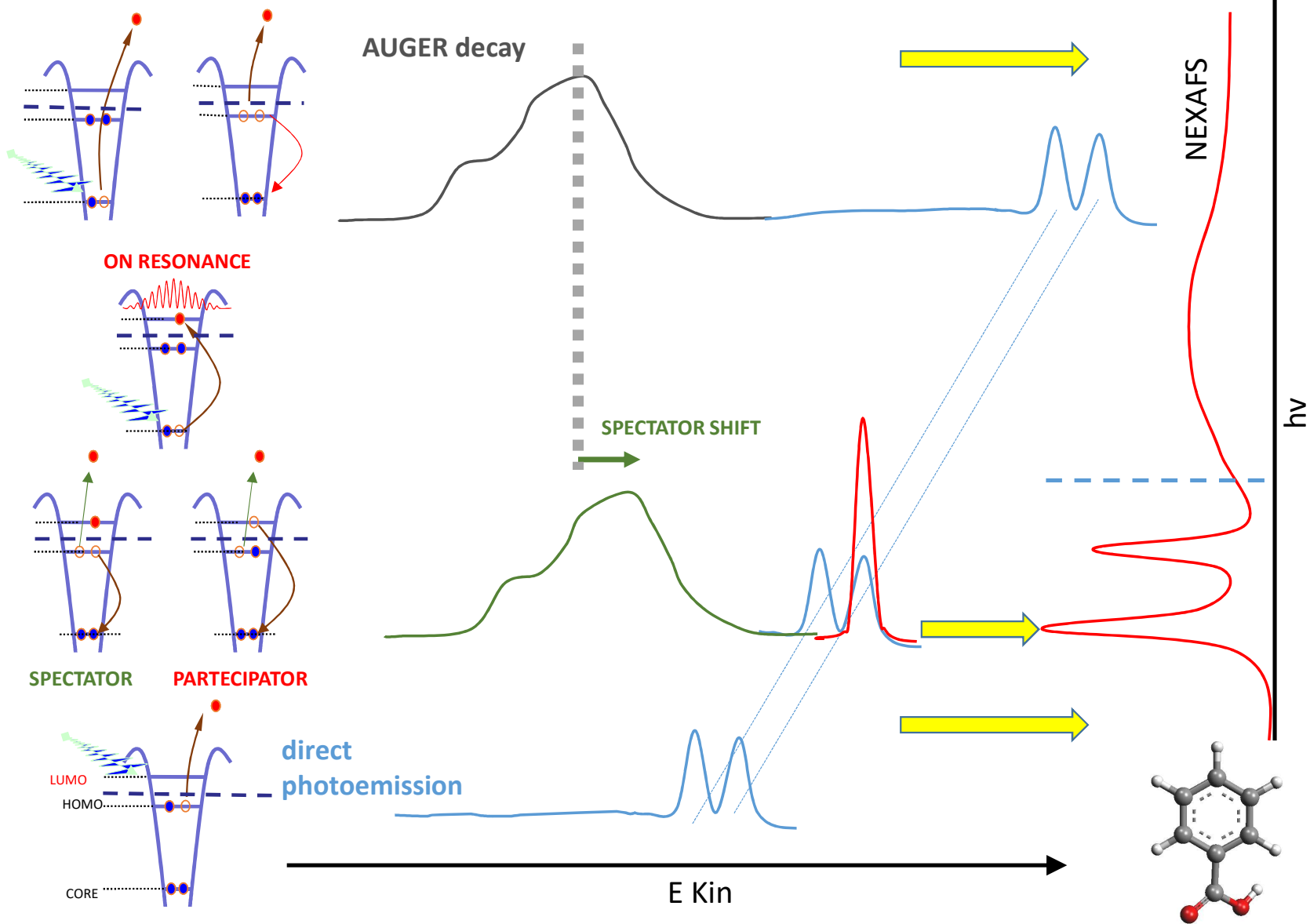
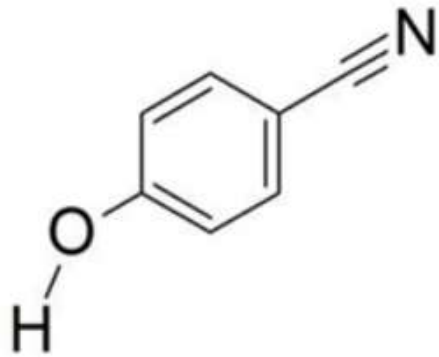


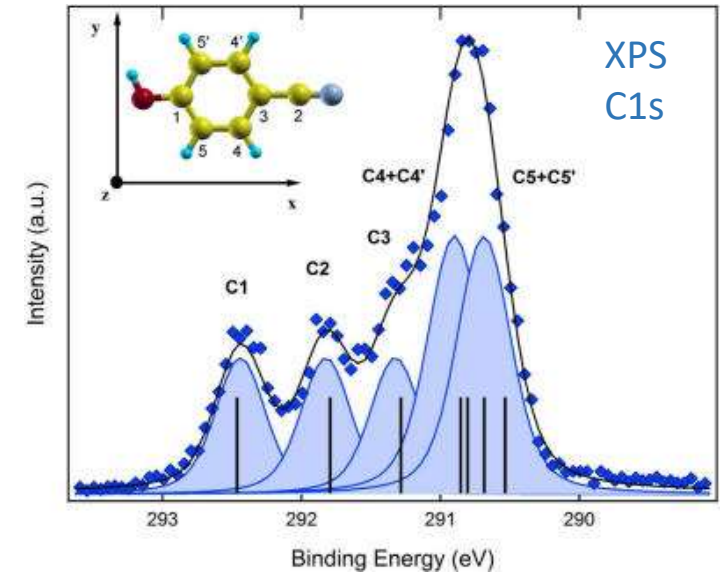
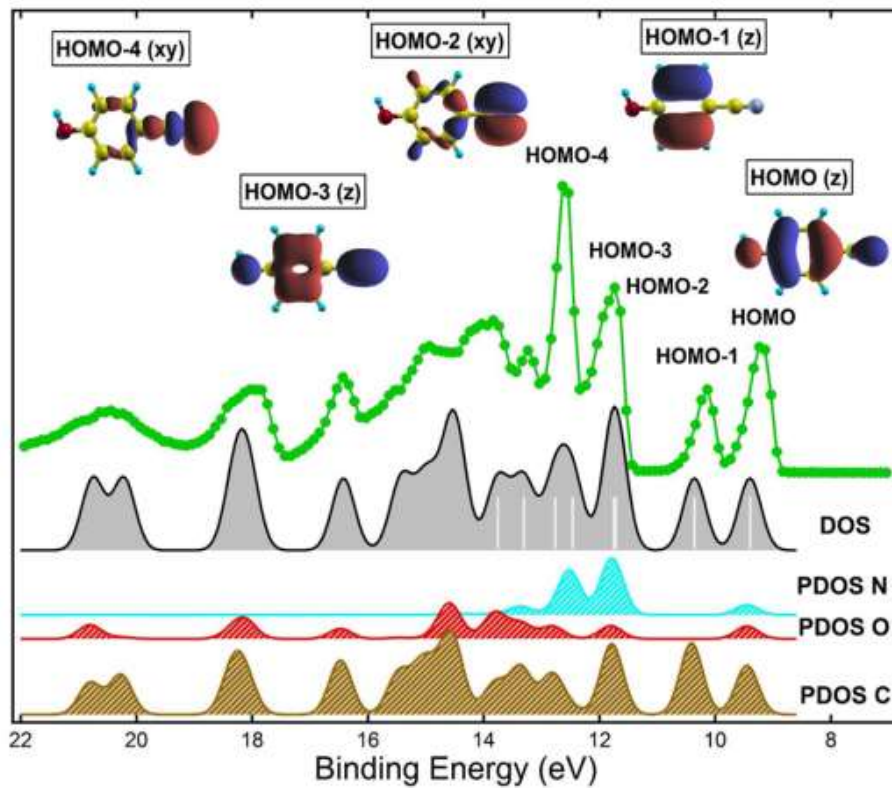
RESPES : Resonant photoemission Spectroscopy

Resonant photoemission spectroscopy

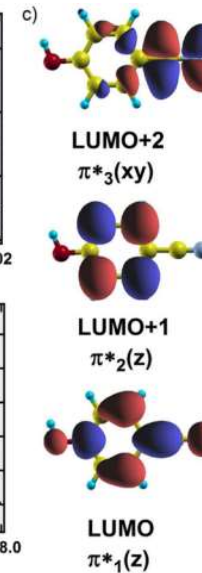
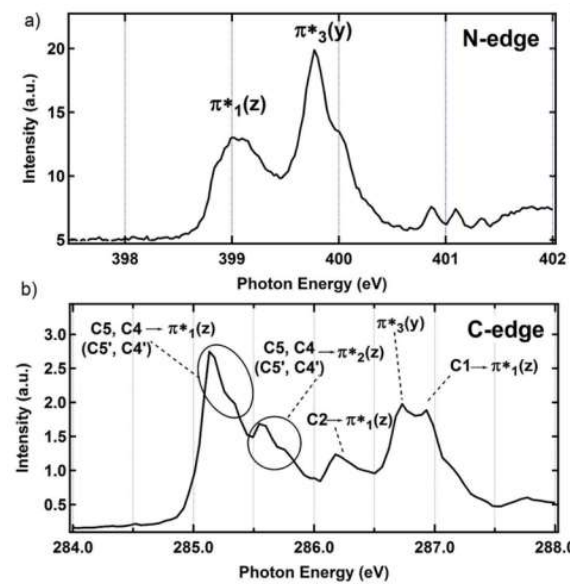


