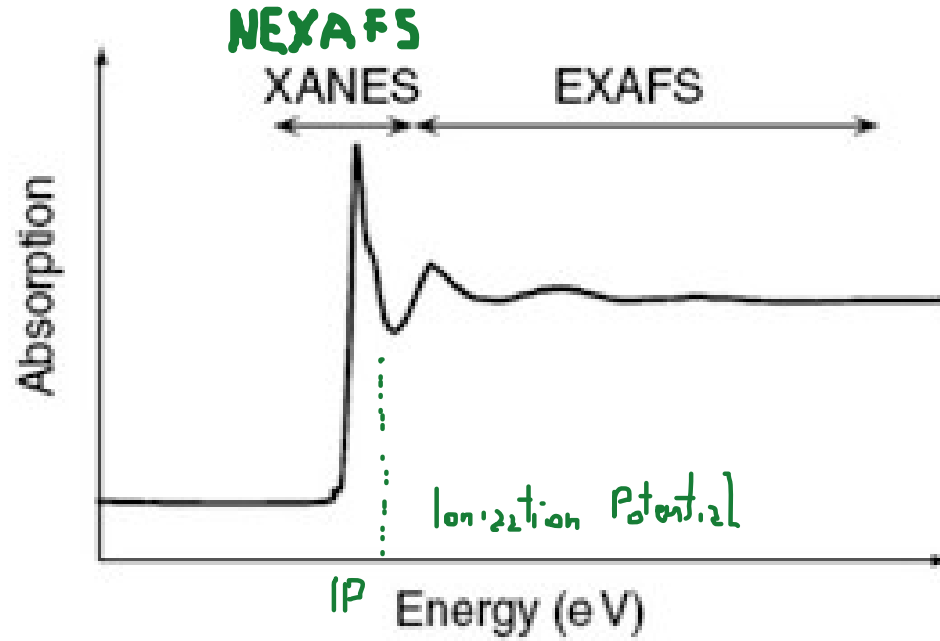


## Adsorbimento a soglia



Prossimità delle soglie

XANES

X-ray Absorption Near Edge Structure

NEXAFS

Near Edge X-ray Absorption Fine Structure

---

$$1. \quad \sigma(h\nu, k) \propto \sum_{|f\rangle} |\langle f | \hat{e}_z \cdot \vec{r} | i \rangle|^2$$

Fermi's golden rule

$$\vec{E} \propto \vec{E}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$\xrightarrow{\text{dipole approx}} \vec{k} \cdot \vec{r} \ll 1$

Soptie  $O_{1s}$   $h\nu \sim 550 \text{ eV}$   $\left( O_{1s} \sim 530 \text{ eV} \right)$

$$\rightarrow \frac{\lambda}{2\pi} = \frac{1}{k} \sim 3.6 \text{ \AA} \rightarrow kr \approx \frac{0.13}{3.6} \ll 1$$

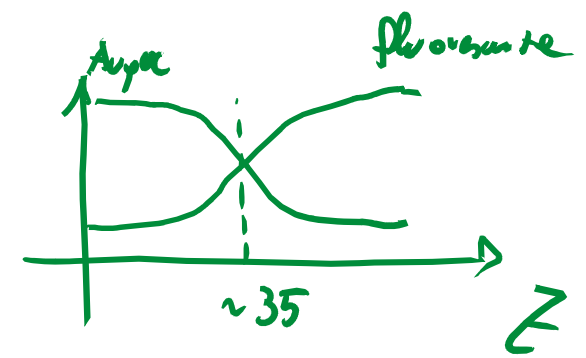
$$|\vec{r}| \approx \frac{2a_0}{Z} = 0.13 \text{ \AA}$$

$$\begin{aligned}
 O_{1s} &\approx 530 \text{ eV} \\
 C_{1s} &\approx 285 \text{ eV} \\
 N_{1s} &\approx 400 \text{ eV} \\
 S_{2p} &\approx 162 \text{ eV}
 \end{aligned}$$

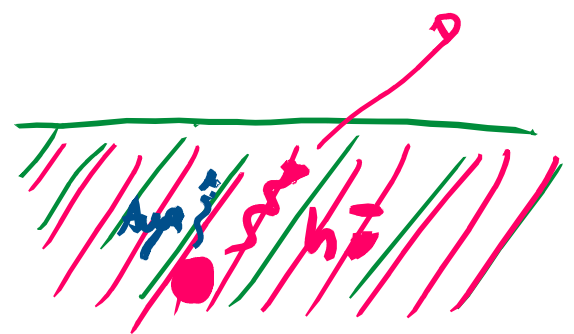
1.

misuro il prodotto della diseccitazione:

- 1. Auger
- 2. fotoni fluorescente



$h\nu$ , variabile



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

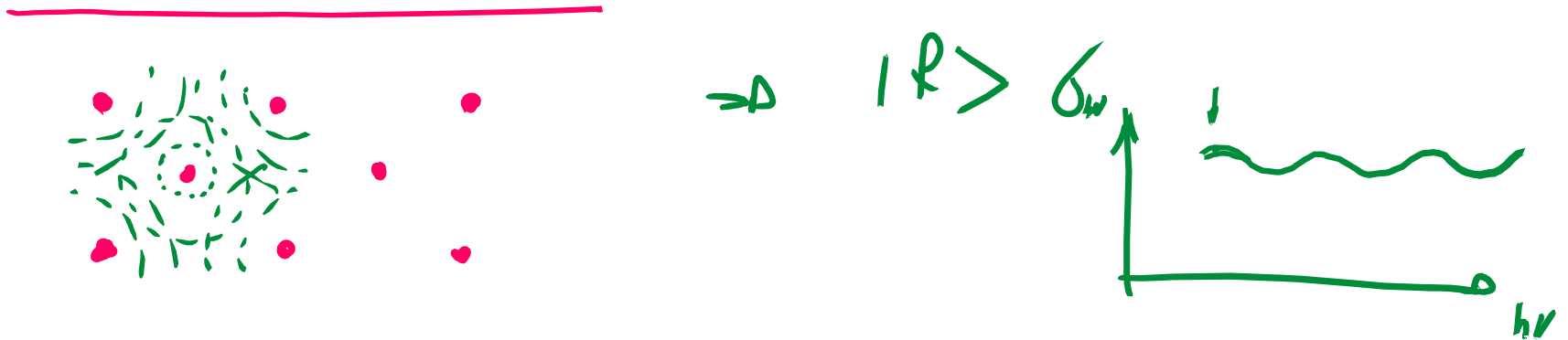
3. Total yield → tutti gli e<sup>-</sup> che uscono dal campione  
 → drain current

## 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  $h\nu$  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.

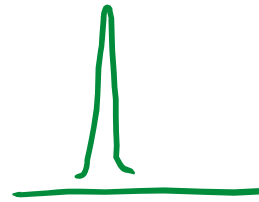
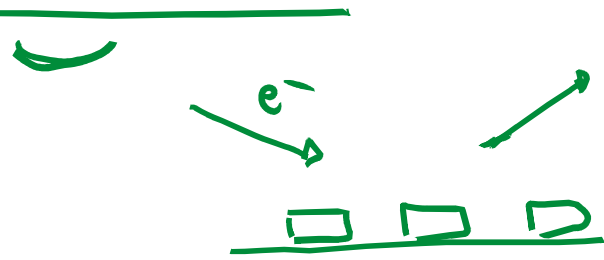
In sostanza, lo stato finale in cui il fotoelettrone viene promosso dipende fortemente dalla disposizione degli atomi circostanti.

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



# ISEELS

# Inner Shell Electron Energy Loss Spectroscopy



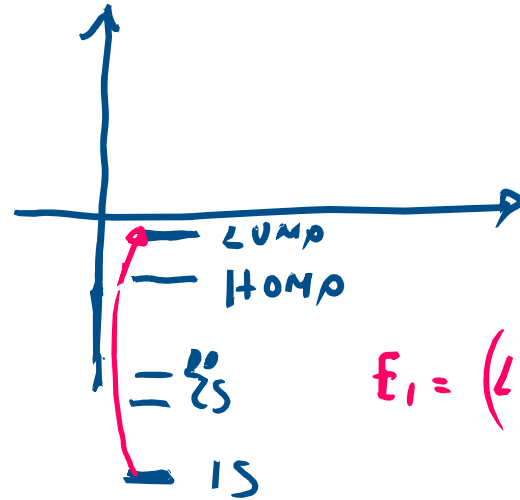
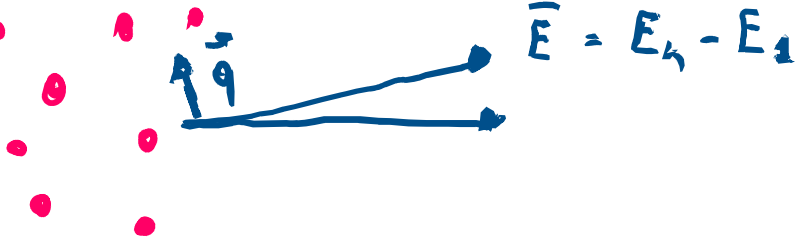
} EELS

## ISEELS

Bethe (1930)

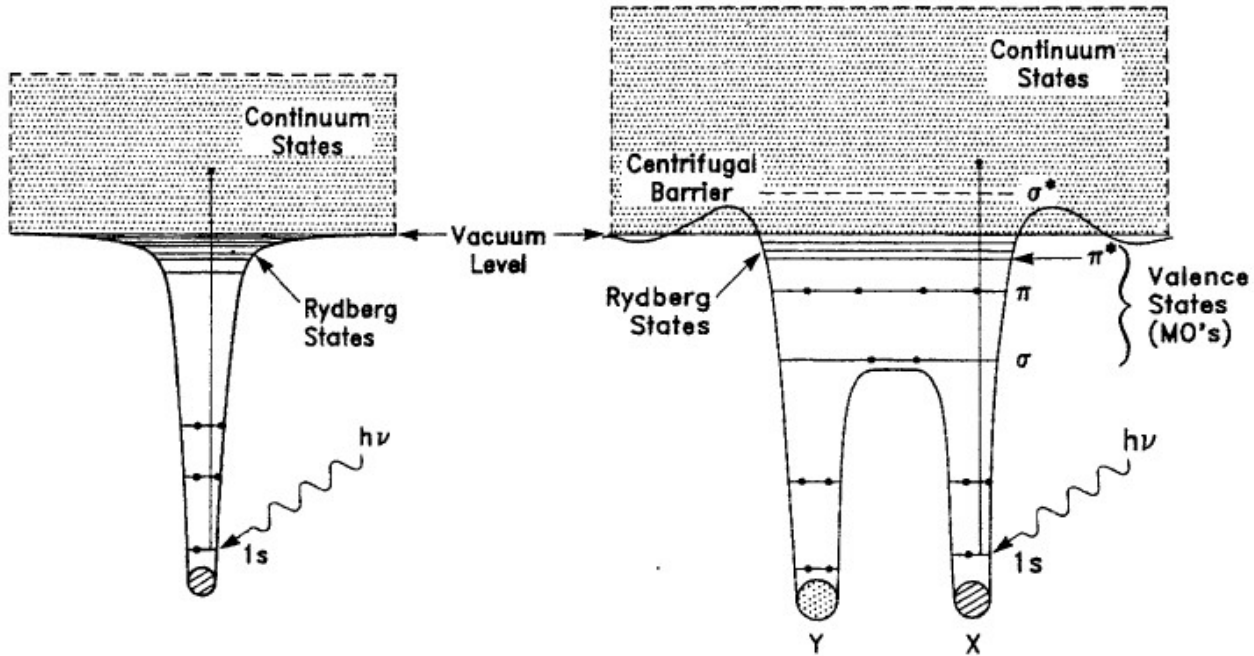
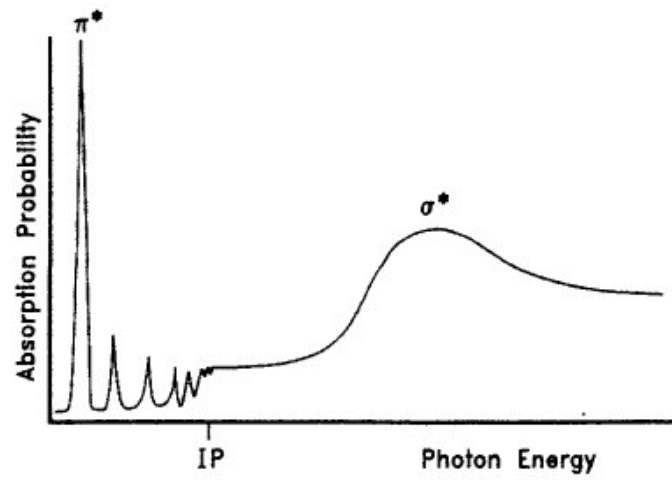
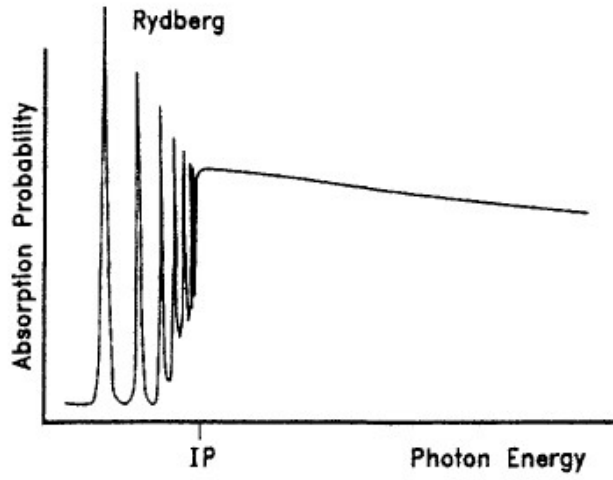
Radio monochromator

