Electron Spectroscopy for Chemical Analysis

Dr. Dmitry Zemlyanov
Purdue Univ. 2007Feb

What is photoemission?

Valence band/orbital



DNA polynucleotides poly(dG)poly(dC)

Dr. M. Furukawa et al.
Phys. Rev. B 75 (2007) 045119

What is photoemission?

Core

- **element analysis**
  - **different energy level for *different element***
- **chemical analysis (ESCA)**
  - **different chemical environments**
  - **between *same elements***

Valence

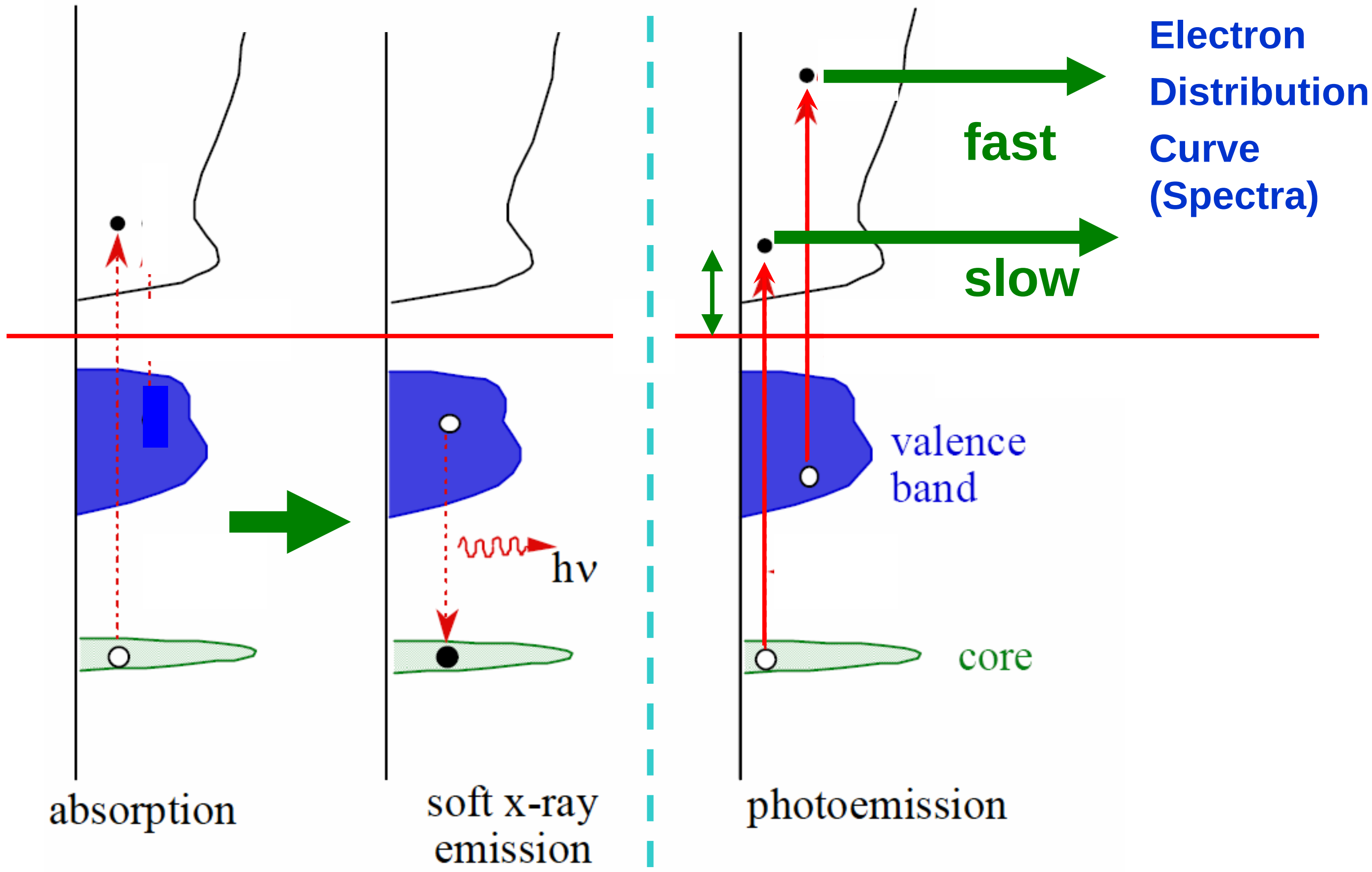
- **valence band**
- **valence orbital**

terminology

photoemission

- **x photon emission (X-ray emission,…)**
- **o photoelectron emission**

photon emission | photoemission



2 steps
photon-in photon-out

1 step
photon-in electron-out

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terminology

photoemission

- **x photon emission (X-ray emission,…)**
- **o photoelectron emission**

photoelectron spectroscopy (PES)

fixed photon energy $h\nu$

$h\nu$ = VUV : UPS (valence)

$h\nu$ = X-ray : XPS (valence, core)

Why SR?

$h\nu$ = synchrotron radiation VUV/X-ray

Why SR PES?

photon energy dependence

wide tunability of SR

(1) escape depth (core, valence)

(2) energy band dispersion (valence)

(3) cross section (valence)

(4) resonance effect (core)

high energy resolution

BE=hν - KE

very high brightness of insertion device SR

very high collimation of insertion device SR

VUV : < 1 meV cf. VUV laser

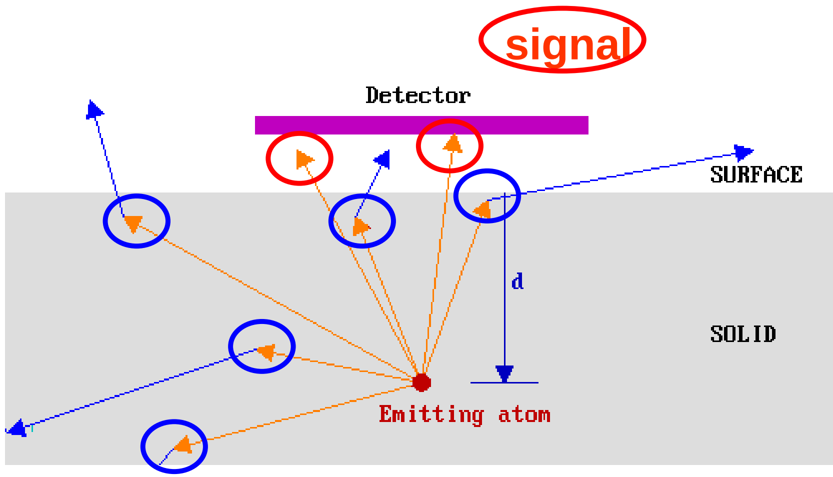
soft X-ray : < 10meV

hard X-ray: < 100meV

Why SR PES? (1) escape depth

noise!

Electron Inelastic Mean Free Path
or Electron Escape Depth

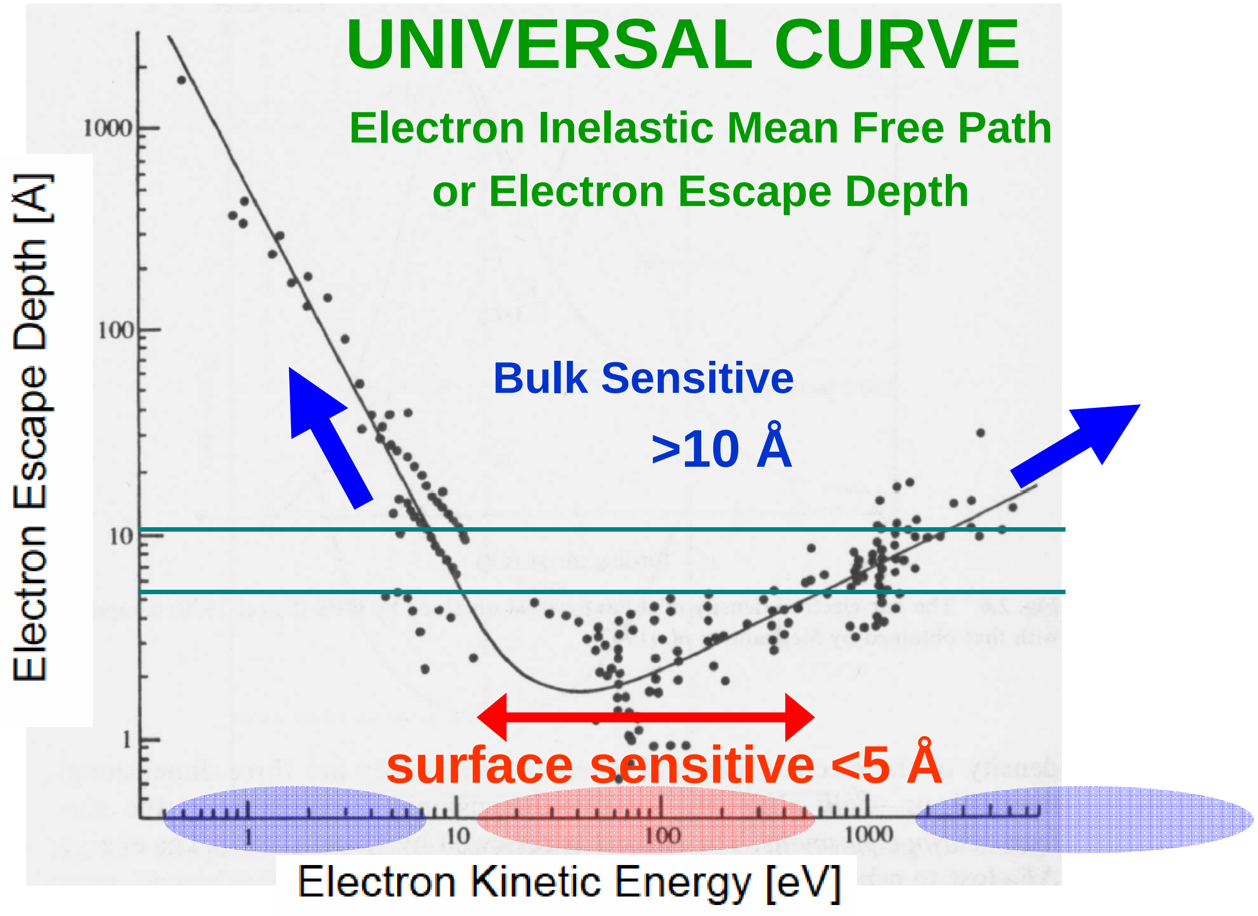


Electron Kinetic
Energy Dependence

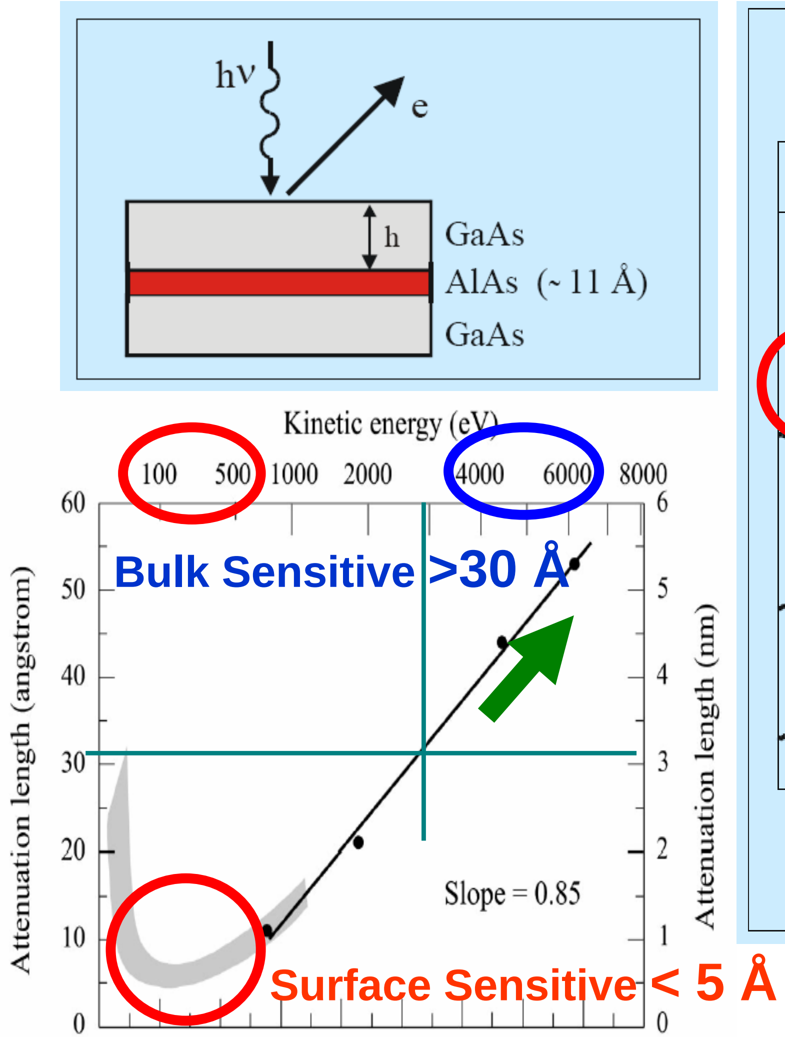
The larger mean free path (depth)
for the larger K.E.

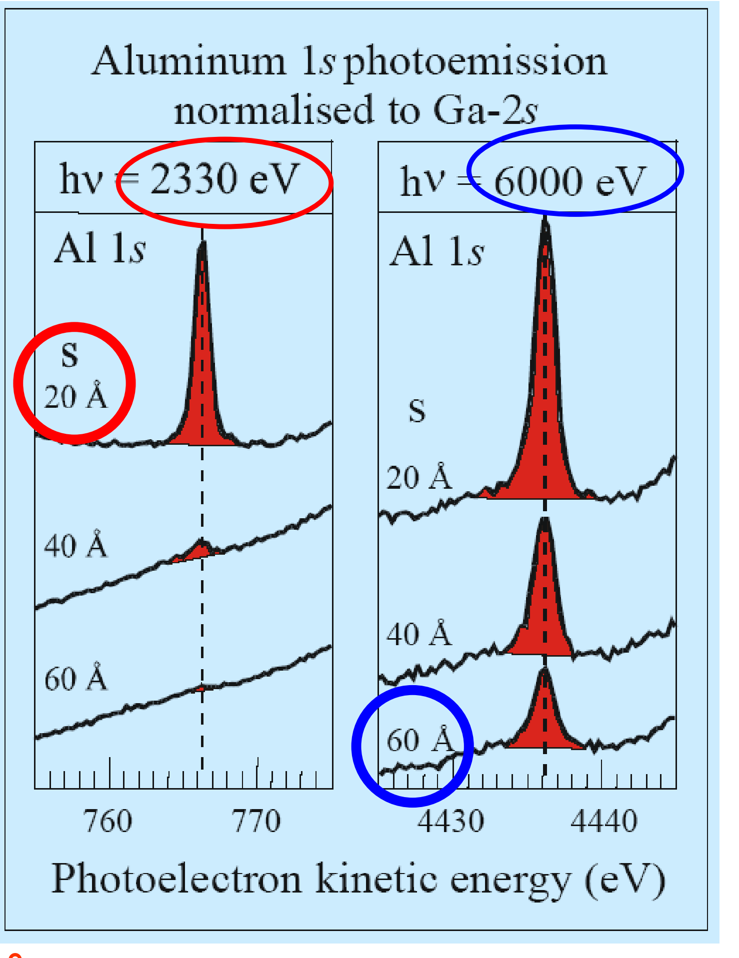
UNIVERSAL CURVE

Why SR PES? (1) escape depth



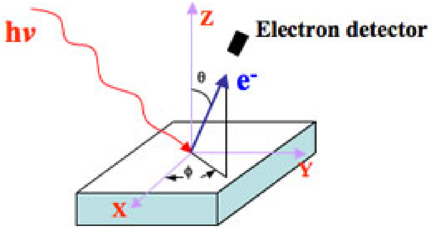
Why SR PES? (1) escape depth





Prof. Lucio Braicovich et al., Appl.Phys.Lett.85(2004)4532

Why SR PES? (2) energy band dispersion



ARPES

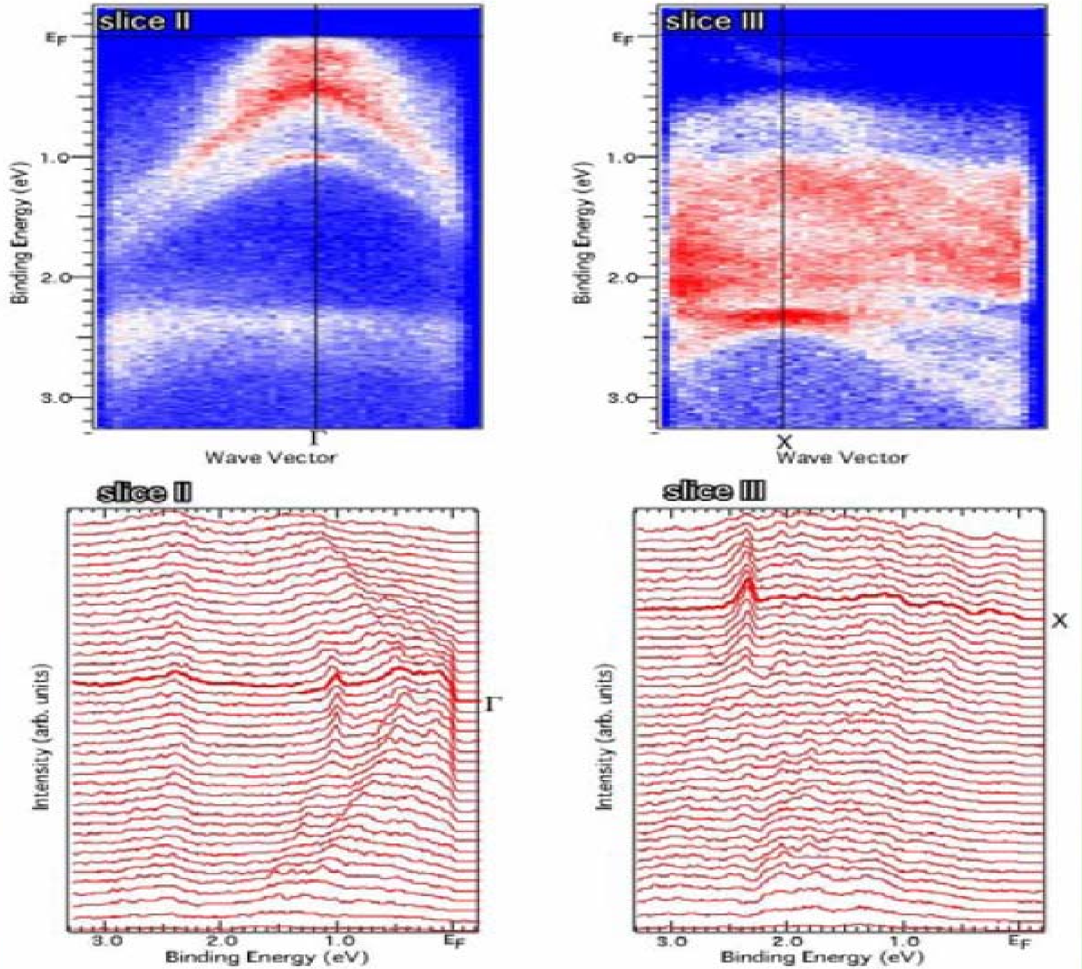
Angle Resolved

PhotoEmission

Spectroscopy

for valence band

[photon energy dependent]

