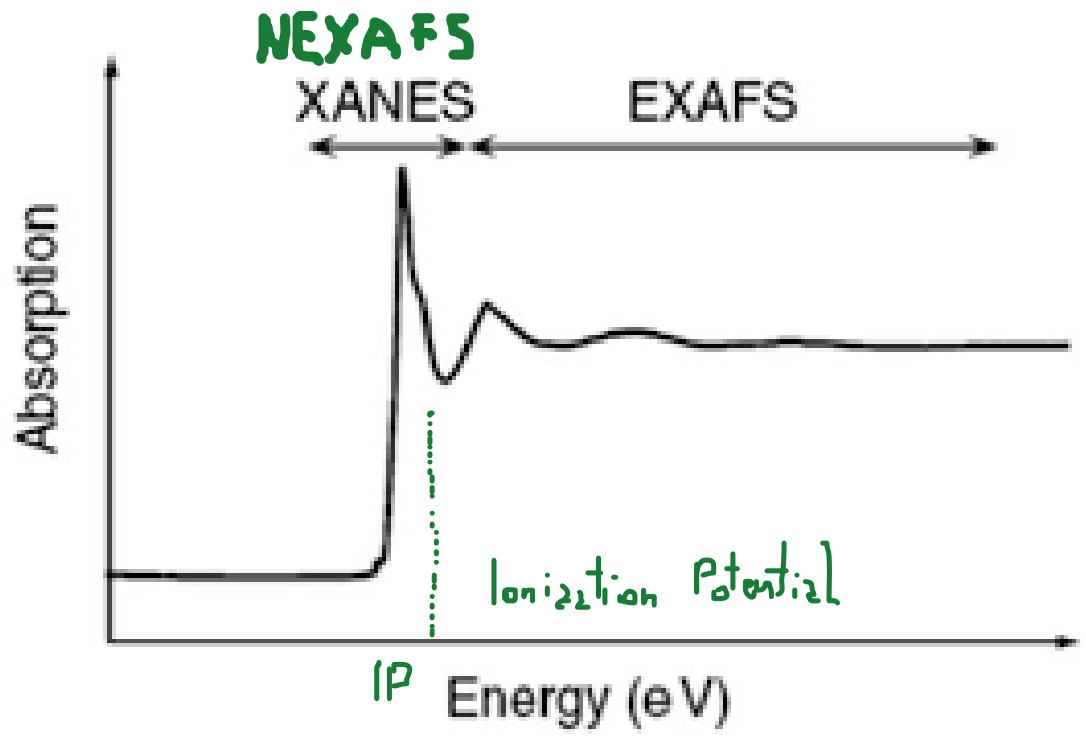
Assorbimento a soglia



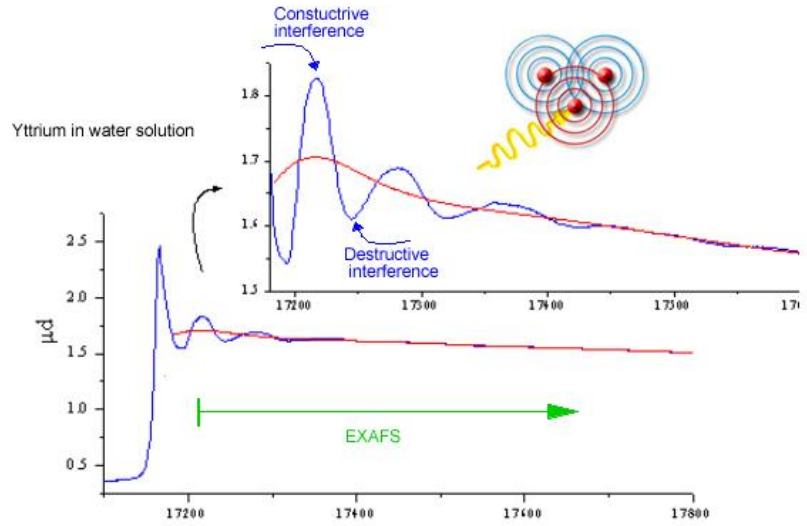
Nell'assorbimento a soglia si misura la probabilità di assorbimento di fotoni la cui energia viene fatta variare nell'intorno di una soglia (esempio soglia k del carbonio (C1s))

Si distinguono due regioni di interesse, una in un intorno di 20-30 eV dalla *Ionization Potential* mi dà informazioni sugli stati non occupati del sistema (tecnica NEXAFS). L'altra….

EXAFS – Extended X-ray Absorption Fine Structure

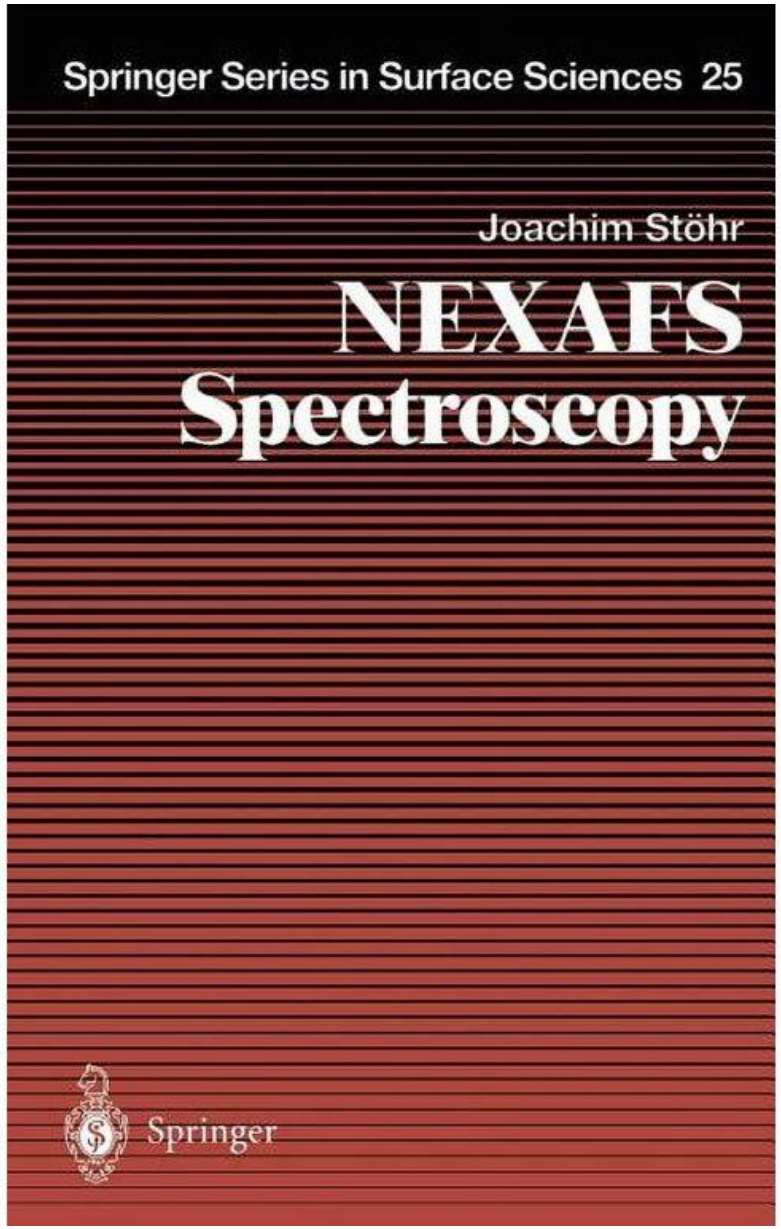
Il fotoelettrone emesso subisce un processo di scattering dagli atomi che sono in prossimità dell'atomo emettitore. Di conseguenza, ci potranno essere, a seconda dell'energia cinetica del fotoelettrone (e quindi a seconda di hv del fotone) delle condizioni di interferenza distruttiva e altre di interferenza costruttiva. Nel primo caso la sezione d'urto di assorbimento sarà minore che nel secondo.
In sostanza, lo stato finale in cui il fotoelettrone viene promosso dipende fortemente dalla disposizione degli atomi circostanti.

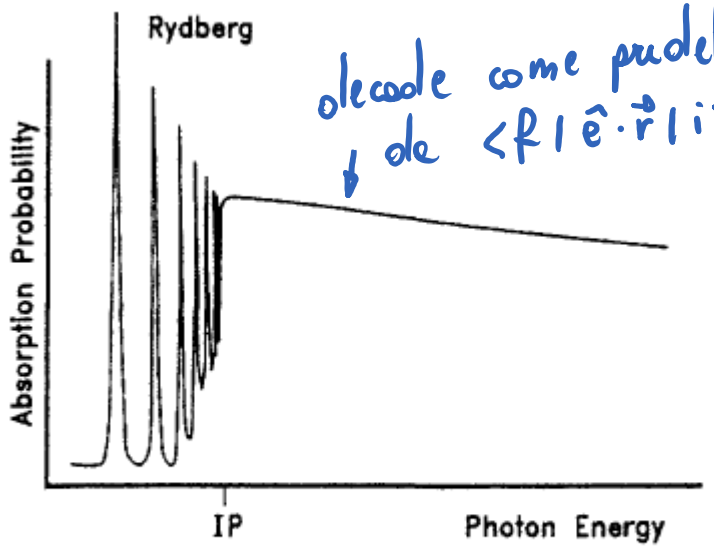
Se io misuro la variazione dell'intensità di assorbimento in funzione di hv ho informazioni sulle distanze tra gli atomi del materiale.



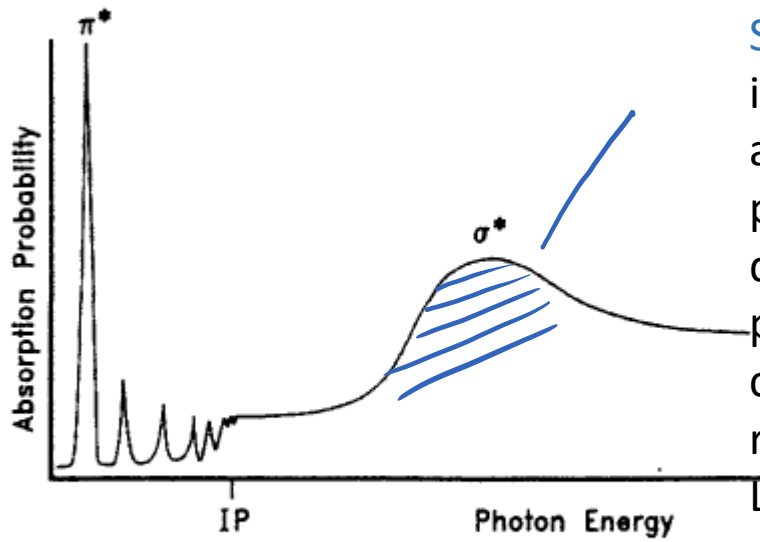
$|f\rangle$ dipende da hv e dall'intorno dell'atomo emettitore

https://www2.ung.si/~arcon/xas/exafs/exafs.htm

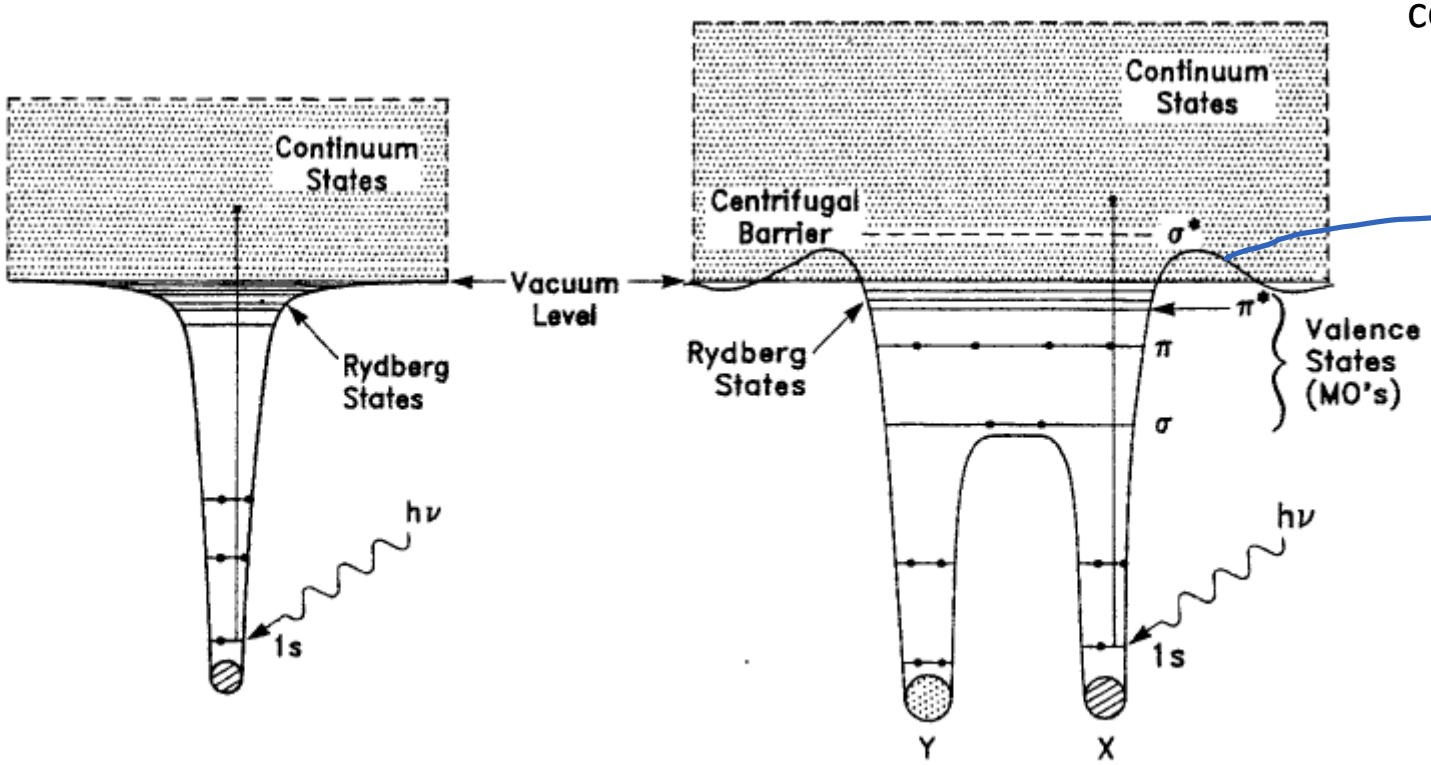

Springer Series in Surface Sciences 25
Joachim Stöhr
NEXAFS
Spectroscopy
Springer



oleoode come prodotto
di $\langle f | \hat{e} \cdot \vec{r} | i \rangle$



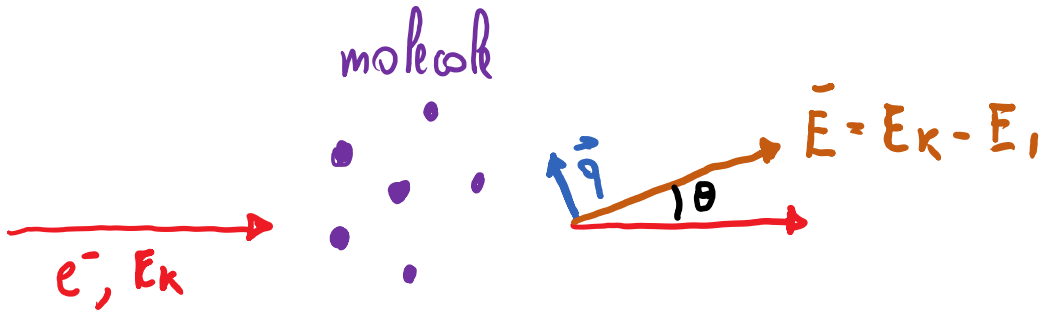
Shape resonance: Nel continuo di stati sopra la ionizzazione, ci sono delle energie poco sopra al livello di vuoto in cui è più probabile promuovere l'elettrone. Un modo per descrivere questi stati è di considerare un potenziale aggiuntivo a quello coulombiano, che è il contributo centrifugo che trovo risolvendo l'equazione di Schrodinger. L'elettrone vivrà qui per un tempo molto breve e poi per effetto tunnel uscirà dalla barriera centrifuga e sarà libero.



Posso vederlo come

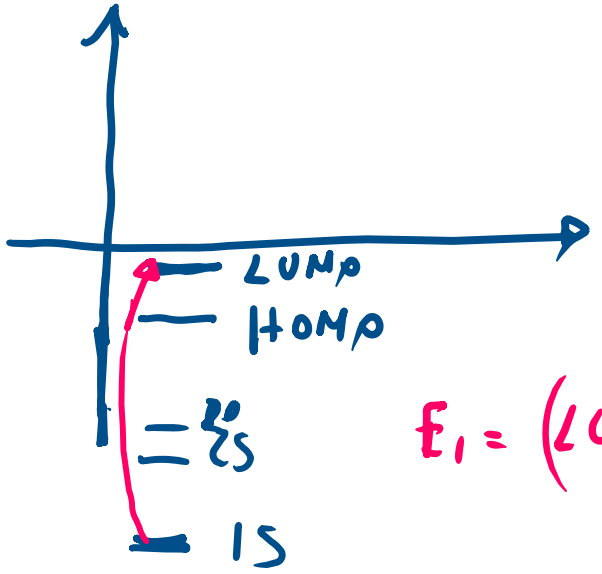
$$V_{eff} = V + \frac{\ell(\ell+1)}{r^2}$$

Un’alternativa alla NEXAFS per evidenziare gli stati elettronici non occupati è la tecnica ISEELS (Inner Shell Electron Energy Loss Spectroscopy). Un elettrone di sufficiente energia cinetica può promuovere elettroni di core in stati non occupato o ionizzarli. In generale il processo è complesso e per descriverlo bisogna tener conto della conservazione dell’energia e del momento.



Misuro elettroni che hanno perso energia

(esempio $E_1 = (LUMO - 1S)$)



Bethe (1930) dimostra che se q è abbastanza piccolo allora:

$$\frac{d\sigma}{dE_1} \propto \sum_{|f\rangle} |\langle f | \hat{e}_q \cdot \vec{r} | i \rangle|^2 \qquad q \cdot r \ll 1$$

$E_1 = (LUMO - 1S)$

Ovvero il processo è descritto in maniera analoga all’eccitazione con fotoni.

Esempio ISEELS:

$E_k = 3\,KeV$, $\theta = 0.5°$ $\Rightarrow$ $Q = 2.4\,\text{Å}^{-1}$

Q deve essere "piccolo" in modo che $\vec{Q}\cdot\vec{r} \ll 1$

Nel caso di O_{1s} $\rightarrow$ $r \approx \frac{a_0}{Z}$ $\longrightarrow$ $Q\,r \approx 0.32$ .... più o meno ci siamo

La tecnica ISEELS ha il vantaggio di essere economica (non mi serve un sincrotrone…) e consente anche di ottenere un ottima risoluzione (0.05 eV).
Però è applicabile solo in condizioni di trasmissione, perché devo avere Q piccoli. Va bene quindi per misure gas-phase ma non per film su superfici….