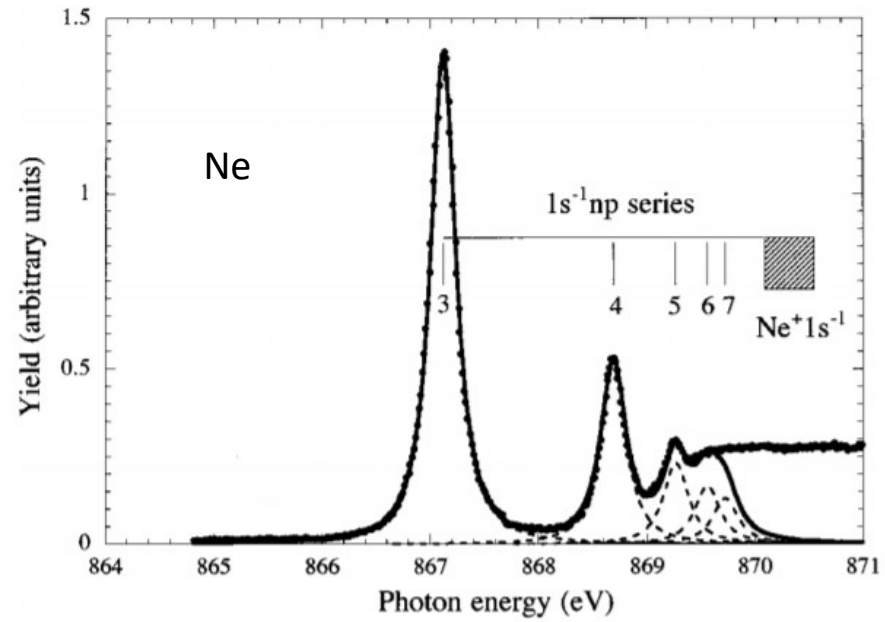
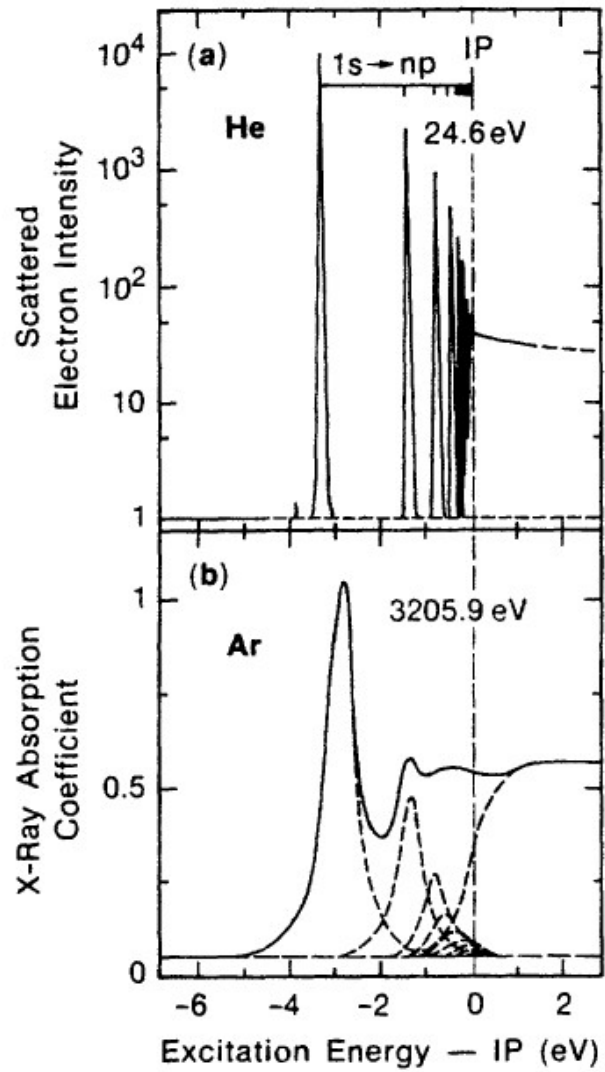
$e^-$ ,  $E_k > E_{shell}$



$$E_i = (LUMO - IS)$$

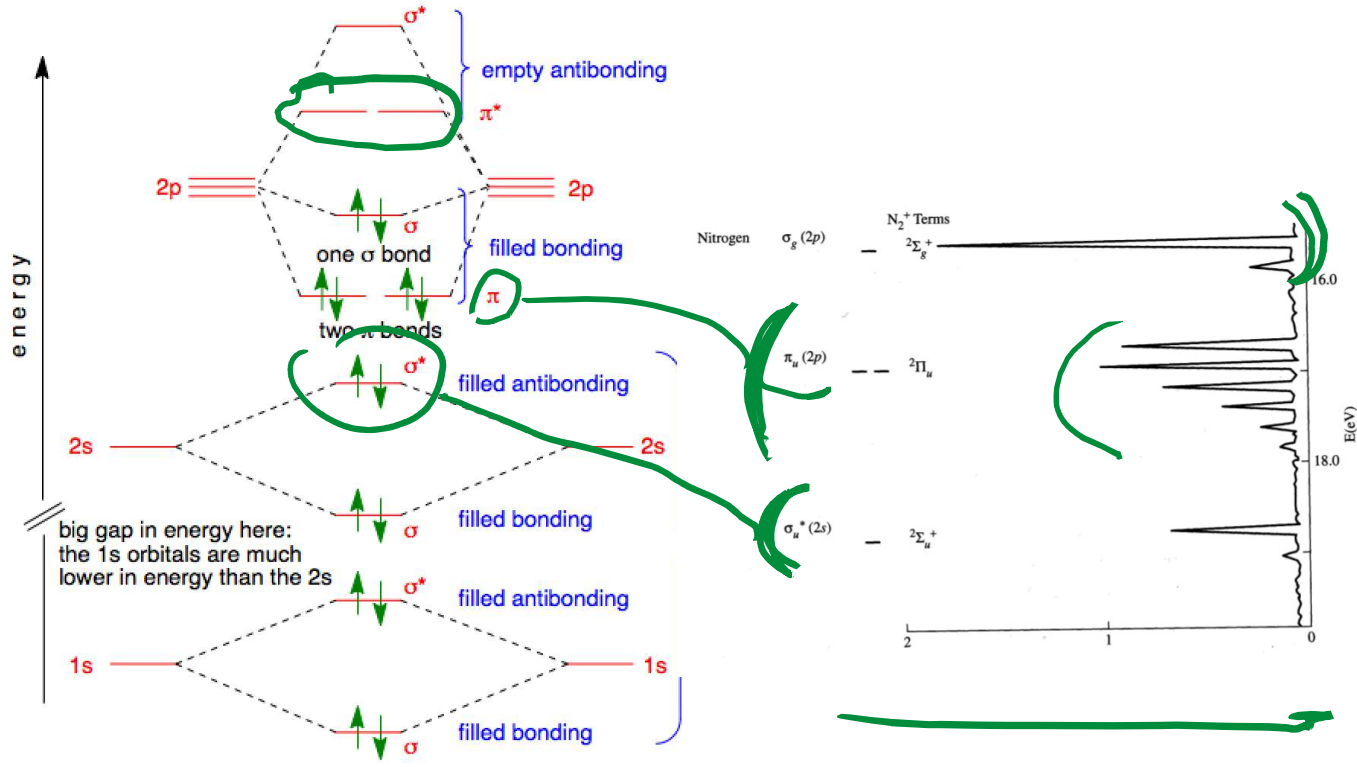
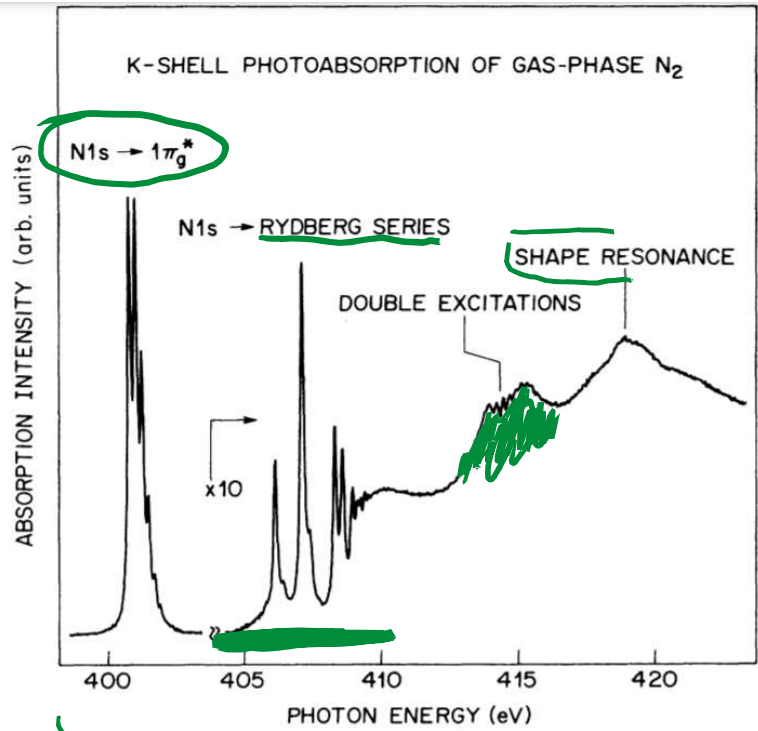
$$\frac{d\sigma_E}{dE_1} \propto \sum_{|i\rangle} |\langle f | \vec{e}_q \cdot \vec{r} | i \rangle|^2 \quad q \cdot r \ll 1$$



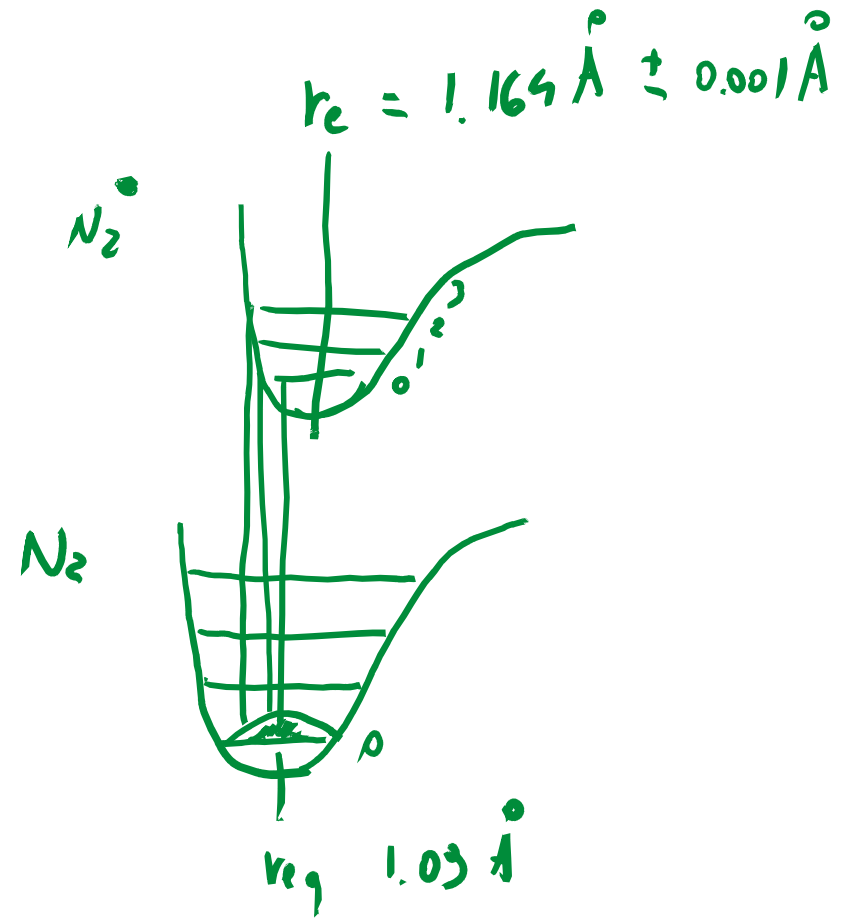
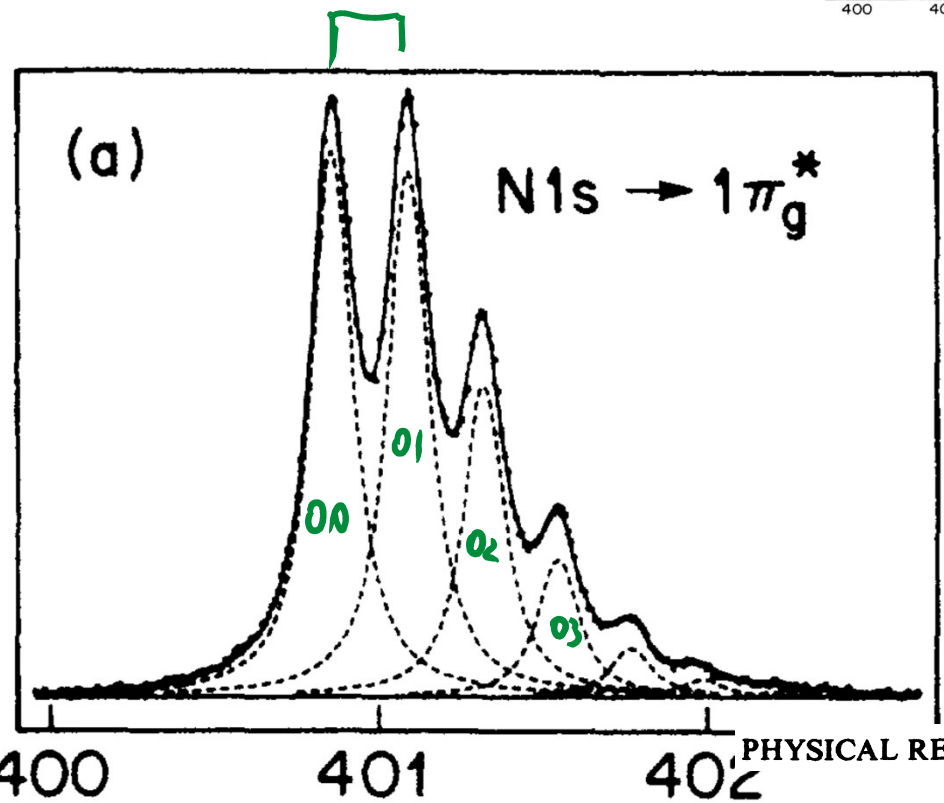
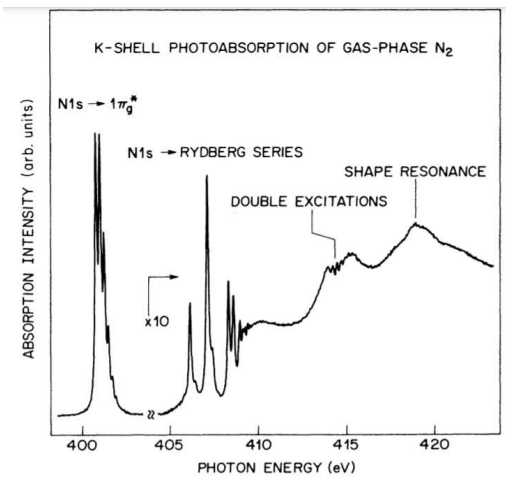


PHYSICAL REVIEW A (1999) 59, 3

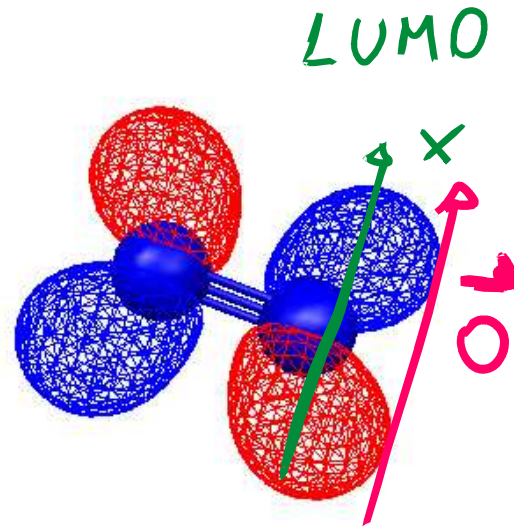
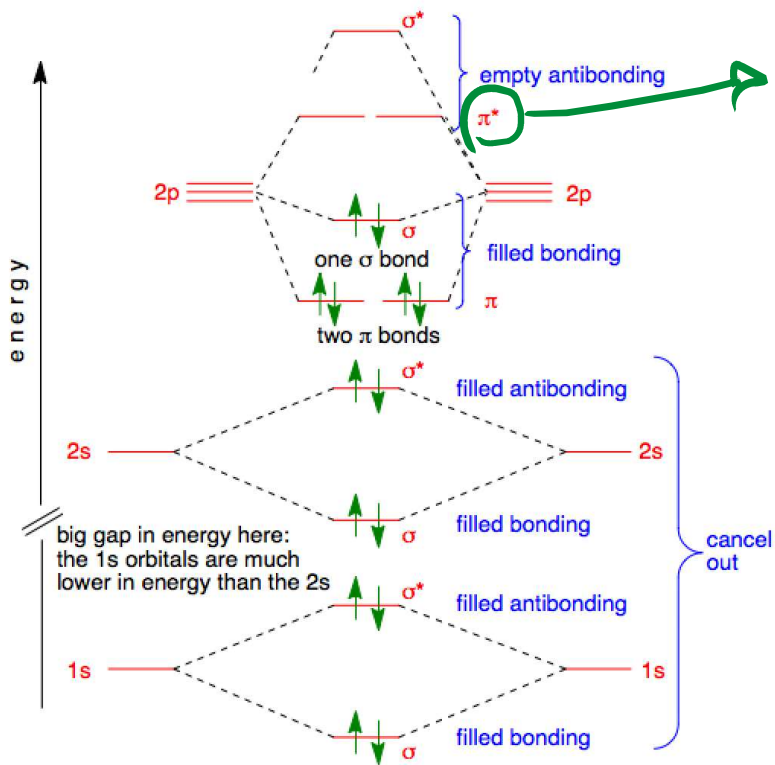
# Molecola di N<sub>2</sub>