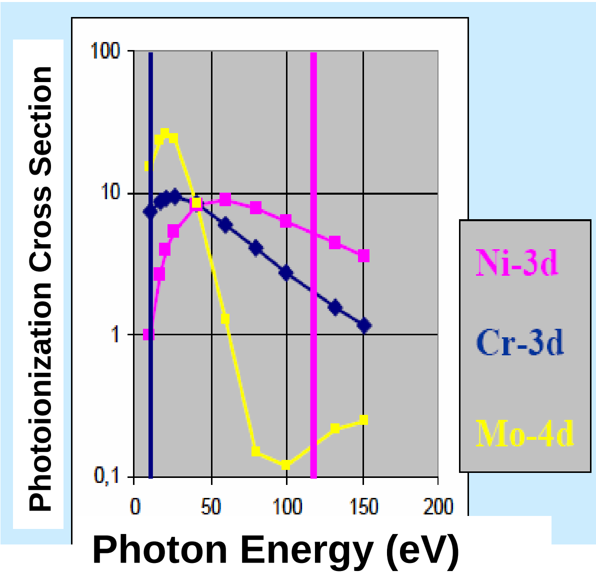


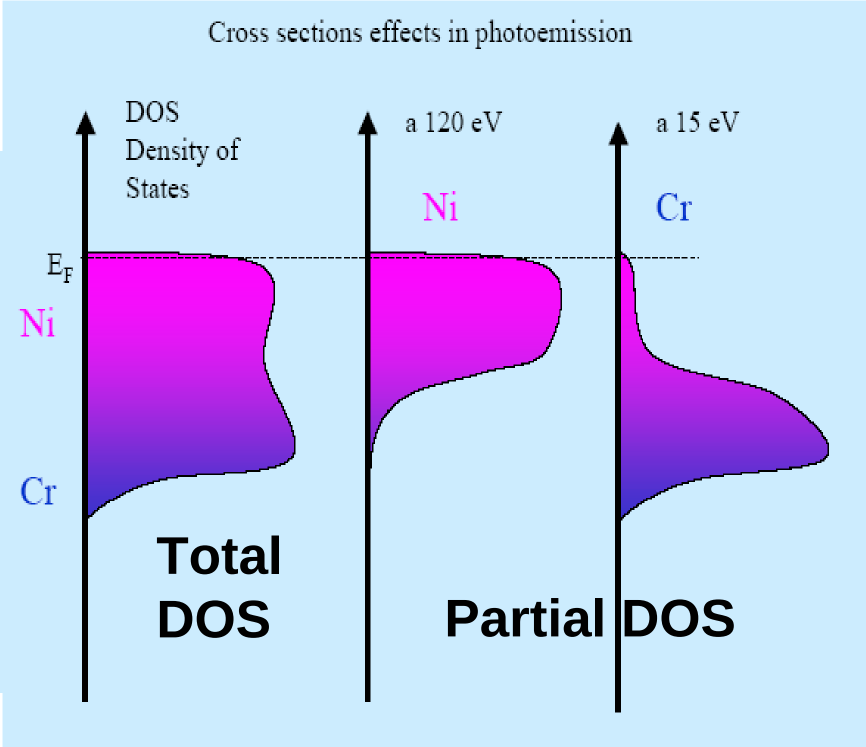
ARPES data of CeSb at 20K obtained by A-1 #0001
Measured by T. Ito, S. Kimura and H. Kitazawa at UVSOR, IMS

Why SR PES? (3) cross section

photon energy dependence of photoionization cross section of TM *valence* electron

(cf. core)





Prof. Lucio Braicovich

Why SR PES? (4) resonance effect

photoionization cross section

= photoabsorption cross section

element-specific photoionization cross section

= core excitation cross section

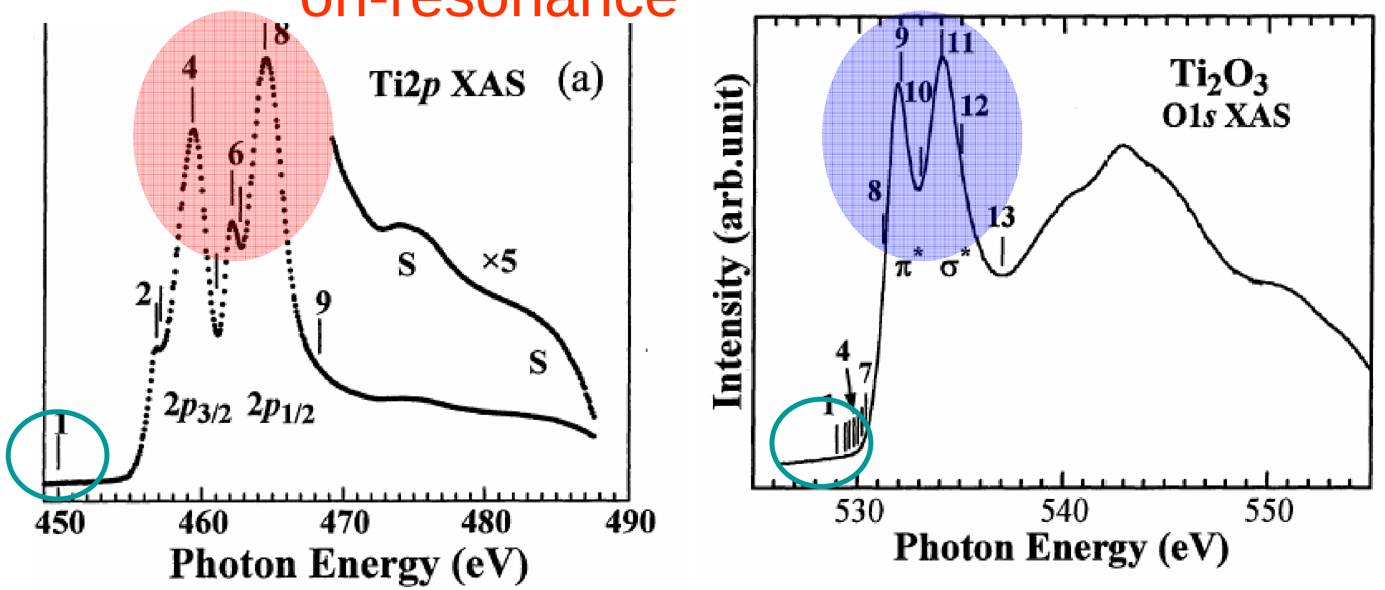
core-to-unoccupied state excitation

= X-ray Absorption Spectroscopy (XAS)

Why SR PES? (4) resonance effect

Ti2p and O1s XAS of Ti_2O_3

on-resonance

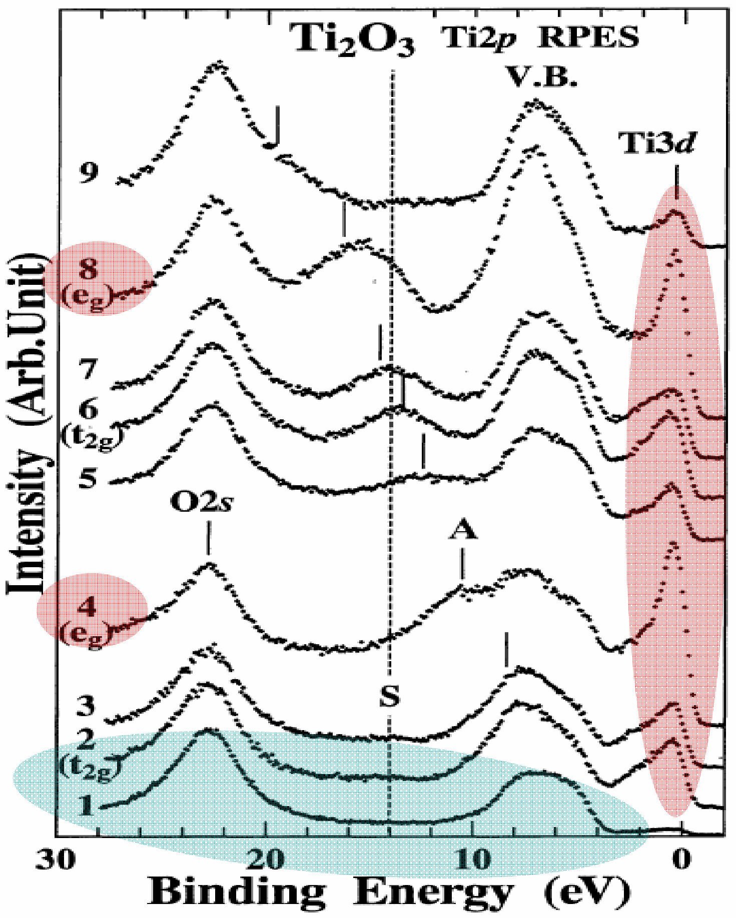


off(non)-resonance

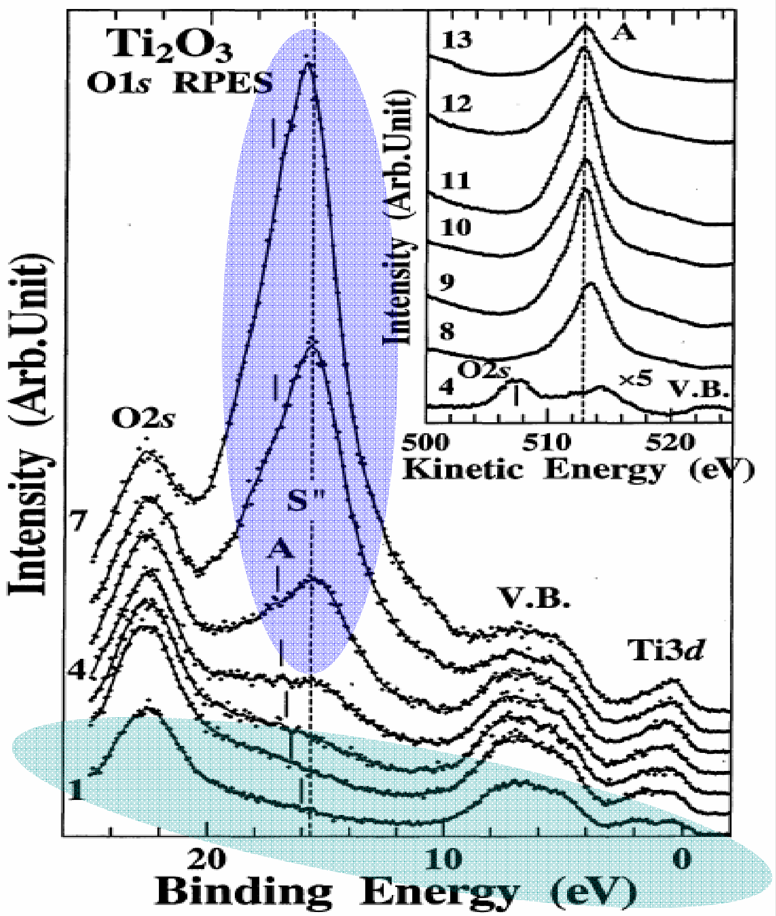
Y. Tezuka et al. JPSJ 66(1997)3153

Why SR PES? (4) resonance effect

Ti 2p resonance

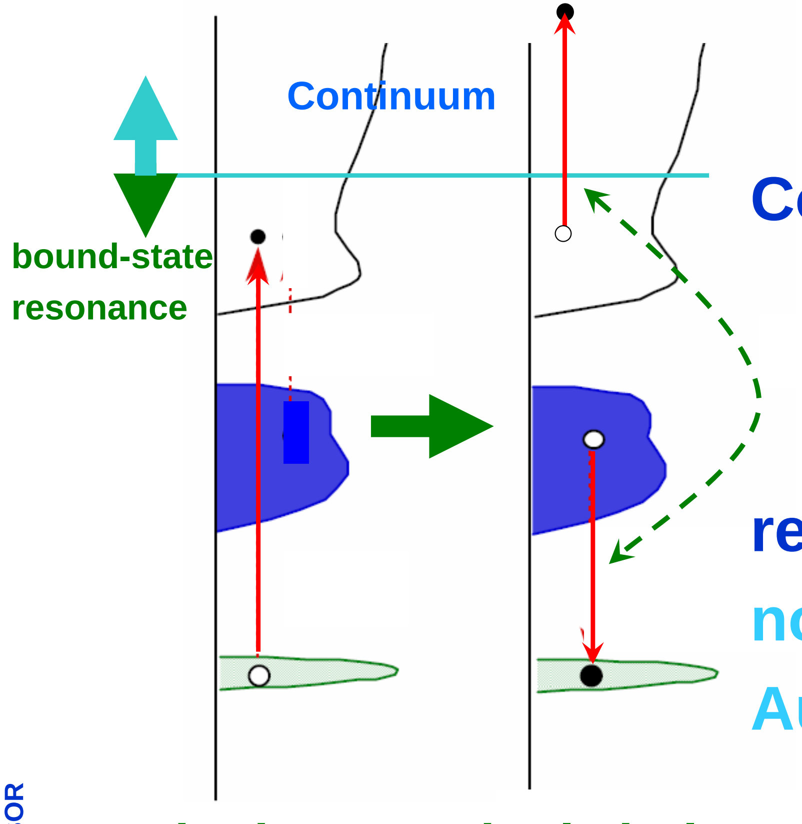


O 1s resonance



Y. Tezuka et al. JPSJ 66(1997)3153

resonant photoemission [1h]



Coulomb decay

intra-atomic

>> interatomic

resonant Auger

non-radiative Raman

Auger-Raman

excitation | **single hole** (*same final state as in non-resonant PES*)

[1h1e] | **[1h]**

linear dependence on hν | **constant BE**

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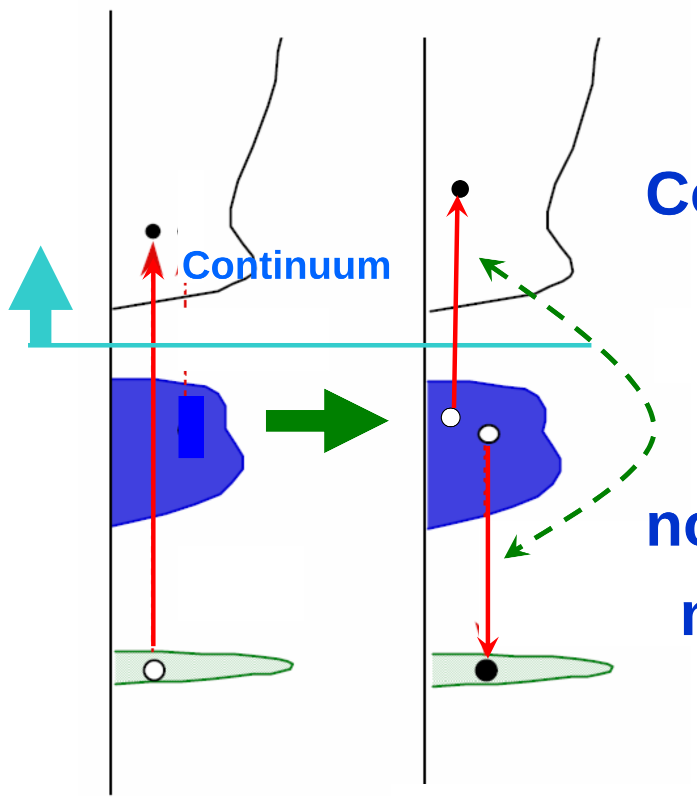
normal Auger decay [2h]



Coulomb decay

intra-atomic

>> interatomic

non-resonant Auger

normal Auger

ionization **[1h]**

double hole **[2h]** (*independent of hν above ionization threshold*)

constant KE

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Why SR PES?

photon energy dependence

wide tunability of SR

(1) escape depth (core, valence)

(2) energy band dispersion (valence)

(3) cross section (valence)

(4) resonance effect (core)

high energy resolution

BE=hν - KE

very high brightness of insertion device SR

very high collimation of insertion device SR

Future of SR PES?