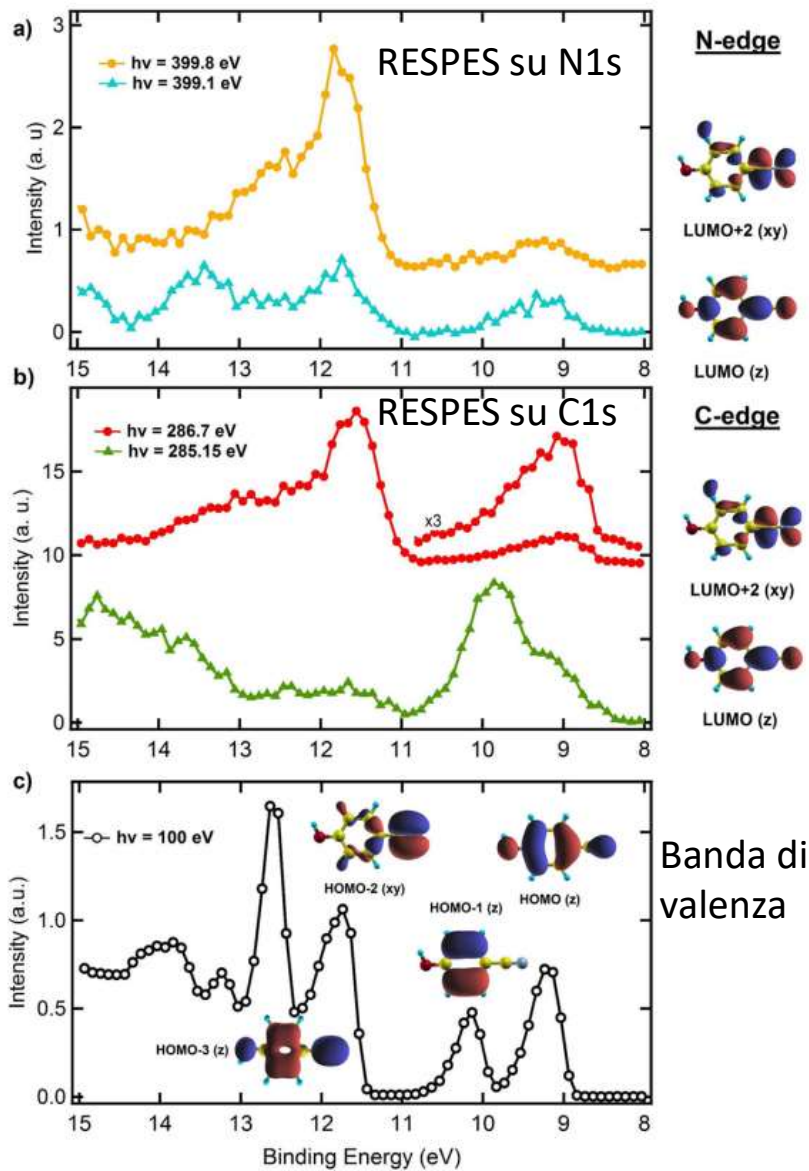


Banda di Valenza



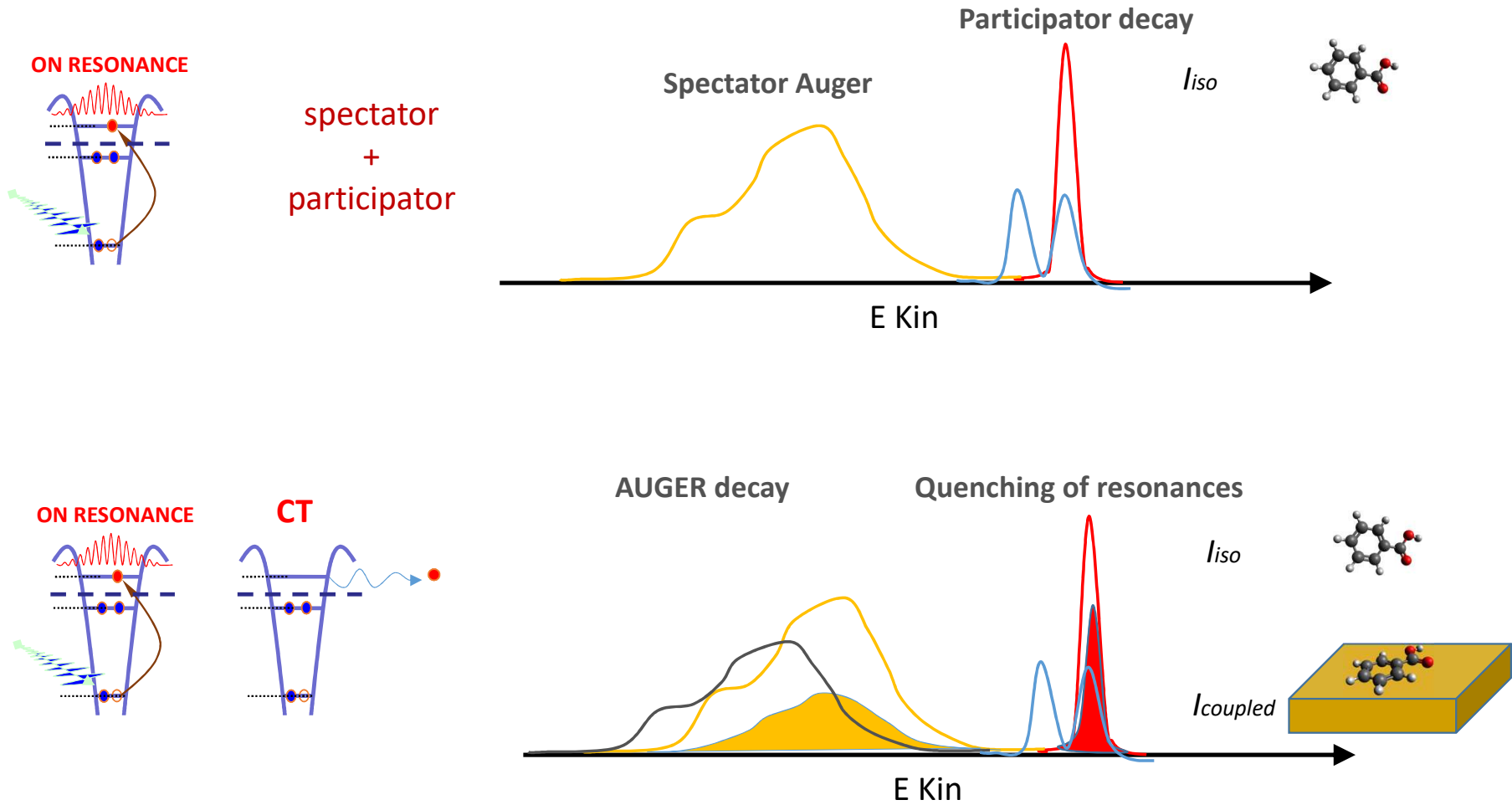
NEXAFS



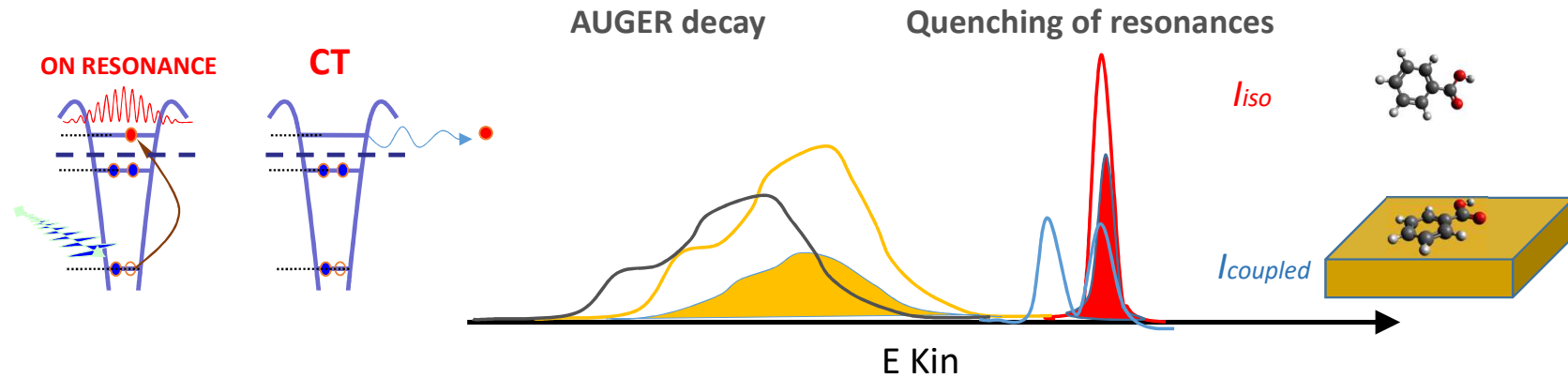


Alle energie di fotone corrispondenti alle transizioni NEXAFS 1s – LUMO(+n), risuonano gli stati HOMO (-n) che hanno un certo overlap. Questo permette un'assegnazione chimica degli stati della banda di valenza.

Electronic coupling: ultra-fast charge delocalization



Electronic coupling: ultra-fast charge delocalization



CT is a tunneling process: $P_{CT}(T) = \int_0^T \frac{1}{\tau_{CT}} e^{-\frac{t}{\tau_{CT}}} dt$ probability CT has occurred at time T

...and competes with core-hole decay: $P_{CH}(T) = \int_0^T \frac{1}{\tau_{CH}} e^{-\frac{t}{\tau_{CH}}} dt$ probability CH has occurred at time T

Probabilità che al tempo t_1 CT non sia avvenuto

$$1 - \int_0^{t_1} \frac{1}{c_{CT}} e^{-\frac{t}{c_{CT}}} dt$$

$$\int_0^T \frac{1}{c_{CH}} e^{-\frac{t}{c_{CH}}} \left(1 - \int_0^{t_1} \frac{1}{c_{CT}} e^{-\frac{t}{c_{CT}}} dt \right) dt,$$

$$= 1 - e^{-\frac{t_1}{c_{CT}}}$$

probabilità che da 0 a T
l'evento sia decade via CT

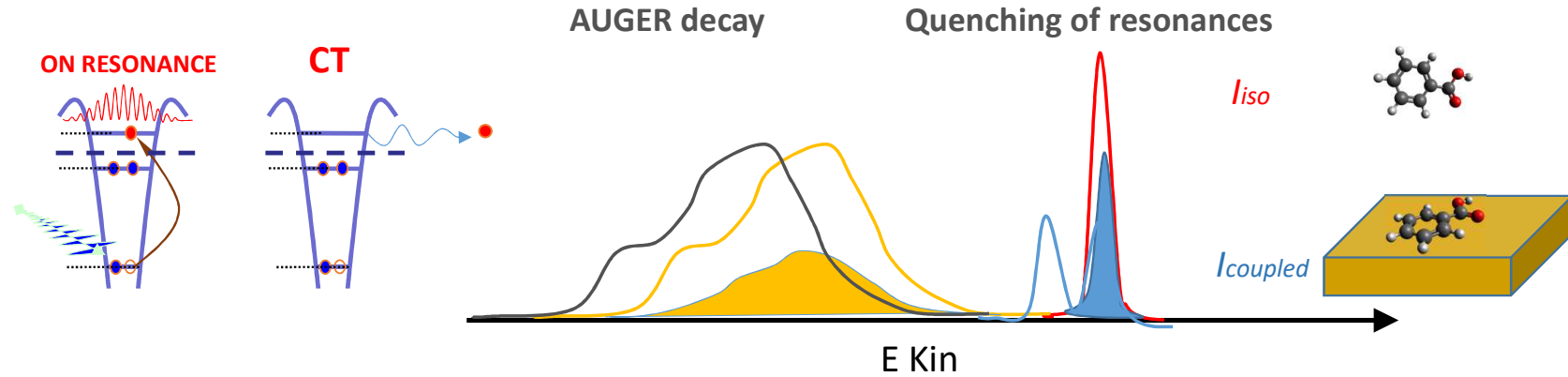
$$= \int_0^T \frac{1}{\tau_{CH}} e^{-t, (\frac{1}{\tau_{CH}} + \frac{1}{\tau_{CT}})} dt, = \frac{\tau_{CT}}{\tau_{CH} + \tau_{CT}} \left[1 - e^{-T (\frac{1}{\tau_{CH}} + \frac{1}{\tau_{CT}})} \right]$$

$T \approx \infty$ (osservo molecole che hanno già subito la disattivazione)
 ($\tau_{CH}, \tau_{CT} \sim 1-100$ fs, io medio su $\sim 0.5, 0.1$ s)

$$P^{NOCT} = \frac{\tau_{CT}}{\tau_{CH} + \tau_{CT}}$$

$$P^{CT} = 1 - \frac{\tau_{CT}}{\tau_{CH} + \tau_{CT}} = \boxed{\frac{\tau_{CH}}{\tau_{CH} + \tau_{CT}} = \frac{I_{iso} - I_{coup}}{I_{iso}}} = P^{CT}$$

Electronic coupling: ultra-fast charge delocalization



Core Hole Clock method

$$\tau_{CT} = \tau_{core} \frac{I_{coupled}}{I_{Iso} - I_{coupled}}$$

τ_{core}

C1s ~ 6 fs

N1s ~ 6 fs

O1s ~ 4 fs



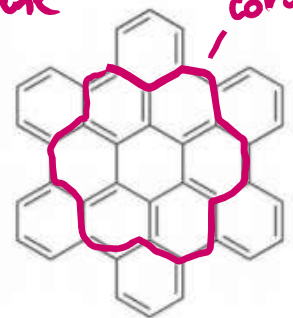
Clock in the 0-50 fs range

P. A. Brühwiler et al., Rev. Mod. Phys. (2002)

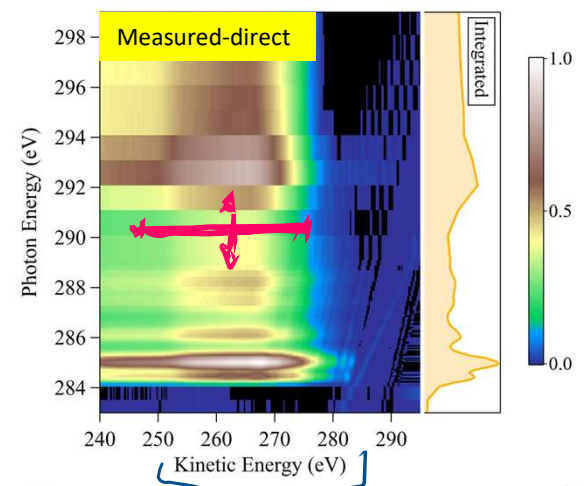
The data analysis: Auger+Spectator+Partecipator

Spectral decomposition

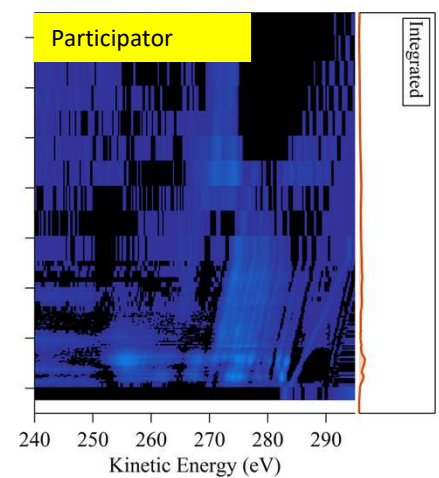
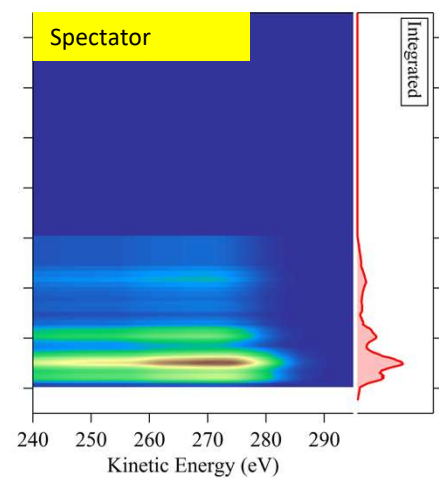
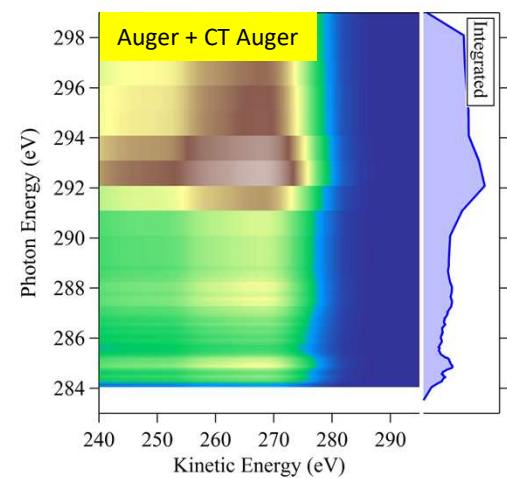
Hexa bands coronarie