1. $\sigma(h\nu, k) \propto \sum_{|f\rangle} |\langle f | \hat{e}_E \cdot \vec{r} | i \rangle|^2$ Fermi's golden rule

$\vec{E} \propto \vec{E}_0 e^{i\vec{k}\cdot\vec{r}}$ $\xrightarrow[\text{dipole}]{\text{approx}}$ $\vec{k}\cdot\vec{r} \ll 1$

soglia O_{1s} $h\nu \sim 550$ eV ($O_{1s} \sim 530$ eV)

$\rightarrow \frac{\lambda}{2\pi} = \frac{1}{k} \sim 3.6$ Å

$|\vec{r}| \approx \frac{a_0}{Z} = 0.07$ Å

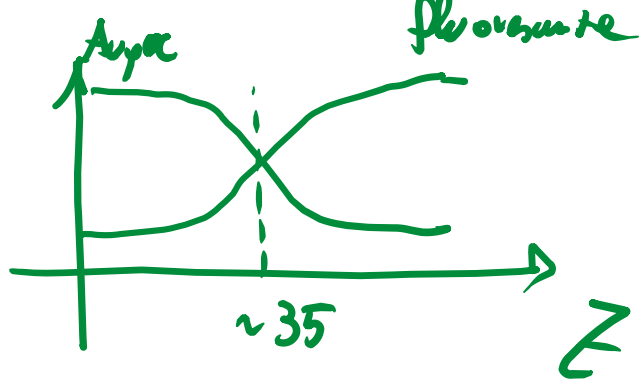
$kr \approx \frac{0.07}{3.6} \ll 1$

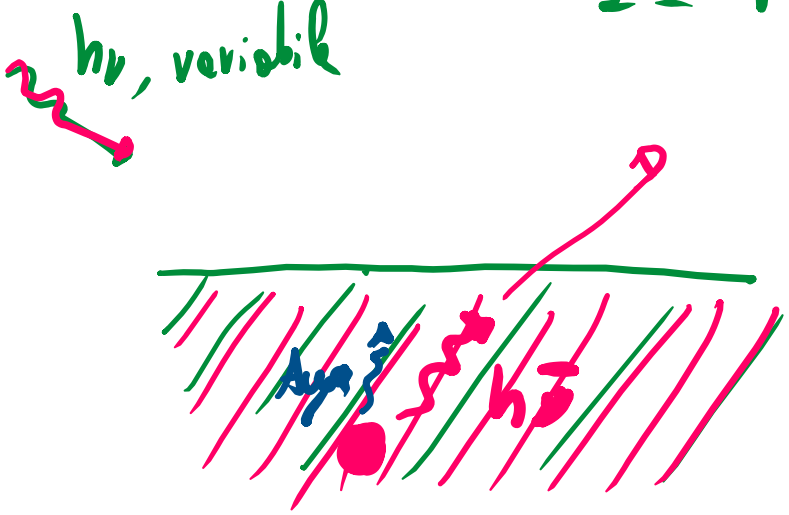
$O_{1s} \approx 530$ eV
$C_{1s} \approx 285$ eV
$N_{1s} \approx 400$ eV
$S_{2p} \approx 162$ eV

1.

misuro il prodotto della diseccitazione:

1. Auger
2. fotoni fluorescenza

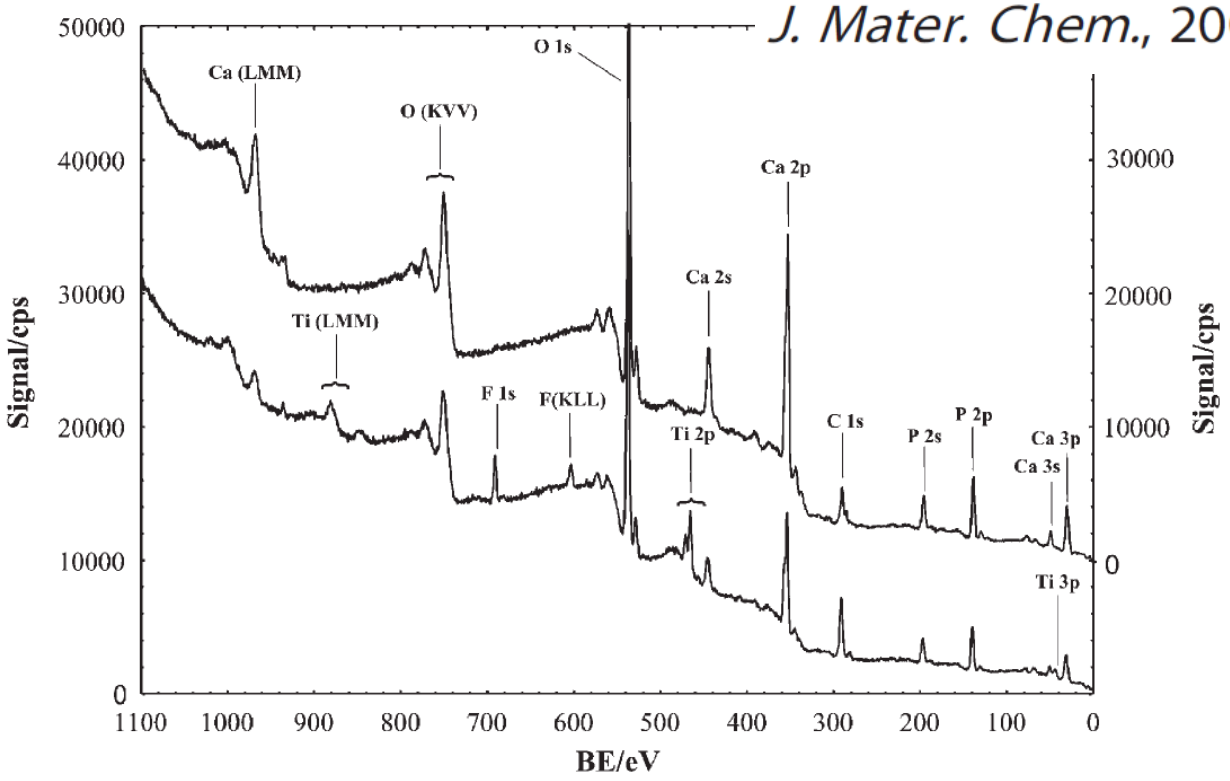




→ $\frac{\text{Auger yield}}{\text{fluorescence yield}}$ è + surface sensitive di:

3. Total yield
   - → tutti gli e⁻ che escono dal campione
   - → drain current

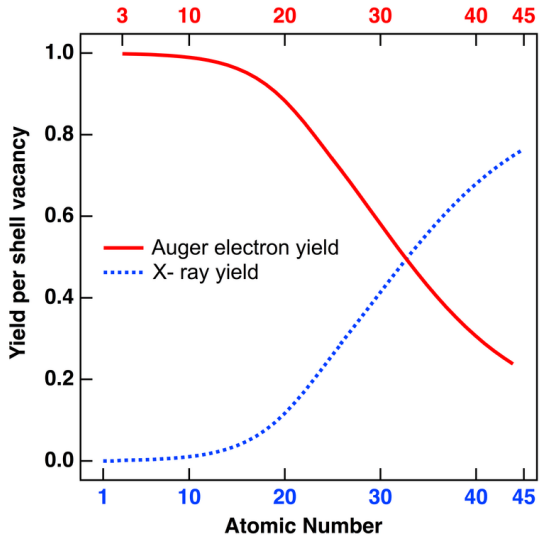
Composizione chimica

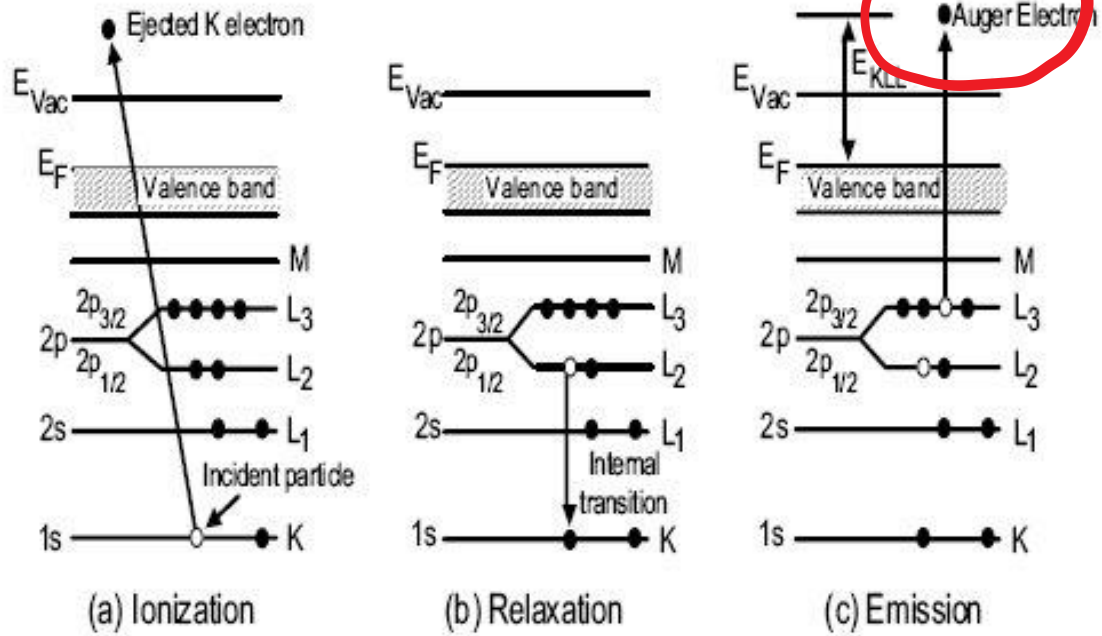


J. Mater. Chem., 2005, **15**, 1626–1636

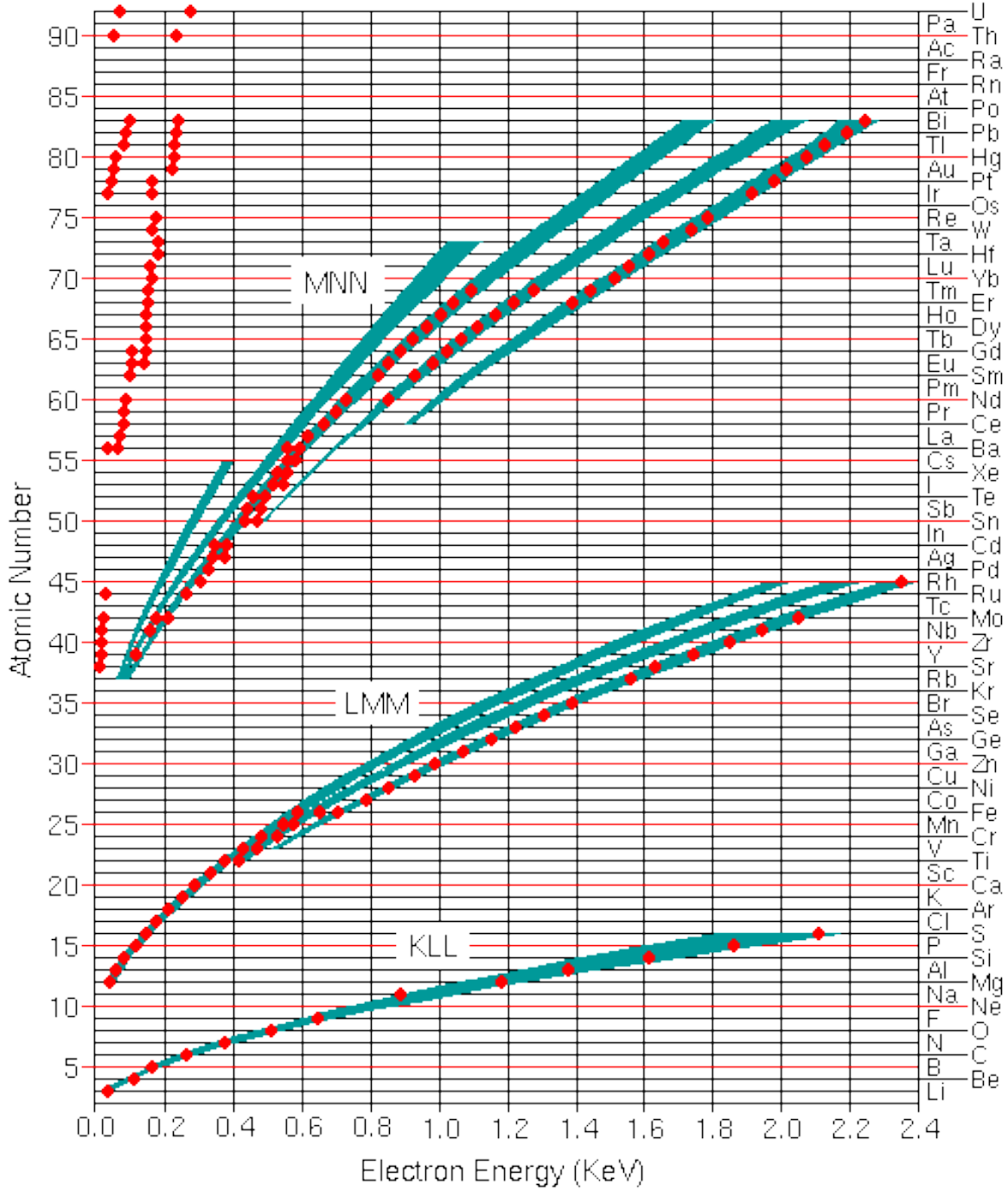
https://srdata.nist.gov/xps/Default.aspx

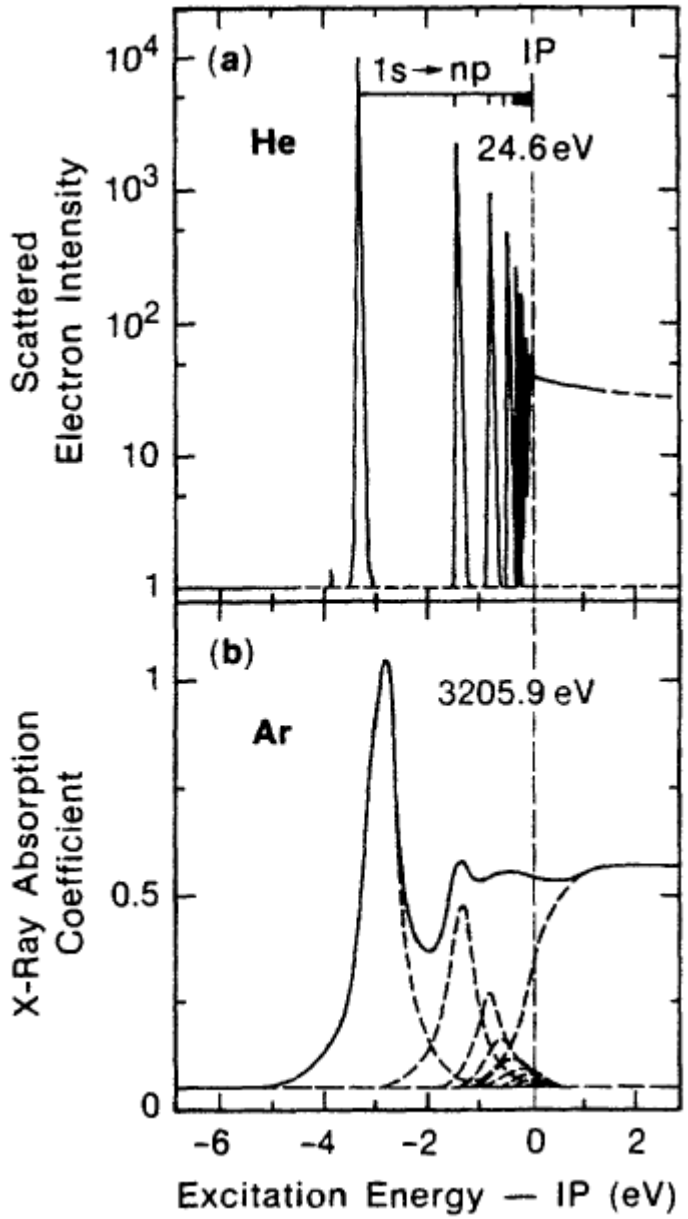
Il processo Auger

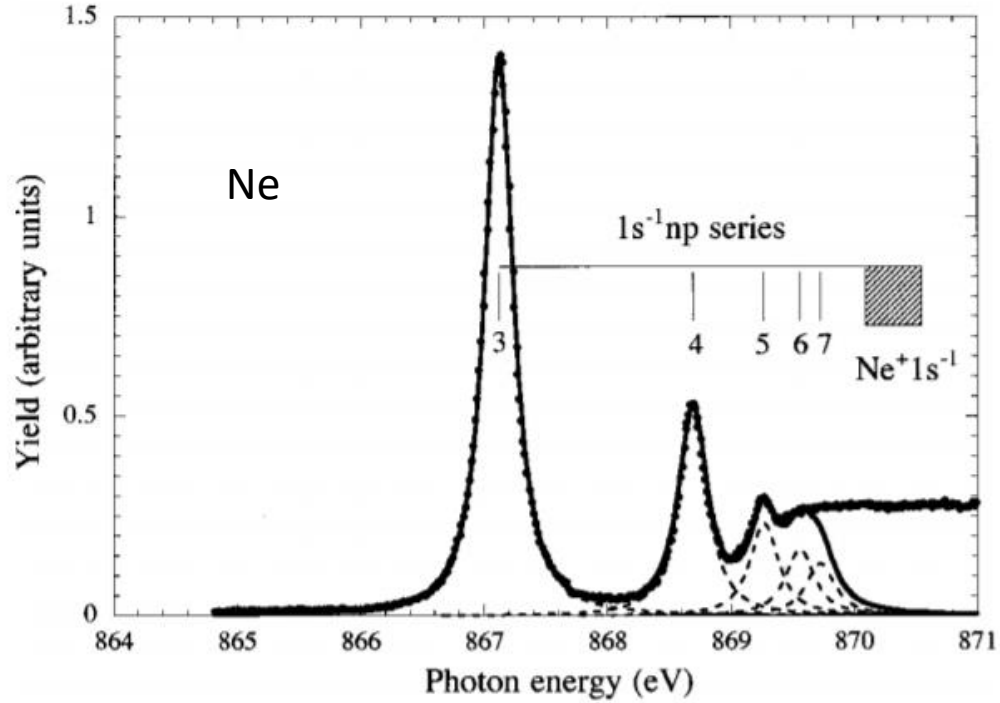




KL_2L_3


MNN
LMM
KLL
Atomic Number
Electron Energy (KeV)
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
U Th Pa Ra Ac Rn Fr Po At Pb Bi Hg Tl Pt Au Os Ir W Re Hf Ta Yb Lu Er Tm Dy Ho Gd Tb Sm Eu Nd Pm Ce Pr Ba La Xe Cs Te I Sn Sb Cd In Pd Ag Ru Rh Mo Tc Zr Nb Sr Y Kr Rb Se Br Ge As Zn Ga Ni Cu Fe Co Cr Mn Ti V Ca Sc Ar K S Cl Si P Mg Al Ne Na O F C N Be B Li

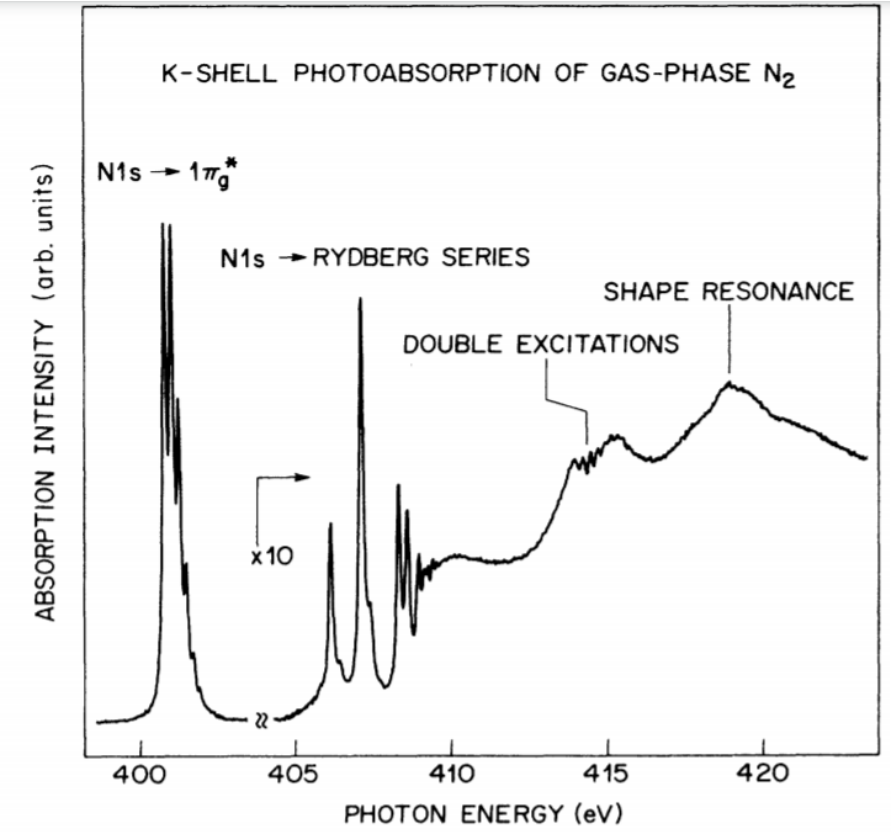


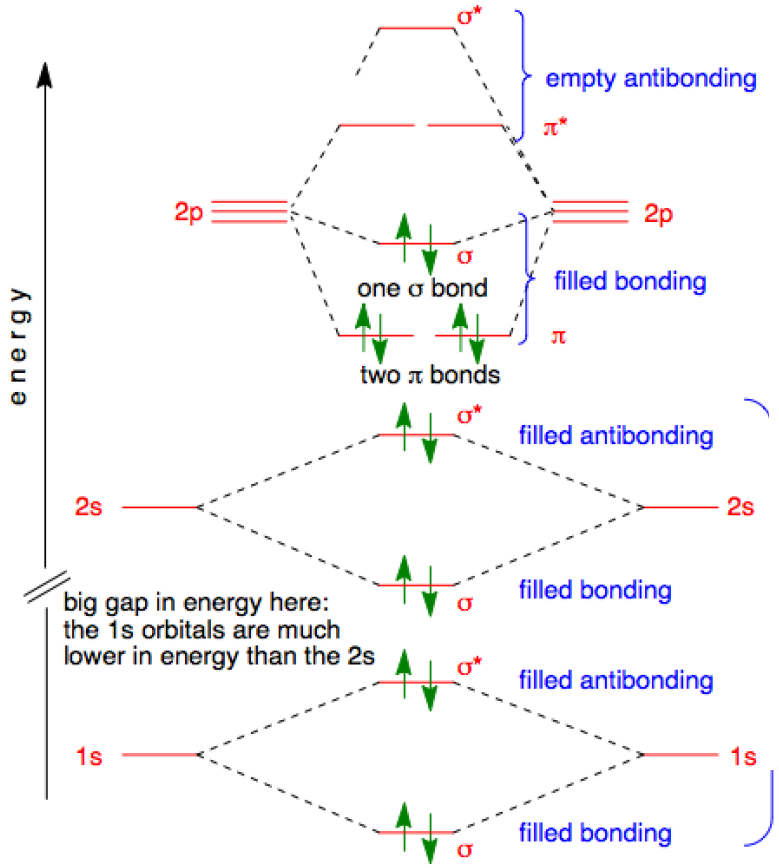


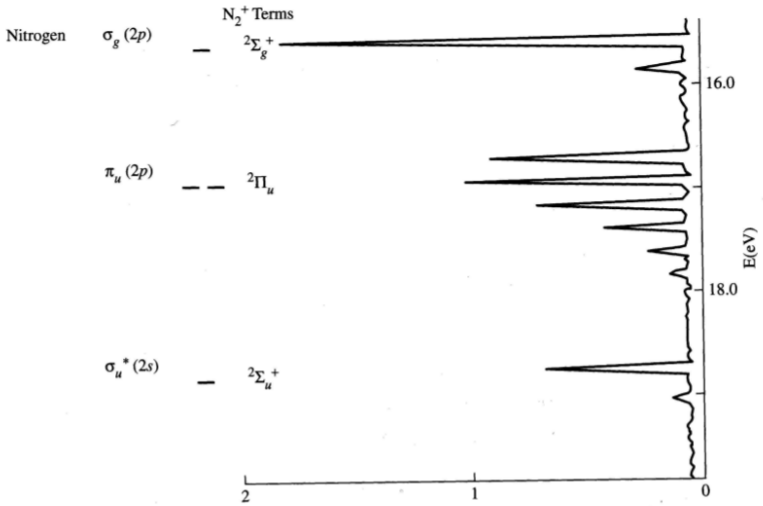
PHYSICAL REVIEW A (1999) 59, 3

All'aumentare di Z diminuisce il tempo di vita della buca 1s che viene creata.
Di conseguenza la larghezza in energia dei picchi aumenta.

