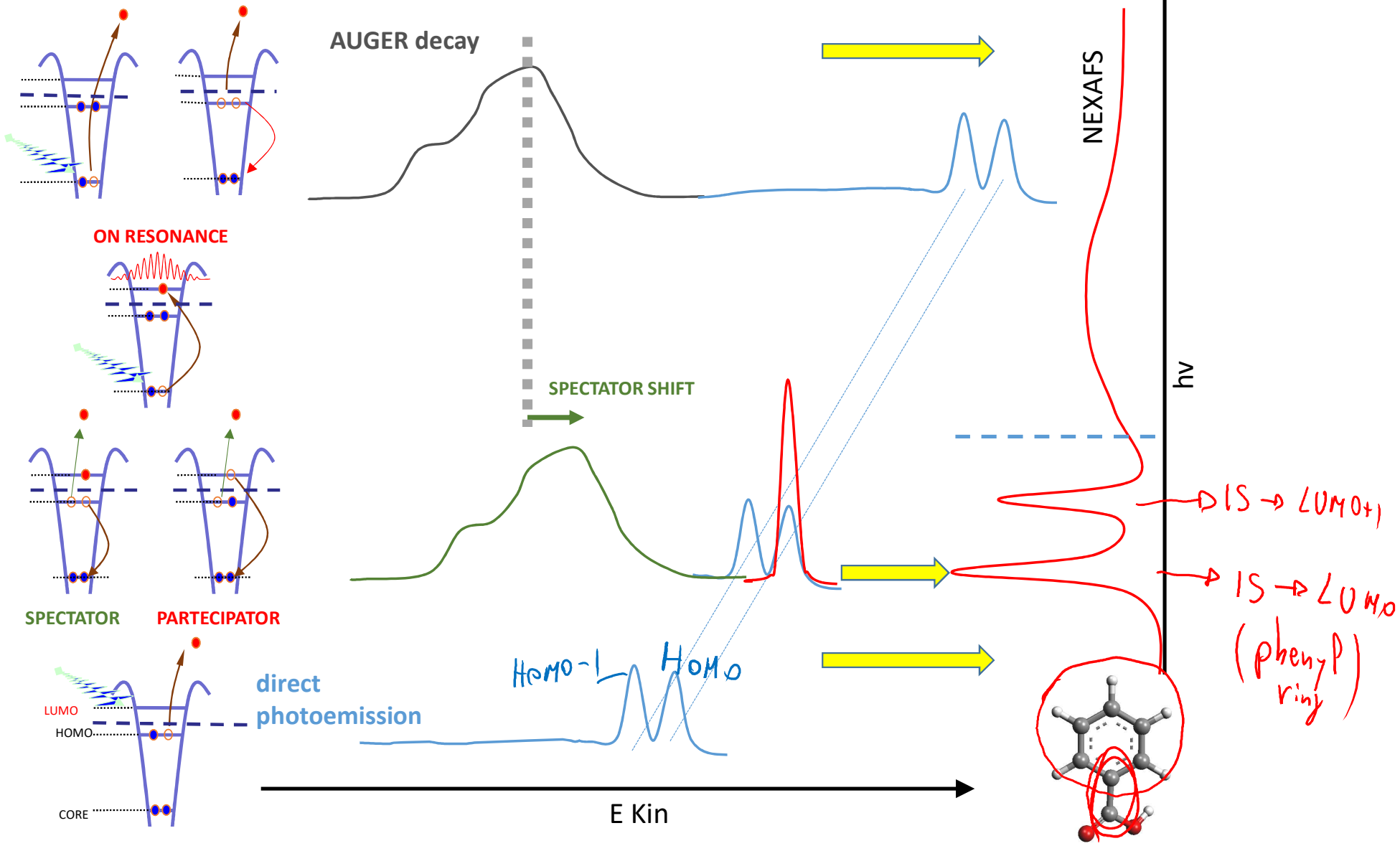
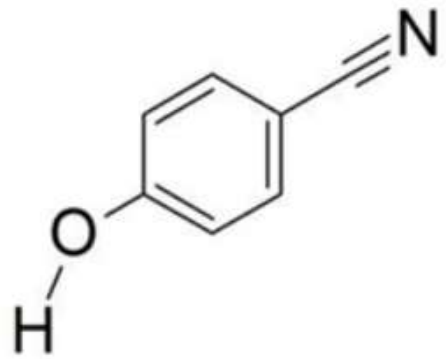
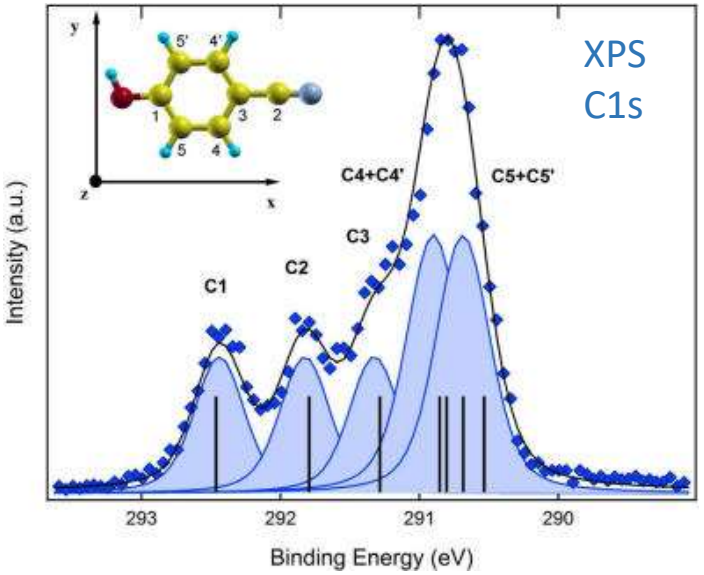
RESPES : Resonant photoemission Spectroscopy

Resonant photoemission spectroscopy

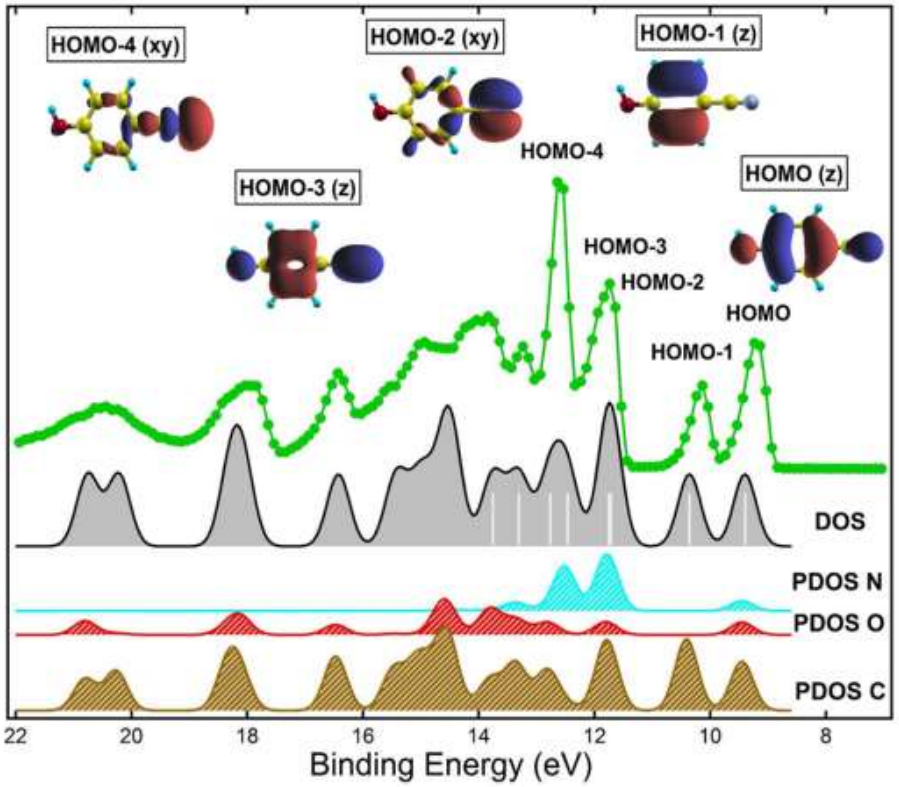




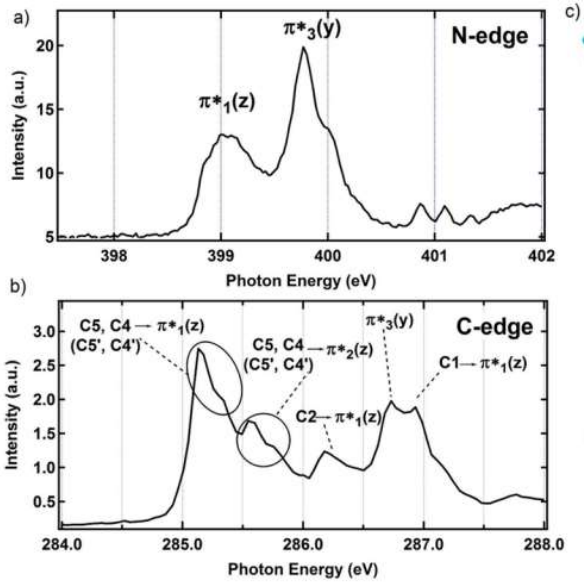
XPS
C1s

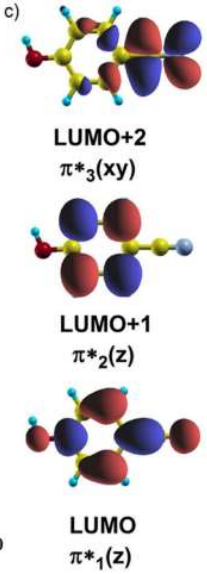


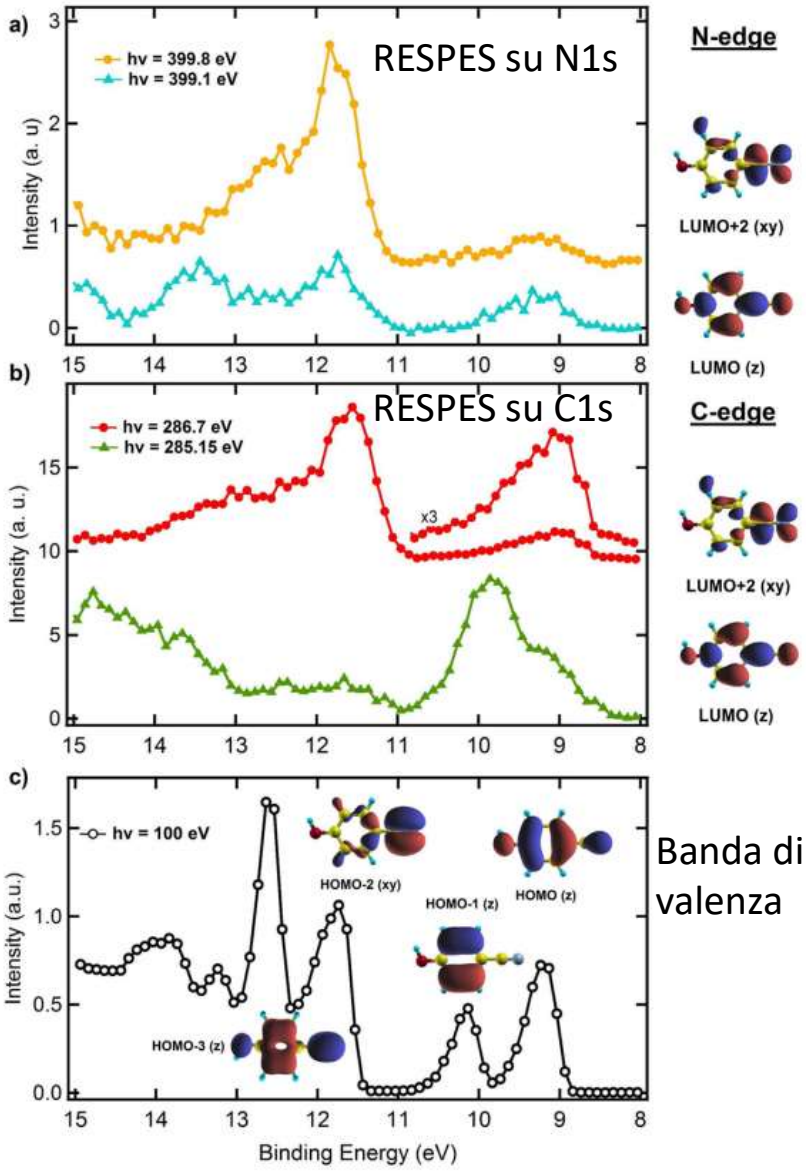
Banda di Valenza



NEXAFS





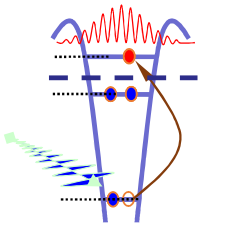


Banda di valenza

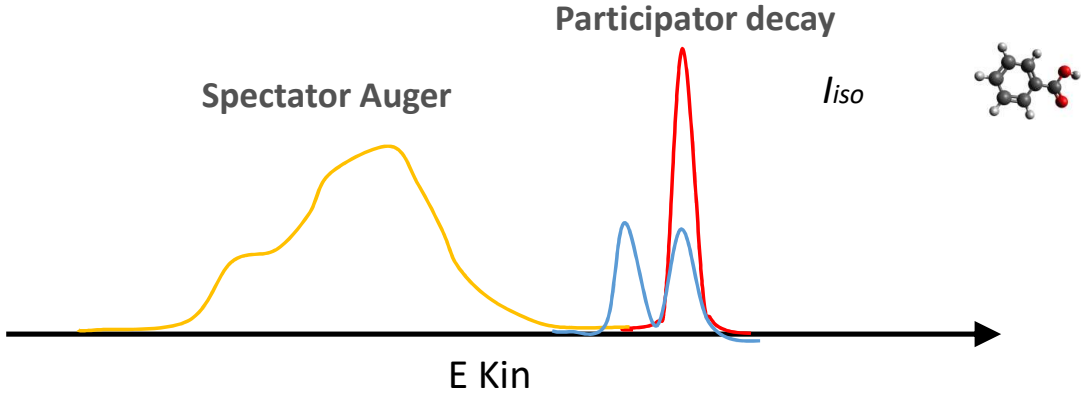
Alle energie di fotone corrispondenti alle transizioni NEXAFS 1s – LUMO(+n), risuonano gli stati HOMO (-n) che hanno un certo overlap.
Questo permette un'assegnazione chimica degli stati della banda di valenza.