high level polarization

high flexibility of insertion device SR

linear and circular (or elliptical)

high space resolution

~ 10nm combined with PEEM, …

high time resolution

~100fs combined with fs laser, …

coherence

long undulator

free electron laser or other types of laser

nonlinear phenomena

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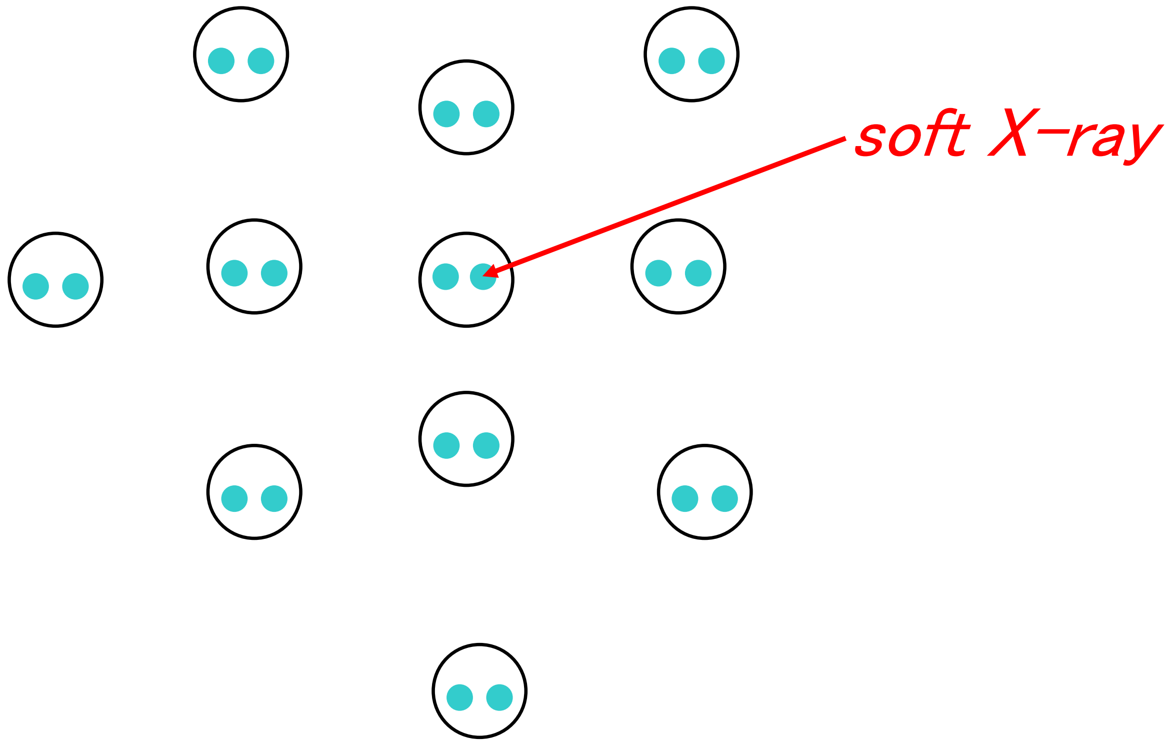
Photoemission 1

Some Topics

TOPIC 1

PES of Kr clusters

photoemission in cluster/solid



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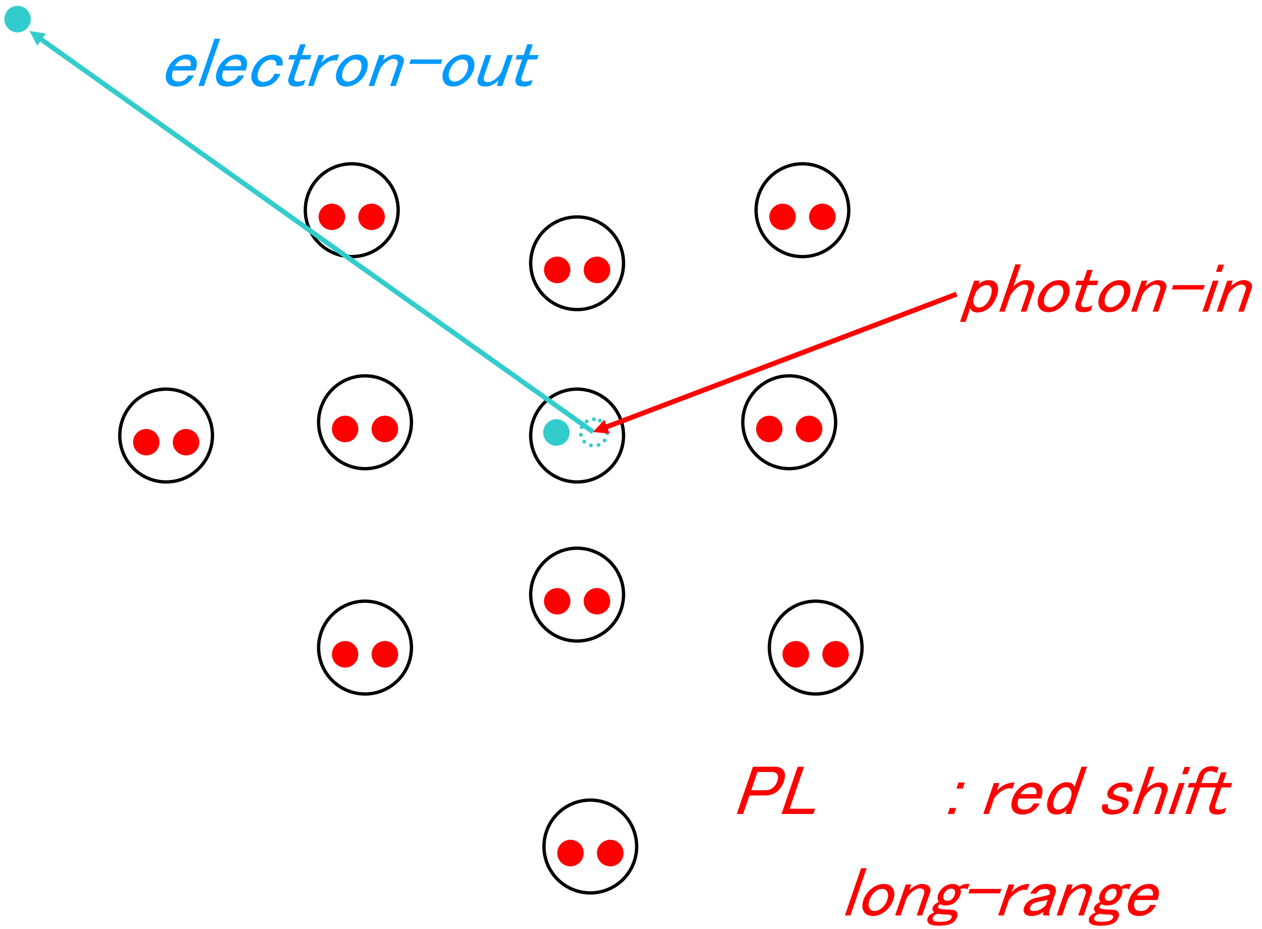
photoemission in cluster/solid



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Kr 3d photoelectron spectra of Kr clusters

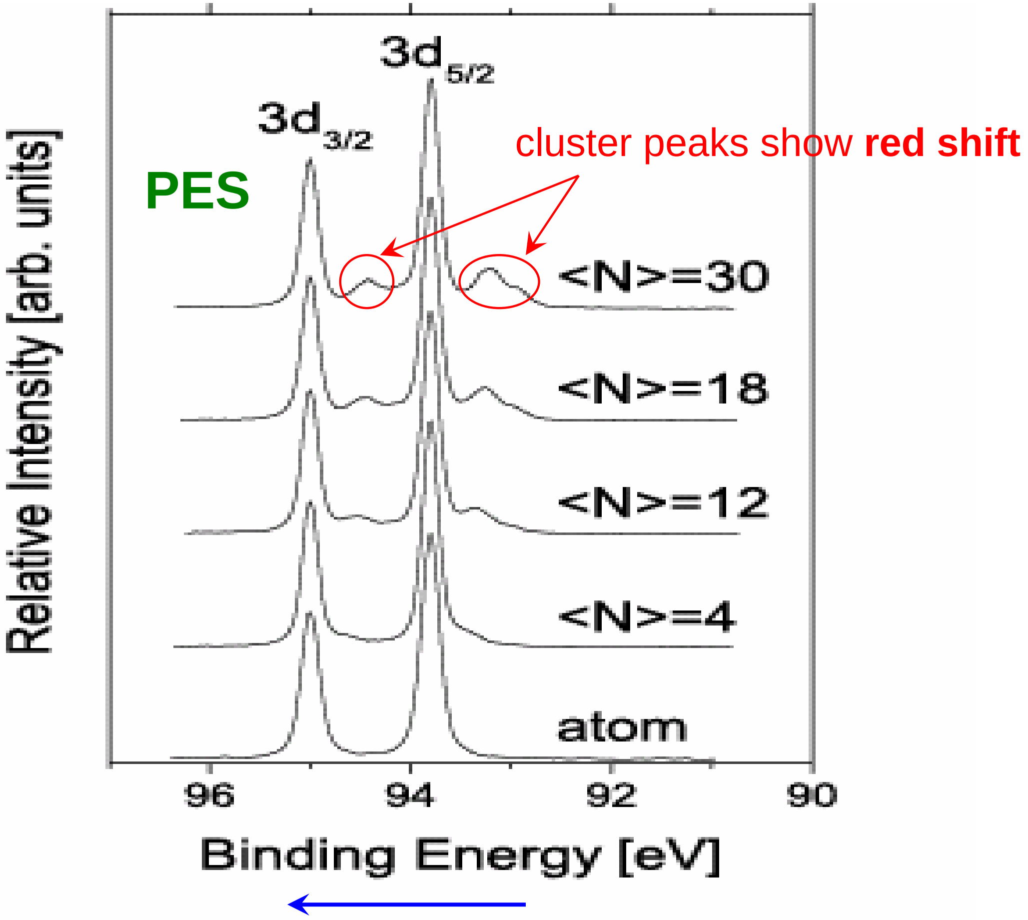

FIG. 1: Comparison of Kr 3d photoelectron spectra of atomic Kr and from a cluster jet, where the average cluster size < N > of Kr clusters is varied between < N > = 4 and < N > = 30.

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Kr 3d peak shift of Kr clusters

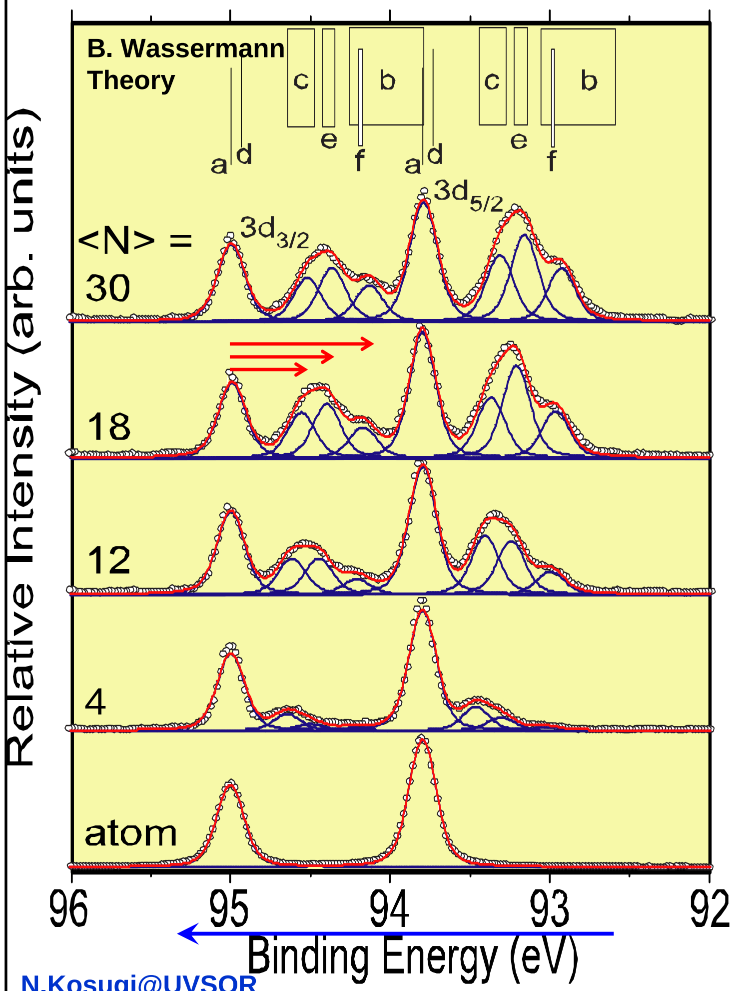

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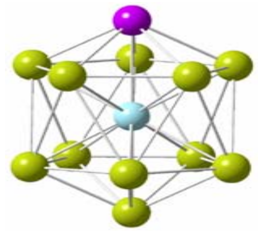
TABLE I: Experimental shifts of the Kr 3d ionization energies relative to the atomic values in meV, as obtained from spectral de-convolutions (see Fig. 2) and plausible assignments (see text). The values in parentheses correspond to the relative intensities of the photoelectron bands of clusters. Averaged values for both spin-orbit components are given. The error limits are estimated to be ± 10 meV

<N>	dimer	corner	edge	face/bulk	
4	-1 (77%)	-334 (14%)	-479 (7%)	-766 (2%)	
12	-2 (52%)	-400 (22%)	-553 (18%)	-792 (8%)	1
18	-4 (42%)	-458 (19%)	-591 (26%)	-818 (13%)	2
30	-5 (41%)	-491 (18%)	-645 (24%)	-874 (16%)	



T.Hatsui, H.Setoyama, N. Kosugi, B.Wassermann, I.L.Bradeanu, E.Rühl, JCP**123** (2005)154304

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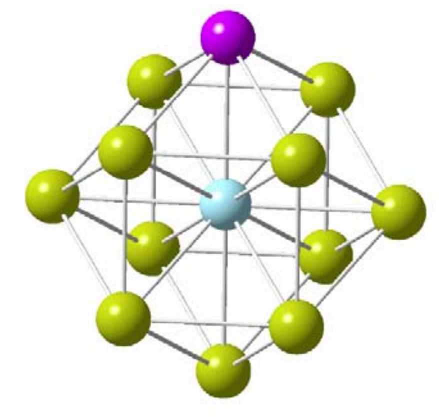
TOPIC 2

PES of Ne clusters

Nonpolar Ne cluster

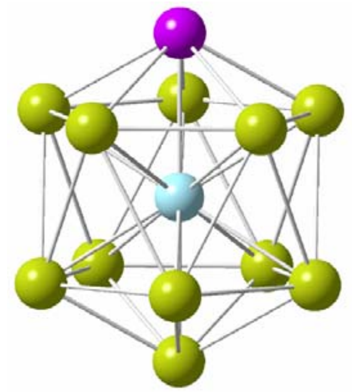
EDGE(5)



bulk(12)

fcc

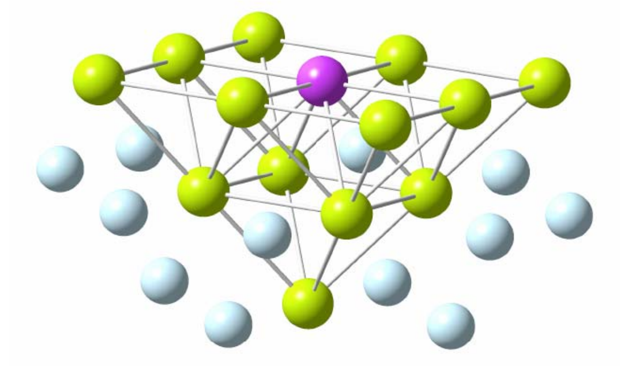
EDGE(6)



bulk(12)

icosahedron

FACE(13)



bulk(18)

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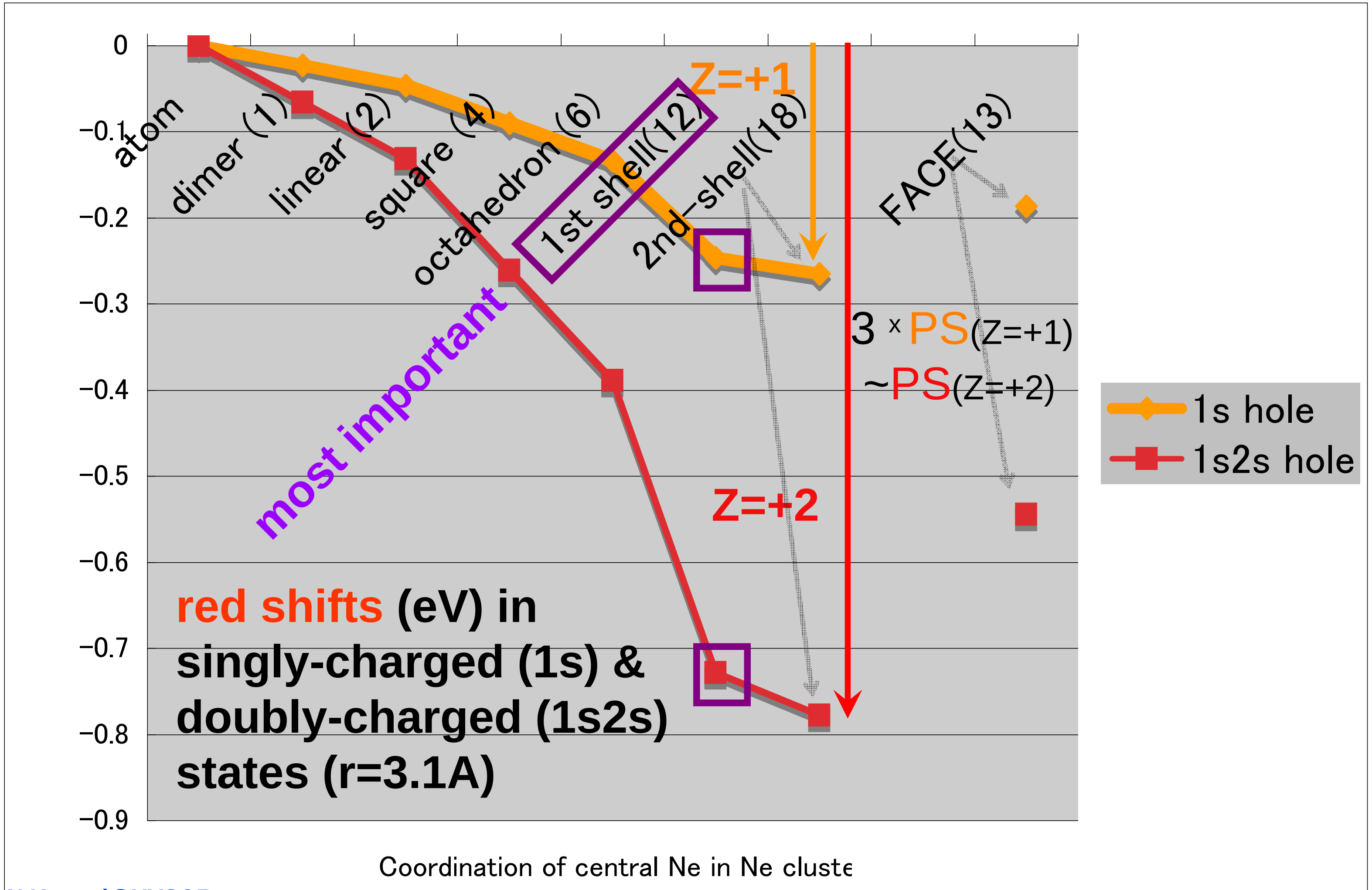
Z=+1/Z=+2 nonpolar (Ne cluster)



