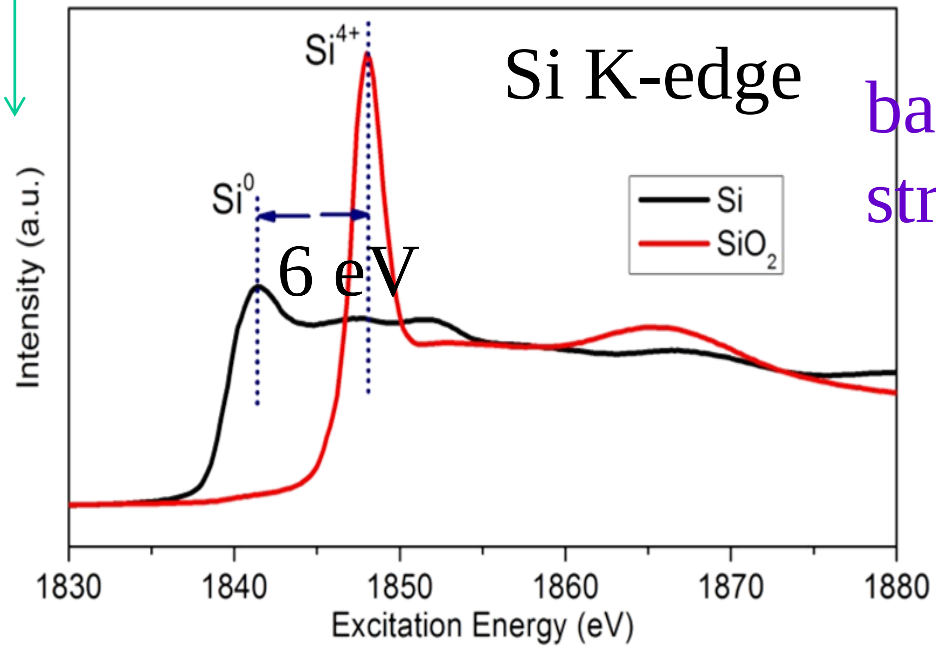
# Information that XAS provides (case study)

μ (E): absorption coefficient

**Oxidation states**: Si and SiO2

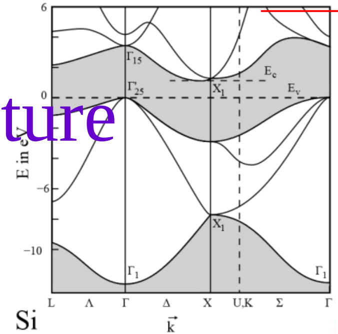


Si K-edge

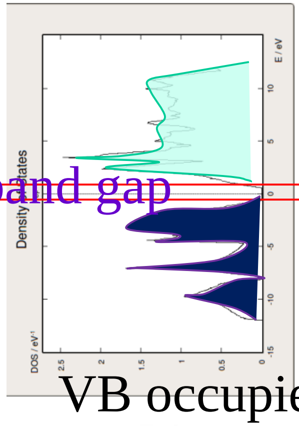
6 eV

crystal structure

band structure



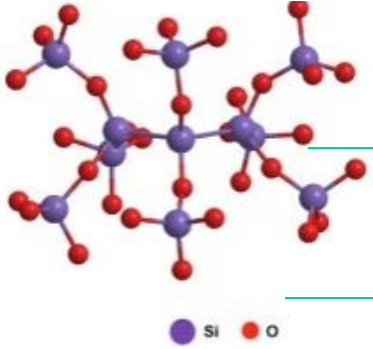
CB unoccupied

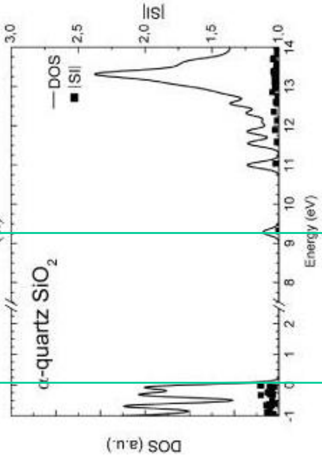


band gap

DOS

VB occupied





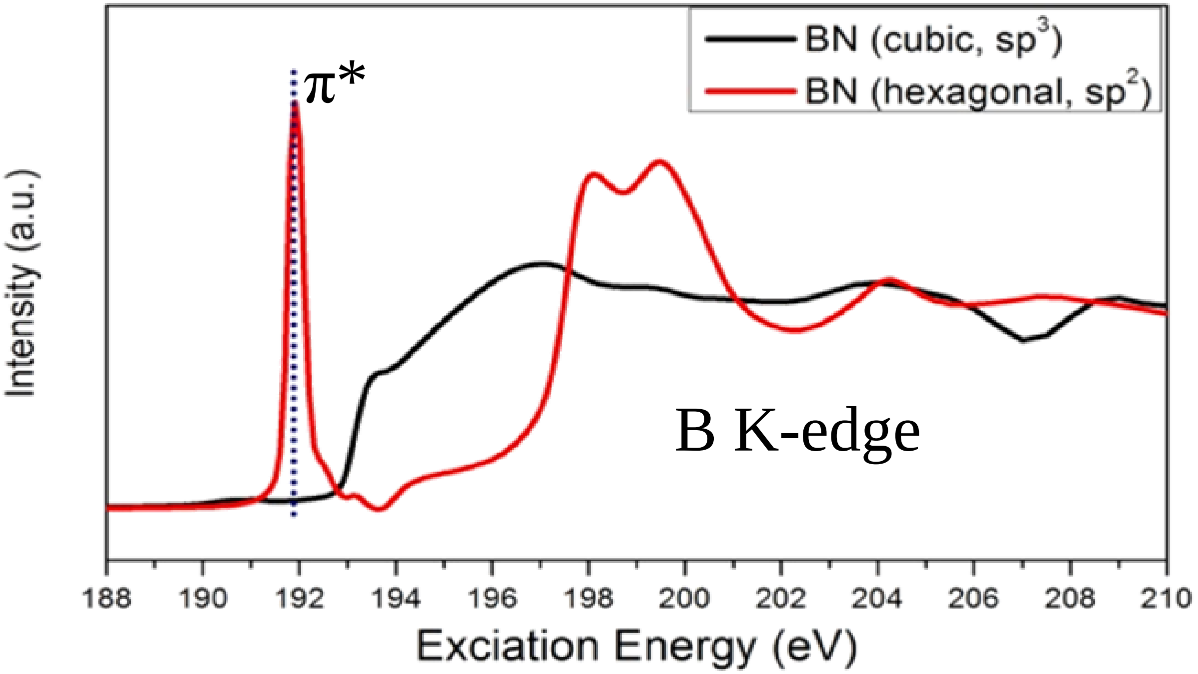
L. Liu., et al *Small*, (2012)15, 2371

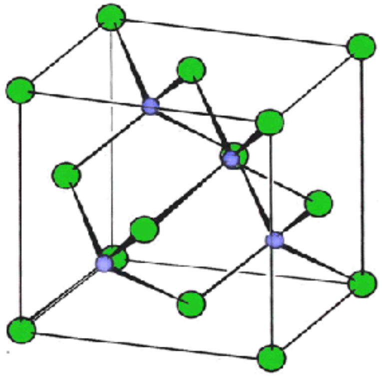
What is the origin of the shift? Oxidation state, ionicity!

# Information that XAS provides

**Hybridization**: sp$^3$ and sp$^2$ hybridized BN

X.-T. Zhou, *Anal. Chem.* (2006) 78, 6314

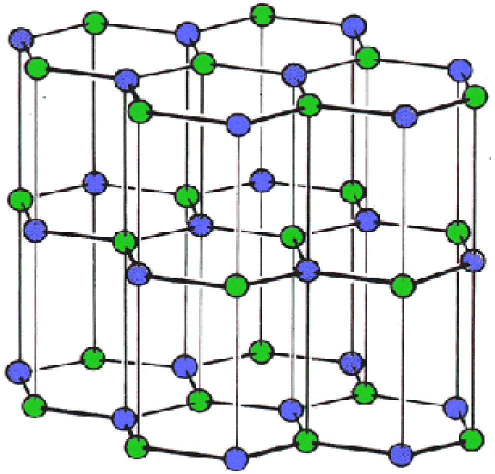


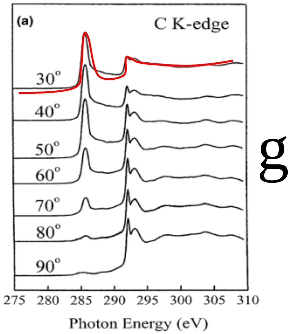


● N

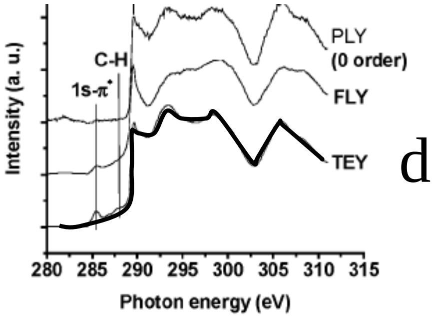
● B

● O





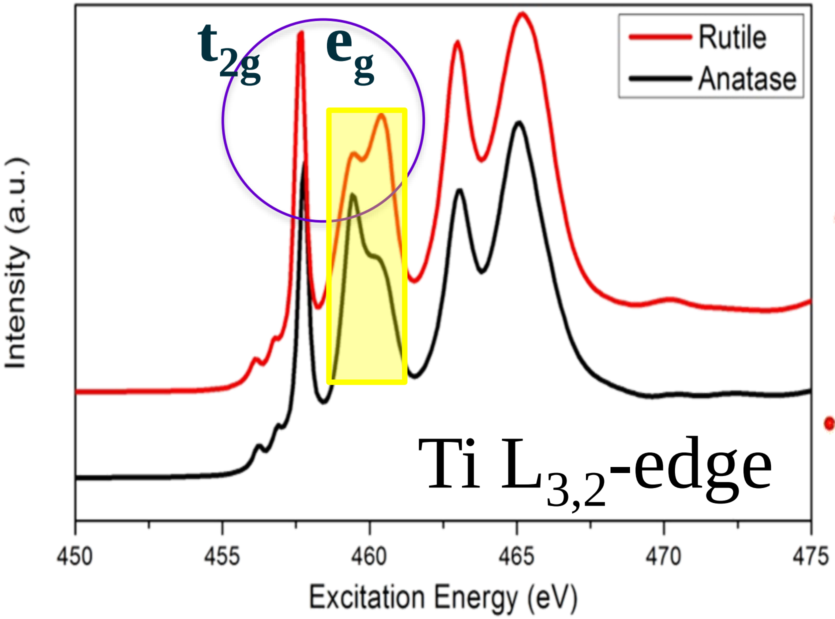
graphite

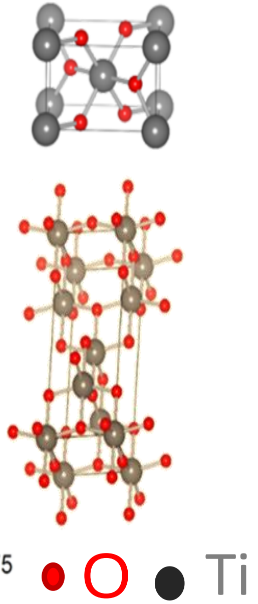


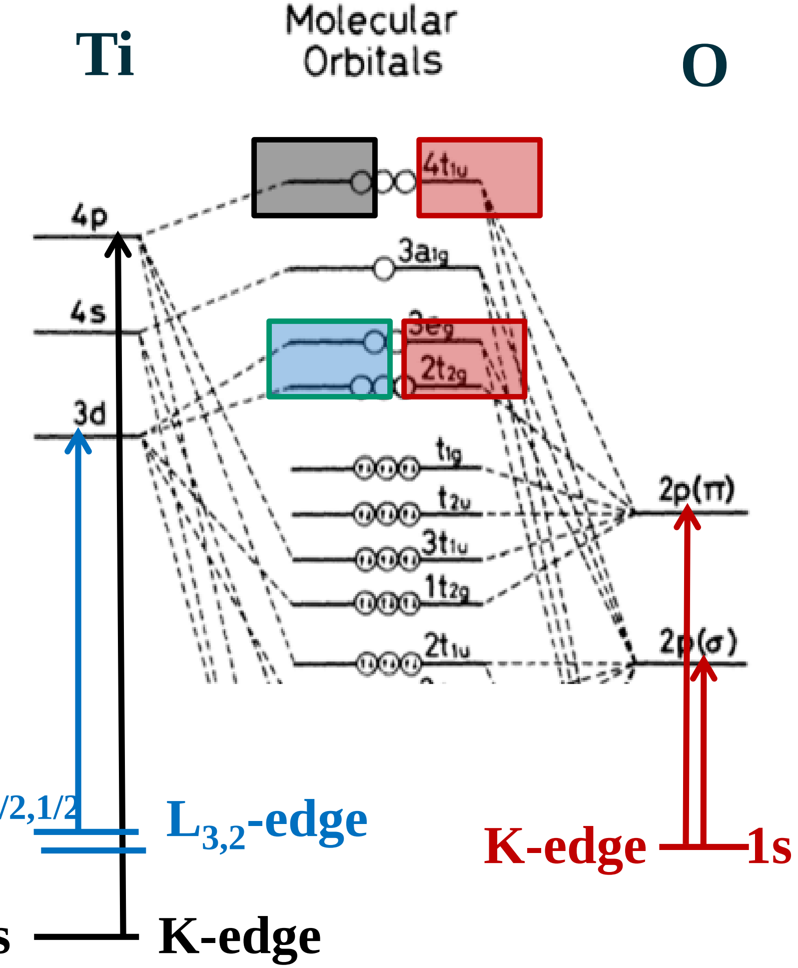
diamond

# Information that XAS provides

## Local symmetry:
## anatase and rutile TiO2

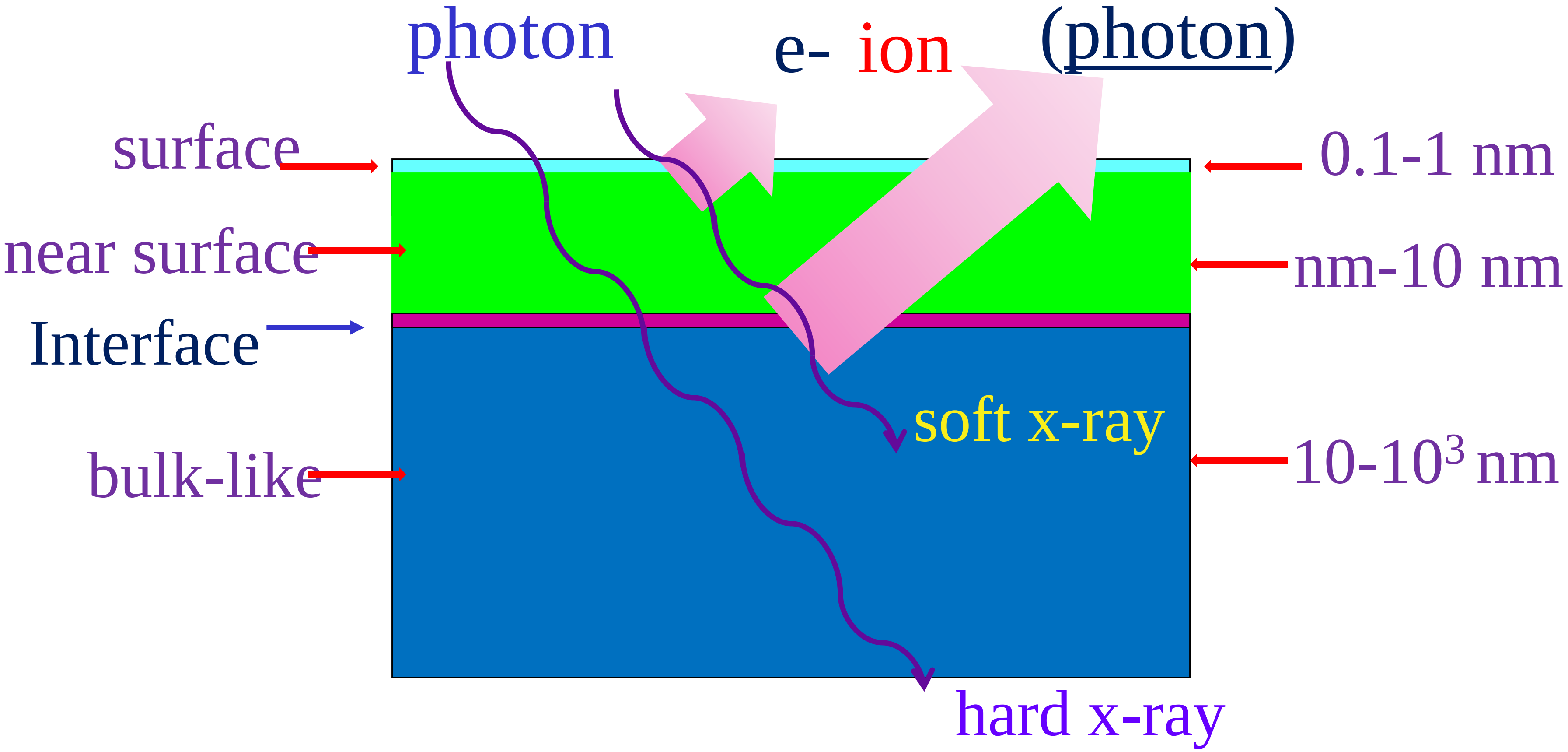






Liu et al. *J. Phys. Chem. C* (2010) 114, 21353

# Soft X-ray vs. Hard X-rays



| | | |
|---|---|---|
| Graphite | 300 eV (K-edge) | $t_1$:160 nm |
| Au | 11919 eV ($L_3$ -edge) | $t_1$: 2.8 μm |

# Soft X-ray energy and core level threshold (binding energy) of element

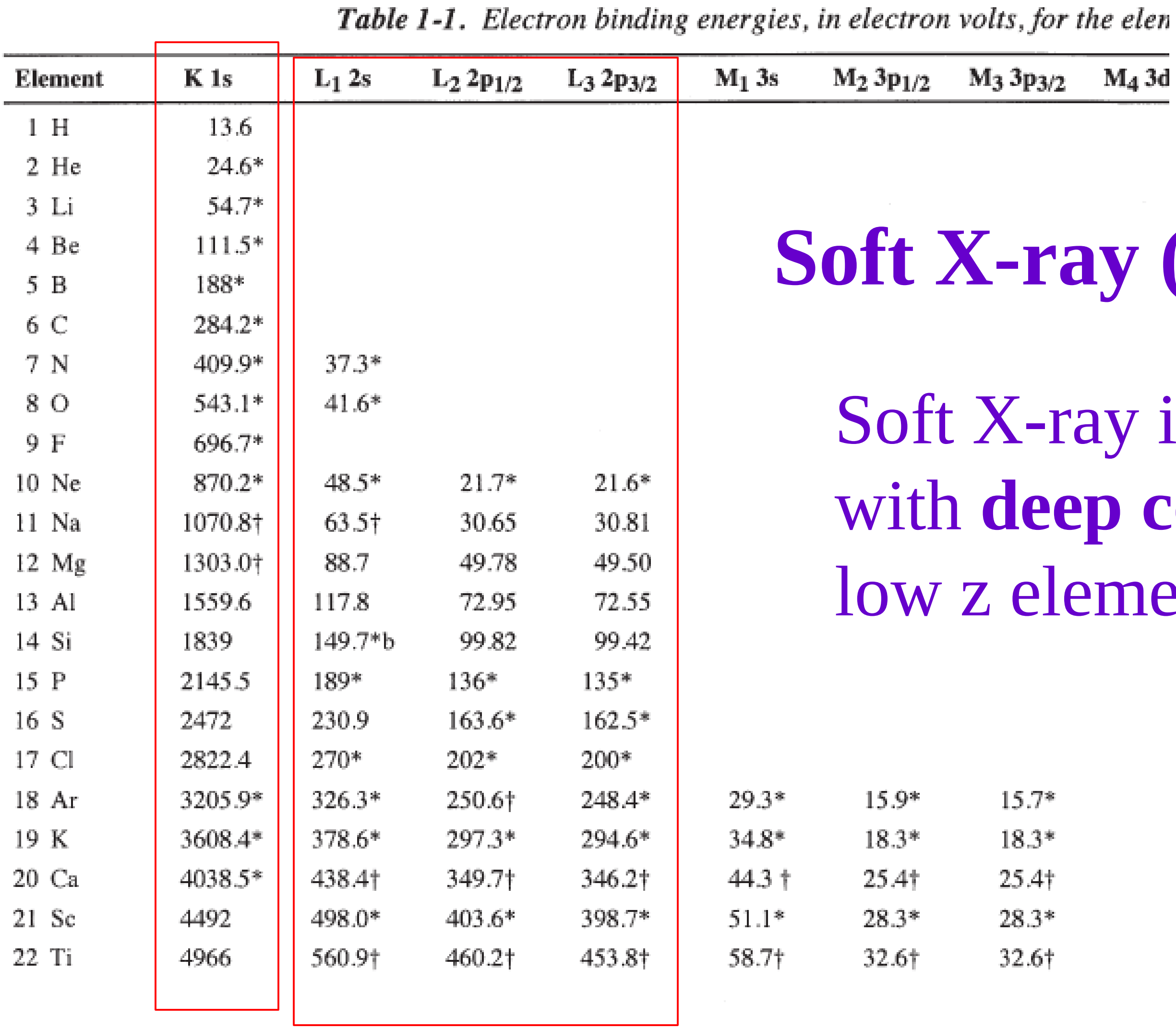


***Table 1-1.*** *Electron binding energies, in electron volts, for the elen*

| Element | K 1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ | $L_3$ $2p_{3/2}$ | $M_1$ 3s | $M_2$ $3p_{1/2}$ | $M_3$ $3p_{3/2}$ | $M_4$ 3d |
|---|---|---|---|---|---|---|---|---|
| 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* | | | | |
| 11 Na | 1070.8† | 63.5† | 30.65 | 30.81 | | | | |
| 12 Mg | 1303.0† | 88.7 | 49.78 | 49.50 | | | | |
| 13 Al | 1559.6 | 117.8 | 72.95 | 72.55 | | | | |
| 14 Si | 1839 | 149.7*b | 99.82 | 99.42 | | | | |
| 15 P | 2145.5 | 189* | 136* | 135* | | | | |
| 16 S | 2472 | 230.9 | 163.6* | 162.5* | | | | |
| 17 Cl | 2822.4 | 270* | 202* | 200* | | | | |
| 18 Ar | 3205.9* | 326.3* | 250.6† | 248.4* | 29.3* | 15.9* | 15.7* | |
| 19 K | 3608.4* | 378.6* | 297.3* | 294.6* | 34.8* | 18.3* | 18.3* | |
| 20 Ca | 4038.5* | 438.4† | 349.7† | 346.2† | 44.3 † | 25.4† | 25.4† | |
| 21 Sc | 4492 | 498.0* | 403.6* | 398.7* | 51.1* | 28.3* | 28.3* | |
| 22 Ti | 4966 | 560.9† | 460.2† | 453.8† | 58.7† | 32.6† | 32.6† | |