Electronic coupling: ultra-fast charge delocalization

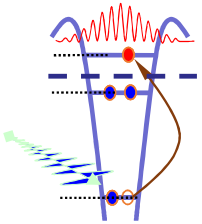
ON RESONANCE



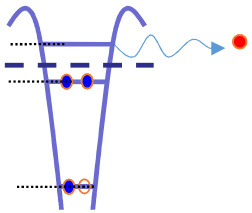
spectator
+
participator

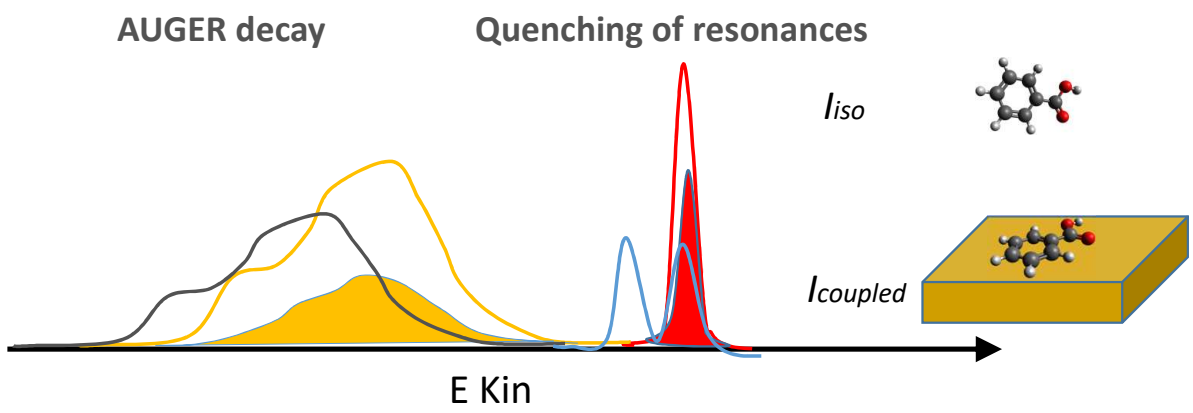


ON RESONANCE

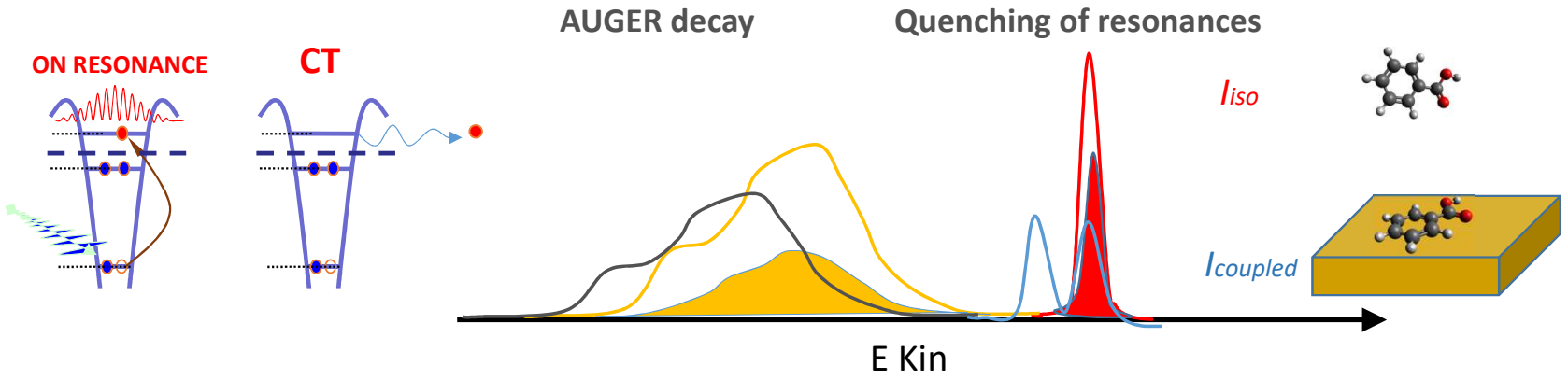


CT





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 occured 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 occured at time T

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

Probabilità che al tempo t_1 CT non sia avvenuto

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

$$\int_0^T \frac{1}{\tau_{CH}} e^{-\frac{t_1}{\tau_{CH}}} \left(1 - \int_0^{t_1} \frac{1}{\tau_{CT}} e^{-\frac{t}{\tau_{CT}}} dt \right) dt_1$$

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

probabilità che da 0 a T
l'eccitazione decada via CH

$$= \int_0^T \frac{1}{\tau_{CH}} e^{-t_1 \left(\frac{1}{\tau_{CH}} + \frac{1}{\tau_{CT}}\right)} dt_1 = \frac{\tau_{CT}}{\tau_{CH} + \tau_{CT}} \left[1 - e^{-T\left(\frac{1}{\tau_{CH}} + \frac{1}{\tau_{CT}}\right)}\right]$$

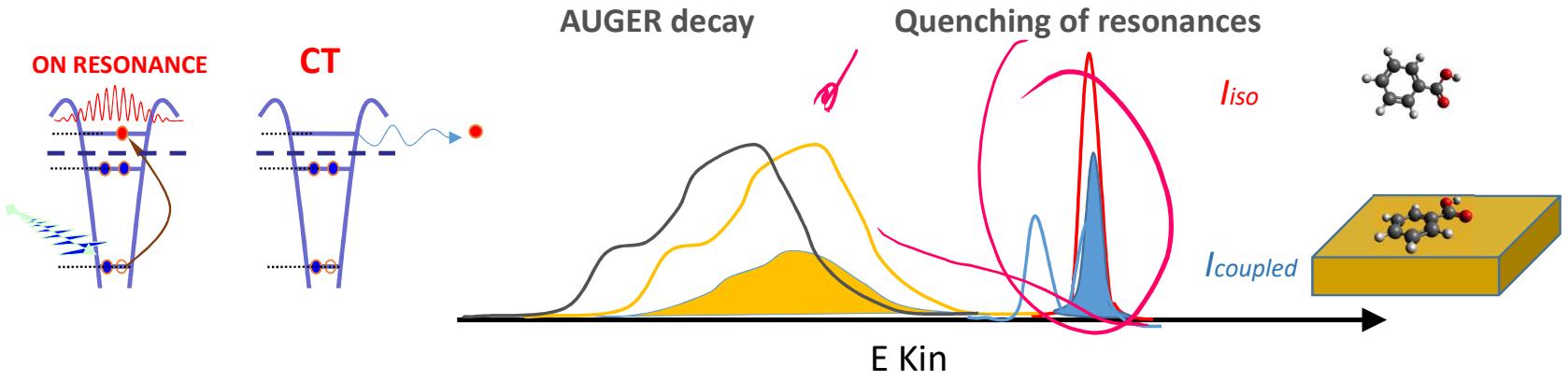
$T \approx \infty$ (ovvero molecole che hanno già subito la dissociazione)

($\tau_{CH}, \tau_{CT} \sim$ 1-100 fs, io medio su $\sim$ 0.5, 0.1 s)

$$P^{NO\ CT} = \frac{\tau_{CT}}{\tau_{CH} + \tau_{CT}}$$

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

Electronic coupling: ultra-fast charge delocalization



Core Hole Clock method

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

τ_{core}

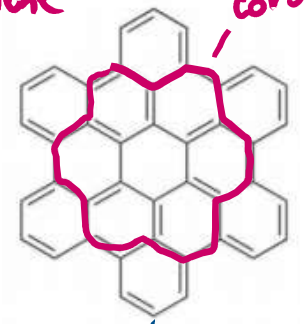
C1s ~ 6 fs
N1s ~ 6 fs
O1s ~ 4 fs

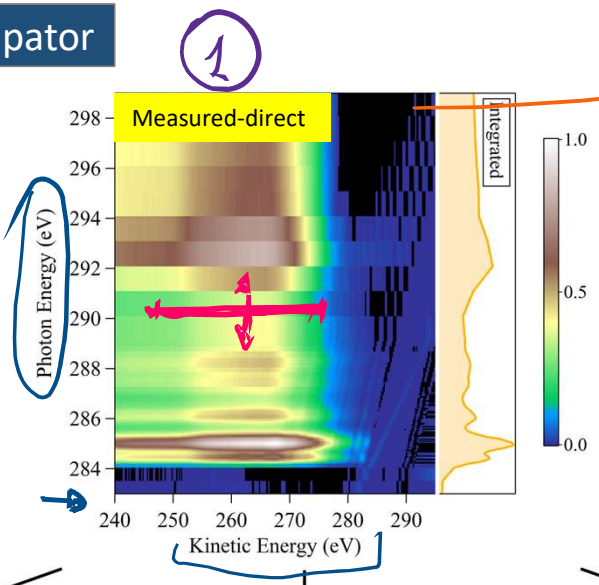
Clock in the 0-50 fs range

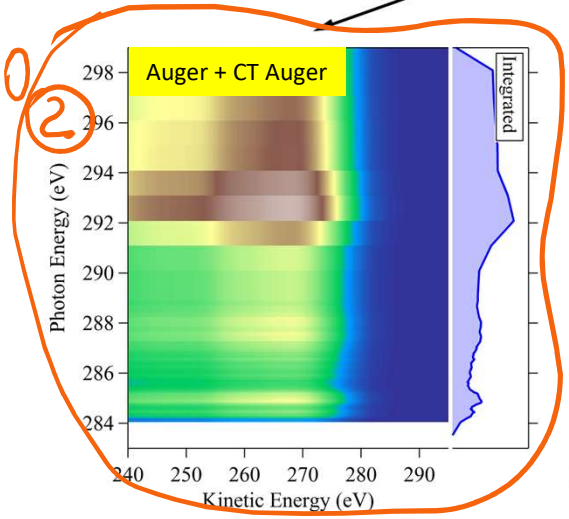
P. A. Brühwiler et al., Rev. Mod. Phys. (2002)

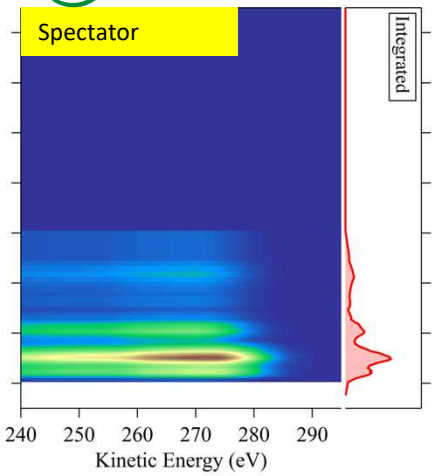
The data analysis: Auger+Spectator+Partecipator

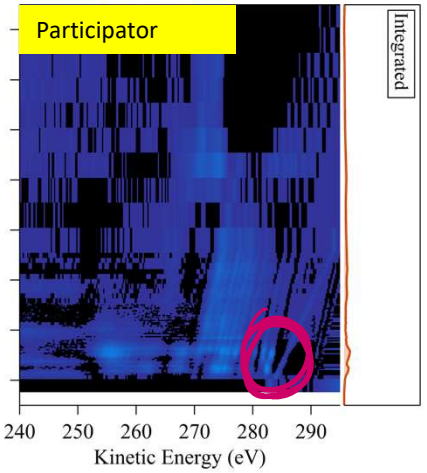
Spectral decomposition







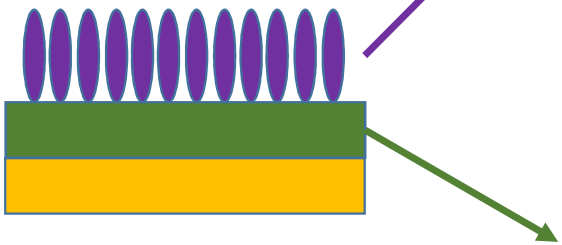


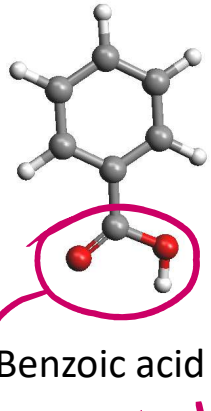


Misurata la mappa RESPES, si individuano le diverse component di decadimento (Auger, Spectator, Participator)
Questo permette di individuare le intensità da utilizzare nel metodo core-hole clock