# Dicroismo



$$I \propto |\langle f | \hat{e} \cdot \vec{r} | i \rangle|^2$$

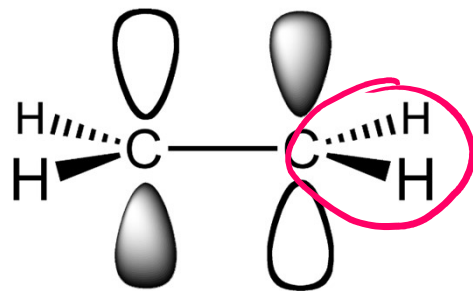
$$\propto |\hat{e} \cdot \langle f | \vec{r} | i \rangle|^2$$

Se  $|i\rangle = 1s$

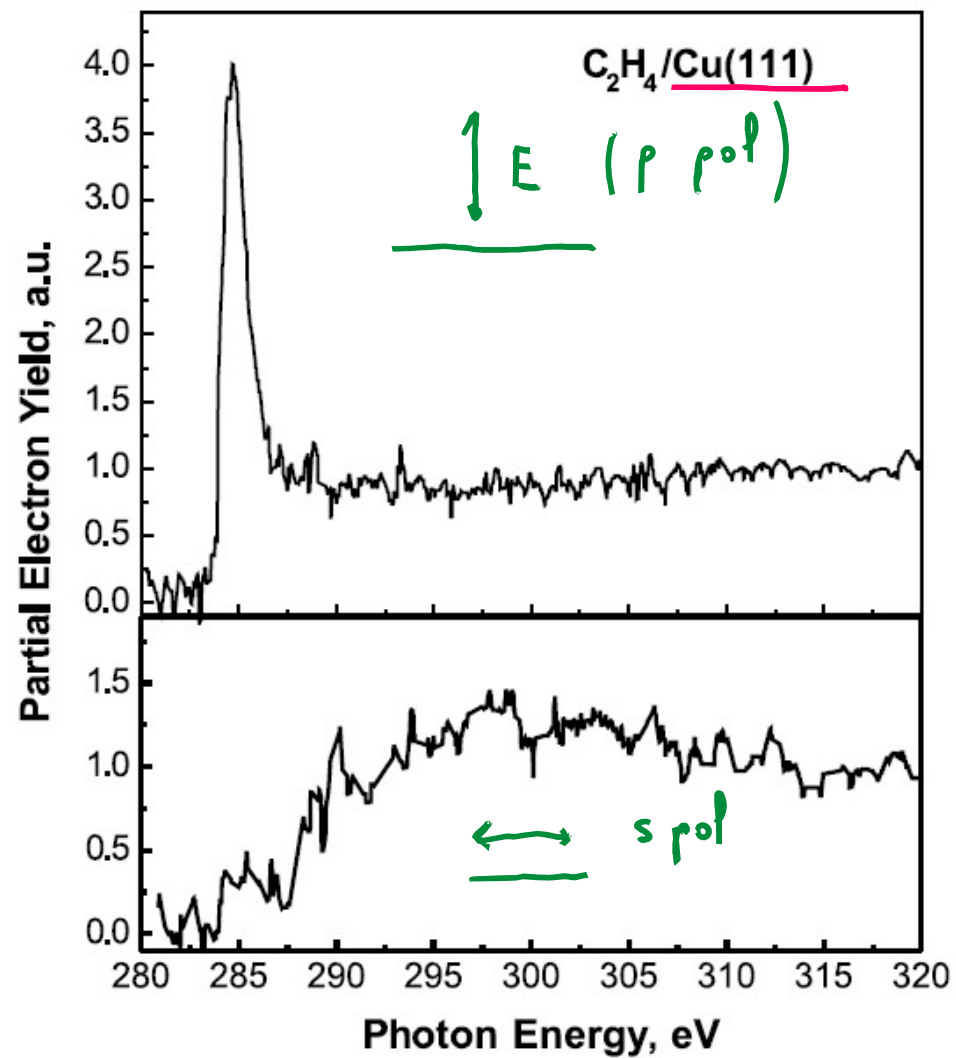
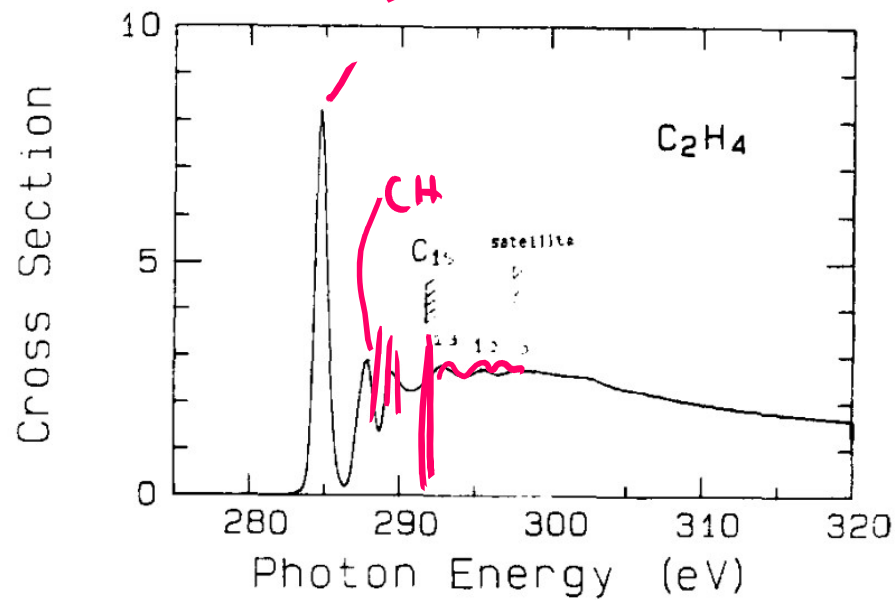
$$\propto |\hat{e} \cdot \vec{0}|^2 \propto \cos^2 \theta$$

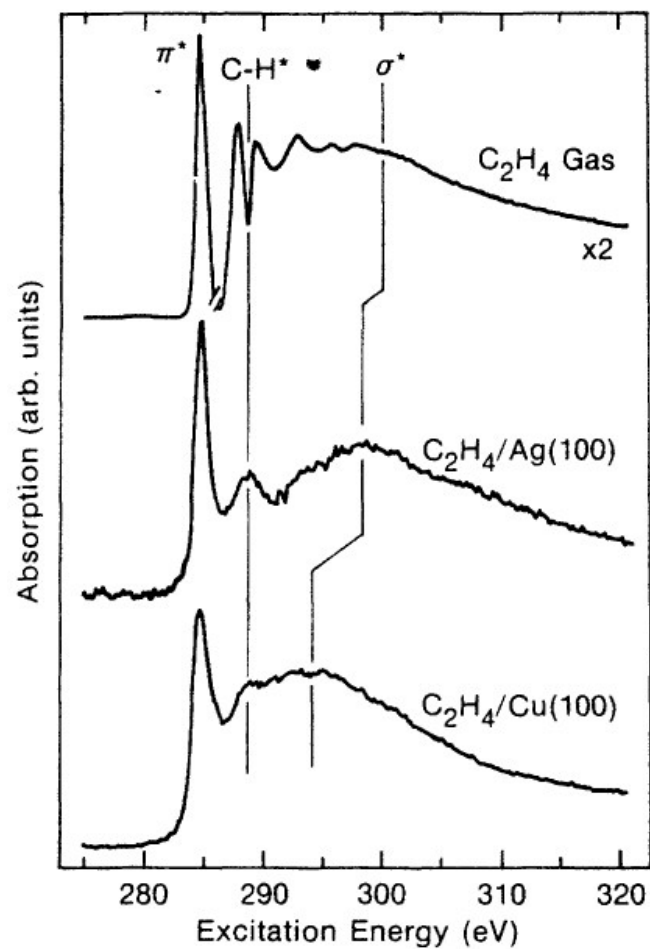
→ si dimostra che ha la simmetria di  $\langle f |$

# Ethylene

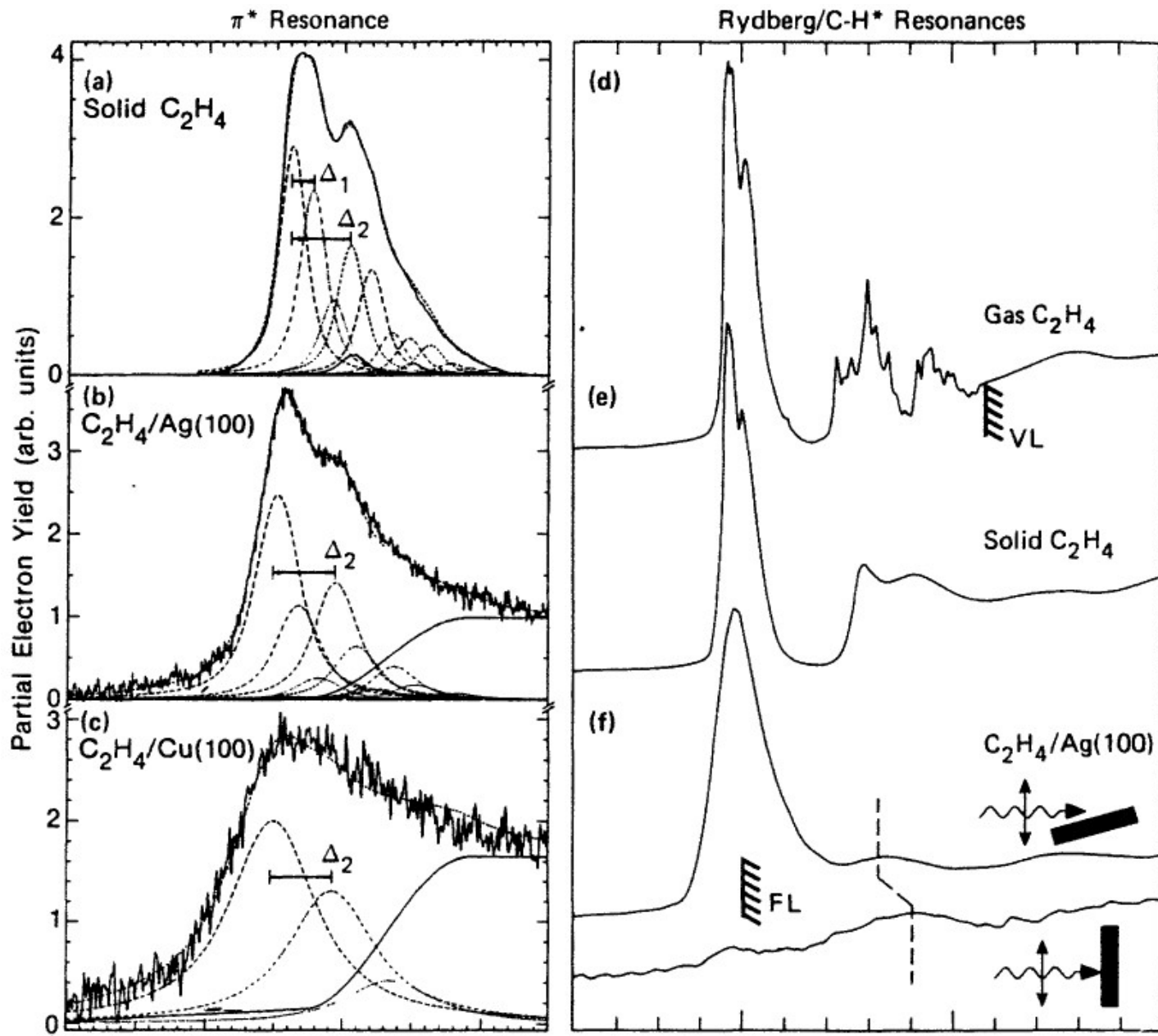


$1s \rightarrow \pi^*$

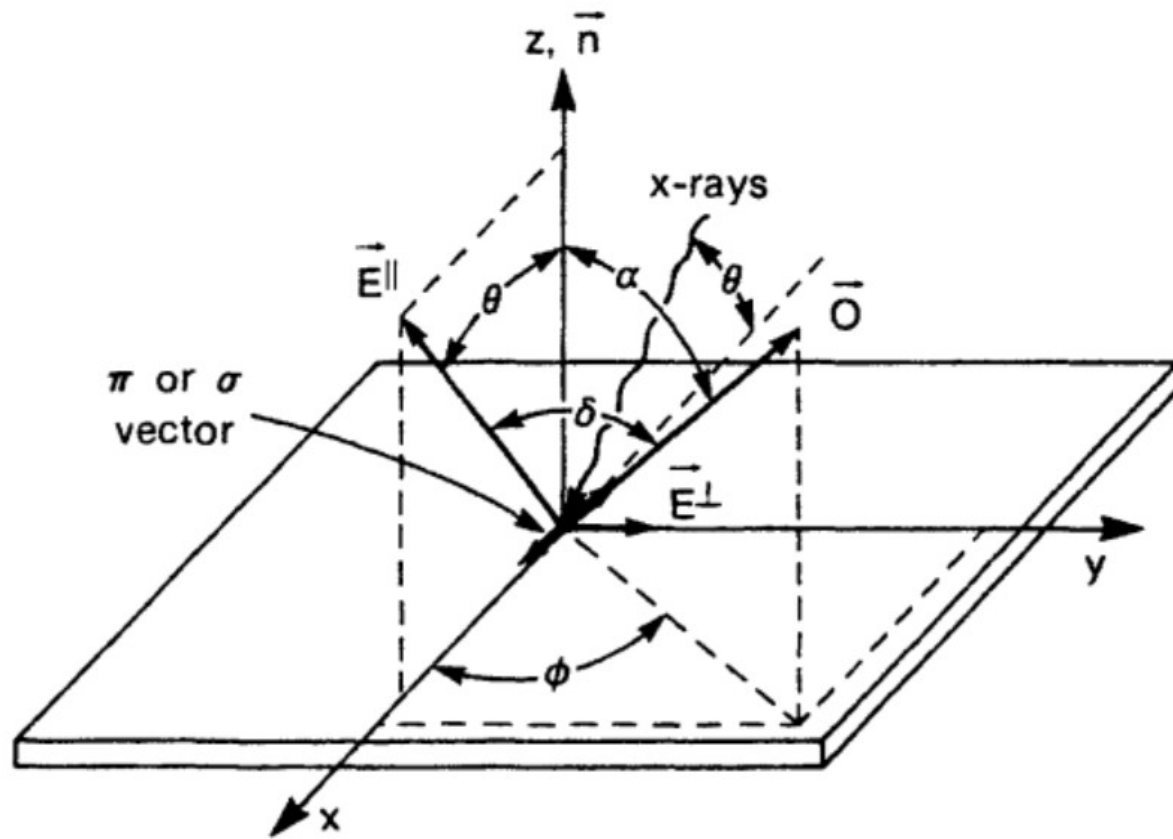




**Fig. 6.2.** K-shell excitation spectra of ethylene ( $C_2H_4$ ) in different environments: (a) free  $C_2H_4$  [6.17, 35], (b)  $C_2H_4$  weakly chemisorbed on Ag(100) at 60 K [6.36], (c)  $C_2H_4$  chemisorbed on Cu(100) at 60 K [6.36, 37]



