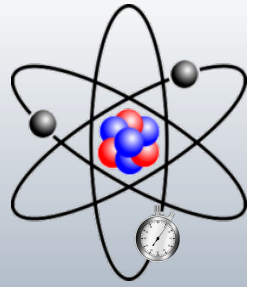
Ultrafast electron transfer at molecular interfaces by core-hole clock spectroscopy

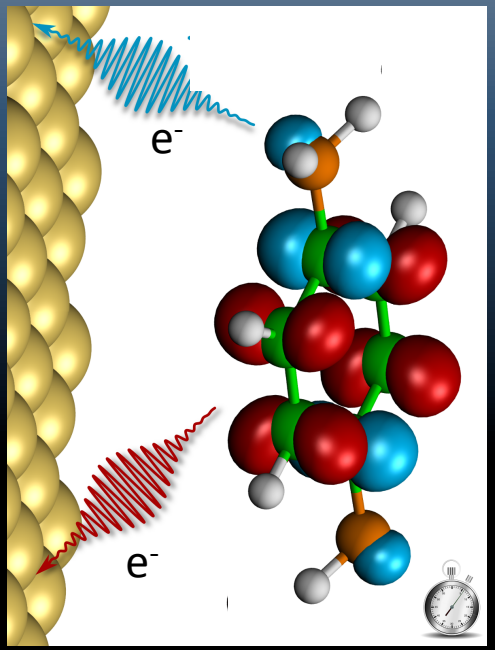
Dean Cvetko
Faculty for mathematics and physics, University of Ljubljana
&
ALOISA beamline, Laboratorio TASC IOM-CNR, Trieste

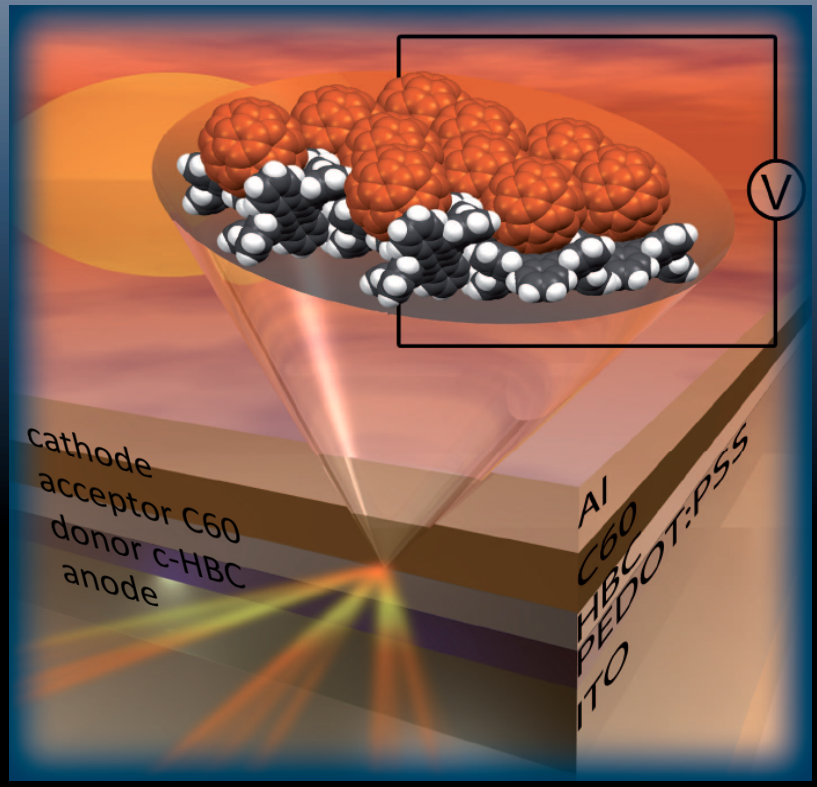
Outline :



Resonant Photoemission and Core Hole Clock = tool to measure CT dynamics across molecular interface with ACME resolution (time, orbital, chemical, atomic site…)

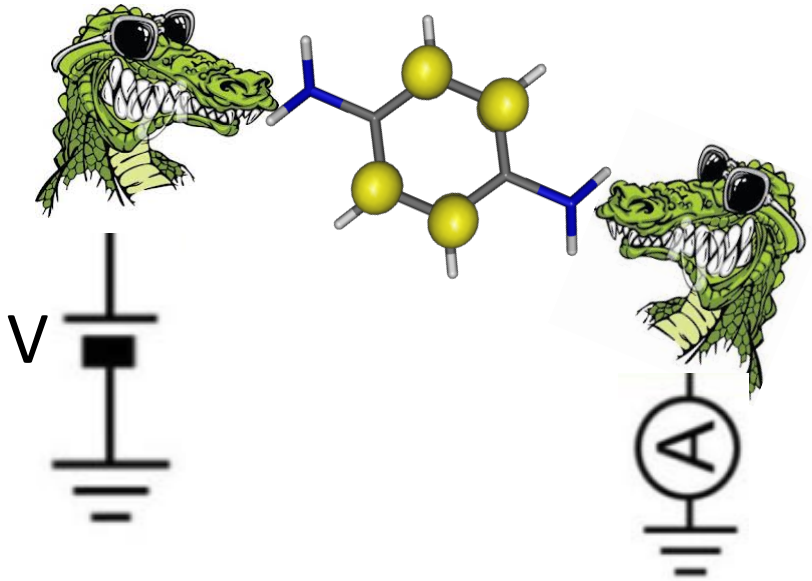
- *BDA/Au(111) - Ultrafast CT with site & orbital resolution, Amine-Au bond.*
- *Fast exciton dissociation in D/A molecular pairs for photovoltaics*





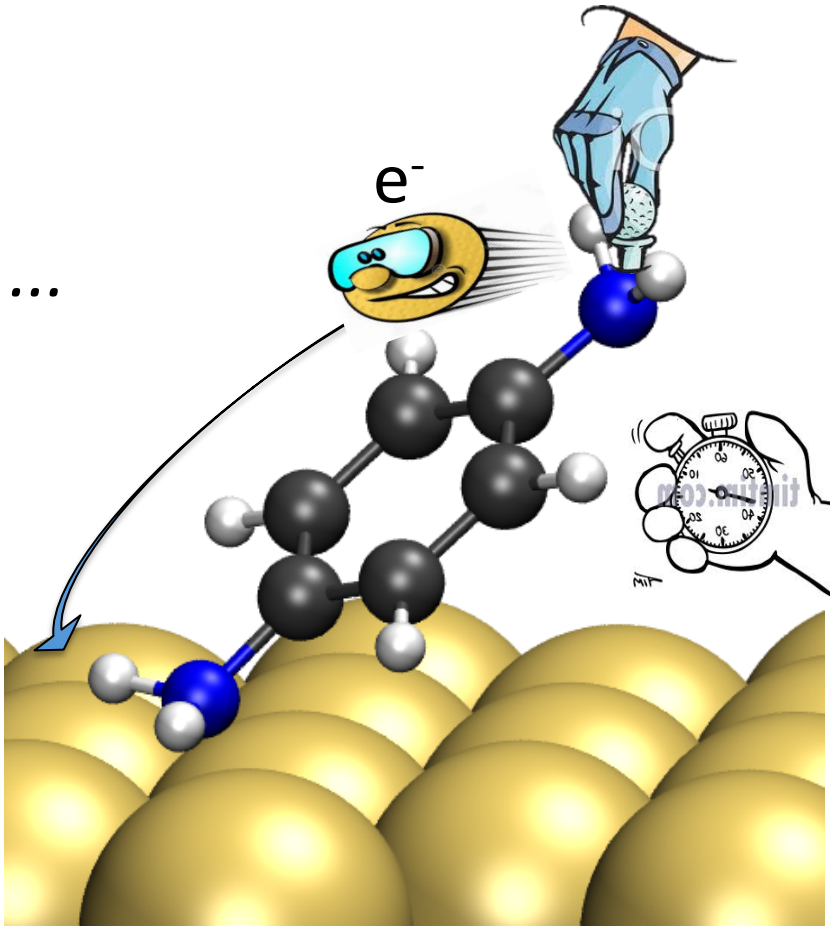
Charge Transport across single molecules is an experimental challenge…..

In an ideal experiment …



- *Metal clips on single molecule….*
- *Apply bias & measure current*
- *Clips on different endgroups => **Fast routes ?***

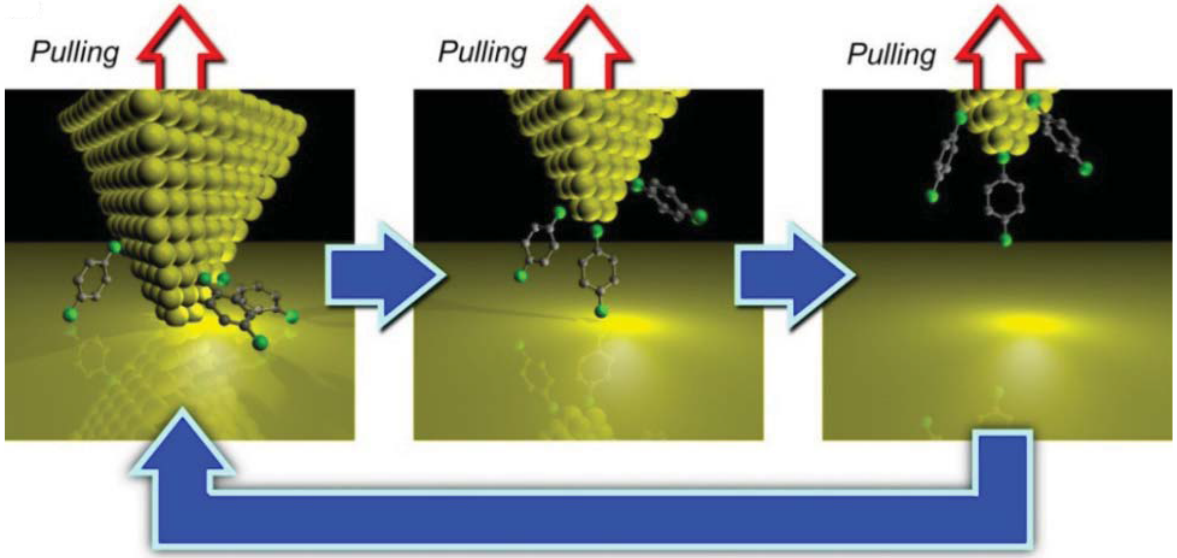
or …

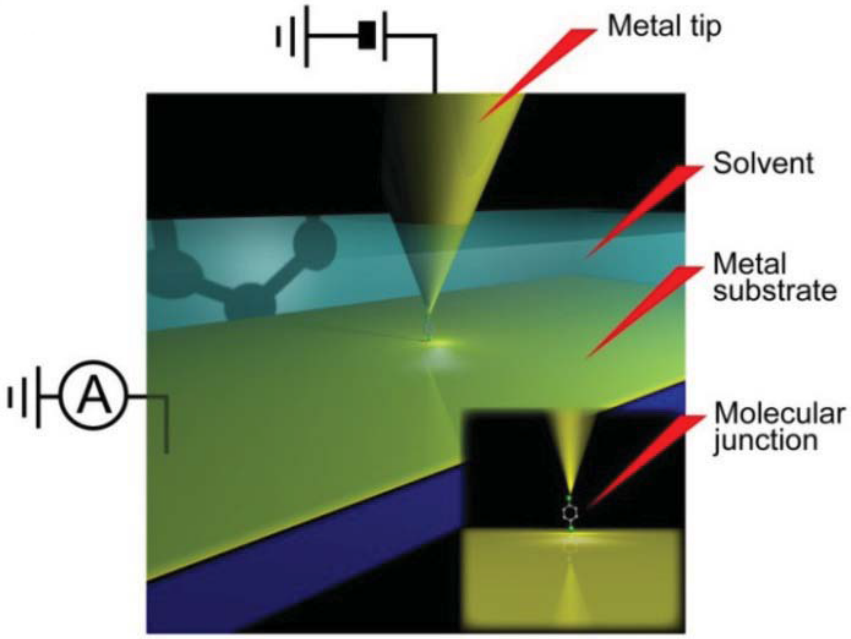


- *Place an e^- on a chosen site at t=0*
- *Measure e^- delocalization time with ultrafast clock…*
- *Change initial site & orbital => **Fast routes ?***

Single molecule conductance can be elegantly measured with STM break junction experiments

As Au tip is retracted from Au electrode, junction gets thinner and current (I) drops in steps, the last being due to Au atomic wire with quantized conductance $G_0=2e^2/h$ ($\approx 7.75 \times 10^{-5}$ S)