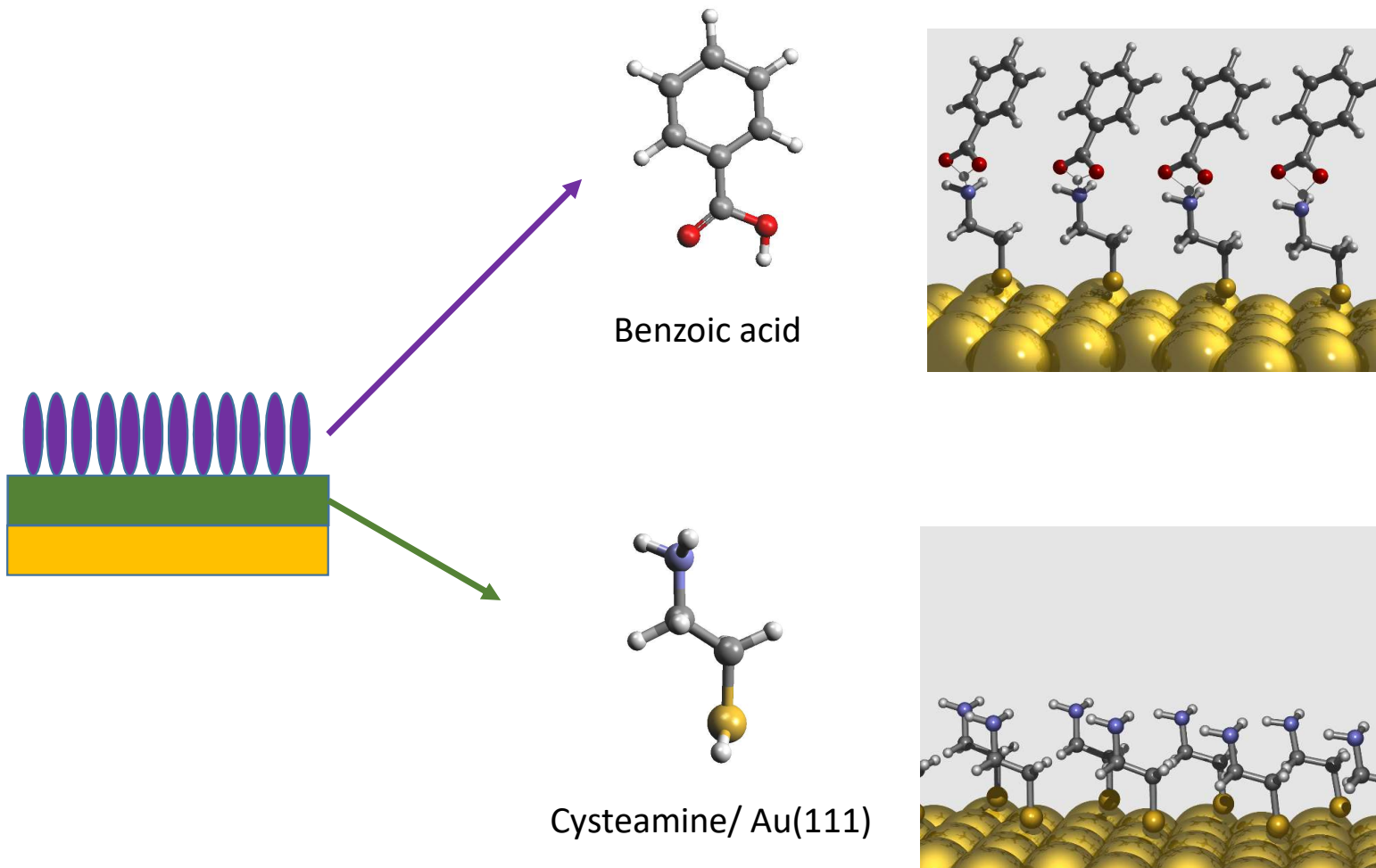
core hole



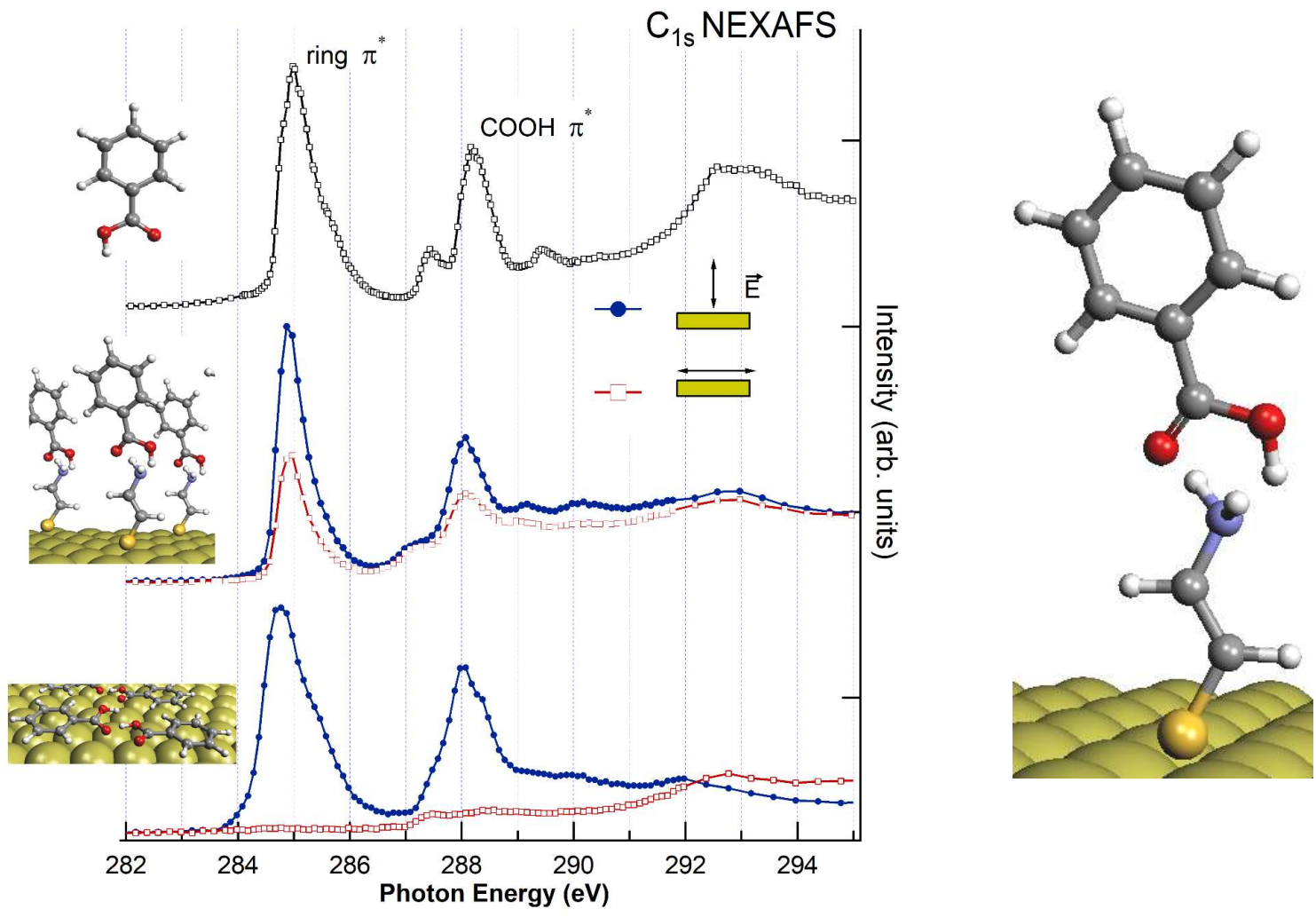
Misurata la mappa RESPES, si individuano le diverse component di decadimento (Auger, Spectator, Partecipator) Questo permette di individuare le intensità da utilizzare nel metodo core-hole clock

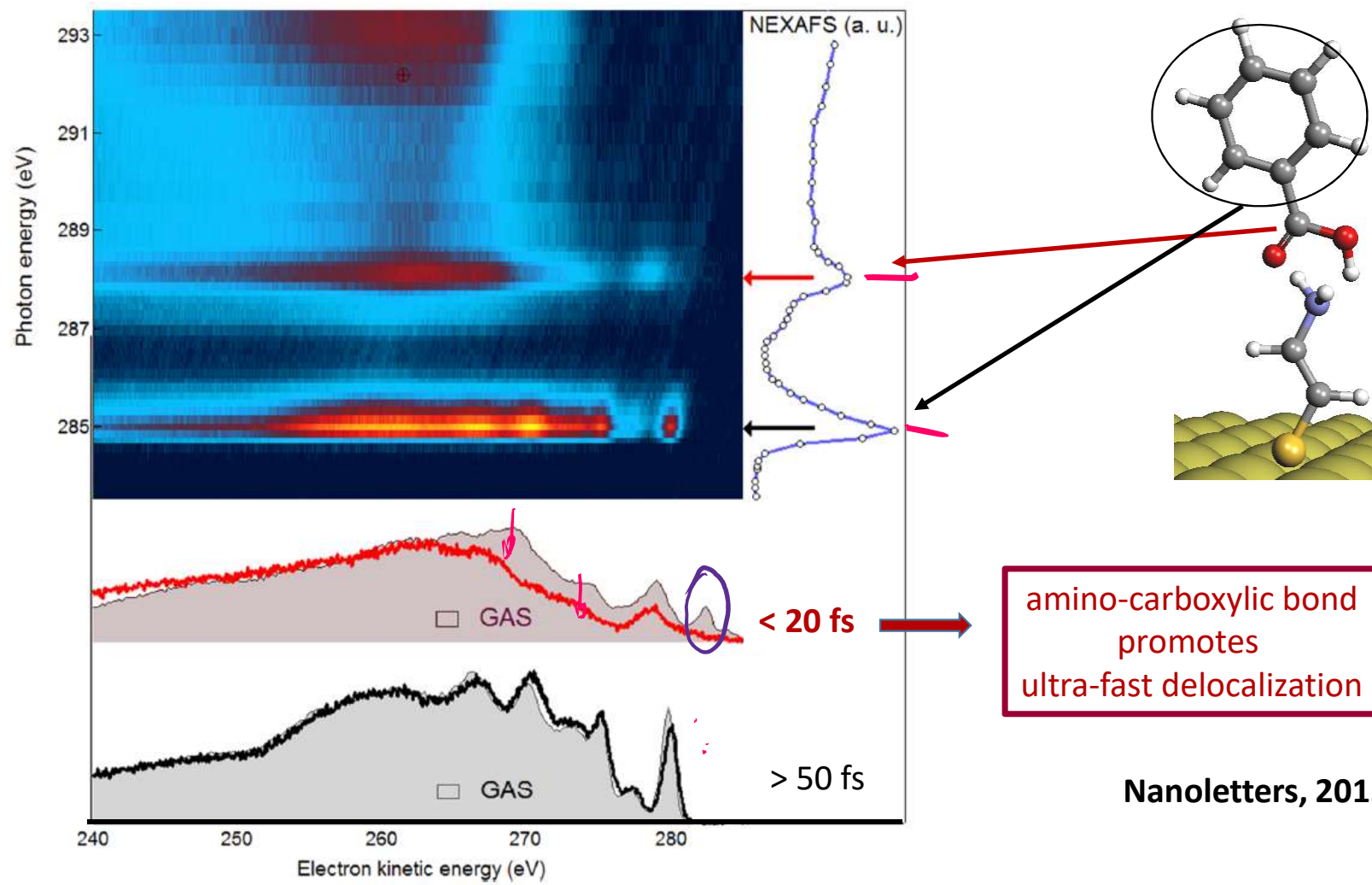


Amino-carboxylic anchoring

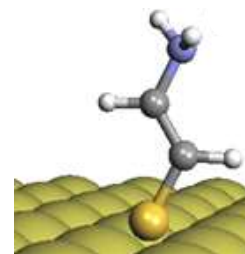
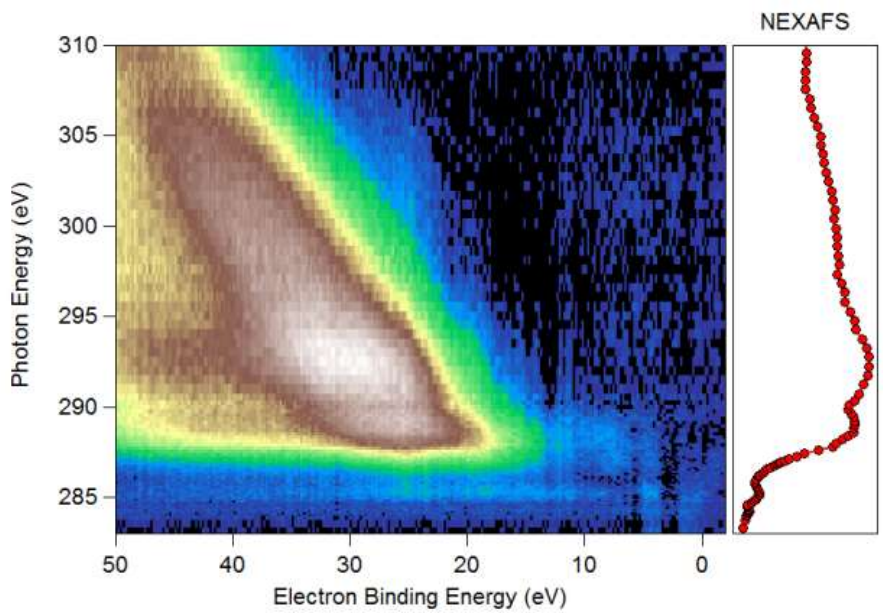
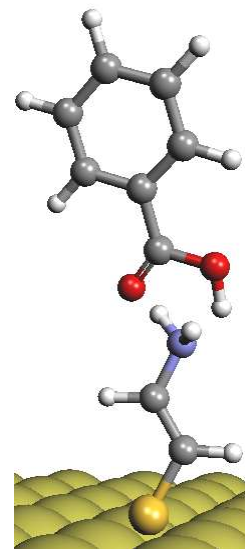
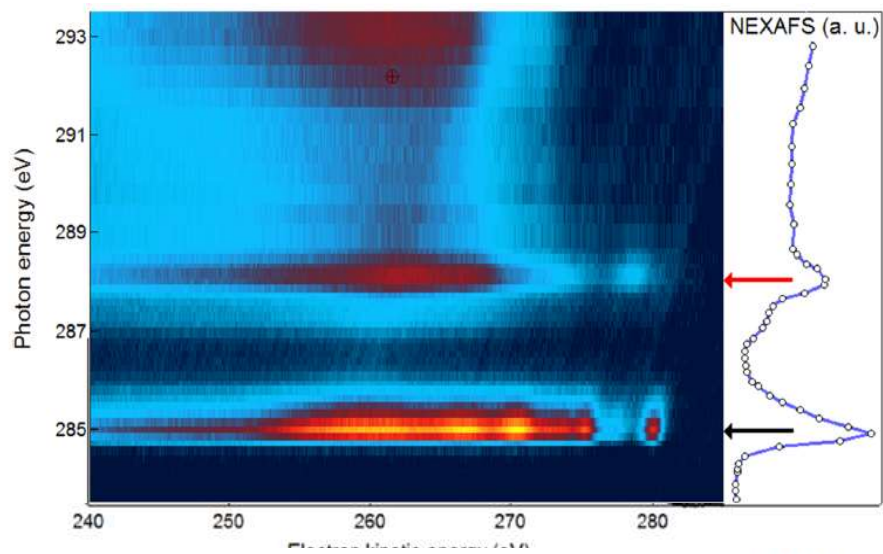