Molecola di N2

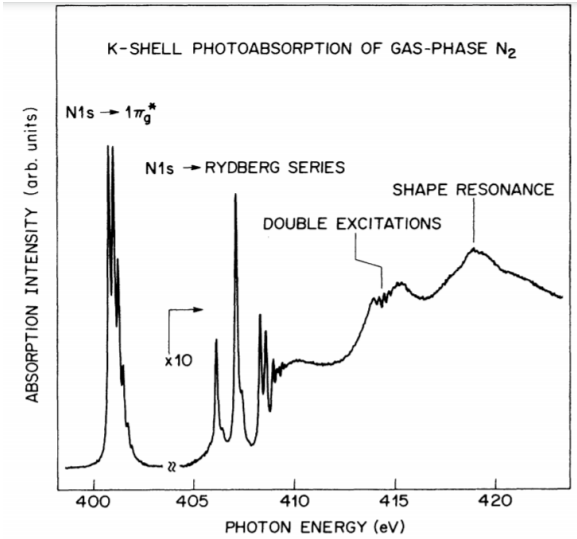




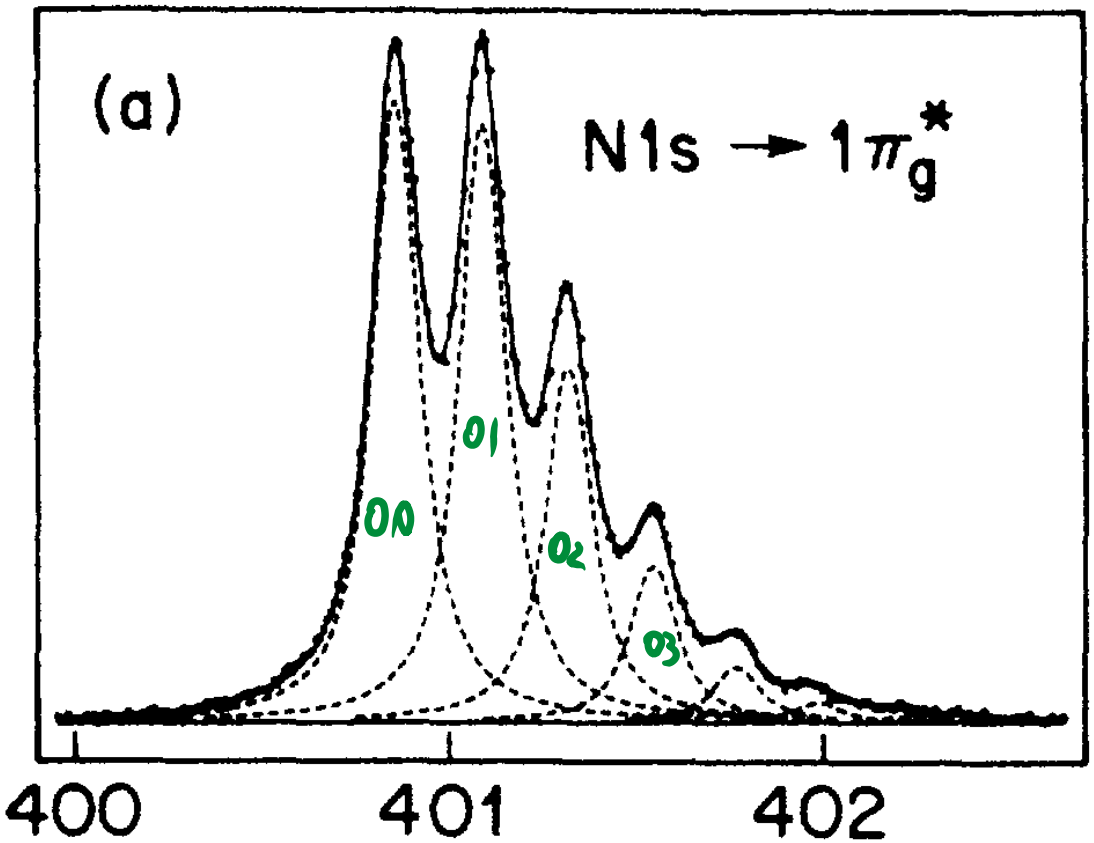


PHYSICAL REVIEW A VOLUME 40, NUMBER 11 DECEMBER 1, 1989

K-shell photoabsorption of the N_2 molecule



The peaks between 400 and 402 eV are the N $1s \rightarrow 1\pi_g^*$ excitation and its vibrational sideband. The features observed between 406 and 410 eV are the N $1s \rightarrow$ Rydberg series transitions. The N $1s$ ionization threshold occurs at 409.938 eV.[12] The area between 413 and 416 eV has been assigned in the literature to double-excitation states that are the shakeups associated with the N $1s \rightarrow 1\pi_g^*$ transition. The broad peak at 420 eV is the σ-shape resonance.



Dicroismo

Nel caso in cui la NEXAFS in una molecola sia misurata su una soglia K, quindi con $|i\rangle = |1s\rangle$, è possibile trovare una ben definita dipendenza della probabilità di assorbimento data dalla regola di Fermi e la geometria dello stato finale.
Innanzitutto, osserviamo che $|f\rangle$ è un orbitale molecolare, si estende in linea di principio su tutta la molecola. Tuttavia, $|i\rangle = |1s\rangle$ è localizzato sull'atomo emettitore. Ne consegue che l'integrale $\mathrm{P} \propto |\langle f|\hat{e}\cdot\vec{r}|i\rangle|^2$ coinvolgerà solo la porzione di $|f\rangle$ localizzata dove esiste anche $|i\rangle$. Ai fini del calcolo di P potrò quindi esprimere $|f\rangle$ come combinazione di orbitali atomici dell'atomo emettitore senza perdere in generalità…
Nel caso di atomi del secondo gruppo, posso coinvolgere gli orbitali n=2 per esprimere $|f\rangle$:

$$|f\rangle = a\,|2s\rangle + b\,|2px\rangle + c\,|2py\rangle + d\,|2pz\rangle$$

Ovvero, dalle coordinate sferiche :

$$|f\rangle = aR_{2s}(r)+R_{2p}(r)(\, b\,\sin\vartheta\cos\varphi + c\,\sin\vartheta\sin\varphi + d\,\cos\vartheta)$$

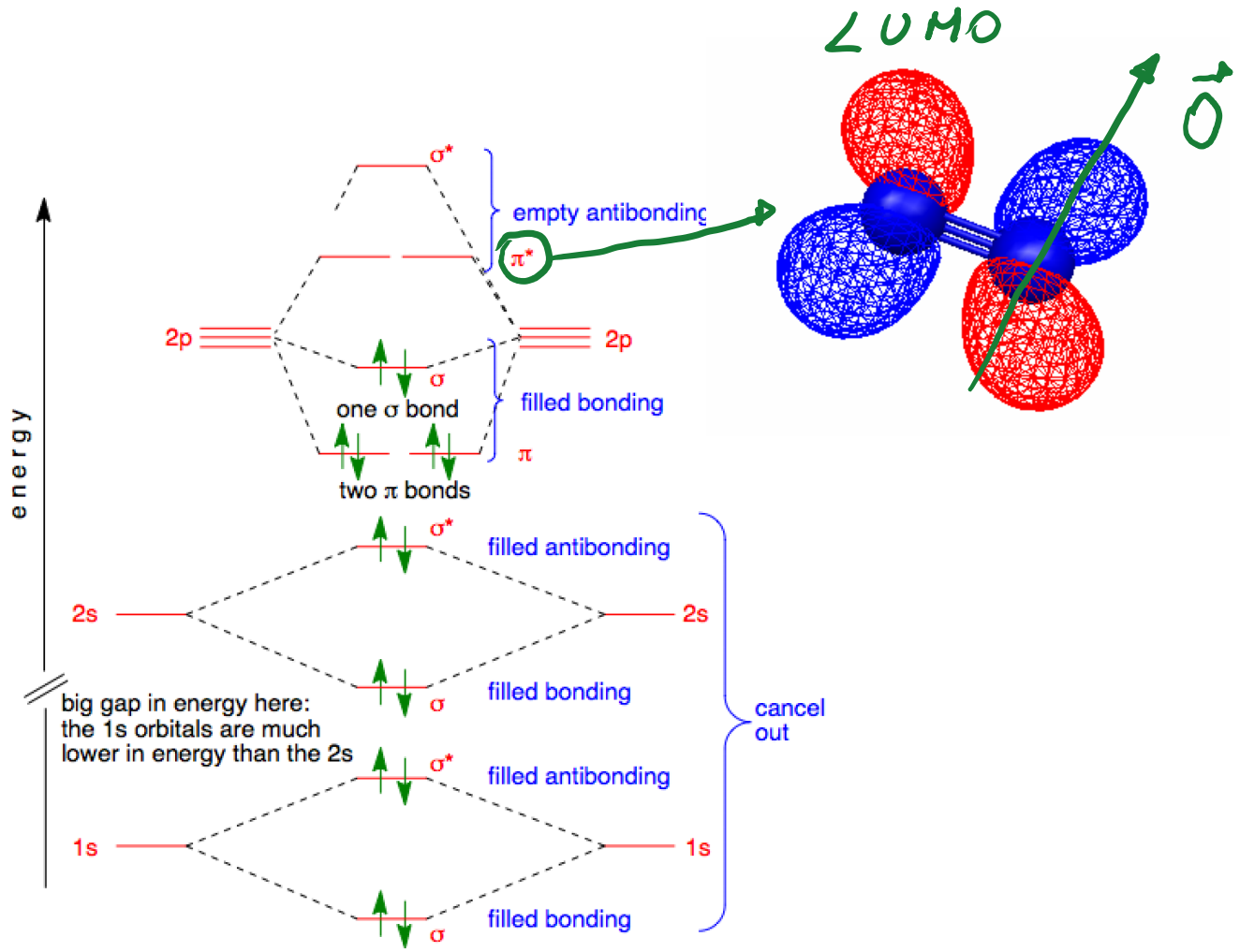
L' operatore posizione $\vec{r}$ inoltre lo potrò esprimere come $\vec{r} = r(\,\hat{x}\sin\vartheta\cos\varphi + \hat{y}\sin\vartheta\sin\varphi + \hat{z}\cos\vartheta)$.

Pertanto:

$\langle f|\hat{e}\cdot\vec{r}|i\rangle = \hat{e}\cdot\langle f|\vec{r}|i\rangle$ e posso scrivere $\langle f|\vec{r}|i\rangle = \int (aR_{2s}(r)+R_{2p}(r)(\, b\,\sin\vartheta\cos\varphi + c\,\sin\vartheta\sin\varphi + d\,\cos\vartheta))\, r \begin{pmatrix}\sin\vartheta\cos\varphi\\ \sin\vartheta\sin\varphi\\ \cos\vartheta\end{pmatrix} (R_{1s}(r))\, r^2\sin\vartheta\; dr\, d\vartheta\, d\varphi$

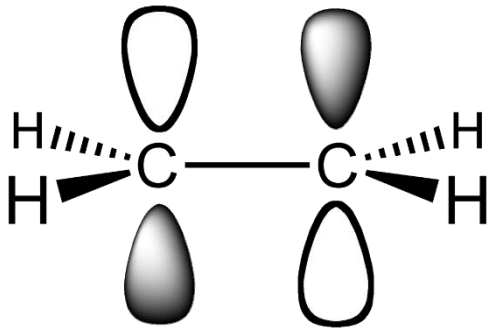
Integrando si ottiene $\langle f|\vec{r}|i\rangle = R\,\frac{4\pi}{3}(b\hat{x} + c\hat{y} + d\hat{z})$ con $R = \int R_{2p}(r)\,(R_{1s}(r))\, r^3\, dr$

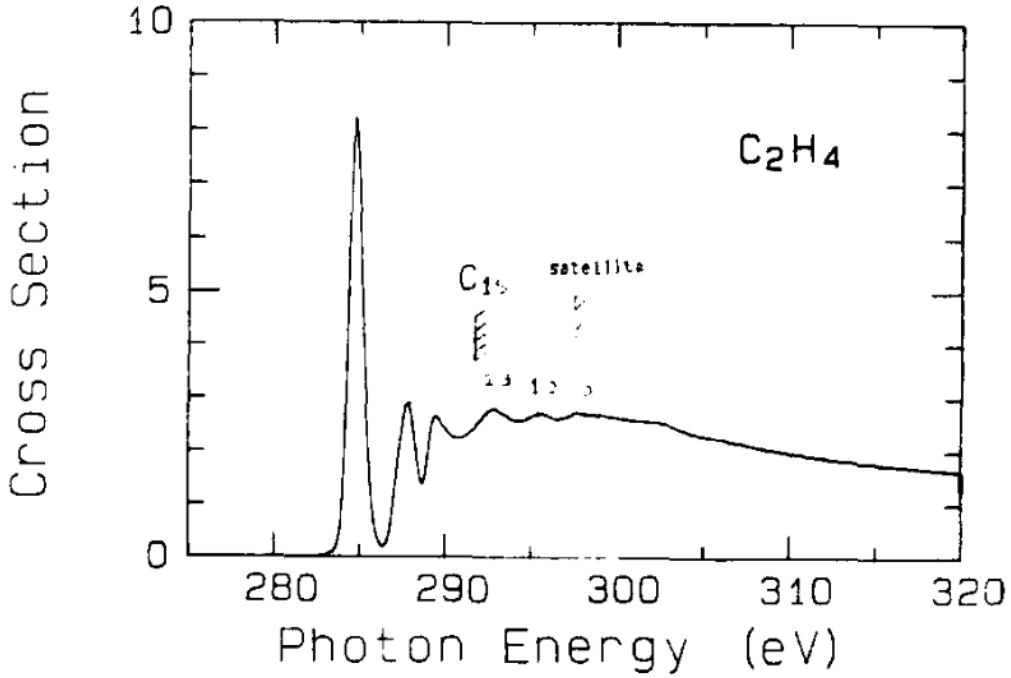
Se definisco questo vettore $\vec{O} = b\hat{x} + c\hat{y} + d\hat{z}$,
la probabilità di assorbimento P sarà $P \propto |\hat{e} \cdot \vec{O}|^2 = cos^2\delta$, con δ angolo compreso tra la direzione che mi descrive l'orbitale e il campo elettrico.

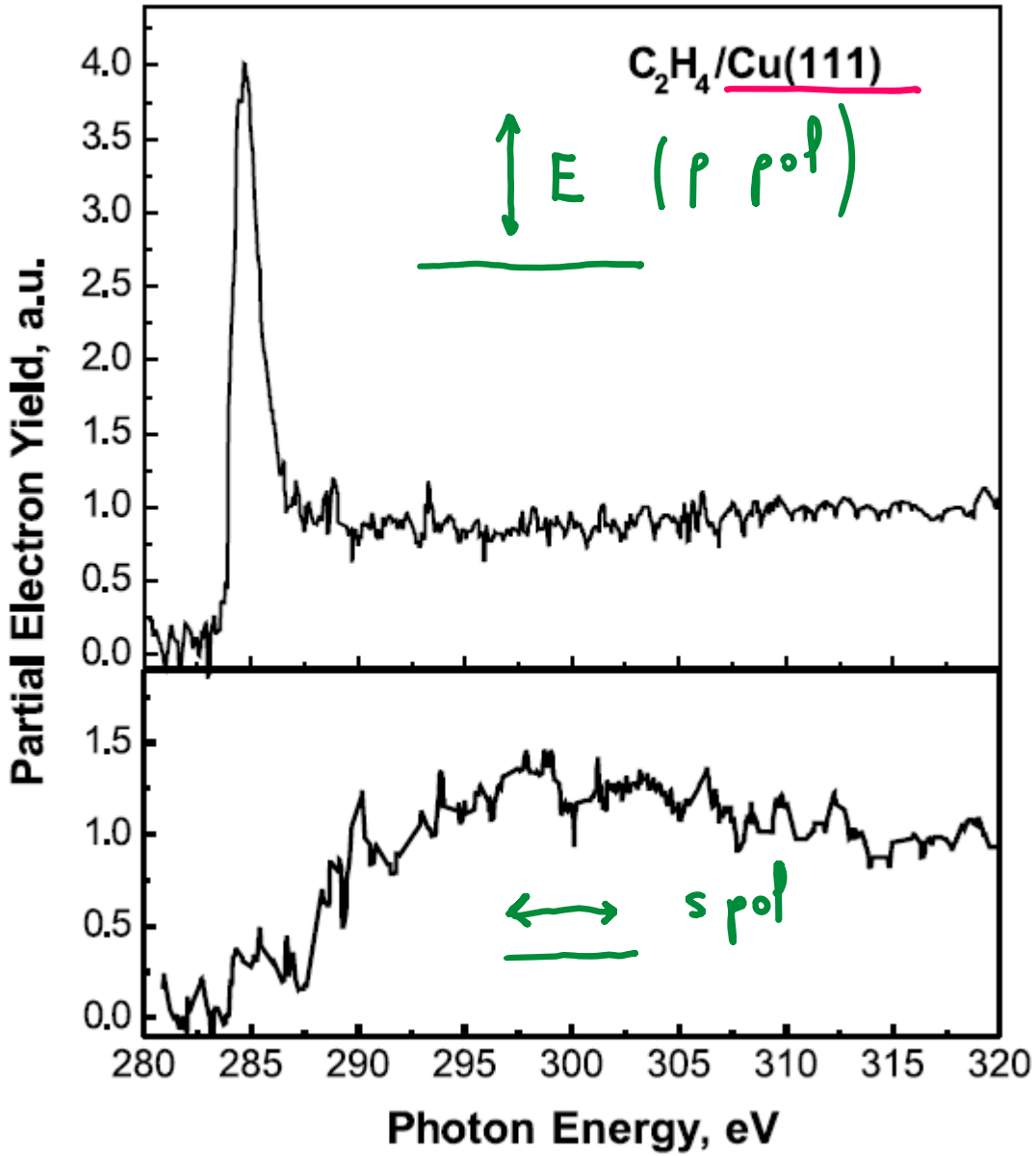


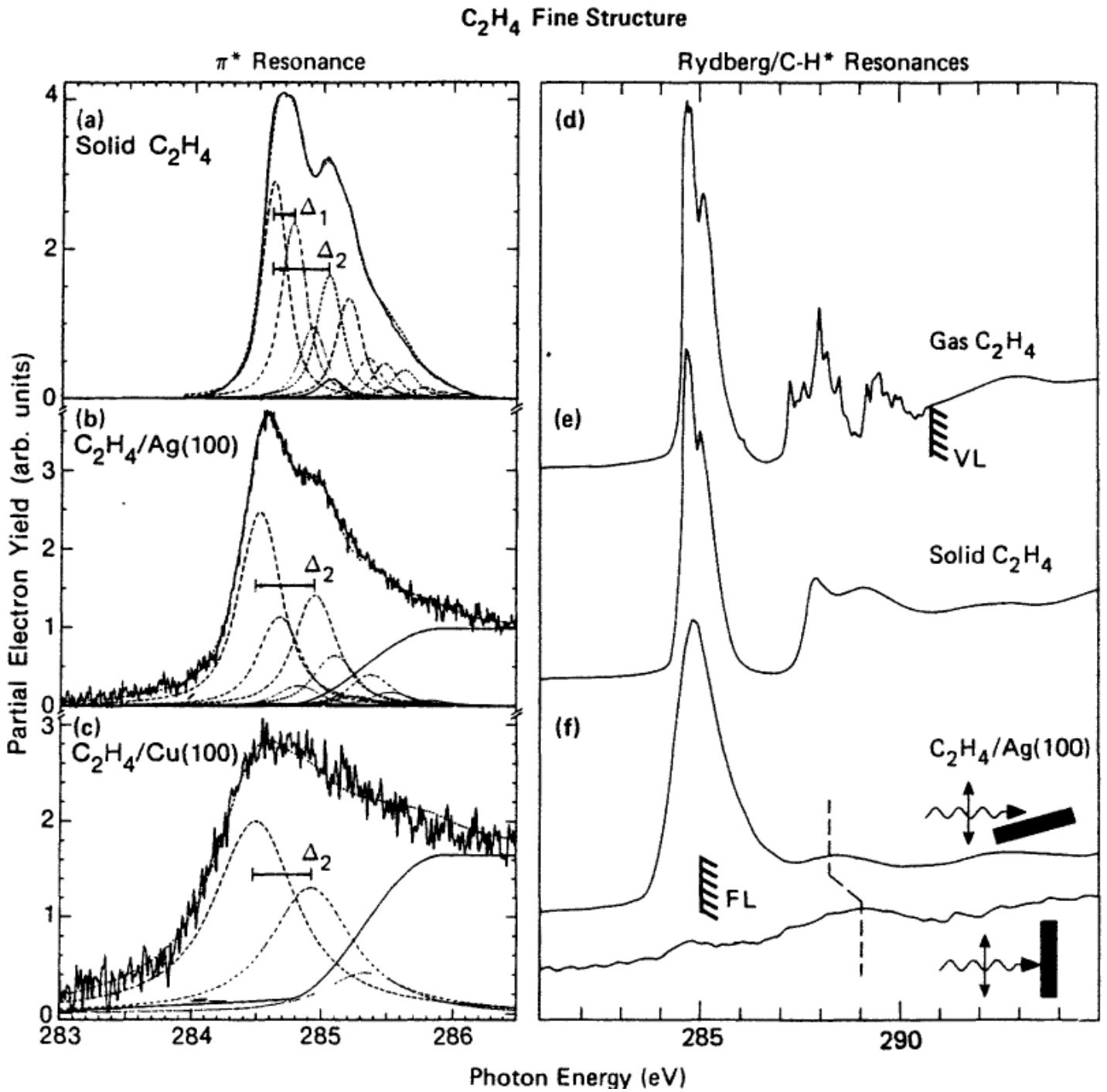
Ad esempio, nel caso della molecola di azoto, se cponsidero le transizioni sul LUMO, $\vec{O}$ sarà un vettore perpendicolare all'asse della molecola.

