Photoemission 1

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What is photoemission?

photon-in electron-out

hv

e−
What is photoemission?

Electron emission

fixed energy
photon
VUV or X-ray

fast

slow

K.E.

B.E.
(I.P.)

hv

hv

BE=hf - KE

photoemission

valence
band

core

ATOM

Molecules/Solids

Electron Distribution Curve (Spectra)
What is photoemission?

Element Analysis

Electron Binding Energy (BE) Ionization Potential (IP) in eV

BE = hν - KE

O 1s
C 1s
Al 2s 2p

valence
What is photoemission?

Carbon 1s electron

Intensity, arb. units

295 290 285 280

Binding Energy, eV

C\textsuperscript{-}F\textsubscript{2}, C\textsuperscript{-}N\textsubscript{3}, OH-C\textsuperscript{-}=O

C\textsuperscript{-}N & C\textsuperscript{-}O

C\textsuperscript{-}C

Residual Hydrocarbons

Peptide constraint

Experimental data Curve-fitting result

ESCA (Kai Siegbahn 1918-2007.7.20)

Electron Spectroscopy for Chemical Analysis
What is photoemission?

Valence band/orbital

DNA polynucleotides poly(dG)poly(dC)
### 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
<table>
<thead>
<tr>
<th>terminology</th>
</tr>
</thead>
<tbody>
<tr>
<td>photoemission</td>
</tr>
<tr>
<td>x  photon emission (X-ray emission,...)</td>
</tr>
<tr>
<td>o  photoelectron emission</td>
</tr>
</tbody>
</table>
photon emission

- absorption
- soft x-ray emission
- 2 steps photon-in photon-out

photoemission

- photoemission
- Electron Distribution Curve (Spectra)
- fast
- slow valence band core
- 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 $h\nu$
  - $h\nu = \text{VUV : UPS (valence)}$
  - $h\nu = \text{X-ray : XPS (valence, core)}$

---

### Why SR?

$h\nu = \text{synchrotron radiation VUV/X-ray}$
### 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

- very high brightness of insertion device SR
- very high collimation of insertion device SR

<table>
<thead>
<tr>
<th>Range</th>
<th>Energy Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>VUV</td>
<td>&lt; 1 meV</td>
</tr>
<tr>
<td>VUV lasersoft X-ray</td>
<td>&lt; 10 meV</td>
</tr>
<tr>
<td>soft X-ray</td>
<td>&lt; 10 meV</td>
</tr>
<tr>
<td>hard X-ray</td>
<td>&lt; 100 meV</td>
</tr>
</tbody>
</table>

\[ BE = h\nu - KE \]
Why SR PES? (1) escape depth

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

UNIVERSAL CURVE
Electron Inelastic Mean Free Path
or Electron Escape Depth

Bulk Sensitive
>10 Å

surface sensitive <5 Å
Why SR PES? (1) escape depth


[Diagram showing escape depth for bulk and surface sensitive analysis]
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)
Why SR PES? (4) resonance effect

- photoionization cross section
  \[ = \text{photoabsorption cross section} \]

- element-specific photoionization cross section
  \[ = \text{core excitation cross section} \]

- core-to-unoccupied state excitation
  \[ = \text{X-ray Absorption Spectroscopy (XAS)} \]
Why SR PES? (4) resonance effect

Ti$_2$p and O$_{1s}$ XAS of Ti$_2$O$_3$

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
resonant photoemission [1h]

- Continuum
- bound-state resonance
- 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 $h\nu$  constant BE
normal Auger decay [2h]

Coulomb decay
intra-atomic
>> interatomic
non-resonant Auger
normal Auger

ionization
[1h]
double hole (independent of hν above ionization threshold)
[2h]

constant KE
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**
- \( \text{BE} = h\nu - KE \)
- very high brightness of insertion device SR
- very high collimation of insertion device SR
<table>
<thead>
<tr>
<th>Future of SR PES?</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>high level polarization</strong></td>
</tr>
<tr>
<td>high flexibility of insertion device SR</td>
</tr>
<tr>
<td>linear and circular (or elliptical)</td>
</tr>
<tr>
<td><strong>high space resolution</strong></td>
</tr>
<tr>
<td>~ 10nm combined with PEEM, …</td>
</tr>
<tr>
<td><strong>high time resolution</strong></td>
</tr>
<tr>
<td>~100fs combined with fs laser, …</td>
</tr>
<tr>
<td><strong>coherence</strong></td>
</tr>
<tr>
<td>long undulator</td>
</tr>
<tr>
<td>free electron laser or other types of laser</td>
</tr>
<tr>
<td>nonlinear phenomena</td>
</tr>
</tbody>
</table>

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<table>
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<th>Photoemission 1</th>
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<td>Some Topics</td>
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</tbody>
</table>
TOPIC 1

PES of Kr clusters
photoemission in cluster/solid

soft X-ray
photoemission in cluster/solid

electron-out

photon-in

PL : red shift
long-range
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 $<N> = 30$. Cluster peaks show red shift.
Kr 3d peak shift of Kr clusters

TA BL E1: 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. Average values for both spin-orbit components are given. The error limits are estimated to be ±10 meV.