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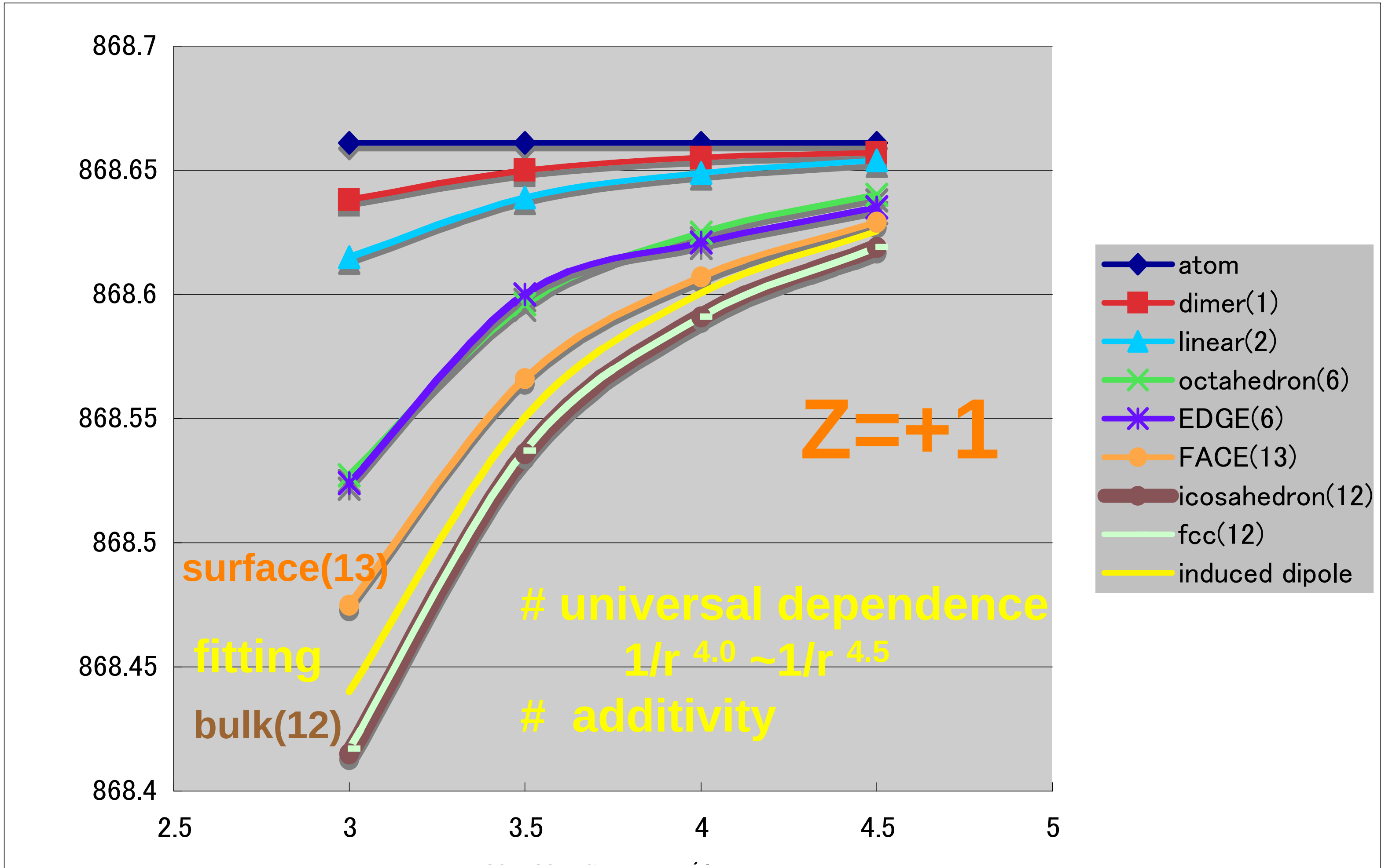
Z=+1 nonpolar (Ne cluster)



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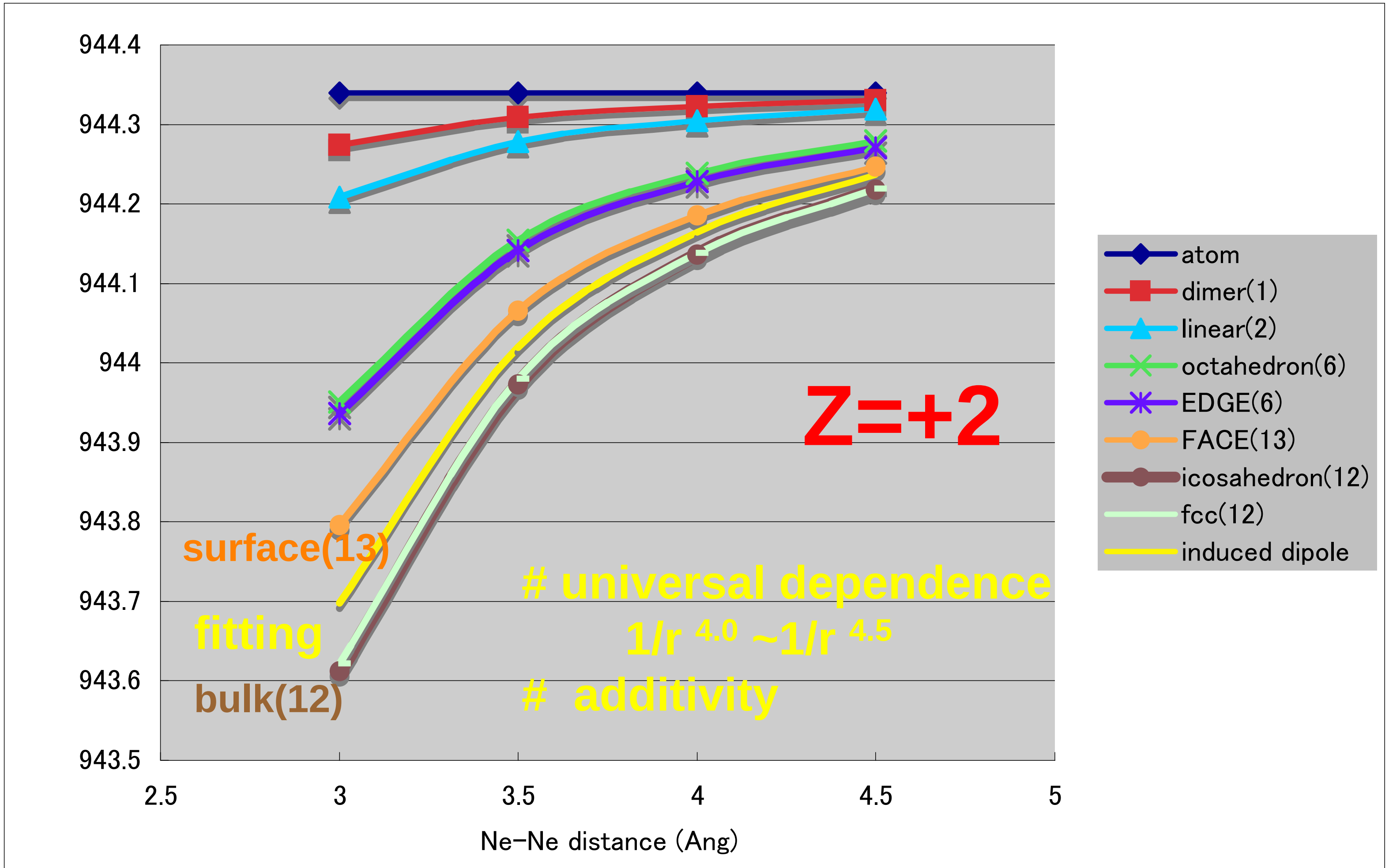
r-dependence in red shift in Ne^{+}(1s)

Z=+2 nonpolar (Ne cluster)



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r-dependence in red shift in Ne^{++}(1s2s)

Z=+1/Z=+2 nonpolar (Ne cluster)

HF calculation (partly MP2)

$\propto - q^{\sim 2} \Sigma_r (1/ r^{\sim 4})$

Induced Dipole

$\propto - N q^2 / r^4$

fcc&icosahedron, surf.&bulk
95% converged at N~2000

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Z=+1 nonpolar (Ne cluster)

Extrapolation from icosahedron
to **N~2000** (bulk, surface)

assuming induced dipole-like dependence ($1/r^4$)

	icosahedron	: surface (face)	: bulk (fcc, icosahedron)
	1	: **1.2**	: **1.9**
Ne^+ (1s)	**0.27 eV**	: **0.33 eV**	: **0.52 eV**

$\Delta E_{sb}(E_{th})$ = **0.19 eV**

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Z=+1 nonpolar (Ne cluster)

VOLUME 93, NUMBER 17 PHYSICAL REVIEW LETTERS week ending 22 OCTOBER 2004

Femtosecond Interatomic Coulombic Decay in Free Neon Clusters: Large Lifetime Differences between Surface and Bulk

G. Öhrwall,[1,*] M. Tchaplyguine,[1,2] M. Lundwall,[1] R. Feifel,[1,†] H. Bergersen,[1] T. Rander,[1] A. Lindblad,[1] J. Schulz,[2] S. Peredkov,[3] S. Barth,[4] S. Marburger,[4] U. Hergenhahn,[4] S. Svensson,[1] and O. Björneholm[1]

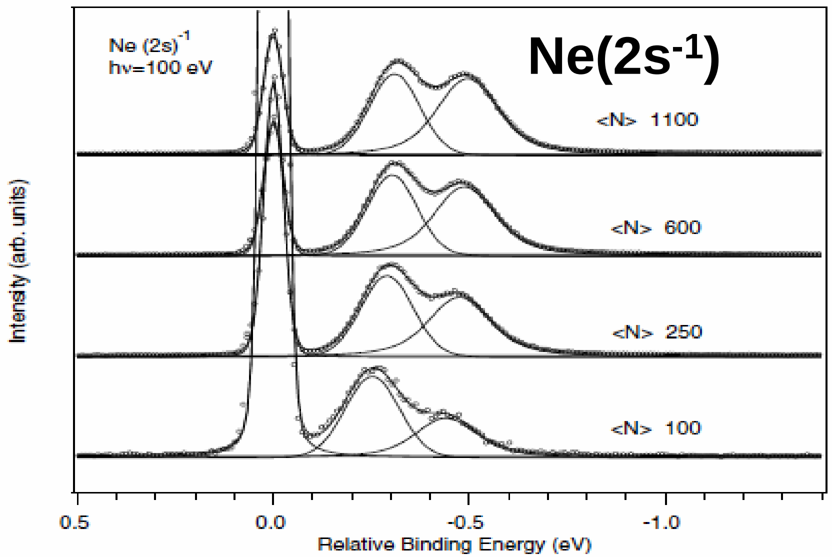

FIG. 3. Photoelectron spectra of the Ne 2s level for clusters of varying sizes, recorded with an experimental resolution of 50 meV. The spectra have been normalized to give the cluster feature at higher binding energy the same intensity. The lower binding energy peak increases with increasing size, indicating that it originates from interior atoms. The cluster features also shift to lower binding energy with increasing size.

$\langle N \rangle$	ΔE_{as}	ΔE_{sb}
100	−253	−189
250	−290	−186
600	−304	−185
900	−307	−187
1100	−310	−186

$\Delta E_{as} \gtrsim 0.3$ eV
$\Delta E_{ab} \gtrsim 0.5$ eV
slowly convenged

$\Delta E_{sb} \sim 0.19$ eV
almost constant

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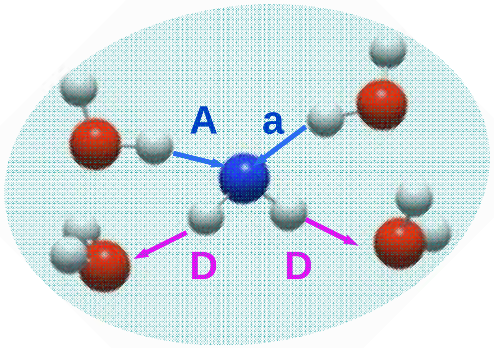
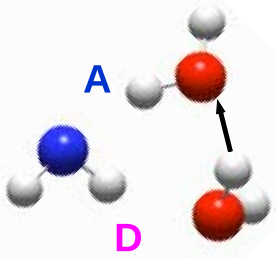
TOPIC 3

PES of liquid water

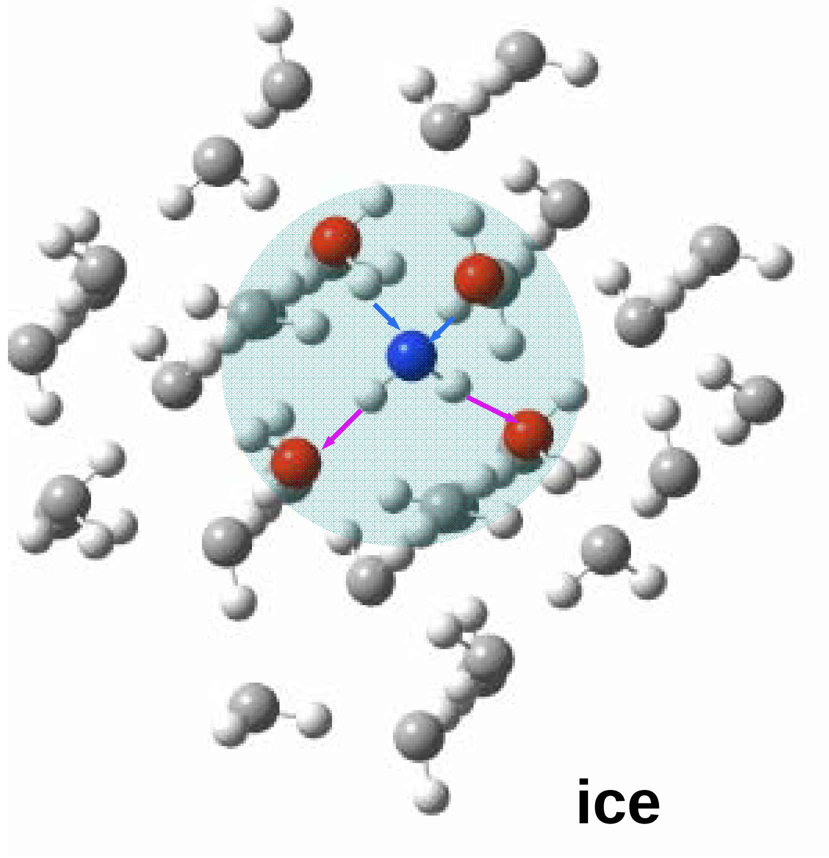
nearest neighbor H_2O structure



DD(Aa)