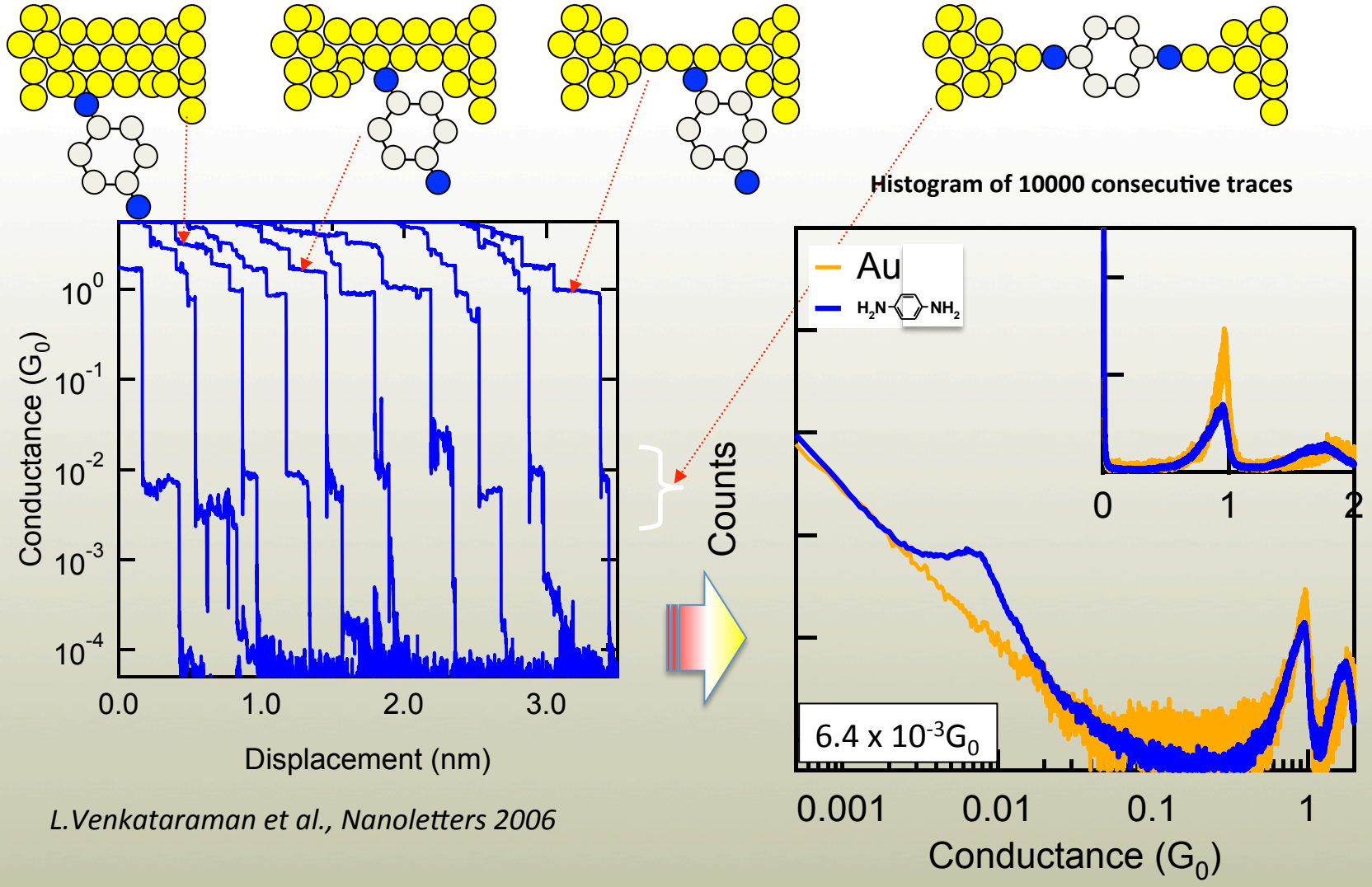




In a solvent, the diluted organic molecules may end up trapped between Au-tip and Au electrode forming single molecule junction with $G < G_0$ conductance. Histogram of several thousands retractions is recorded.

L.Venkataraman et al. Nanoletters, 2006
L.Venkataraman et al., Nature 2006
Y.S.Park, et al. JACS, 2007

1,4 Benzenediamine (BDA) – Amine link group (NH_2)



L.Venkataraman et al., Nanoletters 2006

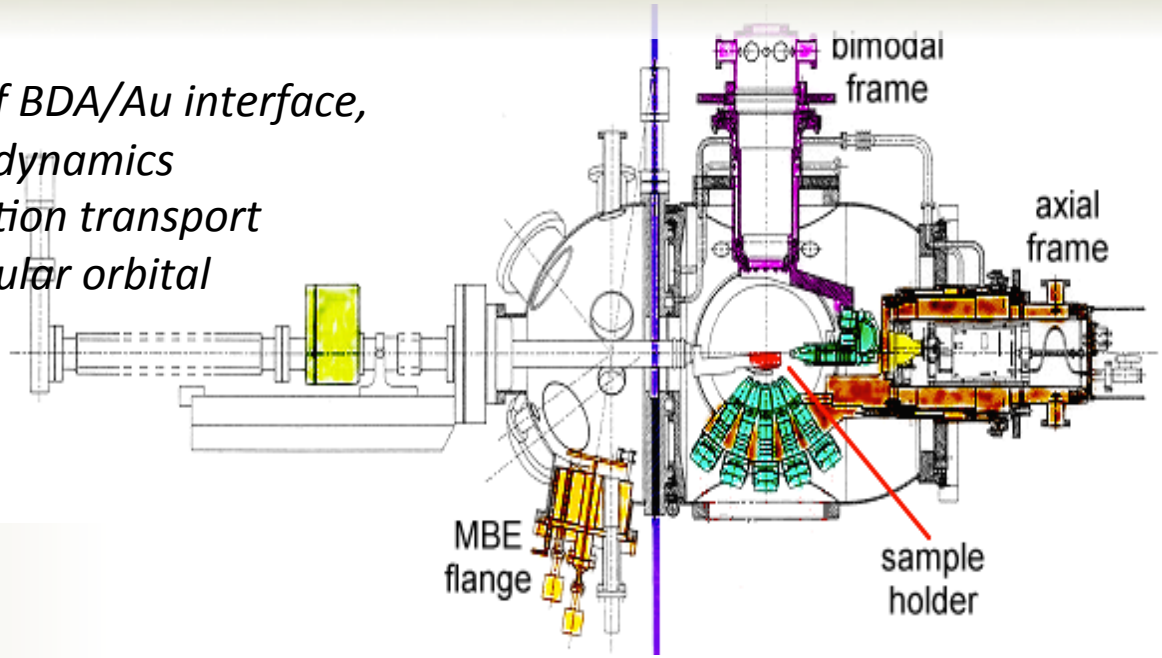
Result: *High molecular conductance thru noncovalent N-Au donor-acceptor bond.*

Issues: *Orbital level alignment? Dominant conductance channel? How fast e- transfers over empty MOs?*

Break junction results vs X-ray spectroscopy ?

Our Aim :

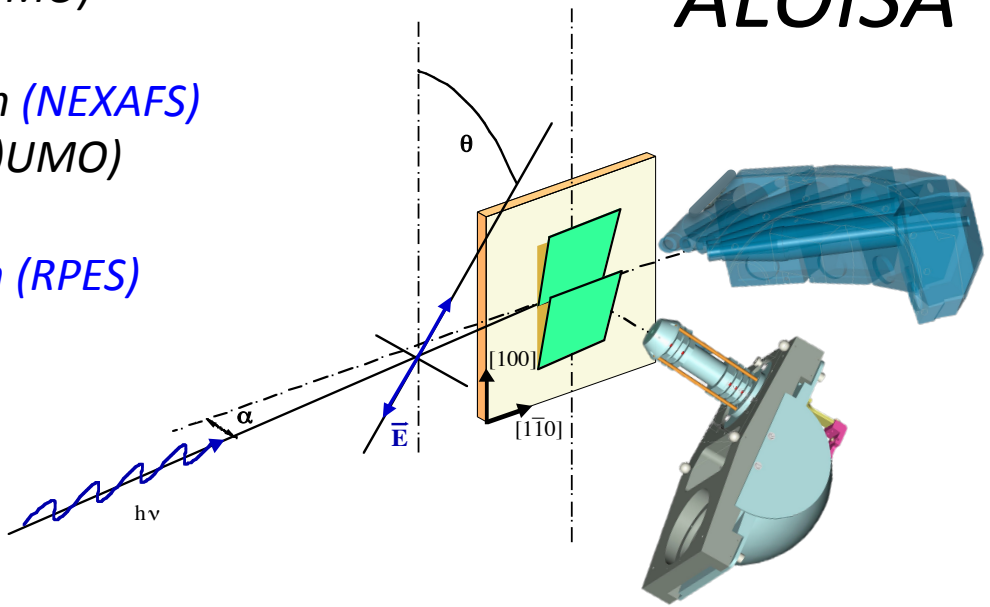
- *Characterize electronic structure of BDA/Au interface,*
- *Determine electron delocalization dynamics*
- ***Role of weak NH_2-Au bond** in junction transport*
- *Identify **"Fast"** vs **"Slow"** CT molecular orbital*



ALOISA

Experimental methods:

- *X ray photoemission (XPS)*
  We probe filled electronic levels (e.g (H)OMO)
- *Variable polarization Near Edge Absorption (NEXAFS)*
  We probe empty electronic levels (e.g. (L)UMO)
- *Valence band and Resonant Photoemission (RPES)*

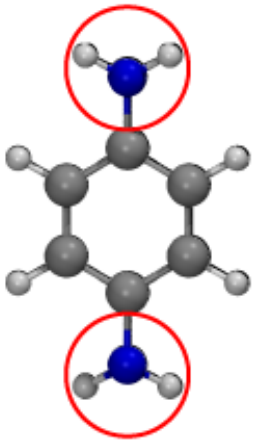


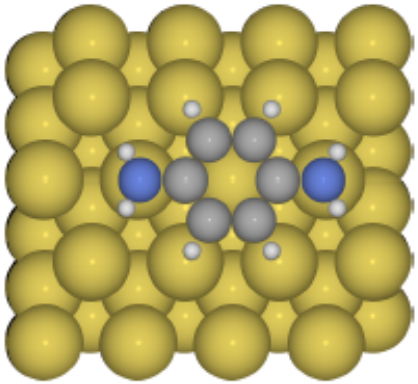
Charge transport dynamics ?

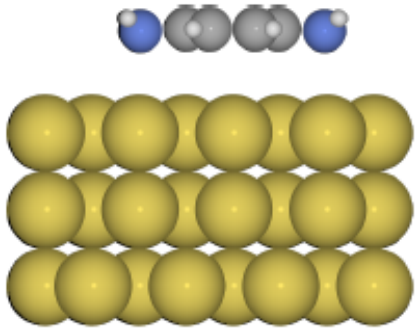
- ***Core-hole-clock** method via RPES*

Break junction results vs X-ray spectroscopy ?

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

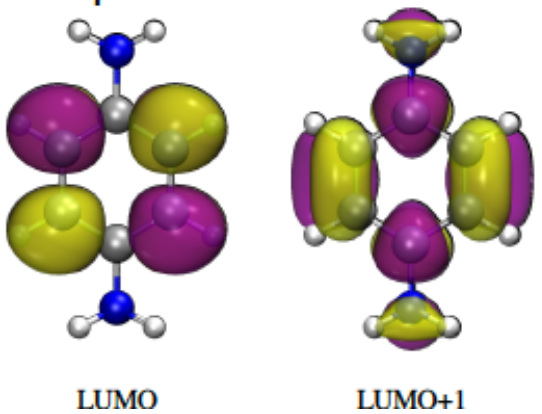






- Two amine groups with donating electron lone-pairs

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



LUMO LUMO+1

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

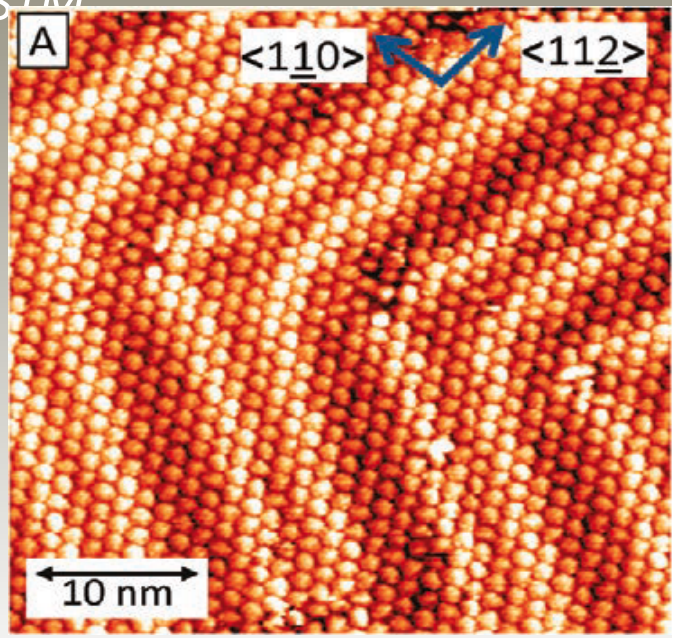
4 electronically distinct systems

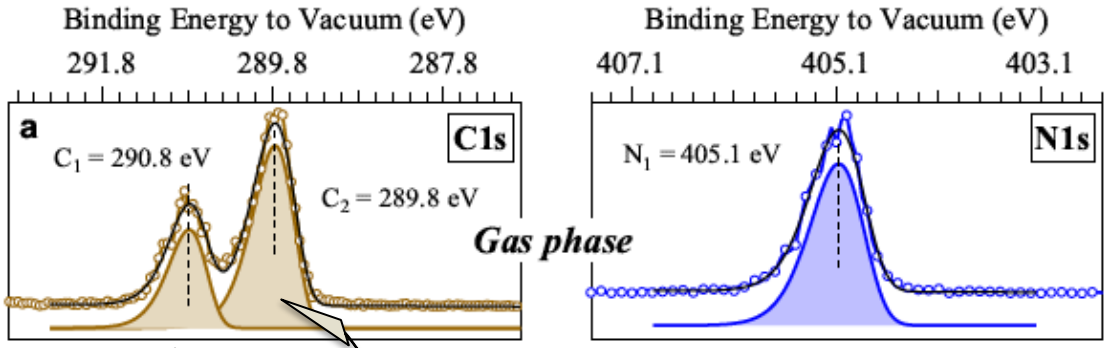
- *Gas phase - isolated*
- *Multilayer - weak VdW*
- *Tilted monolayer - semi-coupled*
- *Flat monolayer - Au-N coupled*