<table>
<thead>
<tr>
<th>&lt;N&gt;</th>
<th>dimer</th>
<th>corner</th>
<th>edge</th>
<th>face/bul k</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>-1 (77%)</td>
<td>-334 (14%)</td>
<td>-479 (7%)</td>
<td>-766 (2%)</td>
</tr>
<tr>
<td>12</td>
<td>-2 (52%)</td>
<td>-400 (22%)</td>
<td>-553 (18%)</td>
<td>-791 (8%)</td>
</tr>
<tr>
<td>18</td>
<td>-4 (42%)</td>
<td>-458 (19%)</td>
<td>-591 (26%)</td>
<td>-818 (13%)</td>
</tr>
<tr>
<td>30</td>
<td>-5 (41%)</td>
<td>-491 (18%)</td>
<td>-645 (24%)</td>
<td>-874 (16%)</td>
</tr>
</tbody>
</table>

B. Wassermann
Theory

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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)

red shifts (eV) in singly-charged (1s) & doubly-charged (1s2s) states (r=3.1Å)

Coordination of central Ne in Ne cluster
Z=+1 nonpolar (Ne cluster)

Z=+1

r-dependence in red shift in Ne⁺(1s)

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# universal dependence
1/r^{4.0} - 1/r^{4.5}

# additivity

surface(13)
fitting
bulk(12)

induced dipole

r-dependence in red shift in Ne⁺(1s)
Z=+2 nonpolar (Ne cluster)

Z=+2

# universal dependence
$1/r^{4.0} \sim 1/r^{4.3}$

# additivity

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

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

HF calculation (partly MP2)
$$\propto - q^2 \Sigma_r \left( 1/ r^4 \right)$$

Induced Dipole
$$\propto - N \frac{q^2}{r^4}$$

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

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**Z=+1 nonpolar (Ne cluster)**

**Extrapolation** from icosahedron to \( N \sim 2000 \) (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  |

\[ \Delta E_{sb}(E_{th}) = 0.19 \text{ eV} \]

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Z=+1 nonpolar (Ne cluster)

ΔE_{as} ≥ 0.3 eV
ΔE_{ab} ≥ 0.5 eV
slowly converged

ΔE_{sb} ~ 0.19 eV
almost constant
TOPIC 3

PES of liquid water
nearest neighbor $\text{H}_2\text{O}$ structure

- $\text{DD}(\text{Aa})$
- $\text{SD}(\text{A})$

$r(\text{O-H}) \sim 1.86\text{A}$

nearest neighbors are most important
Z=+1 polar (H₂O cluster)

H₂O clusters

r-dependence in energy shift in H₂O (1s⁻¹)

Ionization Potentials (eV)

r(O-H)~1.86Å

# universal dependence

1/r 1.5 ~ 1/r 2

r(O-O) ~ r(O-H) + 1Å

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Z=+1 polar (H₂O cluster)

Why blue shift by A & red shift by D?

Point charge fitting to ES potential (CI)

<table>
<thead>
<tr>
<th>Status</th>
<th>Neutral</th>
<th>Ionized</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>-1.10</td>
<td>-0.50</td>
<td>+0.6</td>
</tr>
<tr>
<td>H</td>
<td>+0.55</td>
<td>+0.70</td>
<td>+0.15</td>
</tr>
</tbody>
</table>

0.05e⁻ from O(D)

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**Z=+1 polar (H$_2$O cluster)**

point charge - permanent dipole

\[ \propto \frac{q \mu \cos \Theta}{r^2} \]

HF calculation (partly MP2)

\[ \propto -\frac{1}{r^{-2}} \text{ for Donor site} \]

\[ \propto \frac{1}{r^{-1.6}} \text{ for Acceptor site} \]

Donor is \(~2\) times as strong as acceptor.
Z=+1 polar (H₂O cluster)

H₂O clusters

r-dependence in energy shift in H₂O (1s⁻¹)

Ionization Potentials (eV)

541
540.5
540
539.5
539
538.5
538
537.5
537

1.7
2.1
2.5
2.9
3.3
3.7

donor r(H-O) or acceptor r(O-H)

r(O-O) ~ r(O-H) + 1A

# universal dependence

1/r 1.5 ~ 1/r 2

Z=+1

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### Z=+1 polar (H₂O cluster)

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

#### SD+A

<table>
<thead>
<tr>
<th>1*+2</th>
<th>cluster</th>
<th>0.4 eV red shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*+31</td>
<td>CPMD</td>
<td>0.9 eV(±0.2eV) red shift</td>
</tr>
<tr>
<td>1*+&gt;100</td>
<td></td>
<td>&gt;?0.9eV red shift</td>
</tr>
</tbody>
</table>