coll. **J. Kymissis**, Adv. E. Mat., 2013

Amino-carboxylic anchoring

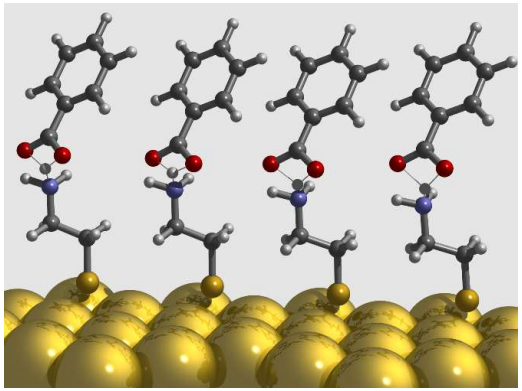


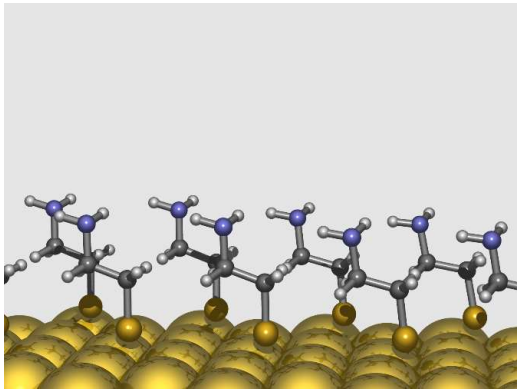


Benzoic acid

COOH affinité chimique

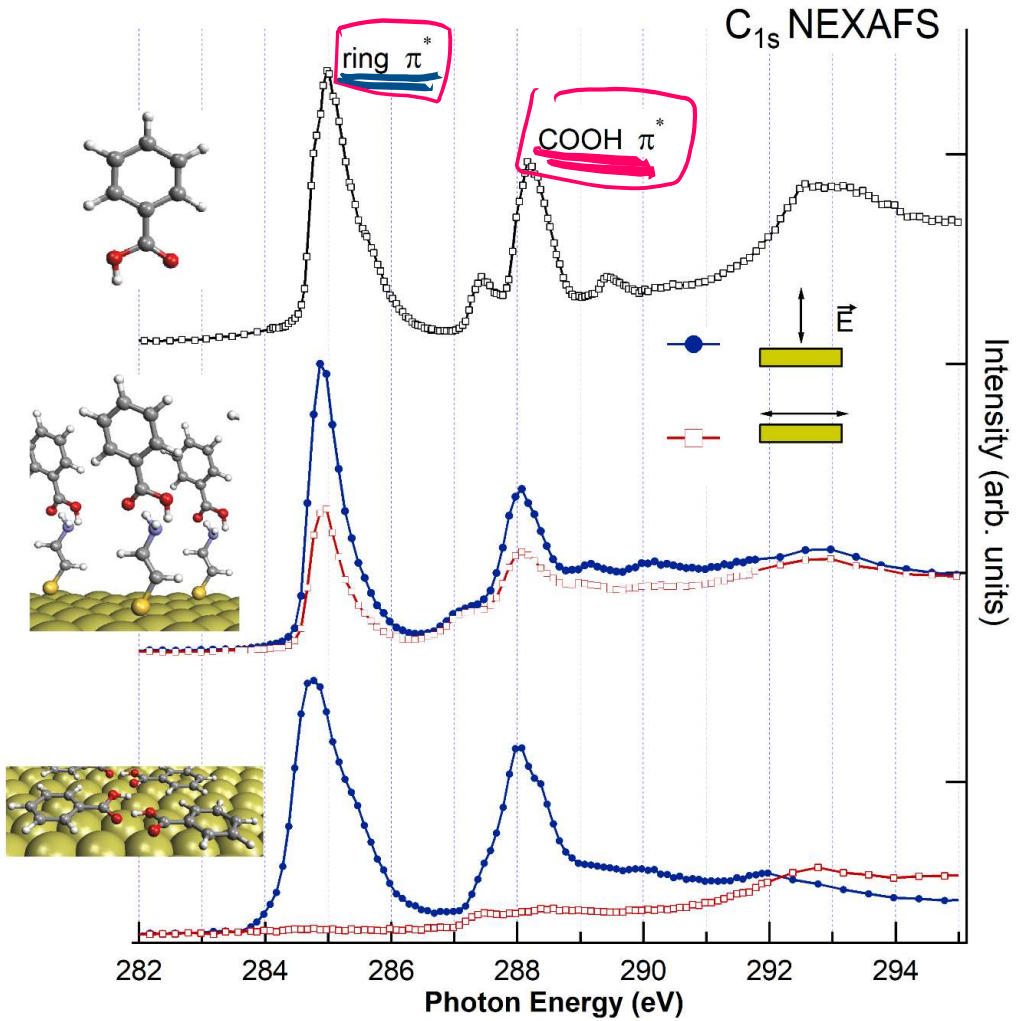
NH_2

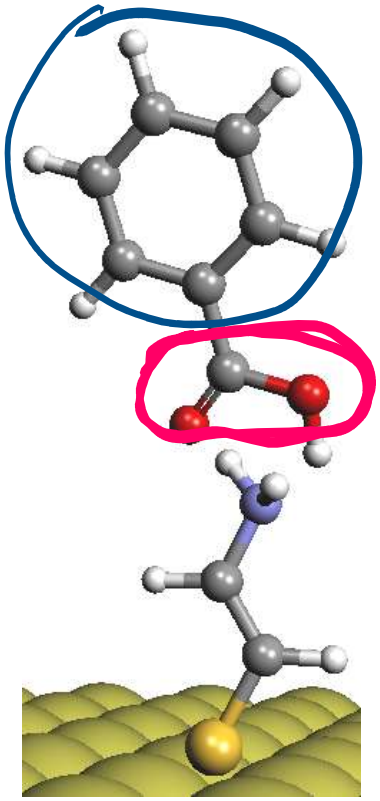


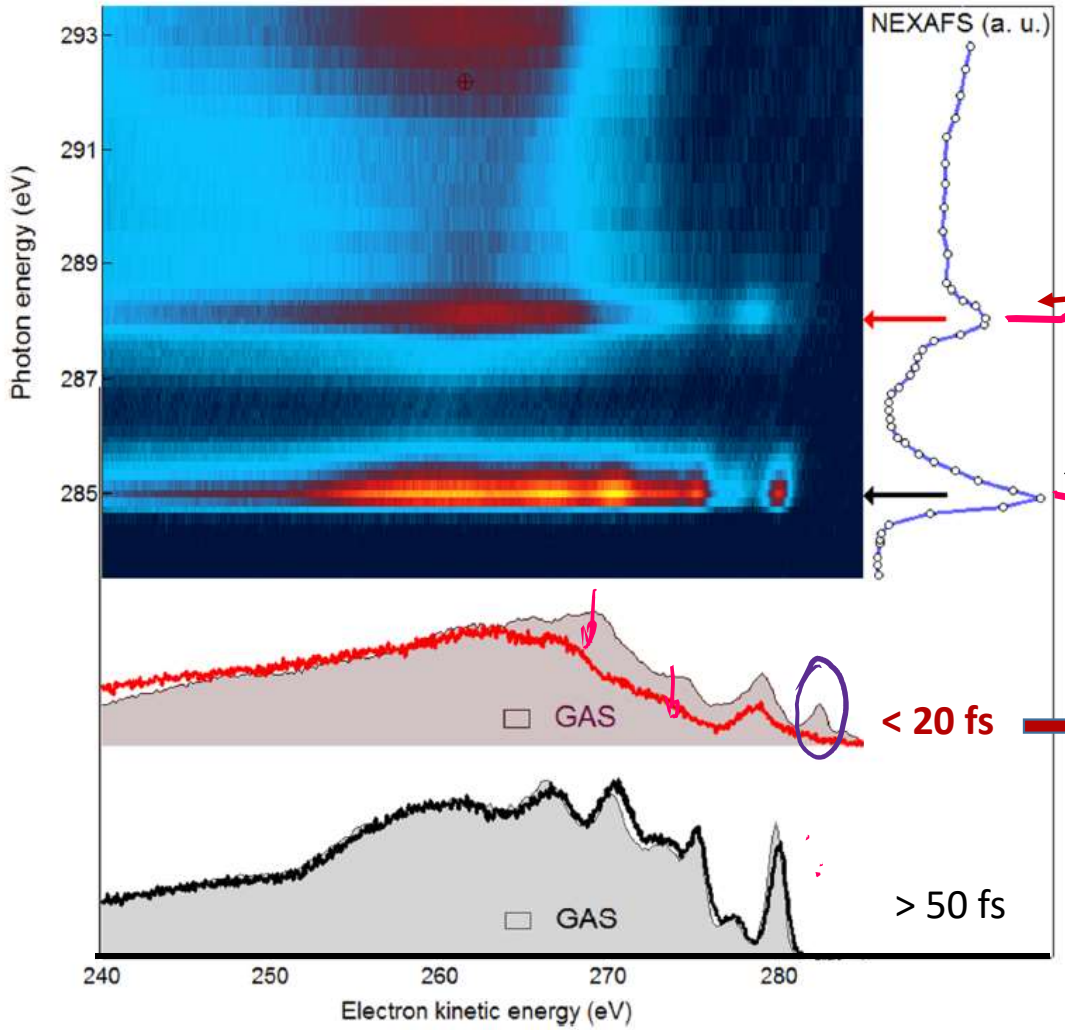


Cysteamine/ Au(111)

The ANCHOR Lab: multi-technique approach

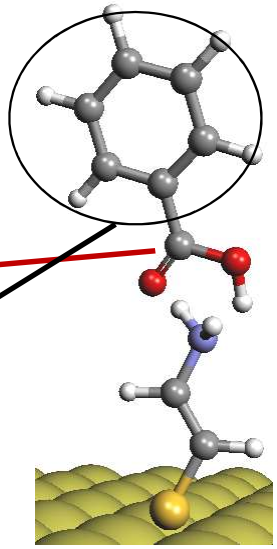






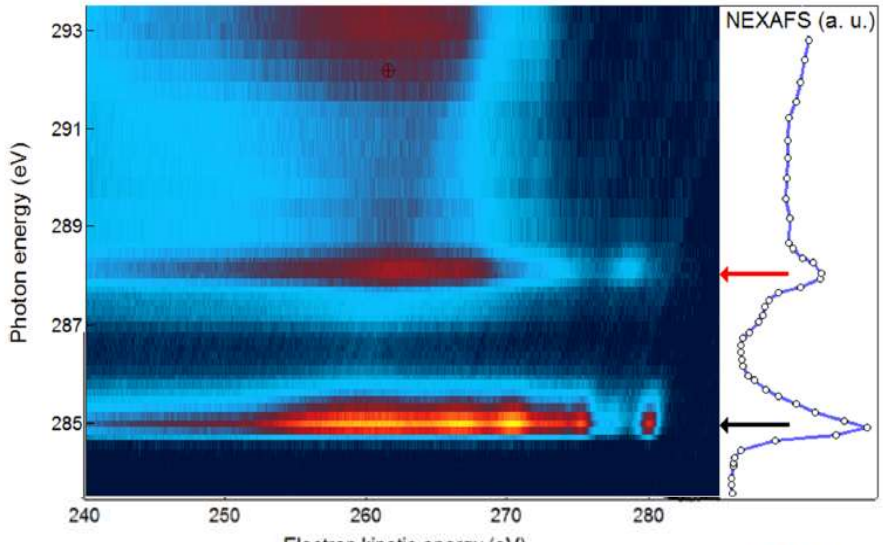
< 20 fs

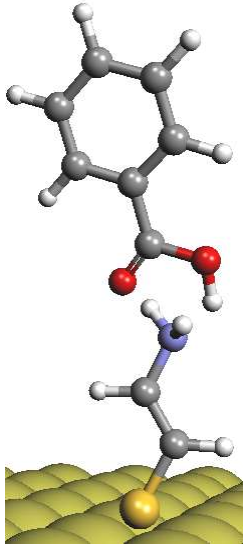
> 50 fs

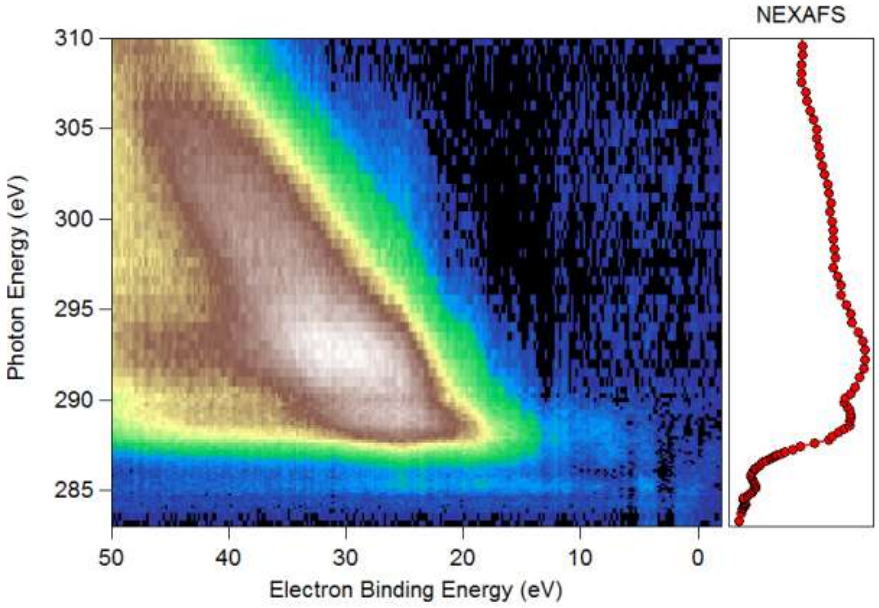


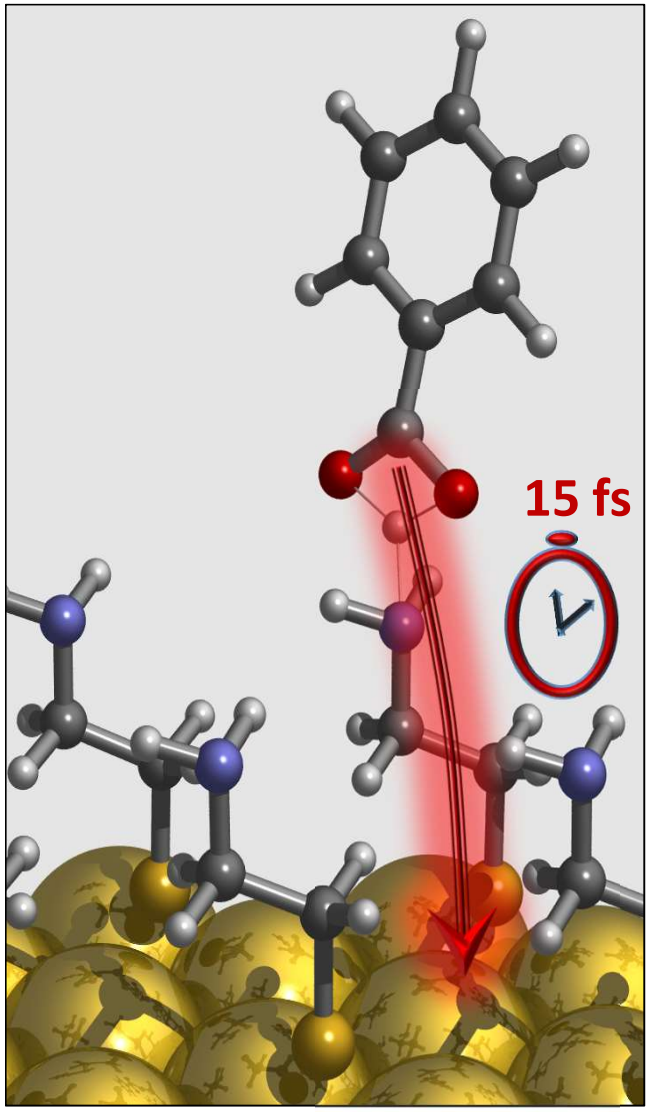
amino-carboxylic bond promotes ultra-fast delocalization