## Dicroismo





CASO two-fob) es. superficie (110)

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

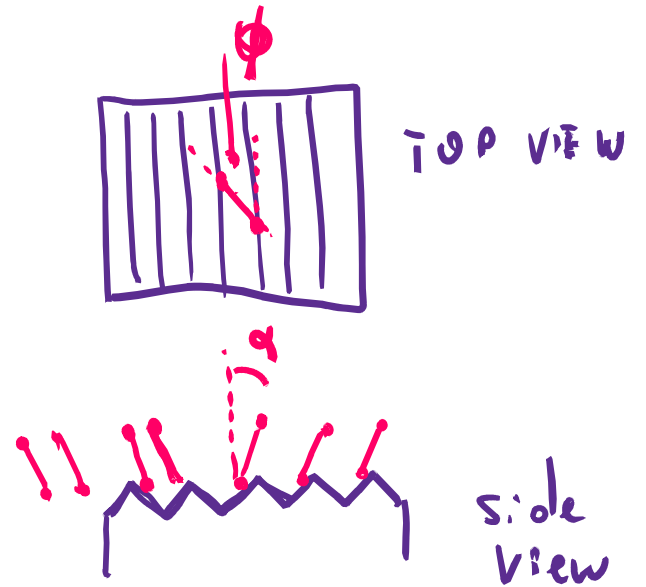
Se scegliamo  $\vec{E}$  in modo che  $\cos \phi = 1$

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

$$\rightarrow \text{se } \boxed{\theta = 45^\circ}$$

$\Rightarrow$  l'intensità diventa indipendente da  $\alpha$

magic angle





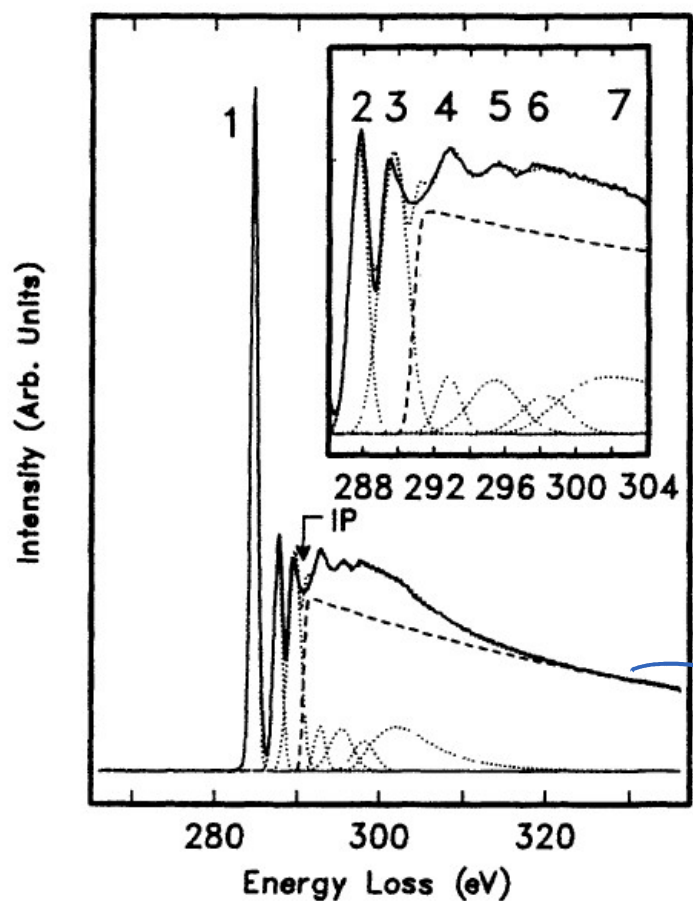
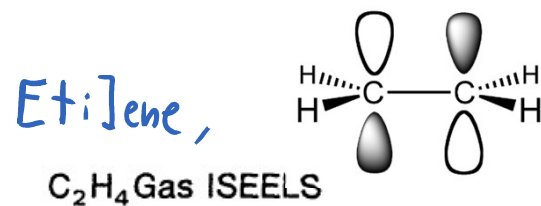
CASO three-fold  $\rightarrow$  (111) FCC

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

se  $\theta = \arctan(\sqrt{2}) = 54.7^\circ$   $\Rightarrow$  magic angle  
(3 fold  $\circ$  n-fold  
 $n \geq 3$ )

Gli step negli spettri NEXAFS : IP step

# IP step



1.  $1s \rightarrow \pi^*$  (LUMO)

2-3.  $1s \rightarrow C-H^*$ , Rydberg

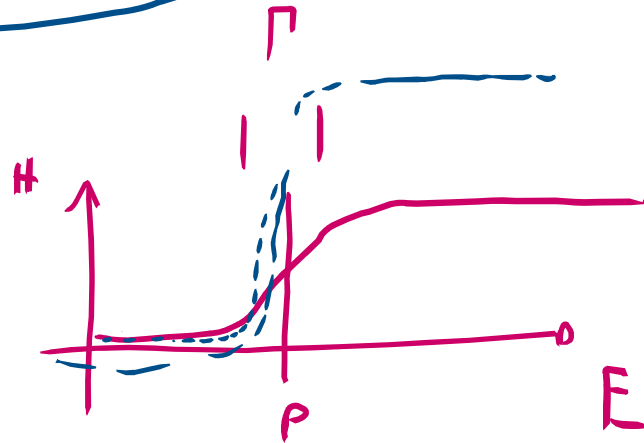
4-6 Multi-electron

7  $C=C \sigma^*$  resonance

decade exponentially

$$\bar{I}_{\text{stop}} = H \left( \frac{1}{2} + \frac{1}{\pi} \arctan \left( \frac{E-P}{\Gamma/2} \right) \right)$$

allegamento Lorentziano



$$I_{\text{step}_{\text{gaussiano}}} = H \left( \frac{1}{2} + \frac{1}{2} \operatorname{erf} \left( \frac{E-P}{\Gamma_G} \right) \right)$$

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$$

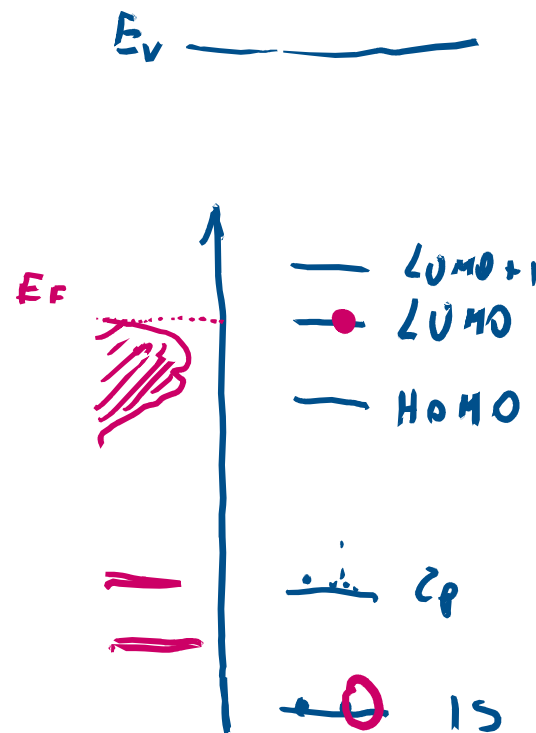
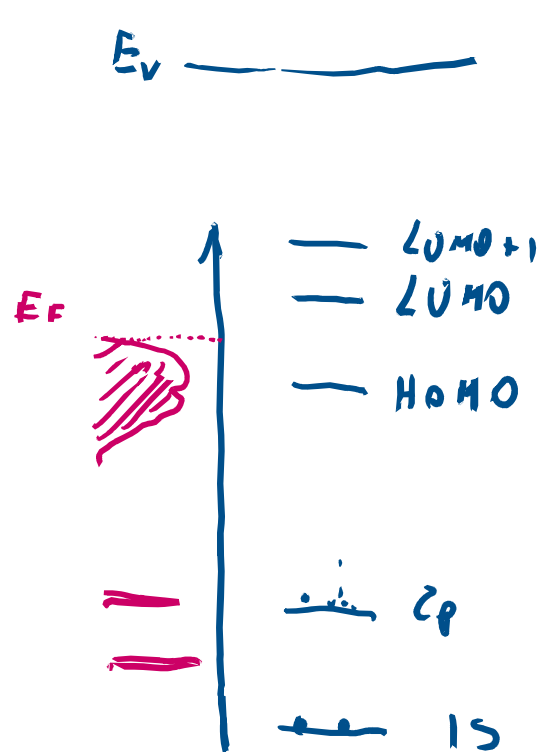
!!  $H$ , stessa dello step (IP step)

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

se  $|1\rangle$  è stato 1s

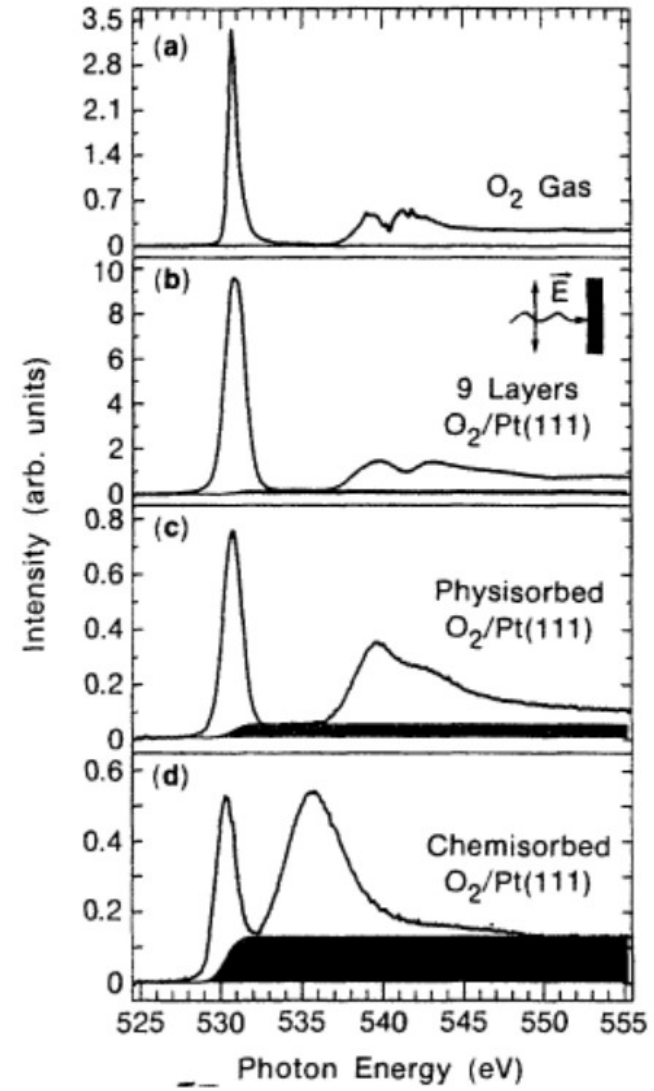
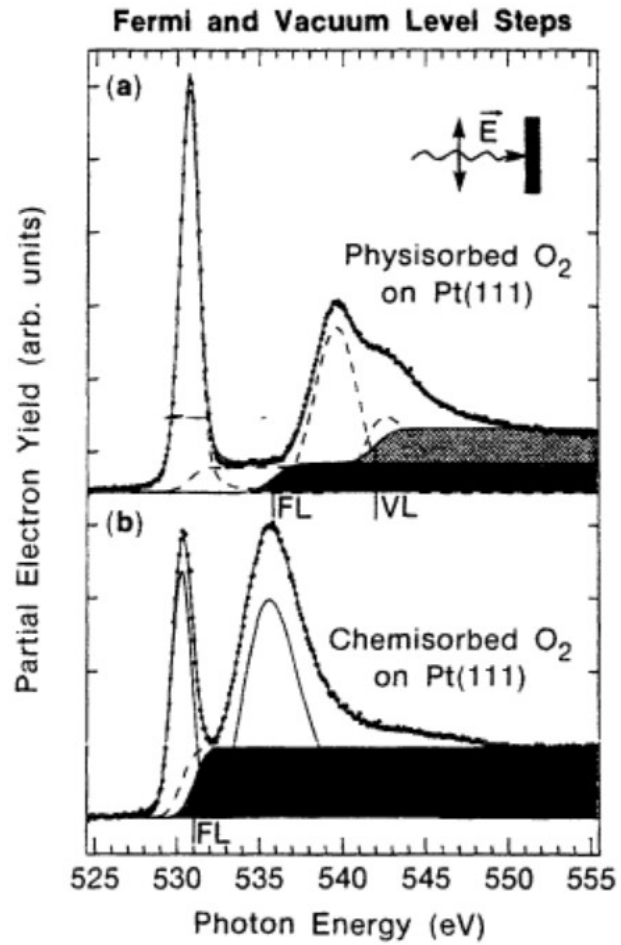
- Gli step negli spettri NEXAFS : Fermi step

## STATO FONDAMENTALE



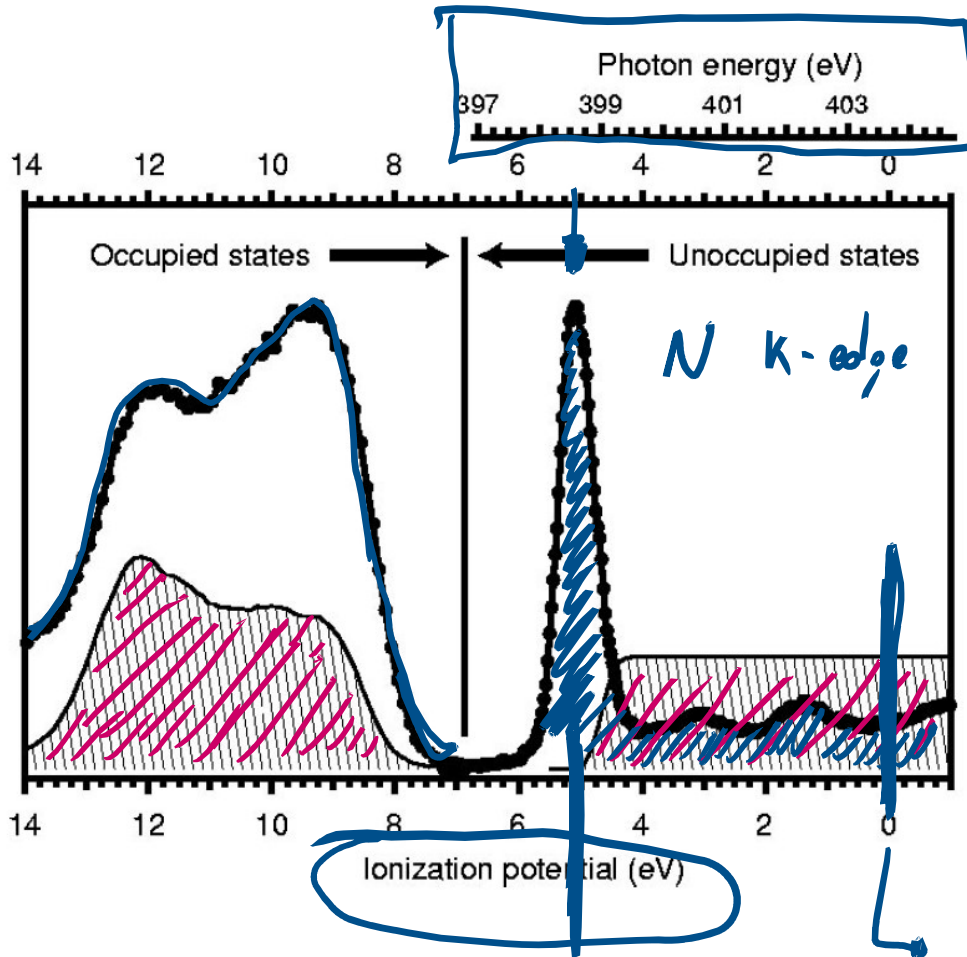
↓ i livelli "scendono" x effetto della buca 1s