## Soft X-ray (< ~5000eV)

Soft X-ray is associated with **deep core levels** of low z elements

# Soft vs Hard X-rays and core level threshold (binding energy) of element

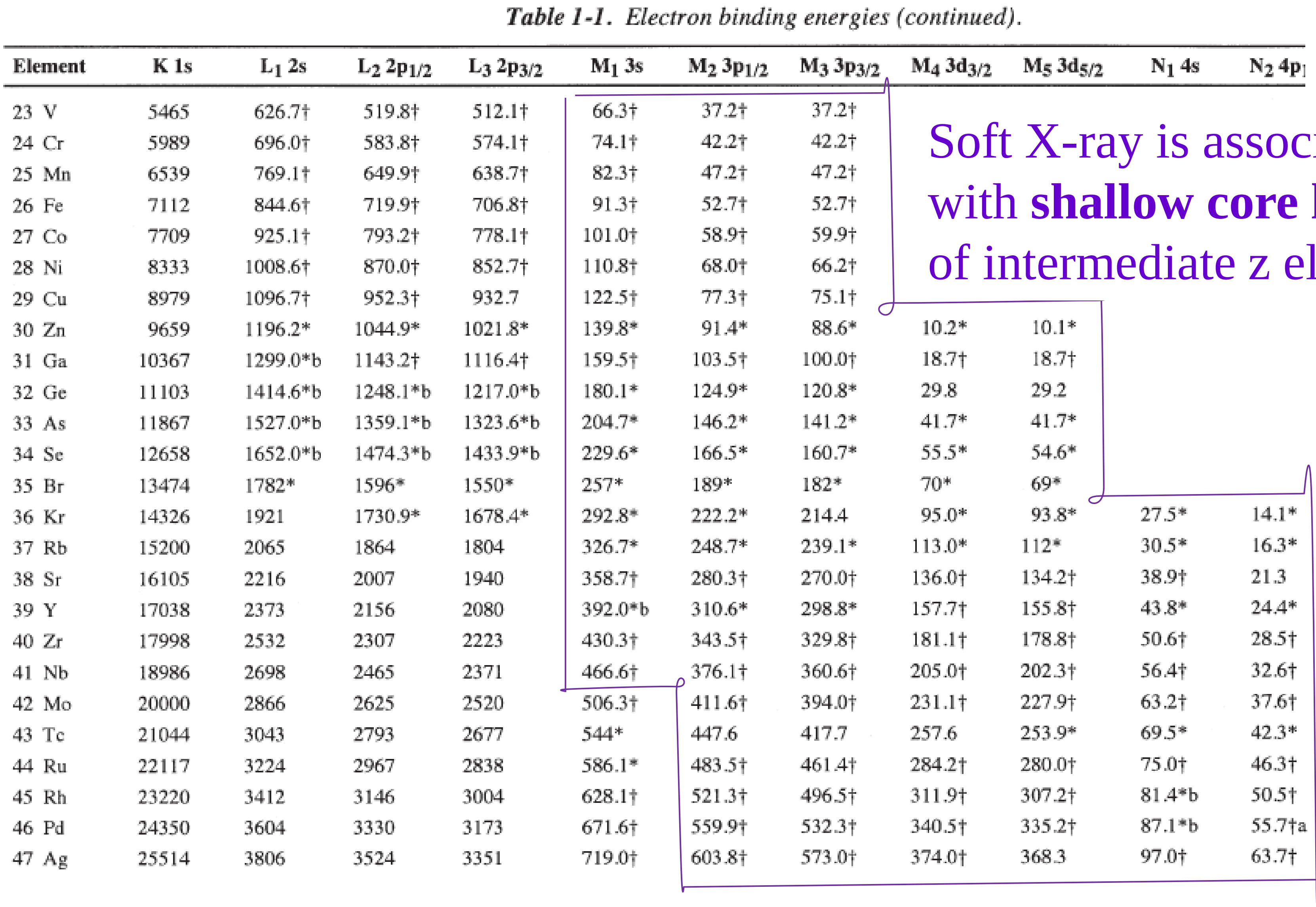


*Table 1-1. Electron binding energies (continued).*

| Element | K 1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ | $L_3$ $2p_{3/2}$ | $M_1$ 3s | $M_2$ $3p_{1/2}$ | $M_3$ $3p_{3/2}$ | $M_4$ $3d_{3/2}$ | $M_5$ $3d_{5/2}$ | $N_1$ 4s | $N_2$ 4p |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 23 V | 5465 | 626.7† | 519.8† | 512.1† | 66.3† | 37.2† | 37.2† | | | | |
| 24 Cr | 5989 | 696.0† | 583.8† | 574.1† | 74.1† | 42.2† | 42.2† | | | | |
| 25 Mn | 6539 | 769.1† | 649.9† | 638.7† | 82.3† | 47.2† | 47.2† | | | | |
| 26 Fe | 7112 | 844.6† | 719.9† | 706.8† | 91.3† | 52.7† | 52.7† | | | | |
| 27 Co | 7709 | 925.1† | 793.2† | 778.1† | 101.0† | 58.9† | 59.9† | | | | |
| 28 Ni | 8333 | 1008.6† | 870.0† | 852.7† | 110.8† | 68.0† | 66.2† | | | | |
| 29 Cu | 8979 | 1096.7† | 952.3† | 932.7 | 122.5† | 77.3† | 75.1† | | | | |
| 30 Zn | 9659 | 1196.2* | 1044.9* | 1021.8* | 139.8* | 91.4* | 88.6* | 10.2* | 10.1* | | |
| 31 Ga | 10367 | 1299.0*b | 1143.2† | 1116.4† | 159.5† | 103.5† | 100.0† | 18.7† | 18.7† | | |
| 32 Ge | 11103 | 1414.6*b | 1248.1*b | 1217.0*b | 180.1* | 124.9* | 120.8* | 29.8 | 29.2 | | |
| 33 As | 11867 | 1527.0*b | 1359.1*b | 1323.6*b | 204.7* | 146.2* | 141.2* | 41.7* | 41.7* | | |
| 34 Se | 12658 | 1652.0*b | 1474.3*b | 1433.9*b | 229.6* | 166.5* | 160.7* | 55.5* | 54.6* | | |
| 35 Br | 13474 | 1782* | 1596* | 1550* | 257* | 189* | 182* | 70* | 69* | | |
| 36 Kr | 14326 | 1921 | 1730.9* | 1678.4* | 292.8* | 222.2* | 214.4 | 95.0* | 93.8* | 27.5* | 14.1* |
| 37 Rb | 15200 | 2065 | 1864 | 1804 | 326.7* | 248.7* | 239.1* | 113.0* | 112* | 30.5* | 16.3* |
| 38 Sr | 16105 | 2216 | 2007 | 1940 | 358.7† | 280.3† | 270.0† | 136.0† | 134.2† | 38.9† | 21.3 |
| 39 Y | 17038 | 2373 | 2156 | 2080 | 392.0*b | 310.6* | 298.8* | 157.7† | 155.8† | 43.8* | 24.4* |
| 40 Zr | 17998 | 2532 | 2307 | 2223 | 430.3† | 343.5† | 329.8† | 181.1† | 178.8† | 50.6† | 28.5† |
| 41 Nb | 18986 | 2698 | 2465 | 2371 | 466.6† | 376.1† | 360.6† | 205.0† | 202.3† | 56.4† | 32.6† |
| 42 Mo | 20000 | 2866 | 2625 | 2520 | 506.3† | 411.6† | 394.0† | 231.1† | 227.9† | 63.2† | 37.6† |
| 43 Tc | 21044 | 3043 | 2793 | 2677 | 544* | 447.6 | 417.7 | 257.6 | 253.9* | 69.5* | 42.3* |
| 44 Ru | 22117 | 3224 | 2967 | 2838 | 586.1* | 483.5† | 461.4† | 284.2† | 280.0† | 75.0† | 46.3† |
| 45 Rh | 23220 | 3412 | 3146 | 3004 | 628.1† | 521.3† | 496.5† | 311.9† | 307.2† | 81.4*b | 50.5† |
| 46 Pd | 24350 | 3604 | 3330 | 3173 | 671.6† | 559.9† | 532.3† | 340.5† | 335.2† | 87.1*b | 55.7†a |
| 47 Ag | 25514 | 3806 | 3524 | 3351 | 719.0† | 603.8† | 573.0† | 374.0† | 368.3 | 97.0† | 63.7† |

Soft X-ray is associated with **shallow core levels** of intermediate z elements

# Soft X-ray is associated with **shallow core levels** of high z elements

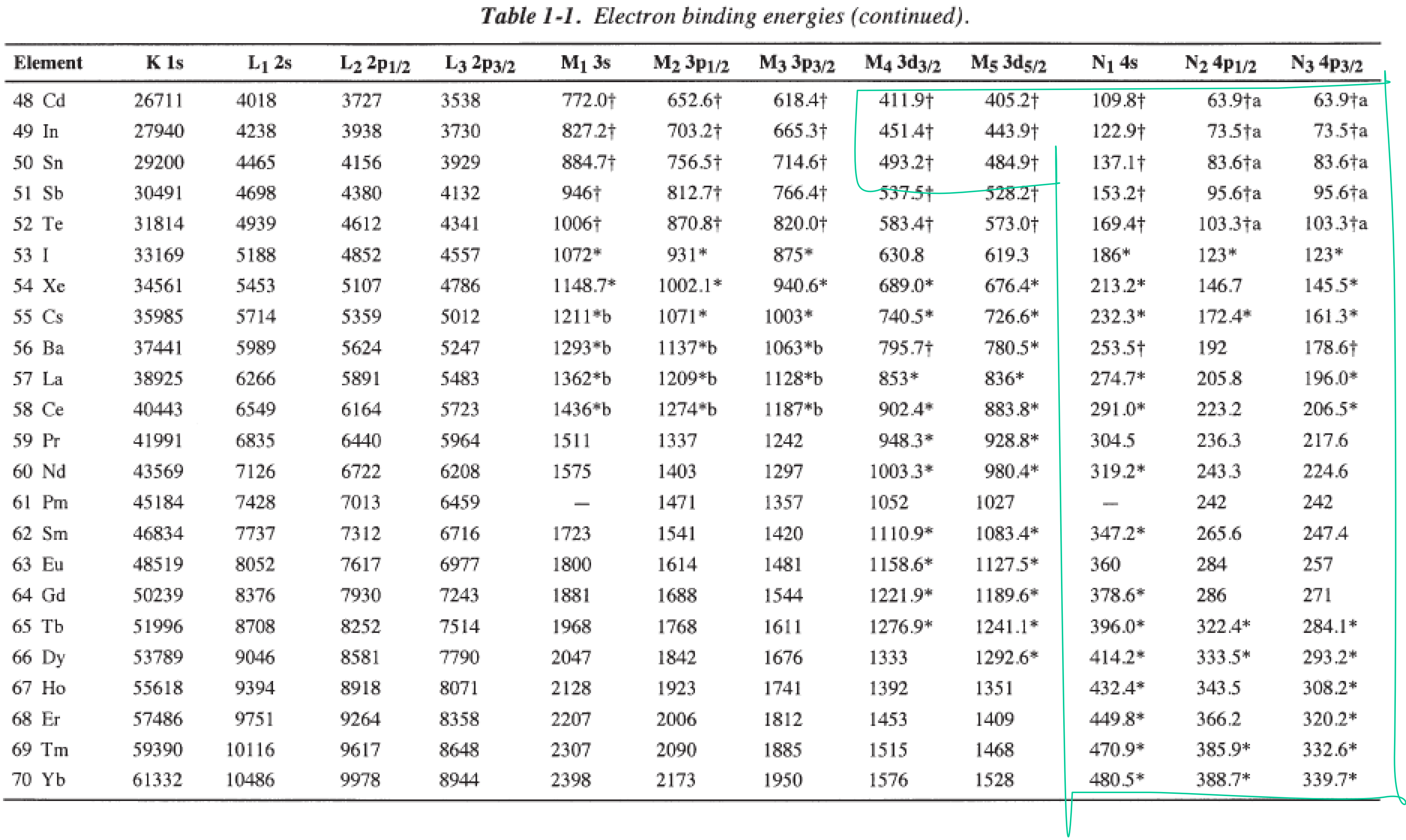


*Table 1-1. Electron binding energies (continued).*

| Element | K 1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ | $L_3$ $2p_{3/2}$ | $M_1$ 3s | $M_2$ $3p_{1/2}$ | $M_3$ $3p_{3/2}$ | $M_4$ $3d_{3/2}$ | $M_5$ $3d_{5/2}$ | $N_1$ 4s | $N_2$ $4p_{1/2}$ | $N_3$ $4p_{3/2}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 48 Cd | 26711 | 4018 | 3727 | 3538 | 772.0† | 652.6† | 618.4† | 411.9† | 405.2† | 109.8† | 63.9†a | 63.9†a |
| 49 In | 27940 | 4238 | 3938 | 3730 | 827.2† | 703.2† | 665.3† | 451.4† | 443.9† | 122.9† | 73.5†a | 73.5†a |
| 50 Sn | 29200 | 4465 | 4156 | 3929 | 884.7† | 756.5† | 714.6† | 493.2† | 484.9† | 137.1† | 83.6†a | 83.6†a |
| 51 Sb | 30491 | 4698 | 4380 | 4132 | 946† | 812.7† | 766.4† | 537.5† | 528.2† | 153.2† | 95.6†a | 95.6†a |
| 52 Te | 31814 | 4939 | 4612 | 4341 | 1006† | 870.8† | 820.0† | 583.4† | 573.0† | 169.4† | 103.3†a | 103.3†a |
| 53 I | 33169 | 5188 | 4852 | 4557 | 1072* | 931* | 875* | 630.8 | 619.3 | 186* | 123* | 123* |
| 54 Xe | 34561 | 5453 | 5107 | 4786 | 1148.7* | 1002.1* | 940.6* | 689.0* | 676.4* | 213.2* | 146.7 | 145.5* |
| 55 Cs | 35985 | 5714 | 5359 | 5012 | 1211*b | 1071* | 1003* | 740.5* | 726.6* | 232.3* | 172.4* | 161.3* |
| 56 Ba | 37441 | 5989 | 5624 | 5247 | 1293*b | 1137*b | 1063*b | 795.7† | 780.5* | 253.5† | 192 | 178.6† |
| 57 La | 38925 | 6266 | 5891 | 5483 | 1362*b | 1209*b | 1128*b | 853* | 836* | 274.7* | 205.8 | 196.0* |
| 58 Ce | 40443 | 6549 | 6164 | 5723 | 1436*b | 1274*b | 1187*b | 902.4* | 883.8* | 291.0* | 223.2 | 206.5* |
| 59 Pr | 41991 | 6835 | 6440 | 5964 | 1511 | 1337 | 1242 | 948.3* | 928.8* | 304.5 | 236.3 | 217.6 |
| 60 Nd | 43569 | 7126 | 6722 | 6208 | 1575 | 1403 | 1297 | 1003.3* | 980.4* | 319.2* | 243.3 | 224.6 |
| 61 Pm | 45184 | 7428 | 7013 | 6459 | — | 1471 | 1357 | 1052 | 1027 | — | 242 | 242 |
| 62 Sm | 46834 | 7737 | 7312 | 6716 | 1723 | 1541 | 1420 | 1110.9* | 1083.4* | 347.2* | 265.6 | 247.4 |
| 63 Eu | 48519 | 8052 | 7617 | 6977 | 1800 | 1614 | 1481 | 1158.6* | 1127.5* | 360 | 284 | 257 |
| 64 Gd | 50239 | 8376 | 7930 | 7243 | 1881 | 1688 | 1544 | 1221.9* | 1189.6* | 378.6* | 286 | 271 |
| 65 Tb | 51996 | 8708 | 8252 | 7514 | 1968 | 1768 | 1611 | 1276.9* | 1241.1* | 396.0* | 322.4* | 284.1* |
| 66 Dy | 53789 | 9046 | 8581 | 7790 | 2047 | 1842 | 1676 | 1333 | 1292.6* | 414.2* | 333.5* | 293.2* |
| 67 Ho | 55618 | 9394 | 8918 | 8071 | 2128 | 1923 | 1741 | 1392 | 1351 | 432.4* | 343.5 | 308.2* |
| 68 Er | 57486 | 9751 | 9264 | 8358 | 2207 | 2006 | 1812 | 1453 | 1409 | 449.8* | 366.2 | 320.2* |
| 69 Tm | 59390 | 10116 | 9617 | 8648 | 2307 | 2090 | 1885 | 1515 | 1468 | 470.9* | 385.9* | 332.6* |
| 70 Yb | 61332 | 10486 | 9978 | 8944 | 2398 | 2173 | 1950 | 1576 | 1528 | 480.5* | 388.7* | 339.7* |

# What edge can soft X-ray probe ?

- Li K-edge (54.7 eV) to ~ Ti K-edge (~5 keV)
- Soft X-ray can access many ***shallow core level*** of many important elements,

  K-edge of C, N, O;

  L, K-edges of Al, Si, S, P, Cl,

  L-edge of 3d metals, L, M-edges of 4d metals, L-edge of Ga, Ge, As, Se and Cd, In, Sn, Sb, Te and

  $N_{4,5}$ edge (giant resonance) of 4f rare-earths

# Soft X-ray vs. hard X-ray

Soft X-ray: shallow penetration depth

- Measurements in transmission is difficult or undesirable
- Yield is normally used !