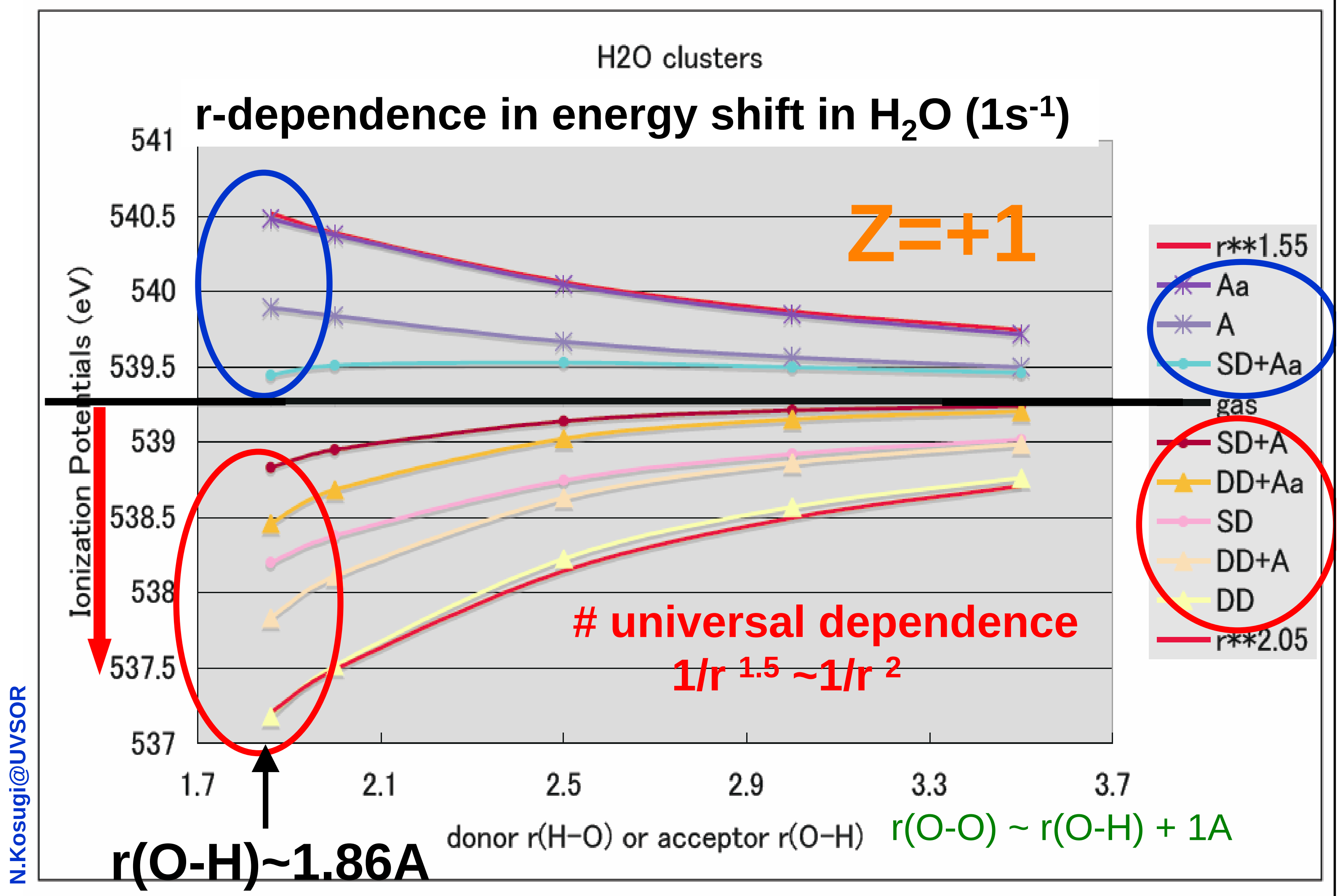
SD(A)



r(O-H)~1.86A

nearest neighbors are most important

$Z=+1$ polar (H_2O cluster)

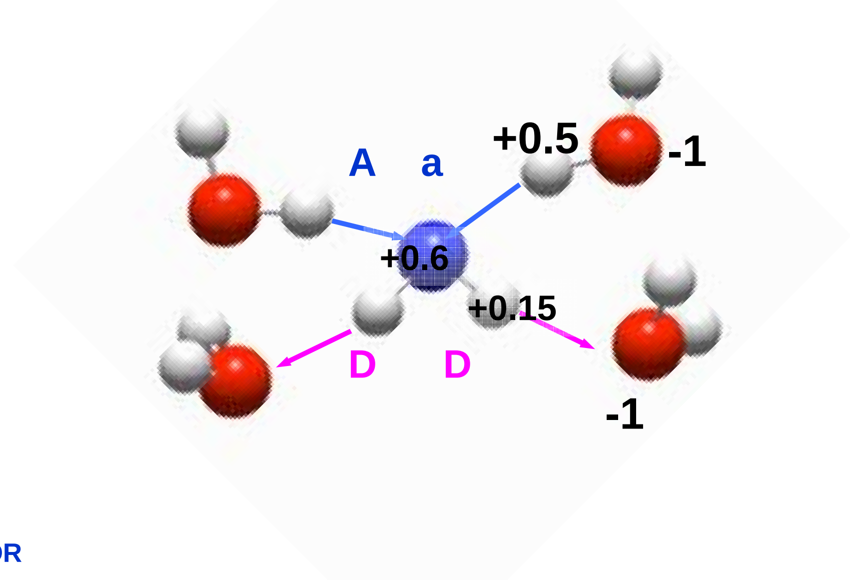


Z=+1 polar (H_2O cluster)

Why blue shift by A & red shift by D ?

point charge fitting to ES potential (CI)

neutral	O(-1.10)	H(+0.55)	
ionized	O(-0.50)	H(+0.70)	0.05e$^-$ from O(D)
Δ	+0.6	+0.15	



Z=+1 polar (H_2O cluster)

point charge - permanent dipole

$\propto q\mu \cos\Theta / r^2$

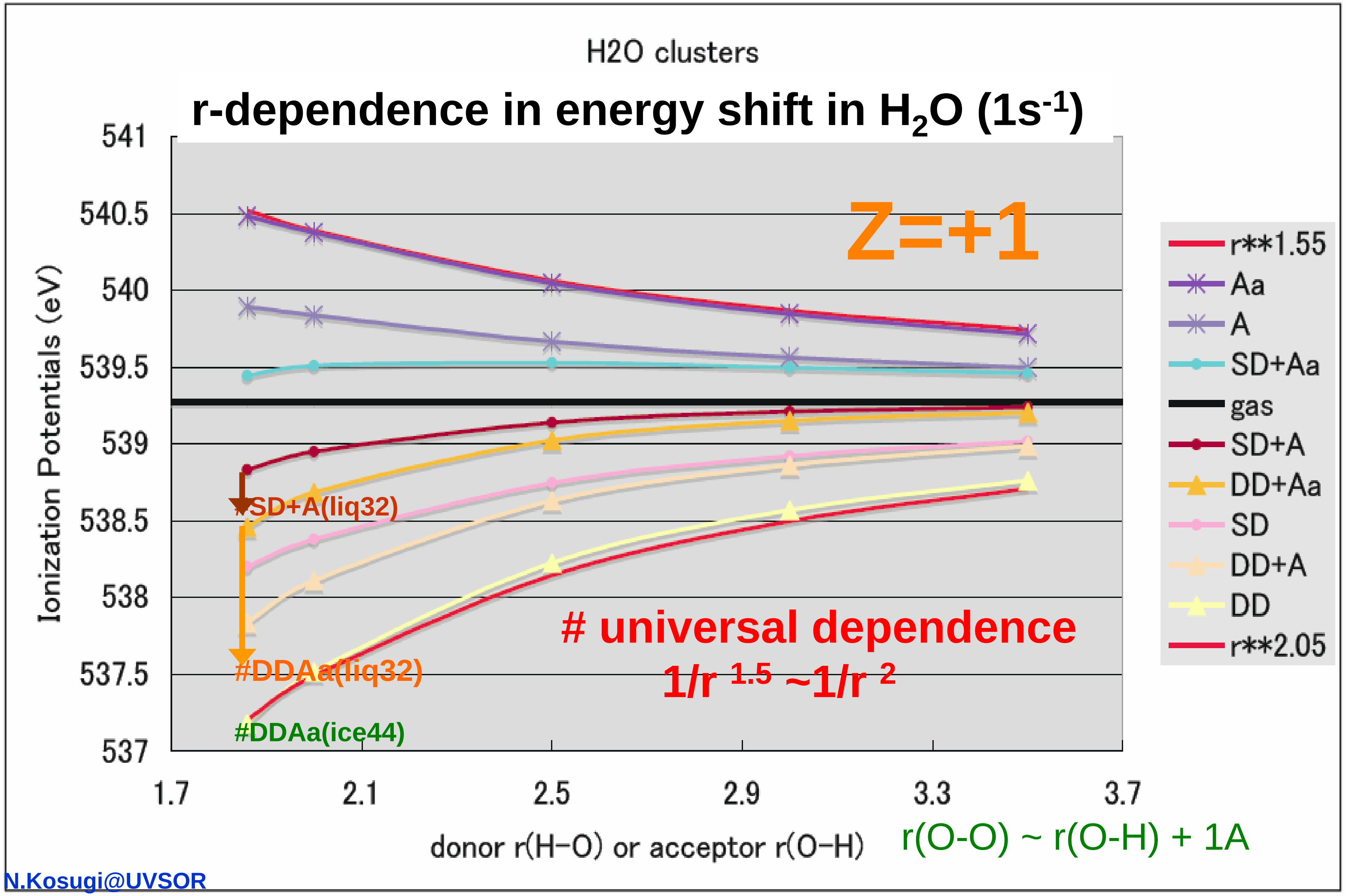
HF calculation (partly MP2)

$\propto -1 / r^{\sim 2}$ for **D**onor site

$\propto +1 / r^{\sim 1.6}$ for **A**cceptor site

Donor is ~2 times as strong as acceptor.

Z=+1 polar (H_2O cluster)



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Z=+1 polar (H_2O cluster)

D(red shift) is stronger than A(blue shift).

SD+A

1*+2	cluster	0.4 eV red shift
1*+31	CPMD	0.9 eV(+/-0.2eV) red shift
1*+>100		>?0.9eV red shift

DD+Aa

1*+4	cluster	0.8 eV red shift
1*+31	CPMD	1.8 eV(+/-0.3eV) red shift
1*+>100		>?1.8 eV red shift
1*+43	ice	2.2 eV red shift

Z=+1 polar (H_2O cluster)

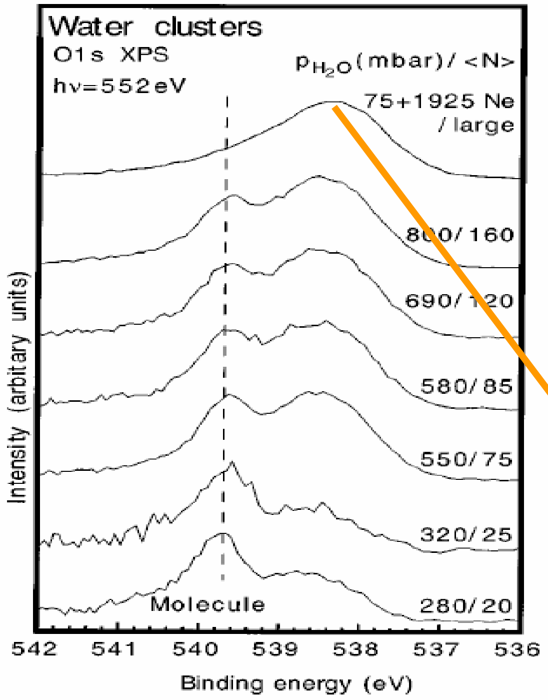
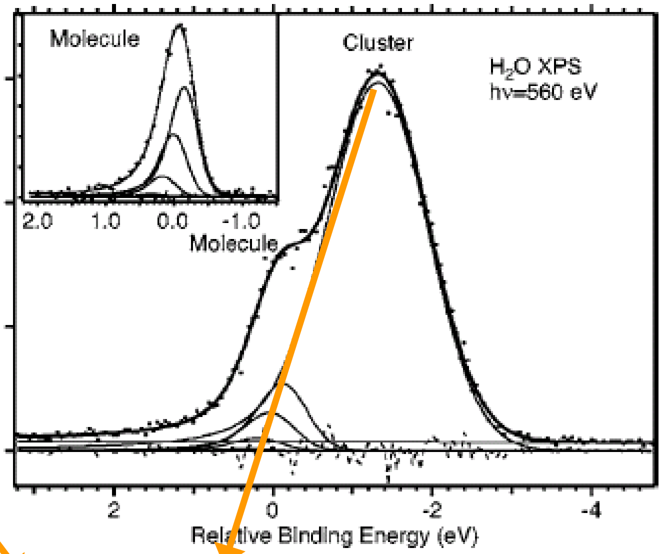


FIG. 1. O1*s* XPS spectra of water clusters produced with various stagnation pressures. The estimated average sizes ⟨*N*⟩ are also indicated. The binding energy of the molecule is indicated by a vertical hatched line.

G. Öhrwall[a] and | J. Chem. Phys. **123**, 054310 (2005)



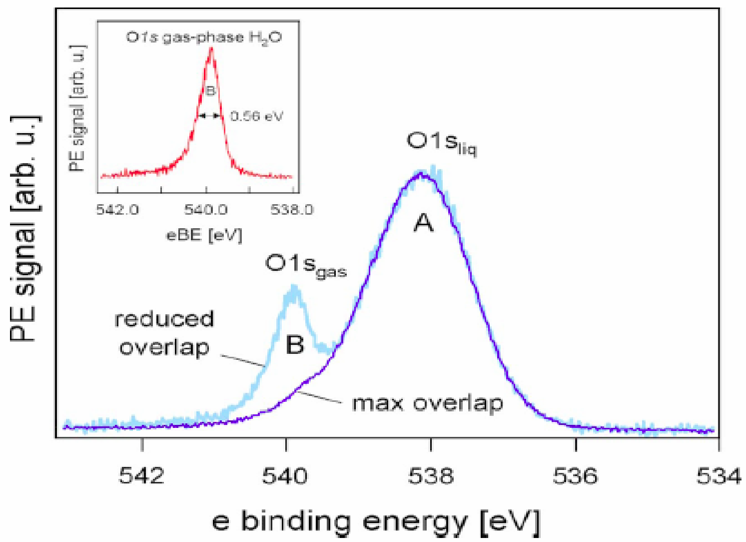
~1.4 eV red shift in cluster

JOURNAL OF CHEMICAL PHYSICS VOLUME 111, NUMBER 2 8 JULY 1999

Between vapor and ice: Free water clusters studied by core level spectroscopy

O. Björneholm,[a] F. Federmann,[b] S. Kakar, and T. Möller

Z=+1 polar (H_2O cluster)



1.77 eV red shift in liquid (surface)

FIG. 1. (Color online) O1*s* PE spectra of liquid water measured at 600 eV photon energy. At maximum overlap between the synchrotron light and the liquid microjet the spectrum almost exclusively contains emission from the liquid phase (peak A at 538.1 eV binding energy). By moving the jet away from the synchrotron beam axis by a few μm, water molecules in both the liquid and gas phases can be simultaneously probed (at lower count rate, though), and the H_2O gas-phase emission (peak B at 539.9 eV) can be used as energy reference. Inset: Spectrum showing component B with negligible liquid-phase contribution, obtained upon further lowering of the liquid jet.

THE JOURNAL OF CHEMICAL PHYSICS 126, 124504 (2007)

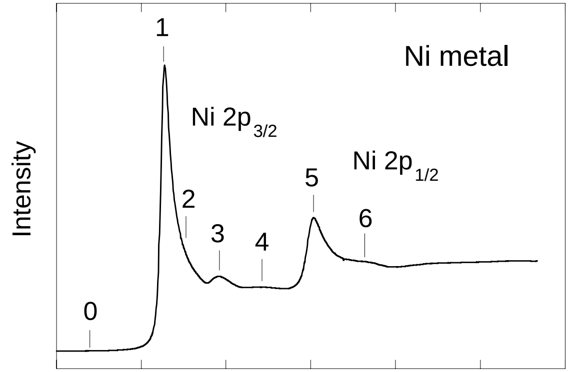
Hydrogen bonds in liquid water studied by photoelectron spectroscopy

Bernd Winter[a)] *Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie,*

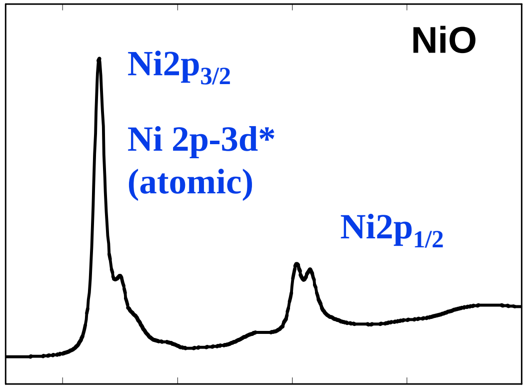
TOPIC 4

Ni 2p resonant PES

Ni2p XAS (resonant absorption)



?