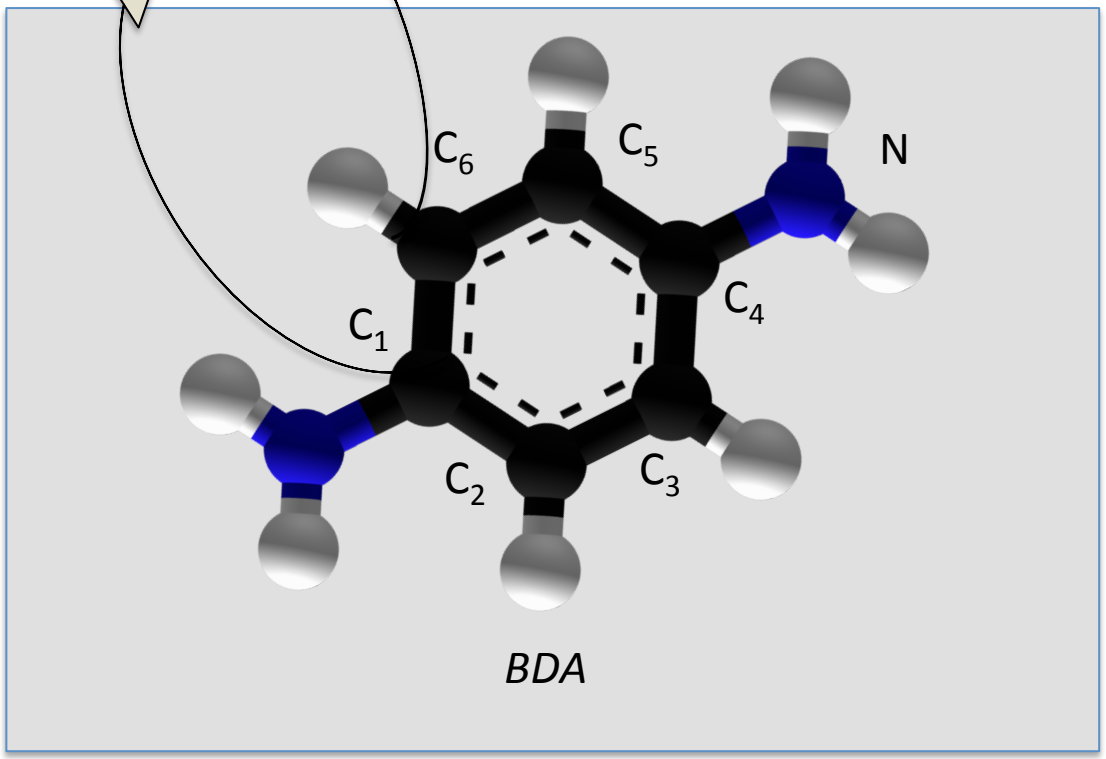
BDA/Au(111) UHV deposition

- T_{Au} = -80C -> *multilayer*
- T_{Au} = -20C -> *tilted monolayer*
- T_{Au} = 20C -> *flat monolayer*

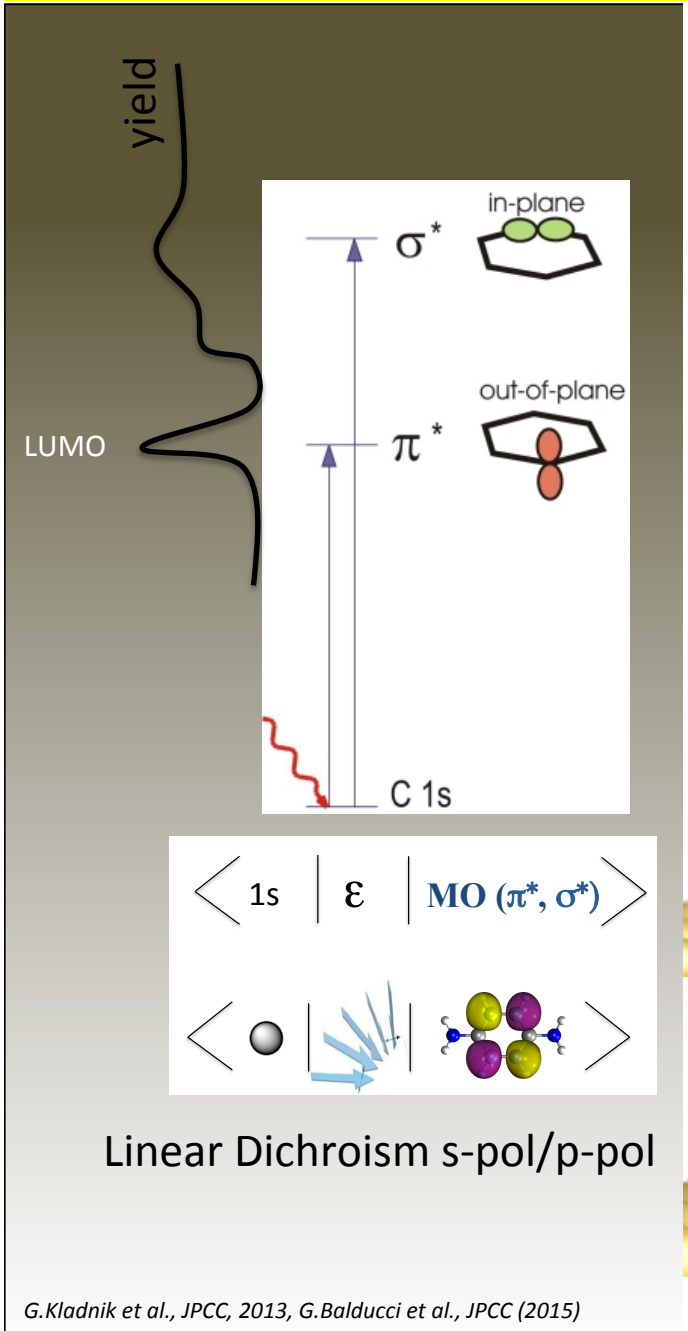
STM

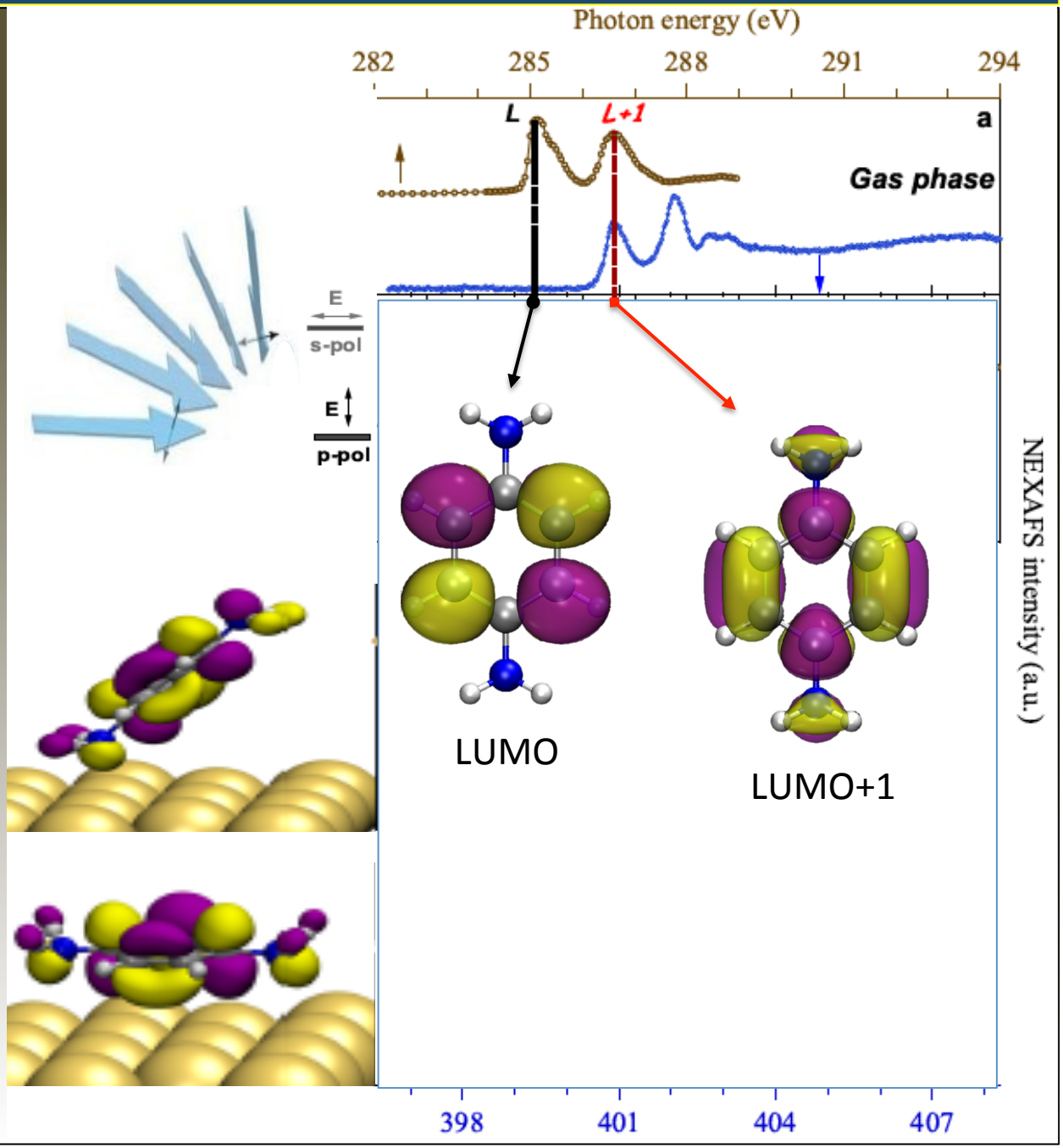






Near-Edge X-Absorption Fine Structure

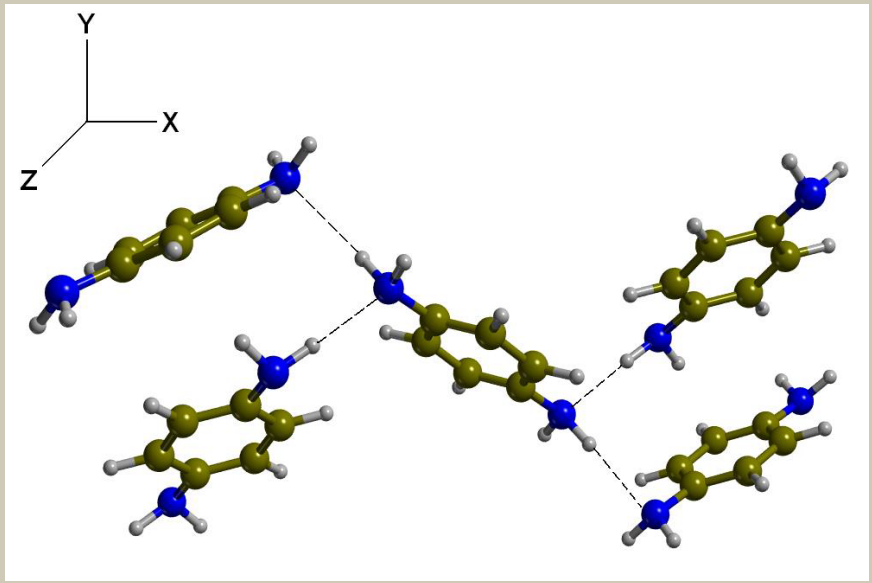


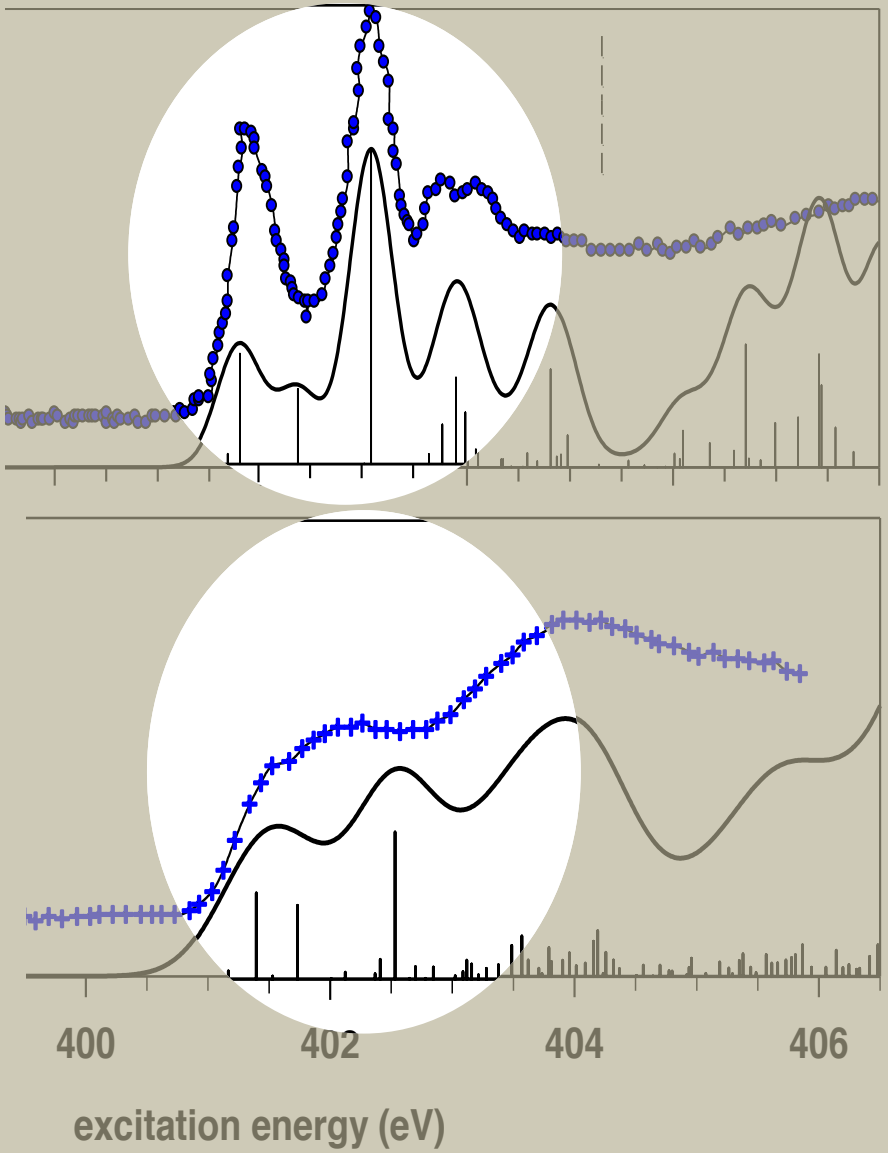


G.Kladnik et al., JPCC, 2013, G.Balducci et al., JPCC (2015)

DFT, Quantum Espresso, PDB0 with VdW for monolayer structure, half core-hole / NEXAFS

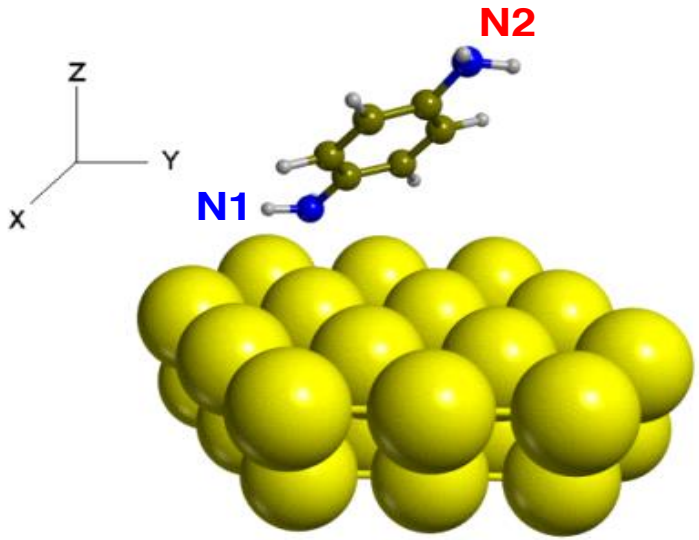
- Suppression of N1s -> LUMO+1 due to weak coupling.
- Can we measure CT from weakly coupled LUMOs?