One absorption length ($\mu t_1 = 1$ or $t_1 = 1/\mu$)

Attenuation length

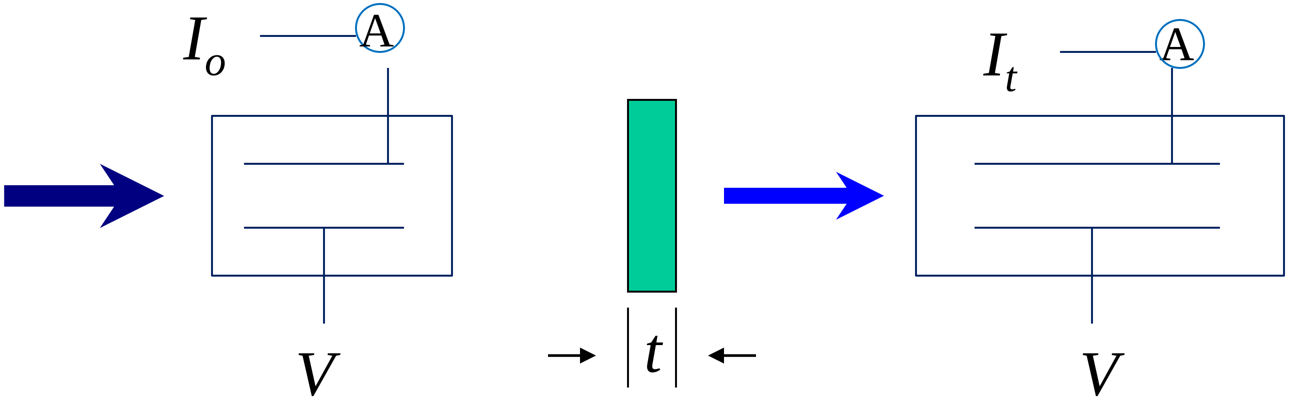
| Element | density(g/cm$^3$) | *hv* (eV) | mass abs (cm$^2$/g) | $t_1$(μm) |
|---|---|---|---|---|
| Si | 2.33 | 1840 (K-edge) | 3.32 ×103 | 1.3 |
| | | 100 (L-edge) | 8.60 ×104 | 0.05 |
| Graphite | 1.58 | 300 (K-edge) | 4.02 ×104 | 0.16 |

# X-ray absorption coefficient and the one-absorption length

- The x-ray absorption coefficient $\mu$ (cm$^{-1}$)

  $\mu = \sigma\rho$ ; $\rho$ (g/cm$^3$), $\sigma$ (cm$^2$/g);

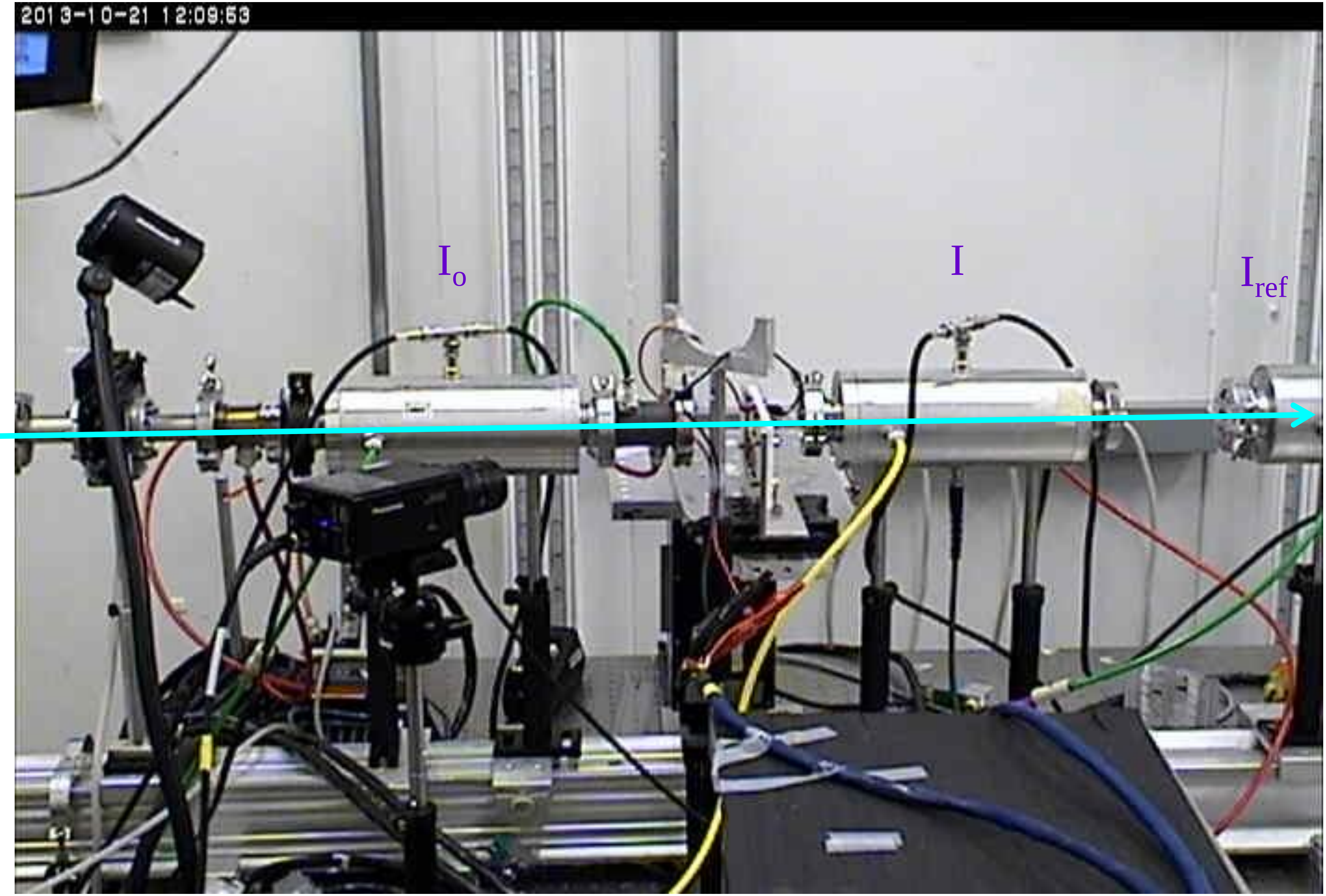
  Beer- Lambert law: Transmission measurements



$$I_t = I_o e^{-\mu t} \quad or \quad \mu t = \ln(I_o / I_t)$$

**Ionization chamber:**

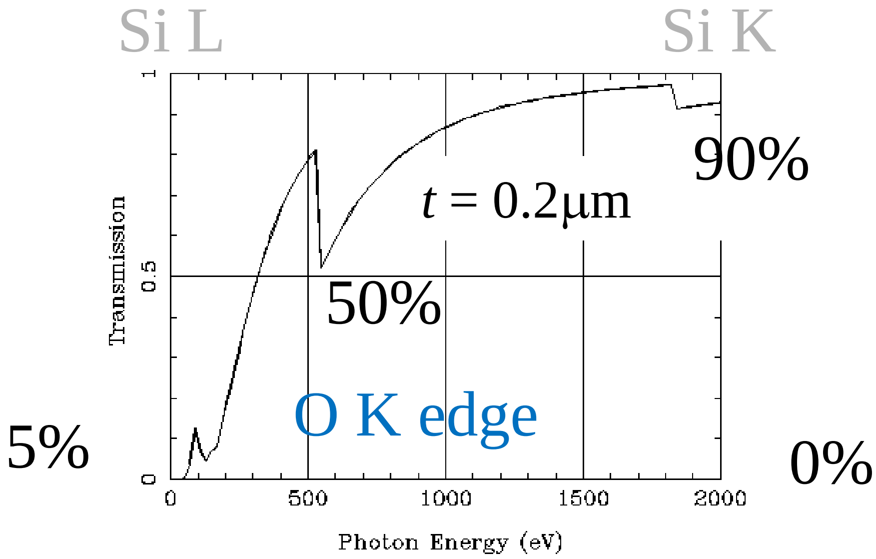
**Can be used to measure absolute photon flux**

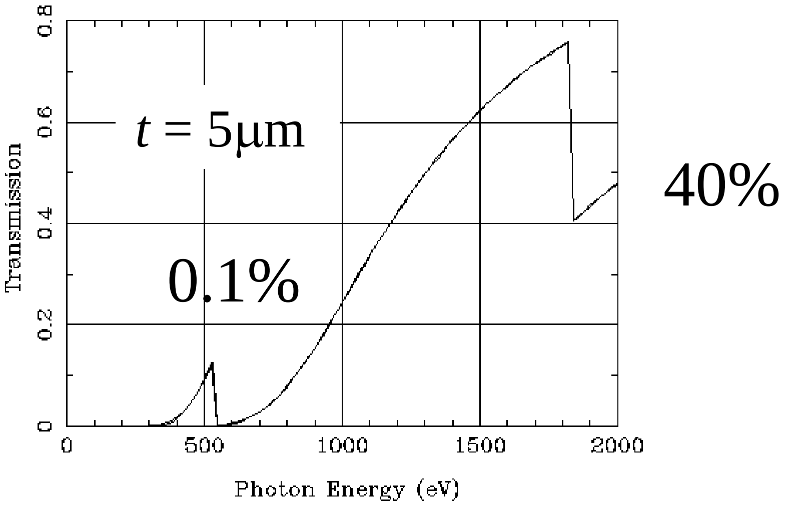

2013-10-21 12:09:53
$I_o$
$I$
$I_{ref}$

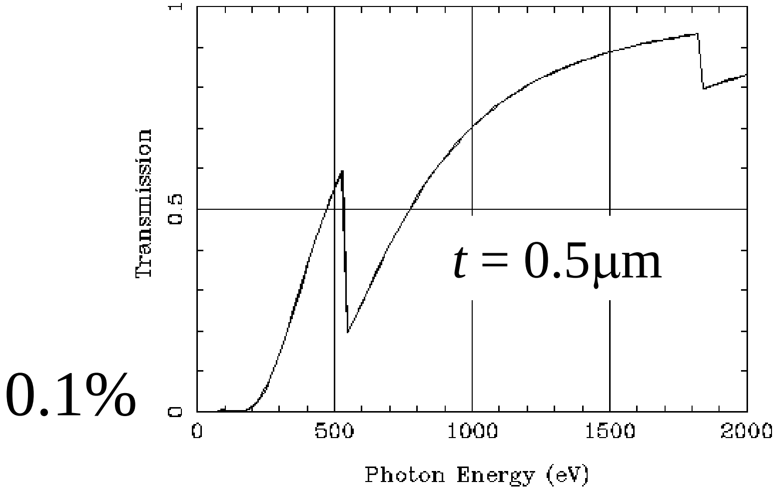
# Experimental considerations

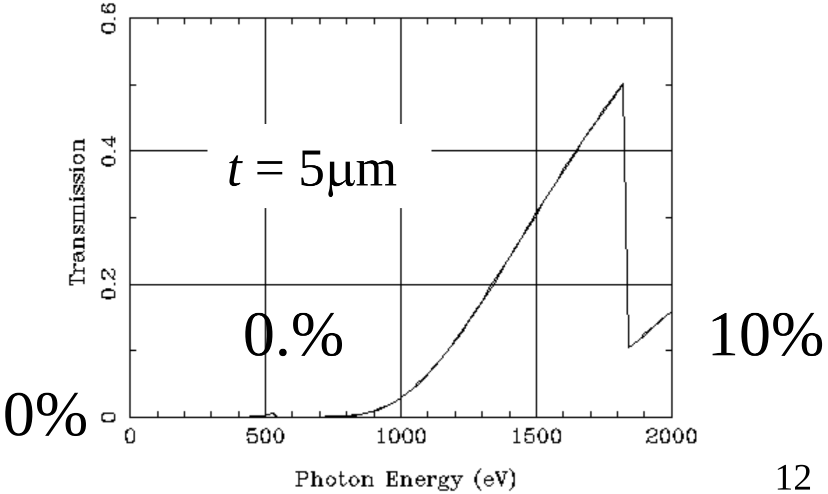
## (transmission is not always practical)

## (i) Suitable sample thickness: $SiO_2$

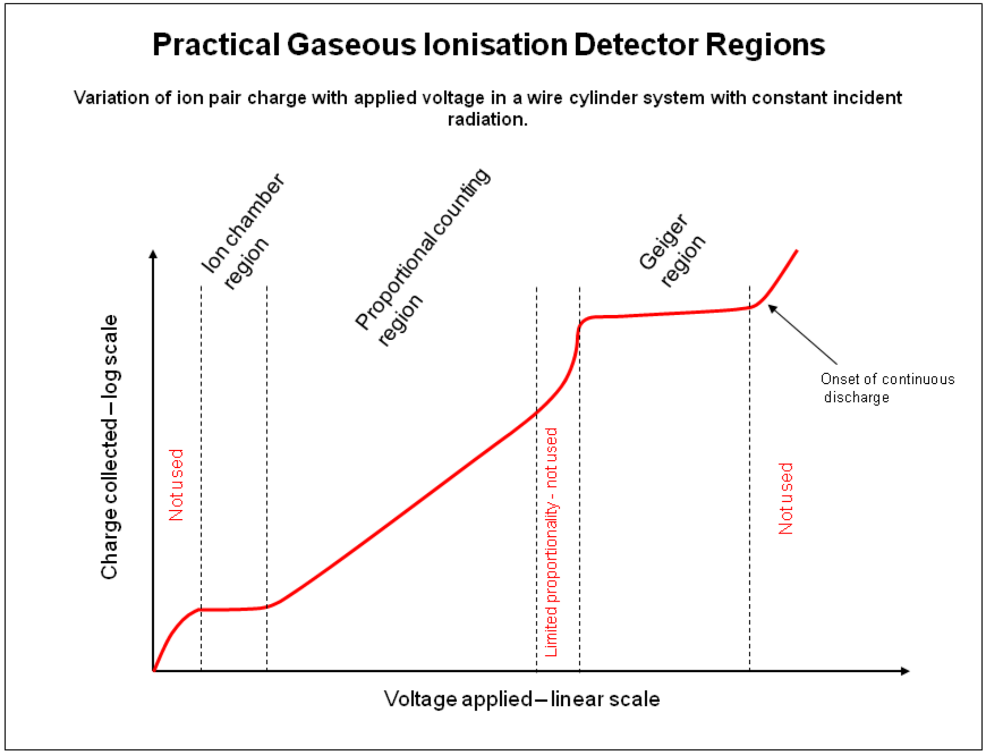






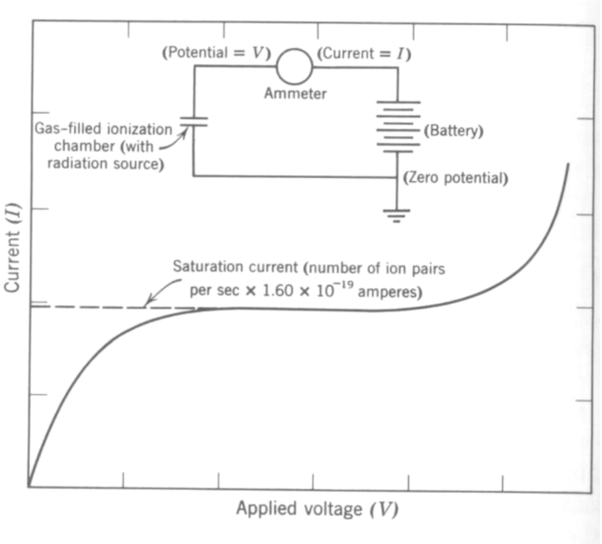


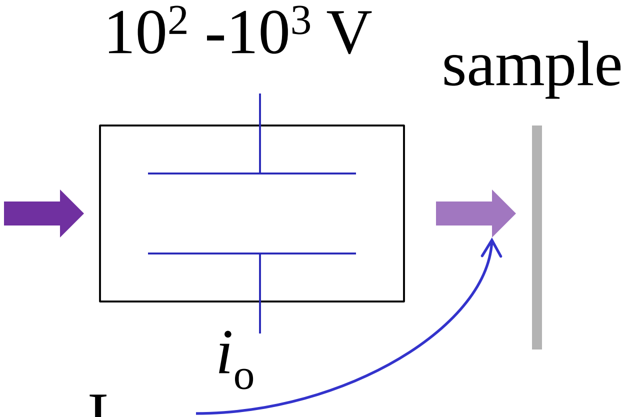
# How does an ion chamber work in X-ray measurements



**Practical Gaseous Ionisation Detector Regions**

Variation of ion pair charge with applied voltage in a wire cylinder system with constant incident radiation.





$$i_o \xrightarrow{\text{W (gas)}} \text{ion pair/sec} \xrightarrow{\mu t\text{ (gas)}} I_o$$

# W and G values of gases

**W value**: energy required to produce one ion pair.

For nitrogen, W = 35.8 eV/ ion pair

**G values**: number of ion pairs produced by 100eV of energy absorbed;
e.g. 100 eV may come from one 100eV photon of 5 20 eV photon or 0.01 10,000 eV photon.

These values are reasonably constant at hard X-ray and gamma ray energies but varies for soft X-ray photons.

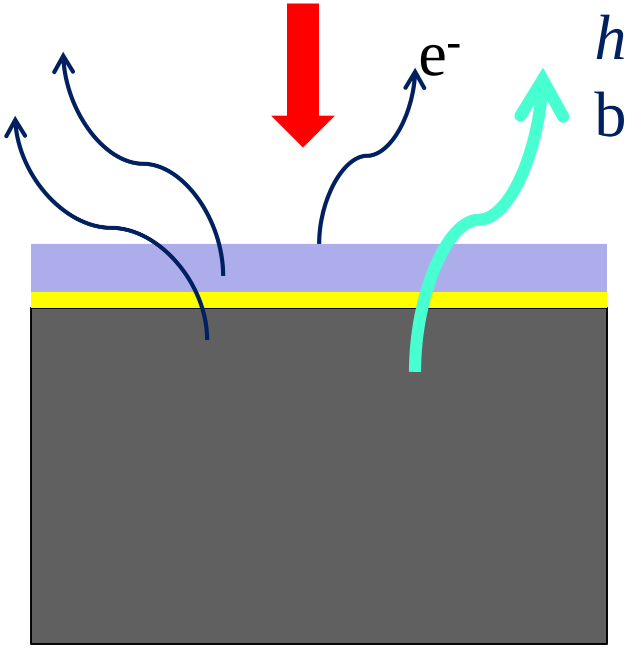
# Experimental considerations

(transmission is not always practical)

## (ii) Specimen geometry

## Thin over layer/multilayer film

*hv* (optical photons) can be surface and bulk sensitive depending on the origin of the luminescence



*hv* (X-ray fluorescence) bulk sensitive

# Why soft x-rays ( ~ 40 - 5000 eV) ?

**Narrow inherent linewidths** (core hole lifetime). Decay often involves the shallow core and valence electrons.

**Shallow penetration depth:** $t_1$( 1/e attenuation) is ~10 – $10^3$ nm. E.g. $t_1$ ~ 60 nm at Si L-edge

**High resolution monochromators** (SGM, PGM): E/ΔE ~10,000 obtainable. e.g. at 300 eV, ΔE= 0.03 eV

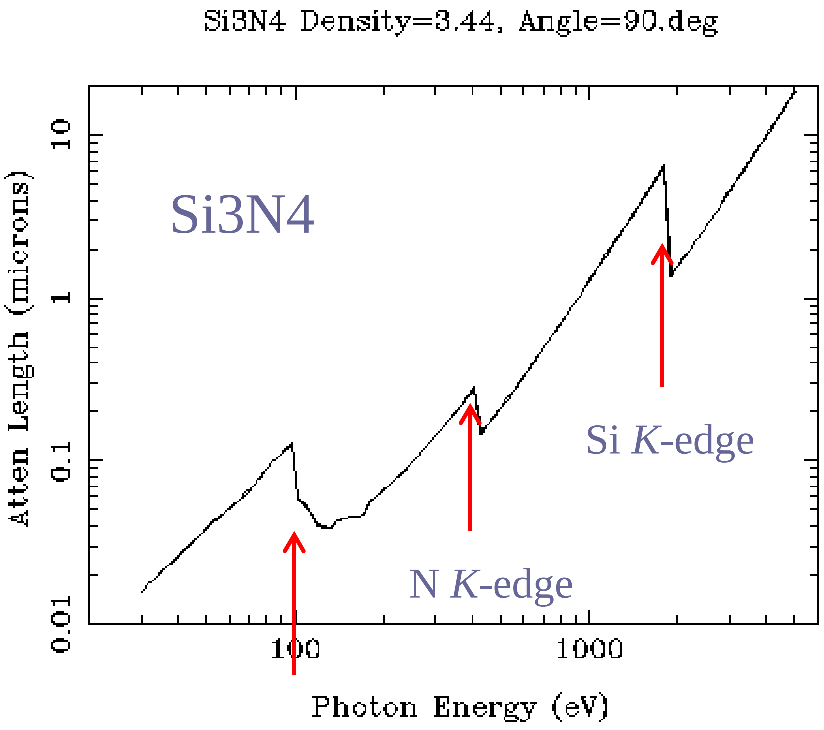
**Chemical and site specificity; depth profile**

# Soft x-ray spectroscopy: unique features

- Yield spectroscopy
  - Electron yield (total, partial- surface sensitive)
  - X-ray fluorescence yield (total, selected wavelength -bulk sensitive)
  - Photoluminescence yield (visible, UV- site specific)
    - XEOL (X-ray excited optical luminescence)
    - TR-XEOL (Time-resolved)
- High energy and spatial resolution
- Excitation of shallow core levels

The near-edge region (XANES/ NEXAFS) is the focus of interest in low z elements and shallow cores