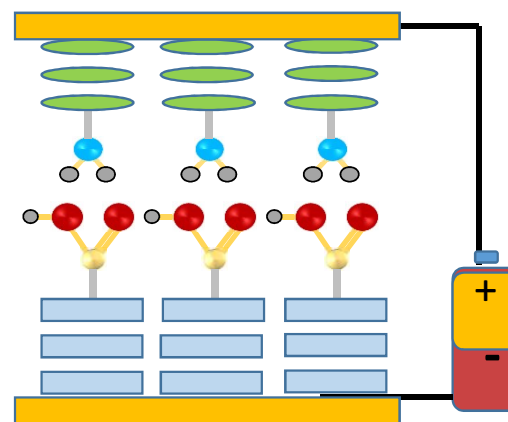
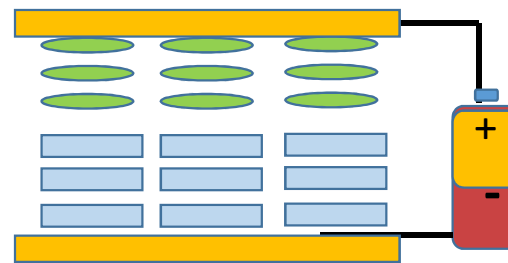
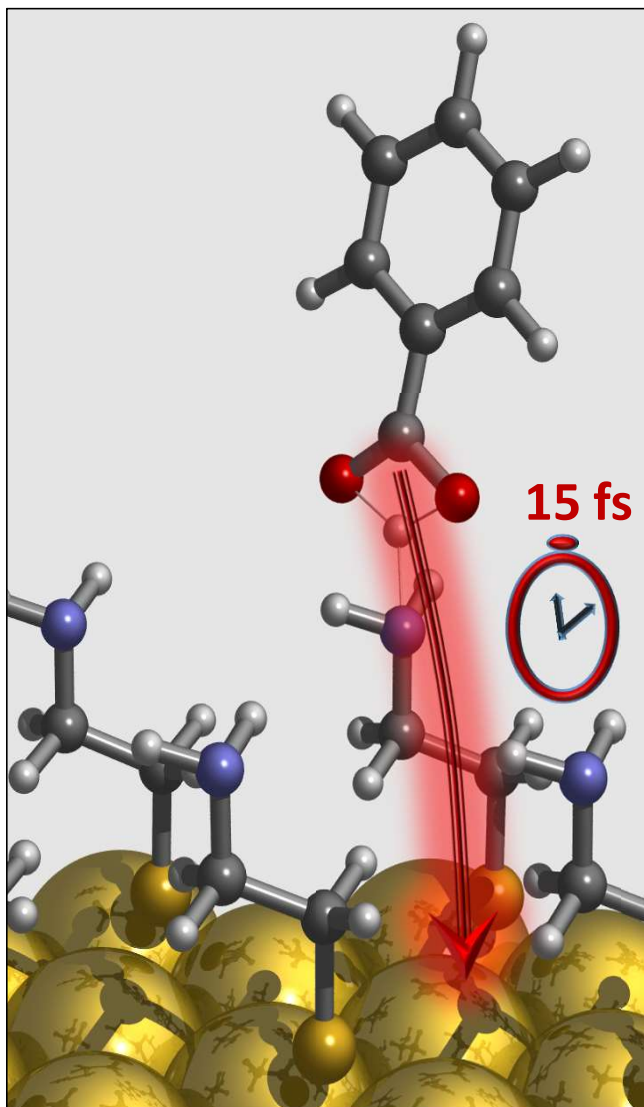
The ANCHOR Lab: multi-technique approach





Nanoletters, 2015

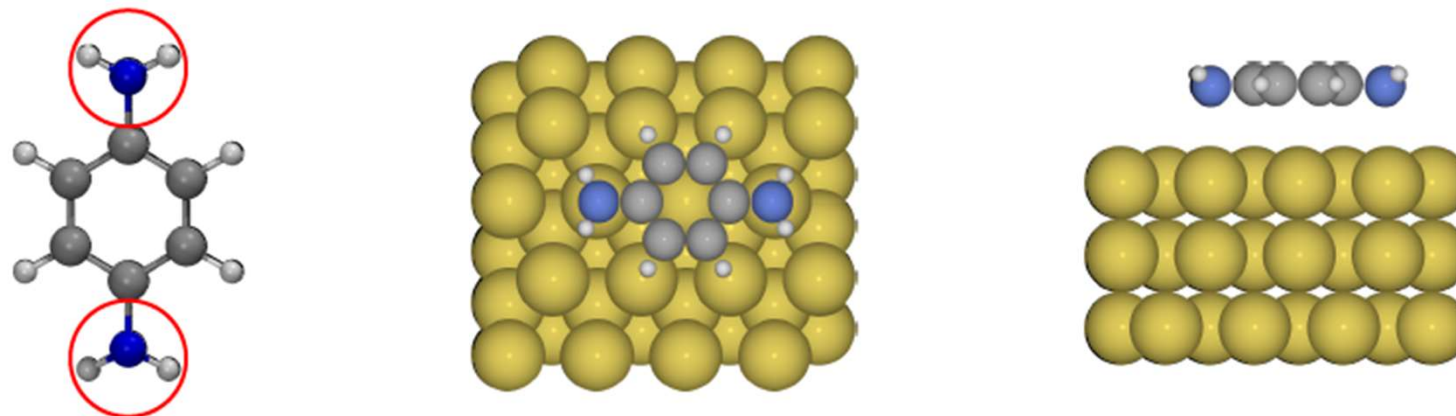




Break junction results vs X-ray spectroscopy

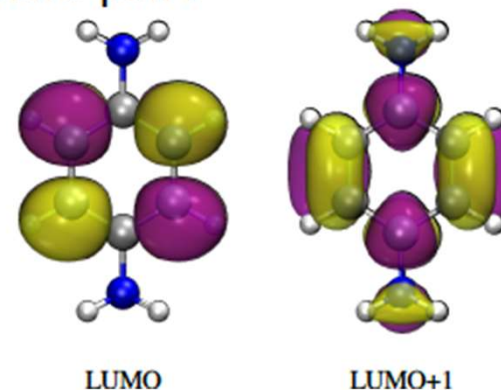
Tracking fast electrons at organic interfaces ...

- Model system 1,4-diaminobenzene (BDA) on Au(111)



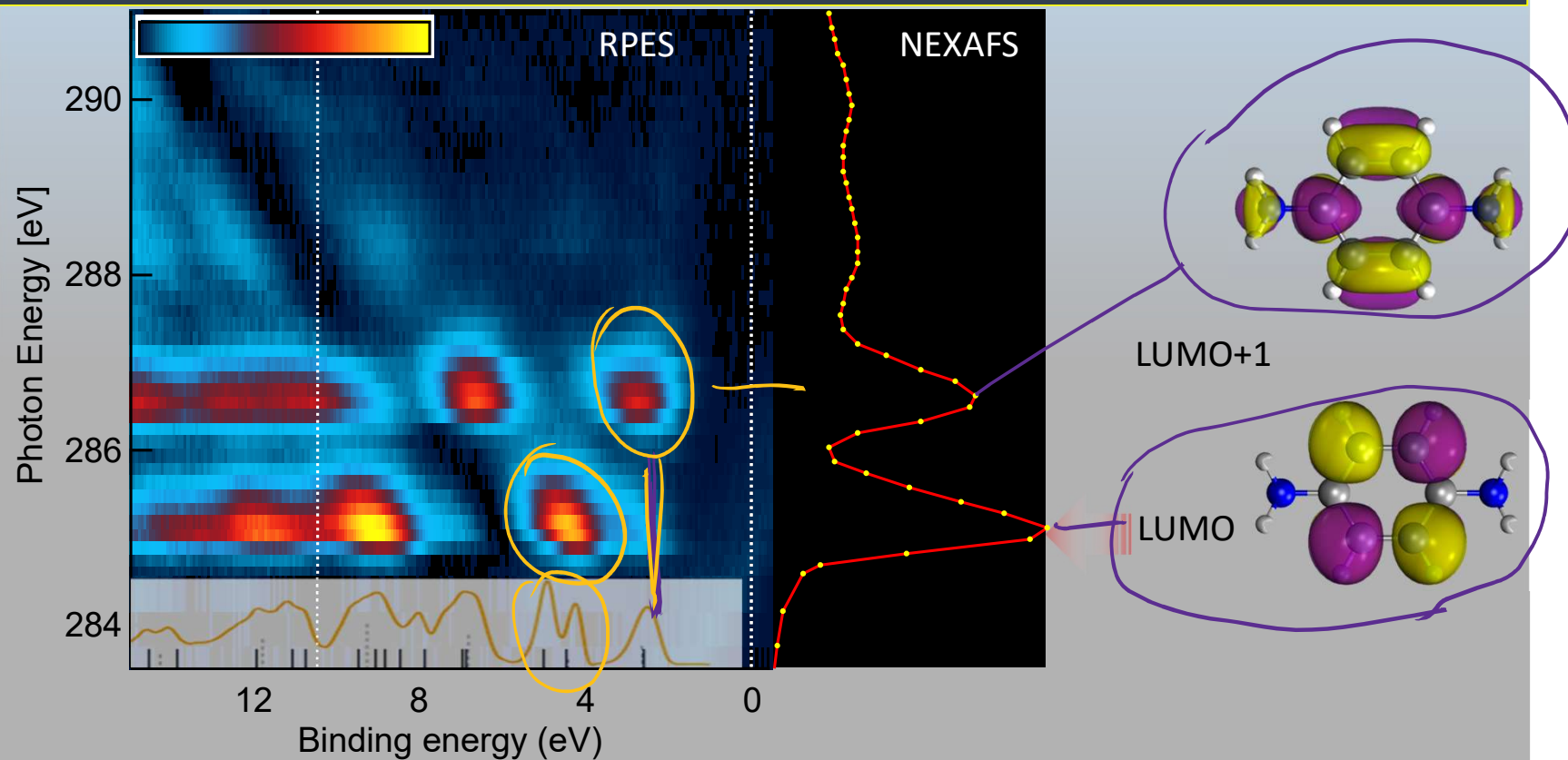
- Two amine groups with donating electron lone-pairs

- We exploit specific LUMO (LUMO+1) symmetry & spatial distribution over the atomic sites



Resonant Photoemission

Tracking fast electrons at organic interfaces ...

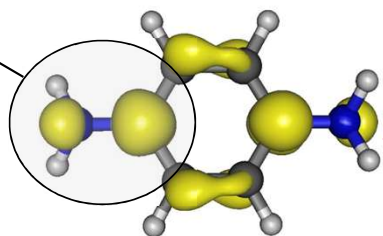


- Measure XPS spectra with $h\nu$ tuned across absorption edge
- VB resonances → Absorption & Hole decay via Autoionization

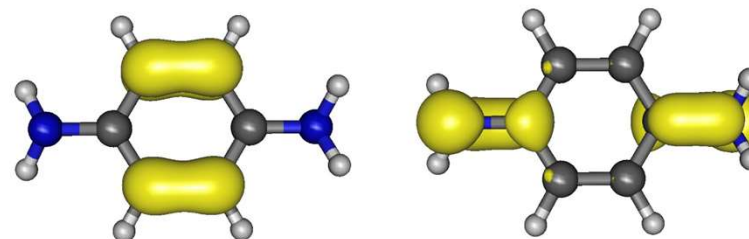
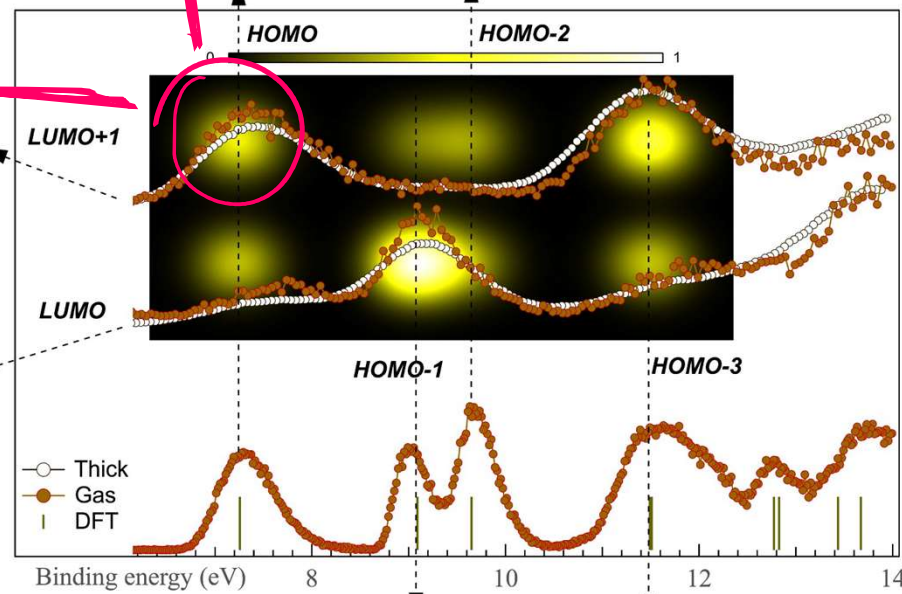
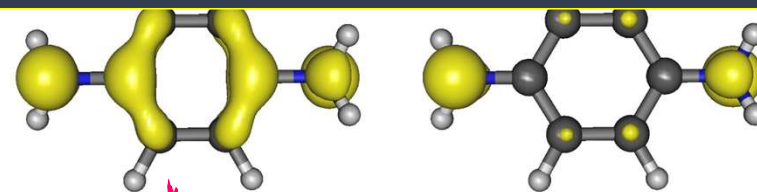
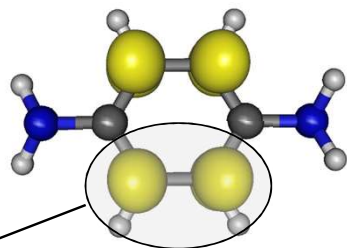
RPES and Orbital Overlap

Tracking fast electrons at organic interfaces ...