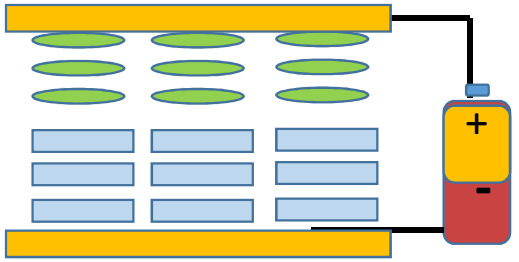
Nanoletters, 2015

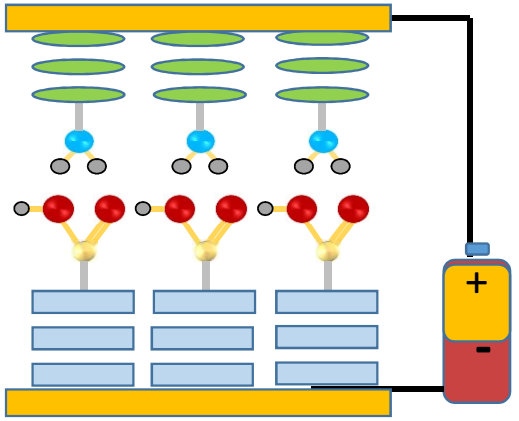

NEXAFS (a. u.)
Photon energy (eV)
293
291
289
287
285
240
250
260
270
280




NEXAFS
Photon Energy (eV)
310
305
300
295
290
285
50
40
30
20
10
0
Electron Binding Energy (eV)


15 fs

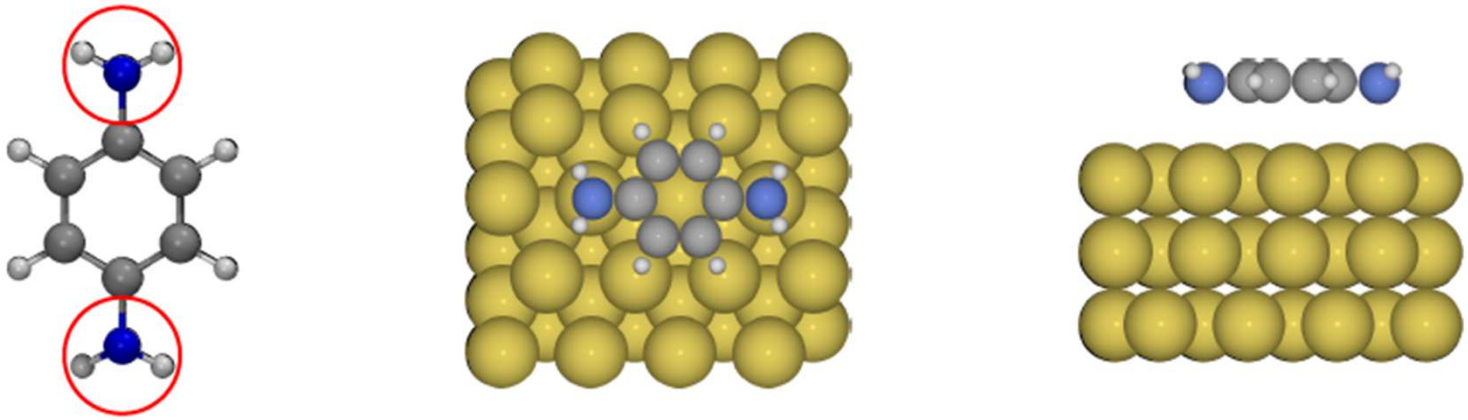

+
-


+
-

Break junction results vs X-ray spectroscopy

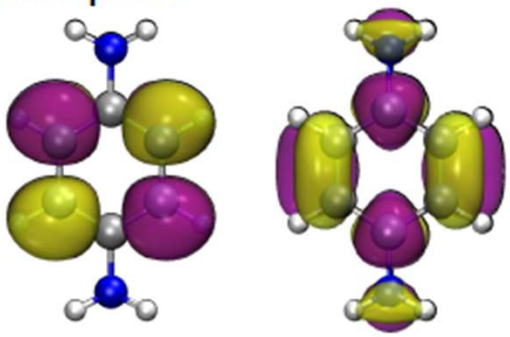
Tracking fast electrons at organic interfaces …

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



- Two amine groups with donating electron lone-pairs

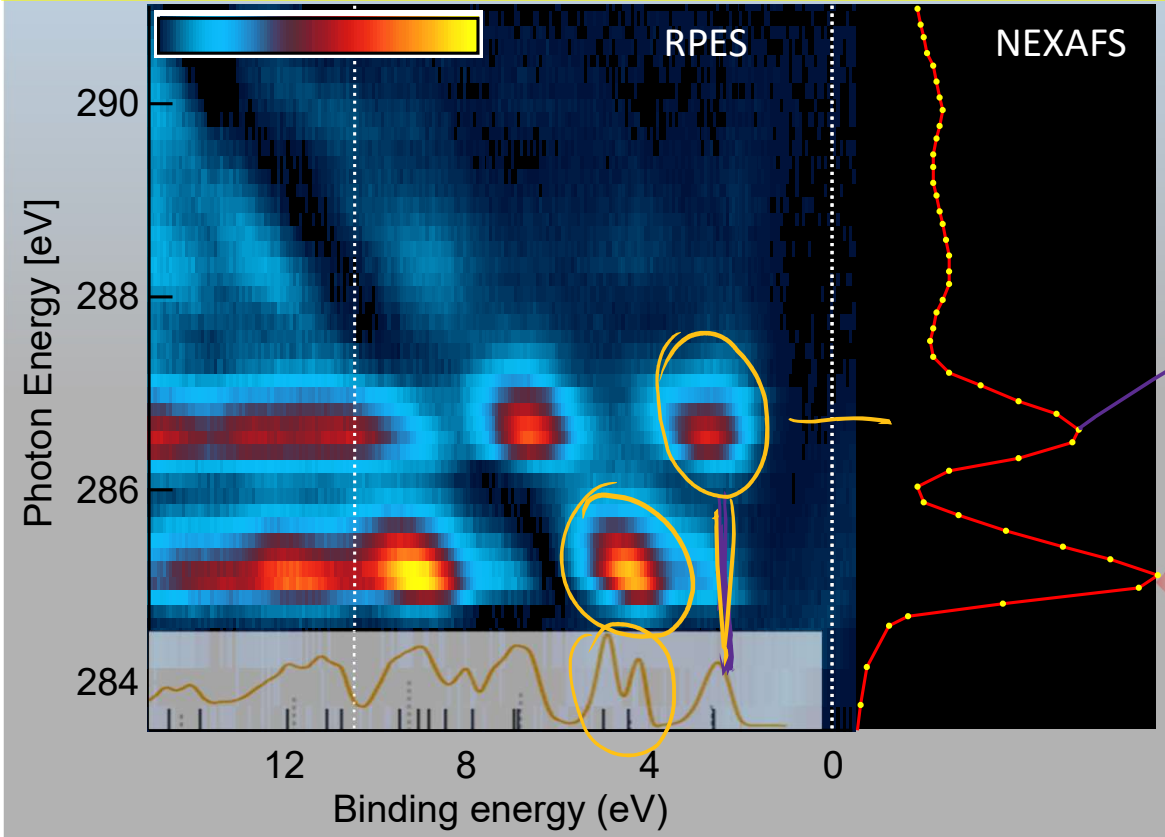
- We exploit specific LUMO (LUMO+1) symmetry & spatial distribution over the atomic sites

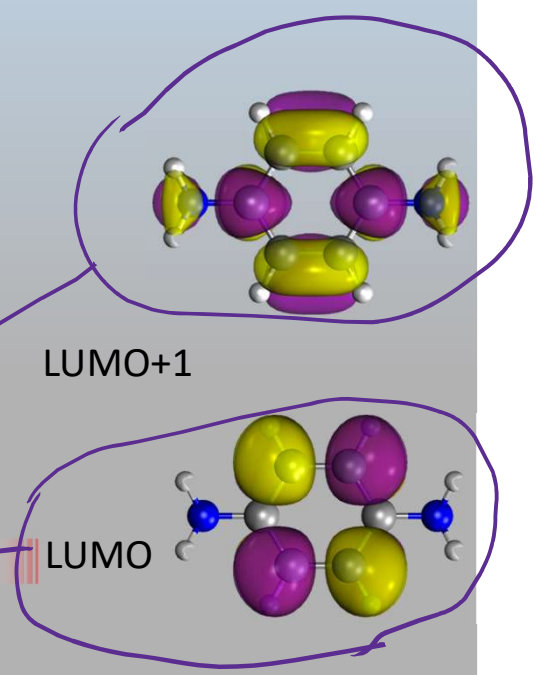


S.Y.Quek et al., Nano Lett., 7 3447 (2007)

Resonant Photoemission

Tracking fast electrons at organic interfaces …

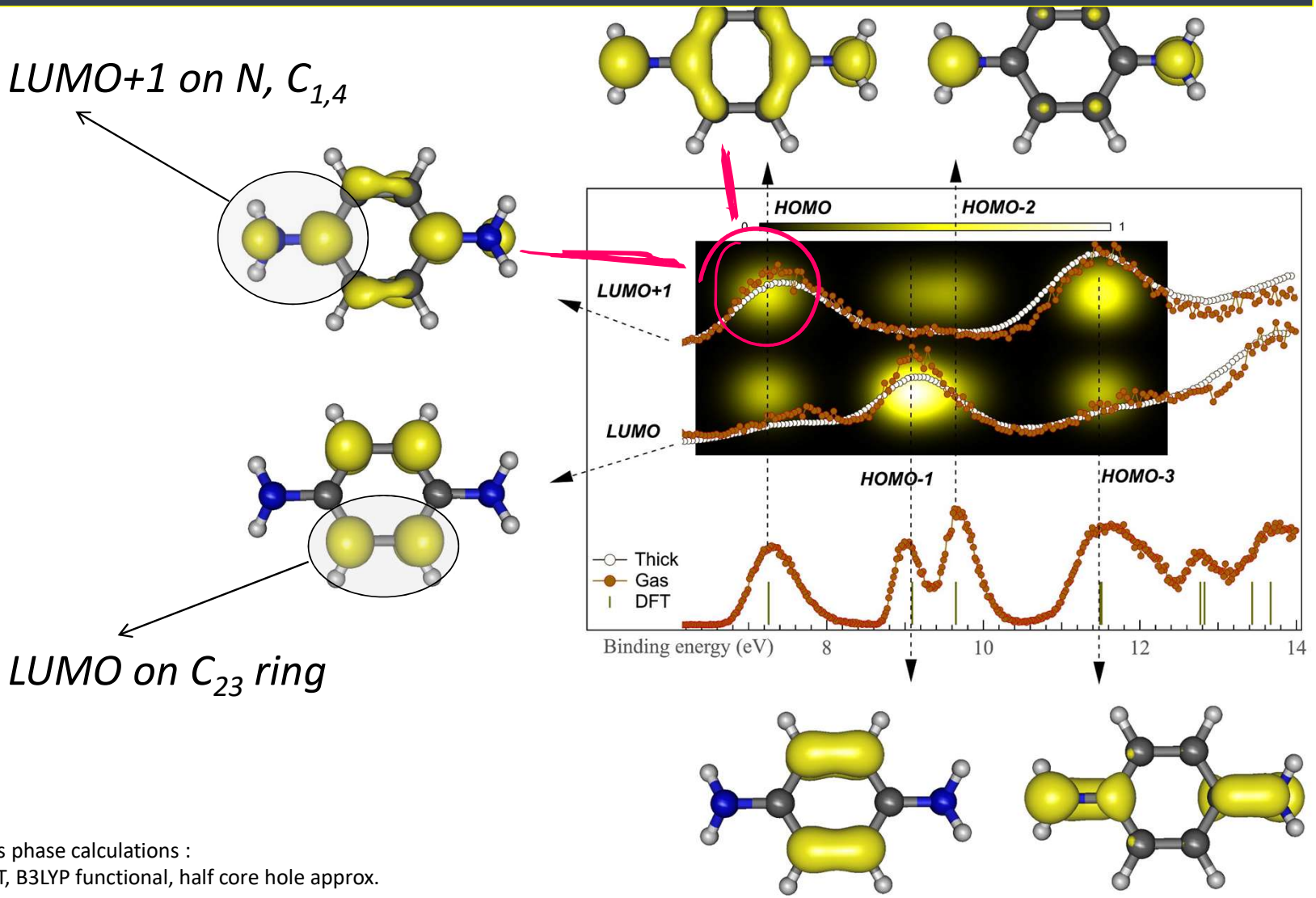




- *Measure XPS spectra with hv tuned across absorption edge*
- *VB resonances* ➔ *Absorption & Hole decay via Autoionization*