# Soft X-ray attenuation

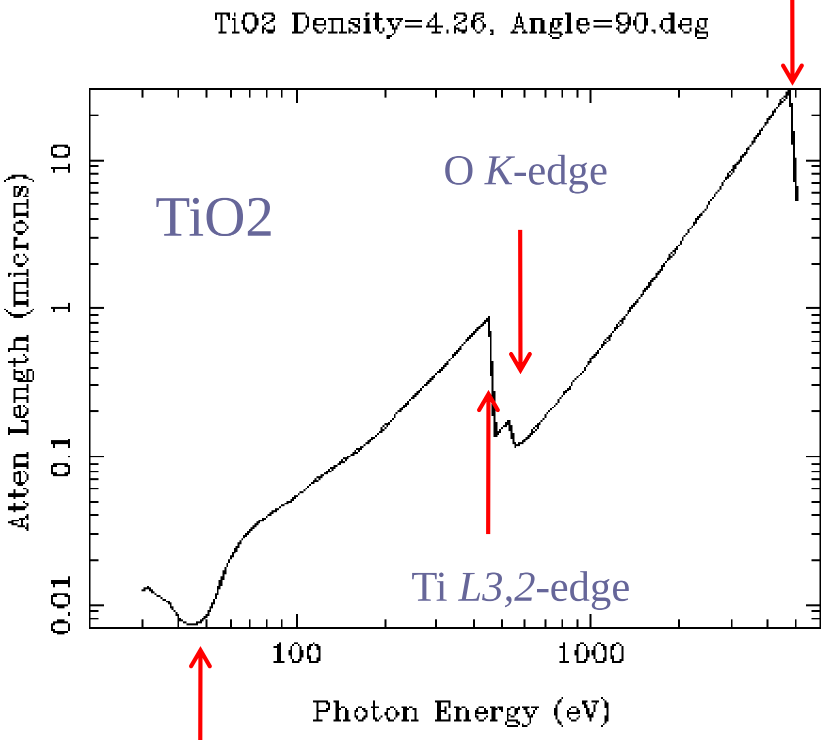


Si3N4

Si *K*-edge

N *K*-edge

Si *L3,2*-edge



TiO2

Ti *K*-edge

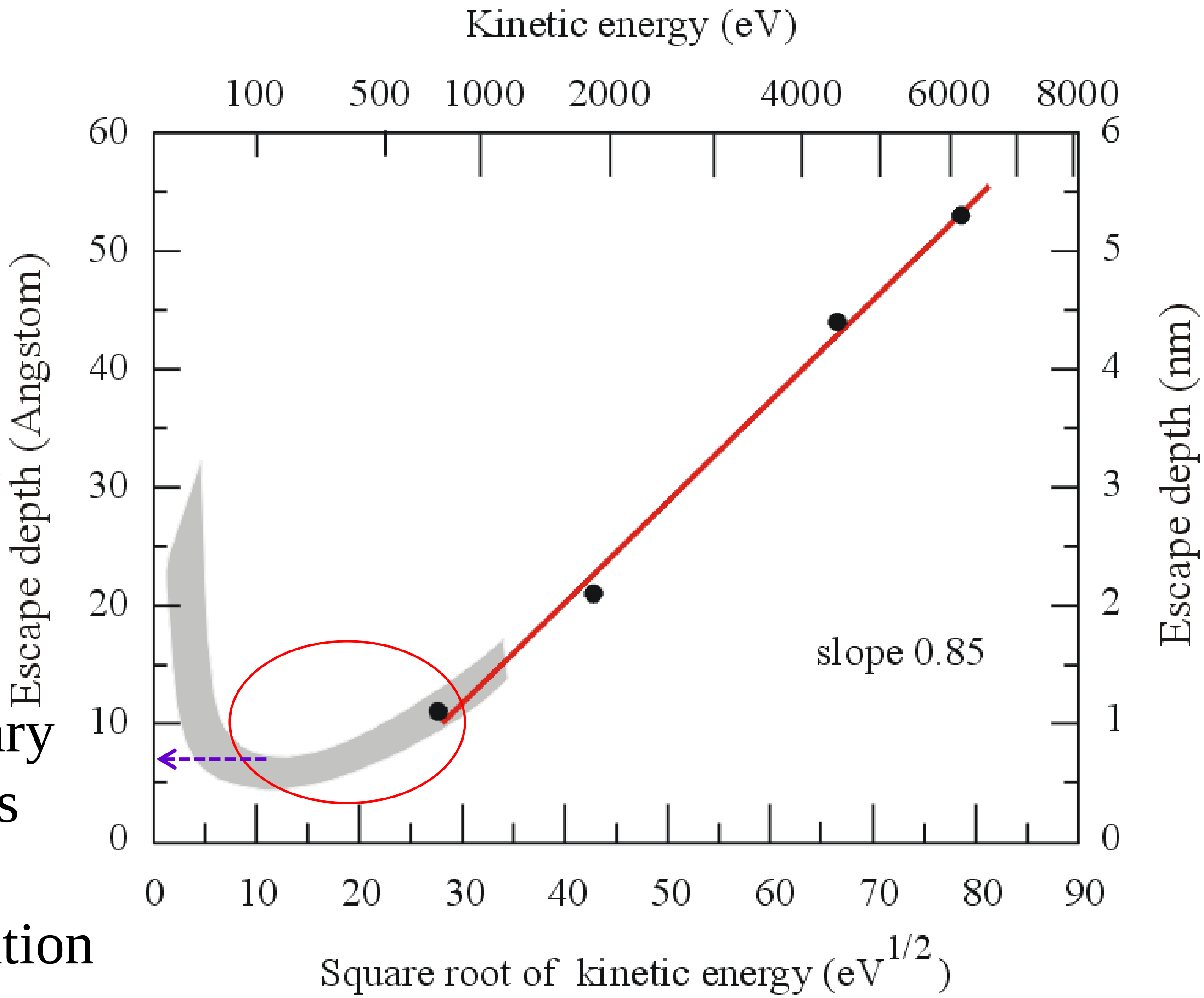
O *K*-edge

Ti *L3,2*-edge

Ti *M*-edge

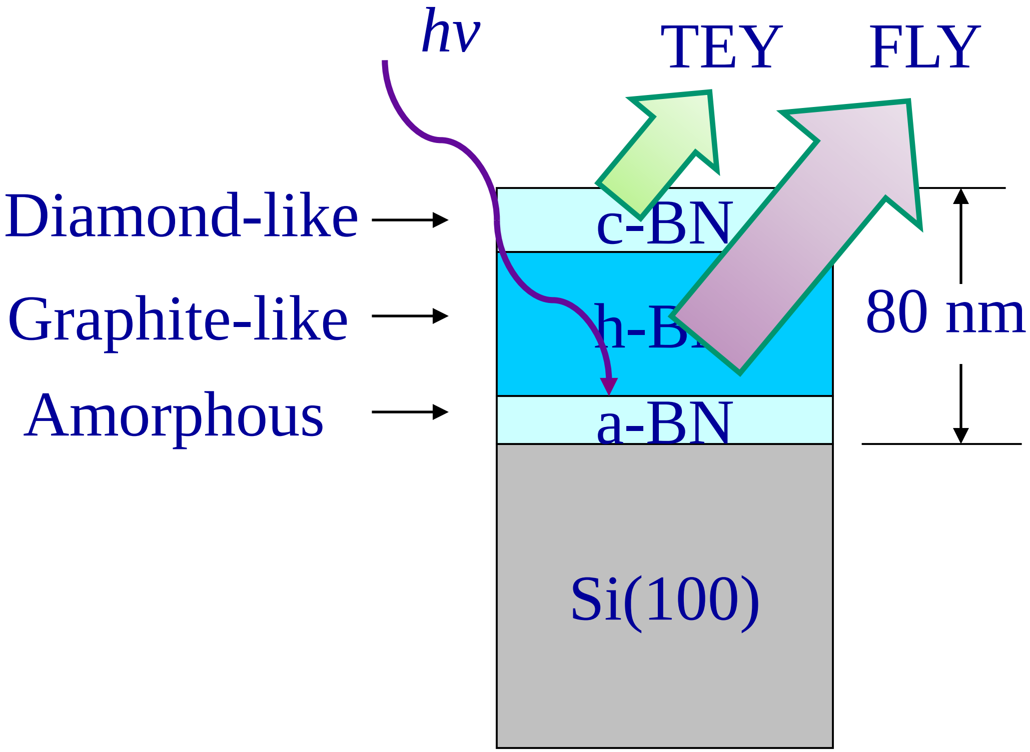
Source: CXRO

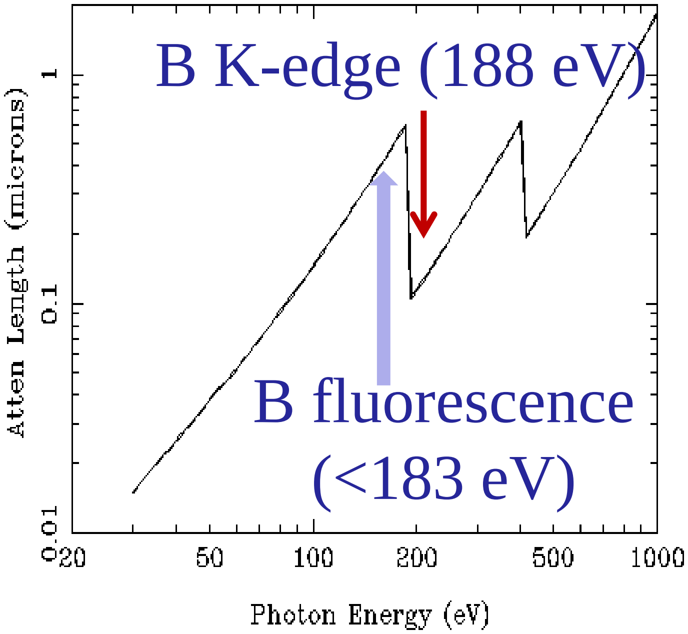
# Surface sensitivity & electron attenuation length



Secondary electrons Main contribution to TEY

# The Interplay of TEY and FLY @ B K-edge



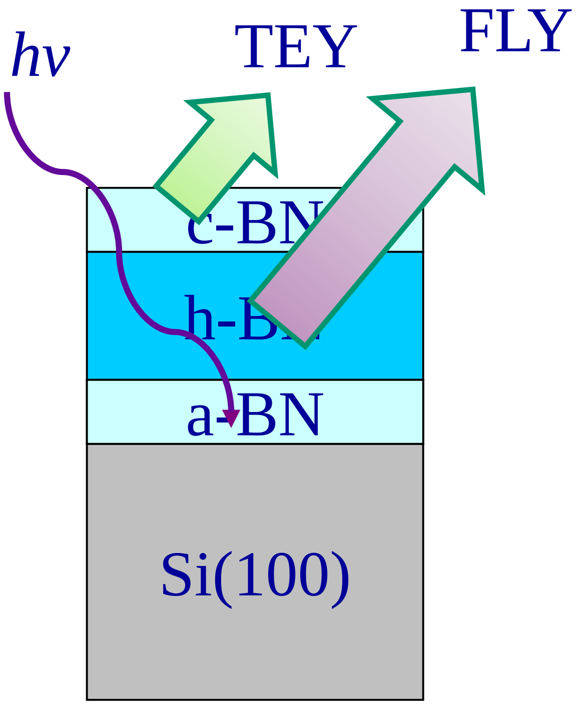


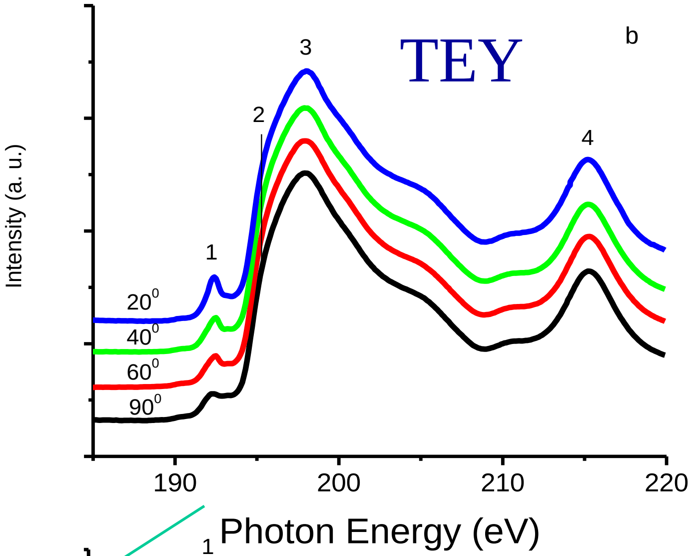
B K-edge (188 eV)

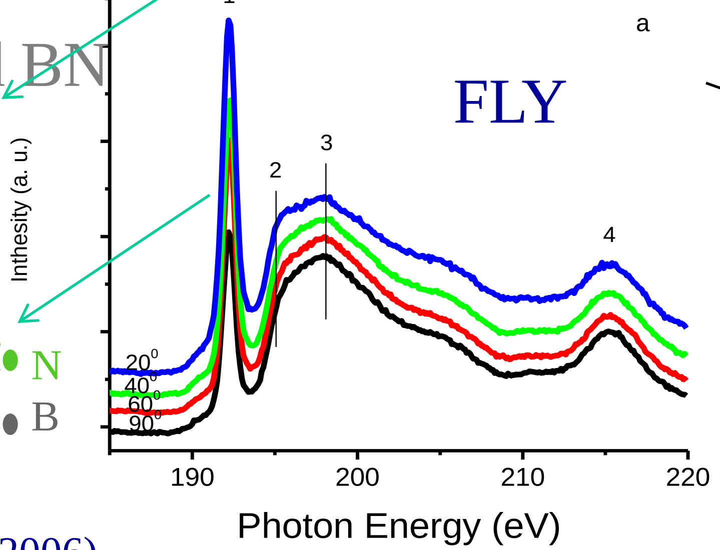
B fluorescence (<183 eV)

Cubic BN film grown on Si(100) wafer ?
Texture of the h-BN underlayer (film)?

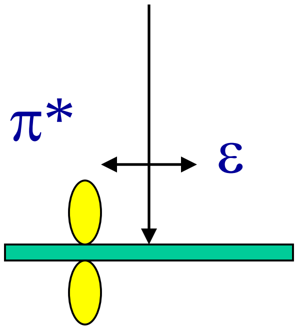
# Boron K-edge





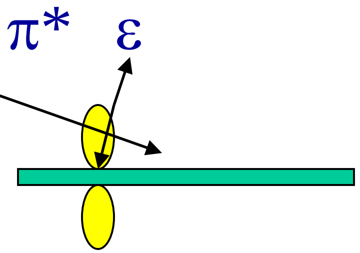


normal (90°)



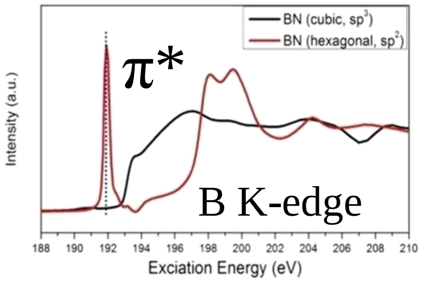
I (1s - π*) minimum

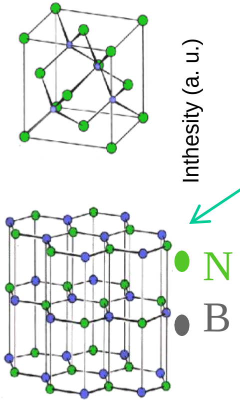
glancing (20°)



I (1s - π*) maximum

sp3 and sp2 hybridized BN





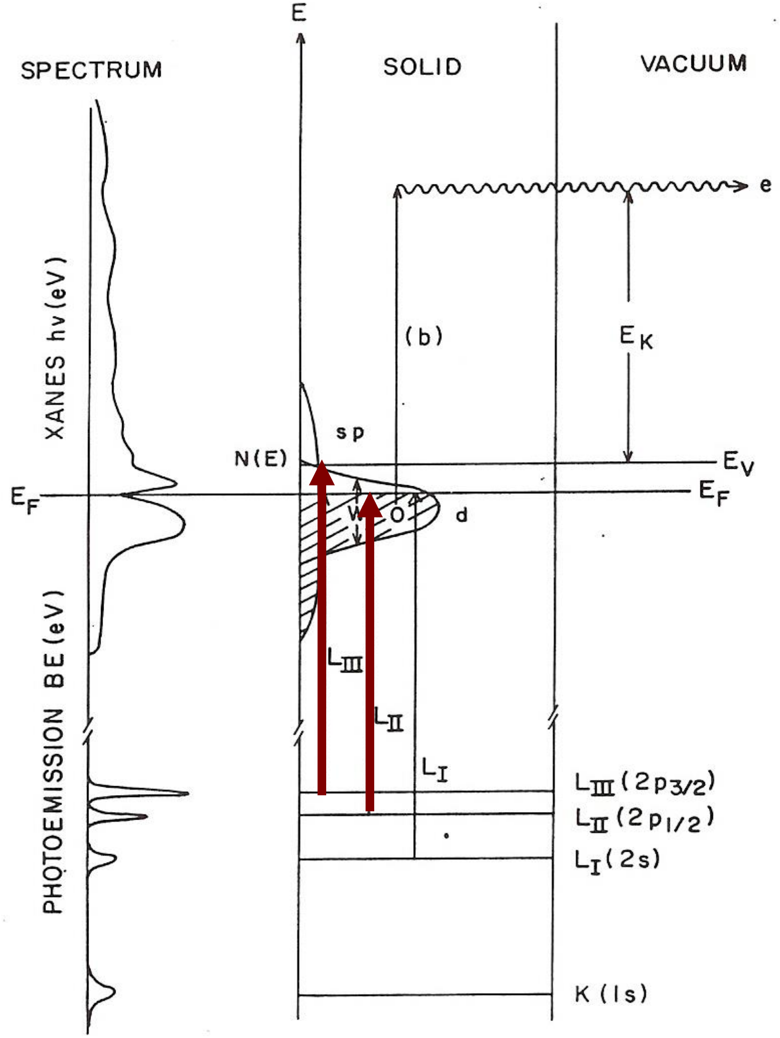
X.T. Zhou et.al. JMR 2, 147 (2006)

# Probing d band metals

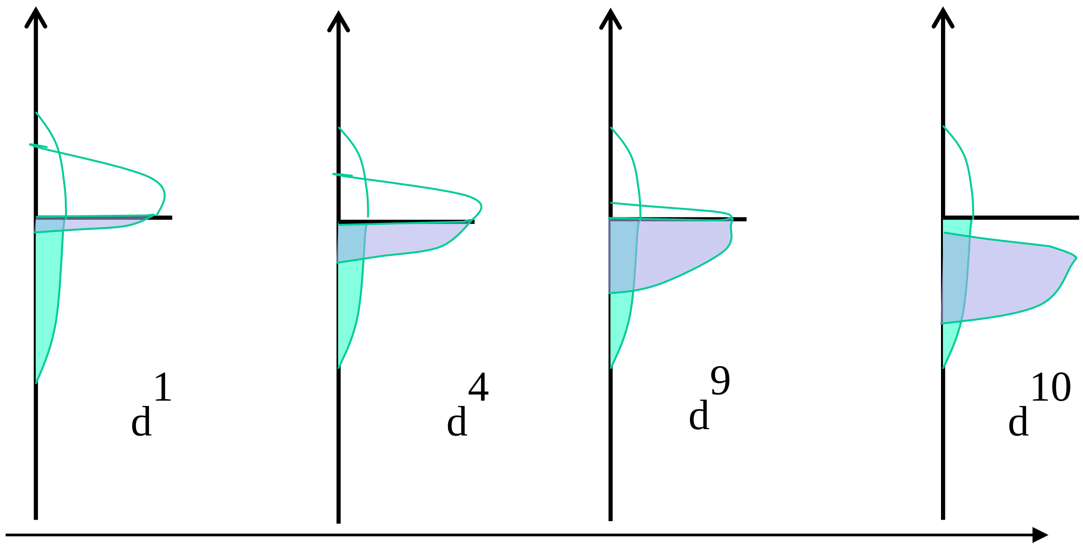
## 3d, 4d and 5d

# d – band metals

The dipole selection rule allows for the probing of the unoccupied densities of states (DOS) of ***d*** character from the 2p and 3p levels – $M_{3,2}$ and $L_{3,2}$-edge XANES analysis (relevance: catalysis)