LUMO+1 on N, C_{1,4}

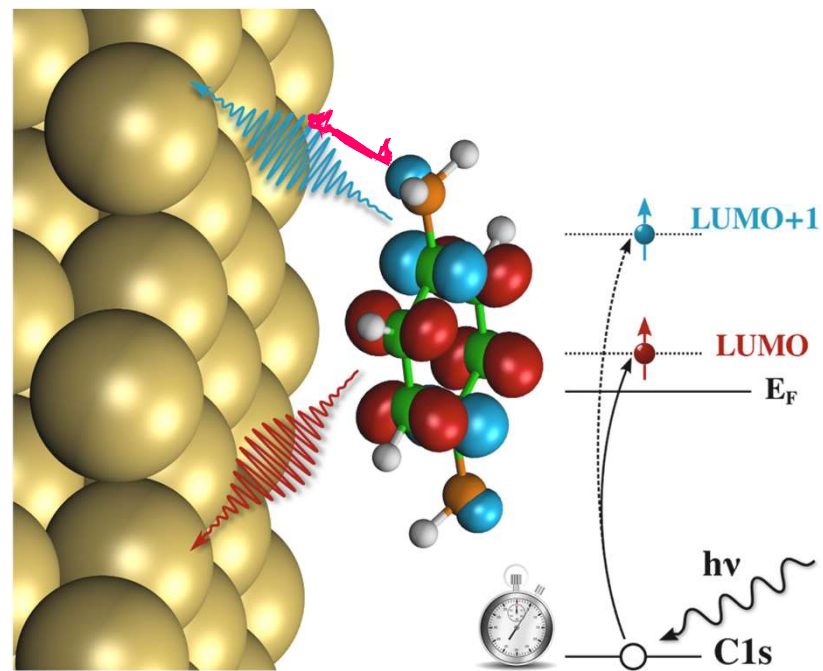
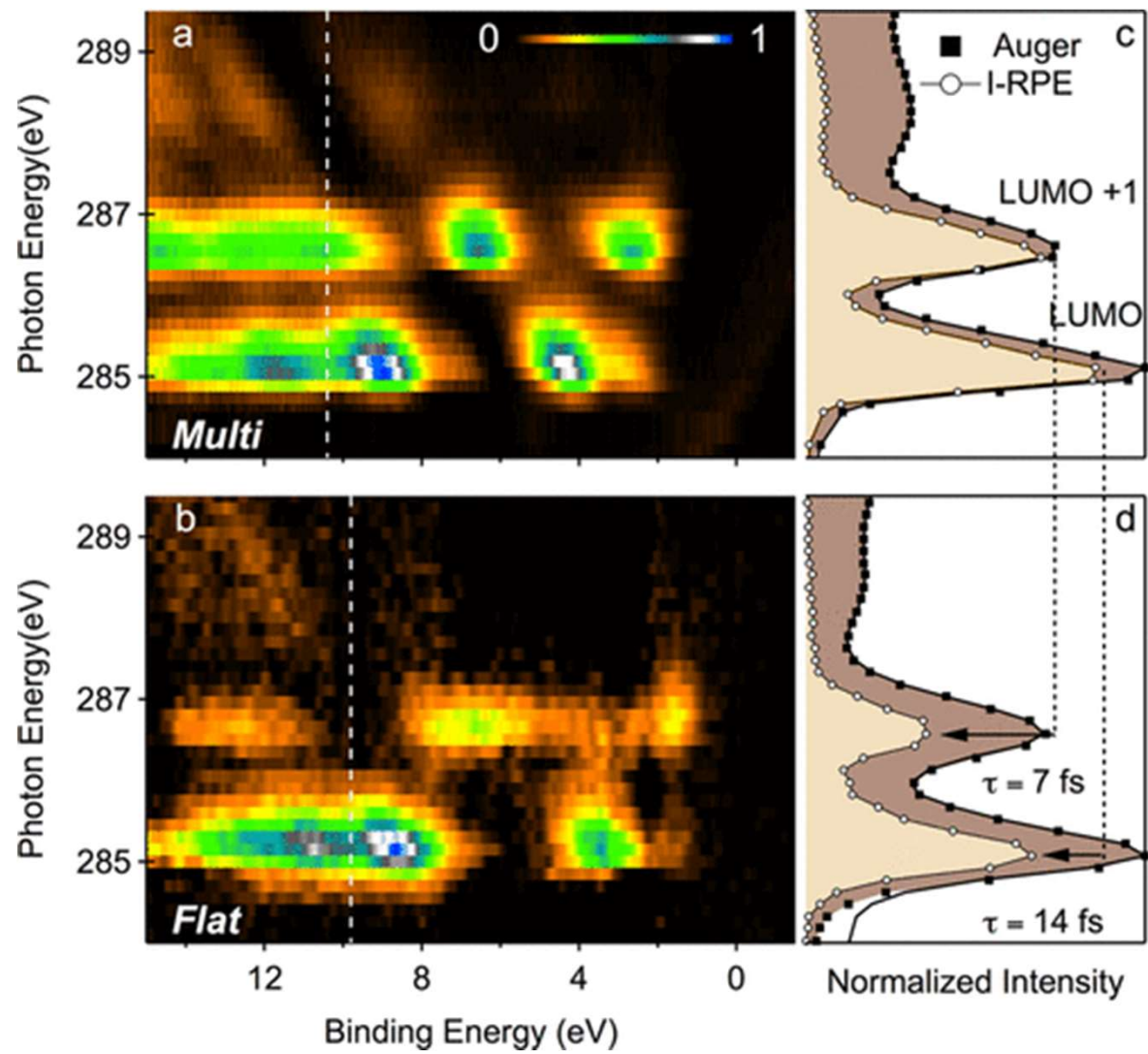


LUMO on C₂₃ ring

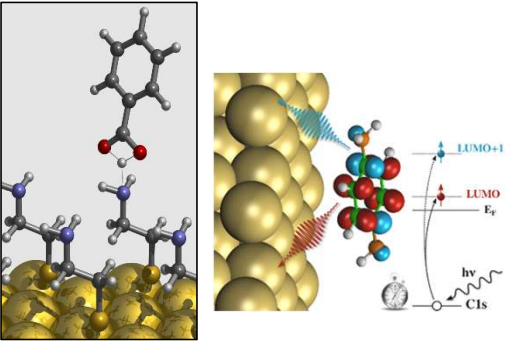
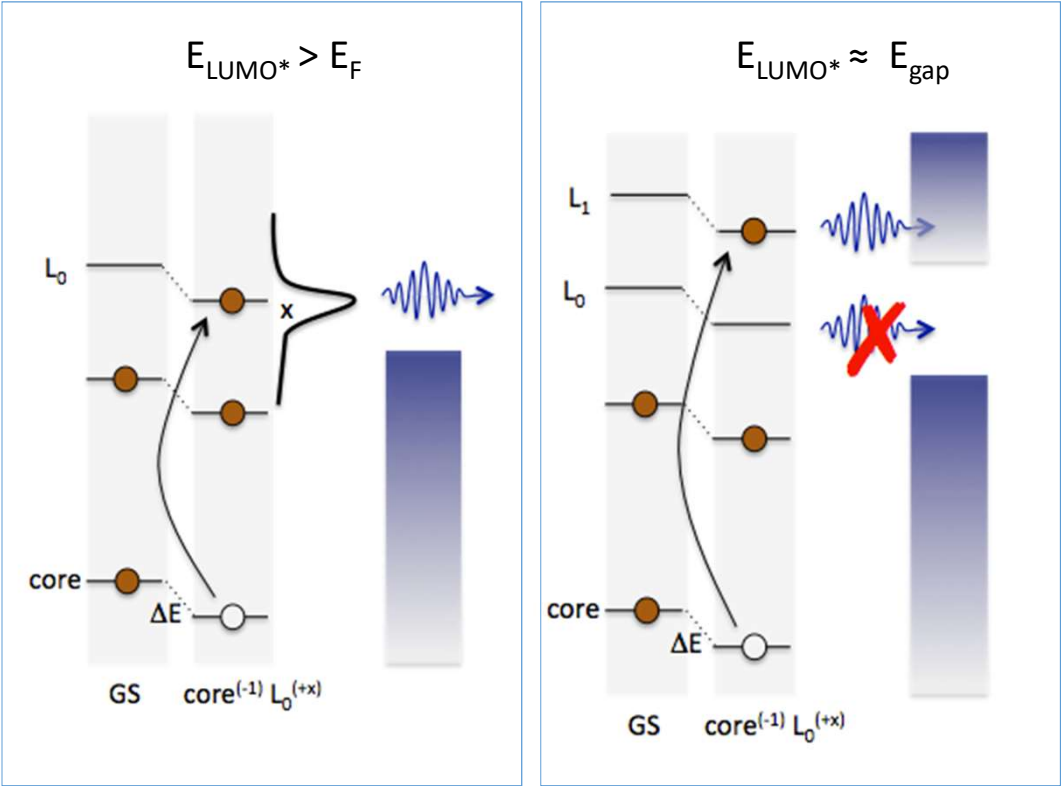


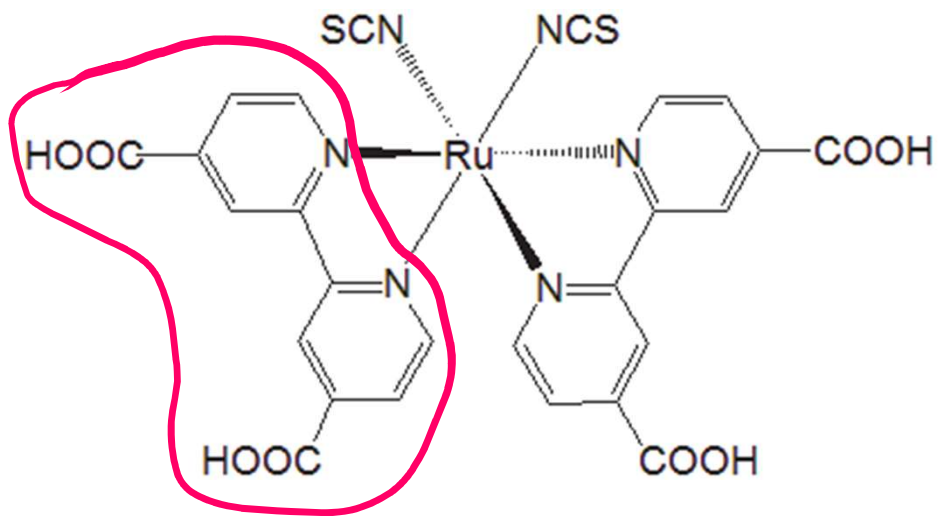
Gas phase calculations :
DFT, B3LYP functional, half core hole approx.

Dell'Angela et al., Nano Lett . (2013)