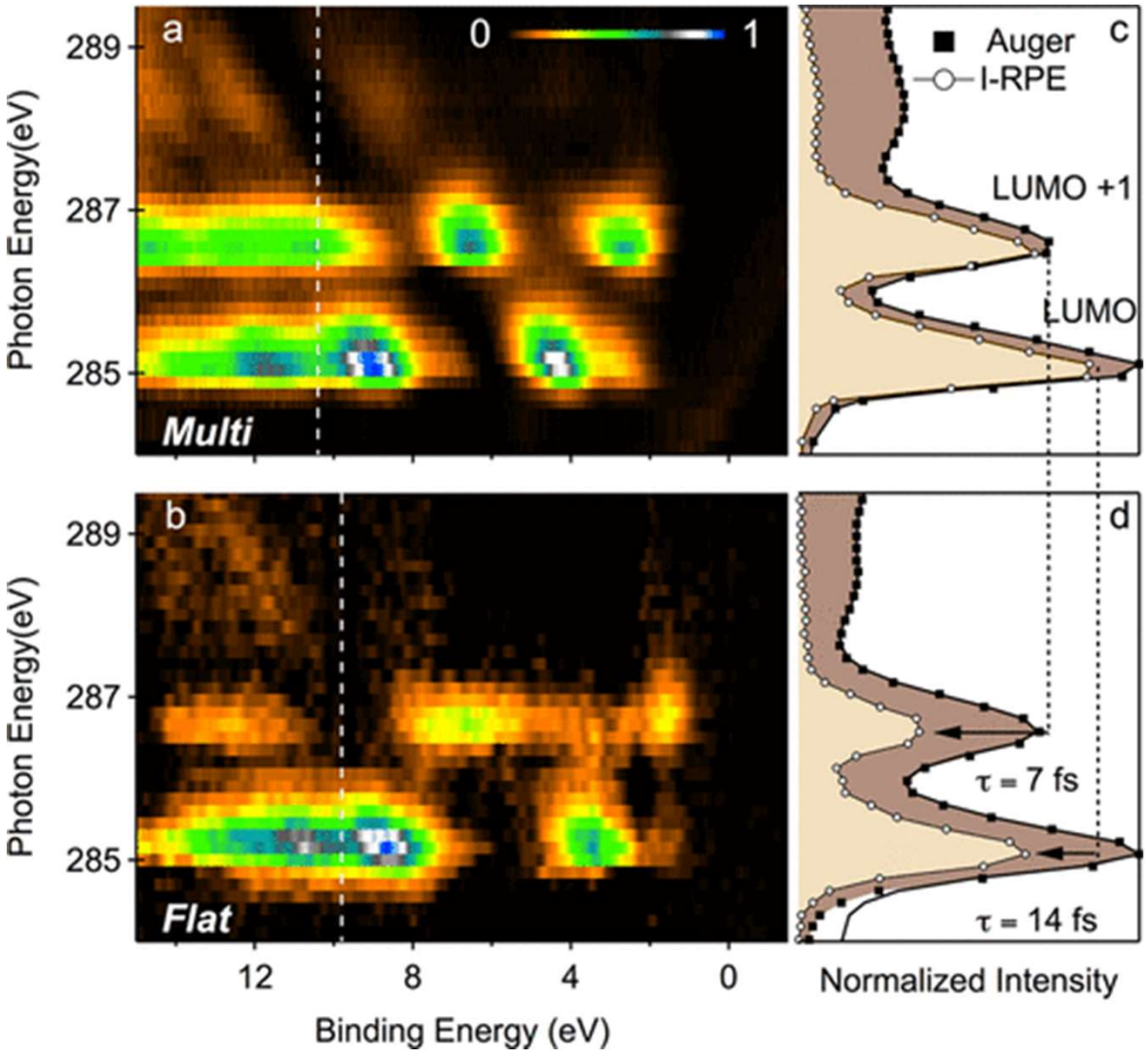
RPES and Orbital Overlap

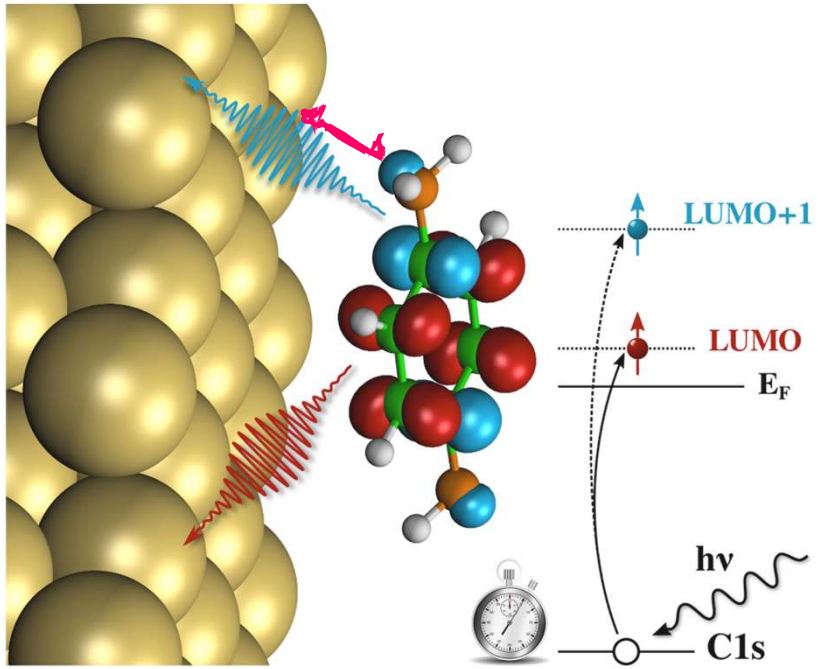
Tracking fast electrons at organic interfaces …



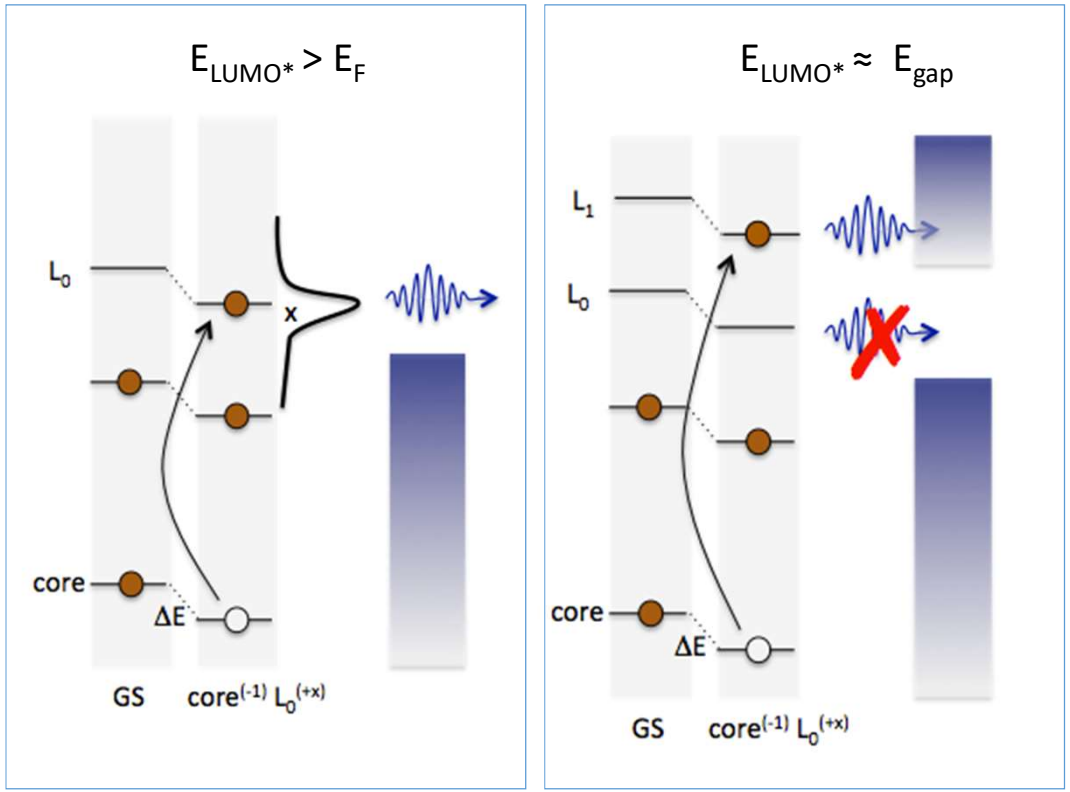
Gas phase calculations :
DFT, B3LYP functional, half core hole approx.

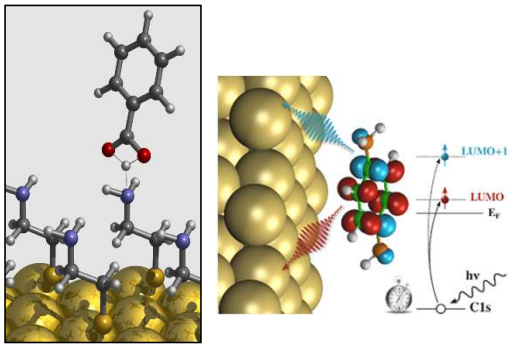
Dell'Angela et al., Nano Lett . (2013)

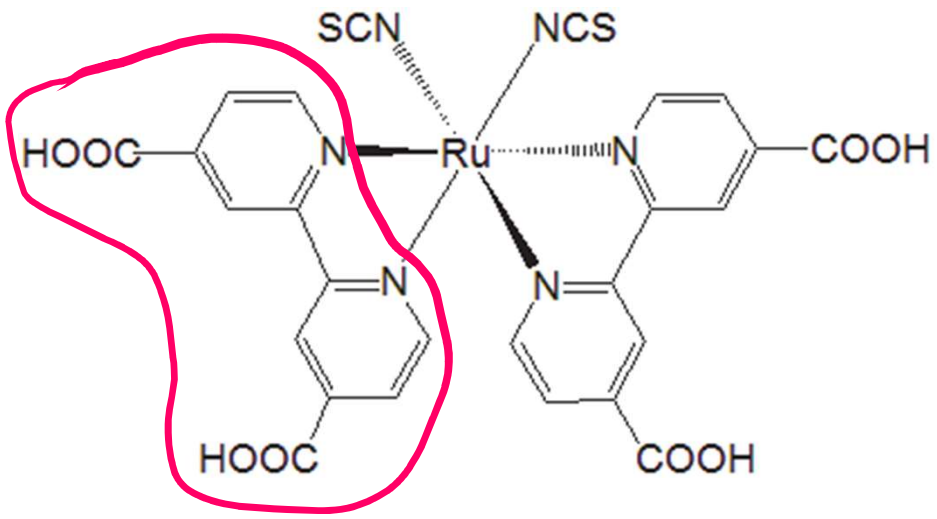

a
0
1
289
287
285
Photon Energy(eV)
Multi
c
Auger
I-RPE
LUMO +1
LUMO
b
Flat
d
τ = 7 fs
τ = 14 fs
12
8
4
0
Binding Energy (eV)
Normalized Intensity