#### DD+Aa

<table>
<thead>
<tr>
<th>1*+4</th>
<th>cluster</th>
<th>0.8 eV red shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*+31</td>
<td>CPMD</td>
<td>1.8 eV(±0.3eV) red shift</td>
</tr>
<tr>
<td>1*+&gt;100</td>
<td></td>
<td>&gt;?1.8 eV red shift</td>
</tr>
<tr>
<td>1*+43</td>
<td>ice</td>
<td>2.2 eV red shift</td>
</tr>
</tbody>
</table>
Z=+1 polar (H$_2$O cluster)

~1.4 eV red shift in cluster
**Z=+1 polar (H$_2$O cluster)**

1.77 eV red shift in liquid (surface)

---

**Hydrogen bonds in liquid water studied by photoelectron spectroscopy**

Bernd Winter$^\text{a}$

$^\text{a}$Max-Born-Institut für Nichtlineare Optik und Kurzzeit-Spektroskopie.
Ni 2p resonant PES
Ni2p XAS (resonant absorption)

Ni 2p XAS

- shoulder structure
- strong correlation
- LMCT shake-up multiplet

Ni2p XAS (resonant absorption)

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Ni2p XAS (resonant absorption)

- molecular system
- Ni2p XAS
- Ni 2p XAS
- • shoulder structure
  strong correlation
- LMCT shake-up multiplet

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**Ni2p XAS (resonant absorption)**

**K₂Ni(CN)₄: ionic**

**Ni₂p XAS (resonant absorption)**

**Ni(Hdmg)₂: neutral**

**molecular system**

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Ni2p XAS (resonant absorption)

- MLCT (Metal-to-Ligand Charge Transfer)
  covalent interaction between ligand $\pi^*$ and Ni 3d

Ni2p XAS (resonant absorption)

Ni 2p$_{3/2}$

K$_2$Ni(CN)$_4$

Ni 2p$_{1/2}$

Ni(Hdmg)$_2$

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

Ni 2p-linagd$^*$ (MLCT)

(in-plane $\pi^*$ & out-of-plane $\pi^*$)
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 dependent on \( h \nu \)
photon emission             photoemission
constant KE $[2h]$  
Continuum  
Coulomb decay
intra-atomic
$\gg$ interatomic
non-resonant Auger
normal Auger

ionization $[1h]$  
double hole $[2h]$

constant KE

(independent of $h\nu$ above ionization threshold)
photon emission             photoemission

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 $h\nu$ constant BE
Ni2p resonant PES

metallic system
[1h] single hole constant BE
[2h] double hole constant KE

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Ni2p resonant PES

Ni2p resonant PES

molecular system
[1h]single hole constant BE & an unusual resonance phenomenon (excitonic feature)

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UVSOR
Resonant photoemission [$1h$]-type

- Bound-state resonance
- Continuum

- Resonant photoemission
- Coulomb decay
- Intra-atomic
  $\gg$ Interatomic
- Resonant Auger

Exciton $[1h1e]$ Single hole $[1h]$

Linear dependence on $h\nu$ Constant BE

(same final state as in non-resonant PES)
resonant photoemission [2h1e]-type

Continuum

resonant photoemission
Coulomb decay
intra-atomic
>> interatomic
resonant Auger

[spectator] Auger decay

exciton  two-hole bound-state
[1h1e]     [2h1e]  (different bound-states dependent on $h\nu$)

UNUSUAL dependence on $h\nu$  NOT constant BE&KE
Ni2p resonant PES

TOPIC 5

S 2p resonant PES
CS₂ S₂p resonant PES

S₂p XAS

PES

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Experiment

UVSOR BL4B
\[ \Delta h\nu = 40 \text{ meV} \]
\[ \Delta k.e = 10 \text{ meV} \]
**CS$_2$ S2p non-resonant PES**

- **Intensity**
- **Binding Energy (eV)**

**X** $^2\Pi_g$

- **3\pi_u**
  - $^1\Sigma_g$
  - 0
- **2\pi_g**
  - 4
- **2\pi_u**
  - 4

**X** $^2\Pi_g$

- **0**
- **3**
- **4**

**A** $^2\Pi_u$

- **0**
- **4**
- **3**

**B** $^2\Sigma_u^+$

- **S1**
- **S1'**

**C** $^2\Sigma_g^+$

- **S2**

**He II**

- Strongly mixed
- Intensity borrowing

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CS$_2$ S2p resonant PES

**Experiment**

UVSOR BL4B

$\Delta h\nu = 40$ meV

$\Delta k.e = 10$ meV

N. Kosugi, J. Elect. Spectrosc.

CS$_2$ S2p resonant PES
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.
Photoemission 1

Thank you!