# Transition metal systematic

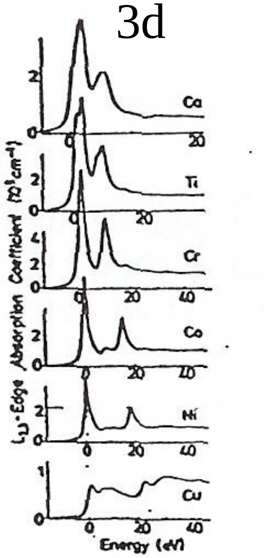


Filling of the d band across the period

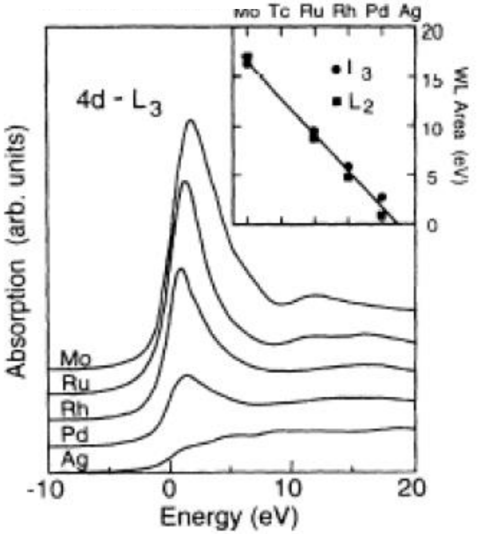
Atom:
ns$^2$(n-1)dx$^n$
Ni:4s$^2$3d$^7$

Metal:
ns$^1$(n-1)d$^{x+1}$
Ni:4s$^1$3d$^8$

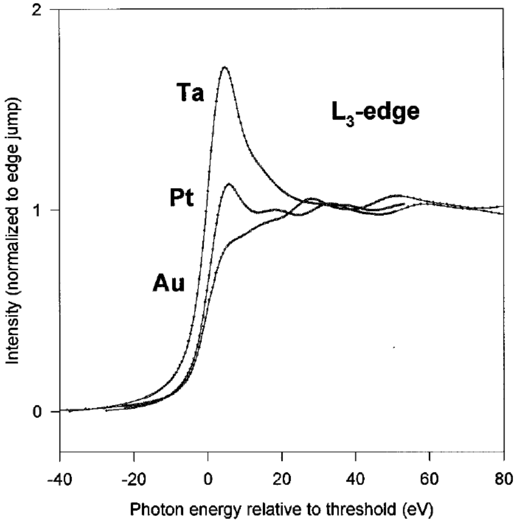
3d



4d



5d



# $L_{3,2}$/$M_{3,2}$ Whiteline and unoccupied densities of d states

- 3d metal: the L-edge WL for early 3d metals is most complex due to the proximity of the $L_3$,$L_2$ edges as well as crystal field effect; the 3d spin-orbit is negligible
- 4d metals: the $L_3$,$L_2$ edges are further apart, WL intensity is a good measure of 4d hole population
- 5 d metals: The $L_3$ and $L_2$ are well separated but the spin orbit splitting of the 5d orbital becomes important, j is a better quantum number than *l*, WL intensity is a good measure of $d_{5/2}$ and $d_{3/2}$ hole populations

# 3d metals

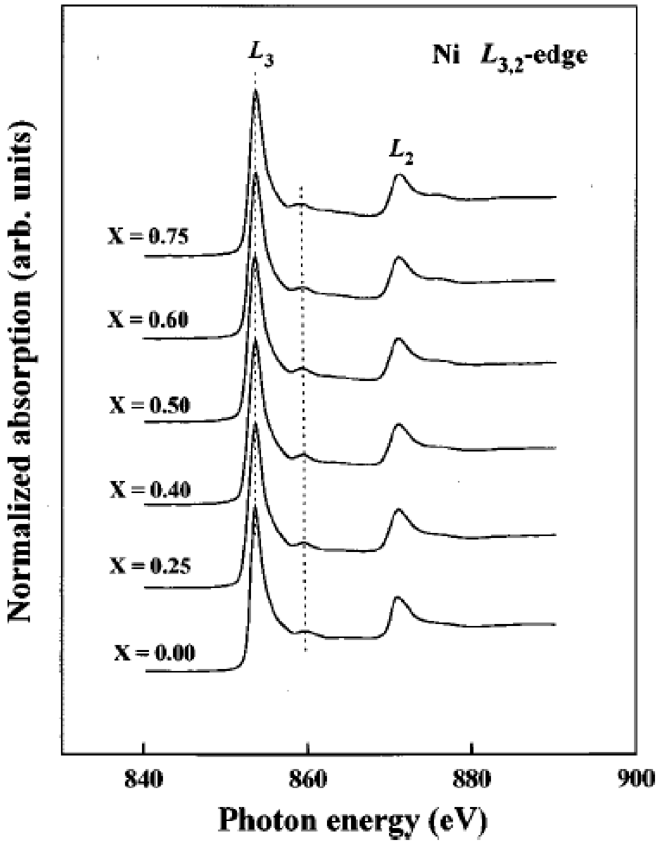


FIG. 2. Normalized Ni $L_{3,2}$-edge x-ray-absorption spectr Ni-Cu alloys and pure Ni metal at room temperature.

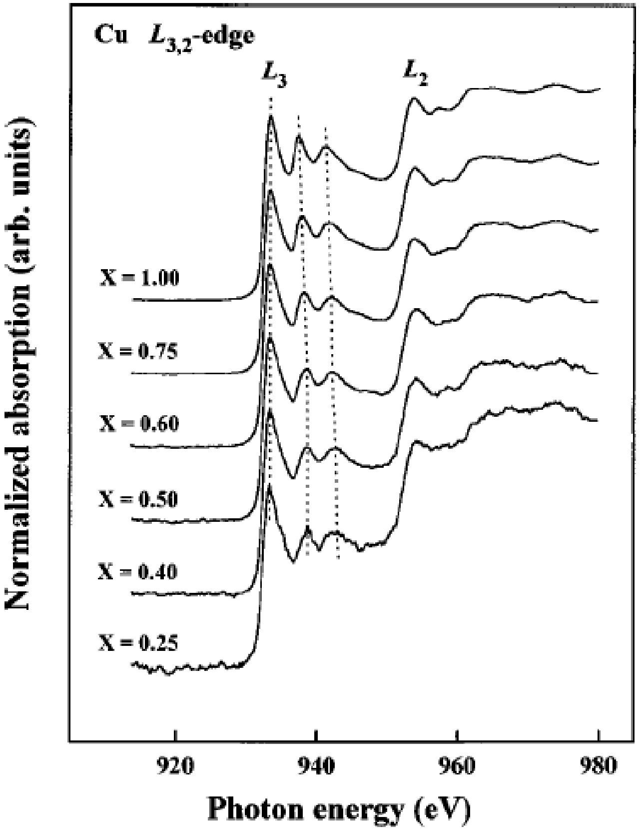
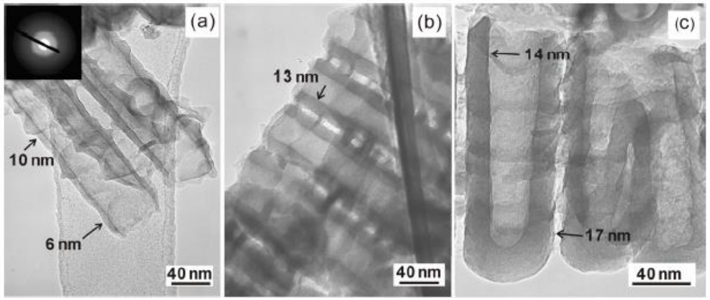


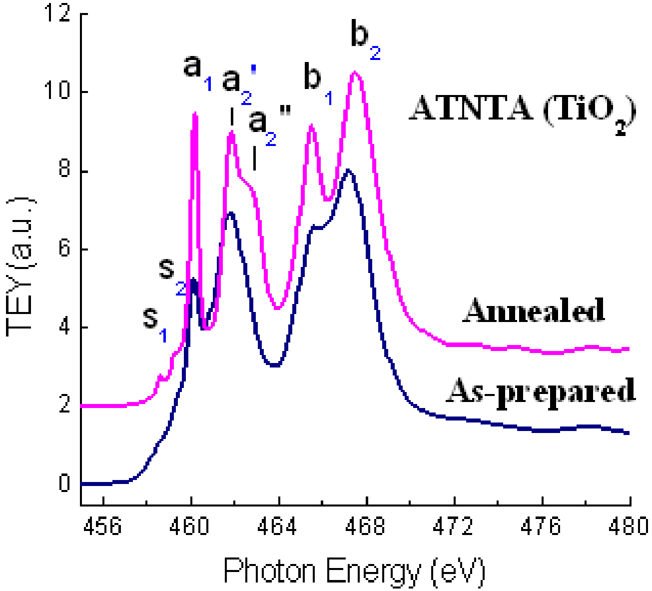
FIG. 3. Normalized Cu $L_{3,2}$-edge x-ray-absorption spectra of Cu alloys and pure Cu metal at room temperature.

Hsieh et al Phys. Rev. B 57, 15204 (1998)

# 3d compounds: $TiO_2$ Nanotube

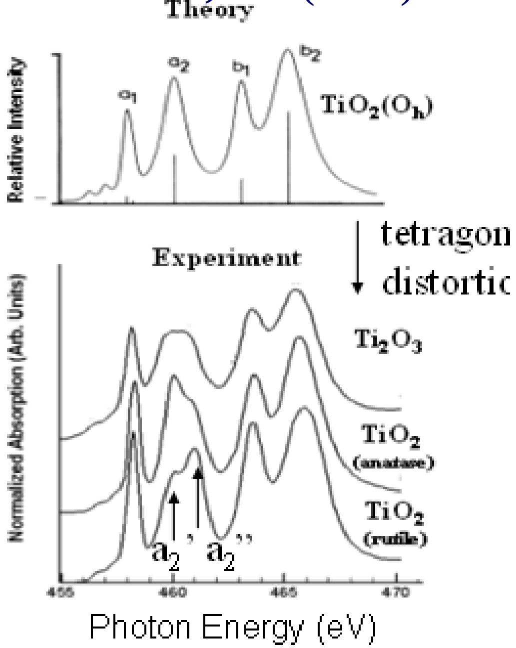


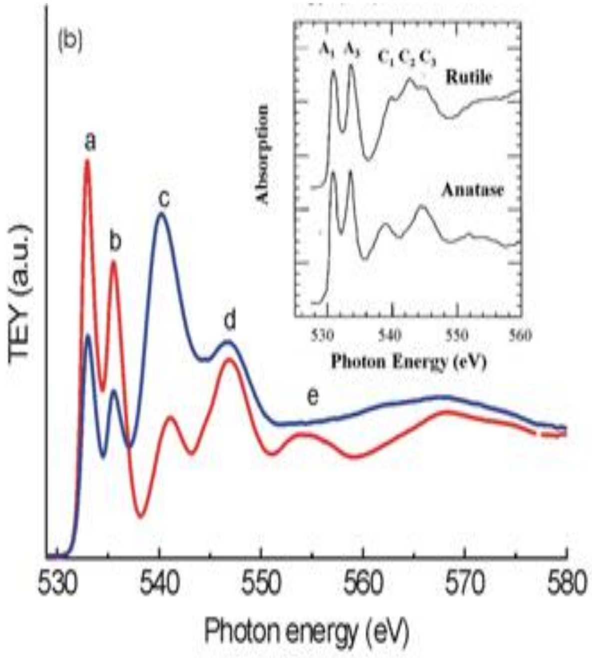
H. Fang et al.
Nanotechnology (2009)



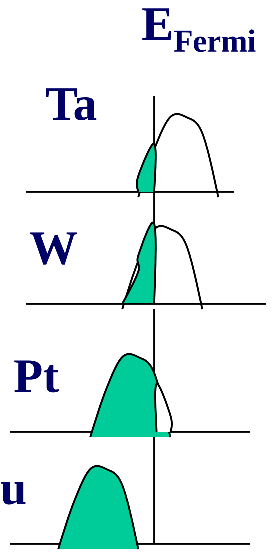
J. Zhou et al. **J. Mater. Chem.,**
19, 6804-6809 (2009)

F.M.F. de Groot, et al.,
**PRB 41,** 928 (1990)

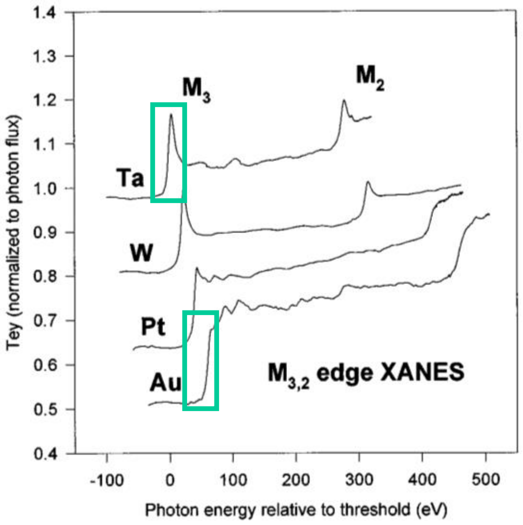


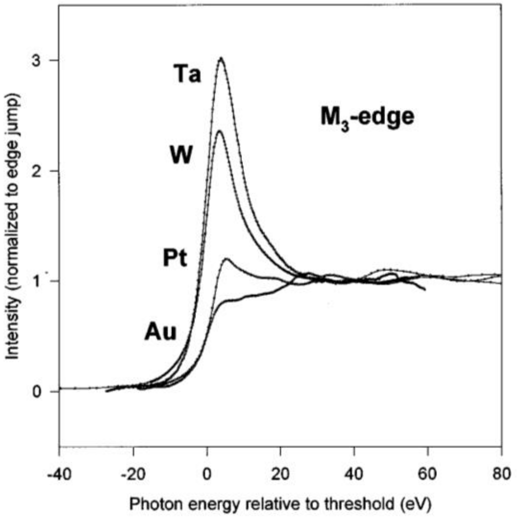


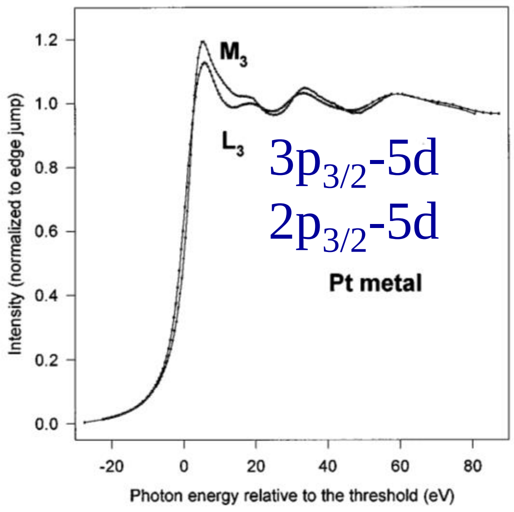
# d- band filling across 4d and 5d row



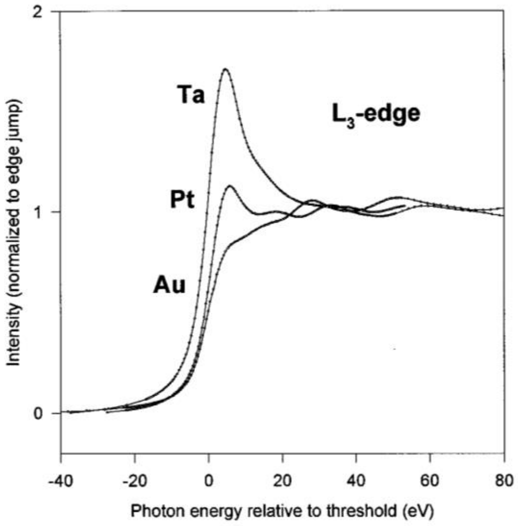
**5d metal d band**







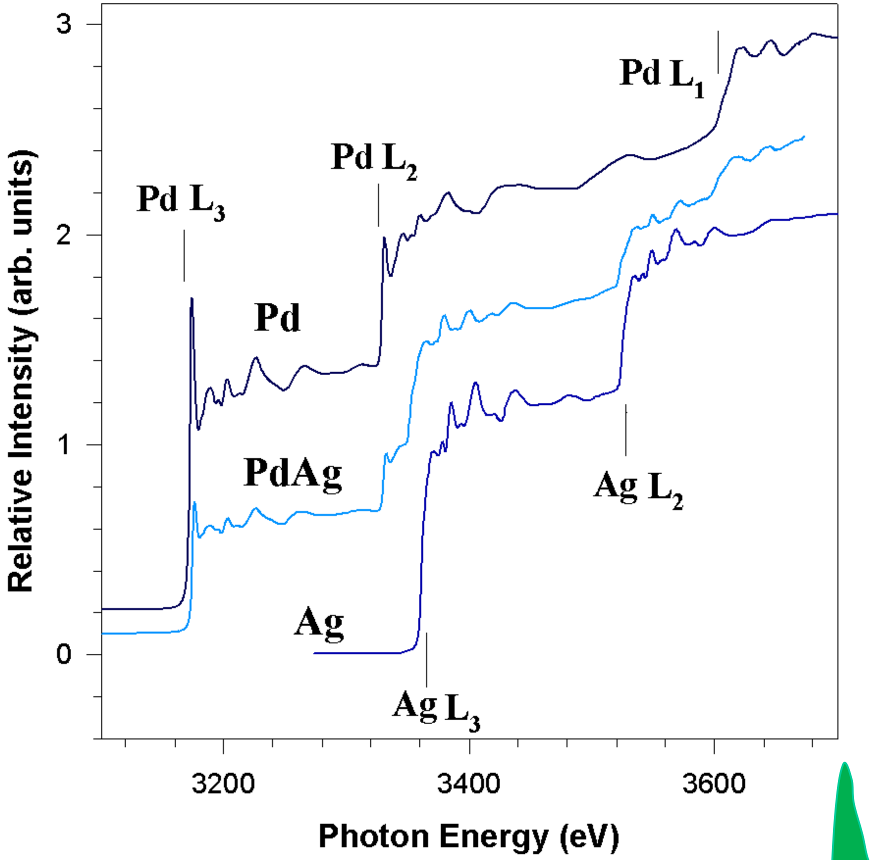
$3p_{3/2}$-5d
$2p_{3/2}$-5d

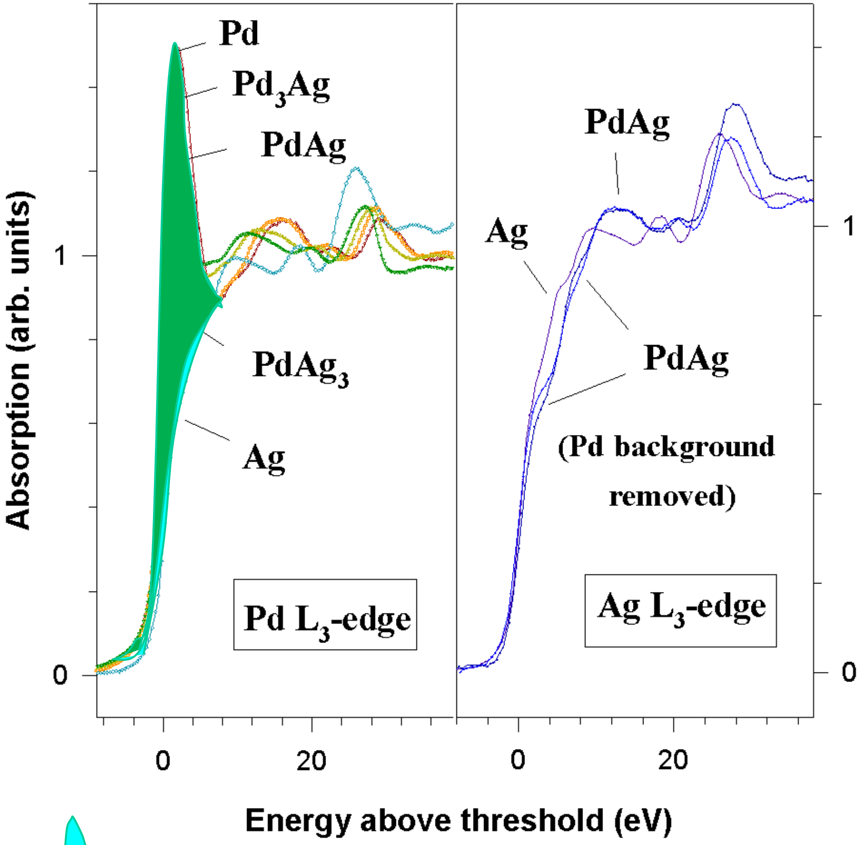


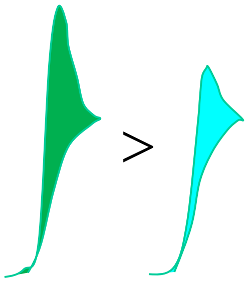
Intensity (area under the curve) of the sharp peak at threshold (white line) probes the DOS