# Fermi step

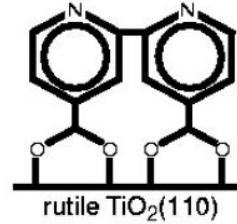


# Allineamento XPS-NEXAFS

*TiO<sub>2</sub> è semiconduttore*

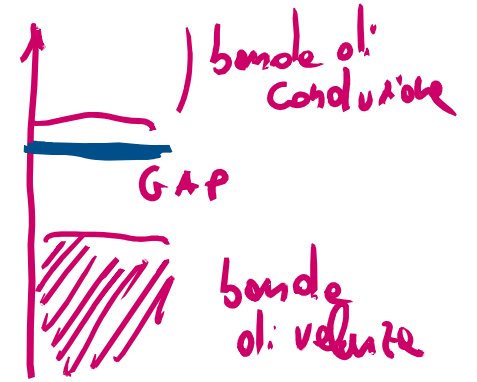


Bi-isonicotinic acid  
on rutile  
TiO<sub>2</sub>(110)

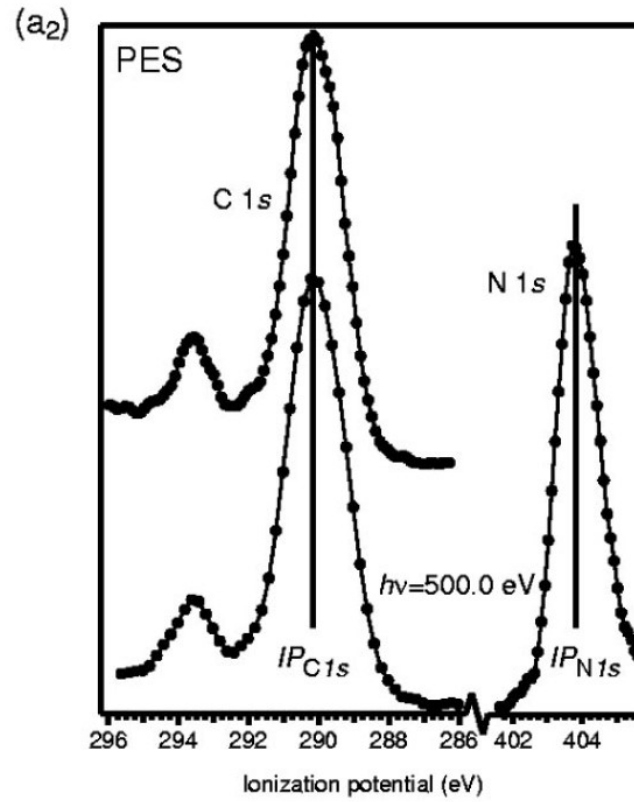
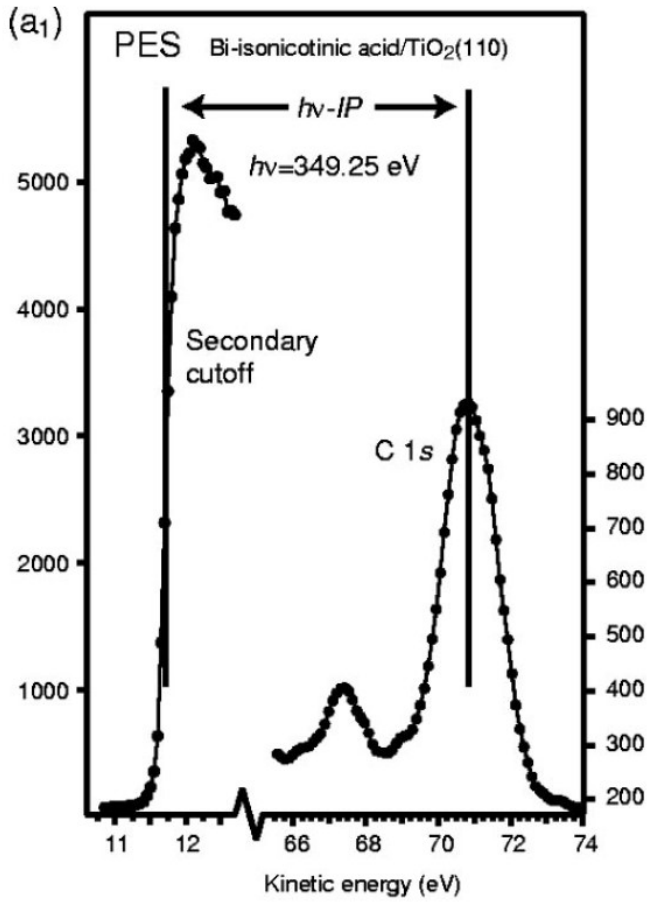


Monolayer:  
 ● PES (occ. states)  
 ● XAS (unocc. states)

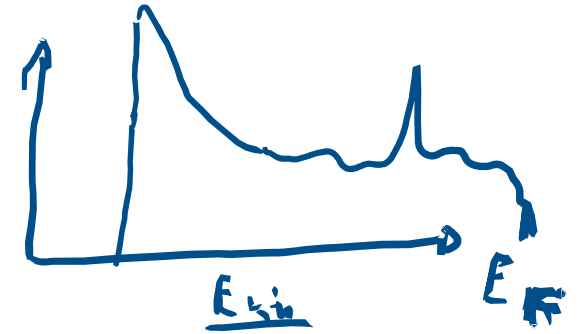
TiO<sub>2</sub> substrate:  
 ▨ PES  
 (valence band),  
 estimate  
 (conduction  
 band)





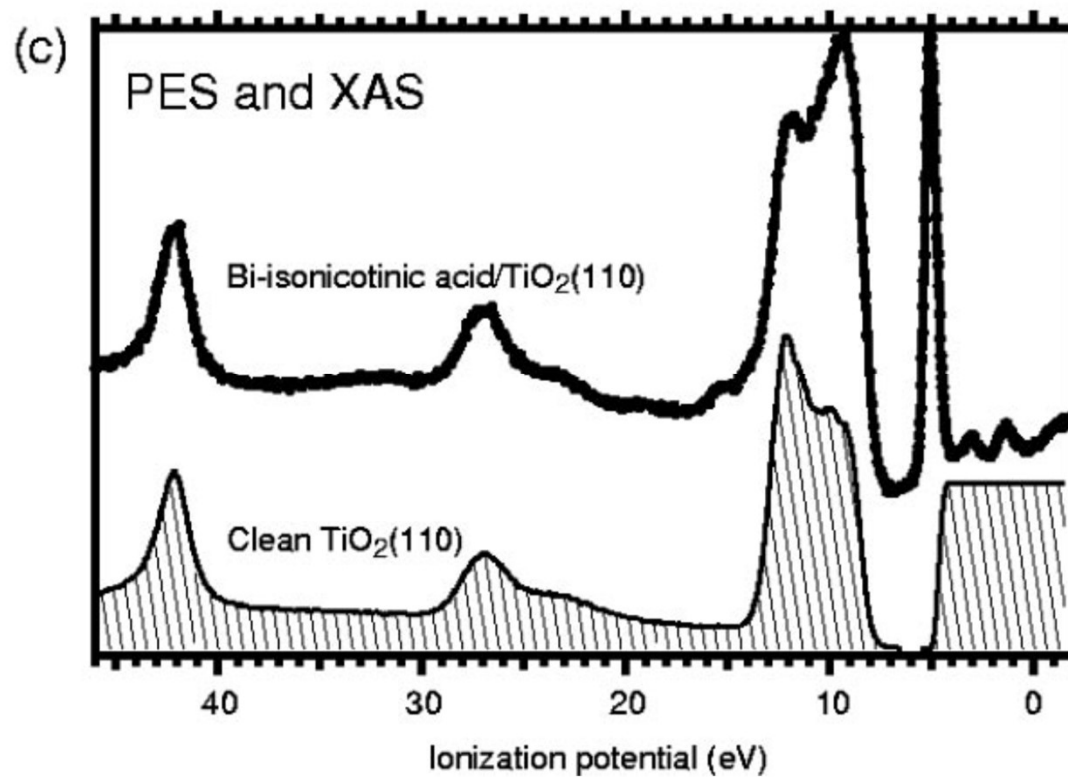
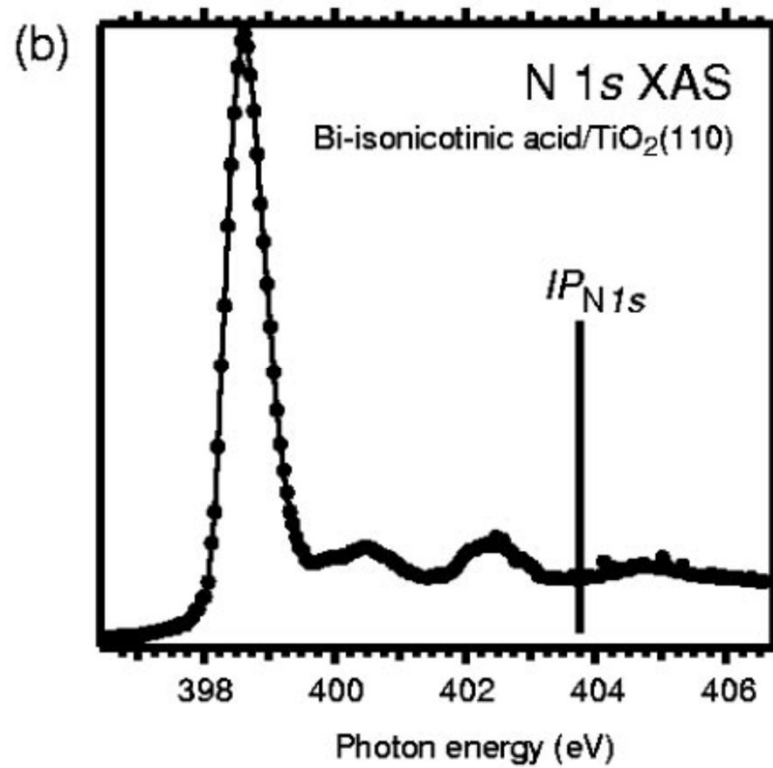


Misure della WF

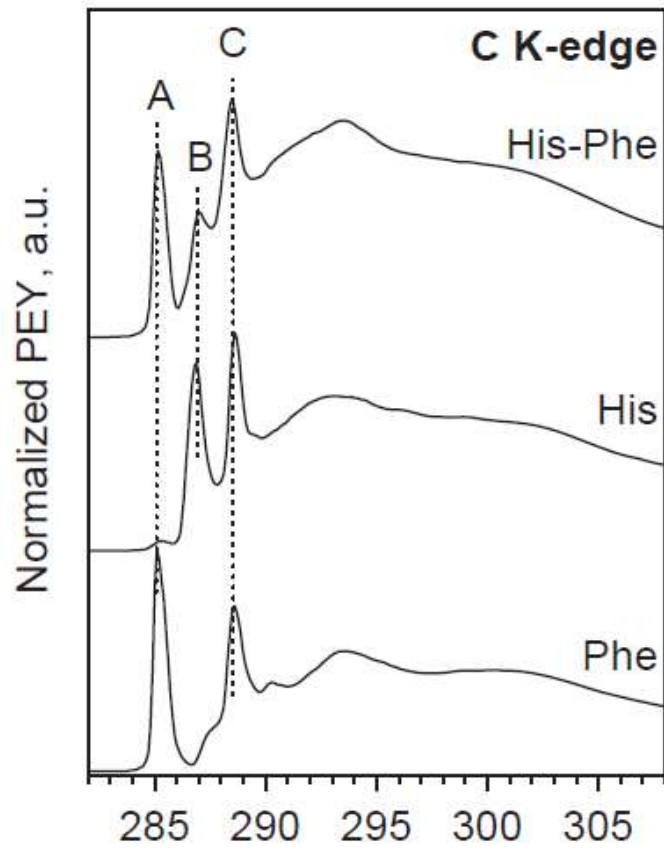
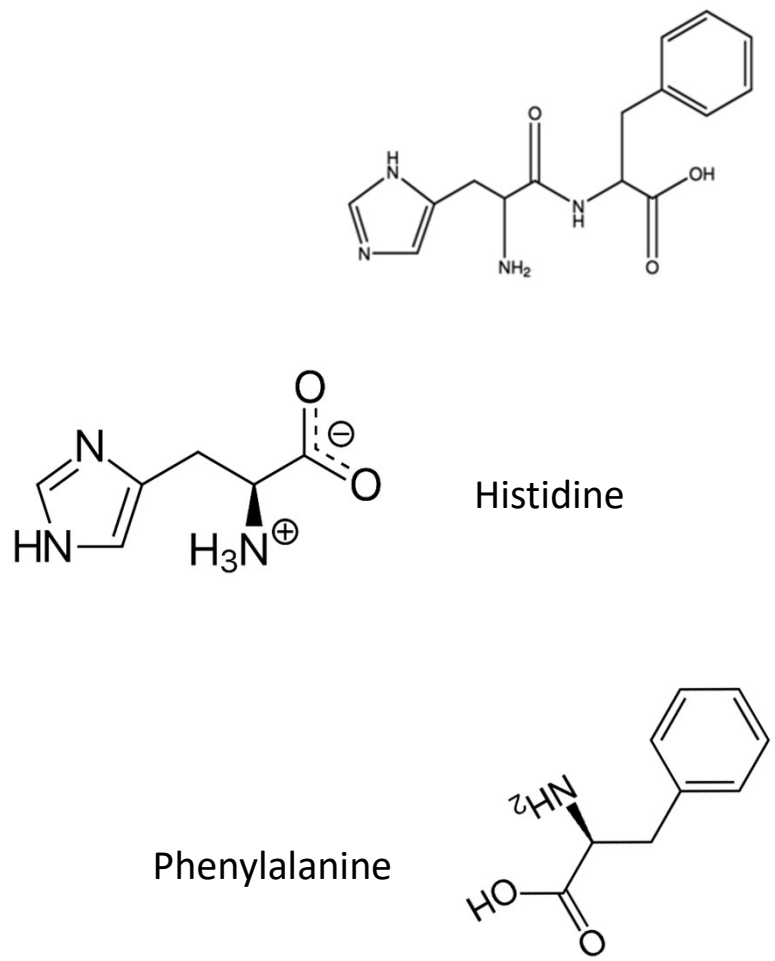