- shoulder structure
  strong correlation
  LMCT shake-up
  multiplet

molecular system

Ni 2p XAS

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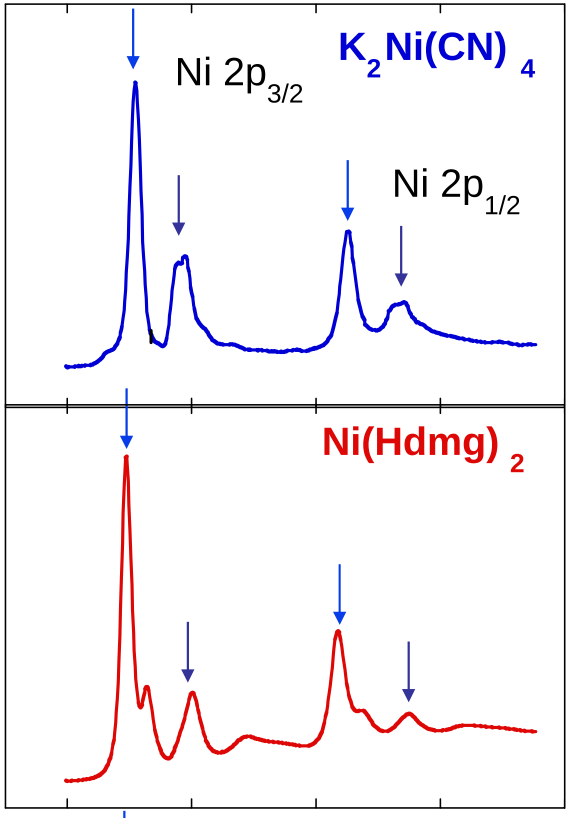
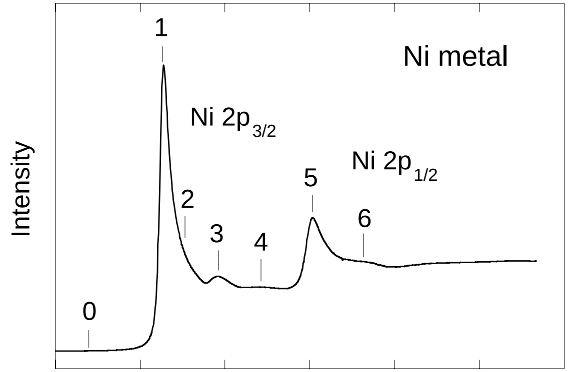
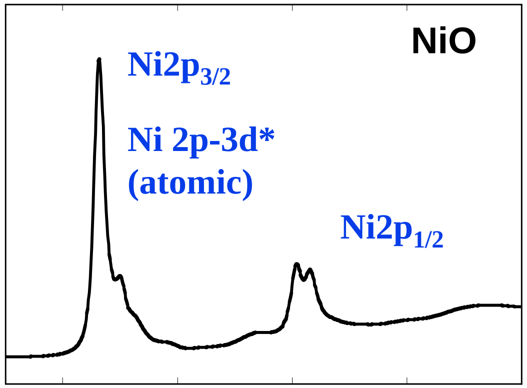
Ni2p XAS (resonant absorption)



molecular system





- shoulder structure
  strong correlation
  LMCT shake-up
  multiplet

Ni 2p XAS

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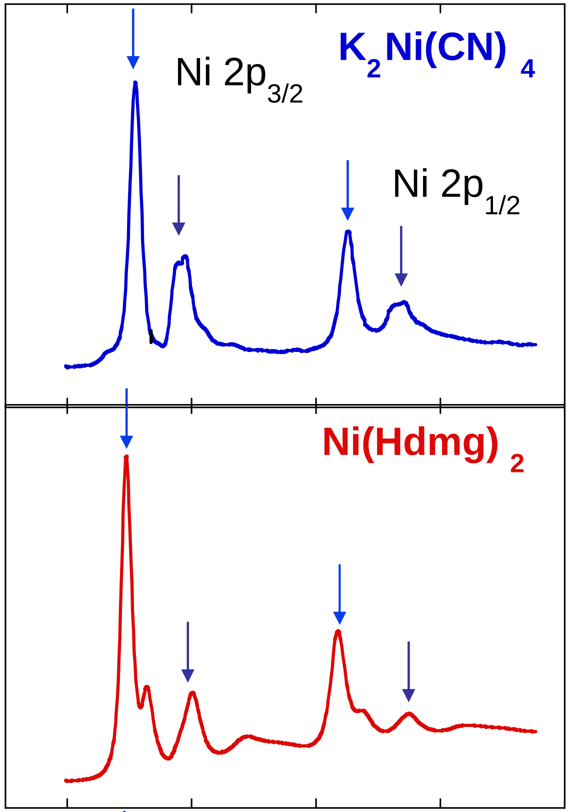
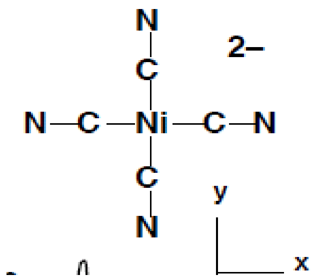
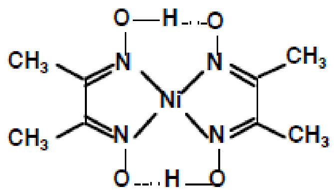
Ni2p XAS (resonant absorption)

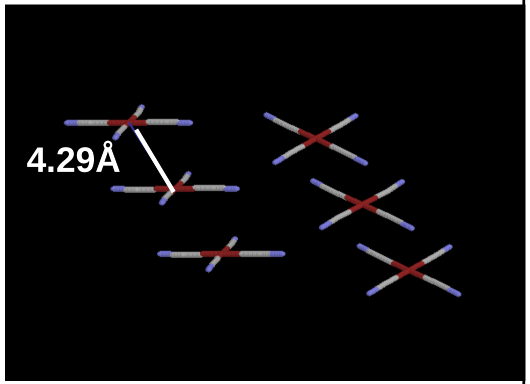


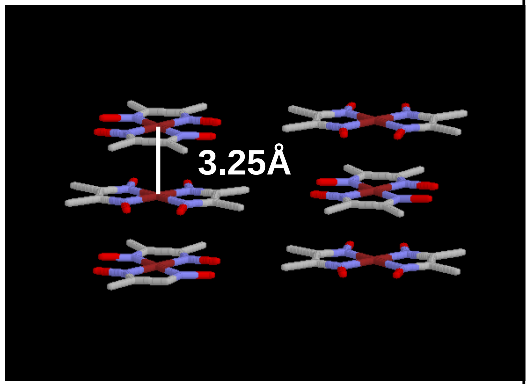


$K_2Ni(CN)_4$: ionic



$Ni(Hdmg)_2$:neutral





molecular system

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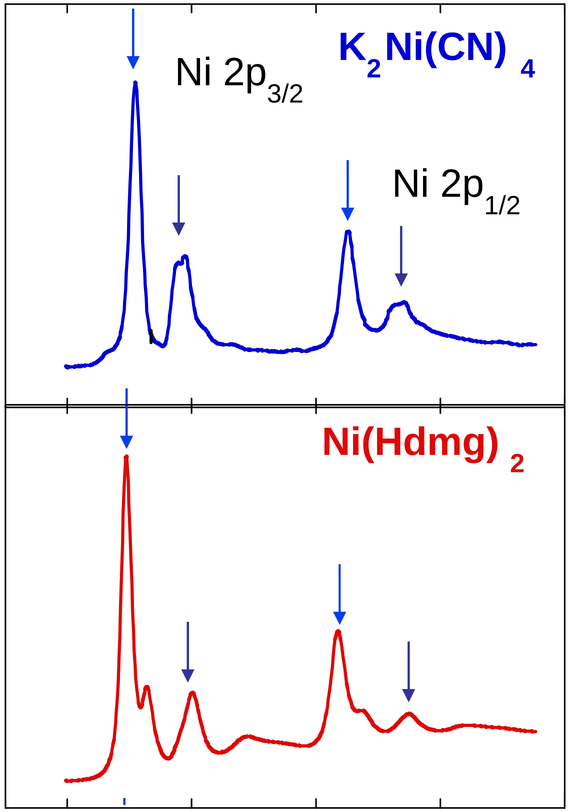
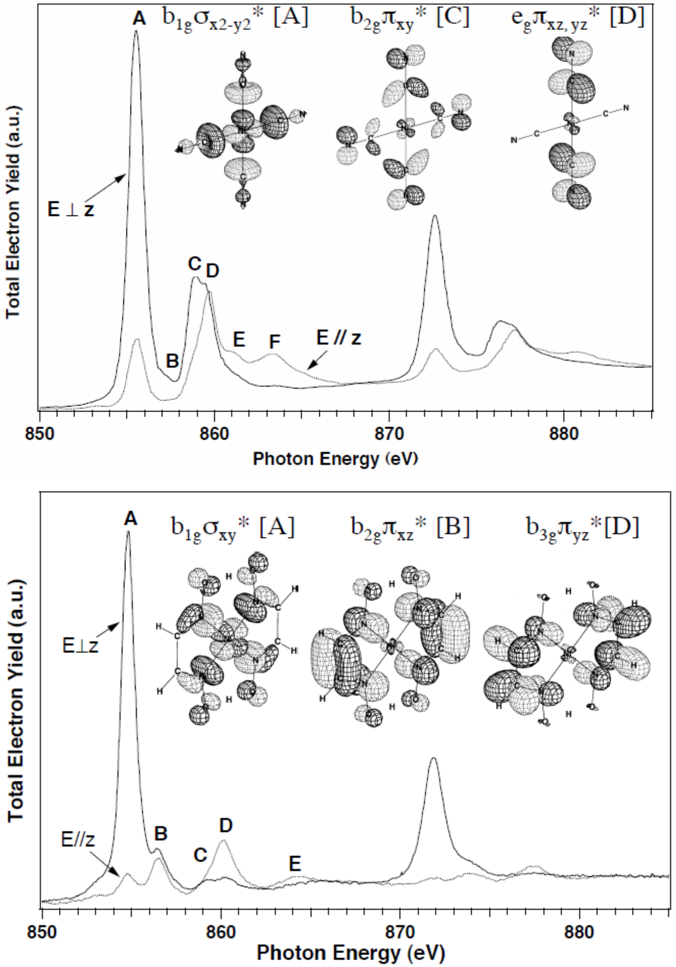
Ni2p XAS (resonant absorption)





- **MLCT**
  (Metal-to-Ligand Charge Transfer)
  covalent interaction
  between ligand π* and Ni 3d

Ni 2p-3d* **(in-plane)**

Ni 2p-linagd* (MLCT) **(in-plane π* & out-of-plane π*)**

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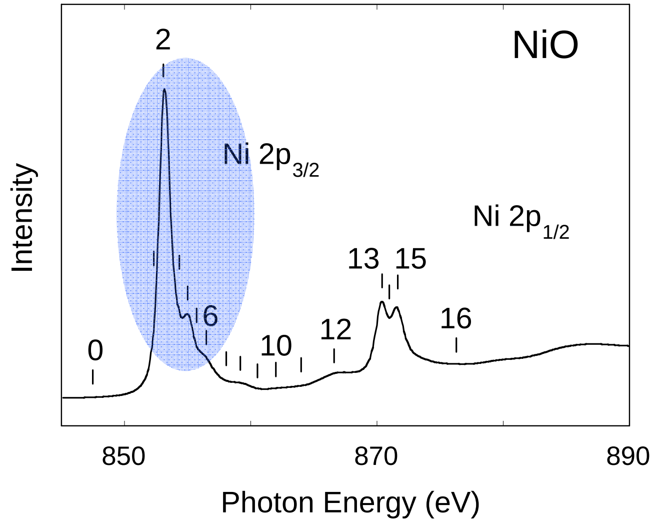
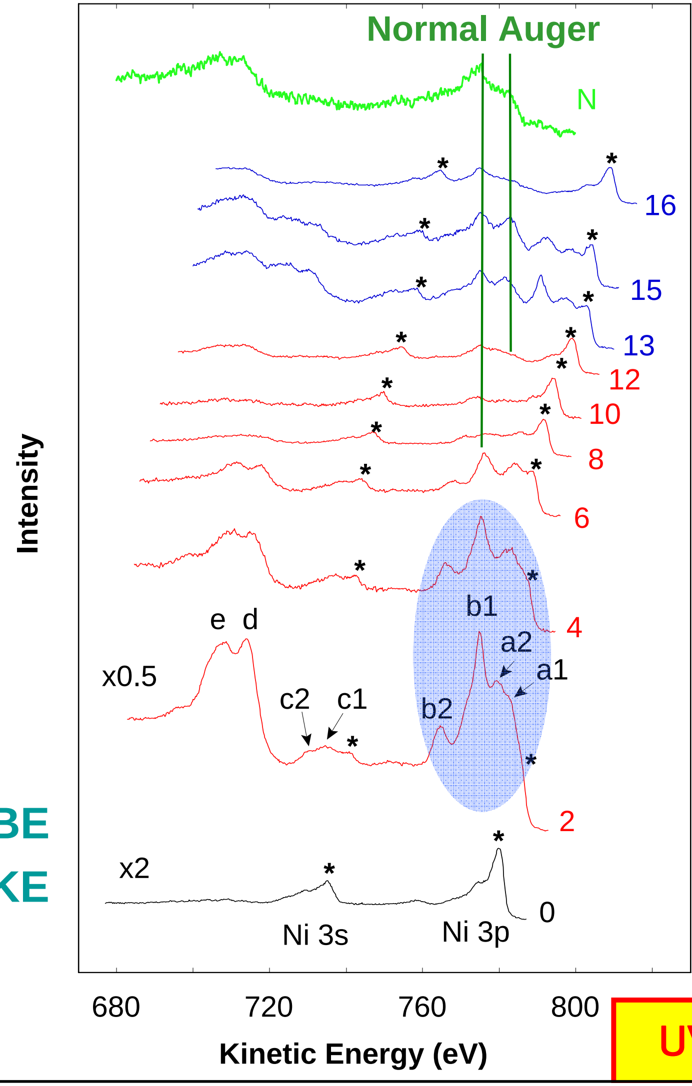
Ni2p resonant PES





correlated system

[1h]single hole **constant BE**

[2h]double hole **constant KE**

& multiplet features

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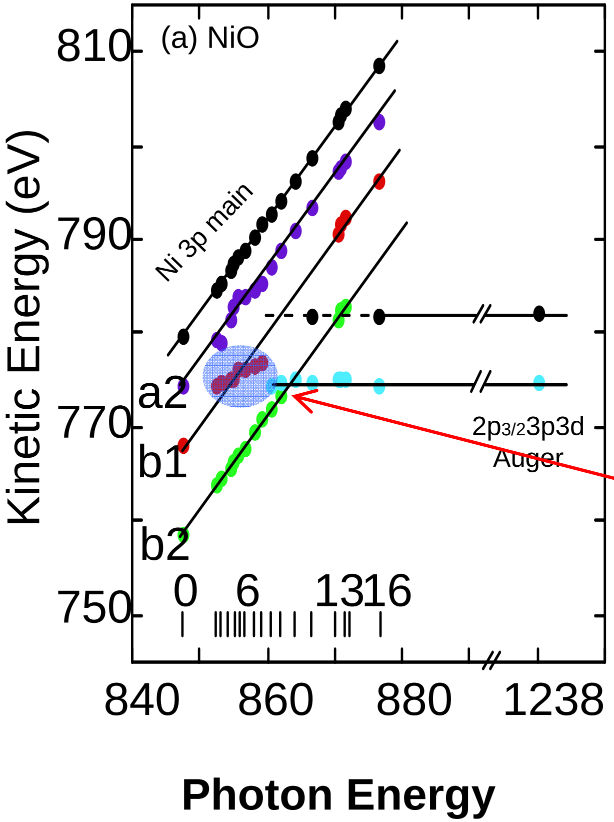
Ni2p resonant PES



[1h]single hole constant BE

[2h]double hole constant KE

&

multiplet features with electron correlation depenedent on hν

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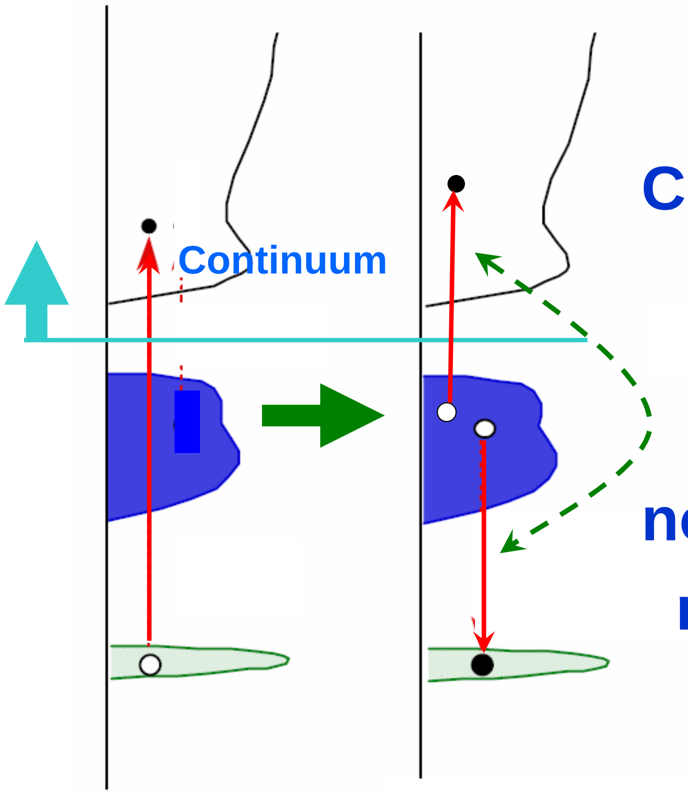
constant KE [2h]



Coulomb decay

intra-atomic

>> interatomic

non-resonant Auger

normal Auger

ionization **[1h]**

double hole ***(independent of hν above ionization threshold)*** **[2h]**

constant KE

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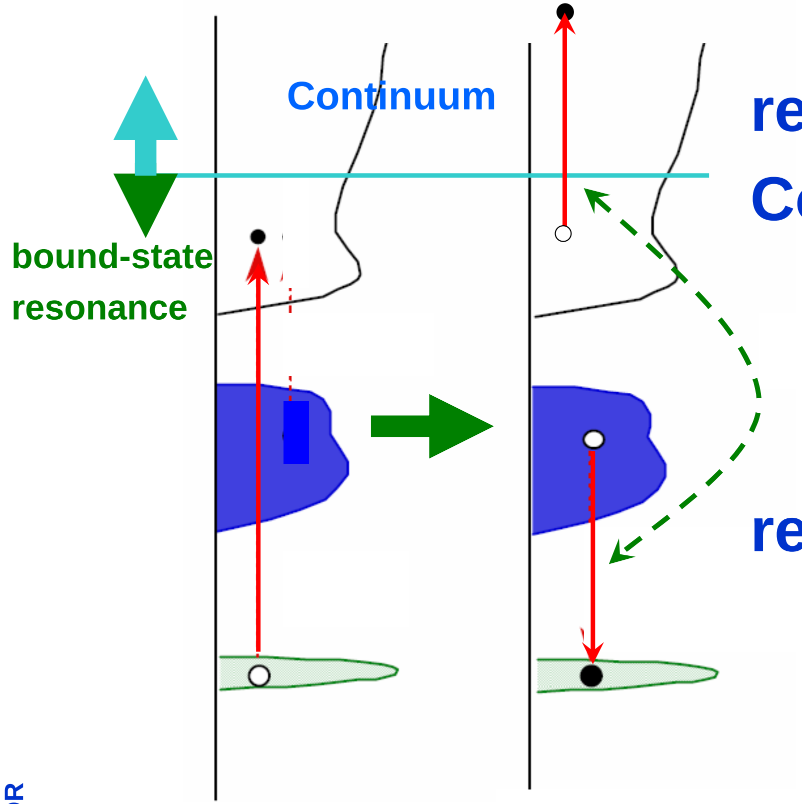
constant BE [1h]



resonant PES

Coulomb decay

intra-atomic

>> interatomic

resonant Auger

excitation | **single hole** (*same final state as in non-resonant PES*)