# d - charge redistribution in 4d metals

## Ag →Pd 4d charge transfer upon alloying



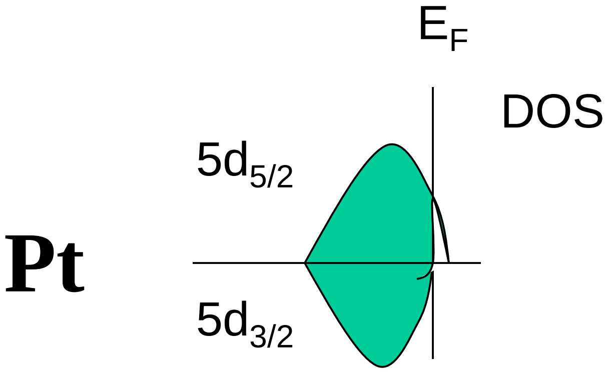




charge transfer to Pd d band
In PdAg$_3$

# Analysis of d hole in Au and Pt metal

In 5 d metals with a nearly filled/full d band such as Pt and Au, respectively, spin orbit coupling is large so $d_{5/2}$ and $d_{3/2}$ holes population is not the same

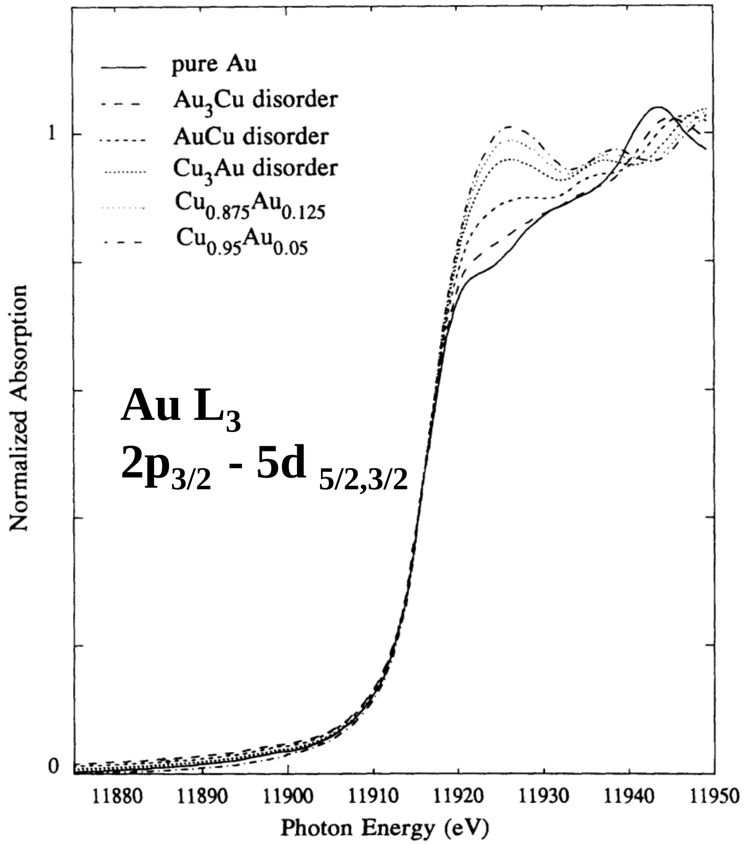


Selection rule: dipole,

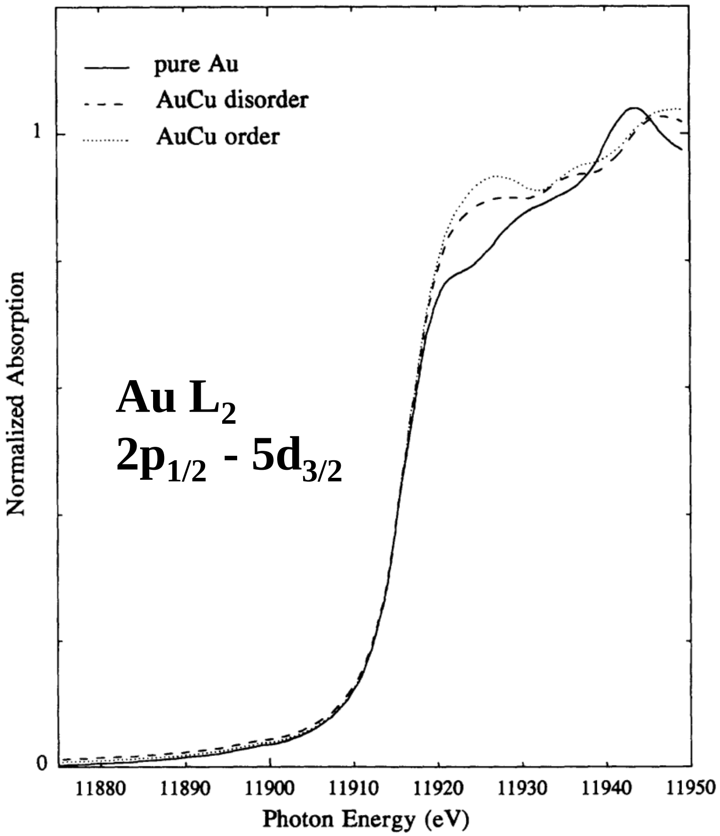
$$\Delta l = \pm 1, \Delta j = \pm 1, 0$$

$$L_3, 2p_{3/2} \rightarrow 5d_{5/2.3/2}$$

$$L_2, 2p_{1/2} \rightarrow 5d_{3/2}$$



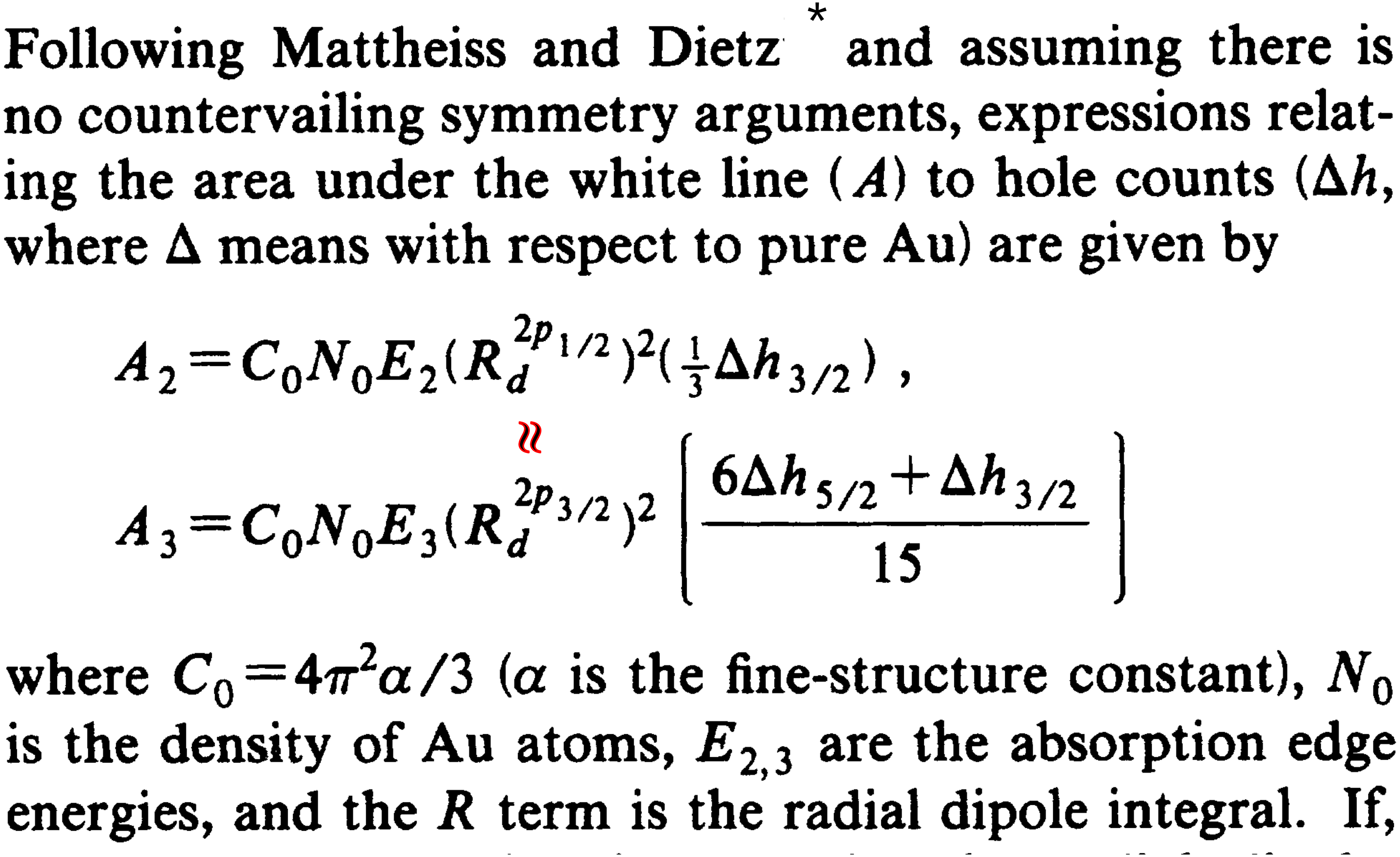
**Au $L_3$**
**$2p_{3/2}$ - $5d_{5/2,3/2}$**



**Au $L_2$**
**$2p_{1/2}$ - $5d_{3/2}$**

$$A_2 = \int [\mu_{L_2}(\text{alloy}) - \mu_{L_2}(\text{Au})] dE \ ,$$

$$A_3 = \int [\mu_{L_3}(\text{alloy}) - \mu_{L_3}(\text{Au})] dE \ .$$



Following Mattheiss and Dietz * and assuming there is no countervailing symmetry arguments, expressions relating the area under the white line ($A$) to hole counts ($\Delta h$, where $\Delta$ means with respect to pure Au) are given by

$$A_2 = C_0 N_0 E_2 (R_d^{2p_{1/2}})^2 (\tfrac{1}{3}\Delta h_{3/2}) \ ,$$

$$\approx$$

$$A_3 = C_0 N_0 E_3 (R_d^{2p_{3/2}})^2 \left[ \frac{6\Delta h_{5/2} + \Delta h_{3/2}}{15} \right]$$

where $C_0 = 4\pi^2\alpha/3$ ($\alpha$ is the fine-structure constant), $N_0$ is the density of Au atoms, $E_{2,3}$ are the absorption edge energies, and the $R$ term is the radial dipole integral. If,

* Phys. Rev. B22, 1663 (1980)

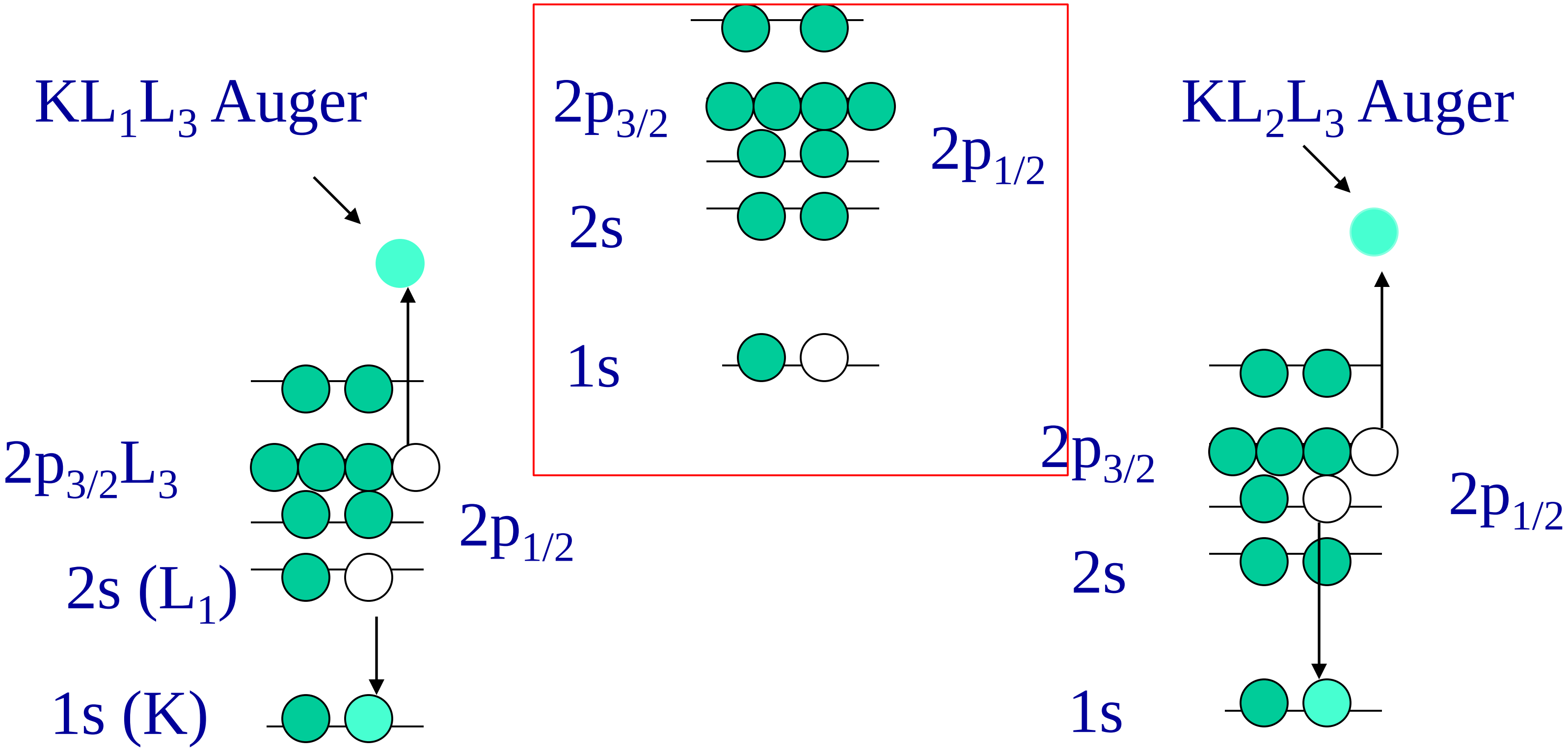
# De-excitation spectroscopy I (Auger)

Core hole decays via two competing channels

- **Auger**
  - normal (*hv* > threshold)
  - Coster- Kronig (hole and e from same shell)
  - Resonant Auger (*hv*~ threshold)
- Fluorescence X-ray
  - normal (*hv* > threshold)
  - XES (x-ray emission, valence e)
  - RIXS (resonant inelastic x-ray scattering, *hv* ~ threshold), RXES (resonant XES)
- Other secondary processes, **fragmentation**/defect creation, luminescence, etc.

# Auger nomenclature

## 1s (K shell) core hole, normal Auger

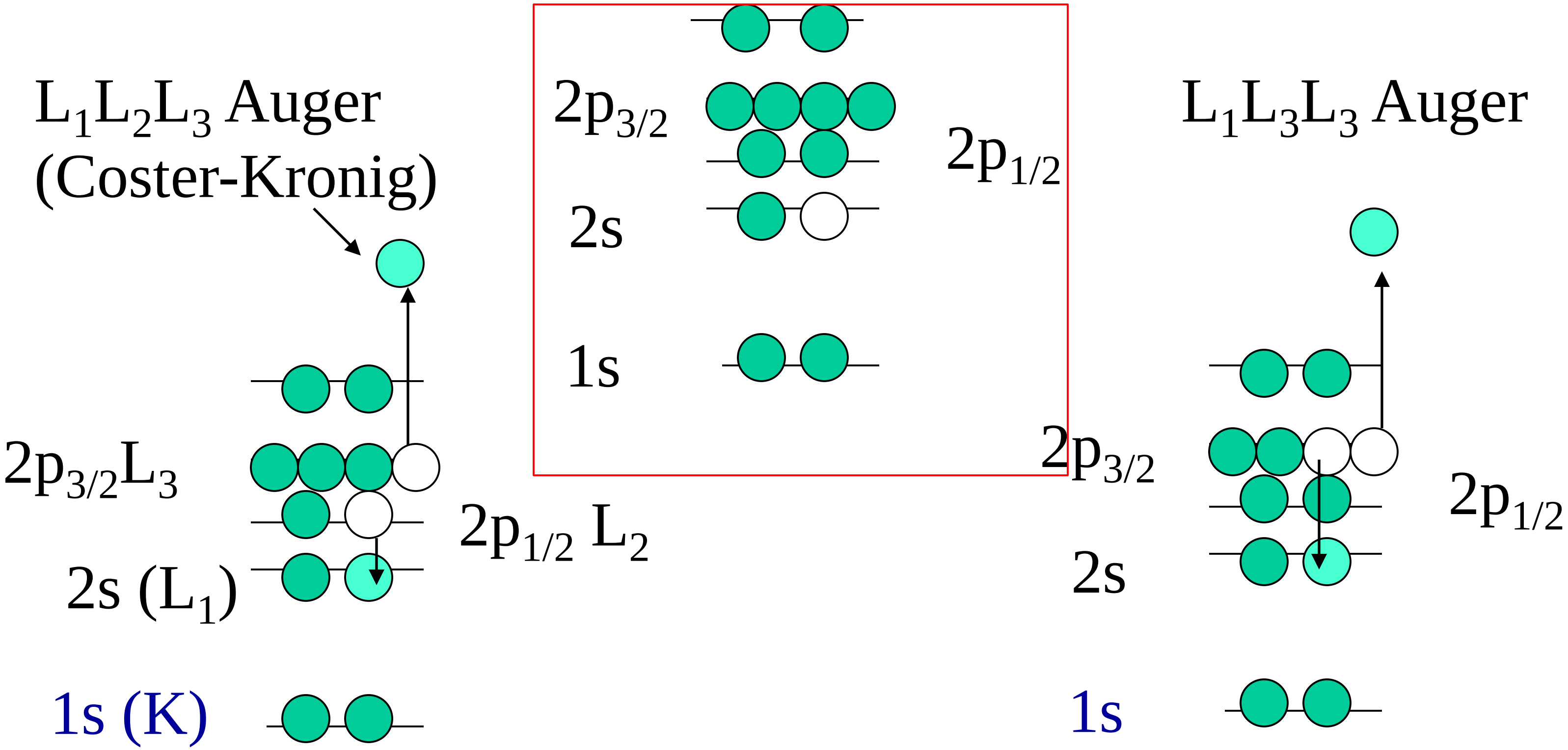


In general, Auger involving n = 2 electrons to fill the 1s hole are called KLL Auger electrons ; selection rule: coulombic

In low z elements, Auger is the dominant decay channel; it determines the life time of the corehole; i.e. that the shorter the lifetime, the broader the peak (Uncertainty Principle).

# Auger nomenclature

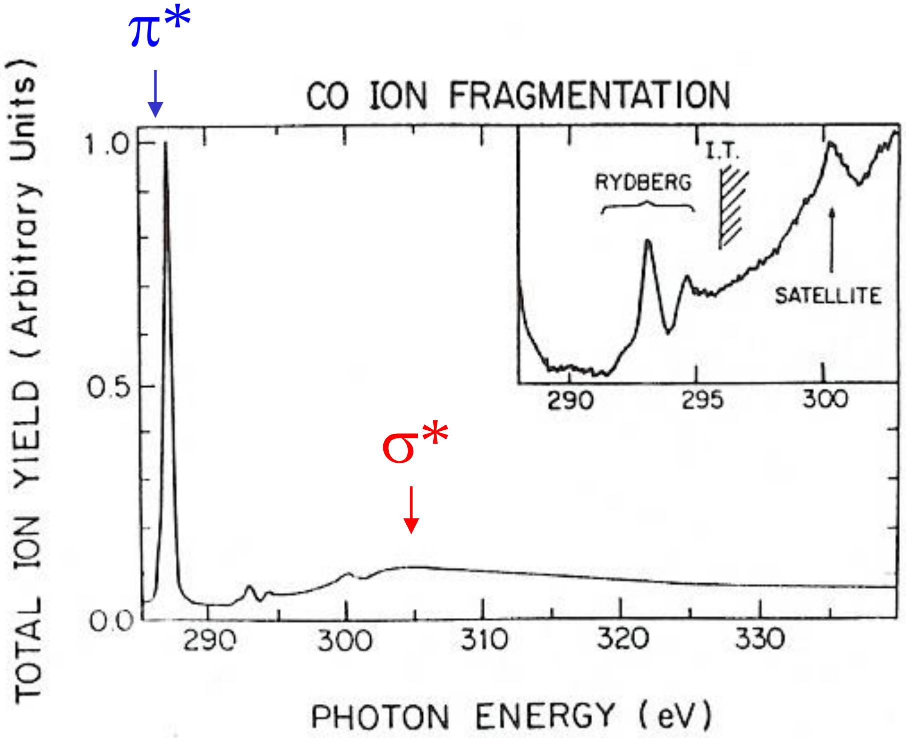
2s ($L_1$) core hole, filled by other L subshell → Coster Kronig



Auger process involving 2 electrons from the shell with the same quantum number n are called Coster-Kronig transitions;
CK transitions are fast; it leads to short life time of the corehole.