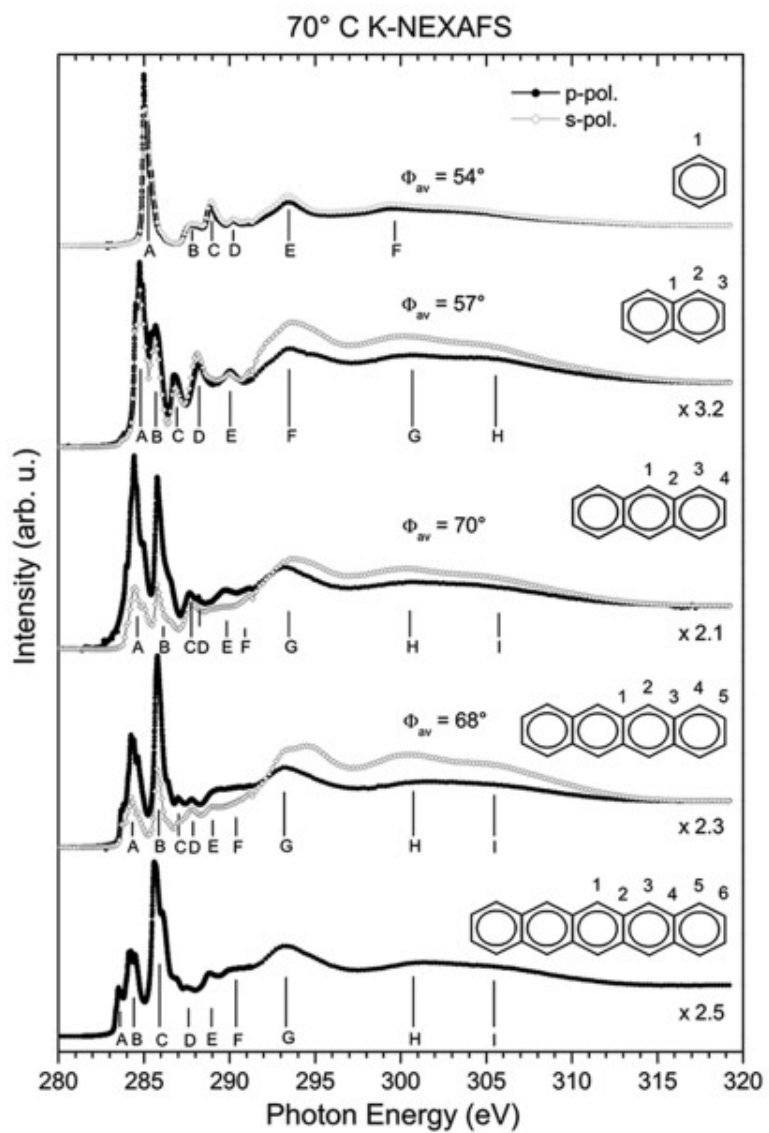
$$= h\nu - WF$$

WF è IP di e<sup>-</sup> all' livello di Fermi



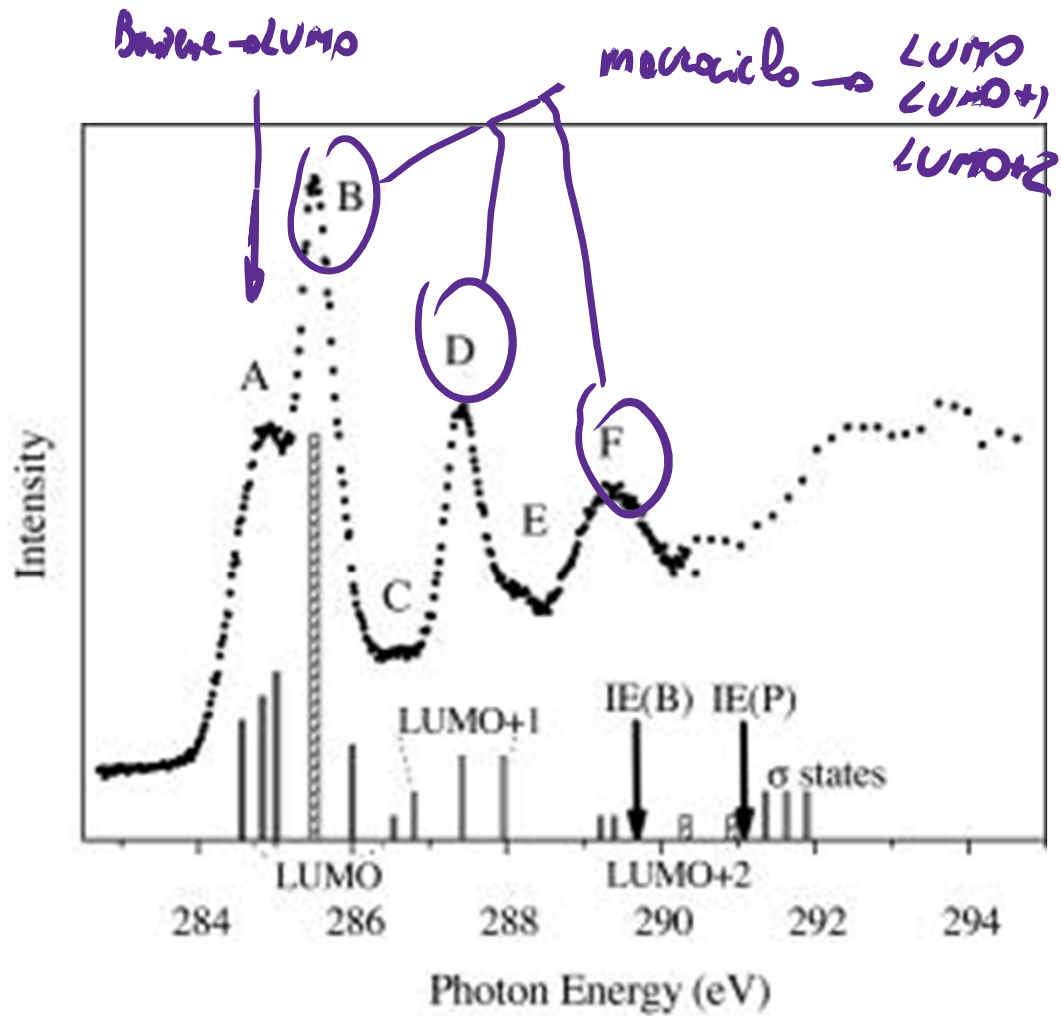
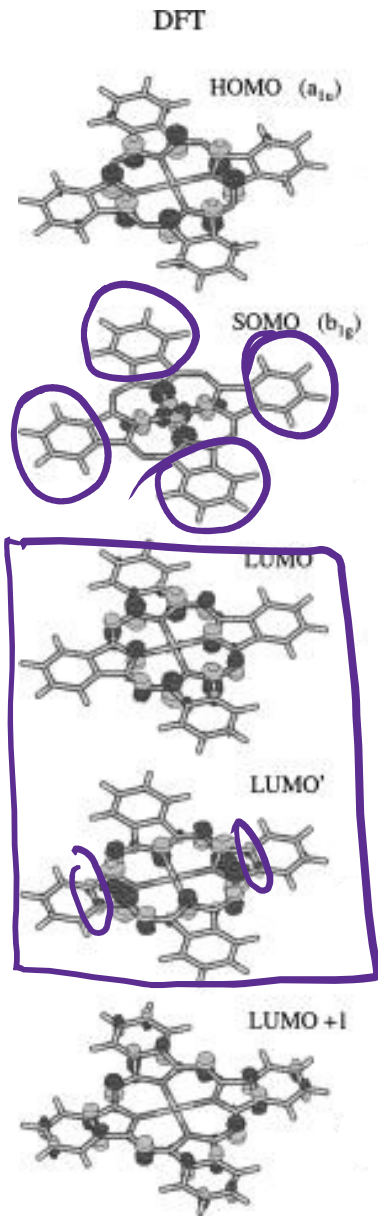
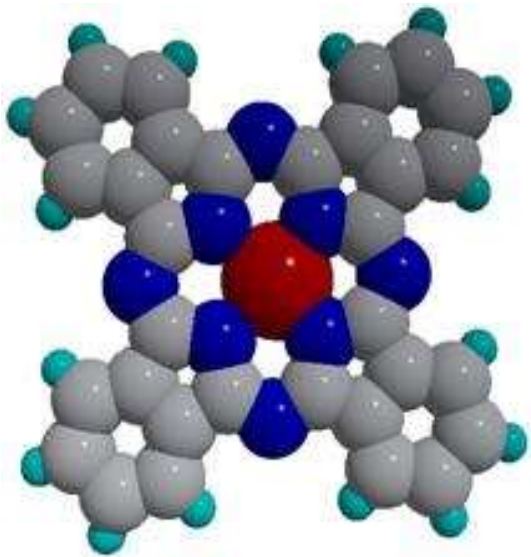
Approccio *building blocks* nell'interpretazione degli spettri



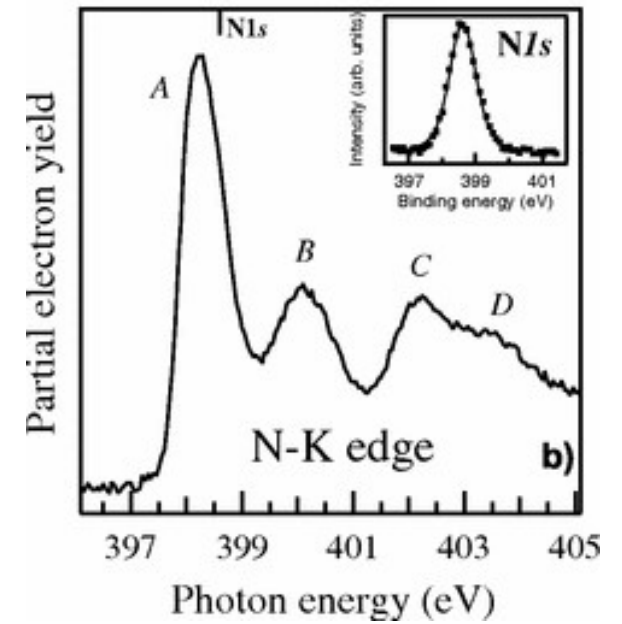
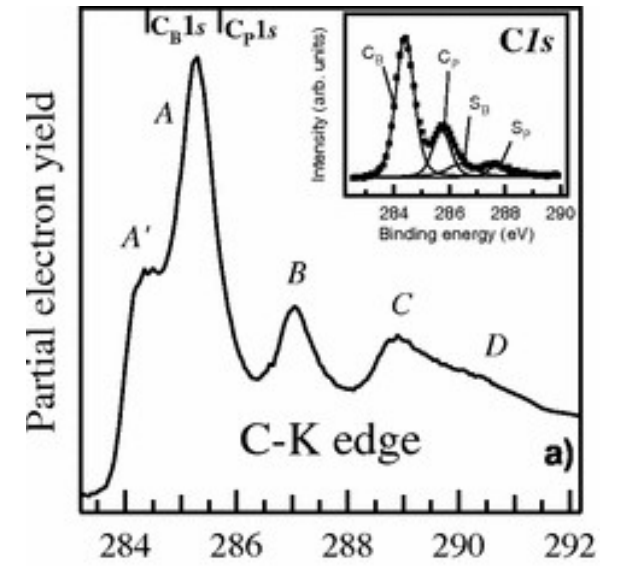
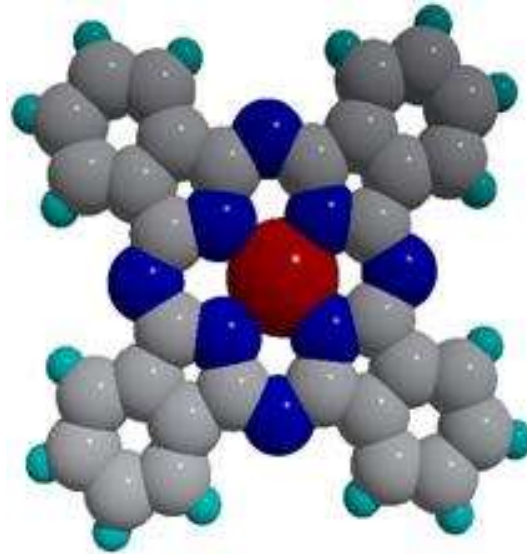
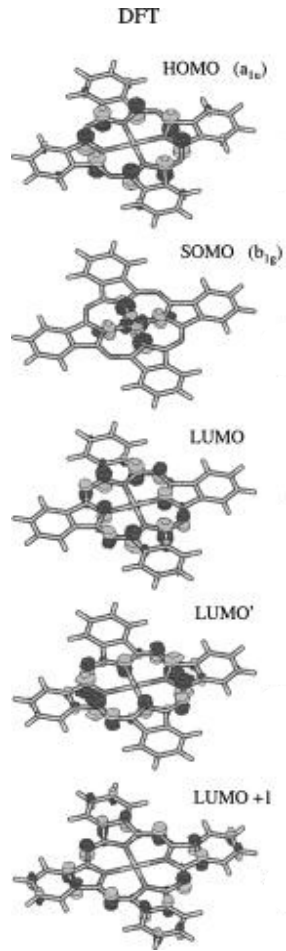