Ethylene


H
H
C
C
H
H


Cross Section
10
5
0
280
290
300
310
320
Photon Energy (eV)
C_2H_4
satellite


C_2H_4/Cu(111)
E (p pol)
s pol
Partial Electron Yield, a.u.
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.5
1.0
0.5
0.0
280
285
290
295
300
305
310
315
320
Photon Energy, eV



In generale, se l'interazione con il substrato aumenta,le componenti NEXAFS si allargano. Questo principalmente è dovuto alla diminuzione del tempo di vita degli stati eccitati.

Δ_1 vibrazionale C-C (150 meV)

Δ_2 C-H (430 meV)

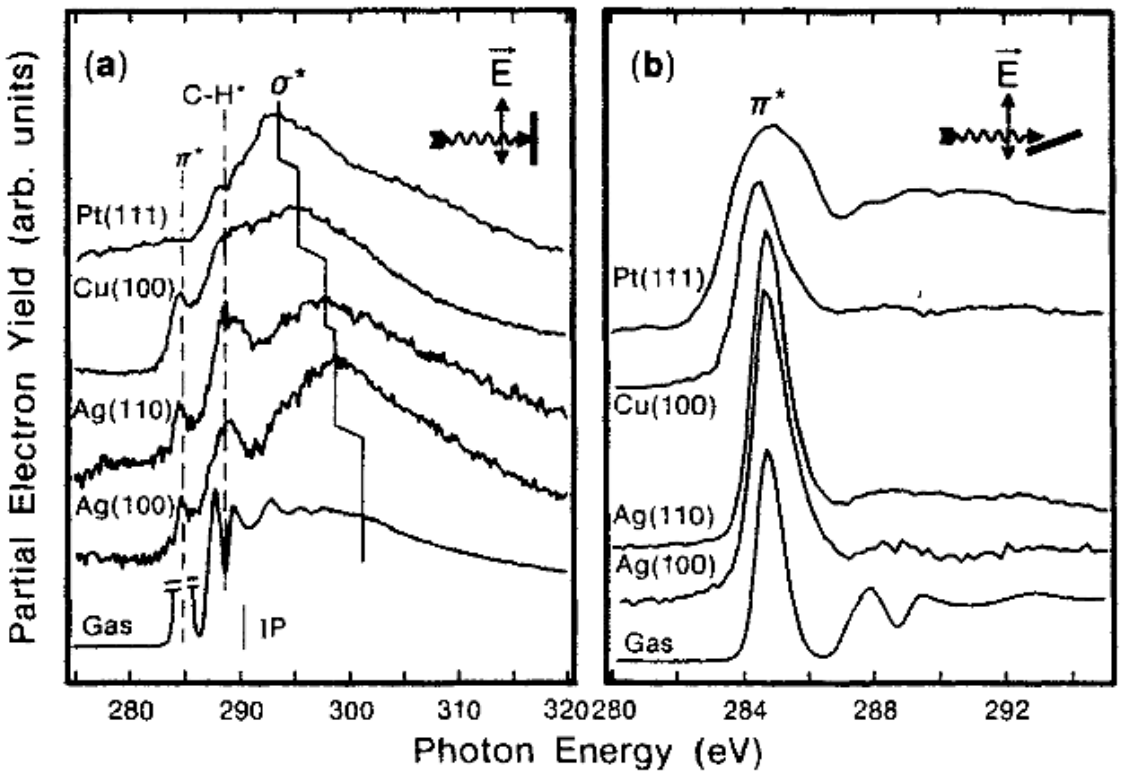
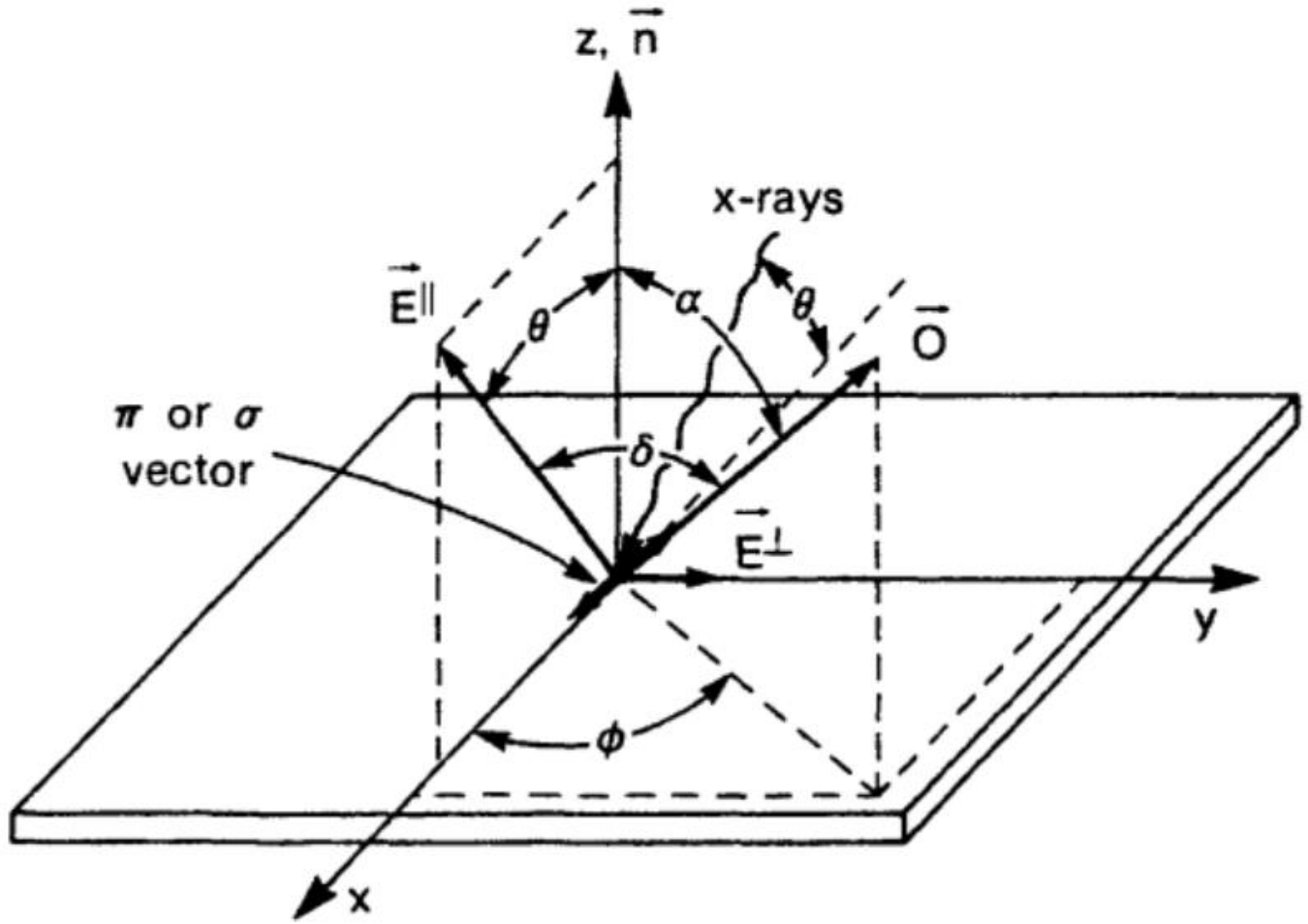


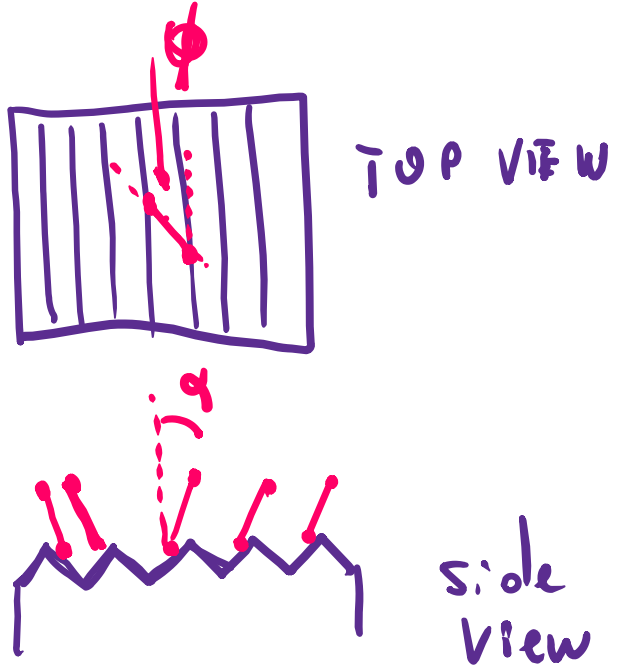
Fig. 8.22. NEXAFS spectra of chemisorbed ethylene on various metal surfaces, Ag(100) [8.78], Ag(110) [8.76], Cu(100) [8.30, 78], and Pt(111) [8.80], recorded at (**a**) normal X-ray incidence and (**b**) 20° grazing incidence. At the bottom the gas phase ISEELS spectrum [8.55] is shown for comparison. In all cases the molecule lies down such that the σ^* resonance is most pronounced at normal incidence and the π^* resonance at grazing incidence. The shift of the σ^* position to lower energy and the broadening of the π^* resonance in going from a Ag to a Pt substrate indicate strengthening of the molecule–substrate and weakening of the intra-molecular C=C bond

L'interazione con il substrato influenza anche la posizione della shape resonance: se aumenta l'interazione con il substrato diminuisce la forza di legame C-C e quindi aumenta la distanza tra i due atomi di carbonio….

Dicroismo


z, $\vec{n}$
x-rays
$\vec{E}^{\parallel}$
θ
α
θ
$\vec{O}$
π or σ
vector
δ
$\vec{E}^{\perp}$
y
ϕ
x

CASO two-fold es. superficie (110)



$$I \propto \cos^2\theta \cos^2\alpha + \sin^2\theta \sin^2\alpha \cos^2\phi$$

Se orientiamo $\vec{E}$ in modo che $\cos\phi = 1$

$$\propto \cos^2\theta \cos^2\alpha + \sin^2\theta \sin^2\alpha$$

$\Rightarrow$ se $\boxed{\theta = 45^\circ}$ $\Rightarrow$ l'intensità diventa indipendente da α

magic angle

CASO three-fold → (111) FCC

$$I \propto \cos^2\theta \cos^2\alpha + \frac{1}{2}\sin^2\theta \sin^2\alpha$$

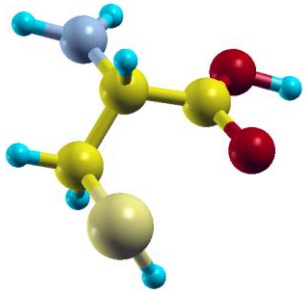
→ non dipende da ϕ (non so determinare l'orientazione azimutale della molecola)

se $\theta = \arctan(\sqrt{2}) = 54.7°$ ⇒ magic angle (3 fold o n-fold $n \geq 3$)

scompare la dipendenza da α !!

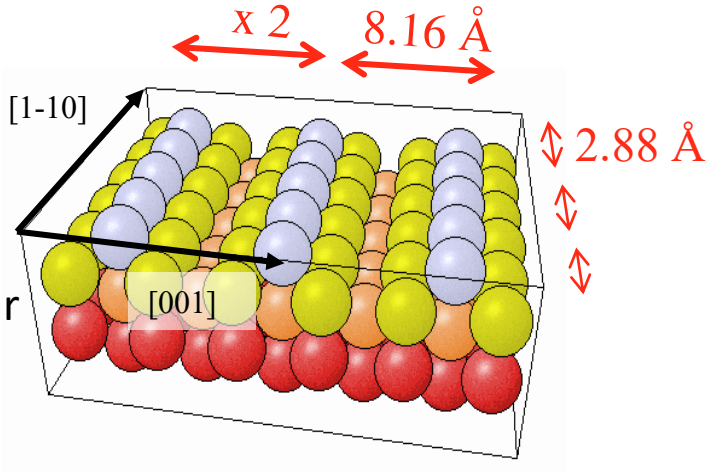
L-Cysteine adsorption on Au(110)

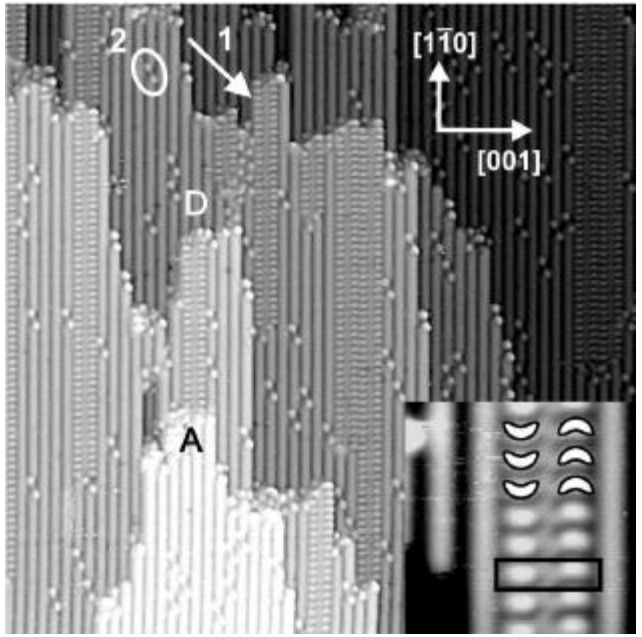
Simple aminoacid
Thiolate bond with substrates



Au(110) surface

- anisotropy in the molecular self assembly process.
- Chirality effects





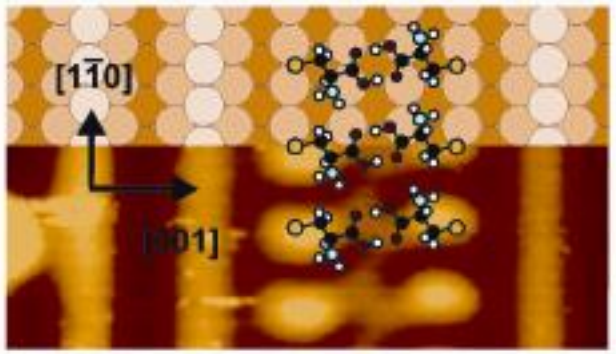
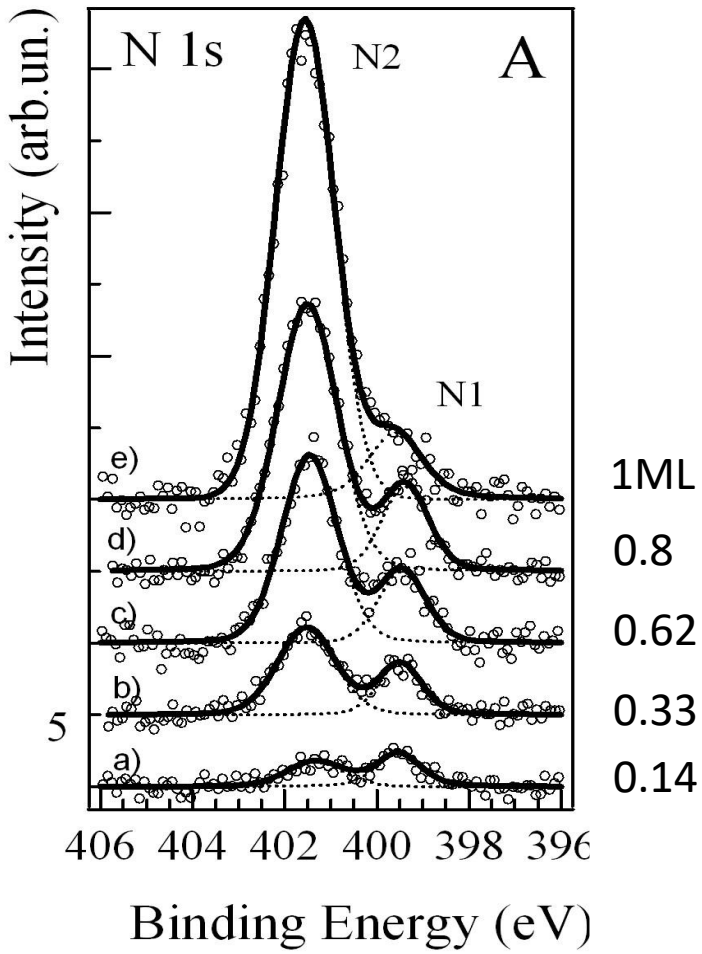


FIG. 3 (color). Most stable cysteine double-row structure, as

Kühnle et al. PRL 93 (2004) 86101

N1s: zwitterionic vs acidic population



1ML

0.8

0.62

0.33

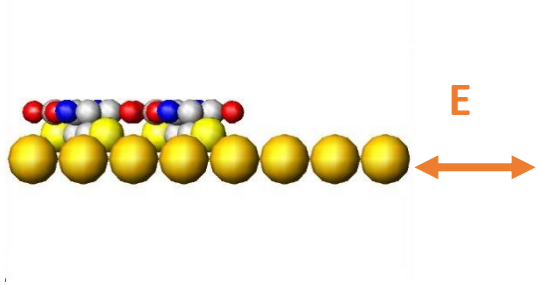
0.14

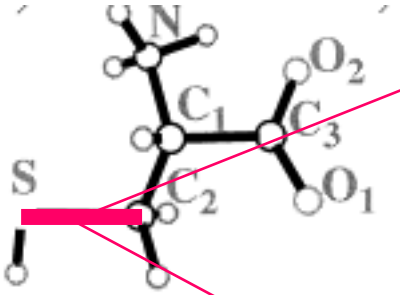
NH_2 399.5 eV

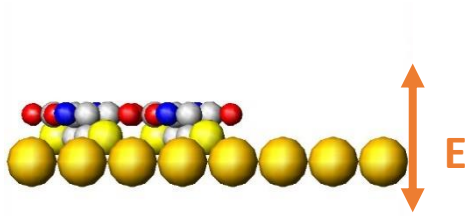
NH_3^+ 401.5 eV

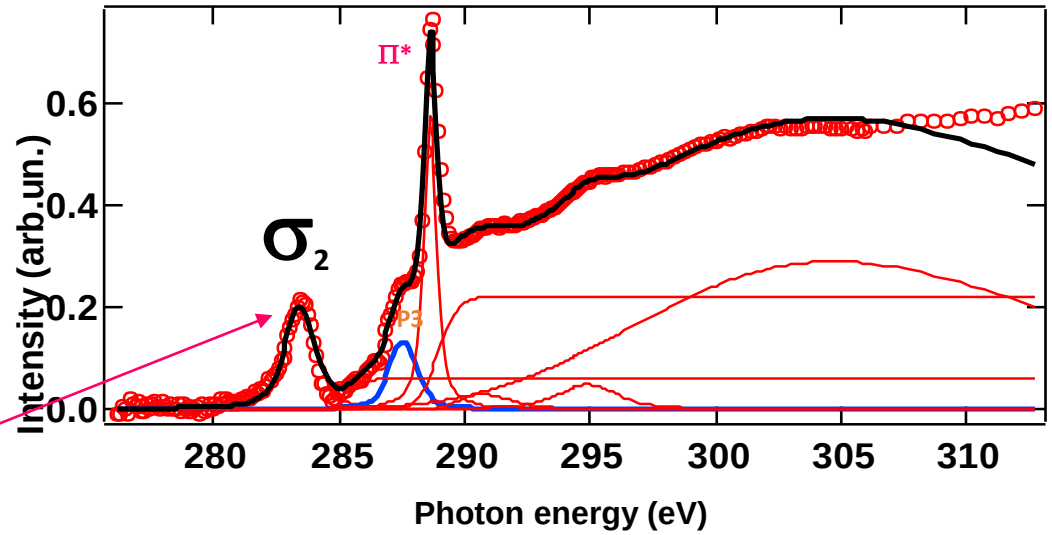
- Total acidic population established at θ < 0.4 ML
- majority of zwitterions for θ > 0.2 ML