CHC and LUMO energy level alignment





Dye N3

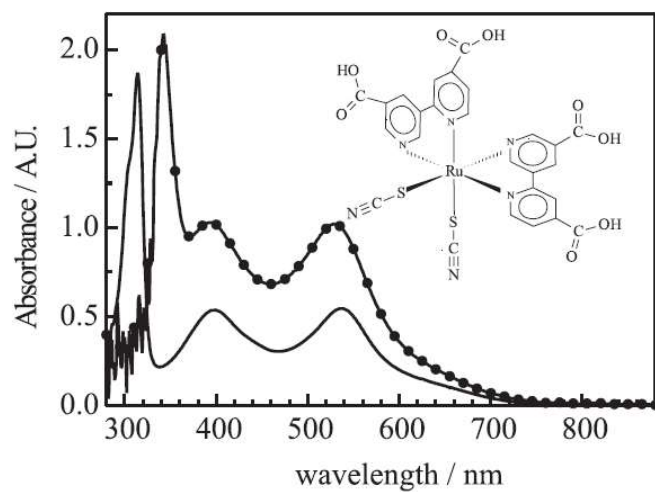
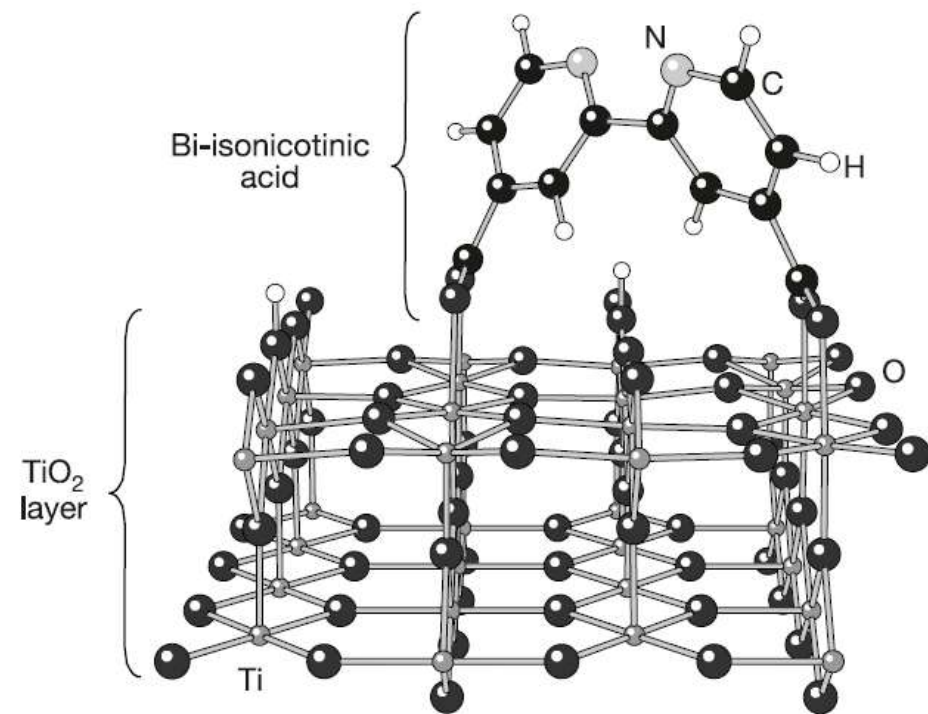
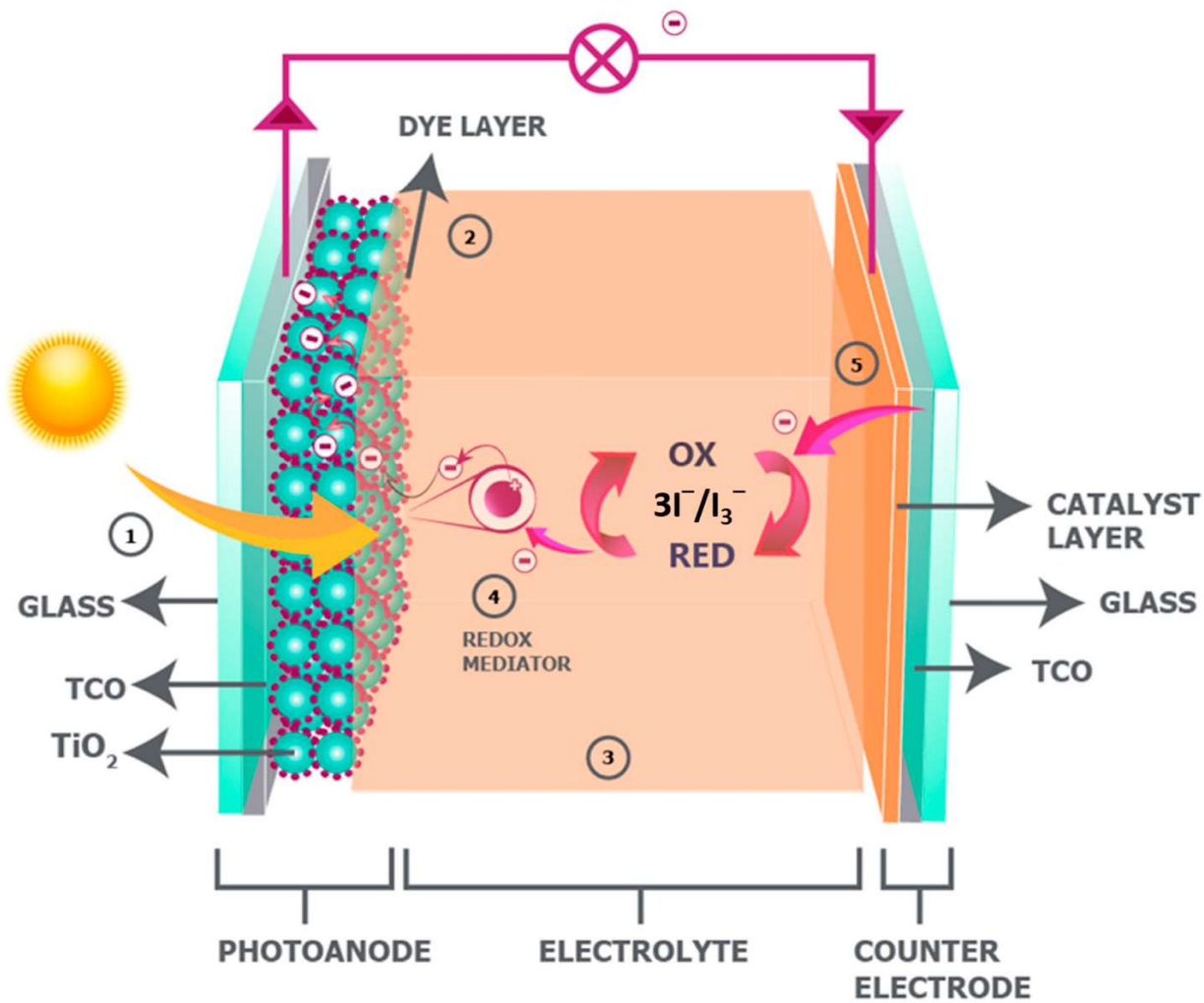


Figure 4. Absorption spectrum of the N3 dye in ethanol solution (—) and of a N3 dye-sensitized nanocrystalline TiO_2 electrode (-•-).



Dye-sensitized solar cell (Cella Grätzel)

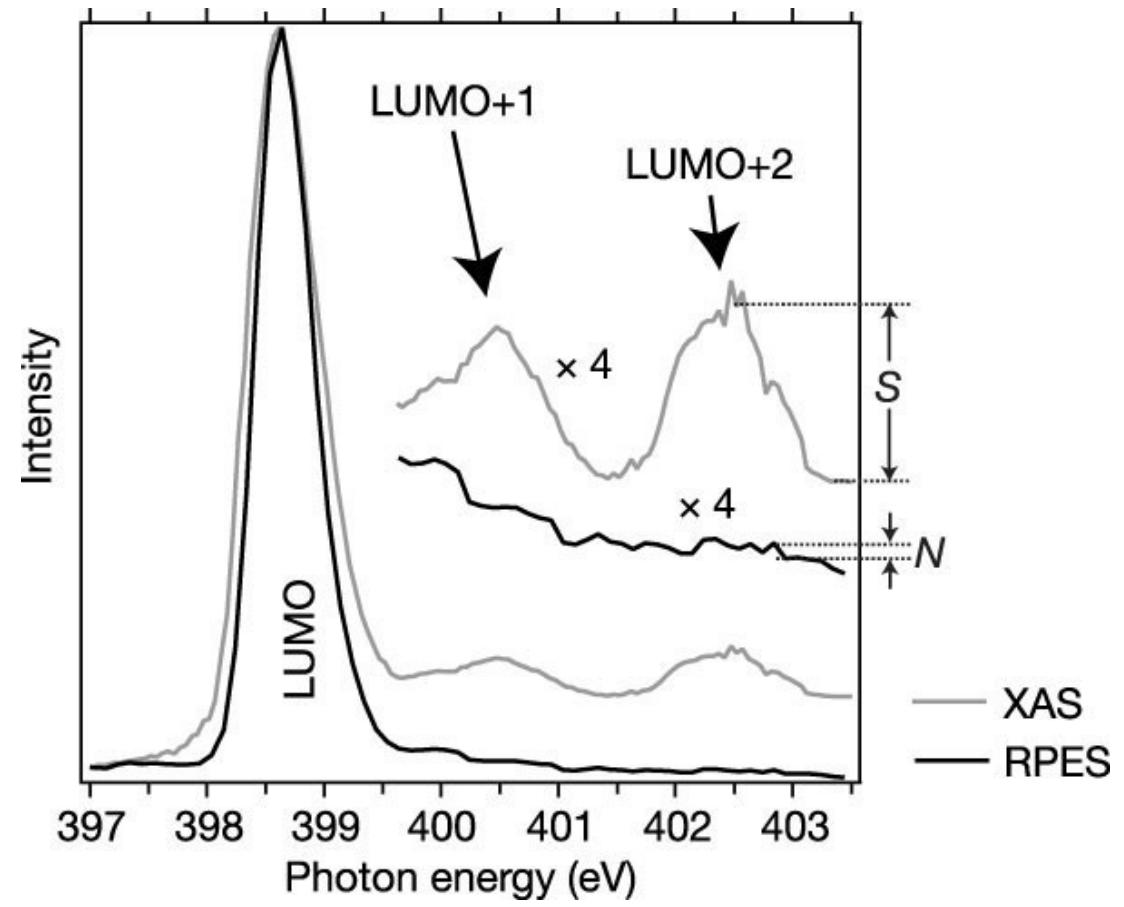
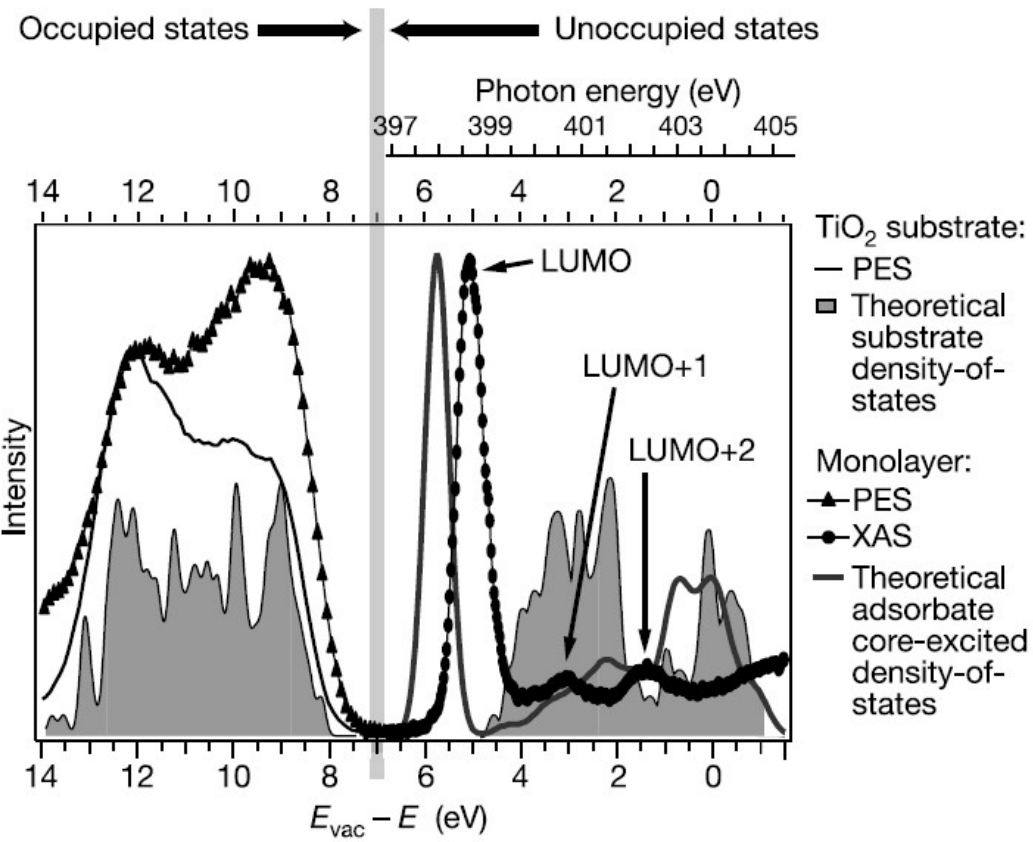


All'interfaccia dye-TiO₂ avviene la separazione dell'eccitone creato dall'assorbimento della luce visibile.

1. Assorbimento fotone (HOMO-LUMO)
2. Trasferimento e⁻ al TiO₂ (banda di conduzione)
3. $2(\text{Dye})^+ + 3\text{I}^- \rightarrow 2\text{Dye} + \text{I}_3^-$
4. L'elettrone viaggia da un elettrodo all'altro
5. $\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$

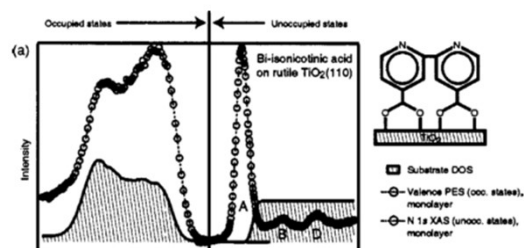
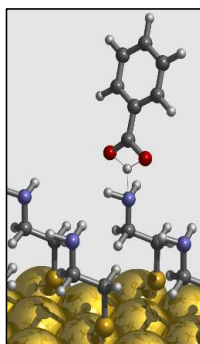
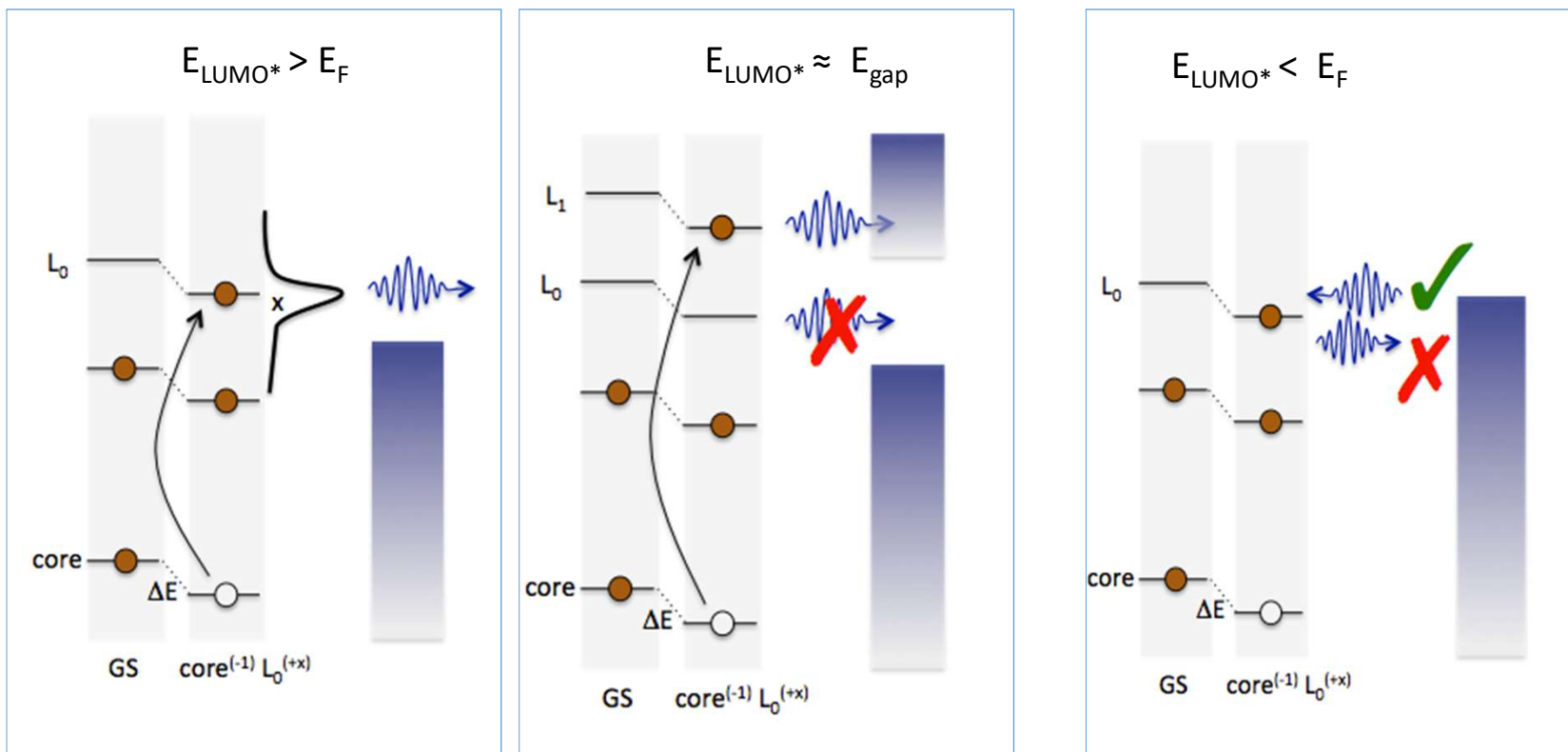
Nota: l'elettrolita è costituito da una soluzione di ioduro in acetonitrile