LUMO+1
LUMO
E_F
hν
C1s

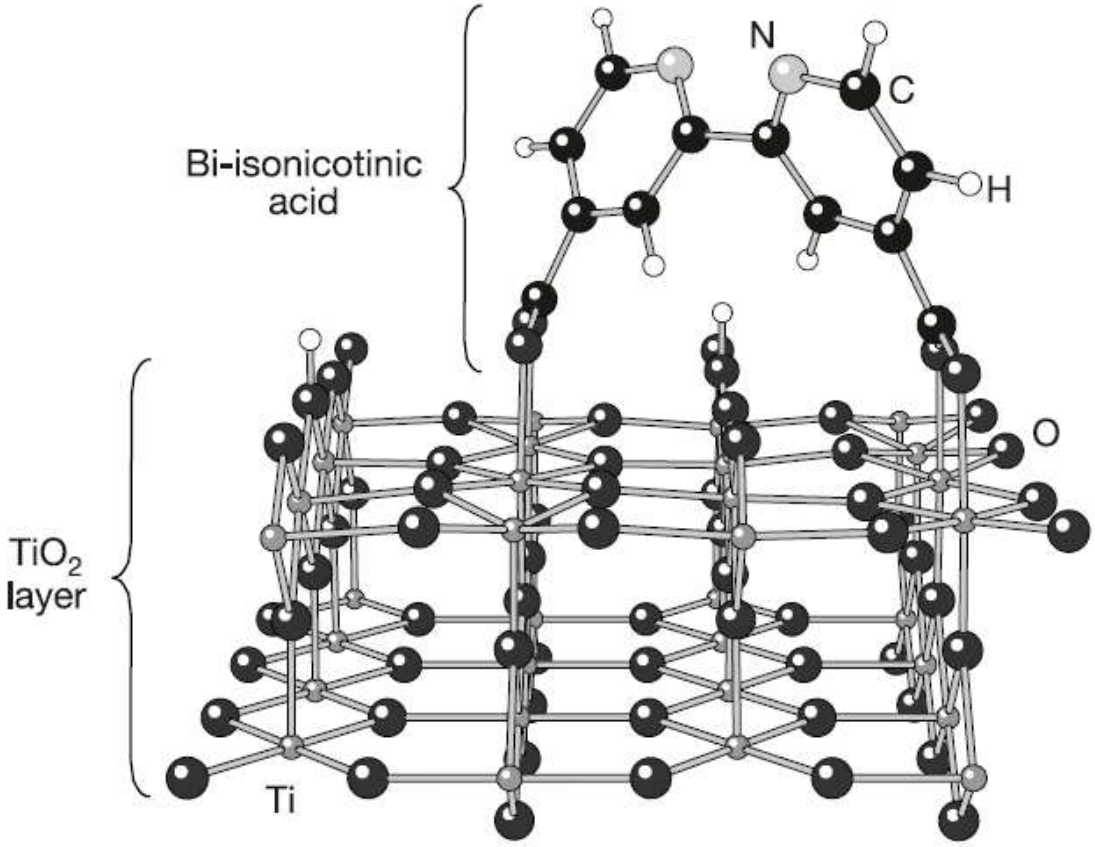
CHC and LUMO energy level alignment





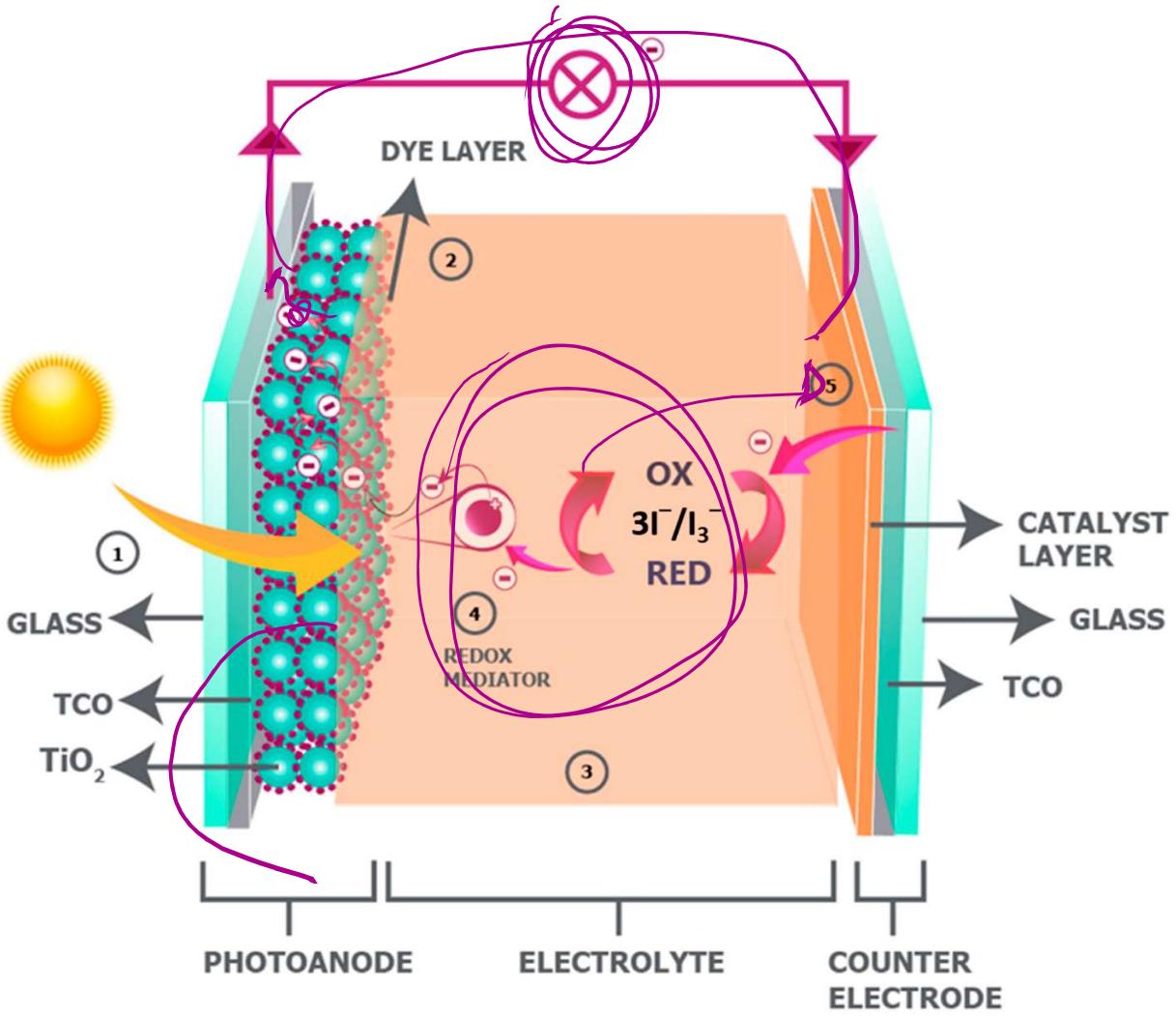

SCN
NCS
HOOC
N
Ru
N
COOH
N
N
HOOC
COOH

Dye N3


Bi-isonicotinic acid
N
C
H
O
TiO_2 layer
Ti

Dye-sensitized solar cell

Cella di Grätzel



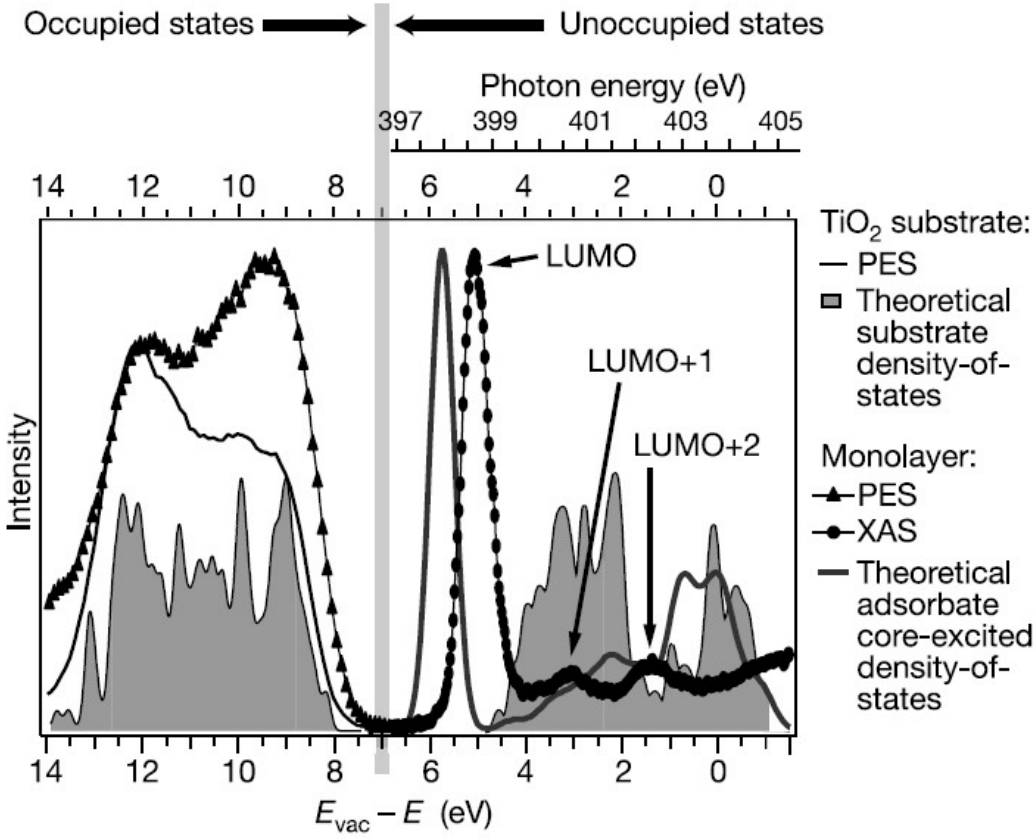
TiO_2

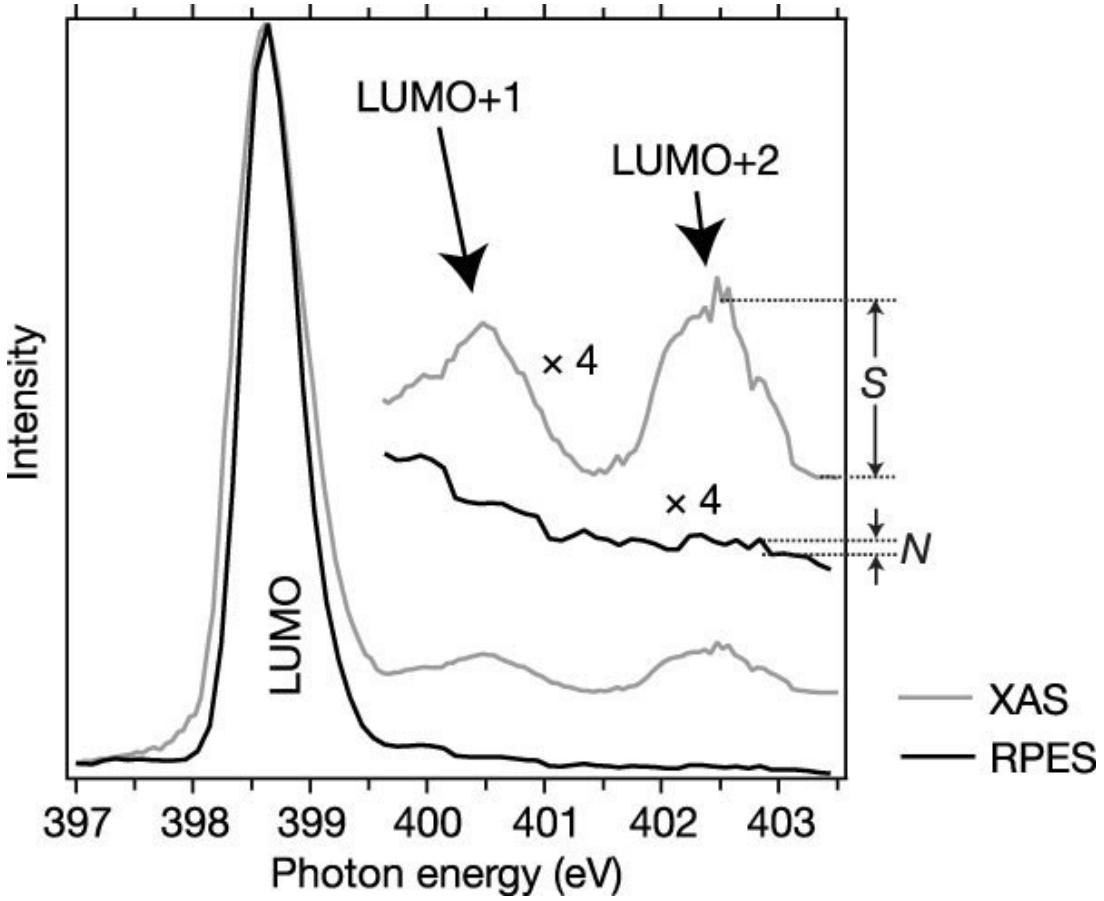
All'interfaccia dye-TiO2 avviene la separazione dell'eccitone creato dall'assorbimento della luce visibile.

$$2(Dye)^+ + 3I^- \rightarrow 2Dye + I_3^-$$

$$I_3^- + 2e^- \rightarrow 3I^-$$

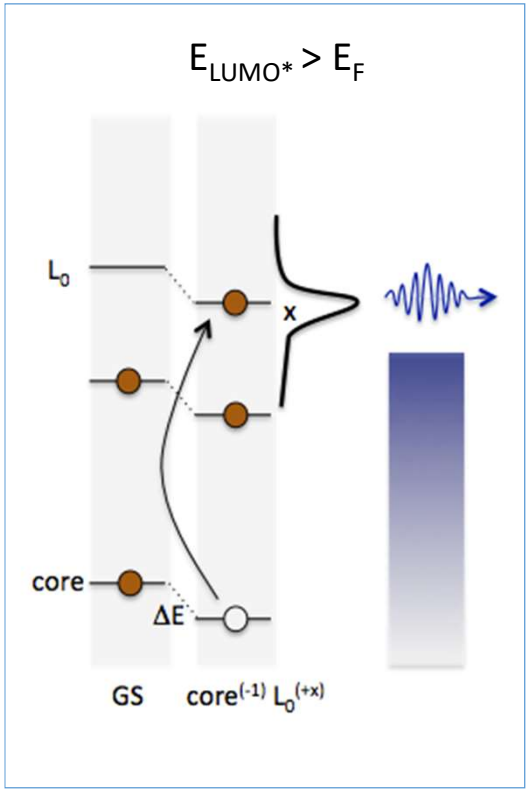
Materials **2019**, *12*, 1998; doi:10.3390/ma12121998

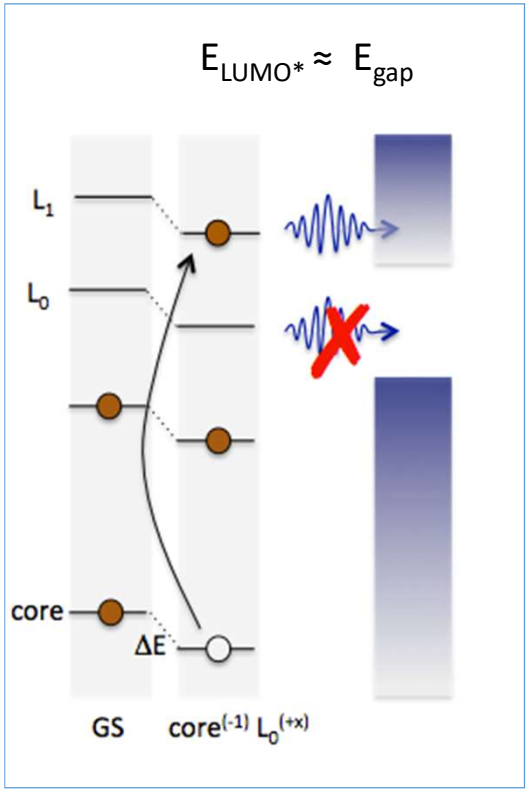


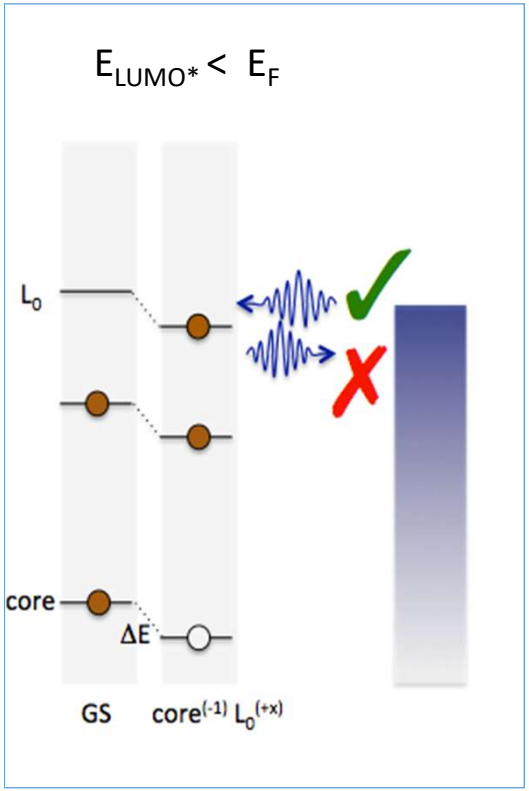


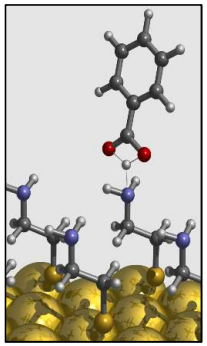
Brittton et al., Phys. Rev. Lett. 109, 017401 2012