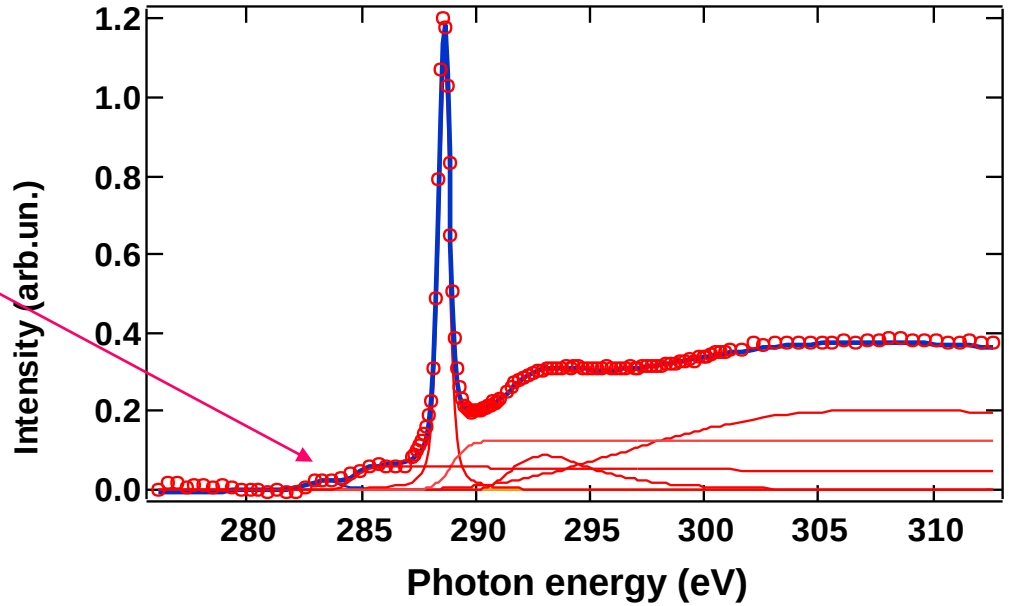
C1s NEXAFS: molecular orientation from polarization dependance



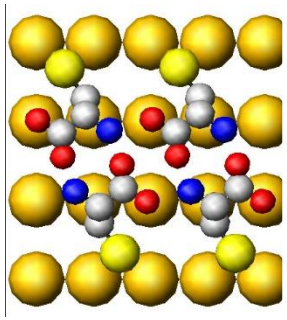




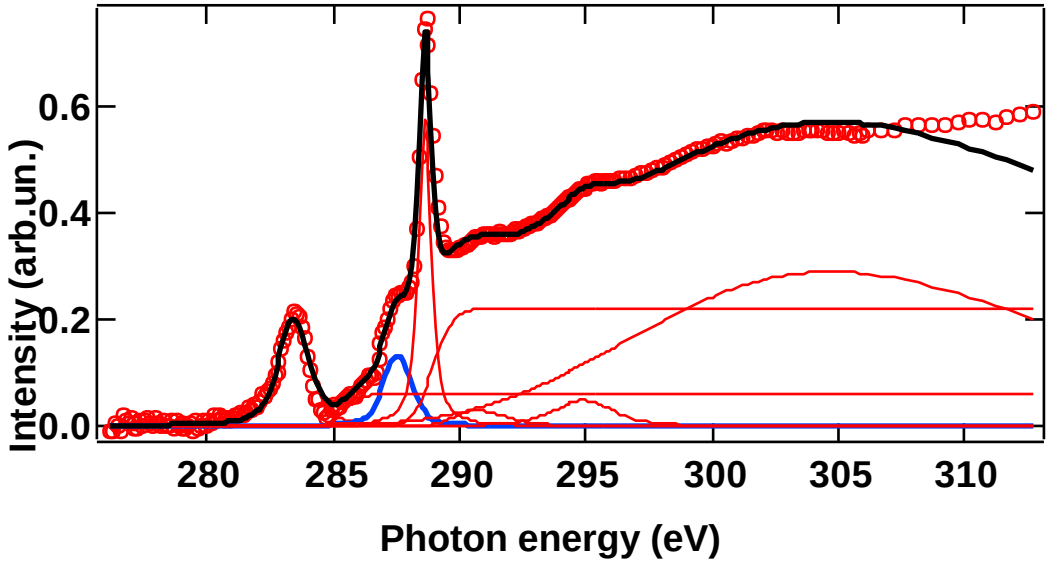




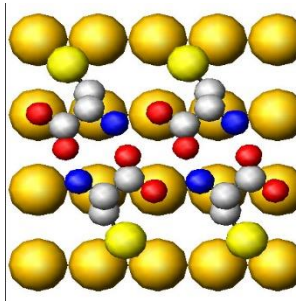
Variable polarization NEXAFS: azimuthal orientation



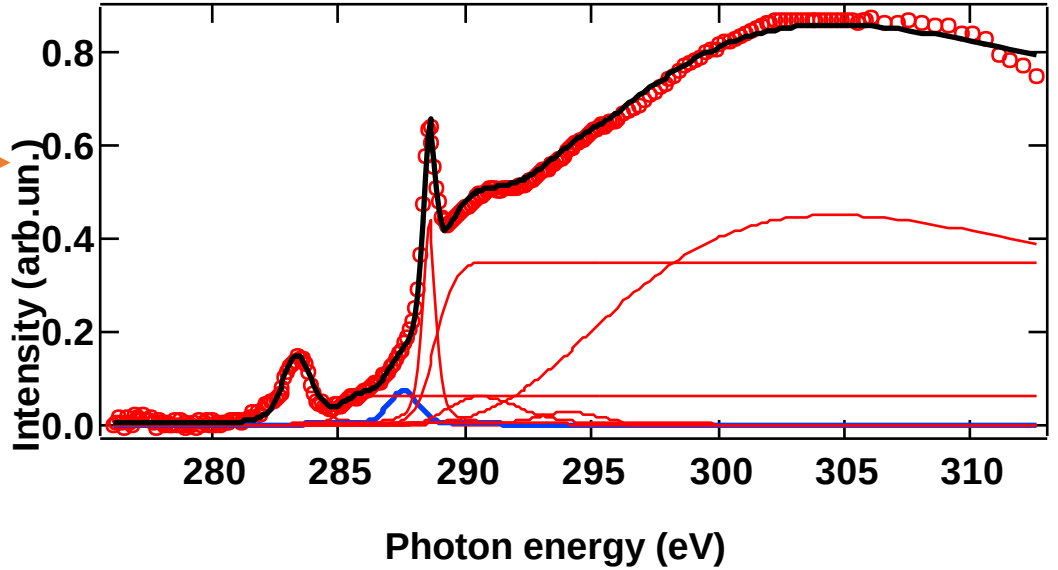
E



P | |

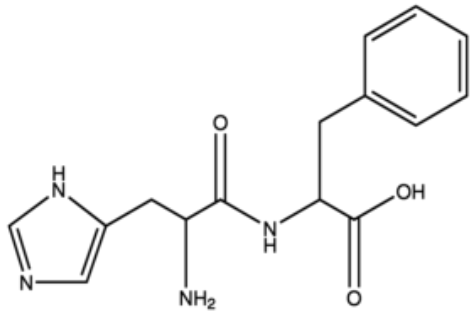


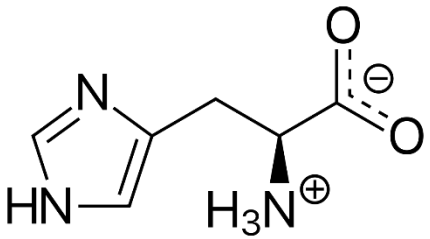
E



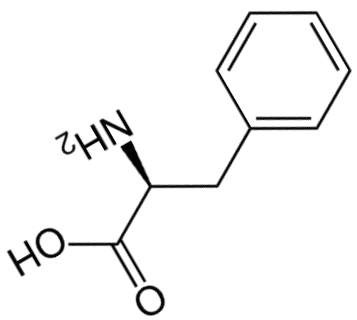
Langmuir, 2006

Approccio *building blocks* nell'interpretazione degli spettri…..