Materials **2019**, *12*, 1998; doi:10.3390/ma12121998



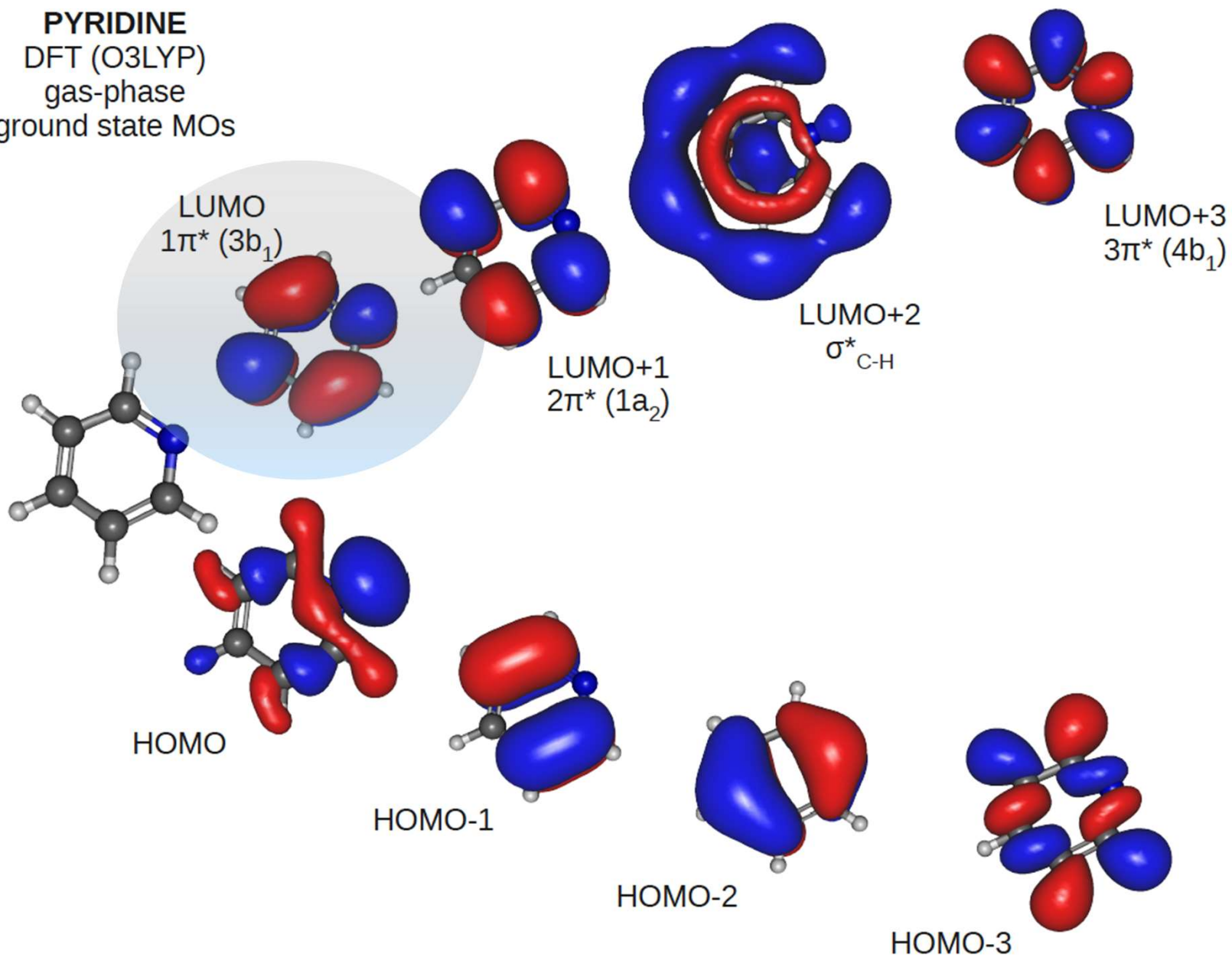
Britton et al., Phys. Rev. Lett. 109, 017401 2012

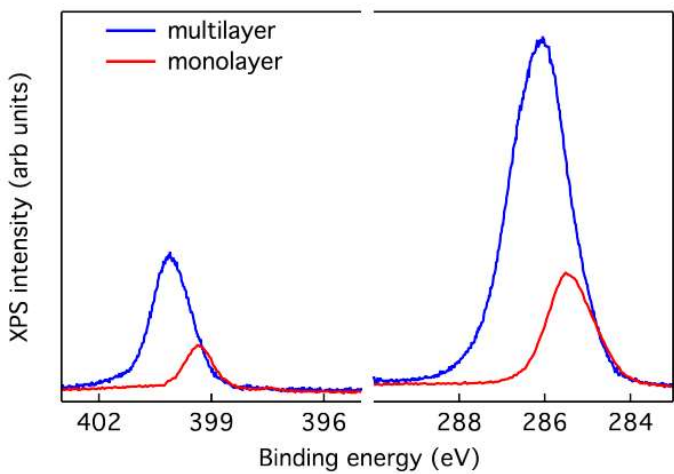
CHC and LUMO energy level alignment



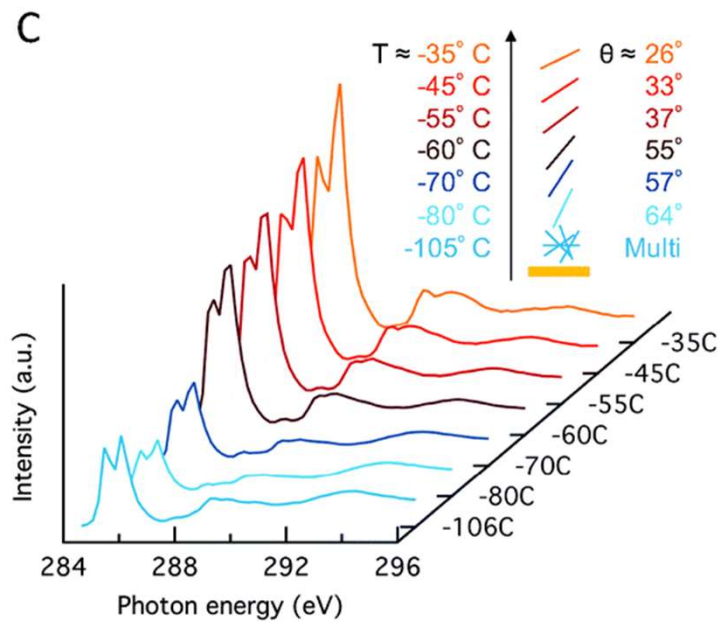
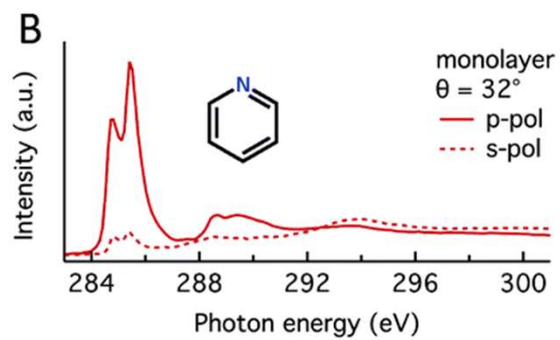
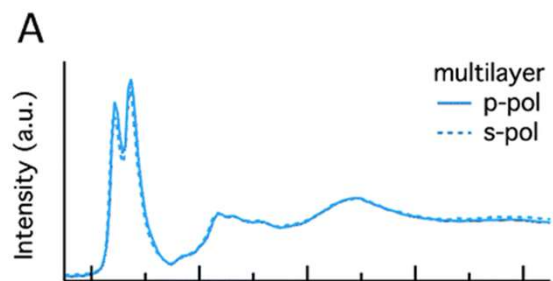
Britton et al., Phys. Rev. Lett. 109, 017401 2012

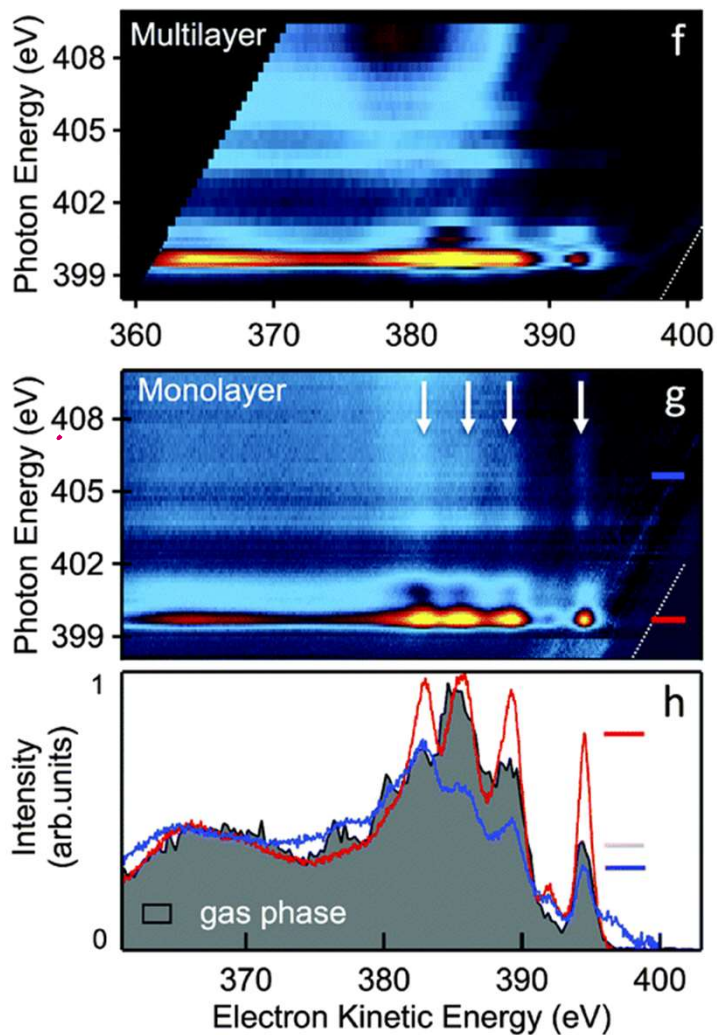
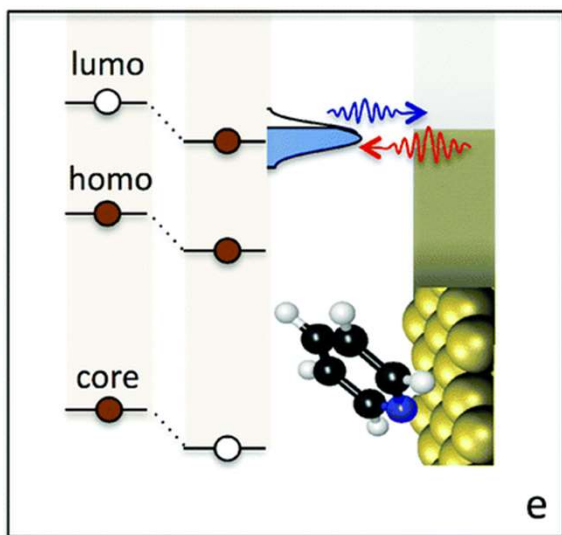
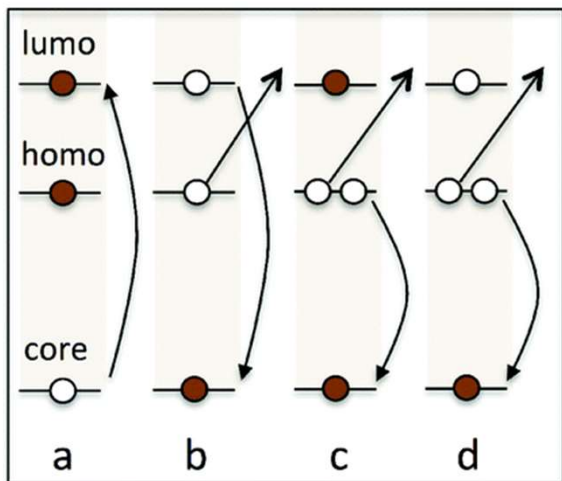
PYRIDINE
DFT (O3LYP)
gas-phase
ground state MOs





Pyridine/Au(111)



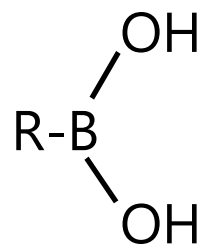


Le frecce bianche indicano l'intensità di tipo participator, che deriva dal trasferimento di un elettrone dal substrato alla molecola ionizzata. Tale processo avviene per $h\nu > IP$ e non è presente ovviamente nel multilayer, dove non c'è contatto delle molecole con il substrato

Spectator shift...