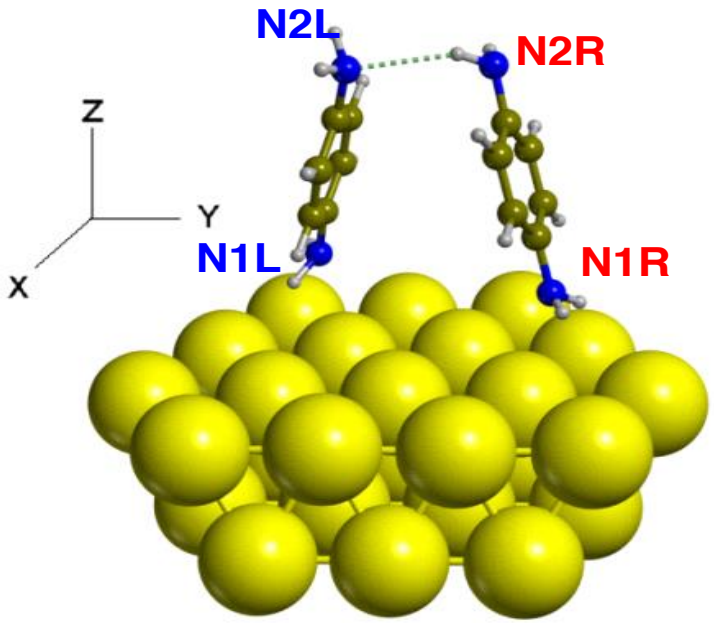


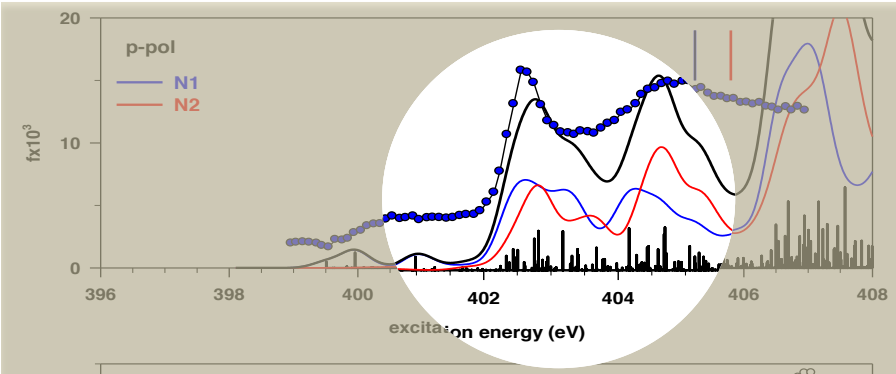


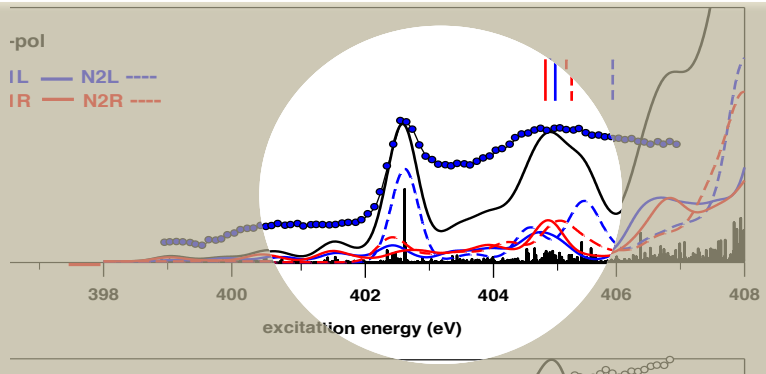
Colapietro et al., J.Phys.Chem., 91, 1728, 1987

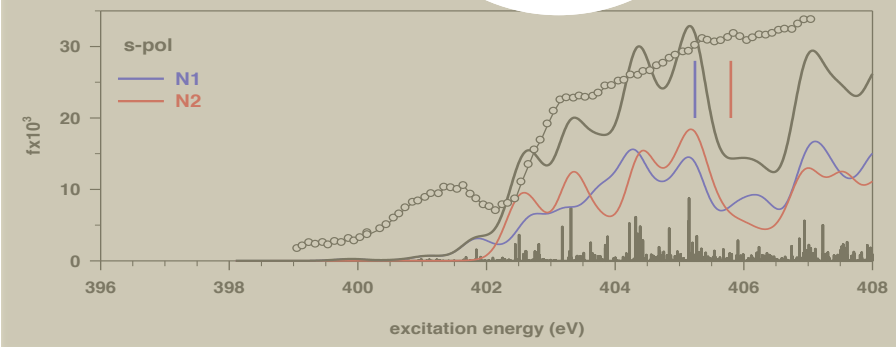
Inter-molecular interactions

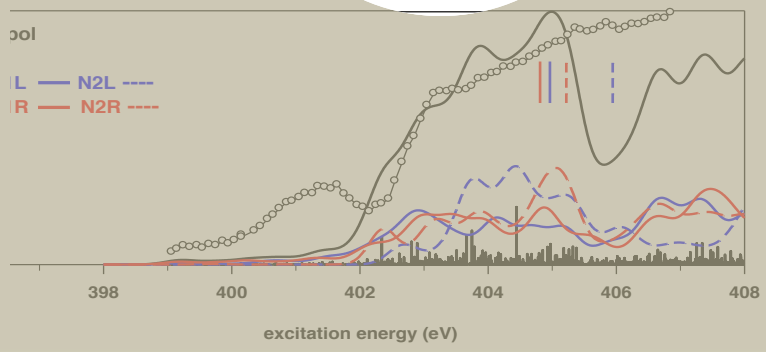












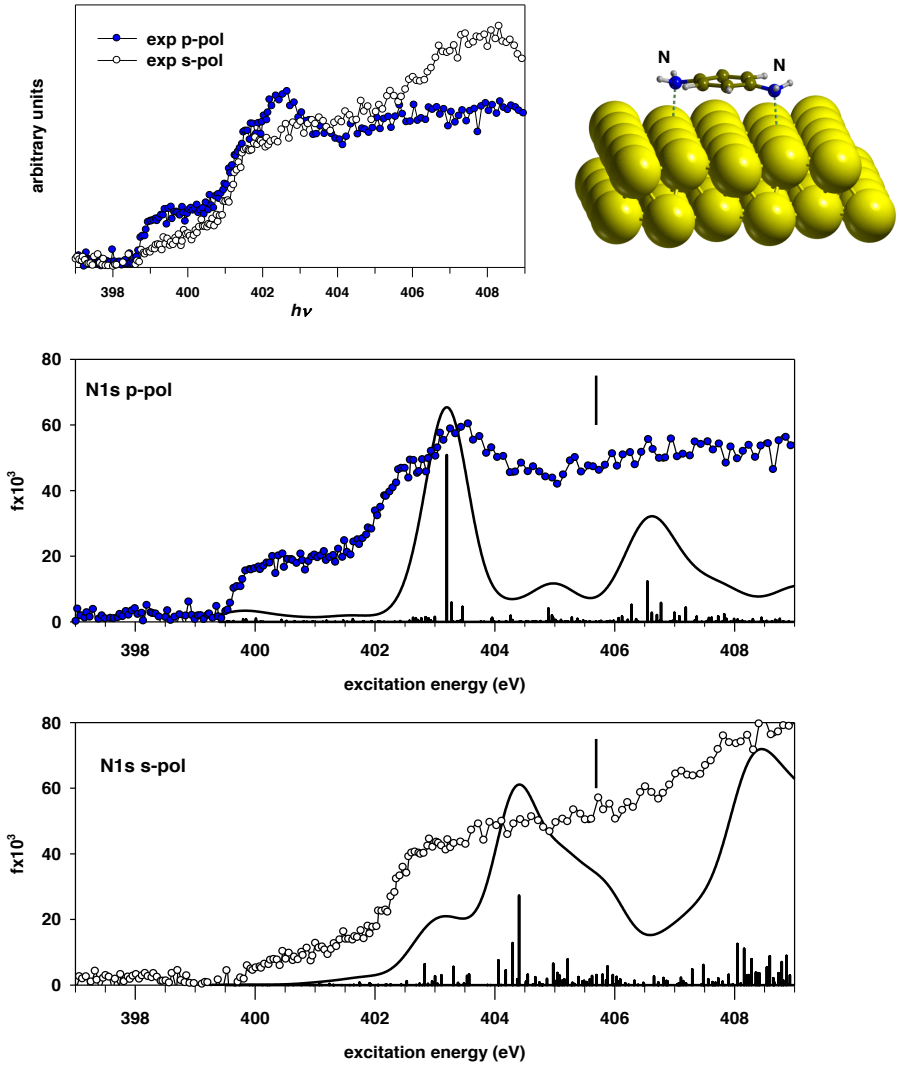
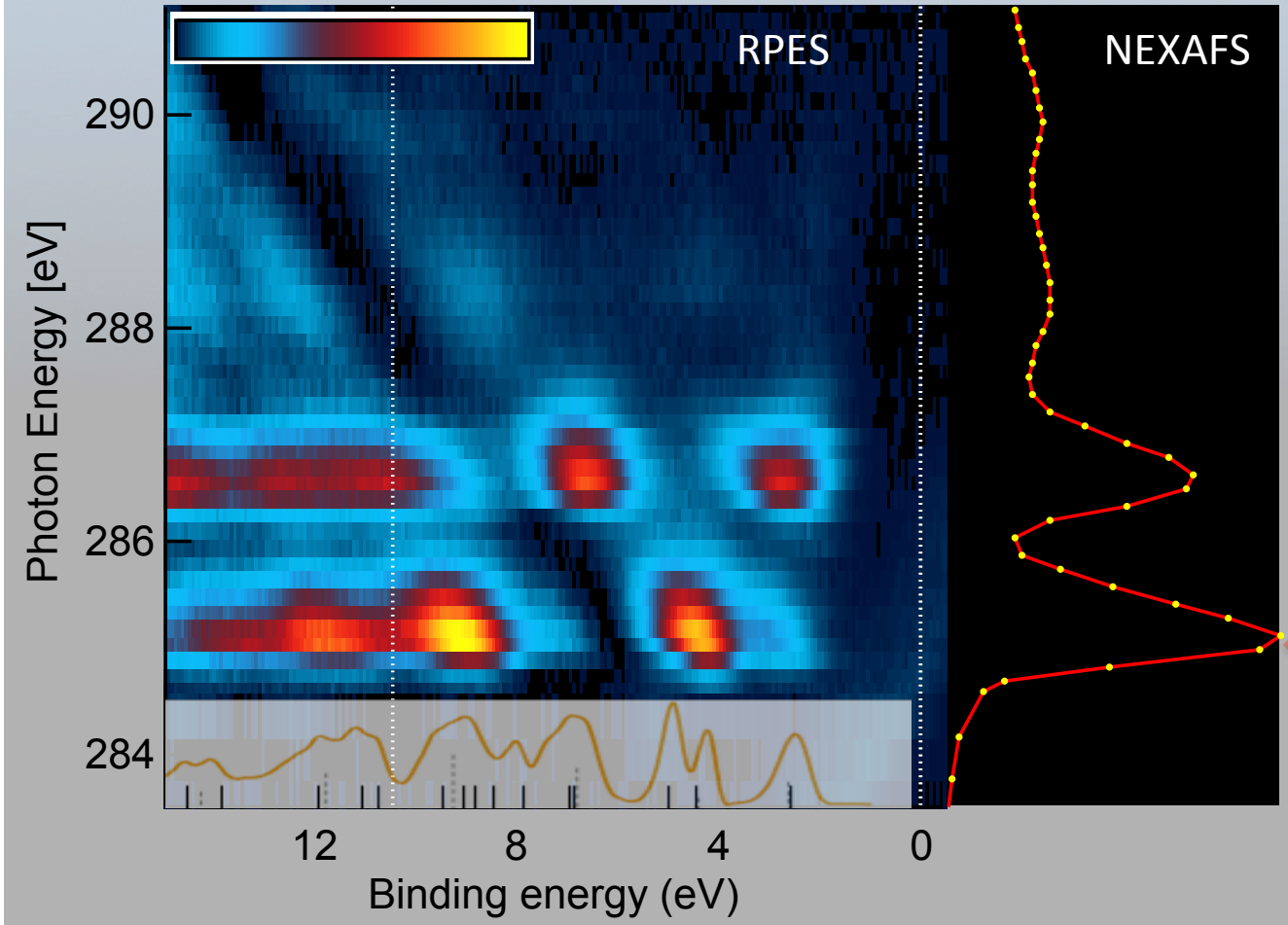
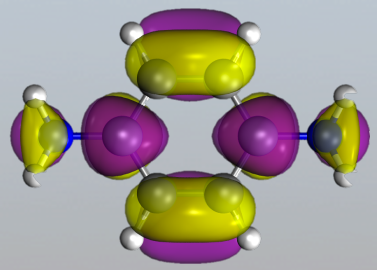
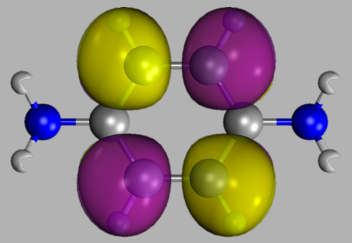

exp p-pol
exp s-pol
arbitrary units
hν
N
N
N1s p-pol
fx10³
excitation energy (eV)
N1s s-pol
fx10³
excitation energy (eV)
Z
Y
X
N1L
N1R
N2R
N2L
p-pol
N1L N2L
N1R N2R
fx10³
excitation energy (eV)
s-pol
N1L N2L
N1R N2R
fx10³
excitation energy (eV)