*J. Phys. Chem. C* 2018, 122, 28692–28701



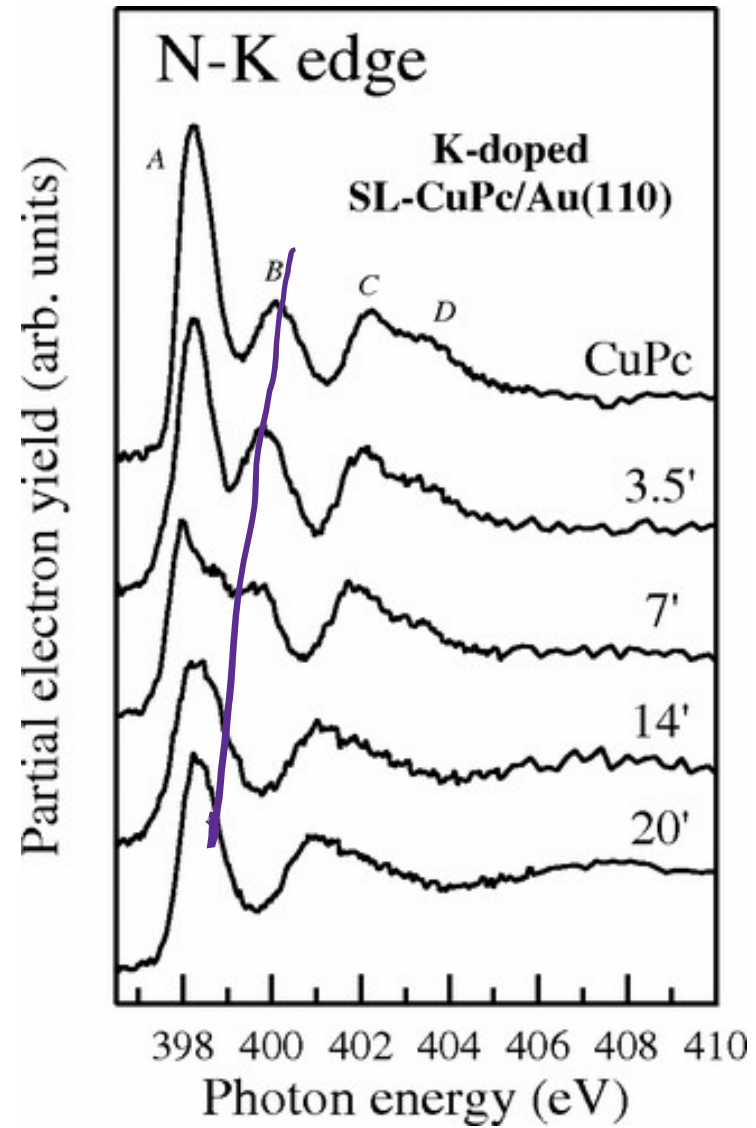
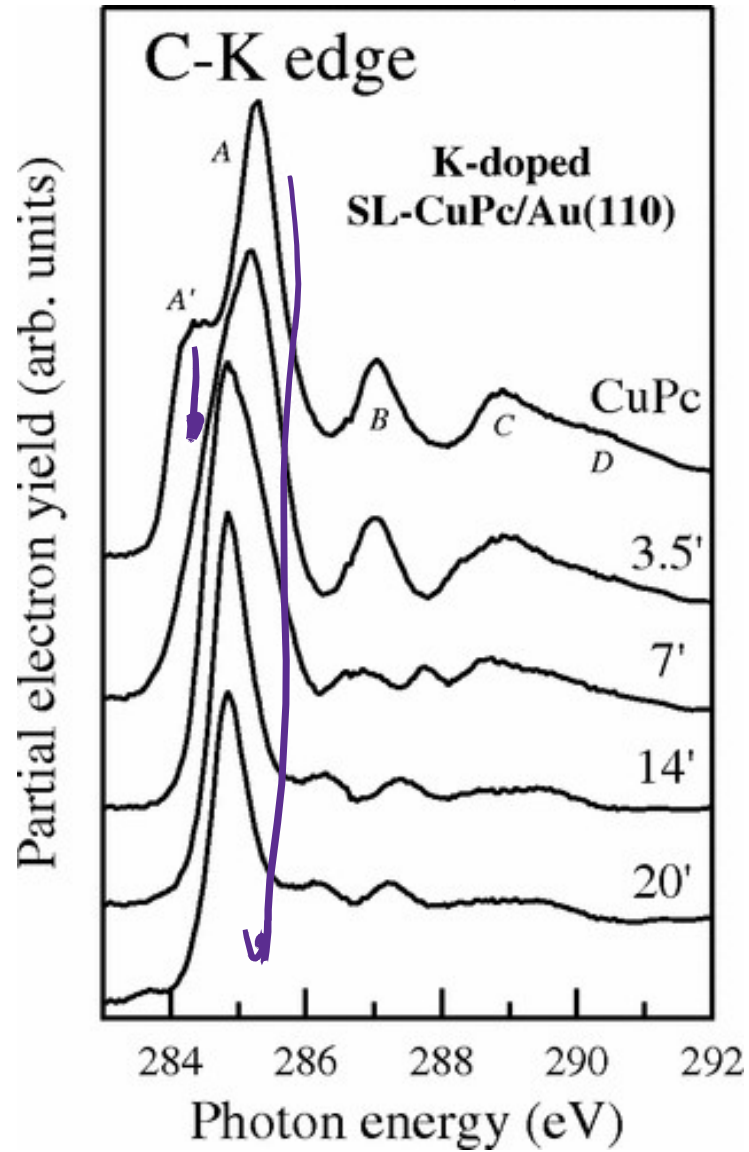


Filling empty states in a CuPc single layer on the Au(110) surface via electron injection

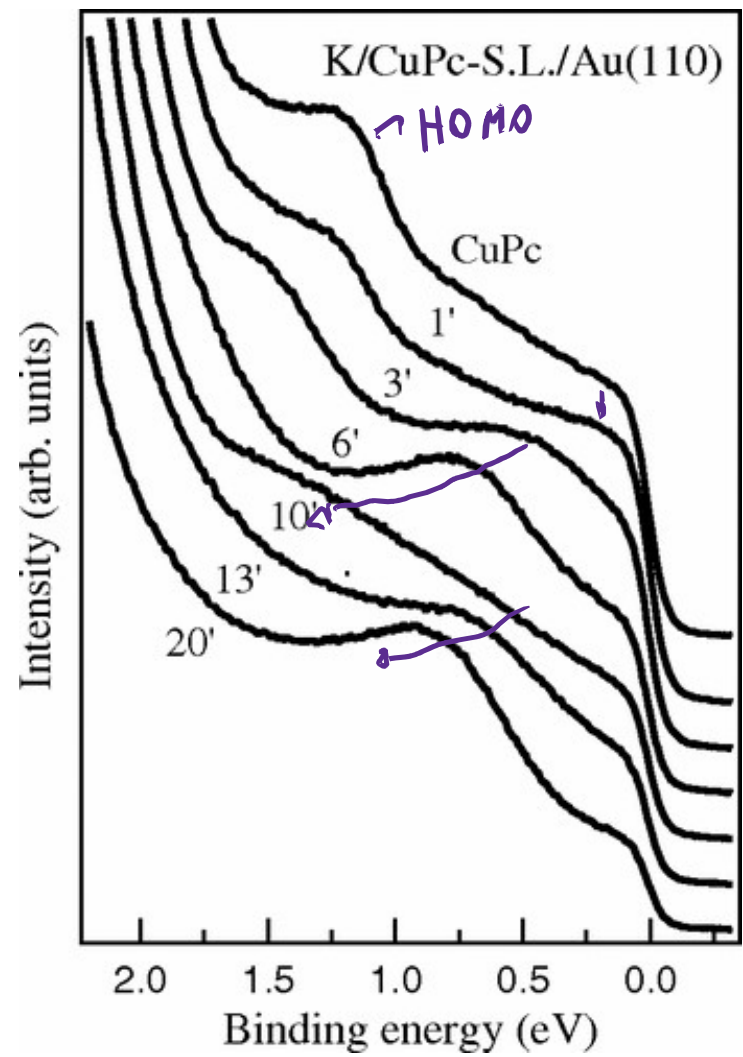




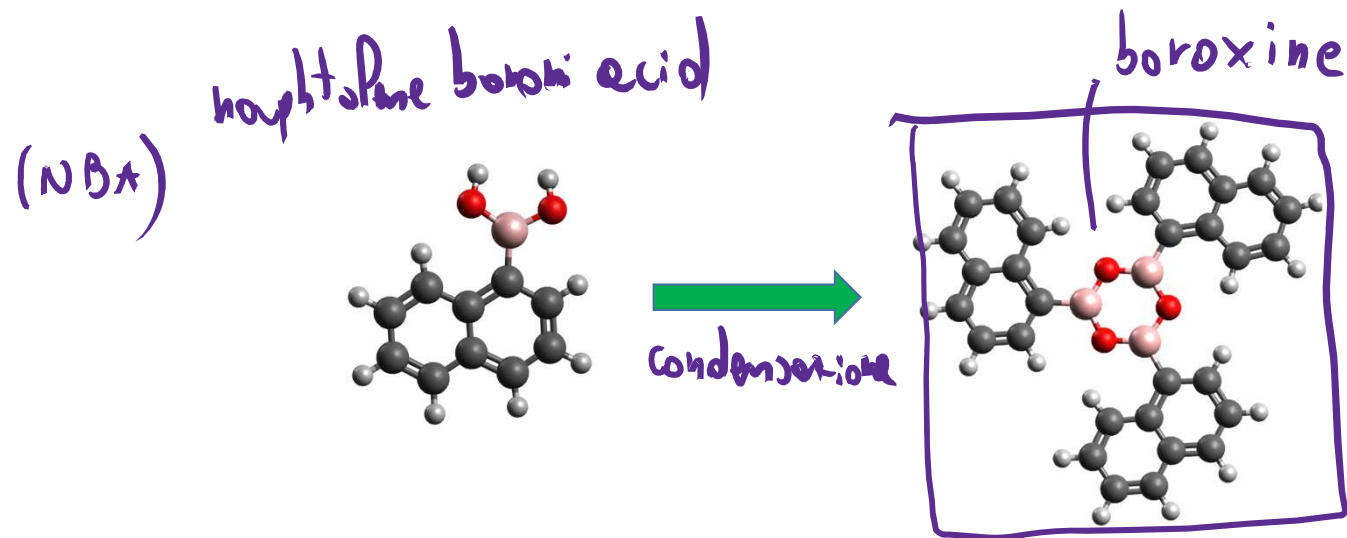
← il doping sposta i livelli



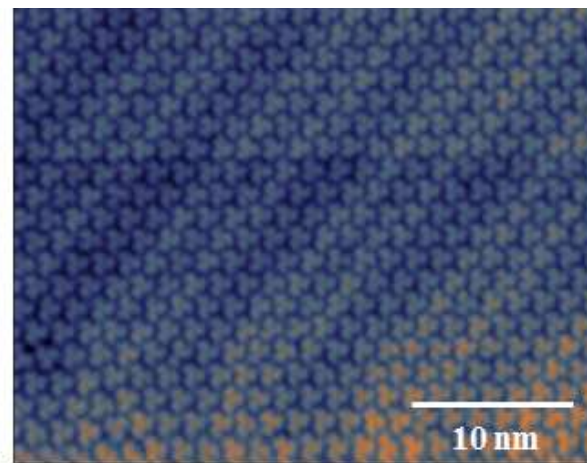
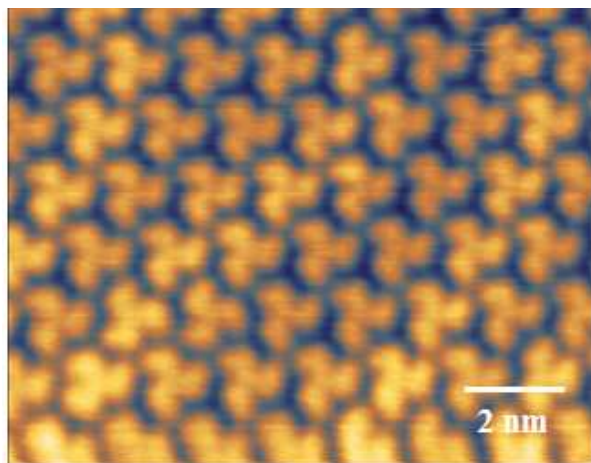




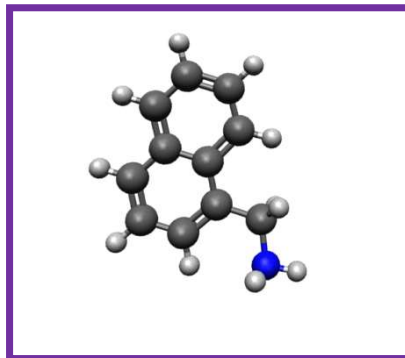
On-surface synthesis of larger molecules



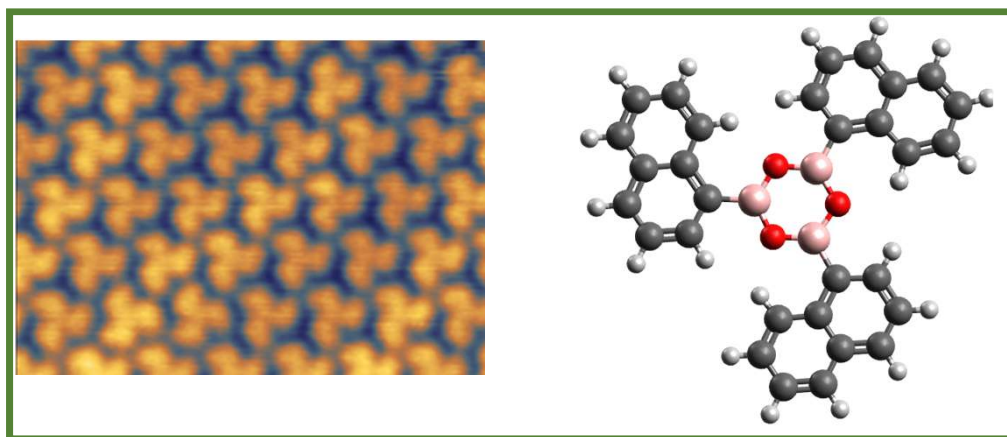
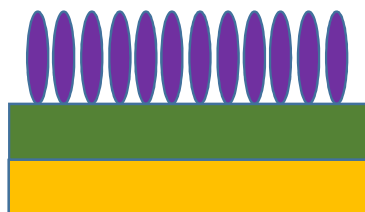
Au(111)



Anchoring platforms?

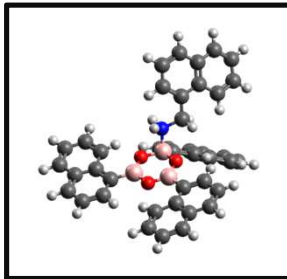
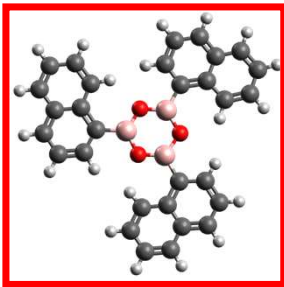


Naphtylmethylamine, NMA

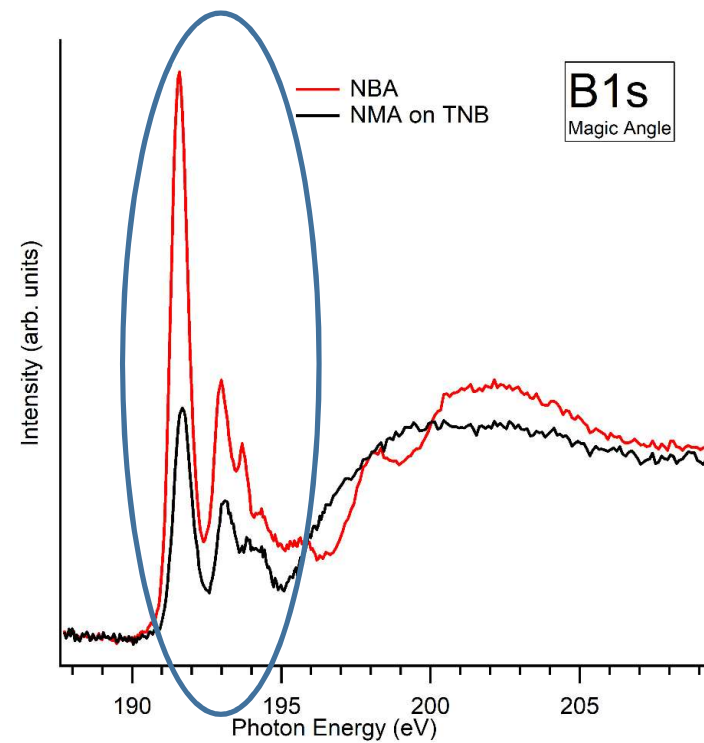
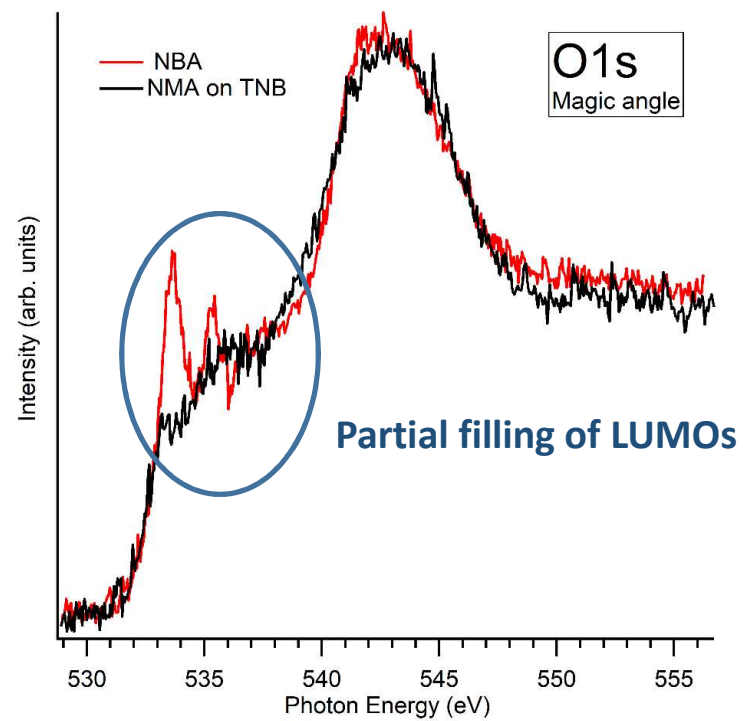


Is boroxine on Au(111) still a Lewis acid?