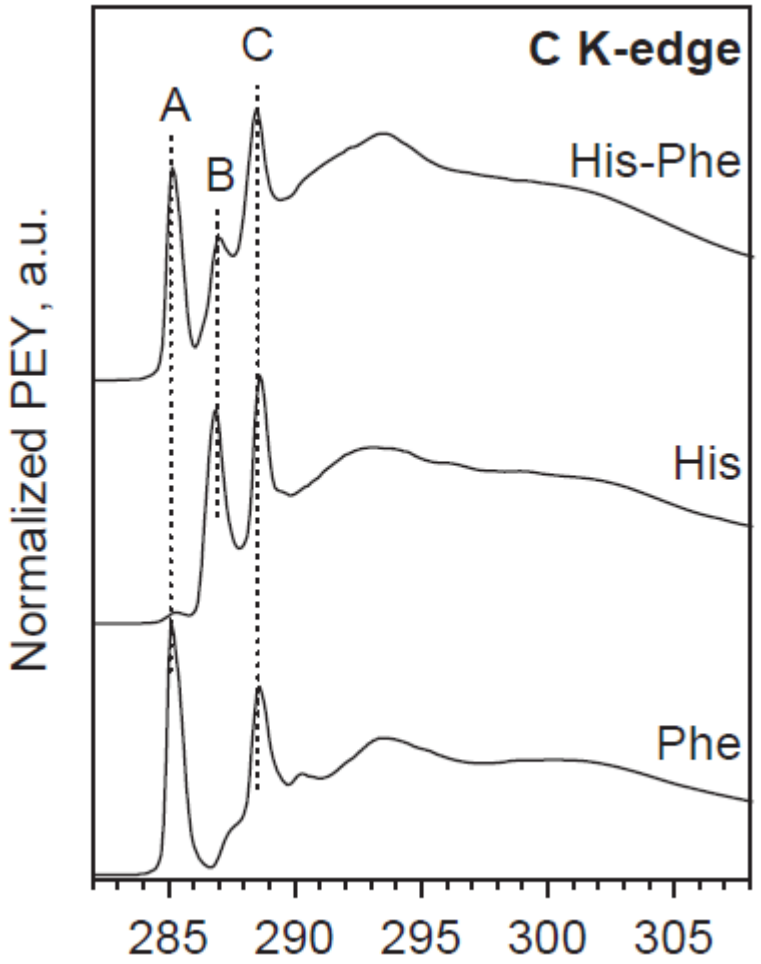


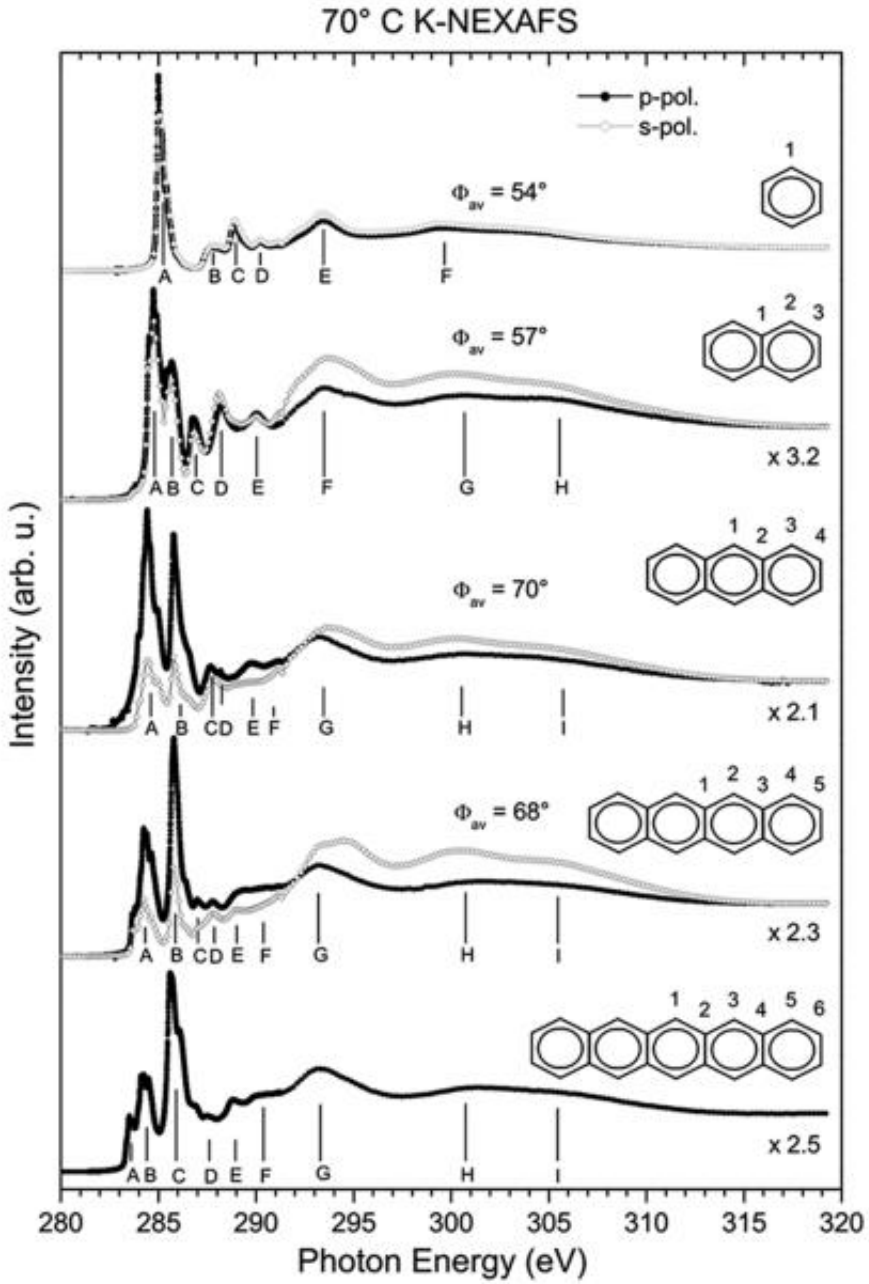


Histidine



Phenylalanine

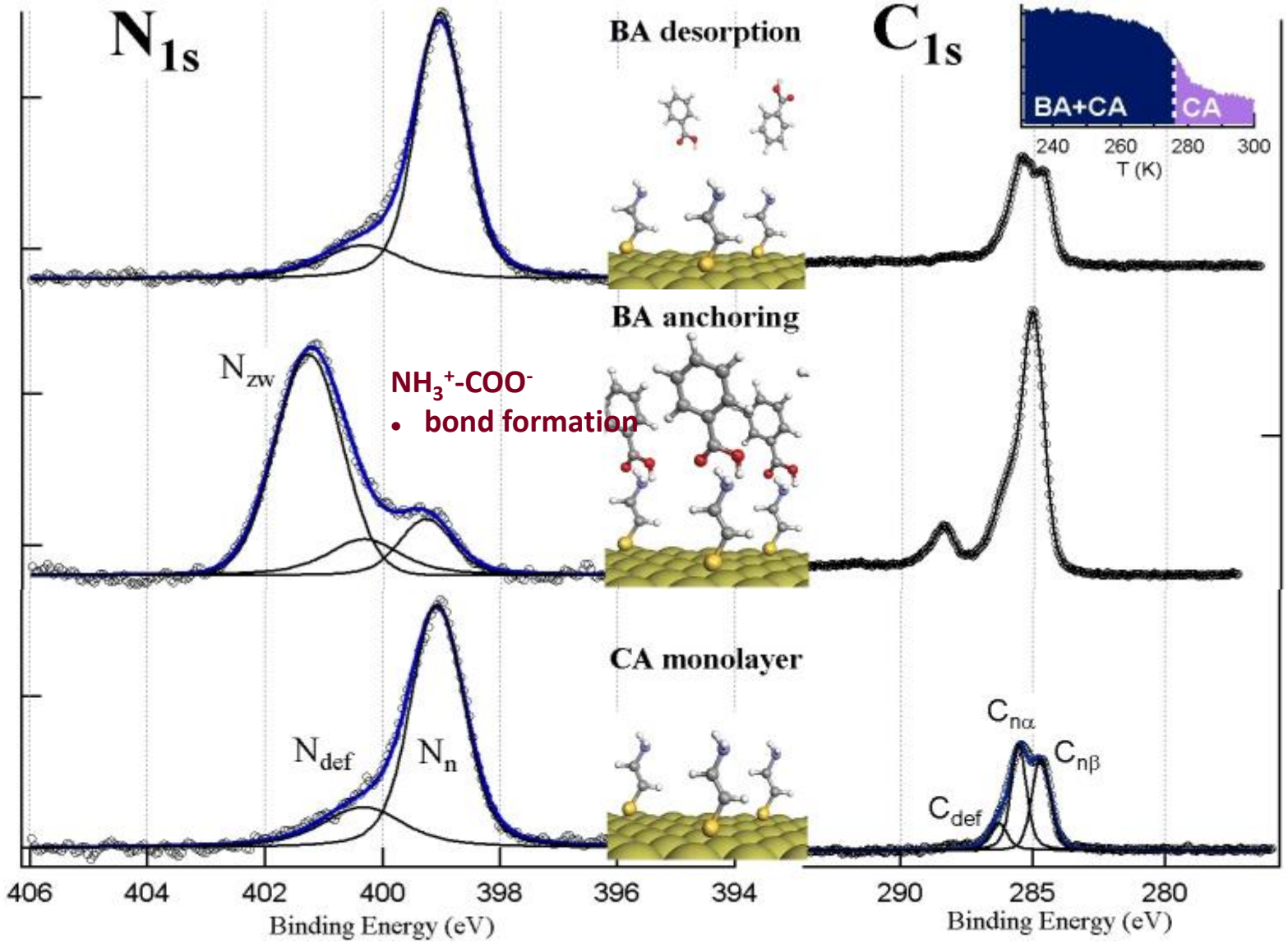


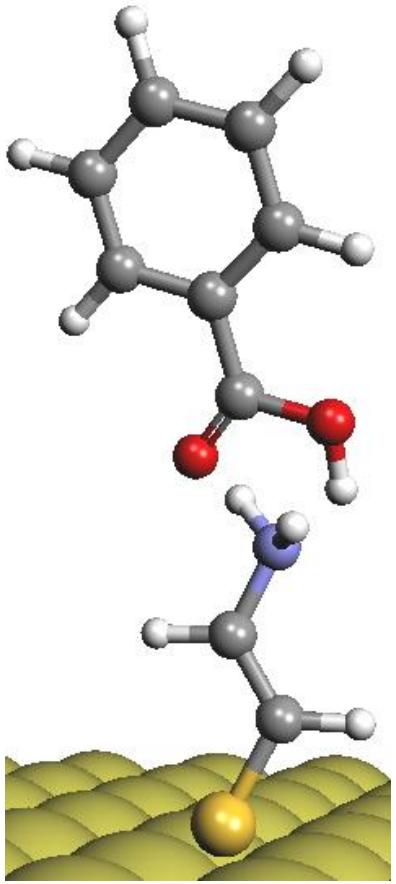


…..non vale per sistemi fortemente coniugati

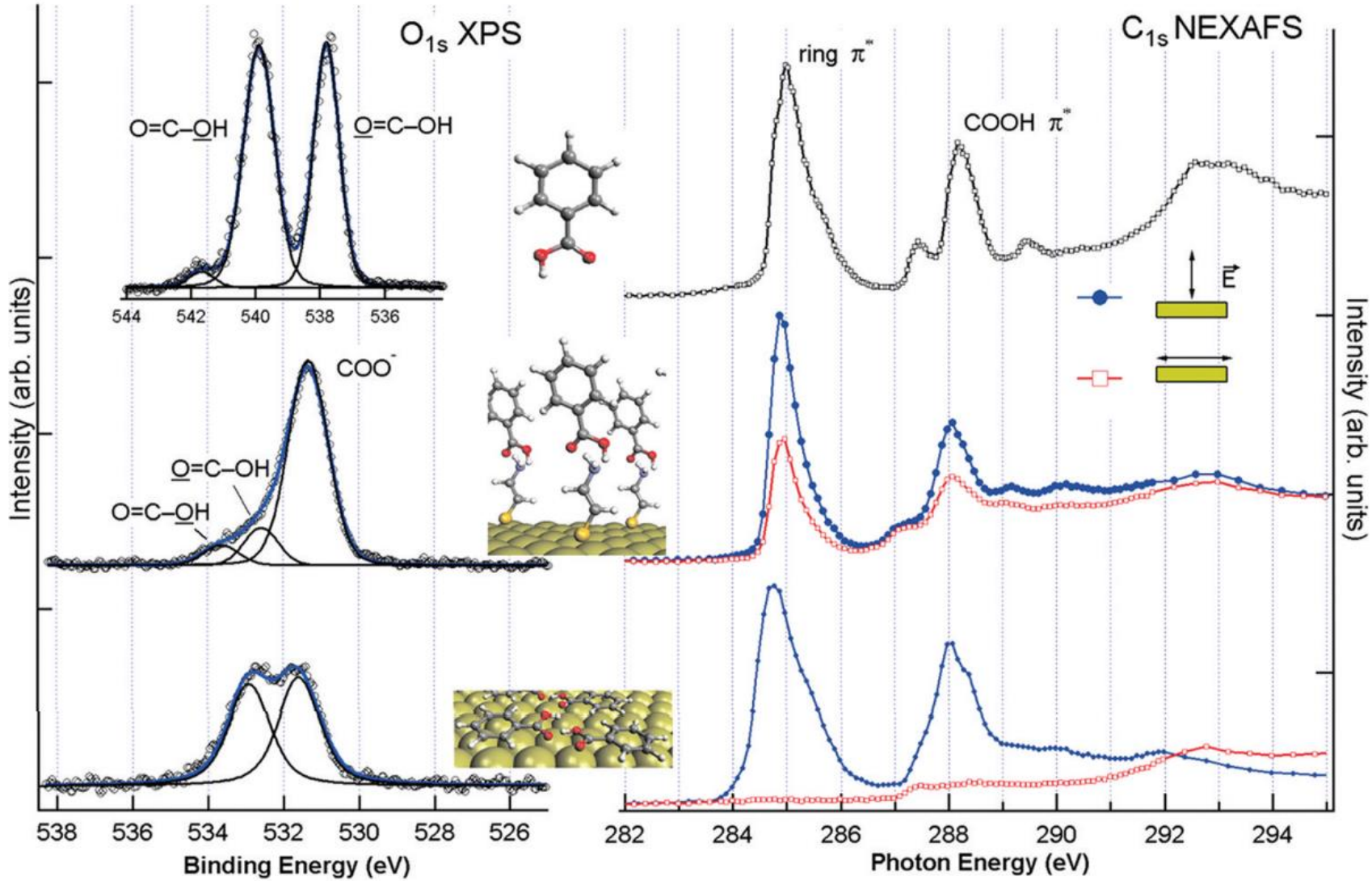
J. Phys. Chem. C 2018, 122, 28692−28701

Anchoring of carboxylic molecules

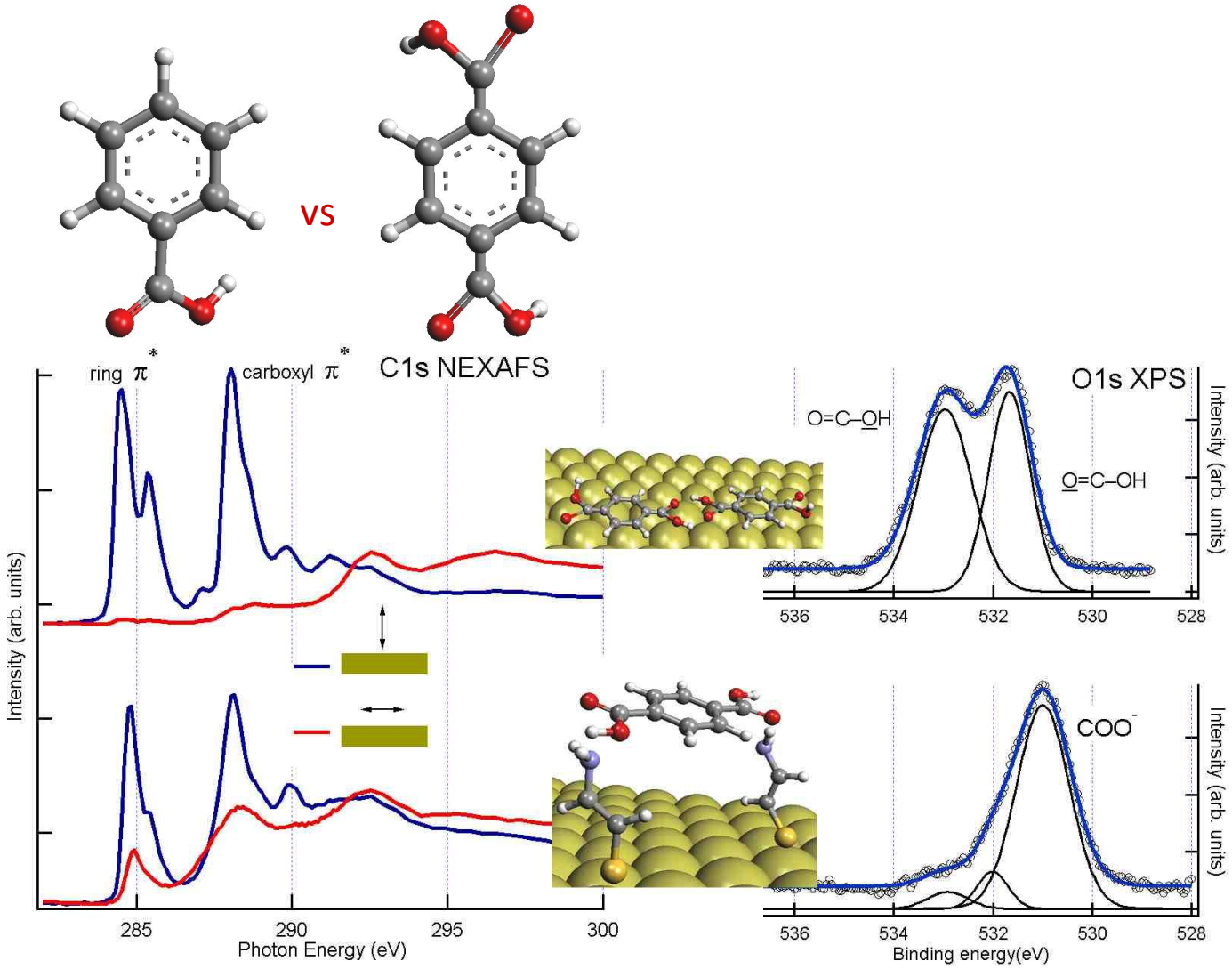




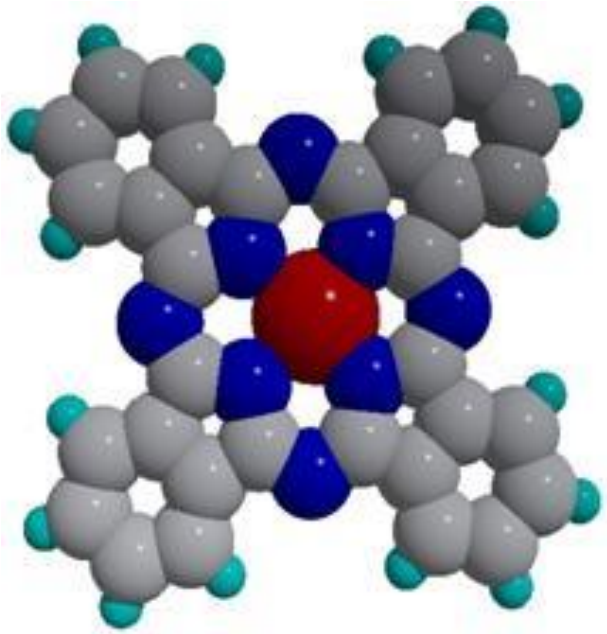
J. Phys. Chem. Lett. **2011**

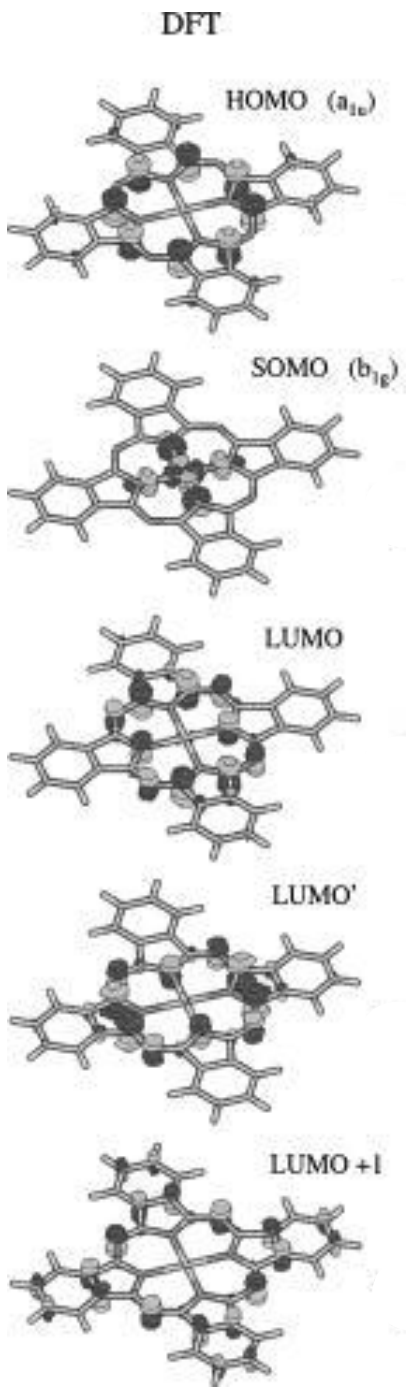

O1s XPS
C1s NEXAFS
O=C–OH
O=C–OH
544
542
540
538
536
COO-
O=C–OH
O=C–OH
ring π*
COOH π*
E
Intensity (arb. units)
Intensity (arb. units)
538
536
534
532
530
528
526
Binding Energy (eV)
282
284
286
288
290
292
294
Photon Energy (eV)

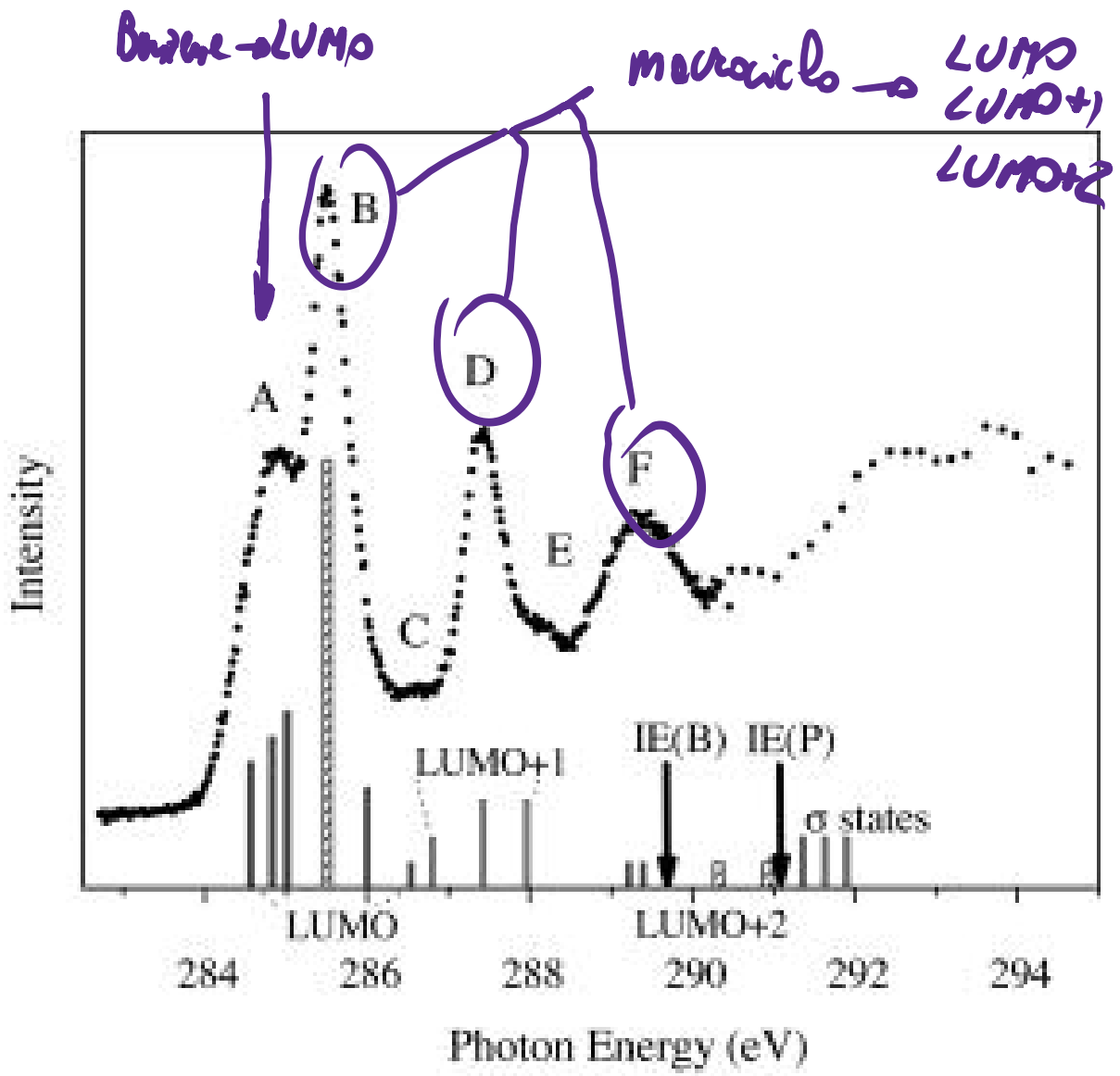
2 Anchoring of carboxylic molecules



PCCP **2012** Morphology changes by selecting the number of anchoring groups

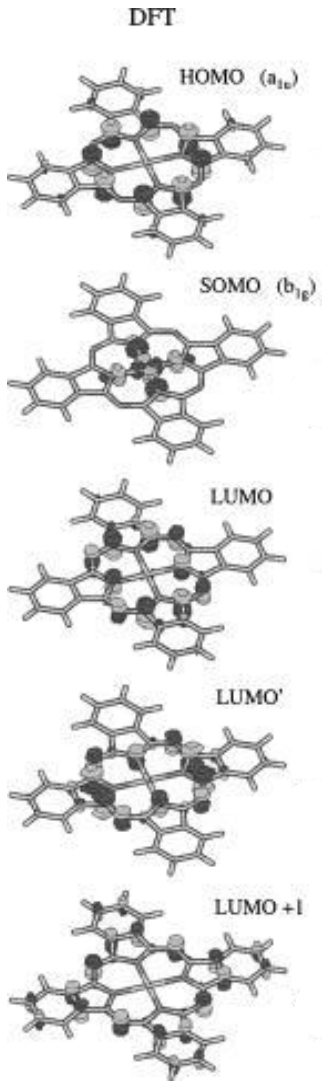


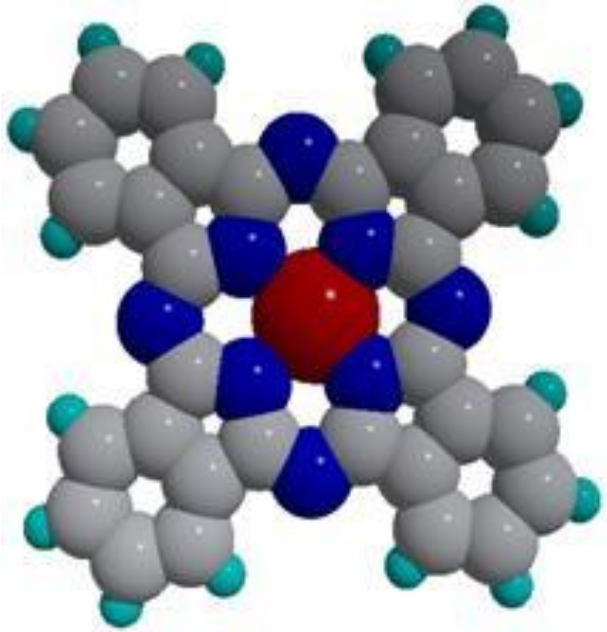

DFT
HOMO (a_{1u})
SOMO (b_{1g})
LUMO
LUMO'
LUMO +1

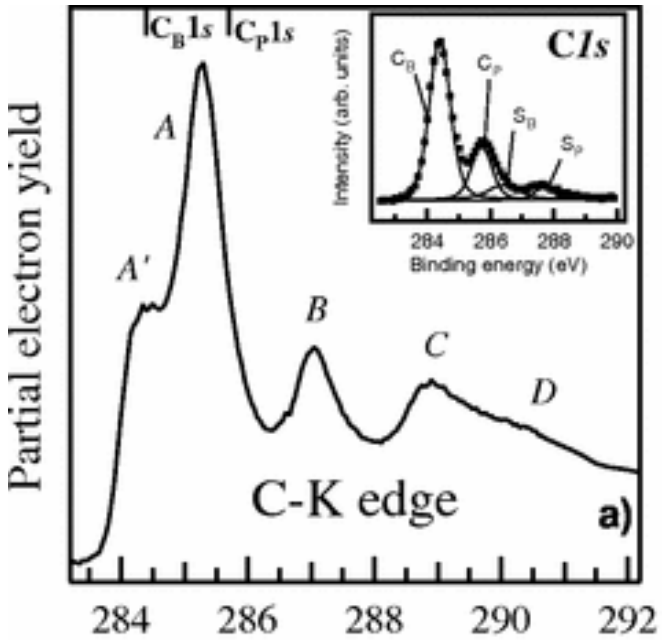

Intensity
A
B
C
D
E
F
LUMO+1
IE(B)
IE(P)
σ states
LUMO
LUMO+2
284
286
288
290
292
294
Photon Energy (eV)

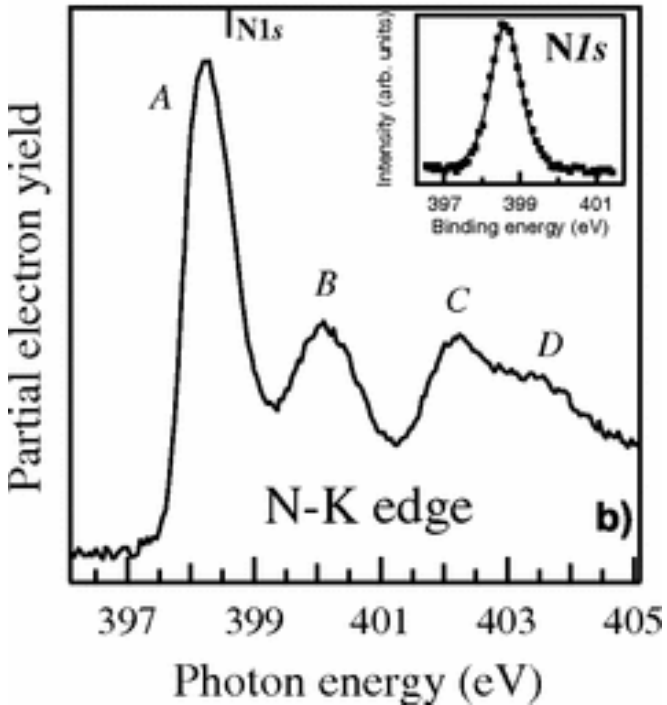
PHYSICAL REVIEW B **79**, 115446 (2009)

Filling empty states in a CuPc single layer on the Au(110) surface via electron injection