Fig.4

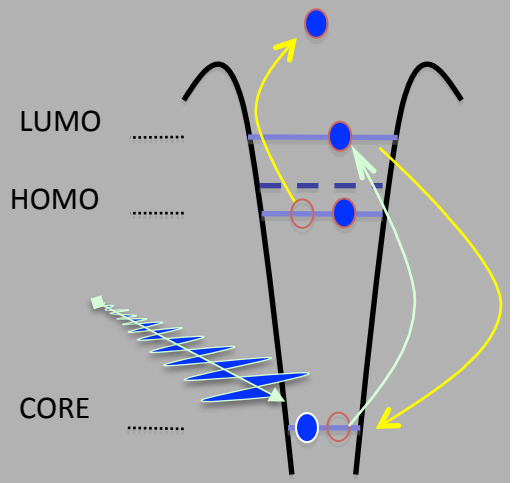




LUMO+1

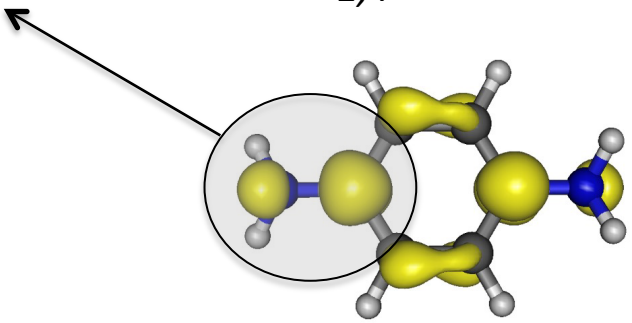


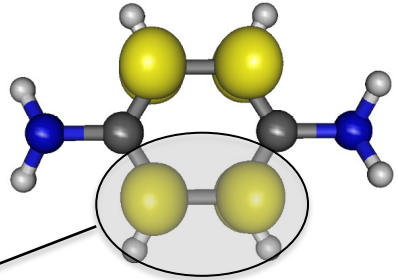
LUMO



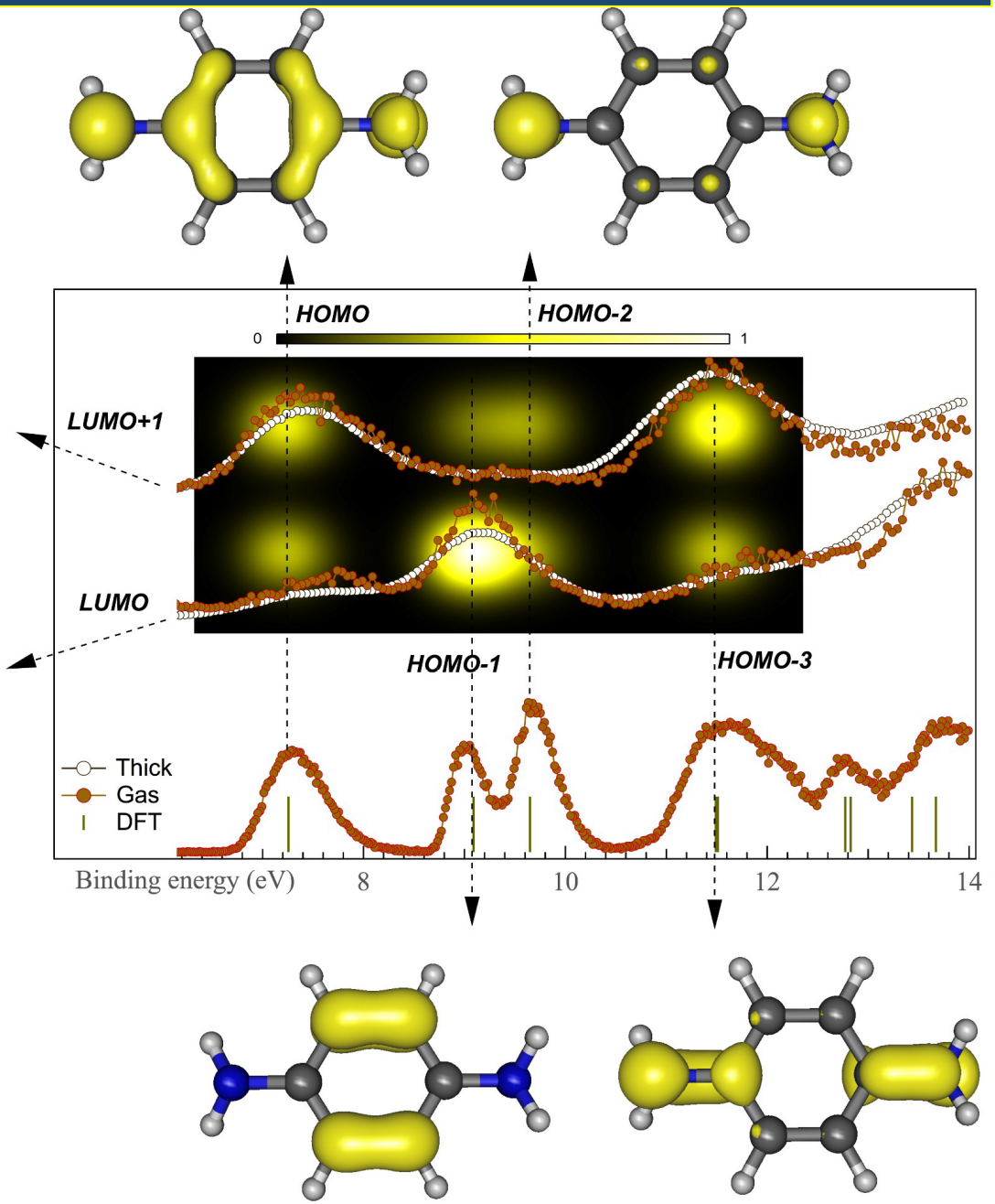
- Two PES channels: Identical final state – e emission + 1 hole in VB
- Resonance: Spatial orbital OVERLAP: Core + LUMO + HOMO

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





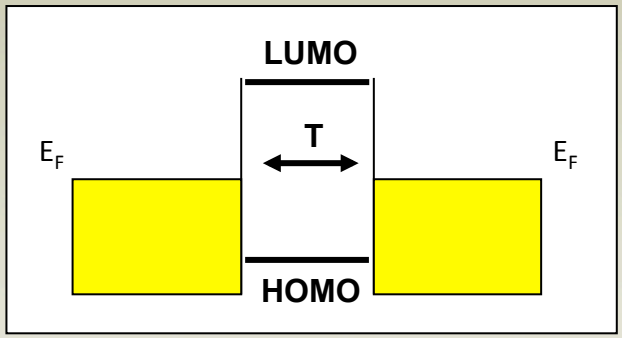
LUMO on C_{23} ring



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

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

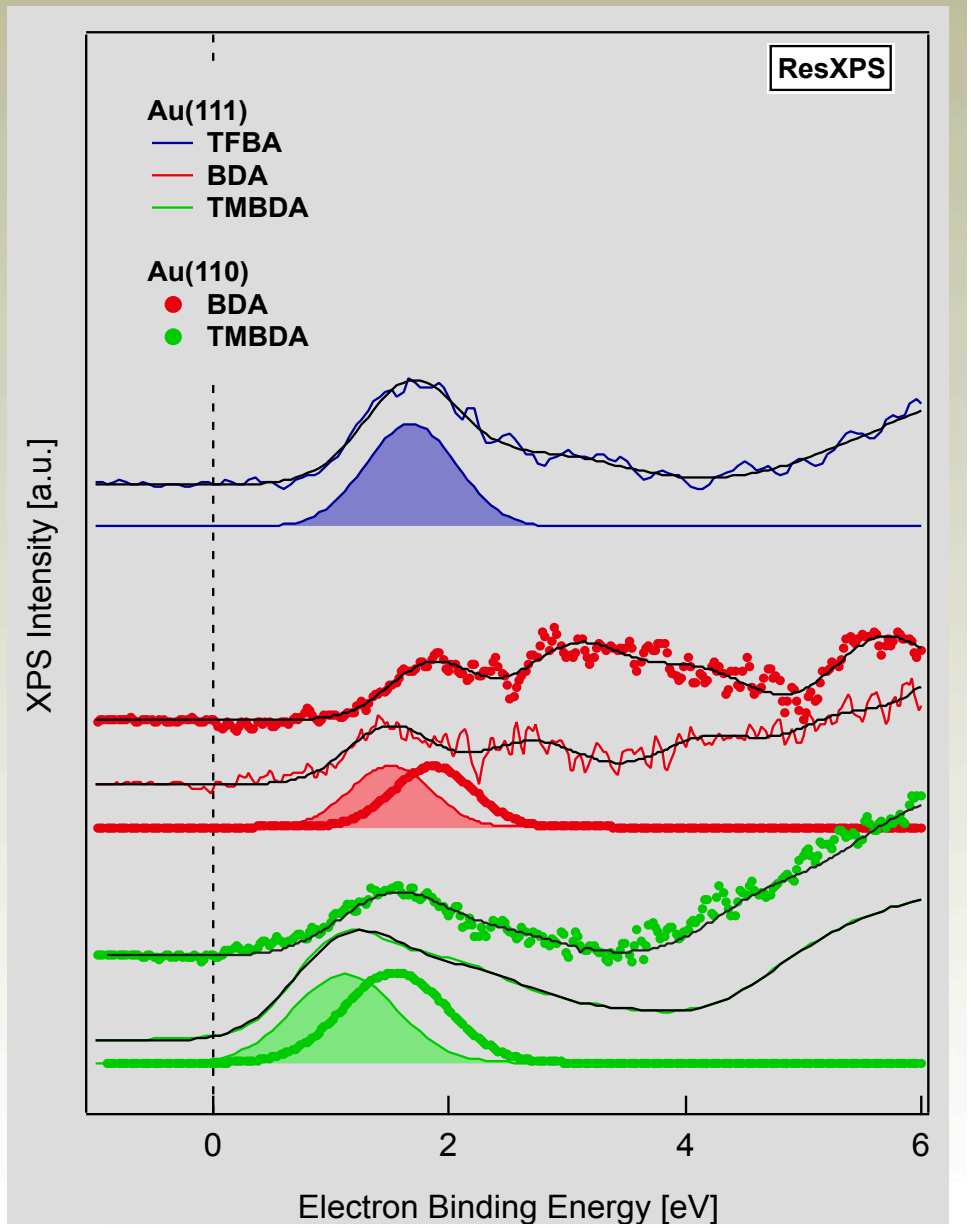
Single molecule conductance is expected to depend on relative position of HOMO, LUMO orbitals:



$$G \propto e^{-\beta L}$$

$$\beta \propto \sqrt{E_F - E_{HOMO}}$$

3 BDA derivatives



$G\ [10^{-2}\ G_0]$	5.5	6.4	8.2

M.DellAngela et al, Nanolett 2009

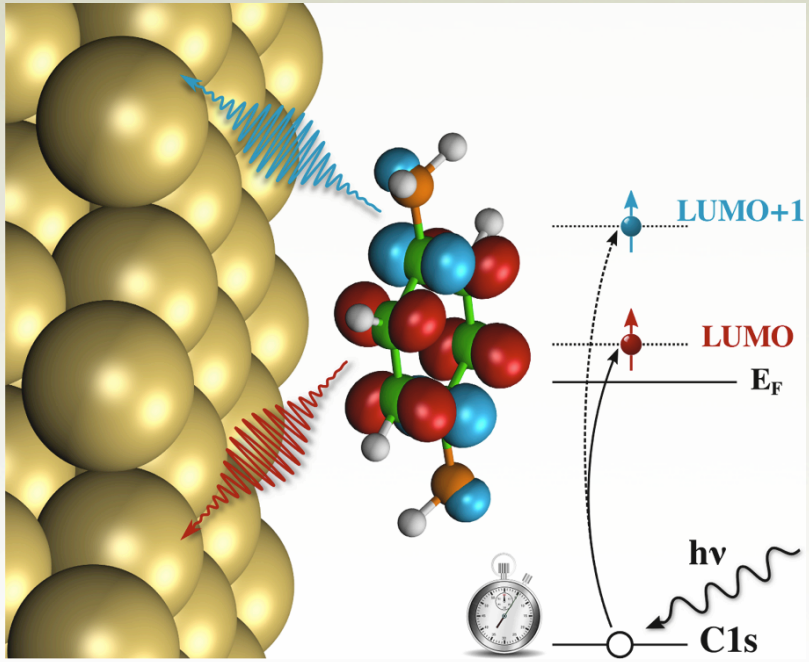
Molecule	measured adsorption energy [eV]	calculated adsorption energy [eV]	HOMO level from E_F [eV] Au(111) UPS	Au(111) Resonant XPS	Au(111) Theory	Au(110) Resonant XPS	Exp. conductance 10^{-3} G_0
	Au(111)	Au(111)					
TMBDA	1.2	0.44	−1.0±0.1	−1.3±0.2	−1.2	−1.6±0.2	8.2±0.2
	Au(111)	Au(111)					
BDA	Au(110) 1.0 1.1	0.36	−1.4±0.1	−1.6±0.2	−1.6	−1.8±0.2	6.4±0.2
	Au(111)	Au(111)					
TFBDA	0.9	0.26	−1.5±0.1	−1.65±0.2	−1.8		5.5±0.2

Table 1 Adsorption energies on Au(111) determined from T-ramp HAS and from DFT-Σ calculations [1,3]. HOMO energy levels relative to E_F from UPS and ResXPS on Au(111) and Au(110) and determined from DFT-Σ [1,3]. STM break junction conductance values from [2].