On- surface boroxination

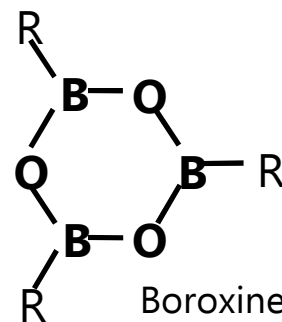
Boronic acid



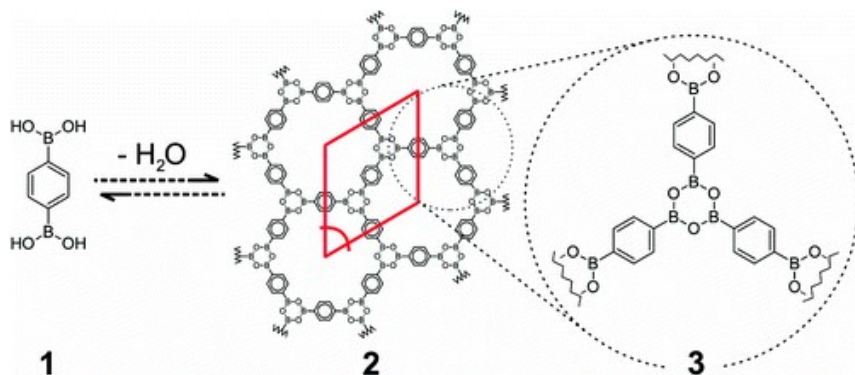
Boroxination



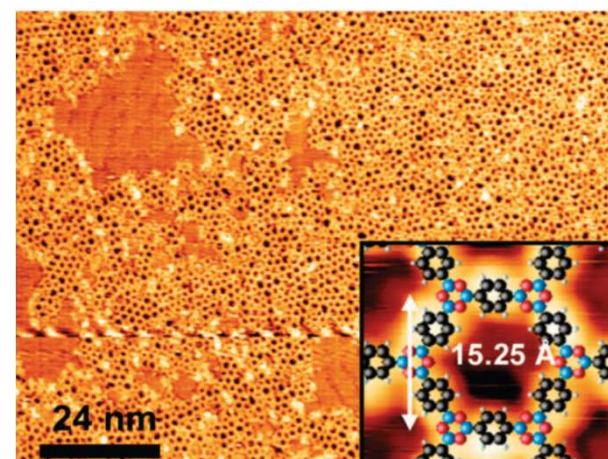
+ 3 H₂O



Boroxine ring

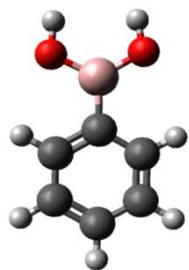


J.F. Dienstmaier et al., ACS Nano, 5, 12, 9737-9745

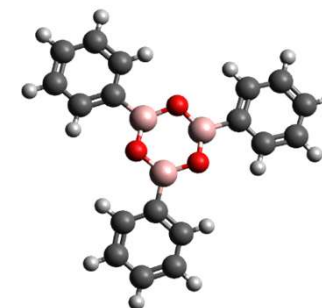
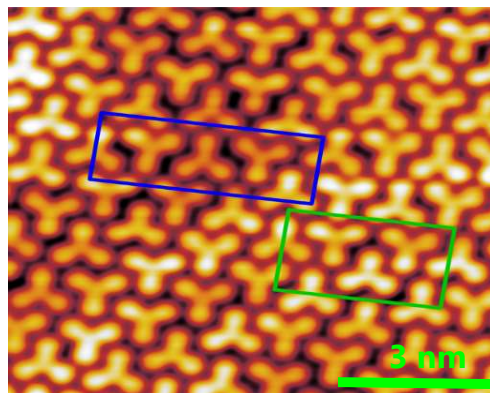


T. Faury et al., J. Phys. Chem. C 2012, 116, 4819-4823

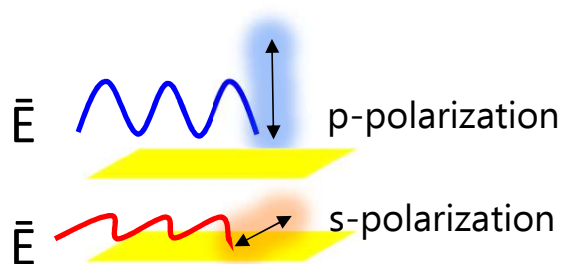
On-surface synthesis of boroxine molecule



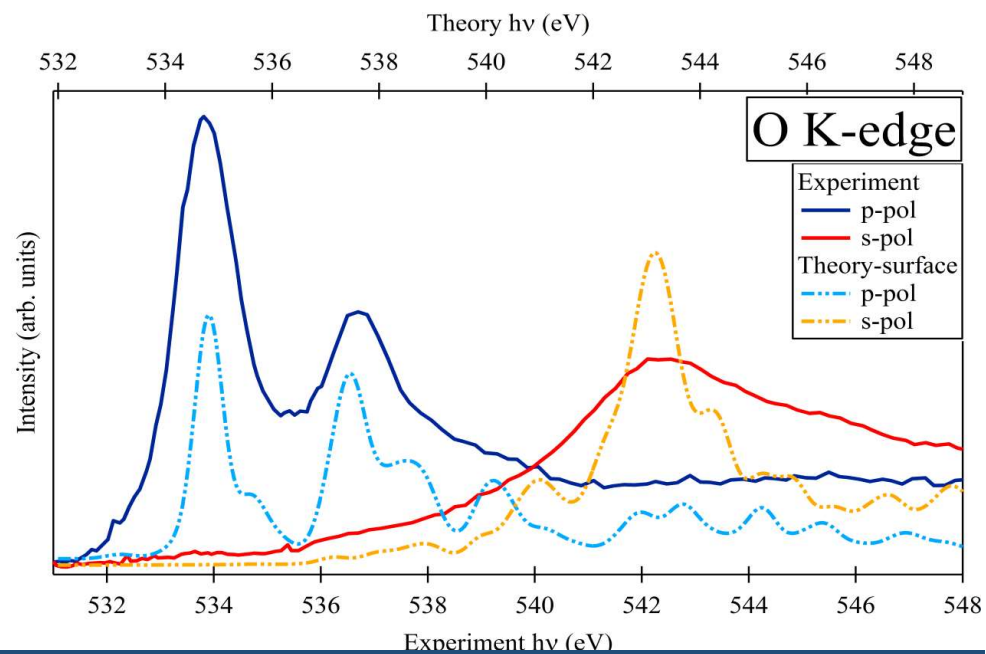
Phenylboronic acid
on Au(111)



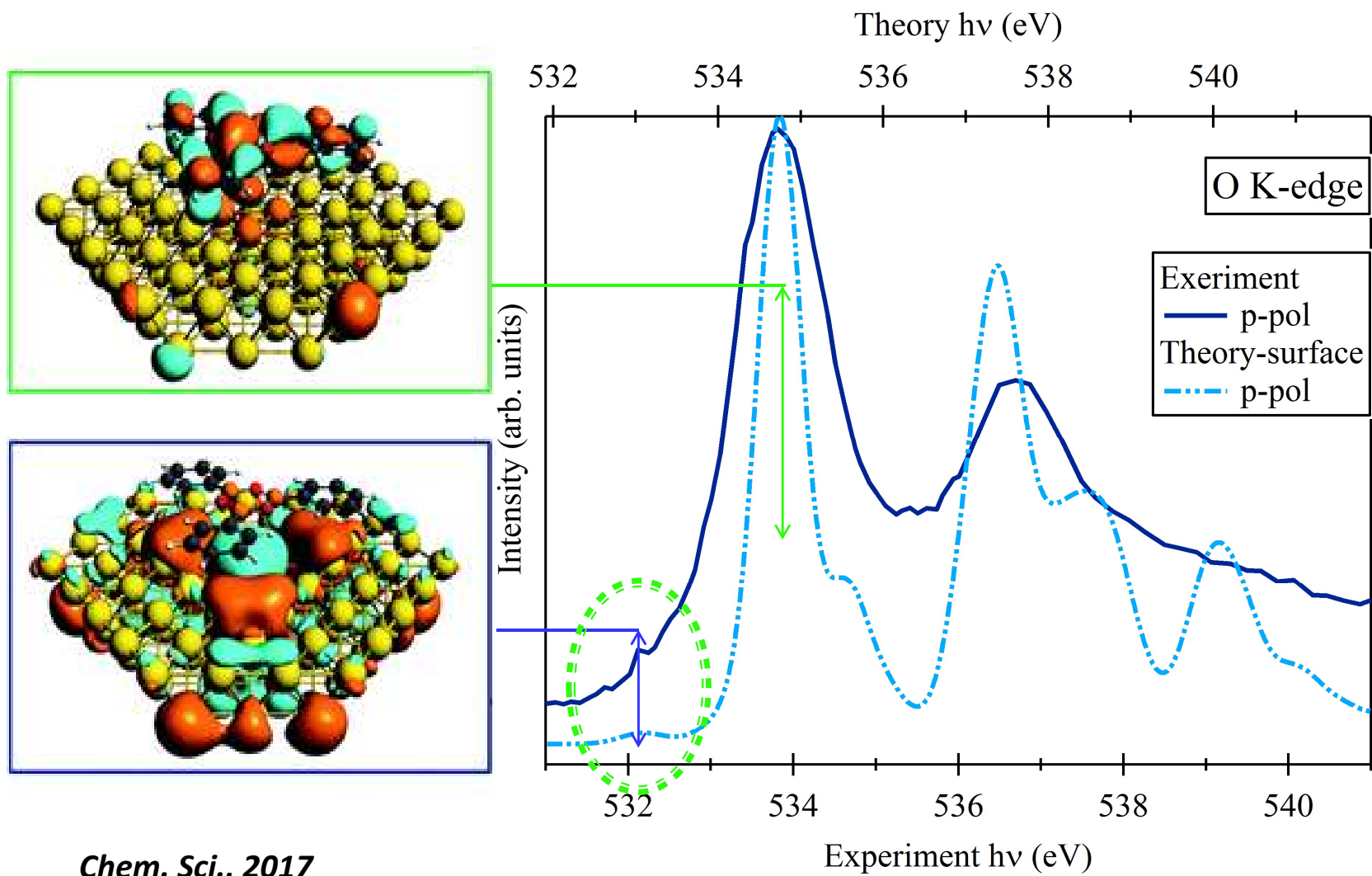
On surface synthesis
Triphenylboroxine



Toffoli et al., **Chem. Sci.**, 2017, 8,
3789-3798

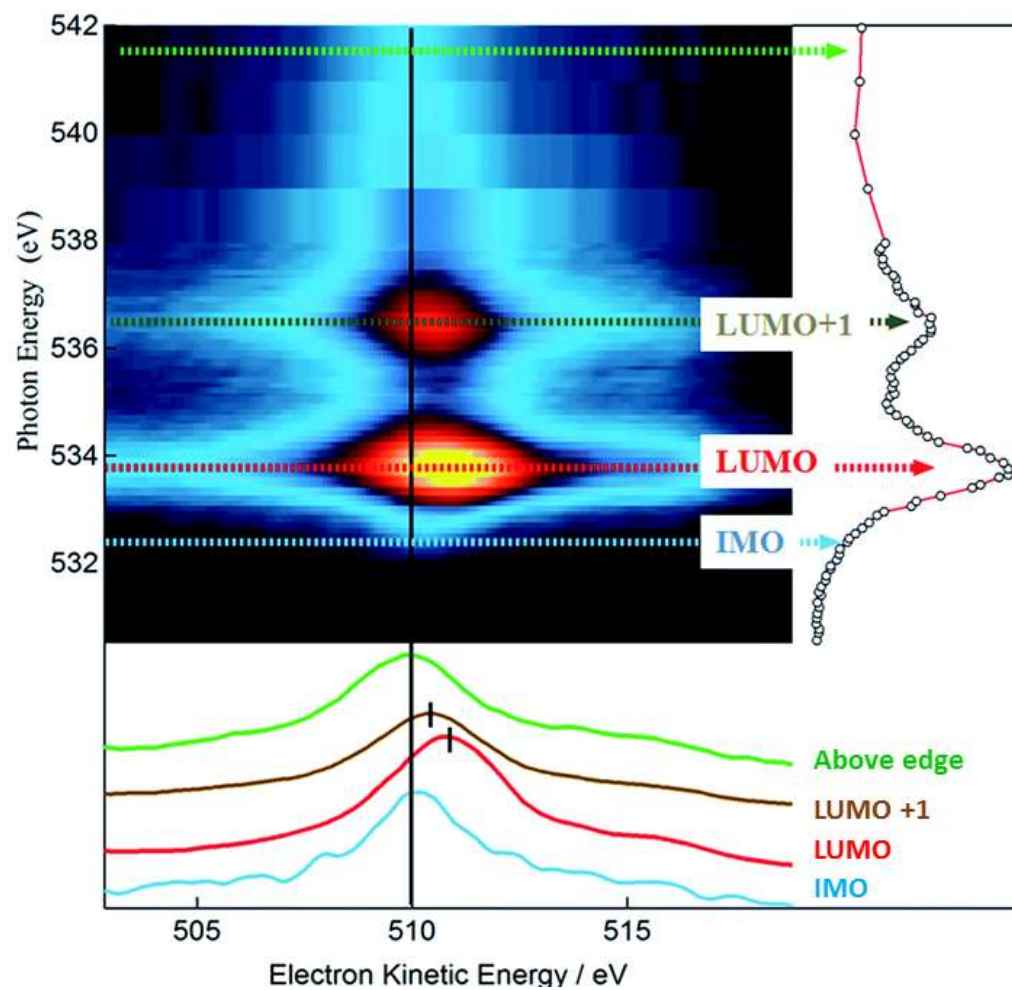


O k-edge NEXAFS + DFT: evidence of interface molecular orbital (IMO)

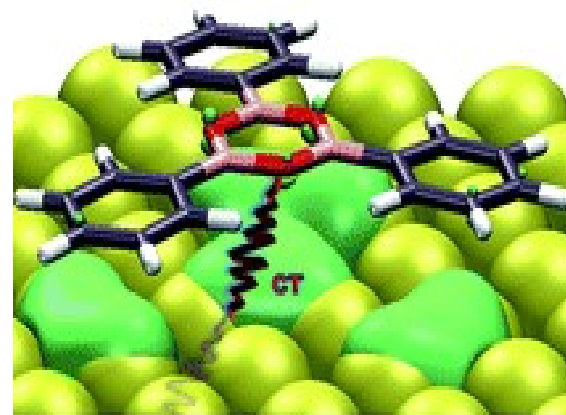


Chem. Sci., 2017

O k-edge RESPEC: IMO promotes ultra-fast charge delocalization



platforms for
ultrafast charge transfer



Toffoli et al., Chem. Sci., 2017, **8**,
3789-3798

Sample Temperature