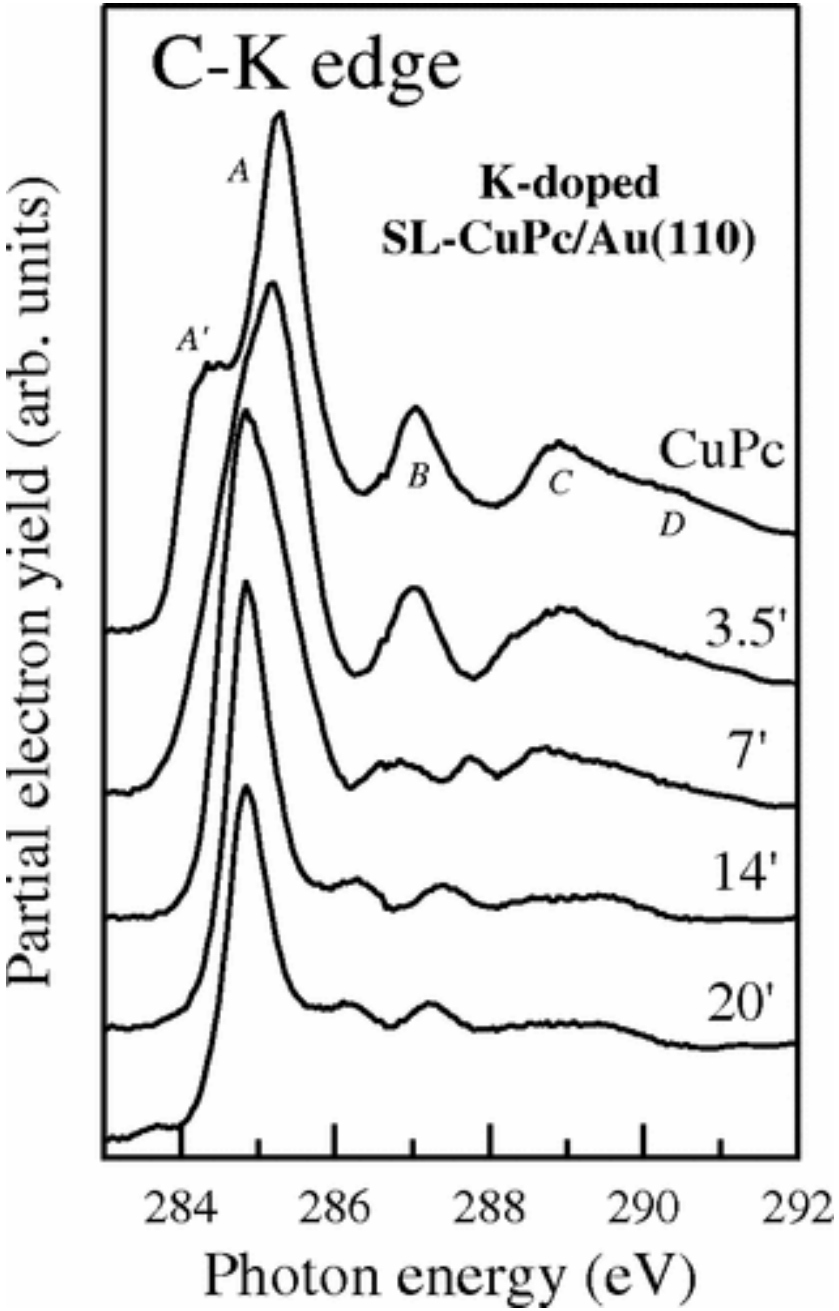


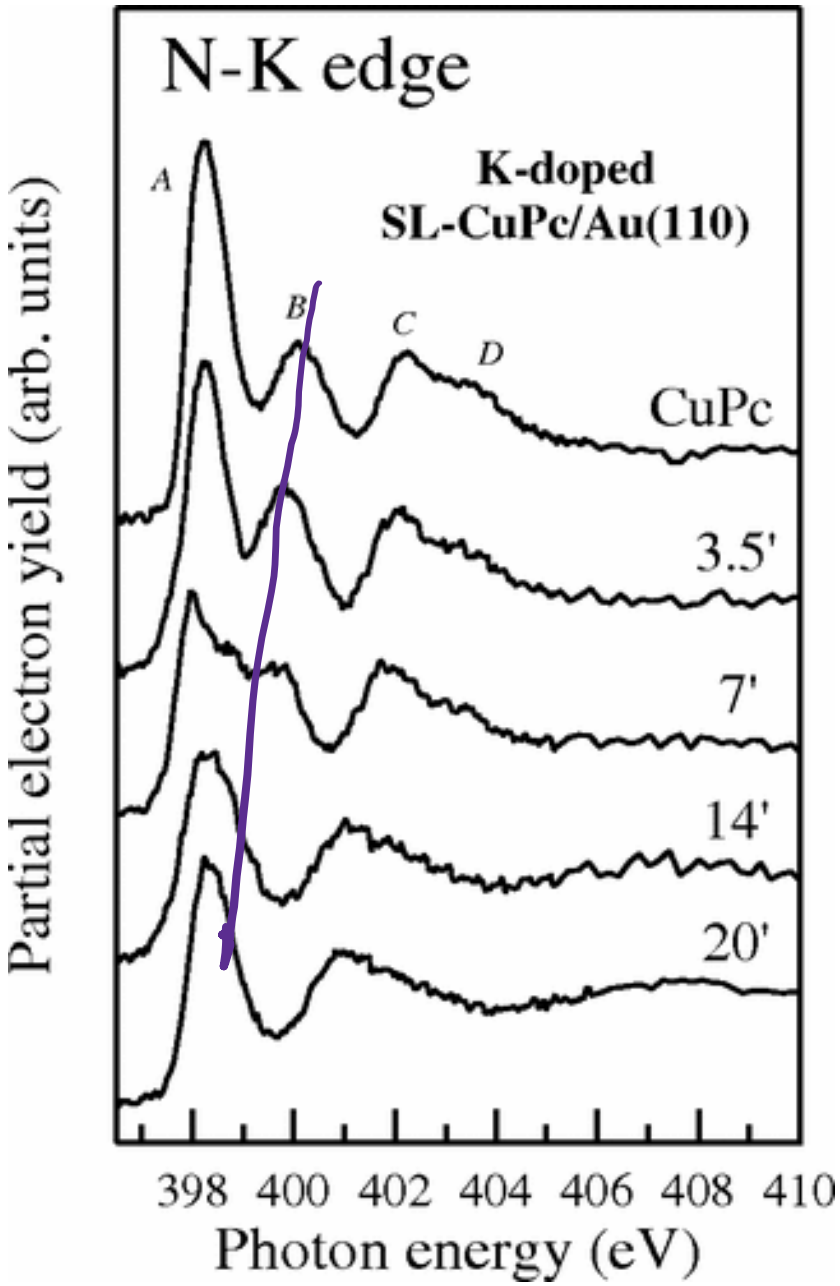


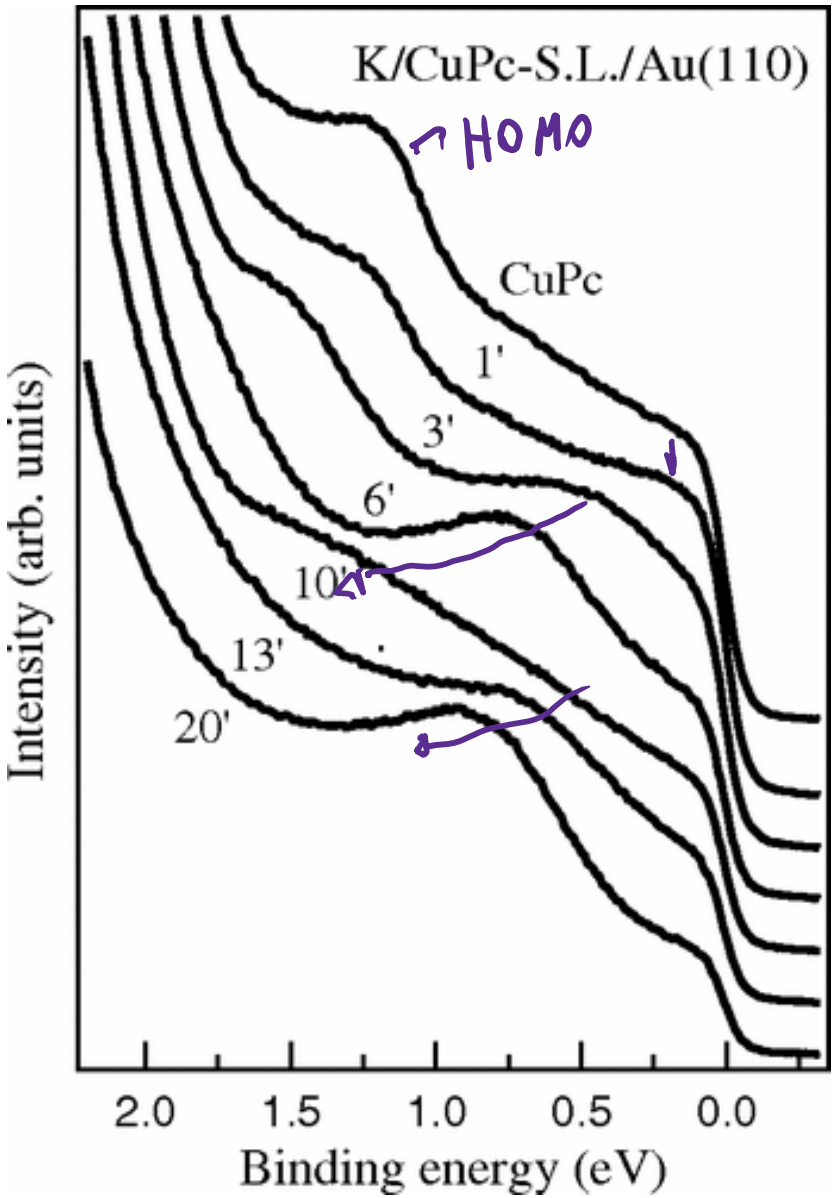




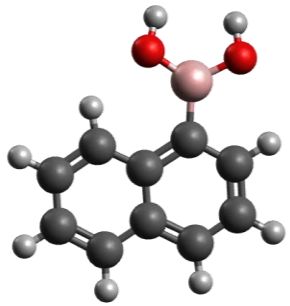
← il doping sposta i livelli





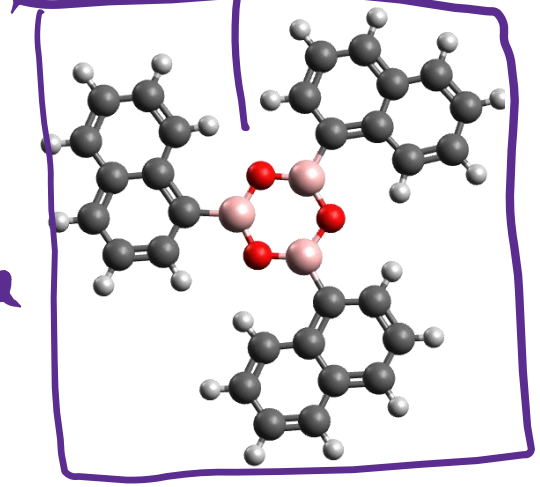

K/CuPc-S.L./Au(110)
HOMO
CuPc
1'
3'
6'
10'
13'
20'
Intensity (arb. units)
2.0
1.5
1.0
0.5
0.0
Binding energy (eV)

(NBA) naphthalene boronic acid

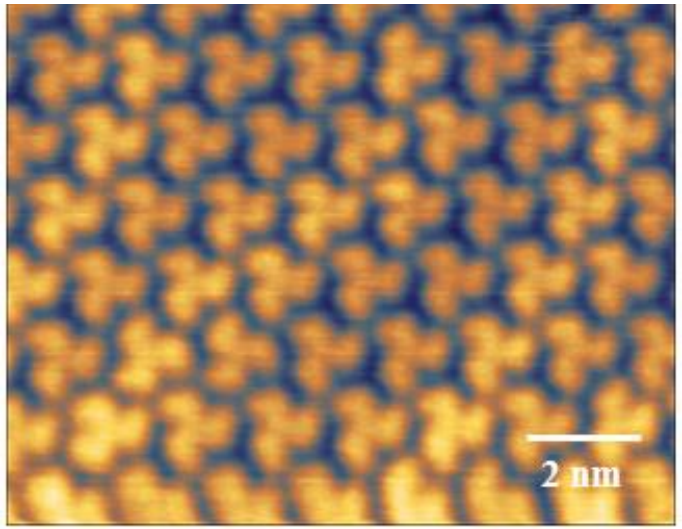


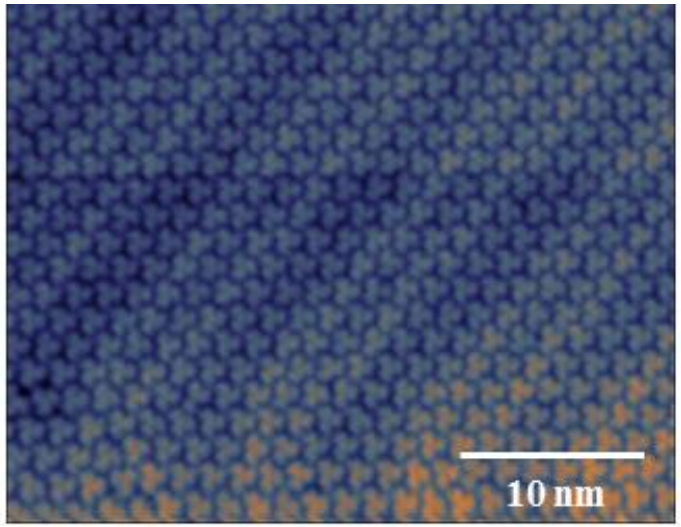
condensation

boroxine

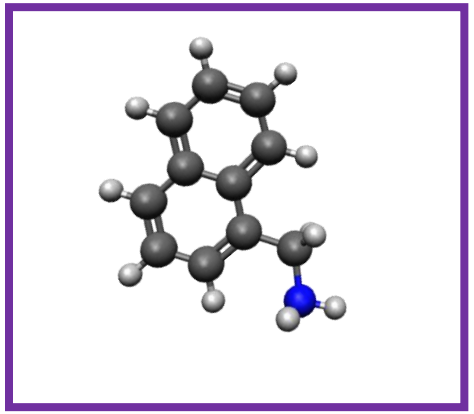


Au(111)

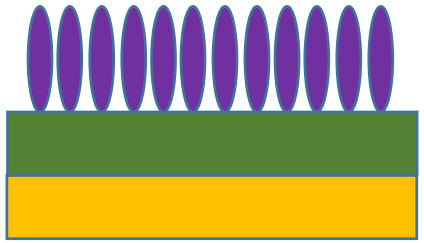


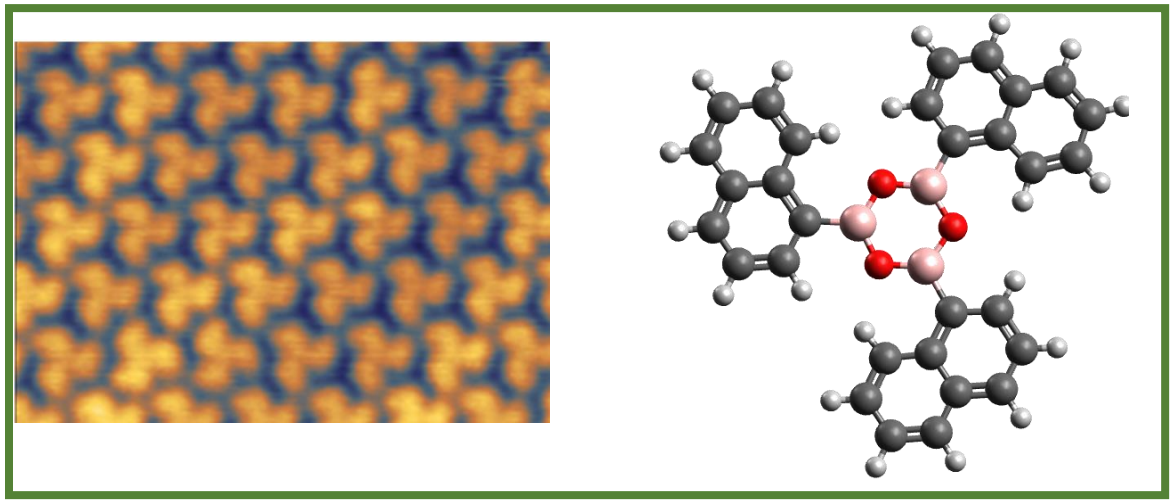


Anchoring platforms?



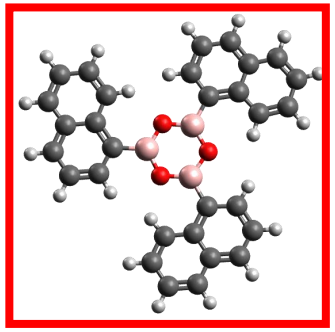
Naphtylmethylamine, NMA

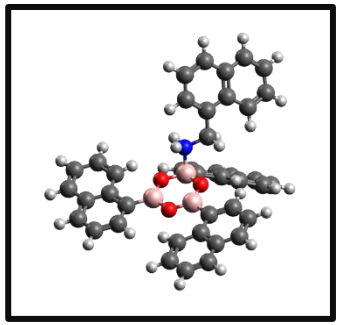




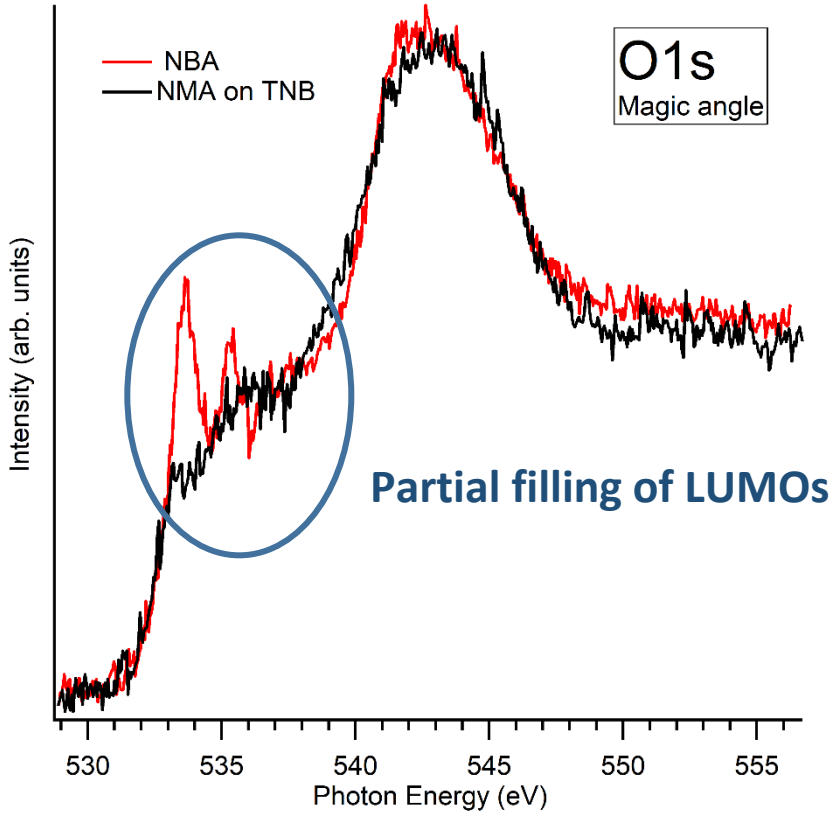
Is boroxine on Au(111) still a Lewis acid?

Anchoring platforms?

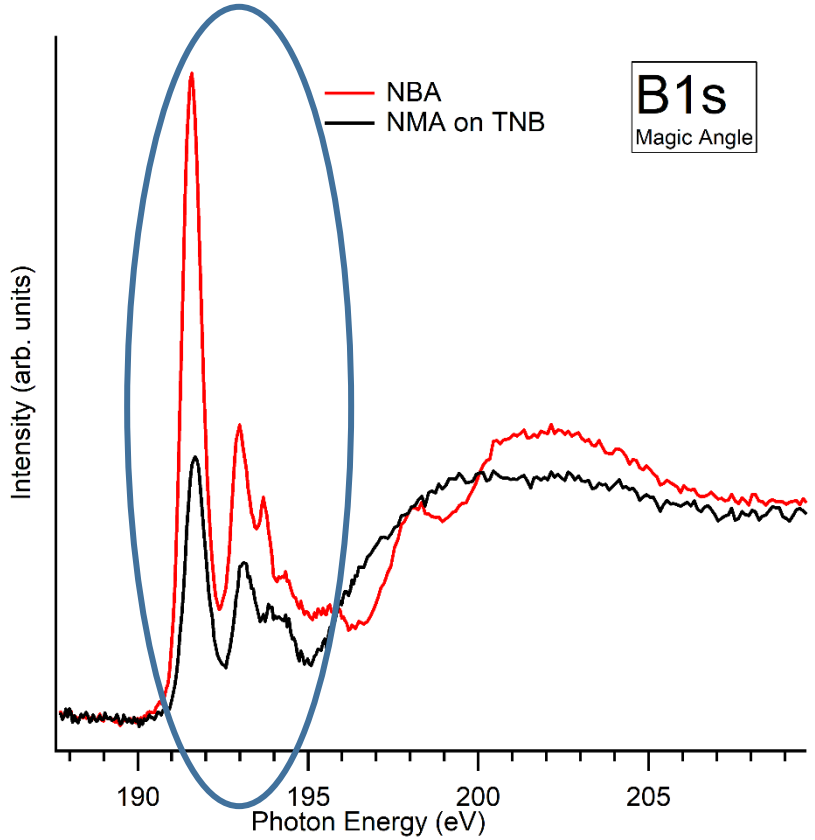




amino-boroxine dative bond



Partial filling of LUMOs

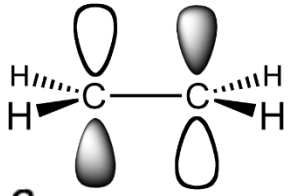


Profili dei picchi e step negli spettri NEXAFS

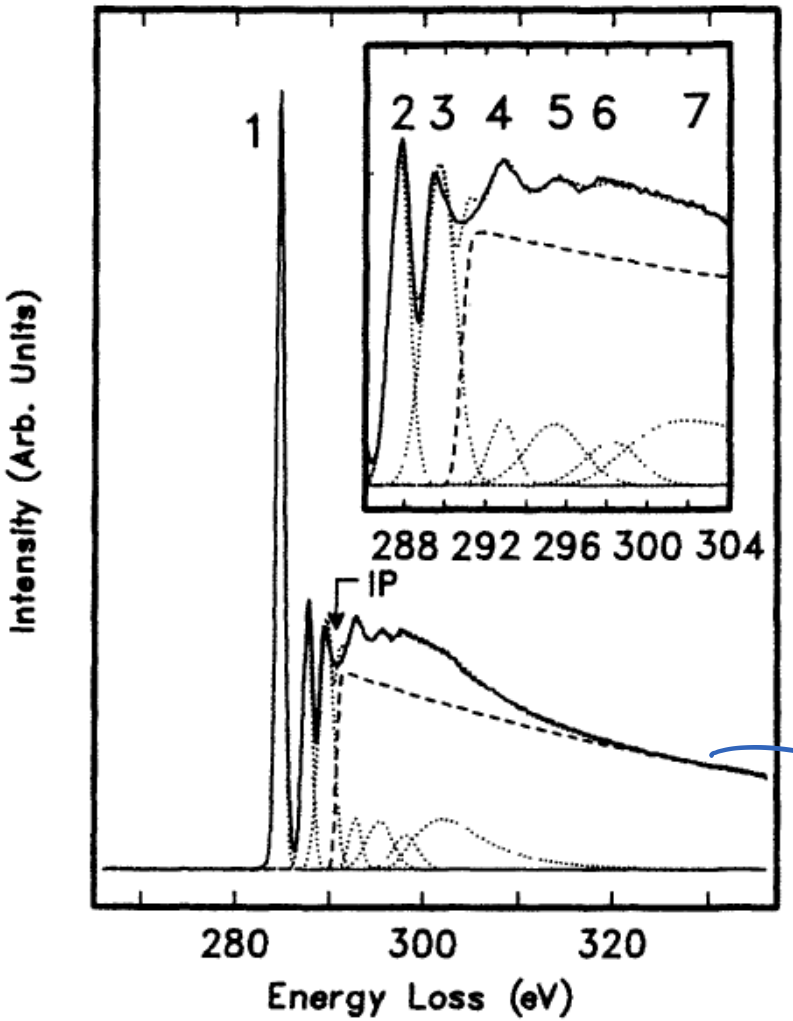
(vedi prima trattazione della forma dei picchi e degli step nella sezione dedicata alla teoria degli Errori)