M.DellAngela et al, Nanolett 2009

Can we access the dynamics of the core excited electron ?

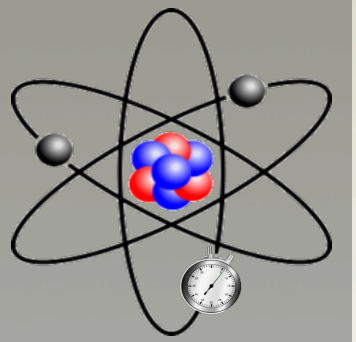
- *Couple BDA to the substrate -> (L)UMO coupled to Au continuum*
- *Orbital level alignment & spatial overlap of (L)UMO ➔ CT across molecular junction*
- Xploit the lifetime of inner shell core-hole to clock the ultrafast electron dynamics.



CORE HOLE CLOCK method

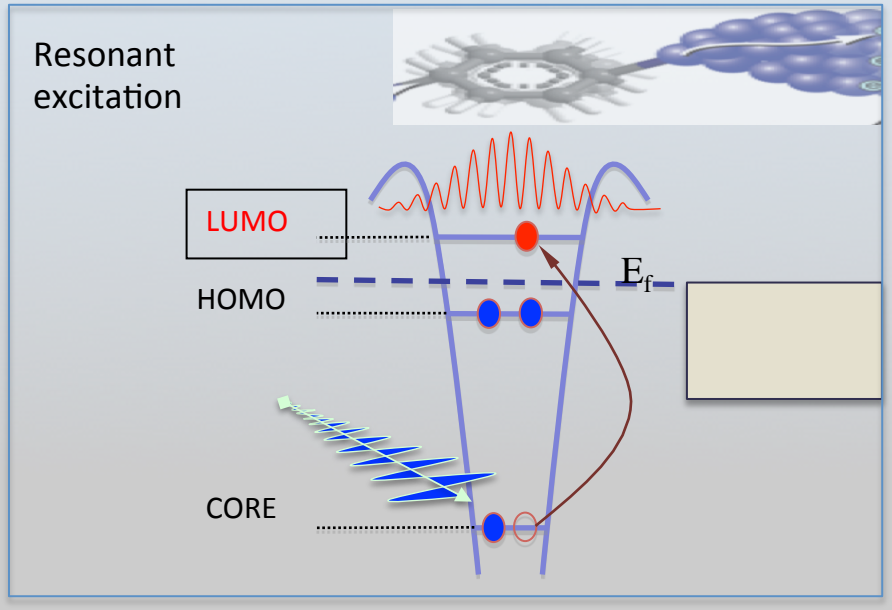
Hole lifetime:

Oxygen KLL: τ = 4 fs.
Nitrogen KLL: τ = 5 fs,
Carbon KLL: τ =6 fs,
Argon $L_3M_{4/5}M_{4/5}$: τ =6 fs;

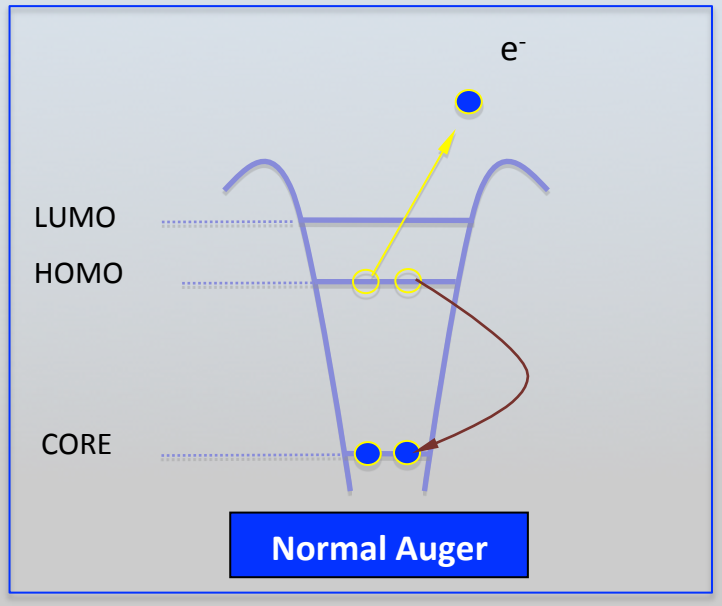


M. Coville et al., Phys. Rev. A (1991), Fohlisch et al, Chem. Phys. (2003).

Core Hole Clock –> *"excited electron" delocalization dynamics*

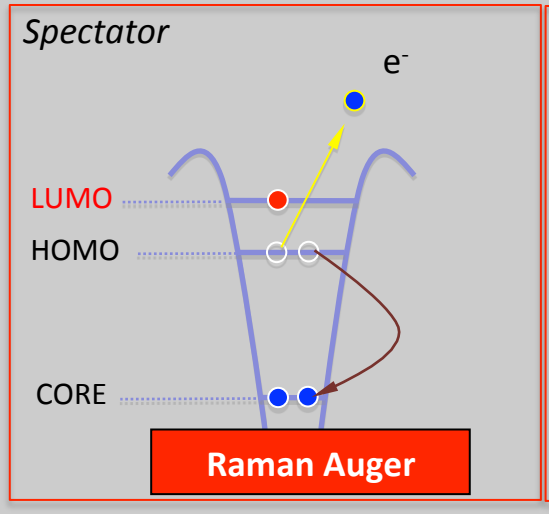


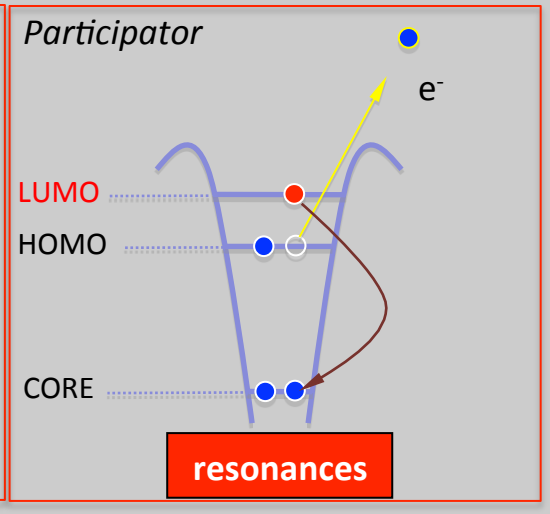
CT

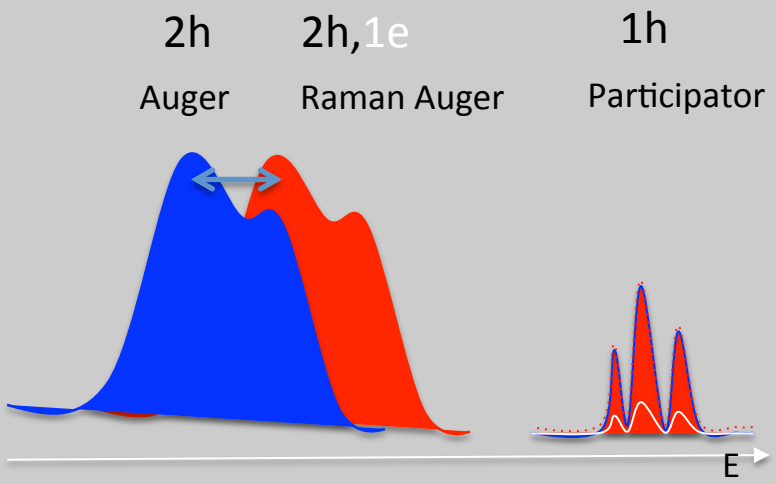


NO CT

Core Hole Decay …



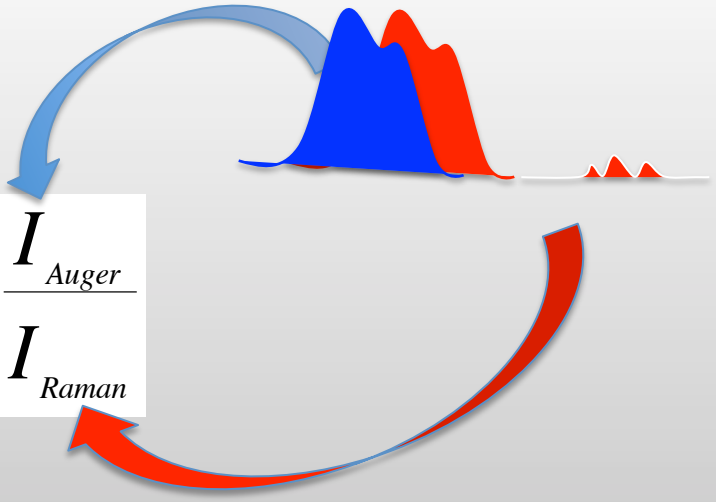




CHC 1 / *Compare Auger vs (spect + part) decay intensity :*

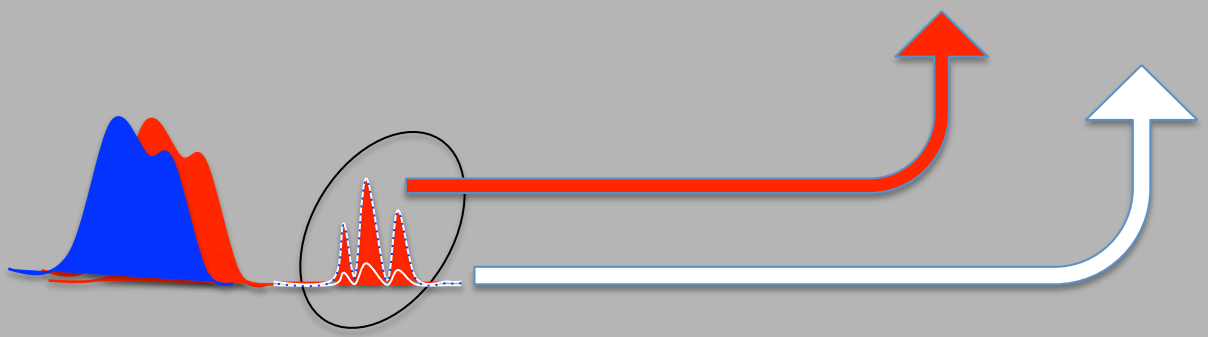
P. A.Brühwiler et al., Rev. Mod. Phys. (2002).

$$\tau_{CT} = \tau_{core}\frac{P_{no\,CT}}{P_{CT}} = \tau_{core}\frac{I_{Auger}}{I_{Raman}+I_{part.}} \cong \tau_{core}\frac{I_{Auger}}{I_{Raman}}$$

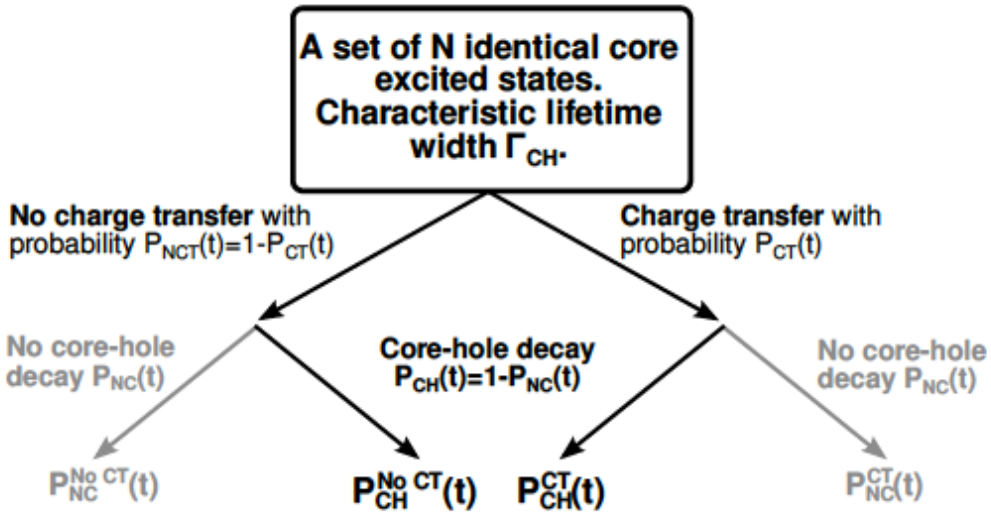


CHC 2 / Compare : ***Coupled*** *&* ***Isolated*** *system (τ = ∞) . RPES quenching in coupled gives CT time.*

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



Decay Channel Branching as a Measure of CT



- Exponential decay law

$$N(t) = N_0 \exp\left(-\frac{t}{\tau}\right) = N_0 \exp\left(-\frac{\Gamma}{\hbar}t\right)$$

- Probability of CT

$$P_{CT}(T) = \int_0^T \frac{\Gamma_{CT}}{\hbar} \exp\left(-\frac{\Gamma_{CT}}{\hbar}t\right) dt$$

- Probability of core-hole decay

$$P_{CH}(T) = \int_0^T \frac{\Gamma_{CH}}{\hbar} \exp\left(-\frac{\Gamma_{CH}}{\hbar}t\right) dt$$

- From conditional probability, i.e., CT before core-hole decay:

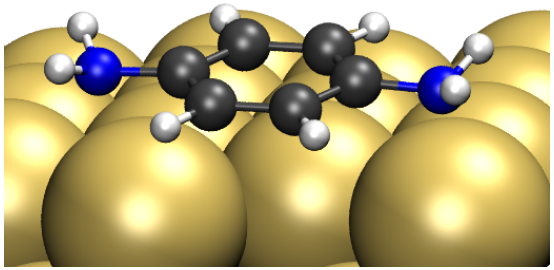
$$P_{CH}^{CT}(T) = \int_0^T \frac{\Gamma_{CH}}{\hbar} \exp\left(-\frac{\Gamma_{CH}}{\hbar}t_1\right) \left[\int_0^{t_1} \frac{\Gamma_{CT}}{\hbar} \exp\left(-\frac{\Gamma_{CT}}{\hbar}t_2\right) dt_2\right] dt_1$$

$$= 1 - \exp\left(-\frac{\Gamma_{CH}}{\hbar}T\right) - \frac{\Gamma_{CH}}{\Gamma_{CH}+\Gamma_{CT}}\left[1 - \exp\left(-\frac{\Gamma_{CH}+\Gamma_{CT}}{\hbar}T\right)\right] \xrightarrow{T\to\infty} \boxed{\frac{\Gamma_{CT}}{\Gamma_{CH}+\Gamma_{CT}}}$$

CHC - Nitrogen of BDA

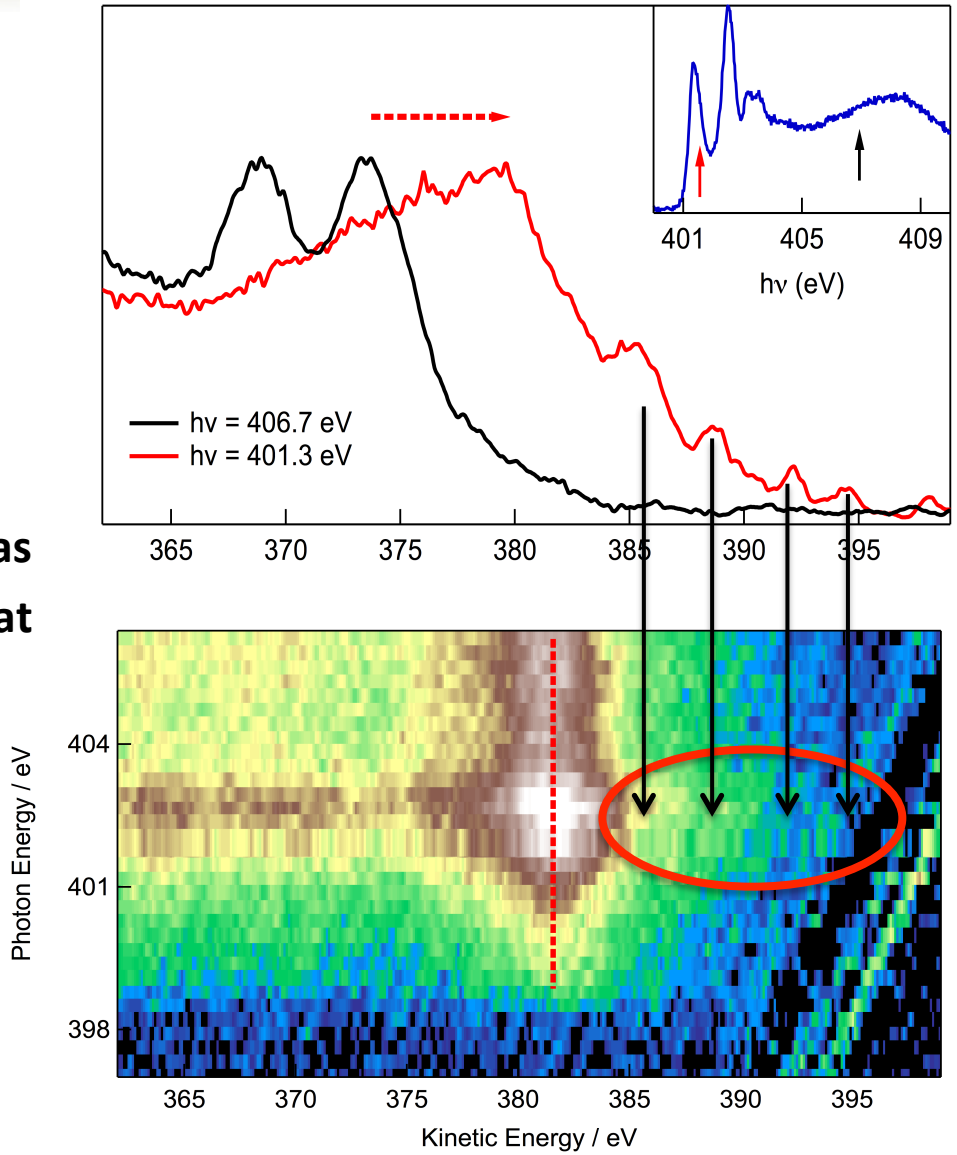
LUMO+1 @ 401.3 eV :

- *6 eV spectator shift Auger-Raman*
- *Participator resonances*



LUMO+1 :

- *No Raman Auger*
- *Participator fully quenched*
- *T < 0.5 fs*

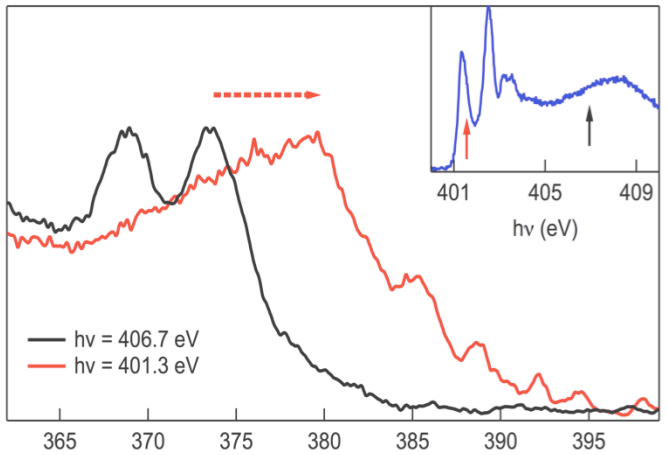


Amine-Au link opens a fast CT channel

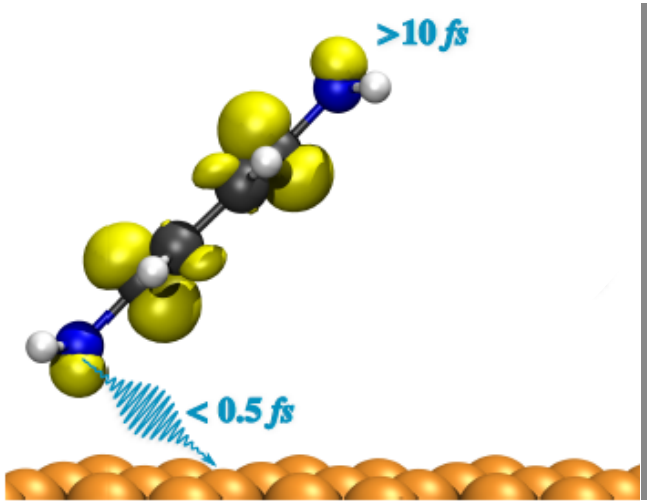
***Tilted ML** at higher coverage*

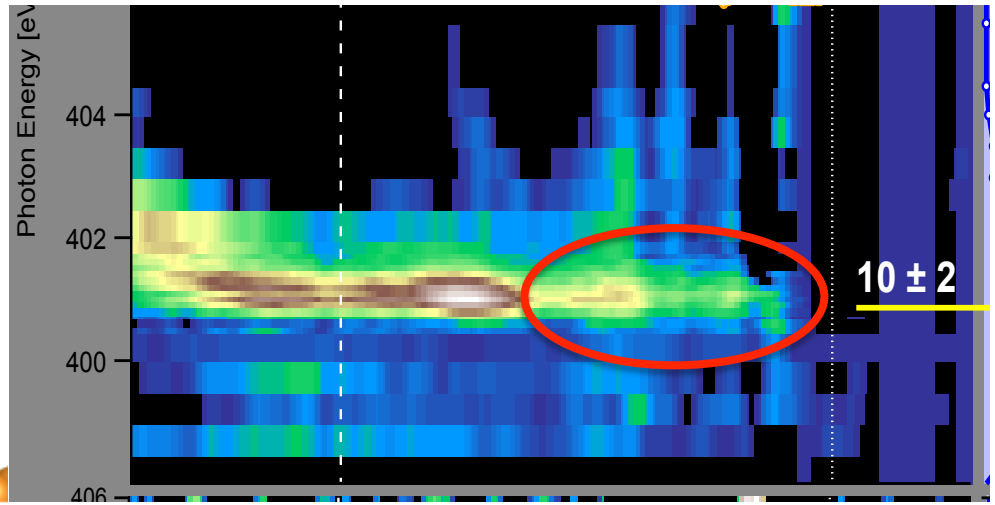
- *2 in-equivalent N atoms.*
- *LUMO+1 resonances not fully quenched: T > 10 fs >> 0.5 fs*
- *Loose N end effectively decoupled*
- *Residual CT through BDA backbone or molecule-molecule interaction ?*