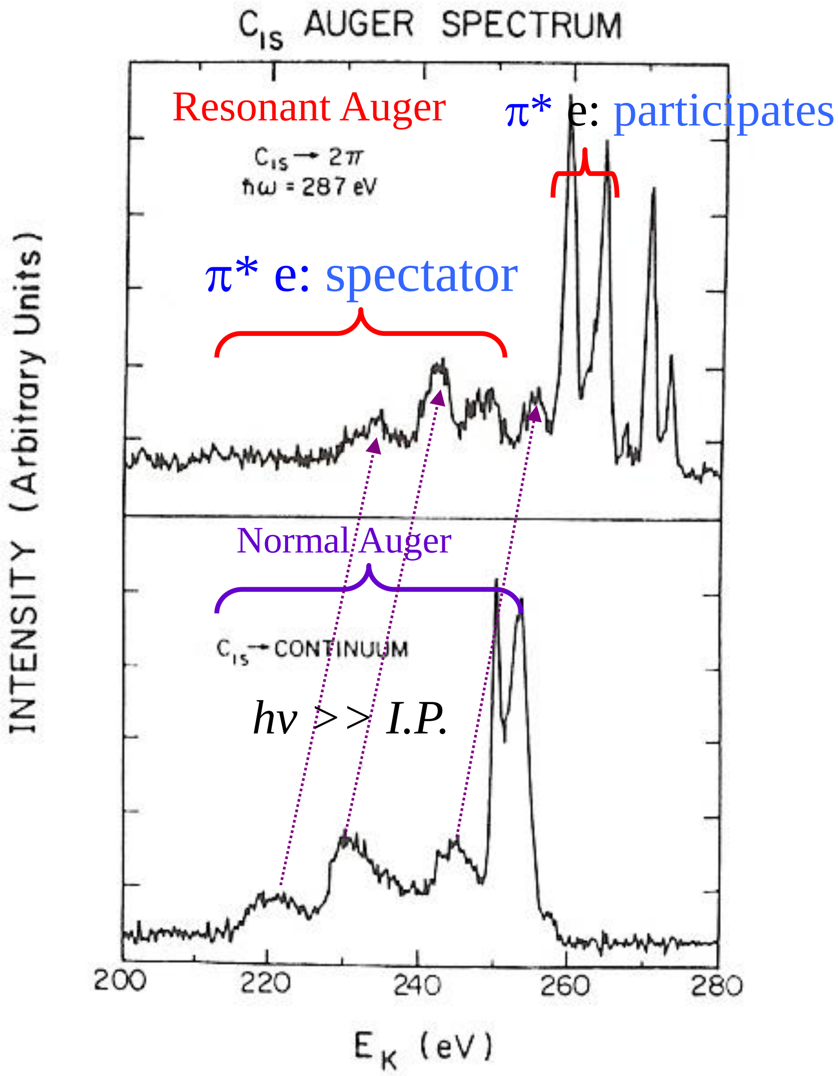
*KE* (Auger) = *BE (1s)* - BE (L) - BE(L’) - *V (2 hole state)*

# Auger in molecular systems



π*

σ*



Resonant Auger

π* e: participates

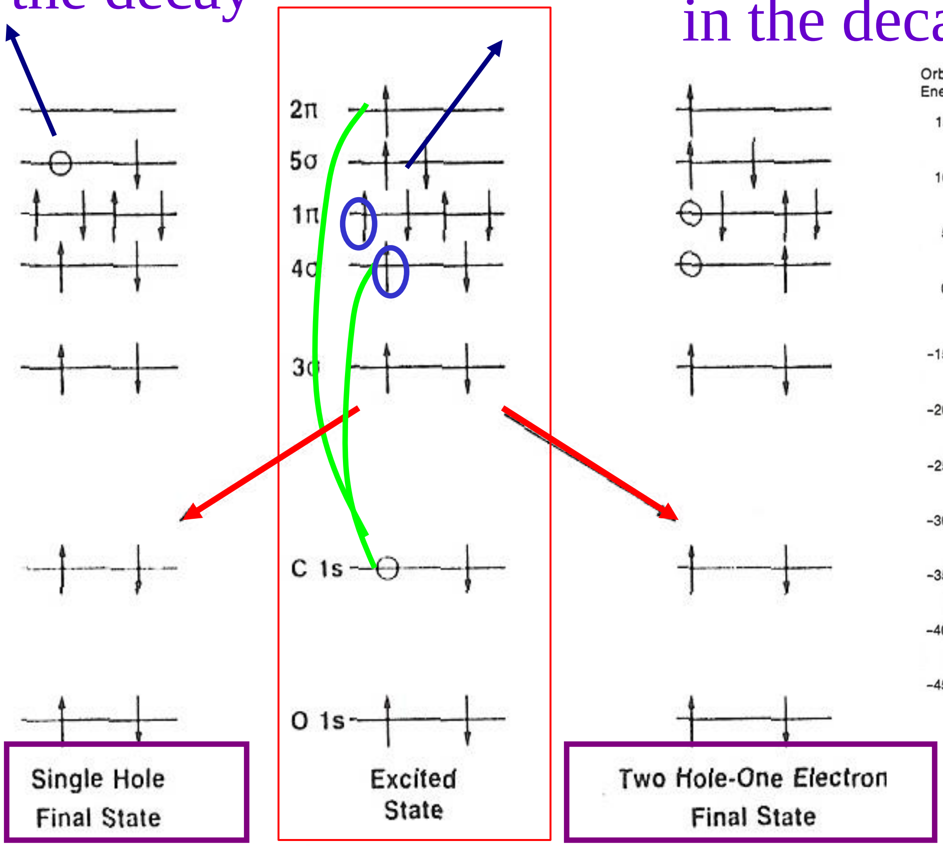
π* e: spectator

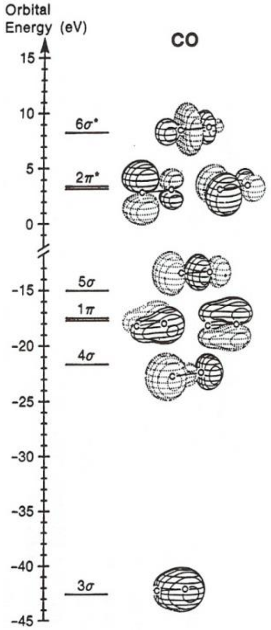
Normal Auger

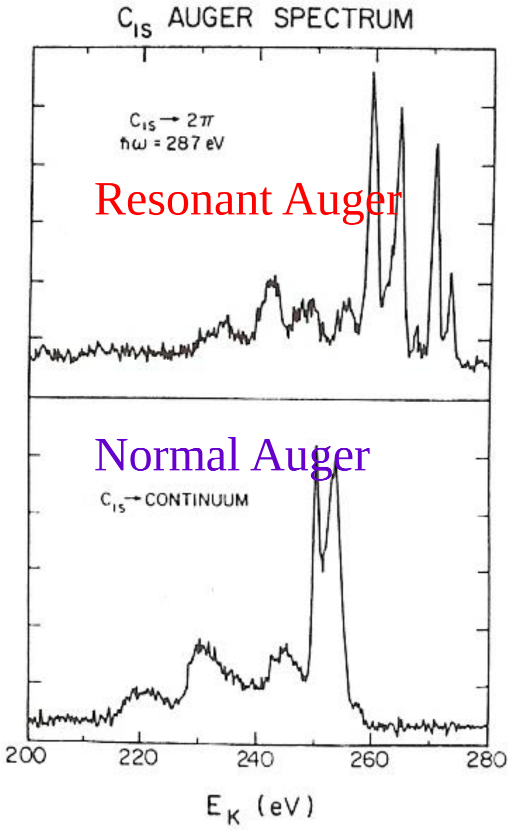
hv >> I.P.

Excited electron participates in the decay

Excited electron acts as a spectator in the decay







Resonant Auger

Normal Auger

Kinetic energy

Resonant photoemission

Note: corresponding normal Auger has a two hole final state without the excited electron acting as the spectator

# Auger electrons excited at resonance

How to identify Auger and photoelectrons ?

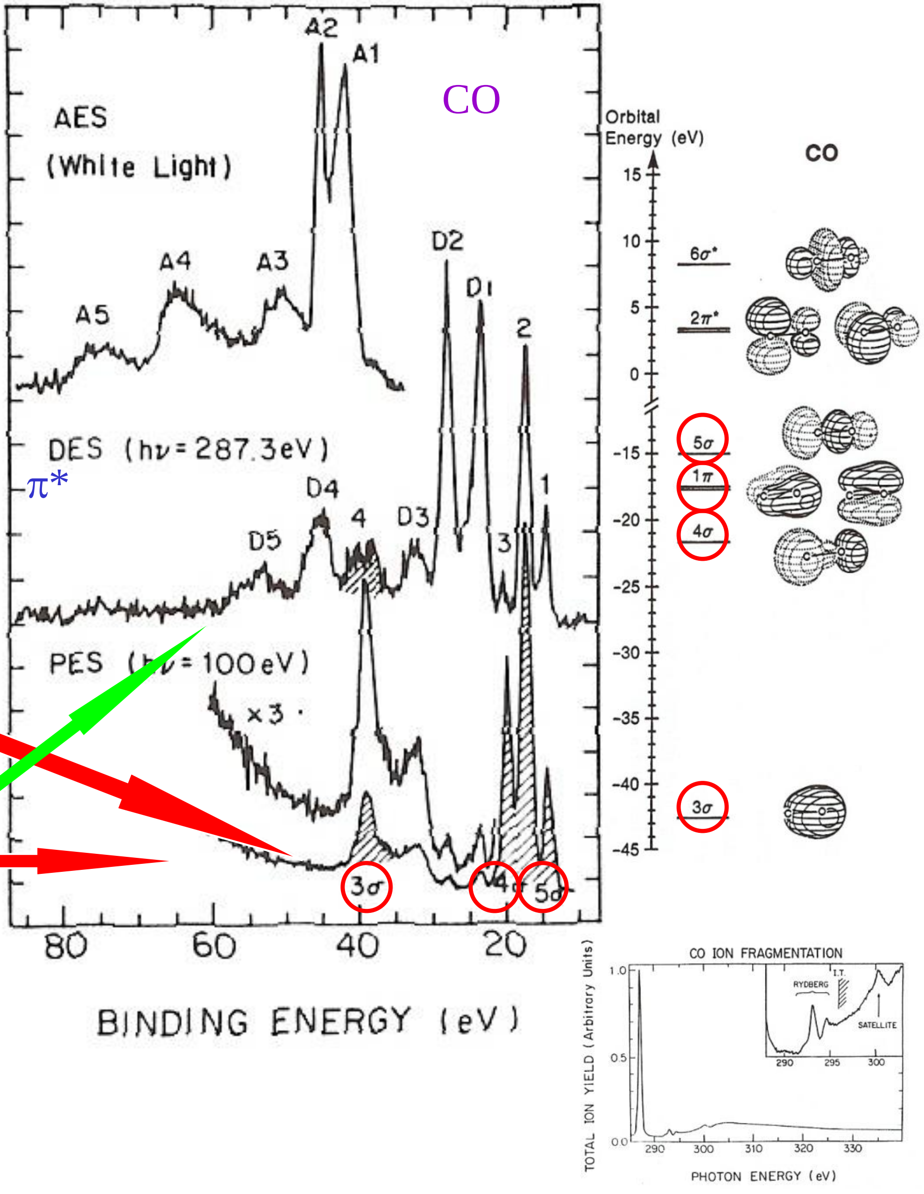
*hv* is significantly above the threshold

i) Normal Auger electrons (2 hole final state) associated with a core hole have constant KE,

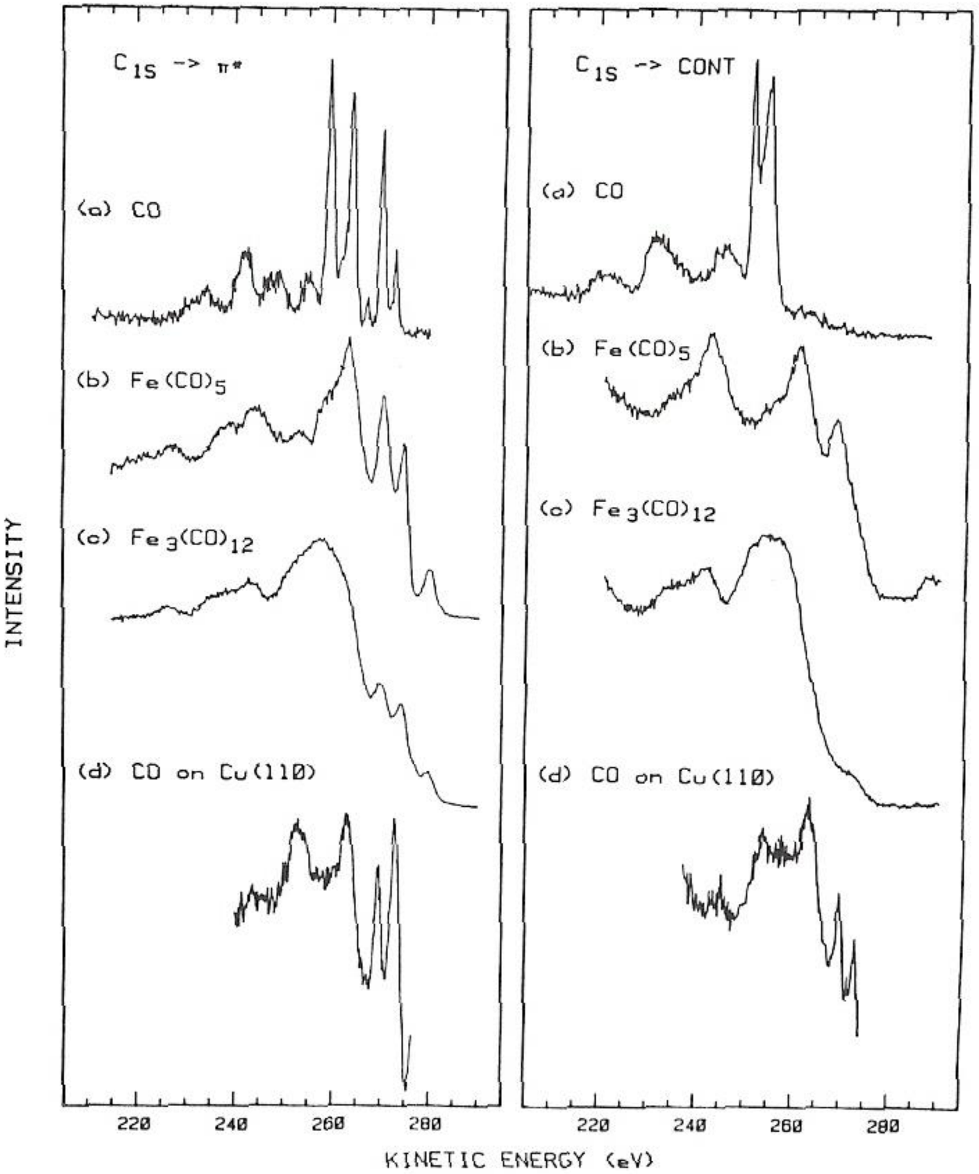
ii) Photoelectrons have constant BE regardless of photon energy. In gas phase, BE = *hv* – KE

Excitation energy significantly below C 1s threshold, no C -KLL Auger

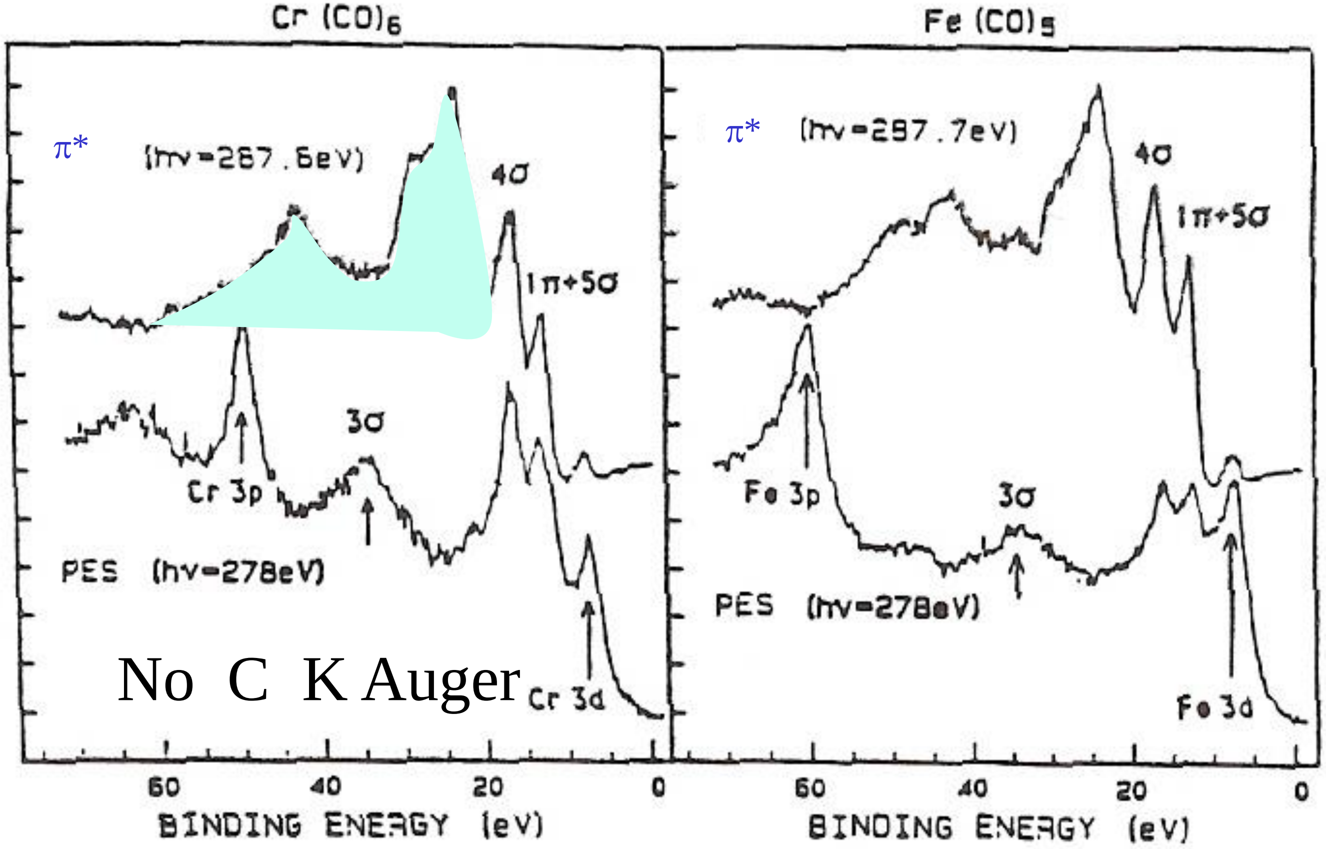
*hv* = resonance energy, Auger Peaks appear at higher kinetic energy (2 hole + spectator electron)



# Other examples



# Resonant Photoelectron and Auger spectroscopy



No C K Auger

XPS of VB at π* resonance, resonant Auger turns on

XPS of VB below π* resonance, no C K-edge Auger

# Resonance in NXAFS/XANES

## (bound to bound transitions)

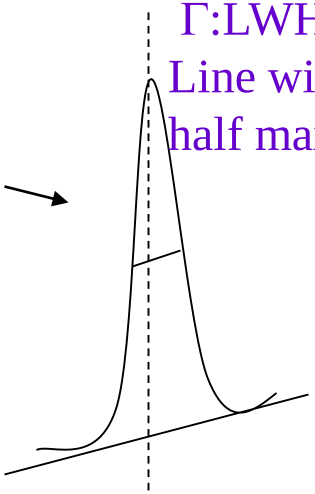
Peak position (E): atomic one-electron energy of the core level modified by chemical environment, to LUMO, LUMO+ transition

e.g. oxidation state, electronegativity etc.