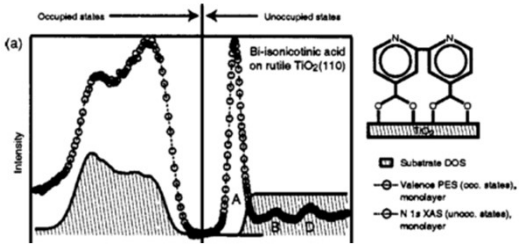
CHC and LUMO energy level alignment



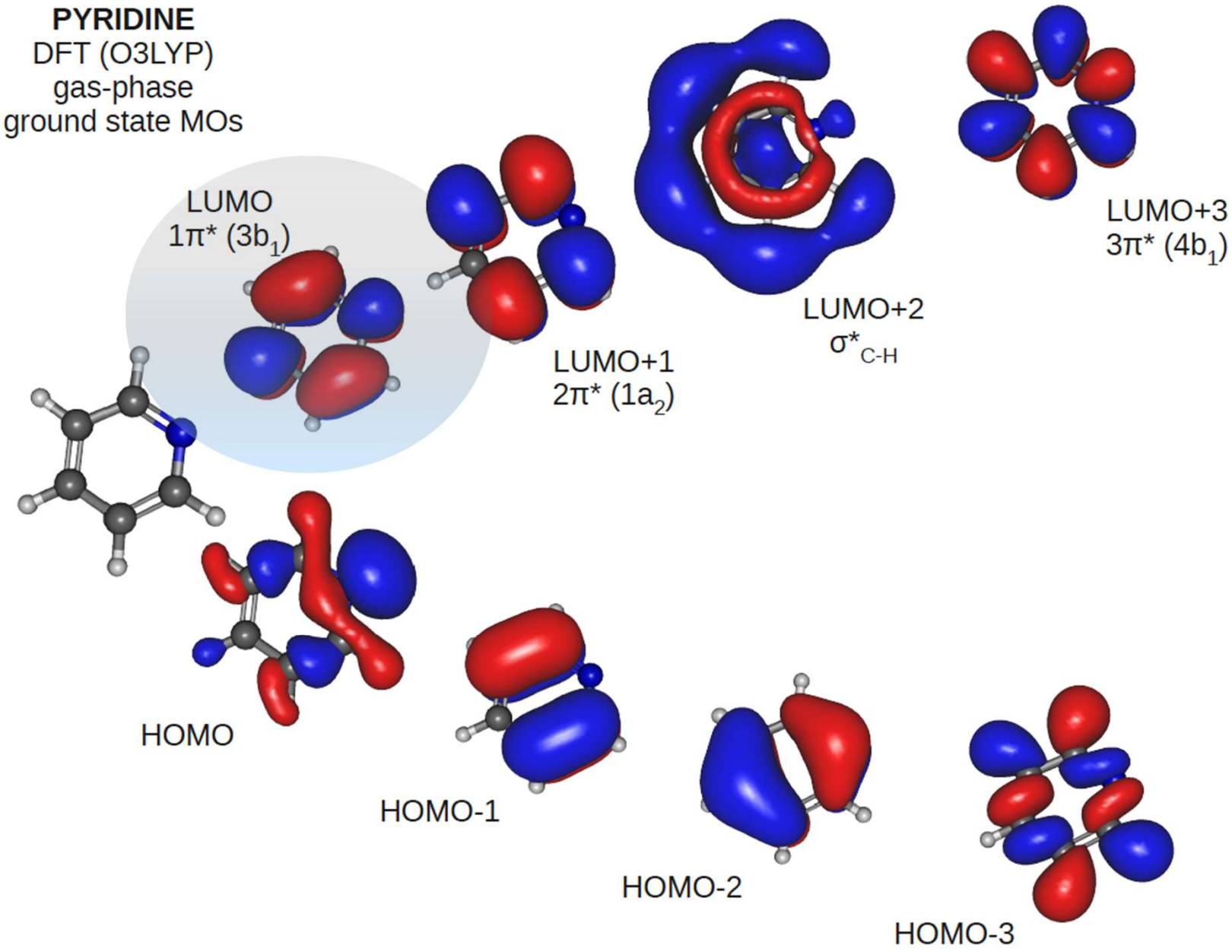


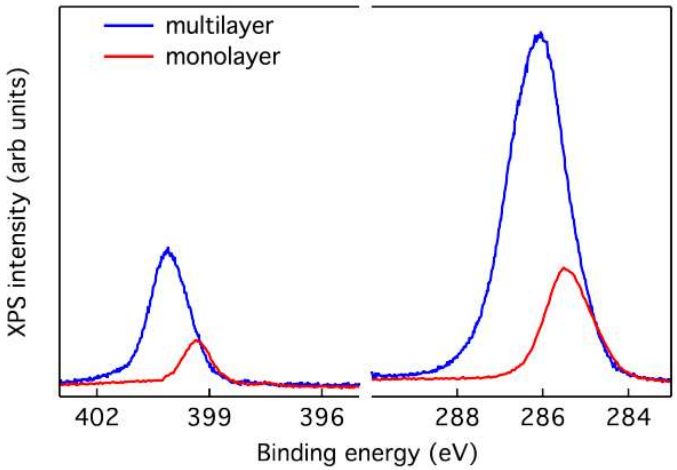




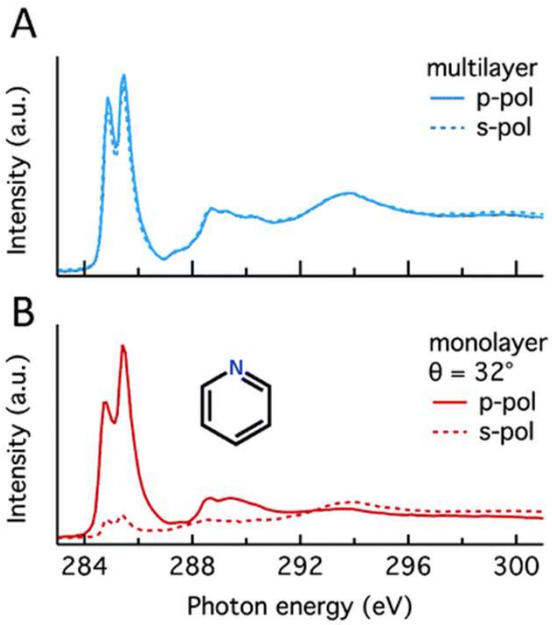


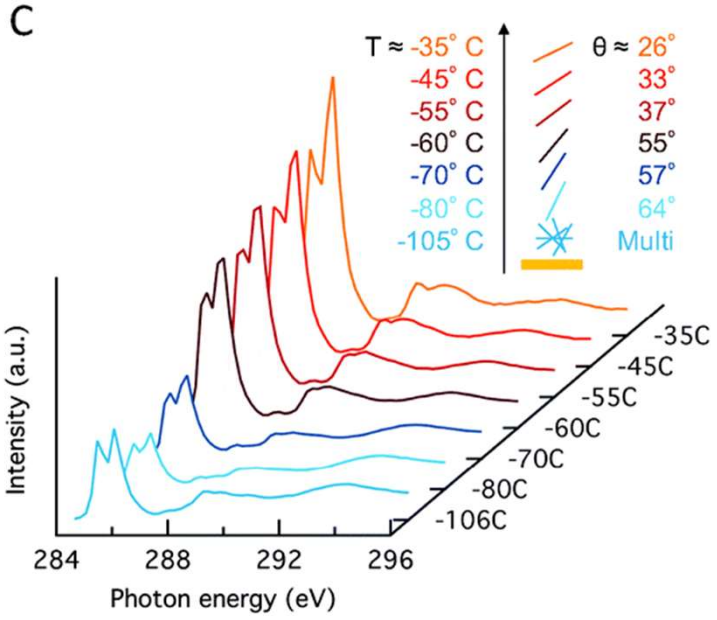
Brittton et al., Phys. Rev. Lett. 109, 017401 2012

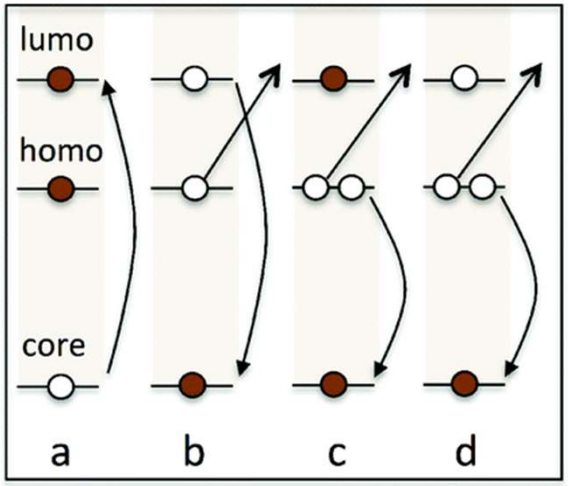

PYRIDINE
DFT (O3LYP)
gas-phase
ground state MOs
LUMO
1π* (3b1)
LUMO+1
2π* (1a2)
LUMO+2
σ*C-H
LUMO+3
3π* (4b1)
HOMO
HOMO-1
HOMO-2
HOMO-3

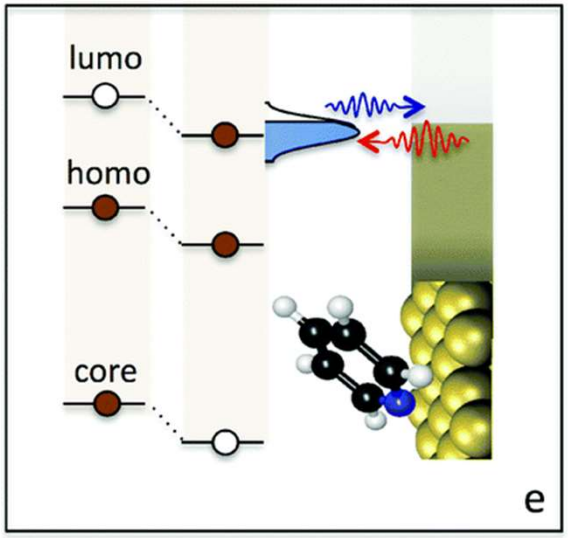


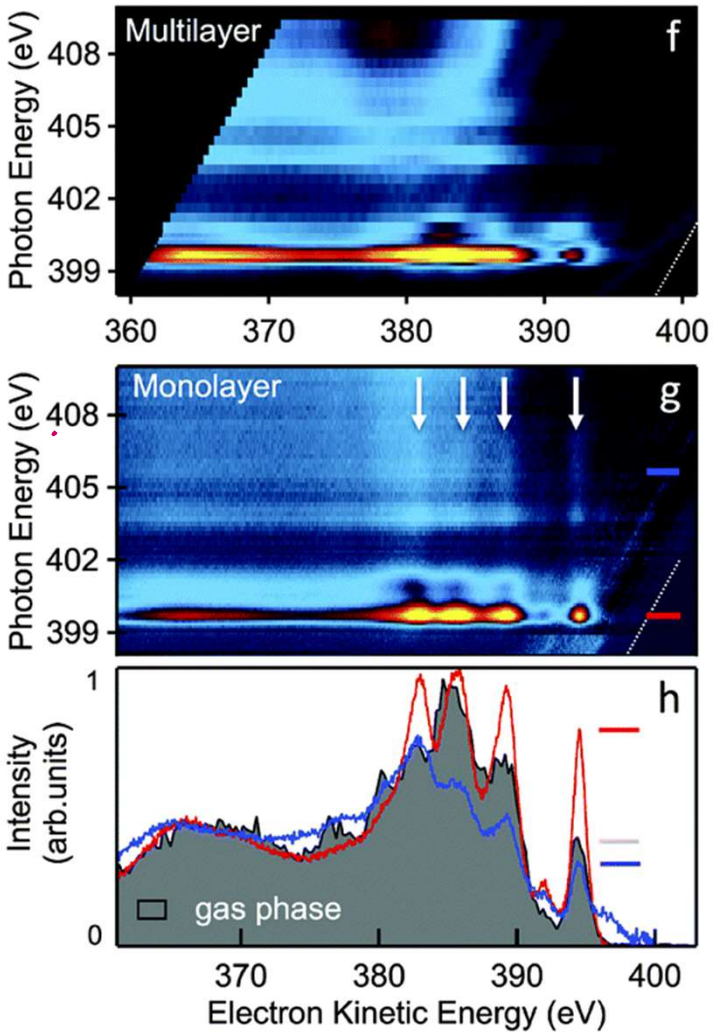
Pyridine/Au(111)









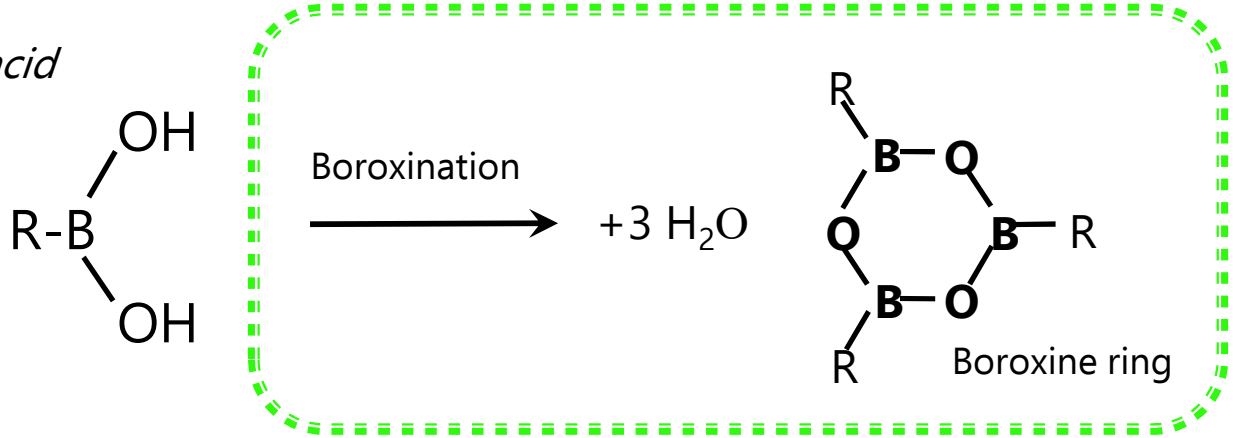


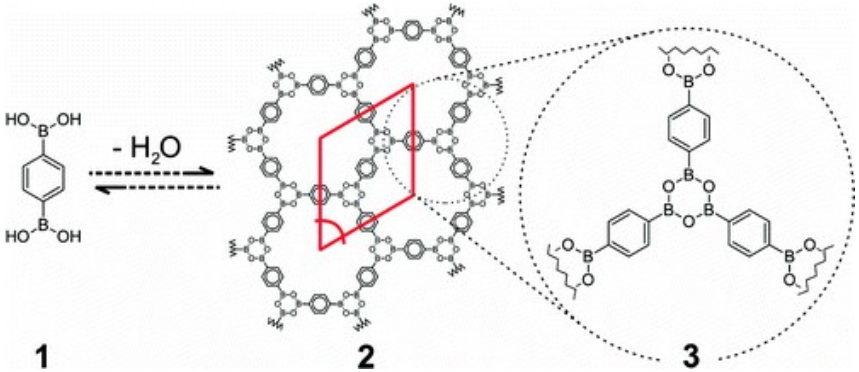
Le frecce bianche indicano l'intensità di tipo partecipator, che deriva dal trasferimento di un elettrone dal substrato alla molecola ionizzata. Tale processo avviene per hv > IP e non è presente ovviamente nel multilayer, dove non c'è contatto delle molecule con il substrato