IP step

Etilene,



C_2H_4 Gas ISEELS



1. IS → π^* (LUMO)

2-3. IS → C-H*, Rydberg

4-6 Multielectron

7 C=C σ^* resonance

→ decade esponenzialmente

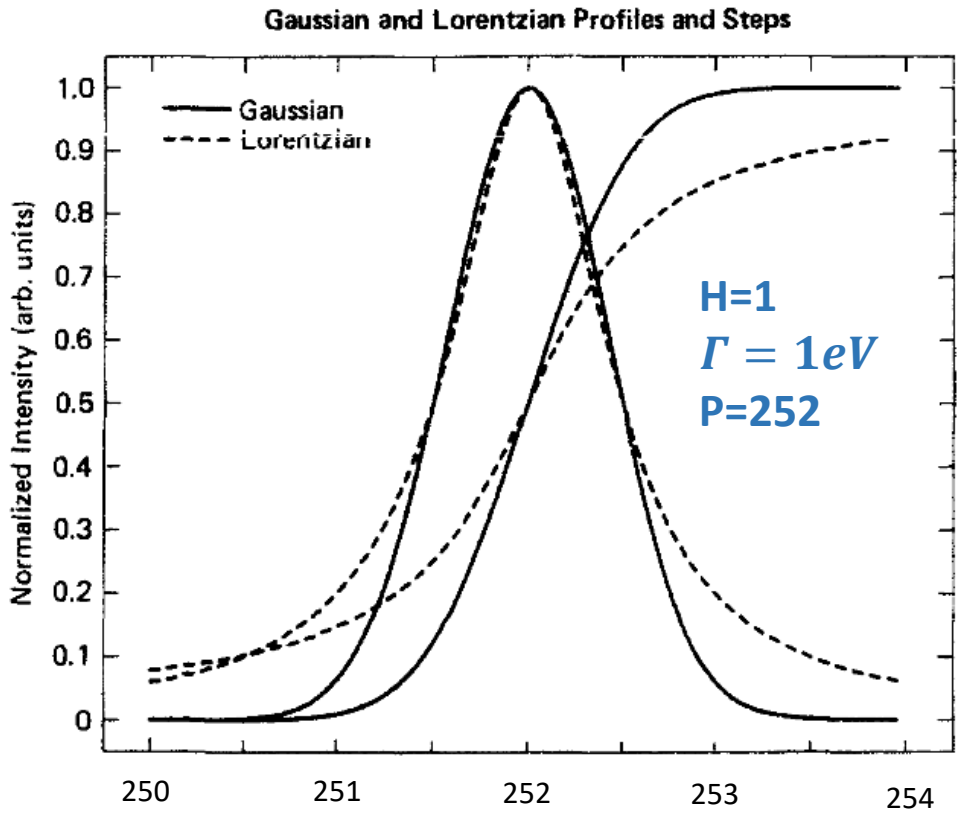
Gli step NEXAFS

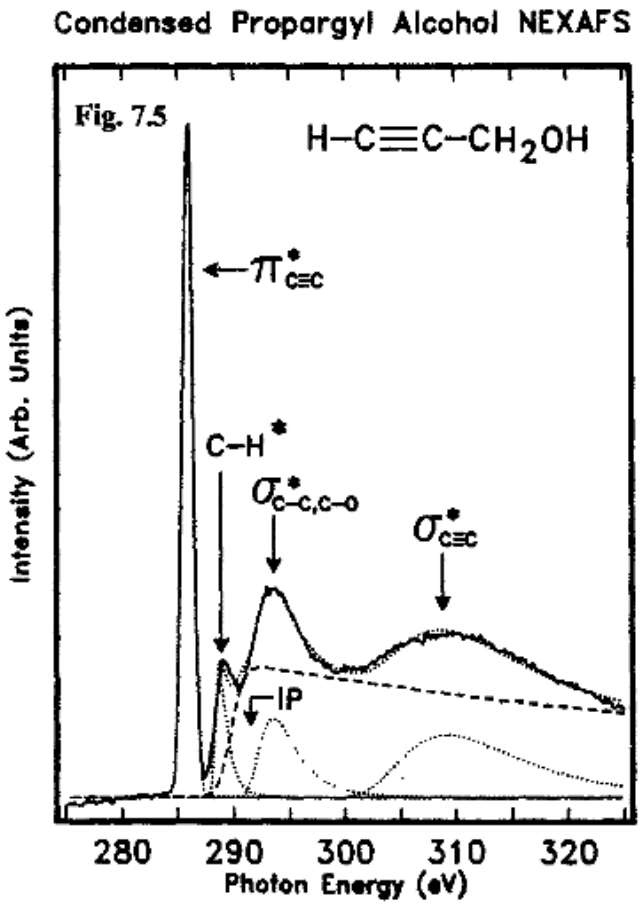
Sia lo step IP che i Fermi step in NEXAFS non sono dei gradini ma hanno un allargamento dovuto al tempo di vita dell'eccitazione. Il loro profilo integrato è una curva lorentziana. Come per la fotoemissione, il profilo misurato sarà la convoluzione con una gaussiana. Essendo gli step sempre sovrapposti a picchi di assorbimento, non è sempre facile individuarne esattamente la forma. Si usano due funzioni per dare dei profili rispettivamente lorentziano e gaussiano:

$$I_{lor} = H\left(\frac{1}{2} + \frac{1}{\pi}\tan^{-1}\frac{(E-P)}{\Gamma/2}\right)$$

$$I_{gauss} = H\left(\frac{1}{2} + \frac{1}{2}erf\,\frac{(E-P)}{\Gamma}\right)$$

$$erf(z) = \frac{2}{\sqrt{\pi}}\int_{o}^{z} e^{-t^2}dt$$





Le shape resonance hanno il profilo di una gaussiana asimmetrica

!! H_I attese dello step (1P step)

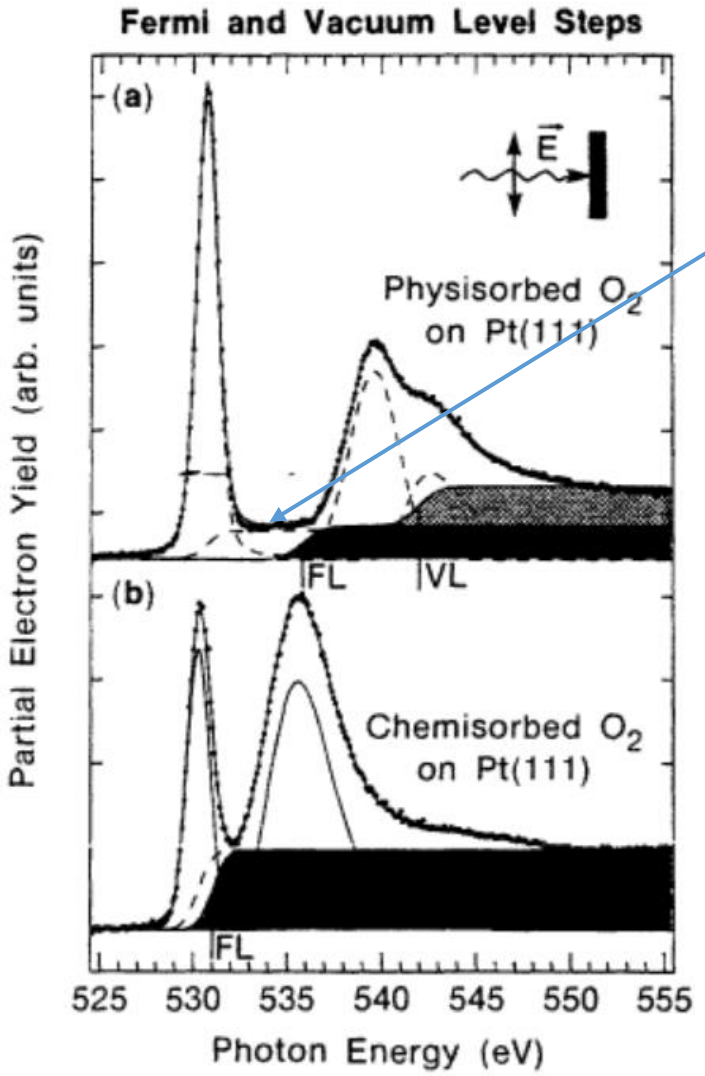
non dipende dalla polarizzazione di $\vec{E}$

se $|i\rangle$ è stato 1s

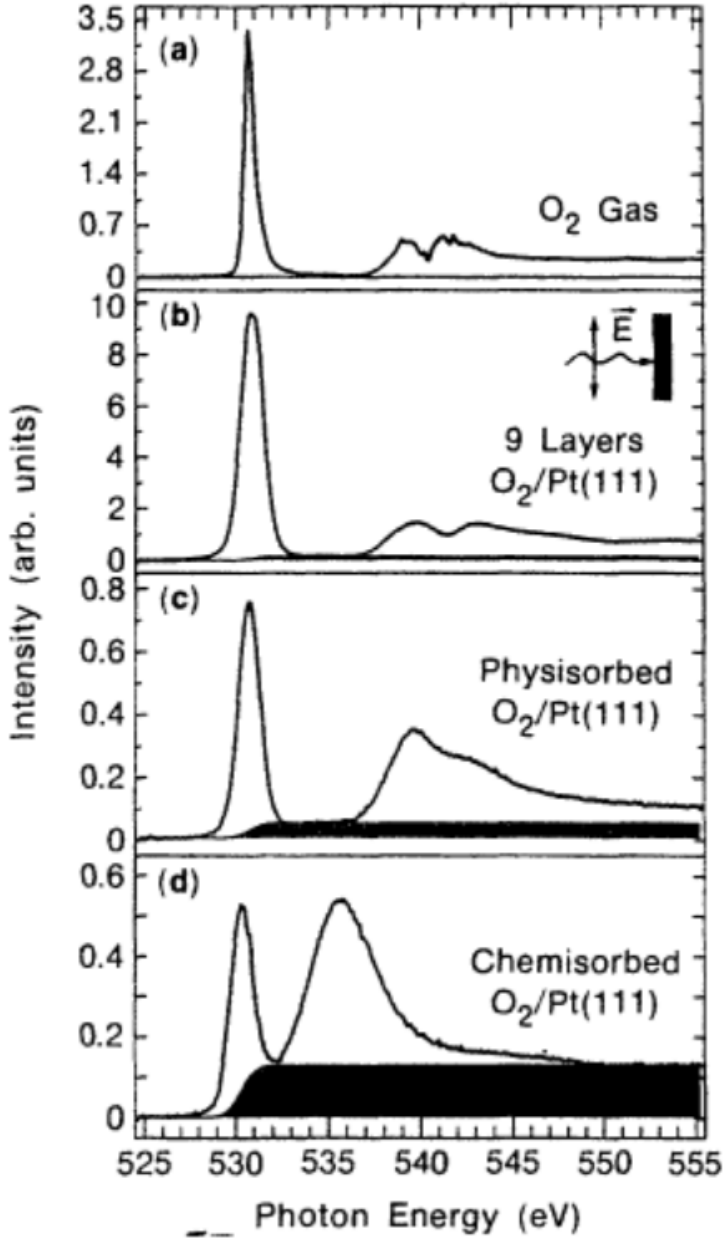
• Gli step negli spettri NEXAFS : Fermi step

Se una molecola è a contatto con la superficie di un metallo, posso avere degli orbitali non occupati ibridi molecola metallo, ad un energia che va dal livello di Fermi in su. Diventa possibile che l'elettrone 1s venga eccitato su uno di questi orbitali. Dal punto di vista della molecola è come se venisse ionizzata ad un potenziale inferiore a quello di ionizzazione. Sperimentalmente registro uno step di intensità all'energia corrispondente al livello di Fermi.

Fermi step



Qui il fit prevede uno step a energie ancora più basse rispetto al livello di fermi. E' da attribuire a fenomeni multielettronici: un primo elettrone viene promosso nel LUMO e un secondo fa un salto dalla banda di valenza al continuo degli orbitali ibridizzati con il metallo al livello di Fermi.



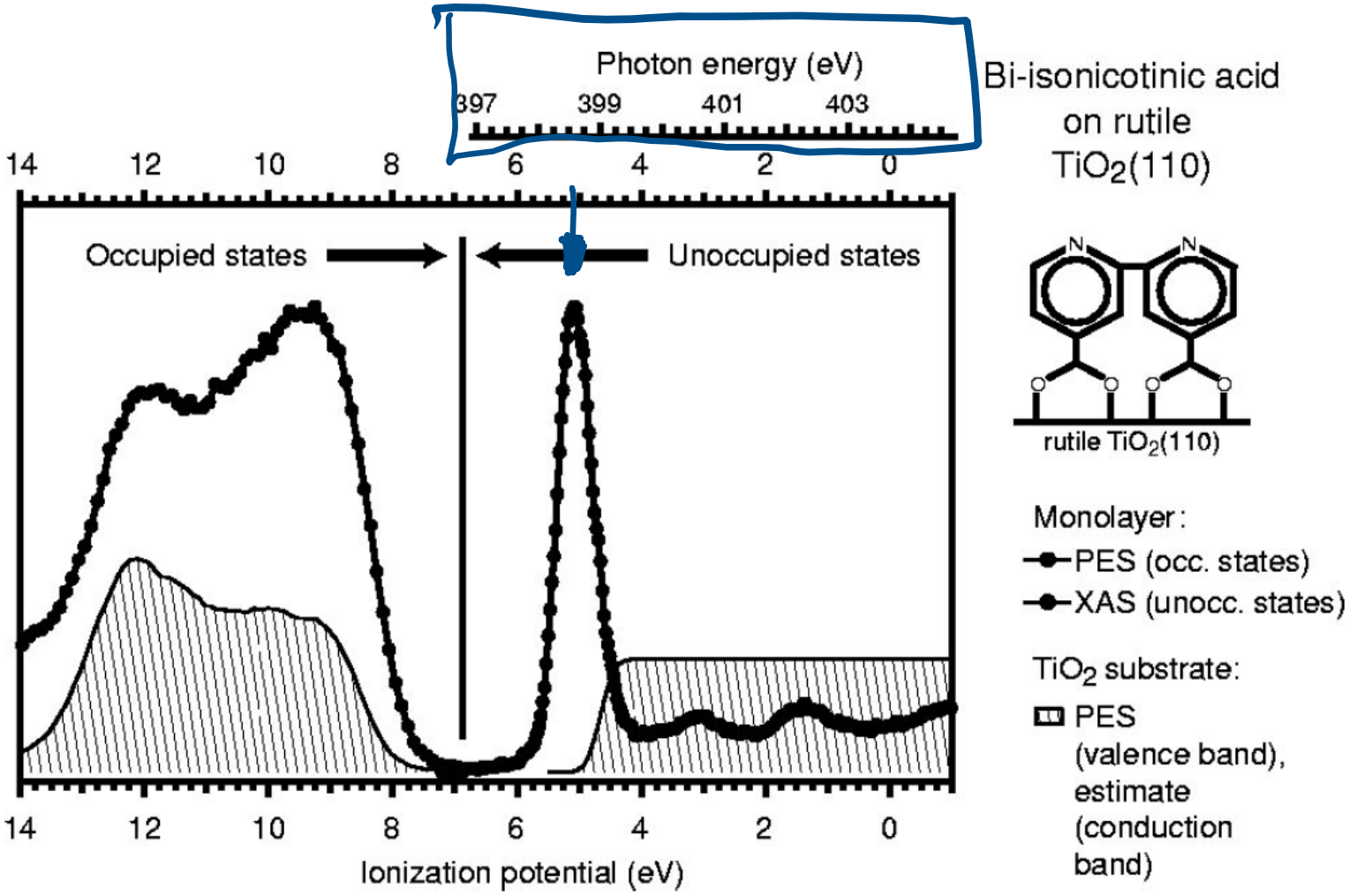
Allineamento XPS-NEXAFS

Fotoemissione ed assorbimento a soglia descrivono la distribuzione in energia degli stati occupati e non occupati, rispettivamente. Per mettere i risultati delle due misure sulla stessa scala delle energie si procede in questo modo:

1. Determino la posizione del potenziale di ionizzazione IP con XPS, mettendo un bias al campione. Posizione IP nello spettro NEXAFS

2. Il livello di Fermi sarà distante da IP di una quantità pari alla funzione lavoro. Allineo XPS rispetto a Nexafs di conseguenza

Allineamento XPS-NEXAFS



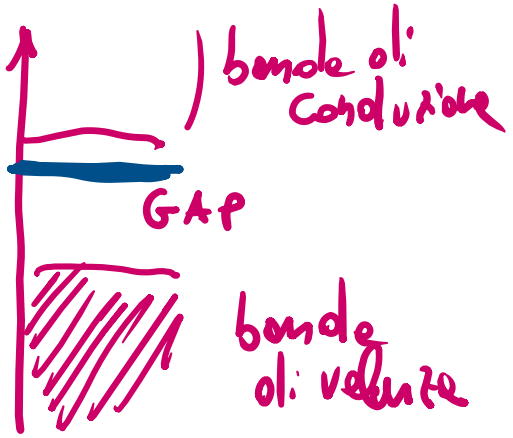
Bi-isonicotinic acid on rutile $TiO_2(110)$

rutile $TiO_2(110)$

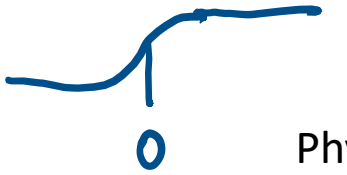
Monolayer:
- PES (occ. states)
- XAS (unocc. states)

TiO_2 substrate:
- PES (valence band), estimate (conduction band)

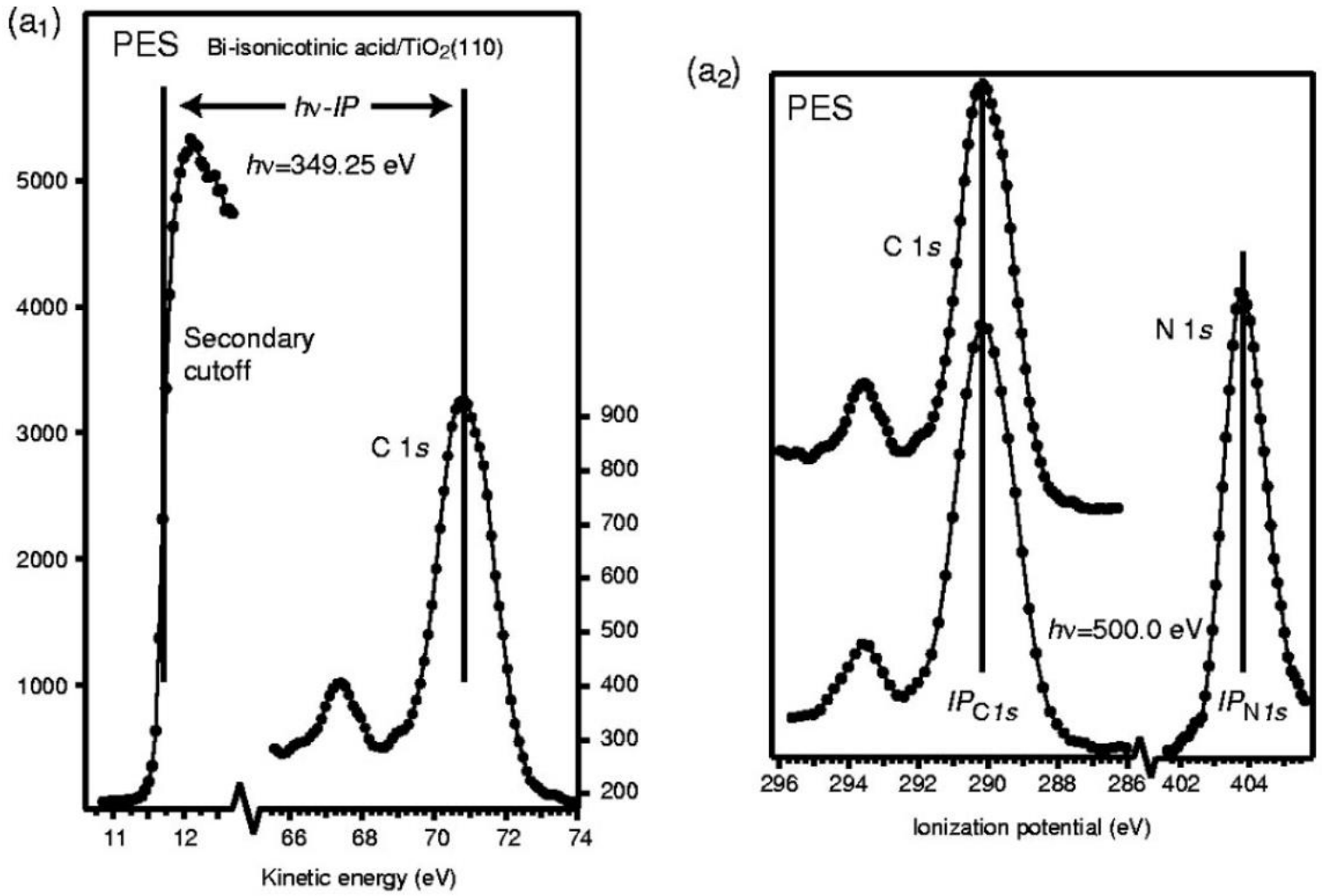
TiO_2 è semiconduttore



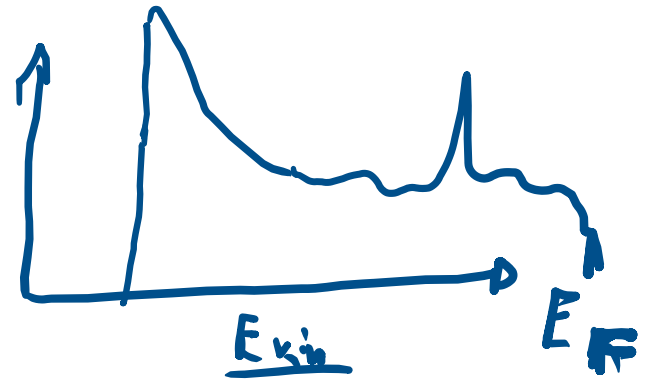
IP :



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Misure della WF



= hν - WF

WF è IP di e⁻ al livello di Fermi

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