[1h1e] | **[1h]**

linear dependence on hν | **constant BE**

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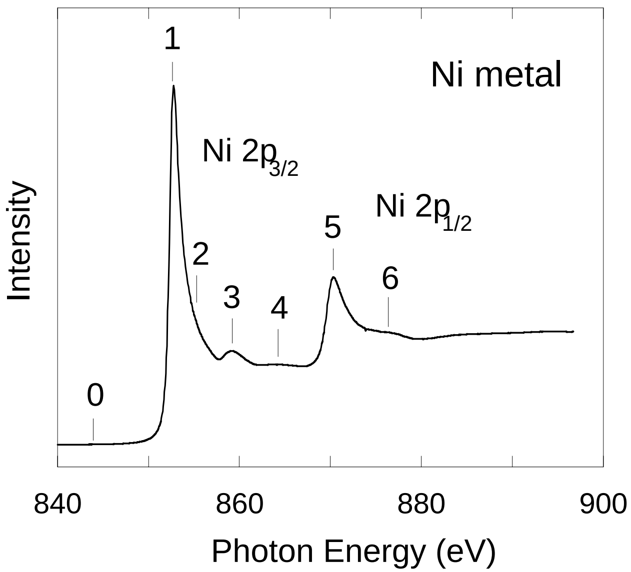
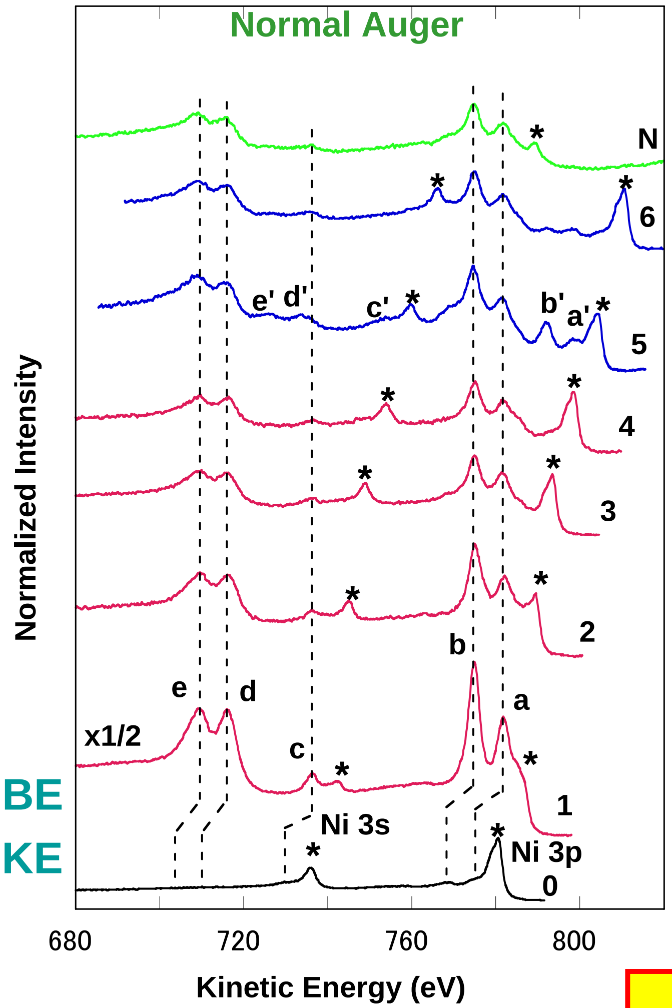
Ni2p resonant PES





metallic system

[1h]single hole constant BE

[2h]double hole constant KE

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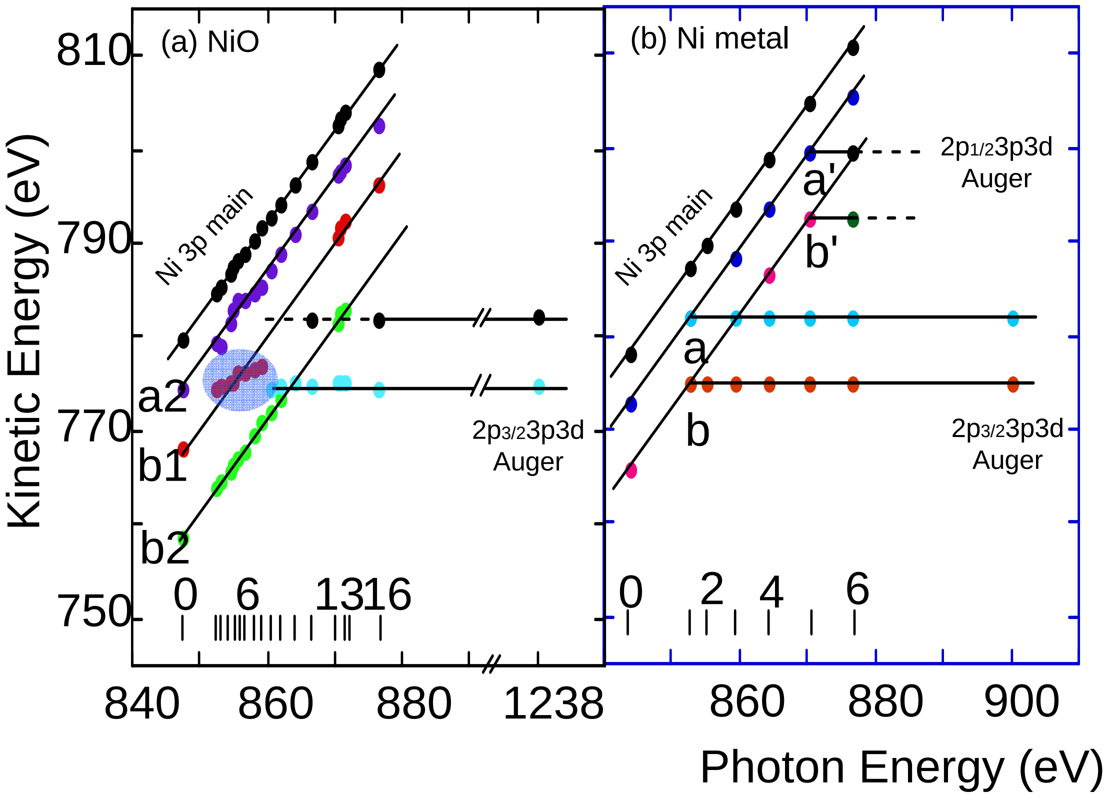
Ni2p resonant PES



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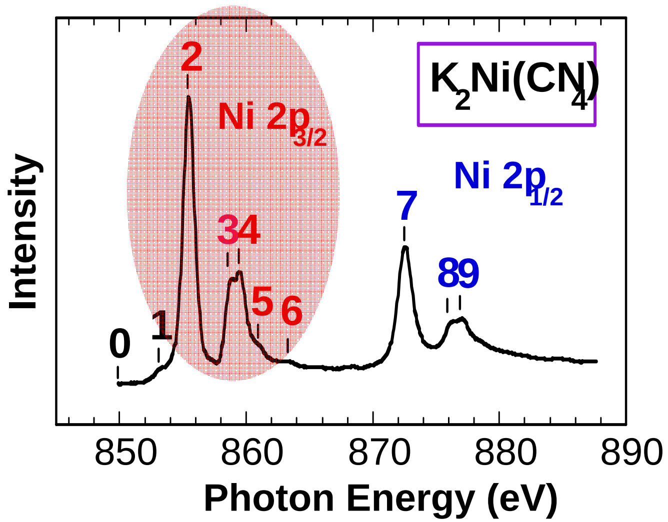
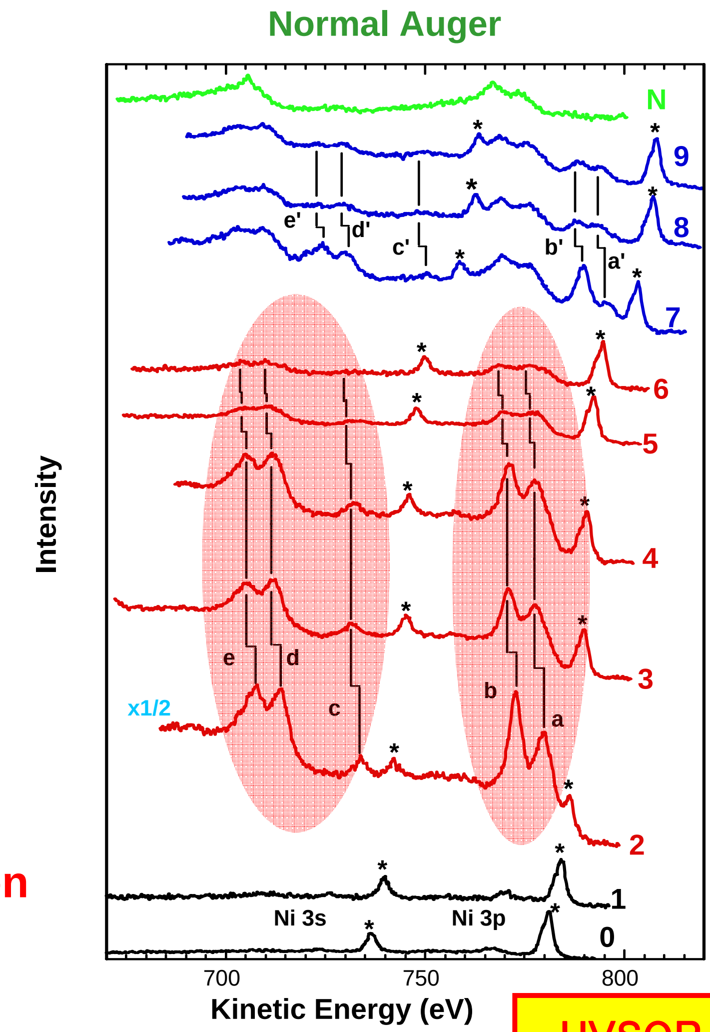
Ni2p resonant PES





molecular system

[1h]single hole constant BE

& an unusual resonance phenomenon
(excitonic feature)

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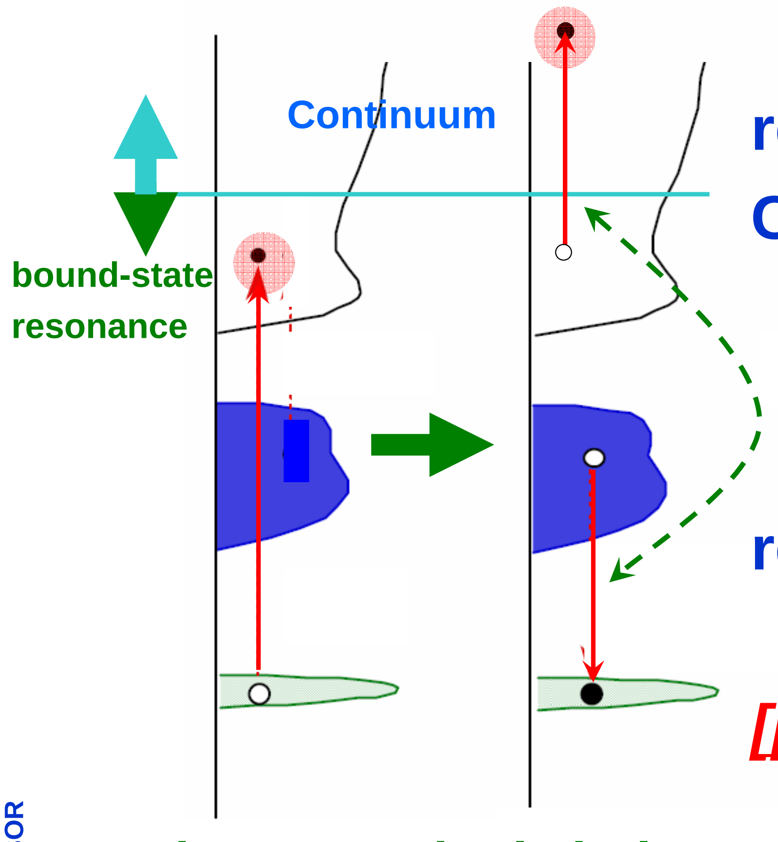
resonant photoemission [1h]-type



resonant photoemission

Coulomb decay

intra-atomic

>> interatomic

resonant Auger

[participant] **Auger decay**

exciton	single hole
[1h1e]	[1h]

(*same final state as in non-resonant PES*)

linear dependence on hν **constant BE**

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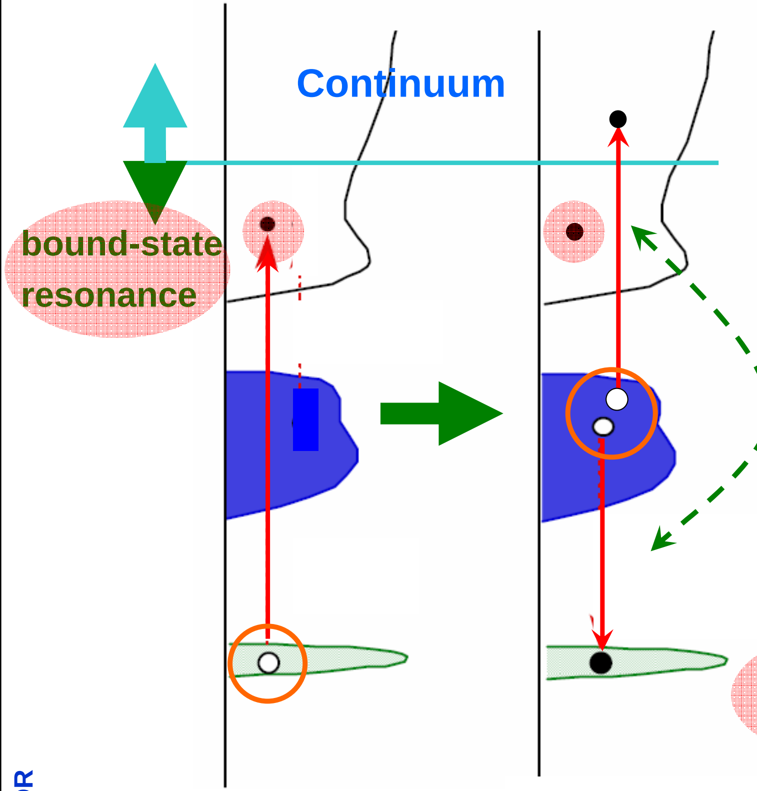
resonant photoemission [2h1e]-type



resonant photoemission

Coulomb decay

intra-atomic

>> interatomic

resonant Auger

[spectator] Auger decay

exciton

[1h1e]

two-hole bound-state

[2h1e]

(*different bound-states dependent on hν*)

UNUSUAL dependence on hν   NOT constant BE&KE

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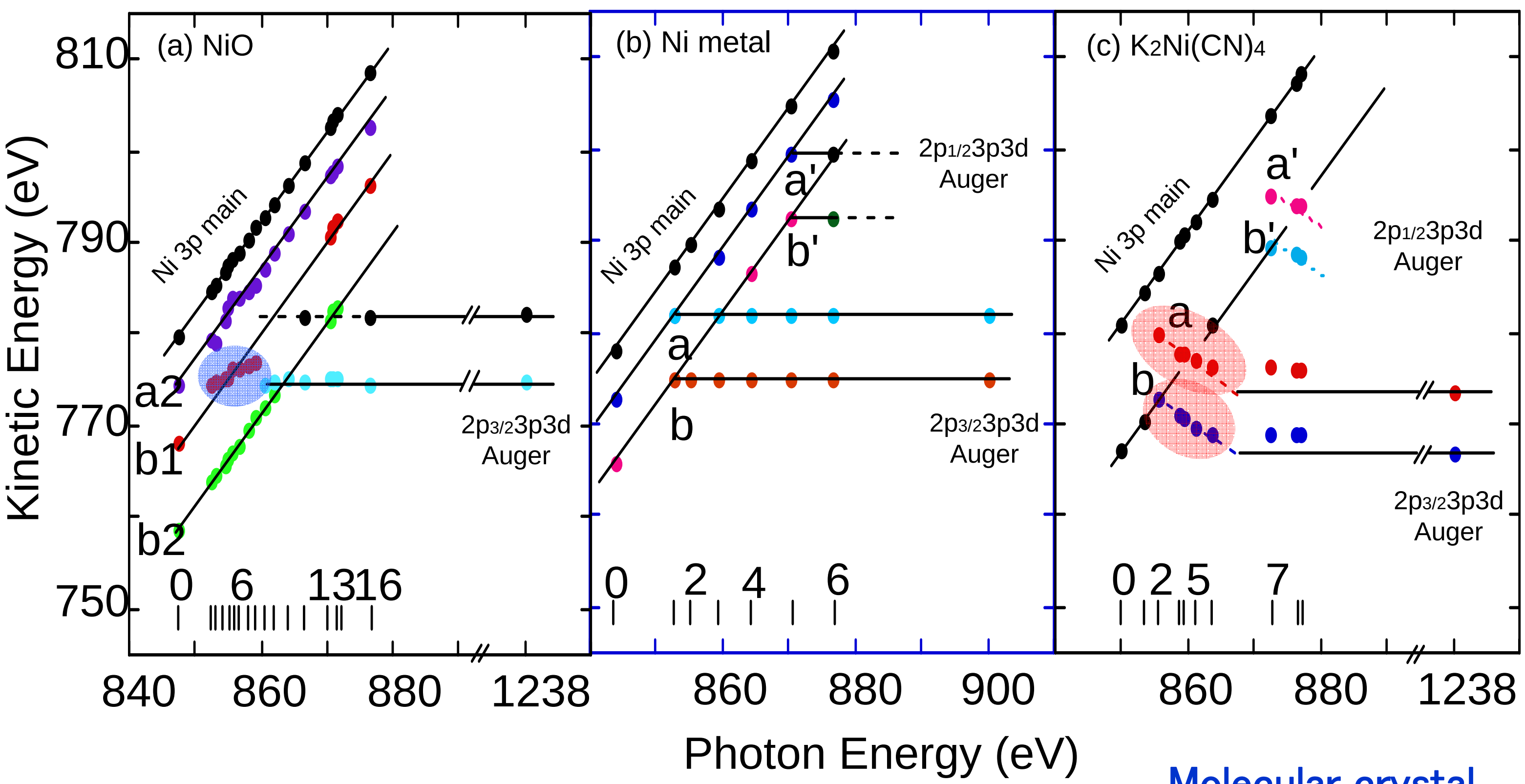
Ni2p resonant PES