## Anchoring platforms?

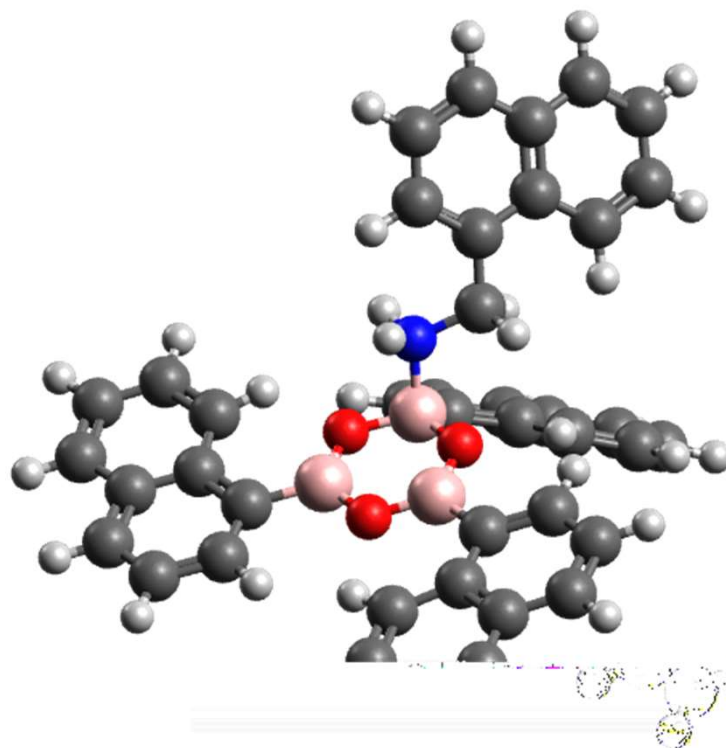


## amino-boroxine dative bond



## Anchoring platforms

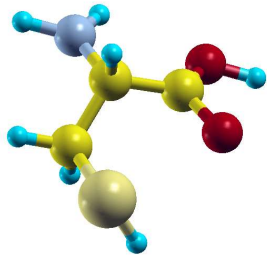
Next step:



Does the bonding promote ultra-fast charge delocalization?

## L-Cysteine adsorption on Au(110)

Simple amino acid  
Thiolate bond with substrates



### Au(110) surface

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

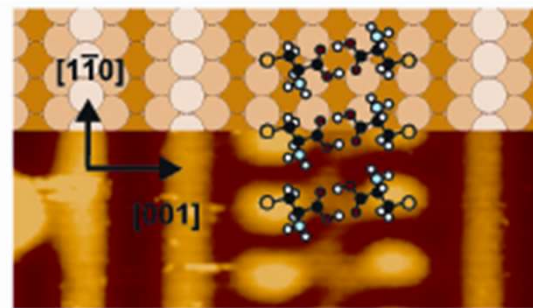
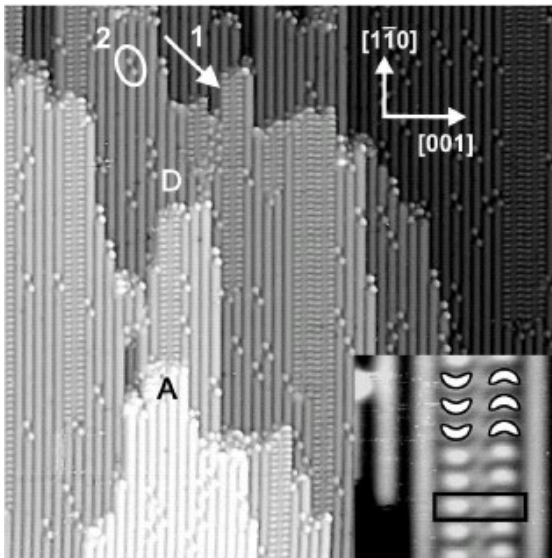
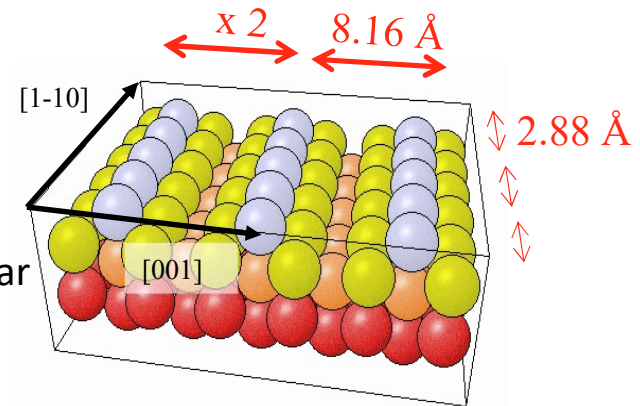
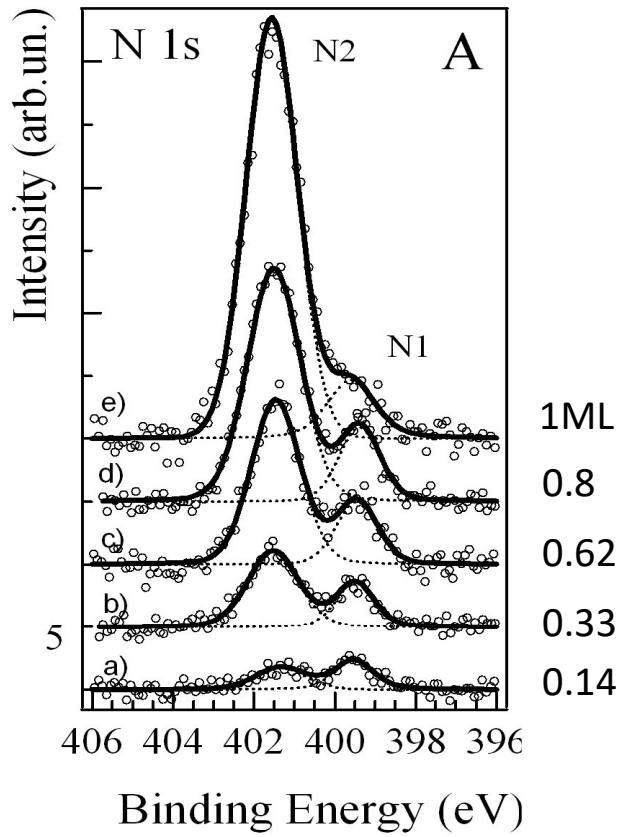


FIG. 3 (color). Most stable cysteine double-row structure, as obtained from the DFT calculations, superimposed onto an

*Kühnle et al. PRL 93 (2004) 86101*

### N1s: zwitterionic vs acidic population



$\text{NH}_2$  399.5 eV

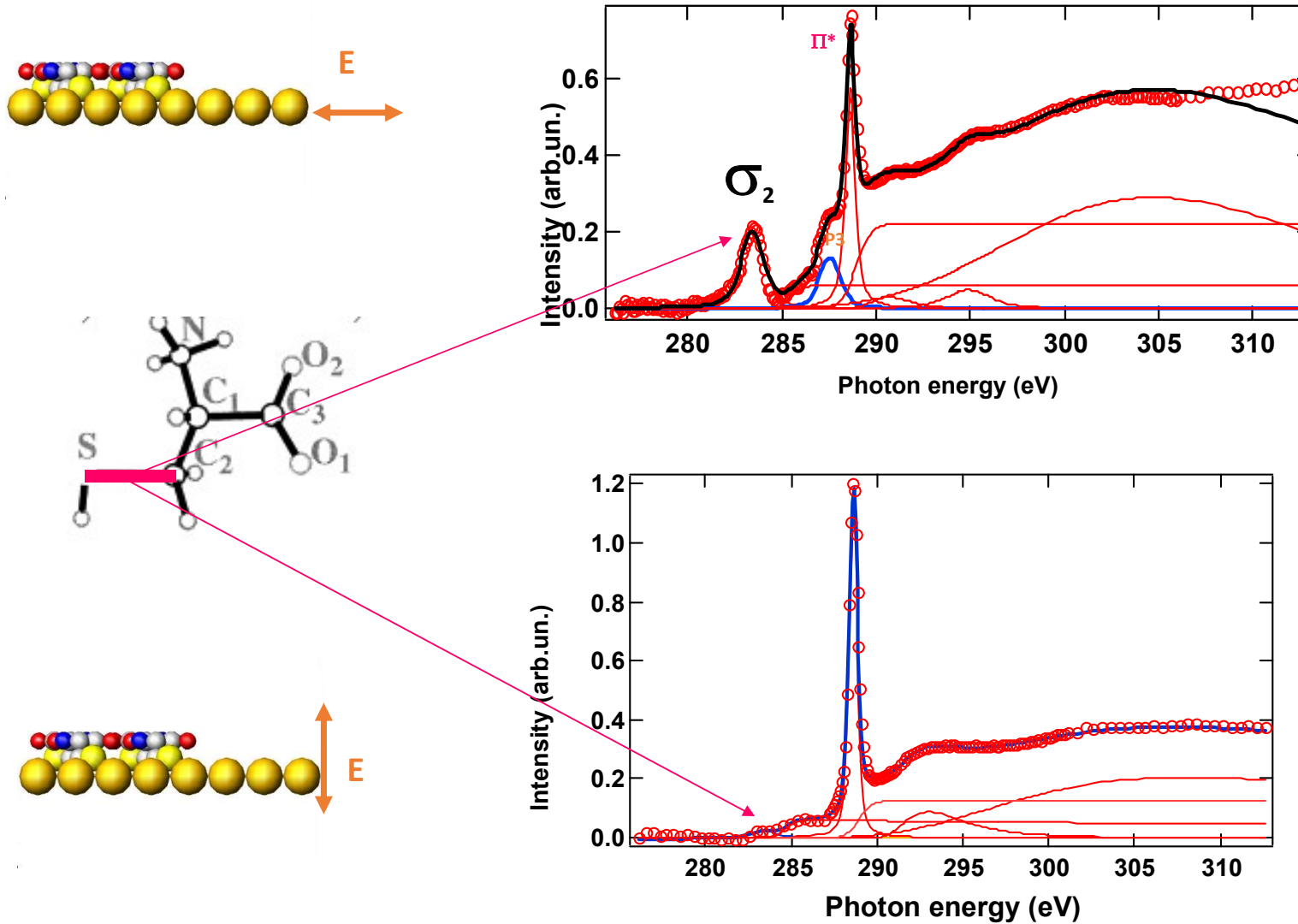
$\text{NH}_3^+$  401.5 eV

- Total acidic population established at  $\theta < 0.4$  ML

- majority of zwitterions for  $\theta > 0.2$  ML

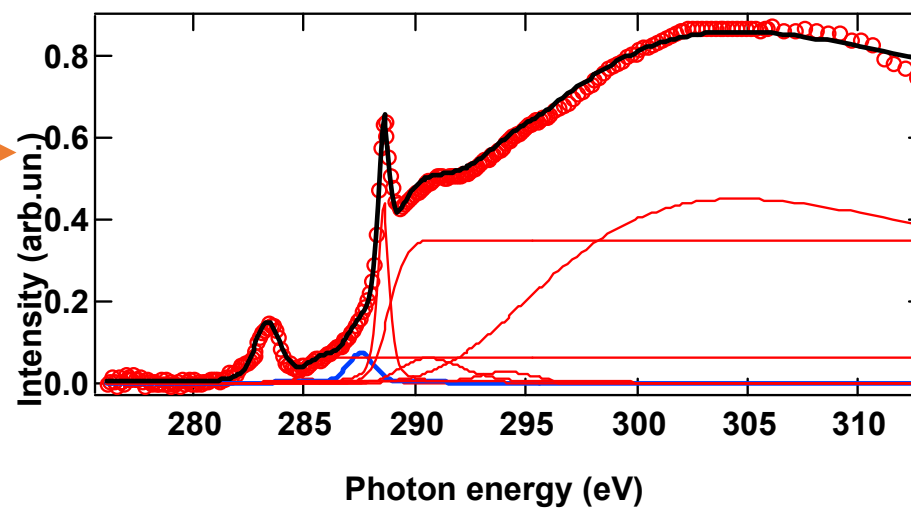
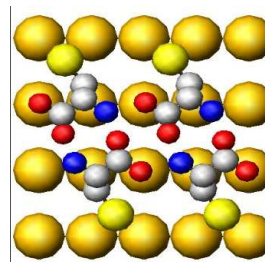
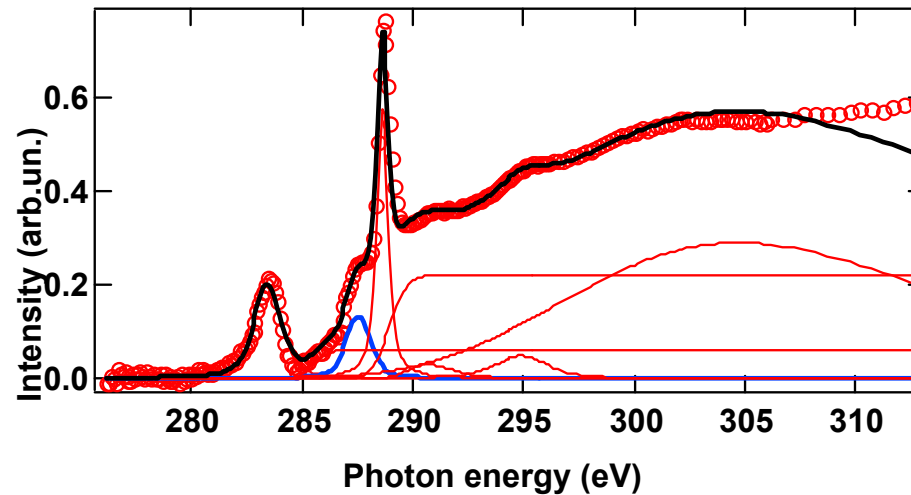
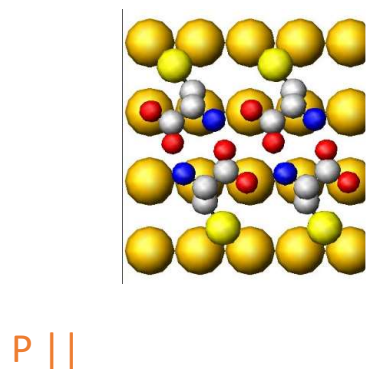


## C1s NEXAFS: molecular orientation from polarization dependence





## Variable polarization NEXAFS: azimuthal orientation



*Langmuir, 2006*