Peak width (Γ ): convolution of core hole lifetime (uncertainty principle), and instrumentation resolution, ΔEI

$$\Delta x \cdot \Delta p = \Delta t \cdot \Delta E_{\tau} \geq \frac{\hbar}{2}$$

$$\Gamma = \sqrt{\Delta E_{\tau}^{2} + \Delta E_{I}^{2}} \rightarrow$$



Γ:LWHM

Line width at half maximum

Lifetime of core hole, τ; lifetime broadening

Peaks intensity (I): (area under the curve)

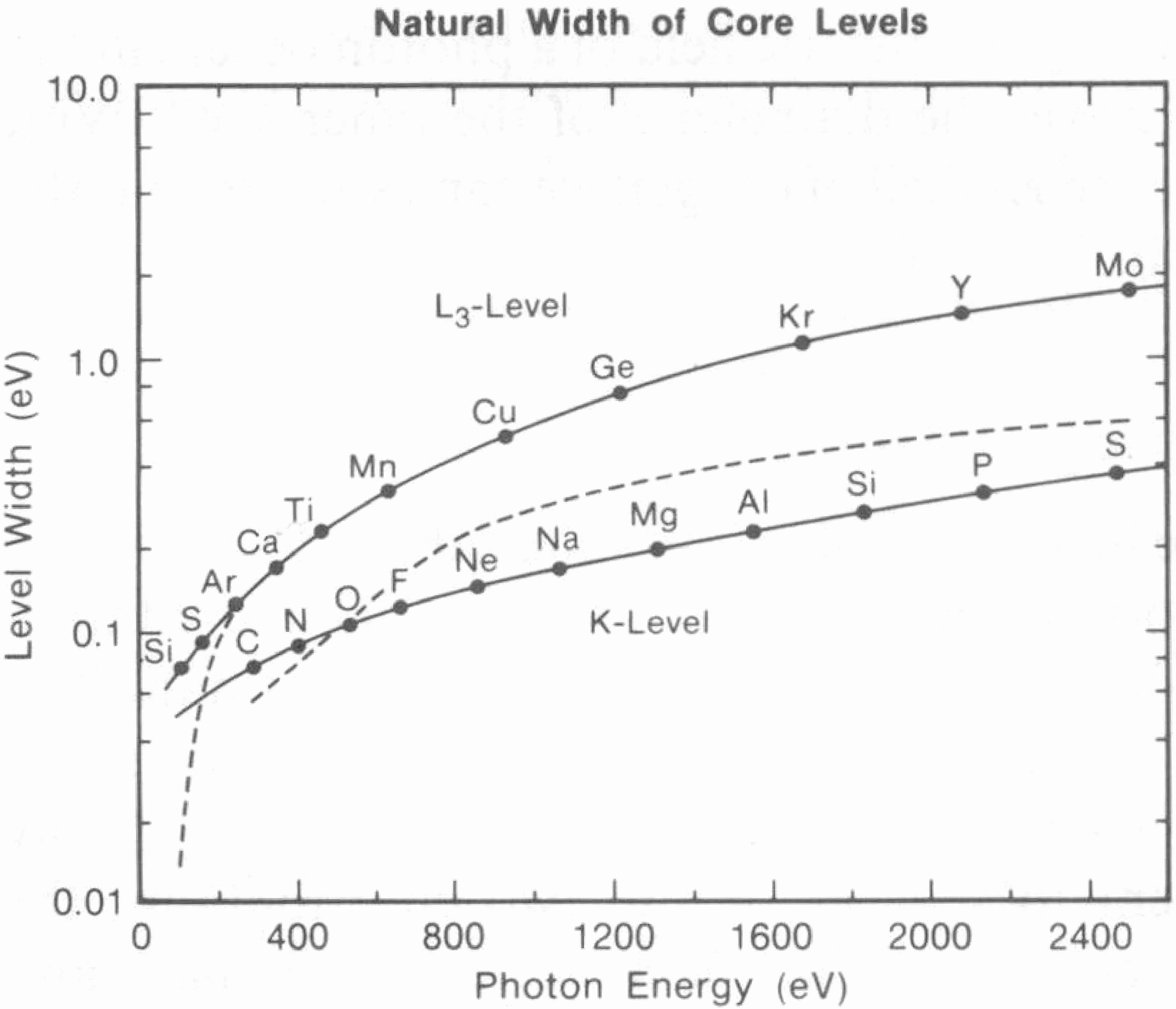
transition matrix element

and the occupancy densities of states

of the final states ρ (E)

$$\left|\langle i|r|f\rangle\right|^{2}$$

Note: in classical theory, the peak intensity is also referred to as oscillator's strength



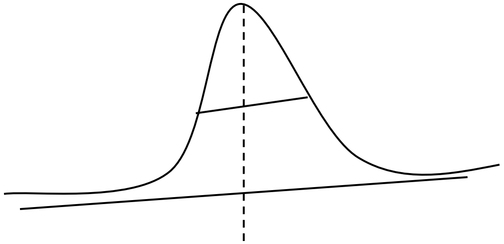
J Stöhr, NEXAFS Spectroscopy

# Resonance in NXAFS/XANES

## (bound to quasi bound transitions)

Peak position (E): atomic one-electron energy of the core level modified by chemical environment to MS state
e.g. qualitatively to semi-quantitatively, inter-atomic distance
Peak width (Γ ): convolution of core hole lifetime (uncertainty principle), band width, instrumentation resolution, $\Delta E_\tau$ , $\Delta E_f$ and $\Delta E_I$
Peaks intensity (I): (area under the curve)
transition matrix element $\left|\langle i|r|f\rangle\right|^2$
and the occupancy densities of states of the final states ρ (E)

$$\Gamma = \sqrt{\Delta E_\tau^2 + \Delta E_f^2 + \Delta E_I^2}$$



Γ:LWHM
Line width at half maximum

# Core hole life time and widths (radiative, X-ray and Auger)

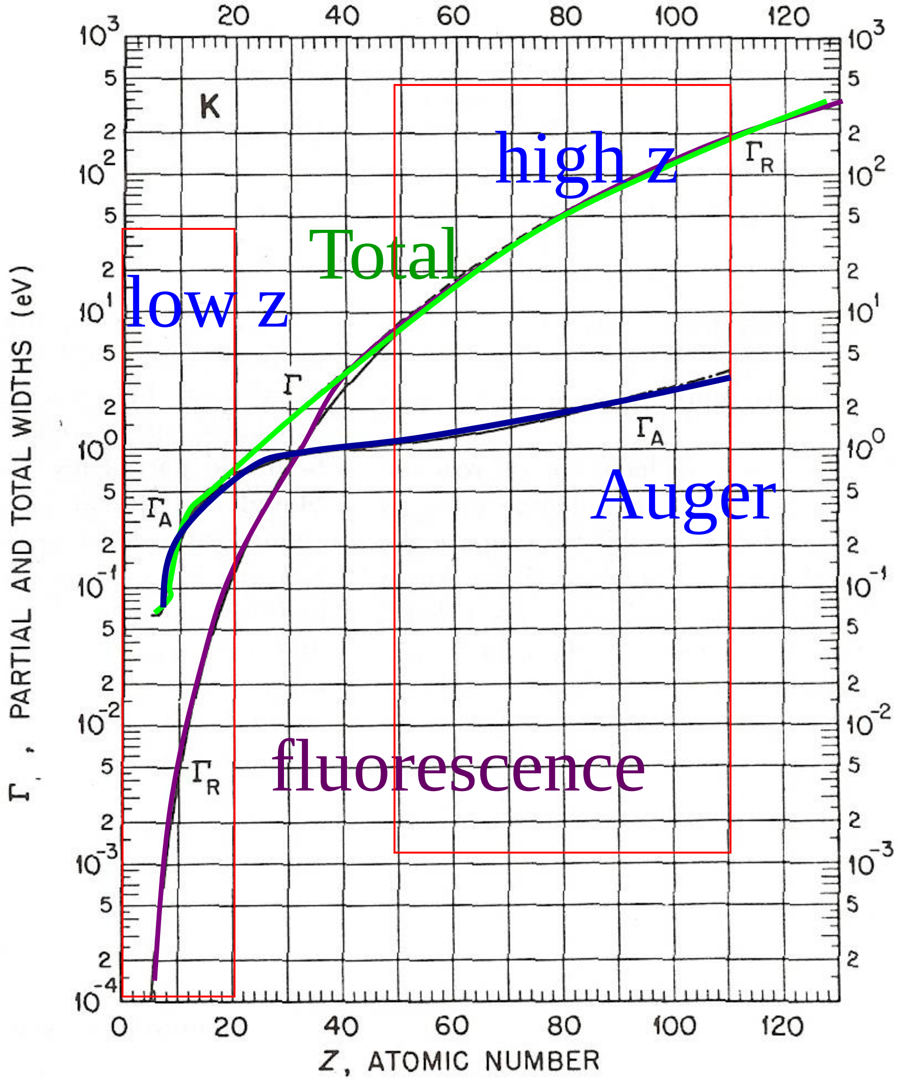


FIGURE 1. Theoretical partial and total atomic level widths for $K$ shell. $\Gamma_A$ = Auger width, $\Gamma_R$ = radiative width, $\Gamma$ = total width. Dot-dash curve represents semi-empirical $\Gamma_A$ curve obtained from adopted $\omega_K$ values and theoretical $\Gamma_R$ curve: $\omega_K \Gamma_A = (1 - \omega_K)\Gamma_R$.

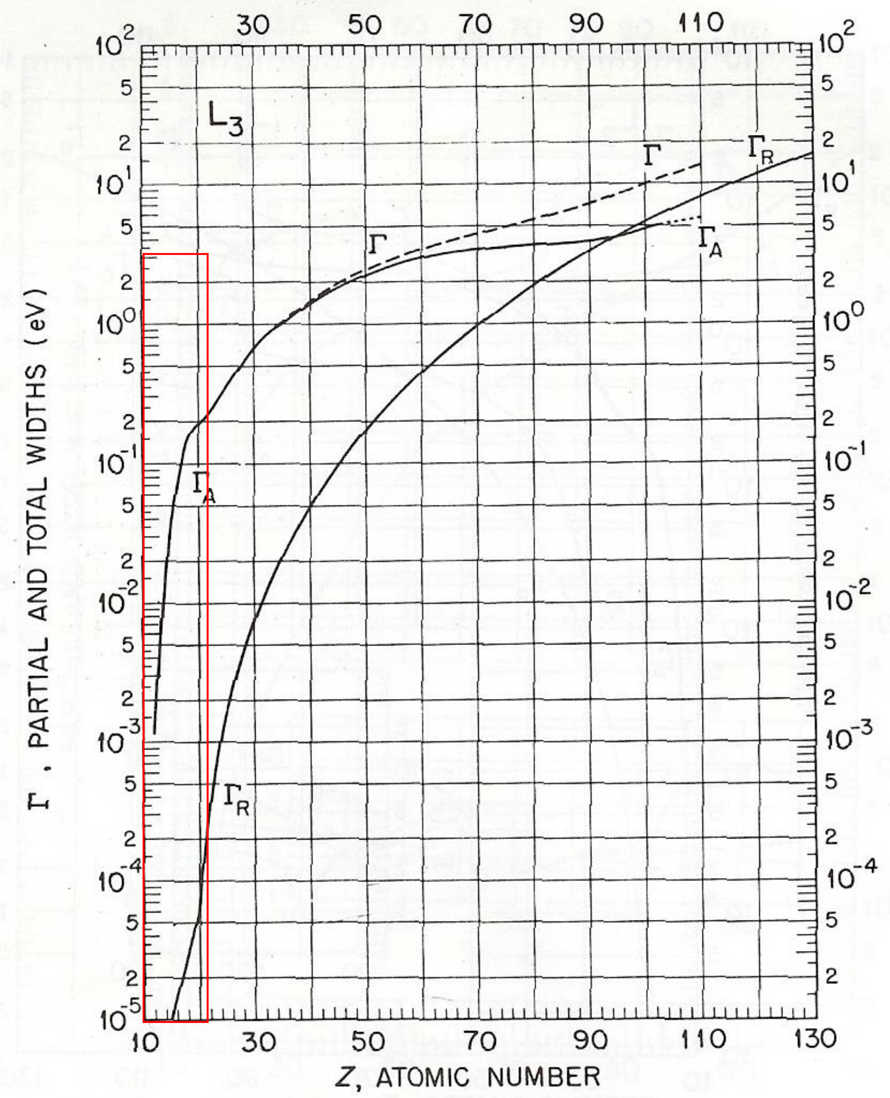


FIGURE 4. Theoretical partial and total atomic level widths for $L_3$ subshell. $\Gamma_A$ = Auger width, $\Gamma_R$ = radiative width, $\Gamma$ = total width.

# Photo-fragmentation of molecules

- One of the more interesting consequence of core hole decay is the fragmentation of molecules (**radiation chemistry, radiation damage)**
- Photo-excitation at selected edges and resonances can lead to ***site specific*** photo-fragmentation of molecules (**photon scalpel**)

# Ion and Auger yield of CO on and off resonance

Time of flight MS

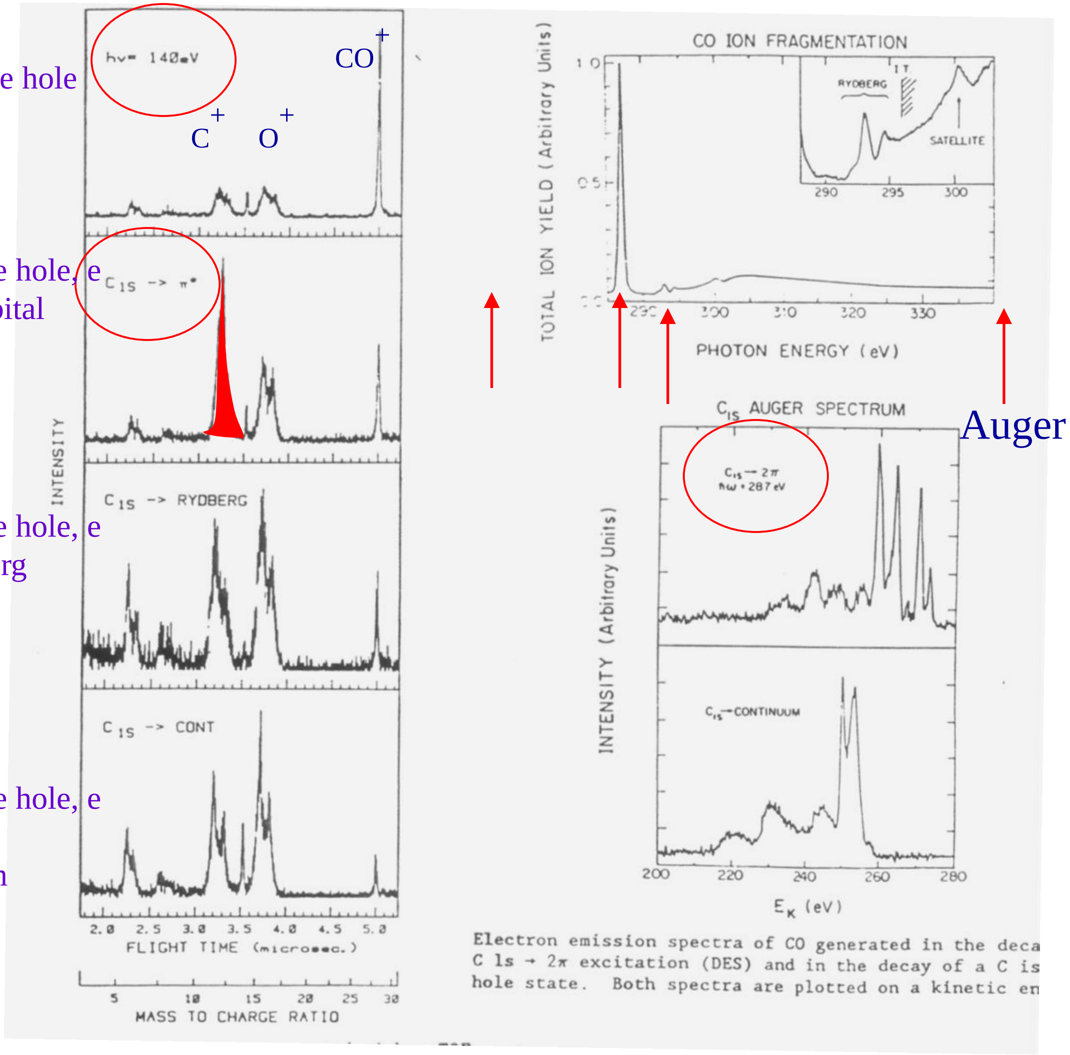
XANES

no core hole

C 1s core hole, e in π* orbital

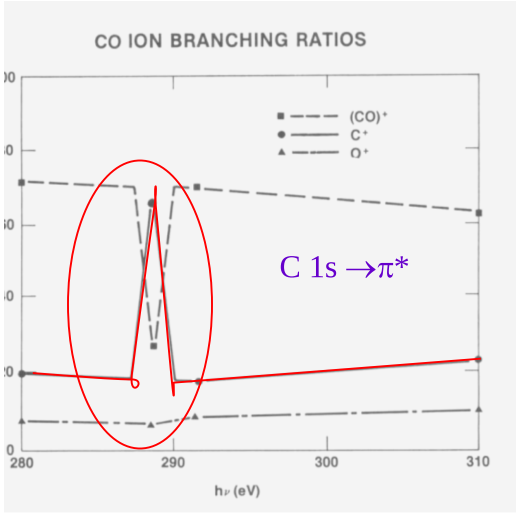
C 1s core hole, e in Rydberg orbital

C 1s core hole, e in contiuum



Electron emission spectra of CO generated in the deca
C 1s → 2π excitation (DES) and in the decay of a C is
hole state. Both spectra are plotted on a kinetic en

Auger



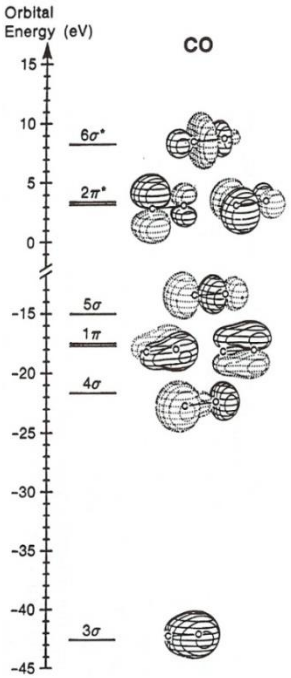
CO+

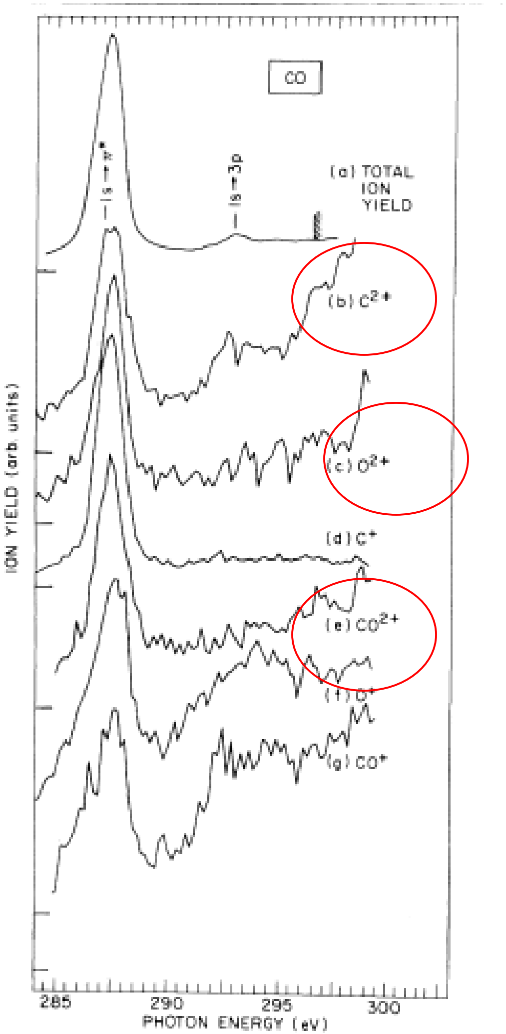
C+

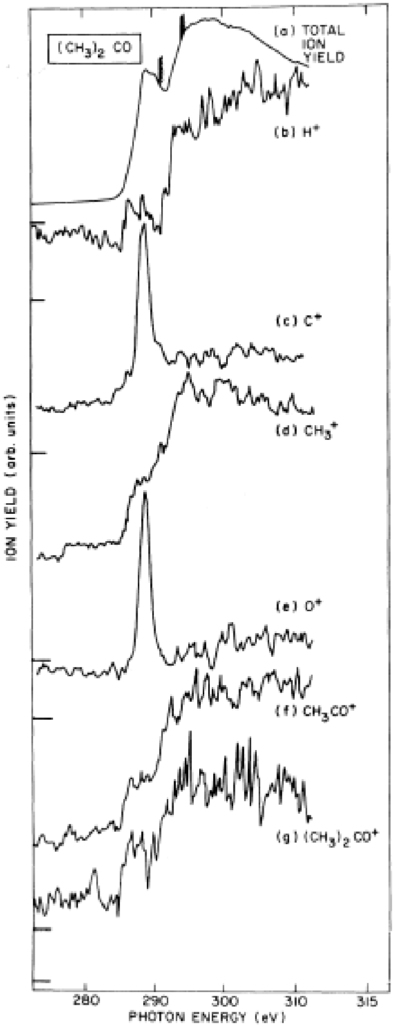
O+

C 1s →π*

# Photo-fragmentation of CO and $(CH_3)_2CO$ at C K-edge







Coulomb explosion:
Moddeman et al.
J. Chem. Phys. 55, 2371 (1971)

Eberhardt et al.
Phys. Rev. Lett.
50, 1038 (1983)

Doubly charge fragments are produced in small molecules