Molecular crystal

→ Conducting polymer

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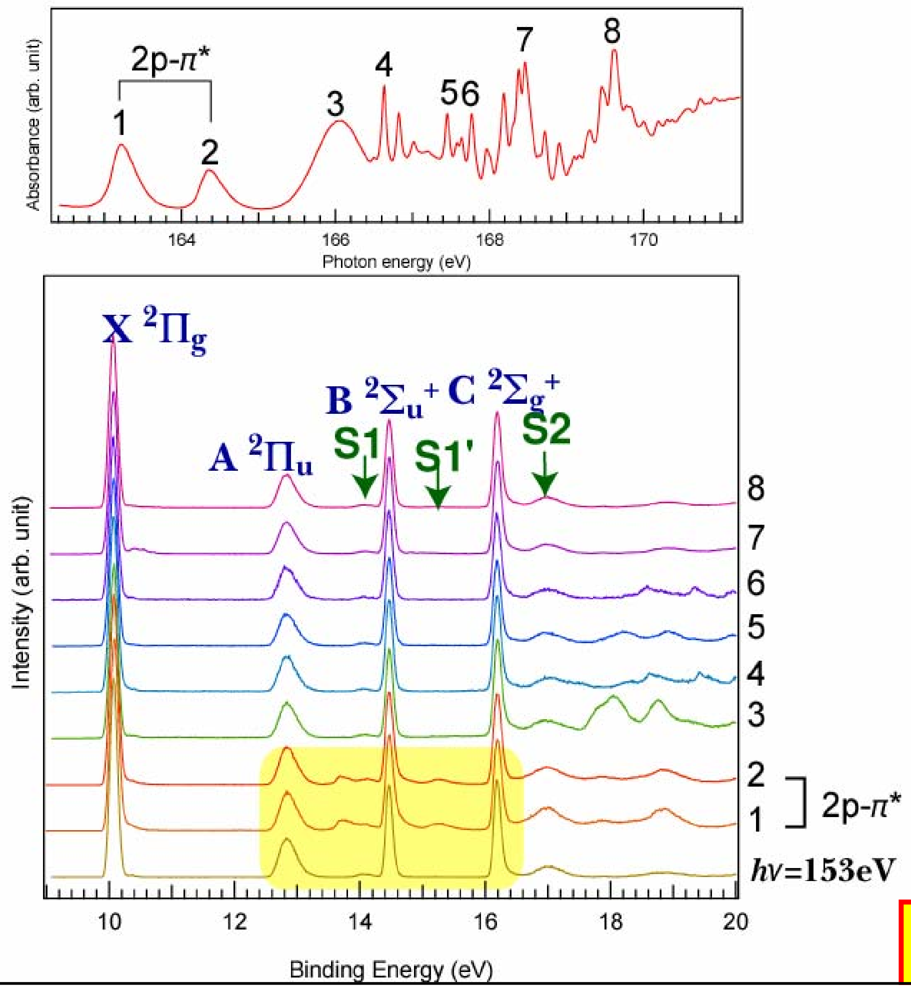
TOPIC 5

S 2p resonant PES

CS_2 S2p resonant PES

S2p XAS

PES



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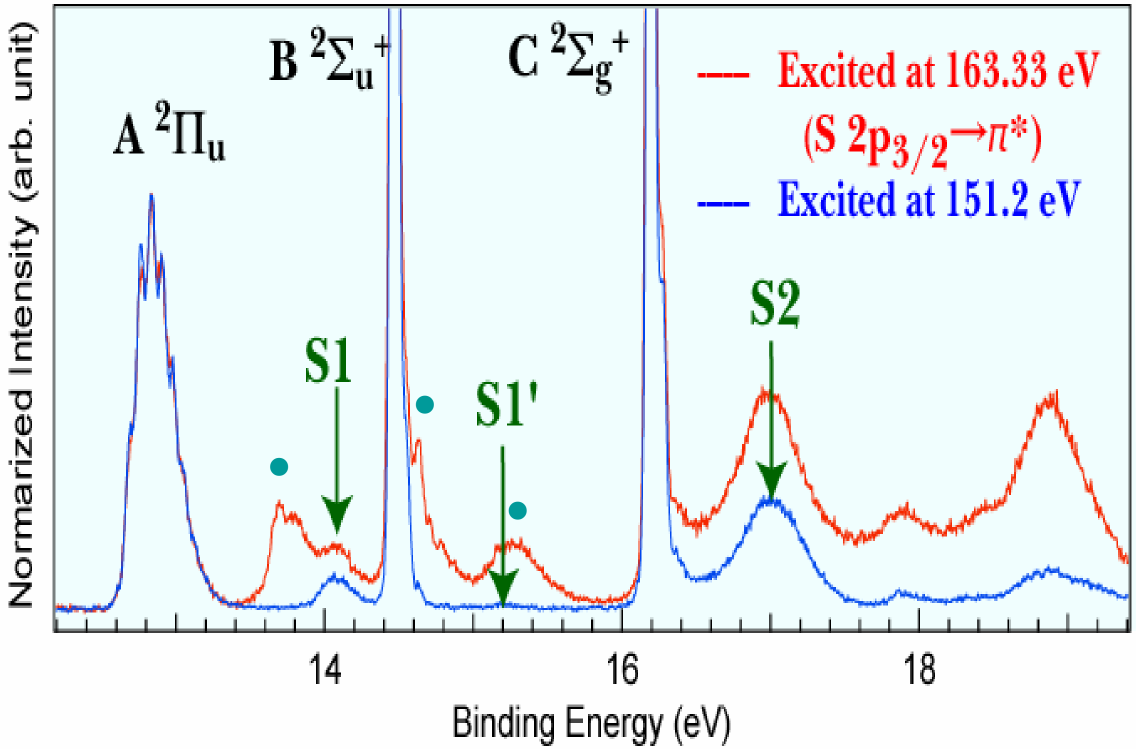
CS_2 S2p resonant PES

Experiment

UVSOR BL4B

$\Delta h\nu$ = 40 meV

$\Delta k.e$ = 10 meV



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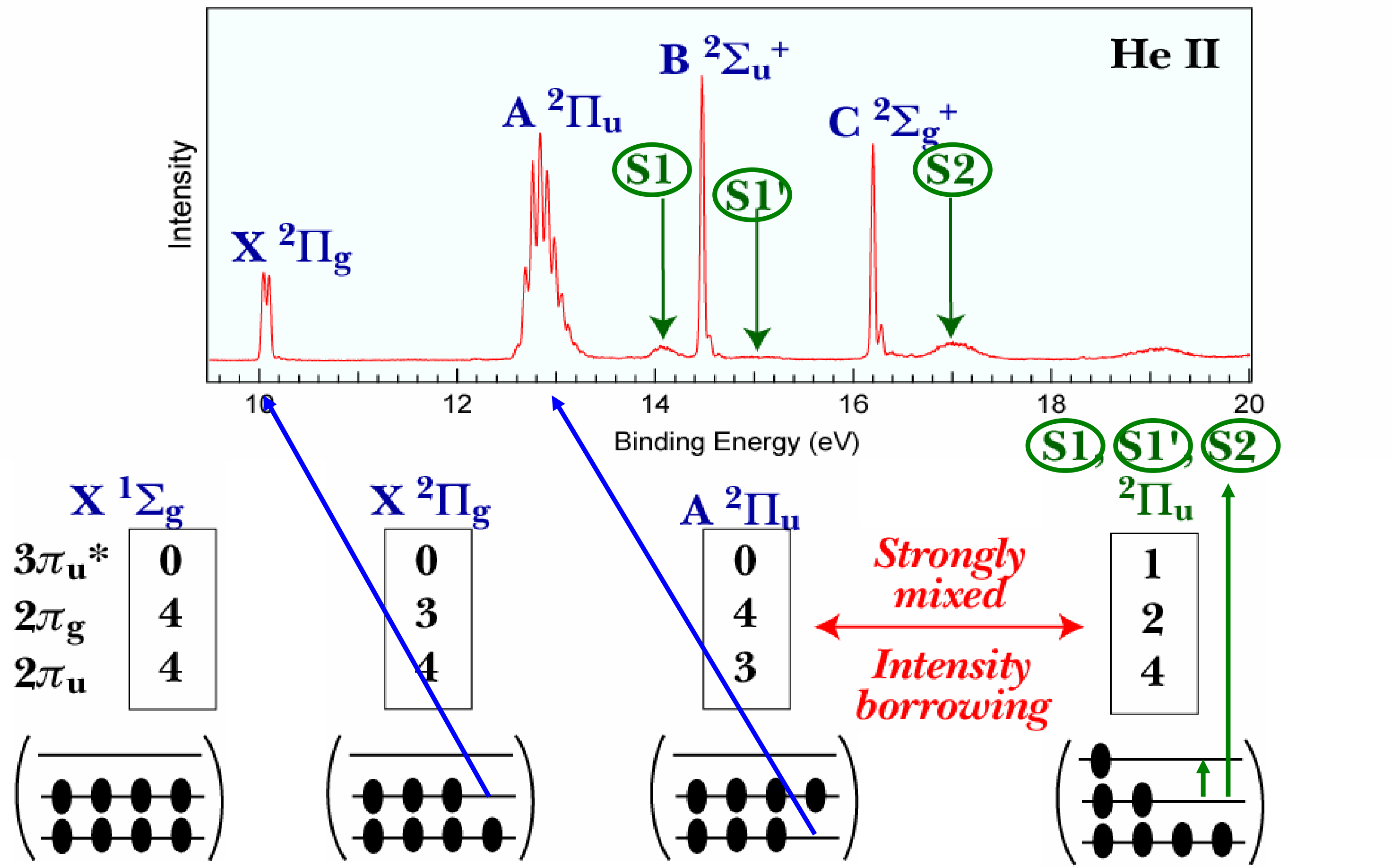
CS_2 S2p non-resonant PES



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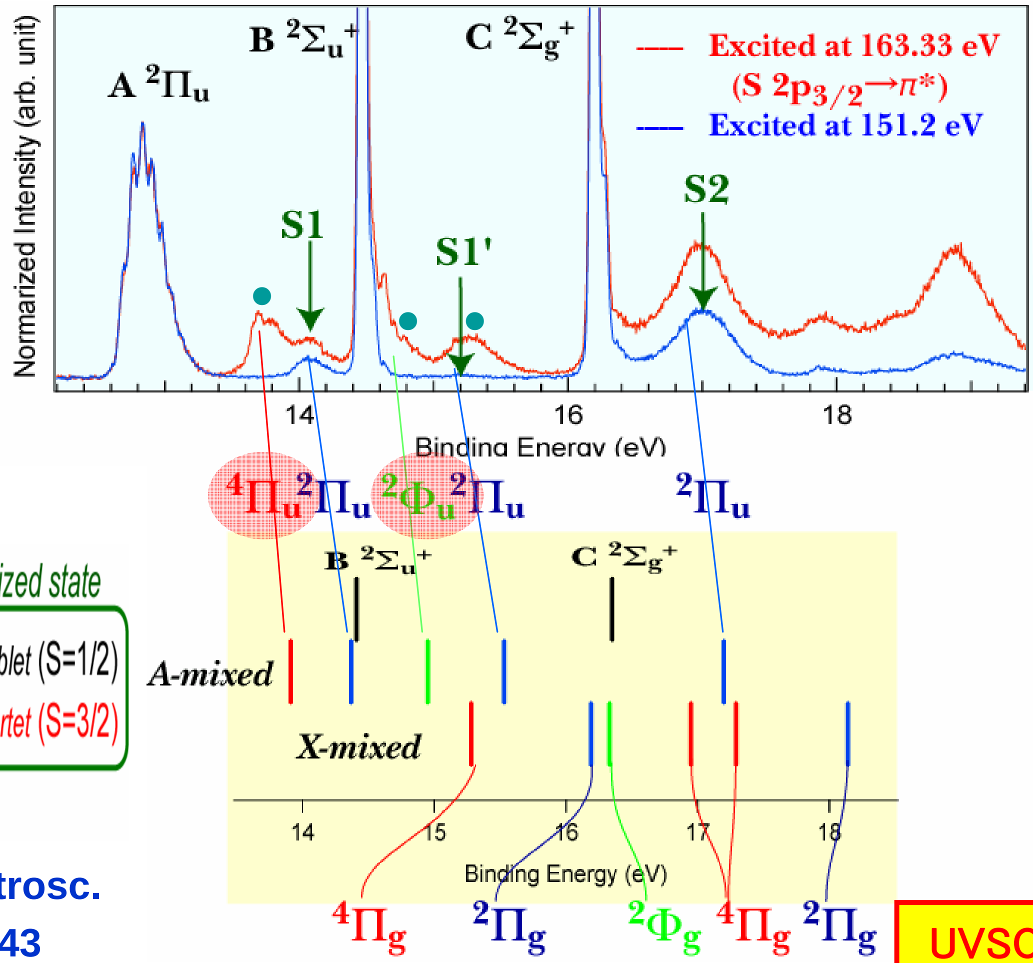
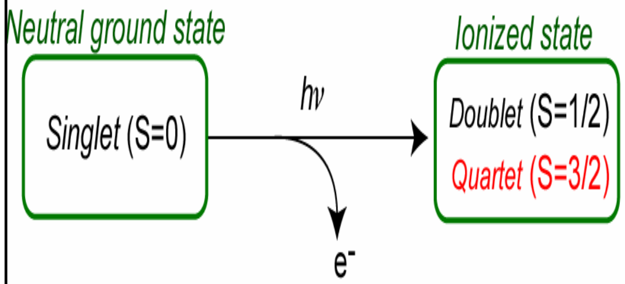
CS_2 S2p resonant PES

Experiment
UVSOR BL4B
$\Delta h\nu$ = 40 meV
$\Delta k.e$ = 10 meV





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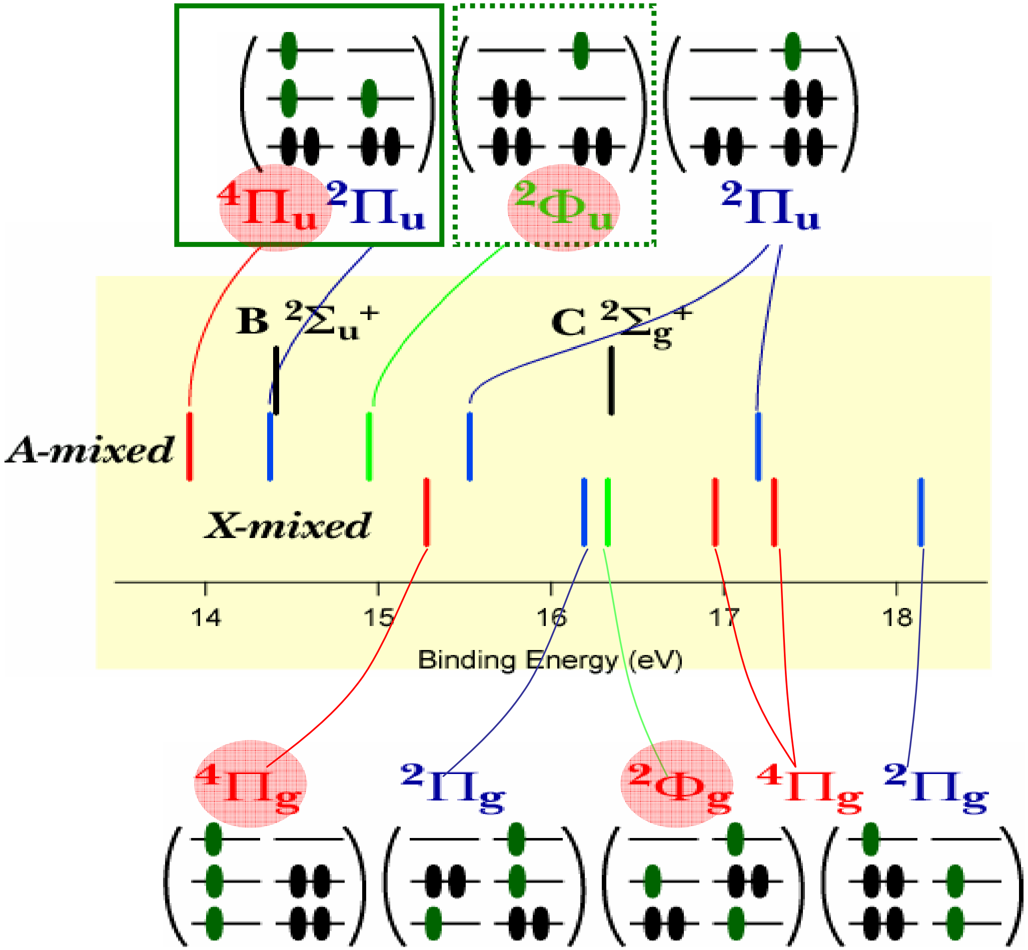
CS_2 S2p resonant PES



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Summary (5 topics)

1. PES of Kr clusters (non-polar)

2. PES of Ne clusters (non-polar)

nearest neighbor interaction is dominant in redshift

extrapolation of interaction from a small cluster model

3. PES of liquid water (polar)

red or blue shift dependent on orientation

4. Ni 2p resonant PES

metallic, correlated, and molecular solids

resonant PES:[2h1e]-type 1e = exciton in molec. solid

[1h]-type single hole = same as in non-resonant PES

5. S 2p resonant PES : [2h1e] = 3 elect. in 3 orbitals

spin-forbidden & symmetry-forbidden states

visible by singlet-triple mixing through spin-orbit int.

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Photoemission 1

Thank you!