Spectator shift…

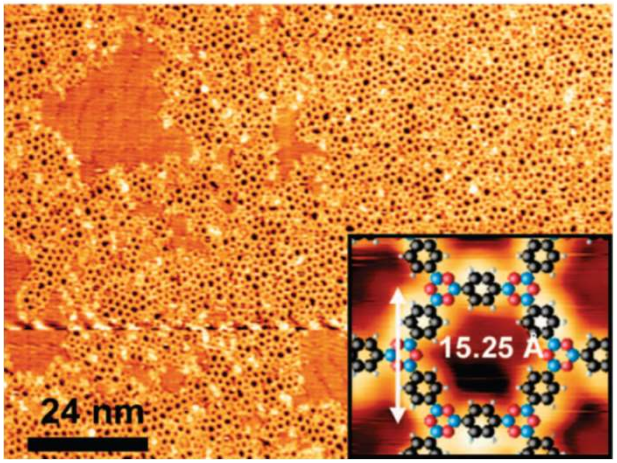
On- surface boroxination

Boronic acid



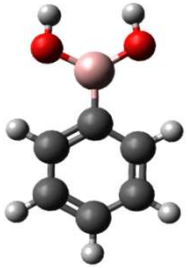


J.F. Dienstmaier et al., ACS Nano, 5, 12, 9737-9745

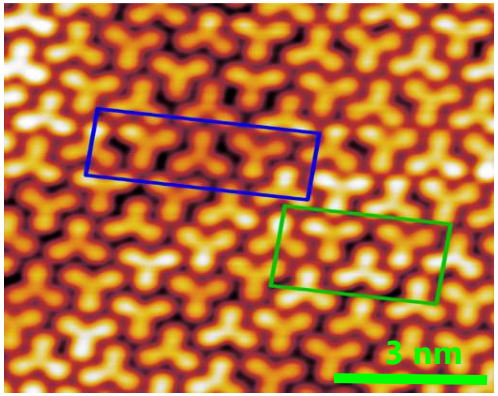


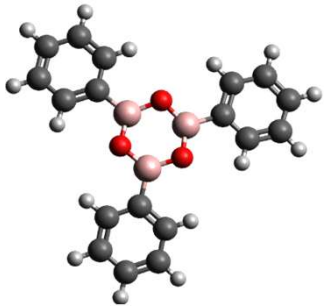
T. Faury et al., J. Phys. Chem. C 2012, 116, 4819−4823

On-surface synthesis of boroxine molecule

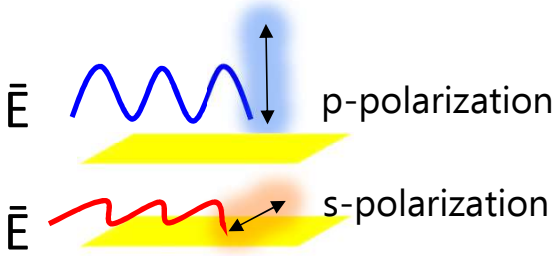


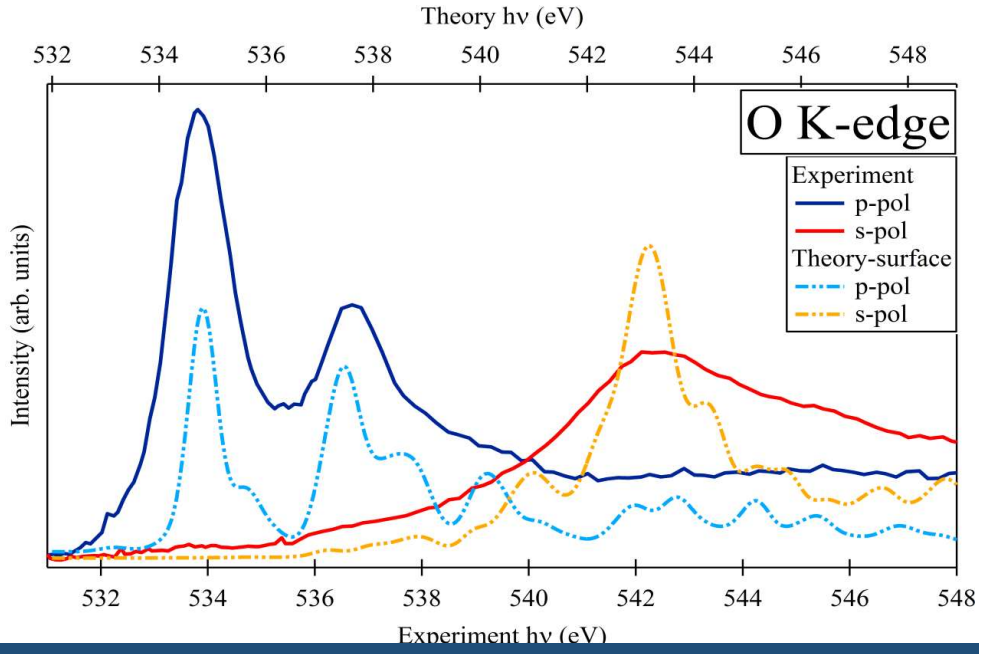
Phenylboronic acid
on Au(111)





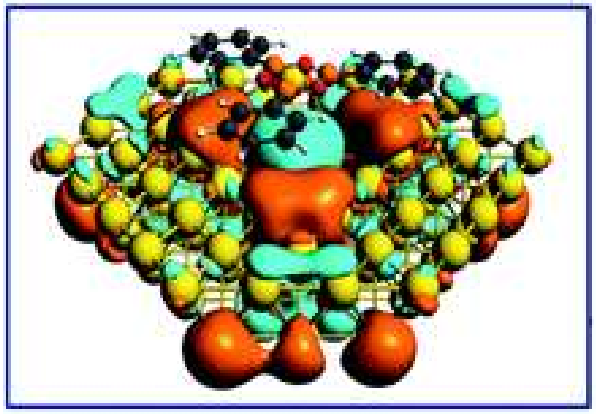
On surface synthesis
Triphenylboroxine

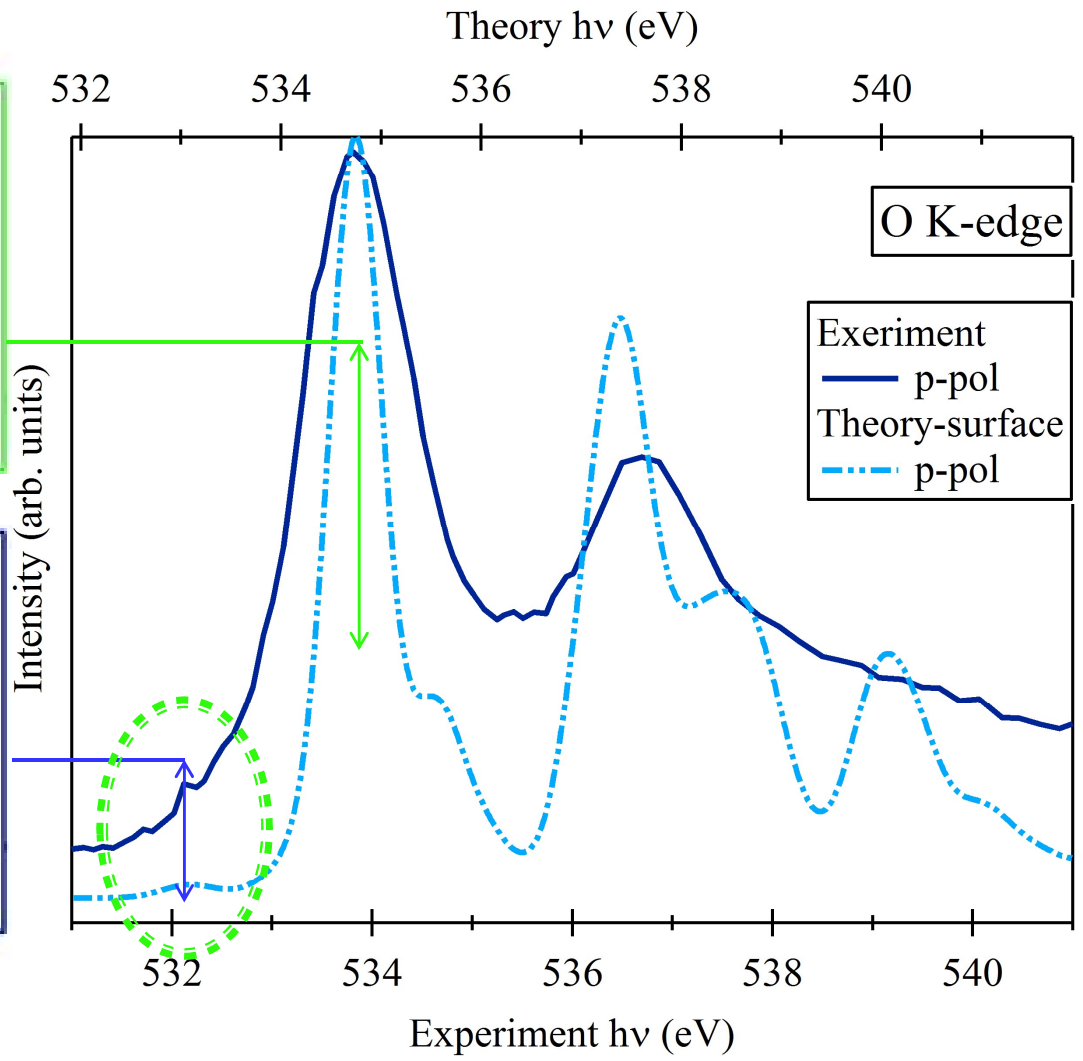




Toffoli et al., **Chem. Sci., 2017**, 8, 3789-3798

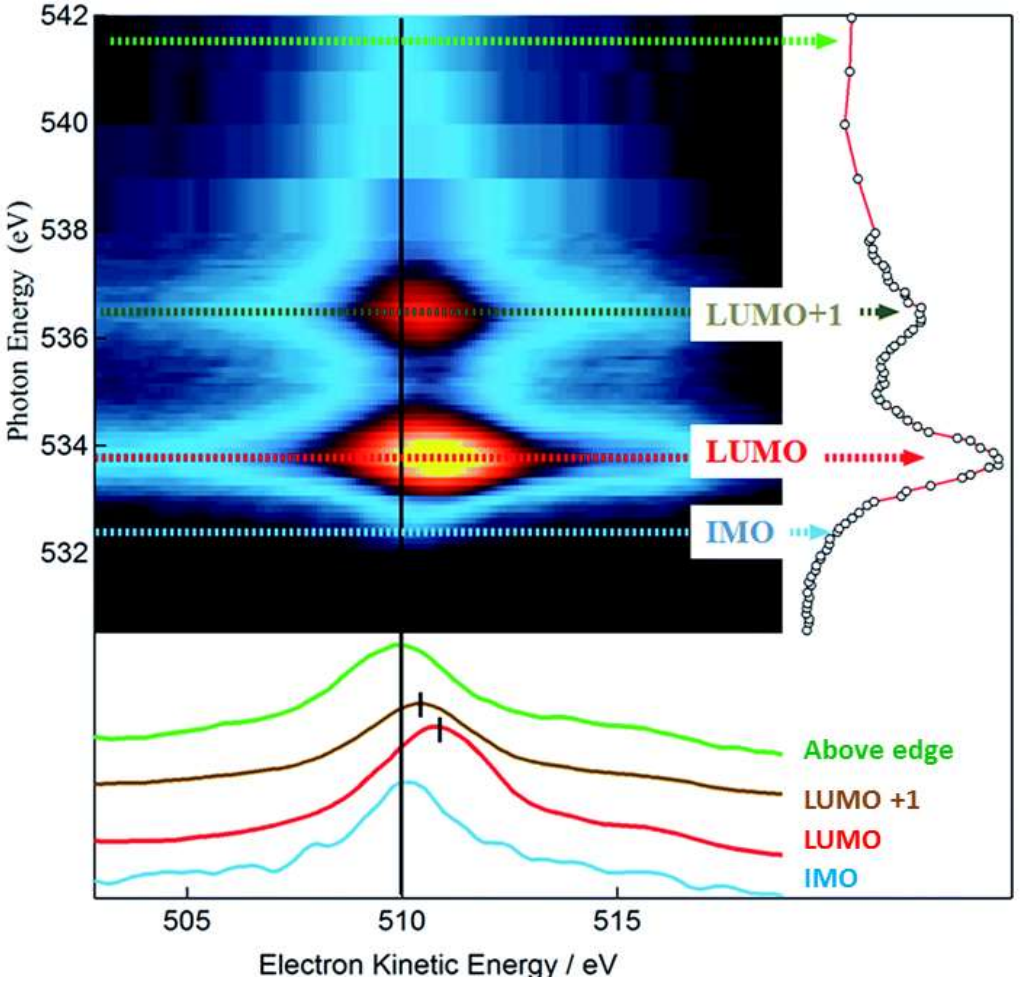
O k-edge NEXAFS + DFT: evidence of interface molecular orbital (IMO)





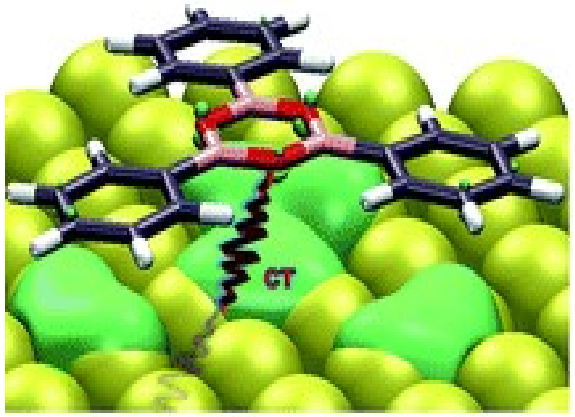
Chem. Sci., 2017

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



platforms for

ultrafast charge transfer



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