Gas

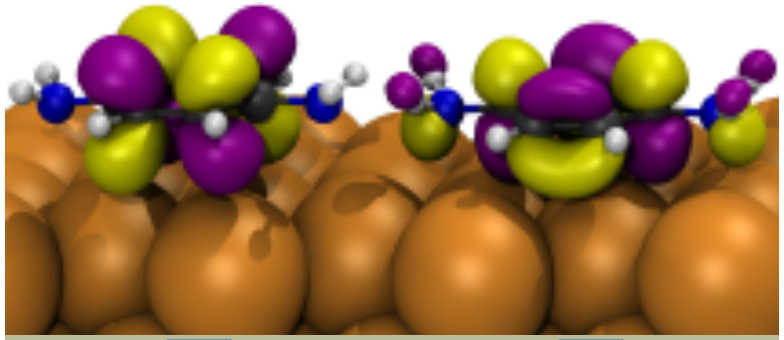


Tilted ML





Flat Monolayer - CT times from Carbon



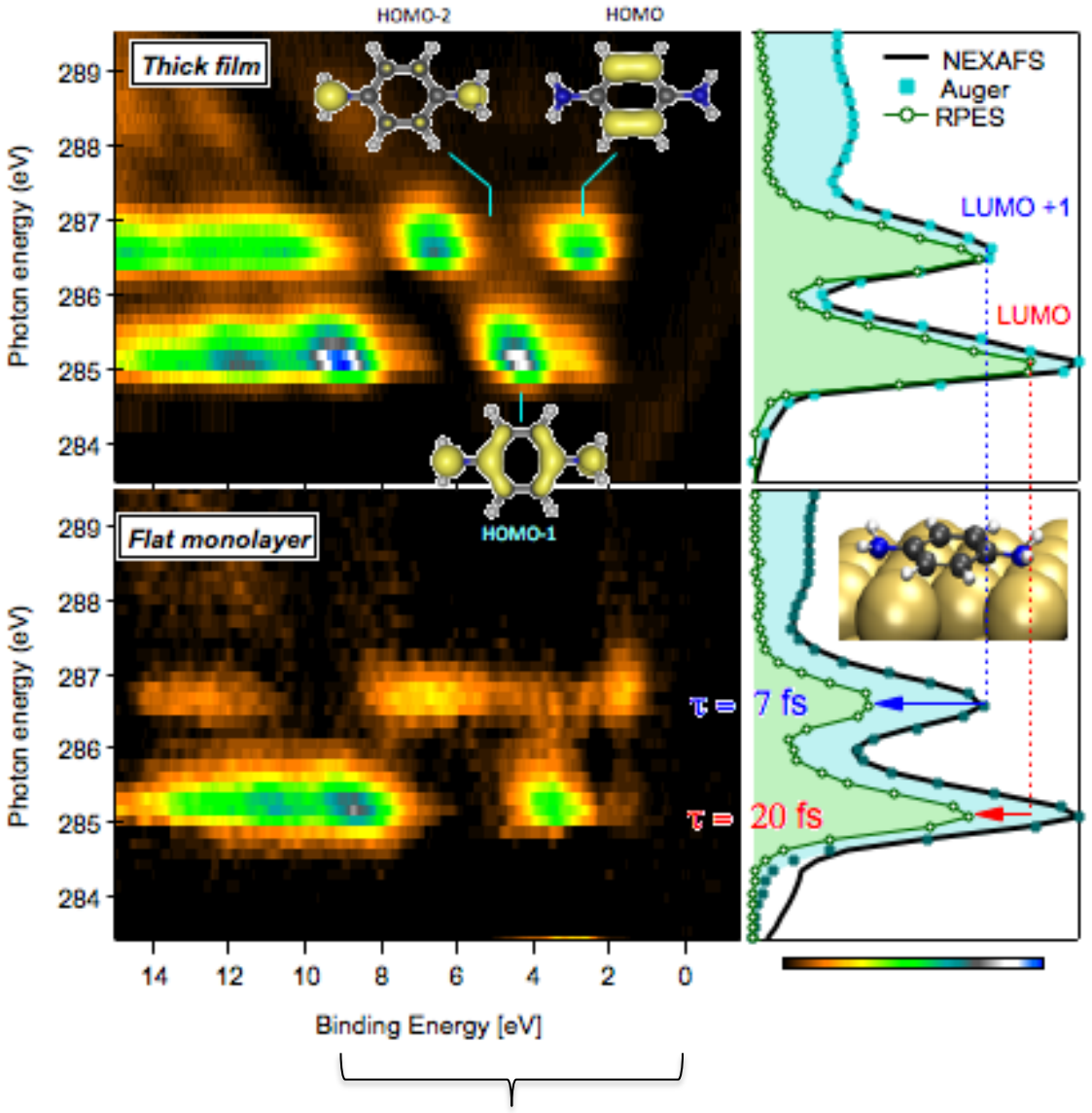
LUMO
inner ring
$C_{2,3}$

T = 20 ±5 fs

LUMO+1
next to NH_2
$C_{1,4}$

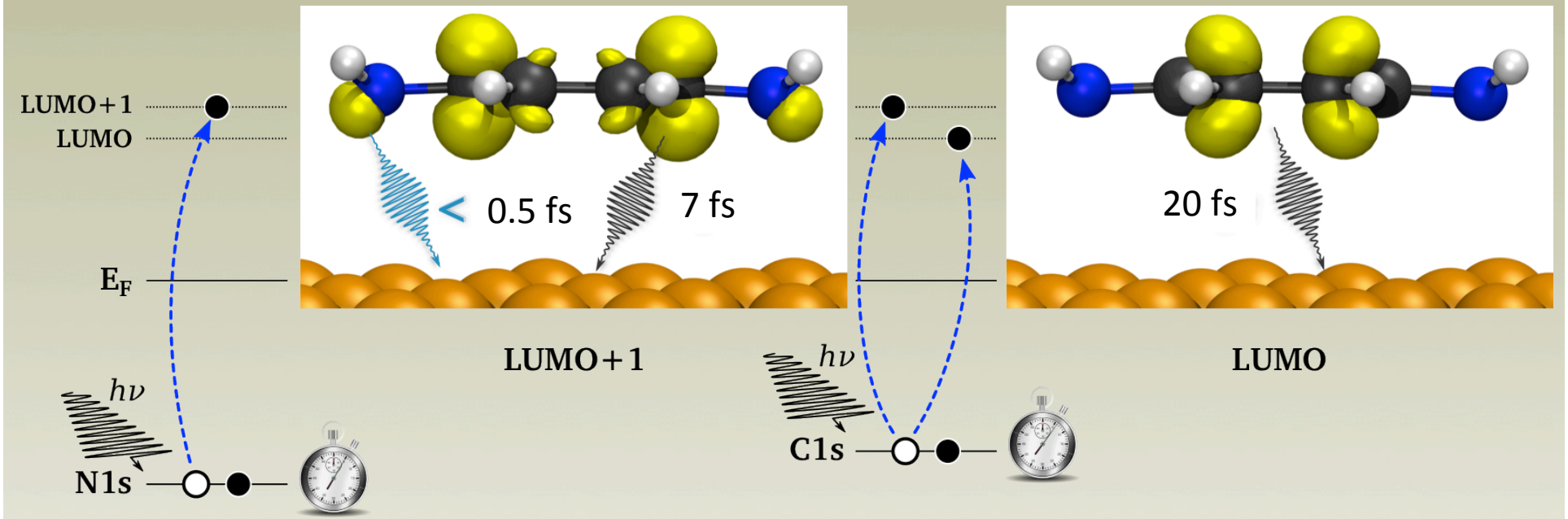
T = 7 ± 2 fs

Amine-Au link opens a fast CT channel from $C_{1,4}$ to Au….



Participator

Summary

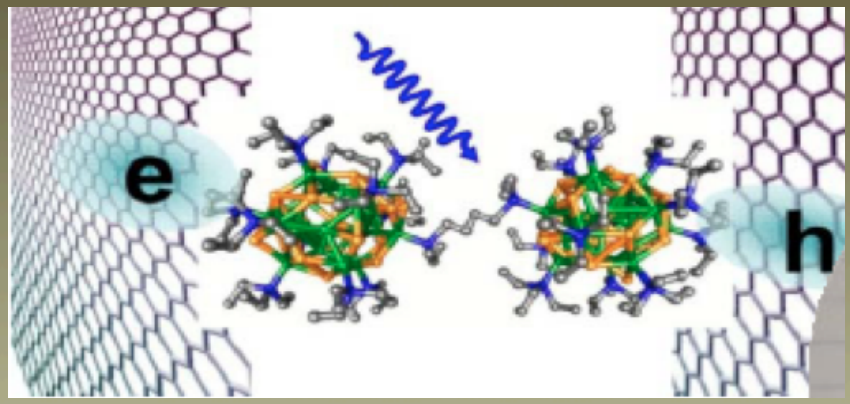


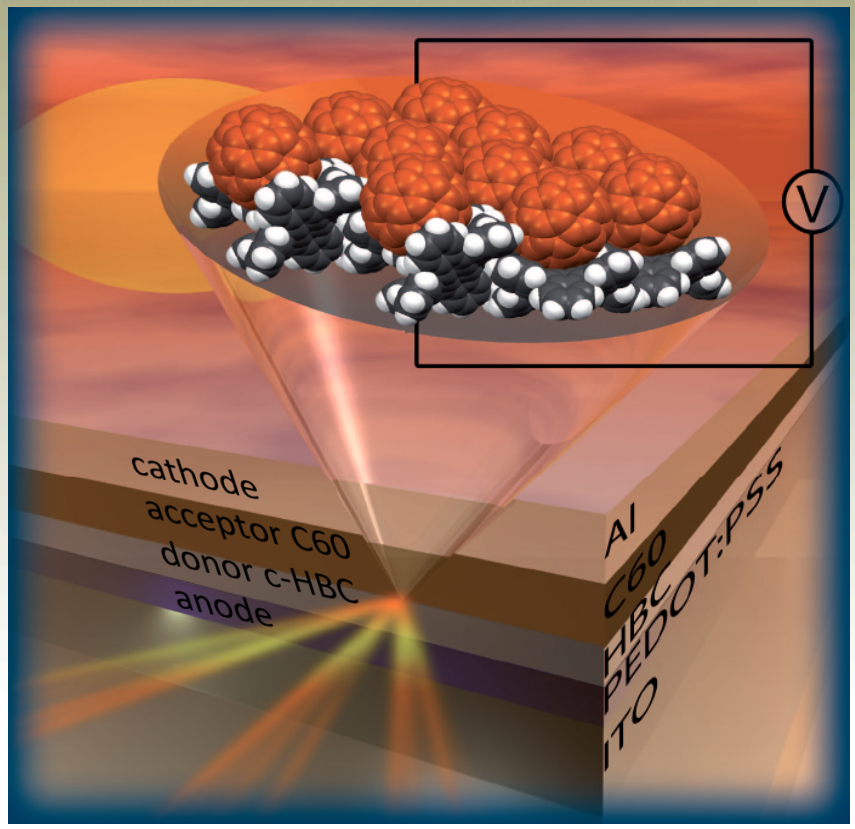
We can "populate" empty orbitals on different atomic sites (N, $C_{1,4}$, $C_{2,3}$) and measure dynamics of electron transfer to Au …

- *Ultra fast CT from orbitals on N coupled to Au (< 500 attos) comparable to covalent bonding … Fast dynamics also over LUMO+1 on $C_{1,4}$.*
- *N-Au donor acceptor bond opens a route for fast interfacial transport.*

II. Donor–Acceptor Shape Matching Drives Performance in Photovoltaics

In OPV the Interface between hole and electron transporting layers is critical for exciton dissociation and charge separation.

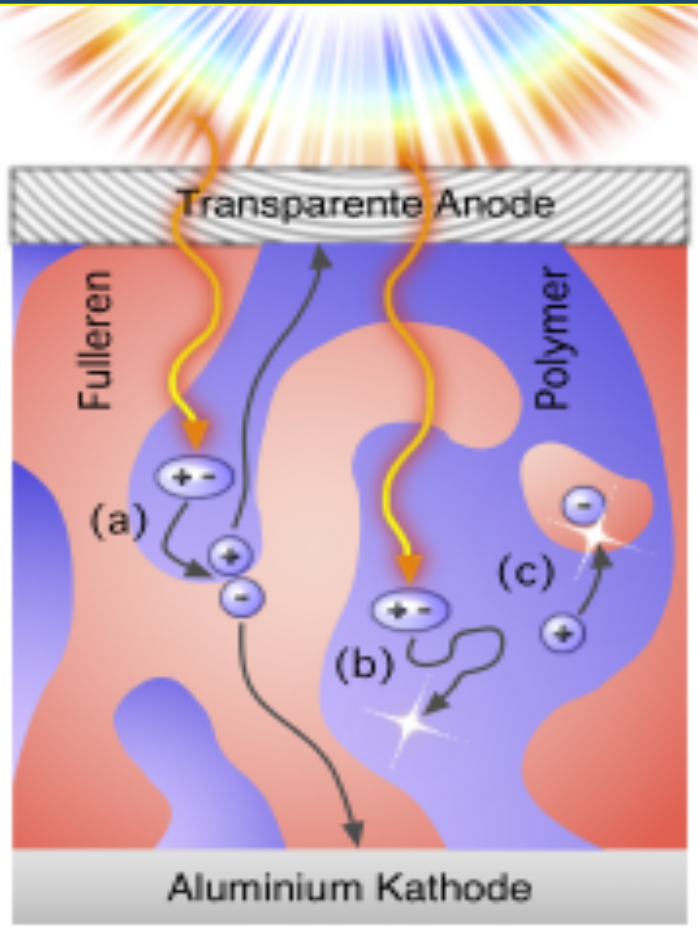


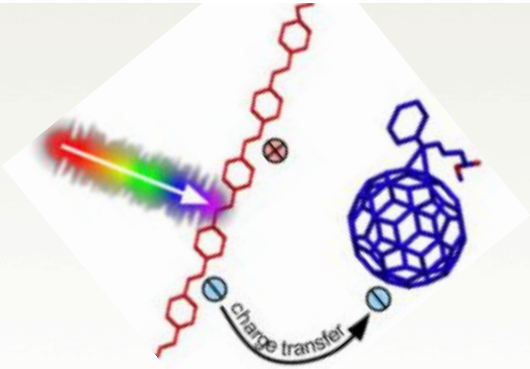


Manipulate microstructure of active layer:

- *Exploit molecular shape–complementarity*
- *Exploit Self-assemblying to nanostructure the heterojunction*
- *Control the interface morphology*

N.J.Tremblay et al., ChemPhysChem 2010, 11, 799 – 803





Principles of organic heterojunction PV

- *Light is absorbed in the active layer of 100nm ➔ exciton creation*
- *Exciton diffuses within lifetime (ns) about 10nm to reach the Donor/Acceptor interface.*
- *Exciton breaks up (10 fs?) into e-h polaron pair, which dissociates and separate charges may reach electrode to generate photocurrent.*

Issues :

- *Optimal D/A phase separation – percolation, inter-twinning, etc. Interface morphology : fine grained (exciton dissoc) and coarse grained (charge-polaron transport)…..*

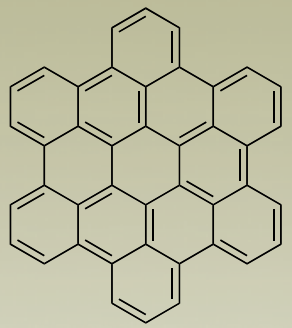
As size of devices approaches nm lenghtscales, single molecule junctions & atomic pathways for CT are important: Molecular arrangement and coupling for exciton breakup:

- *MO of D/A pair - energy level alignment*
- *MO of D/A pair - spatial overlap*

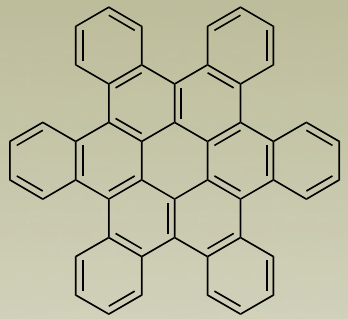
Motivation : Device scale experiments with shape matched D/A assemblies CHC/C_{60}

Hypothesis : Shape matching drives performance of heteroorganic PV device

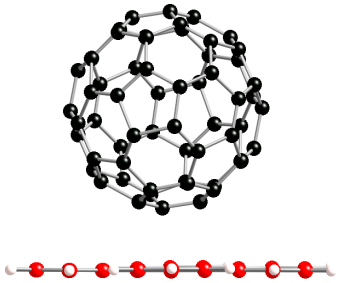
A - Fullerenes (C_{60}, C_{70}) D – Hexabenzocoronenes

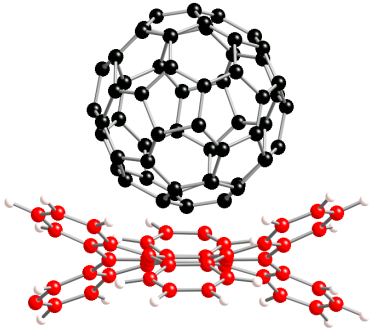


Flat HBC (f-HBC)

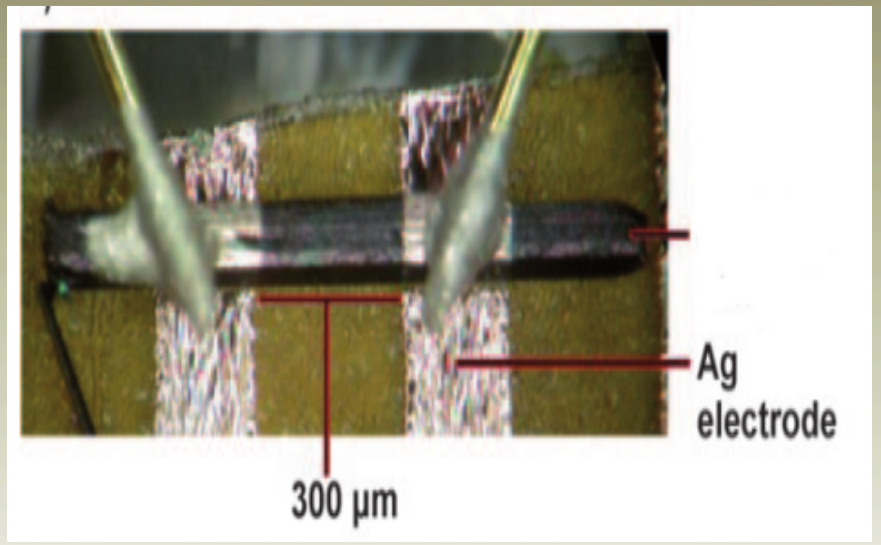


Contorted HBC (c-HBC)





Experimental device performance



PV cell efficiency

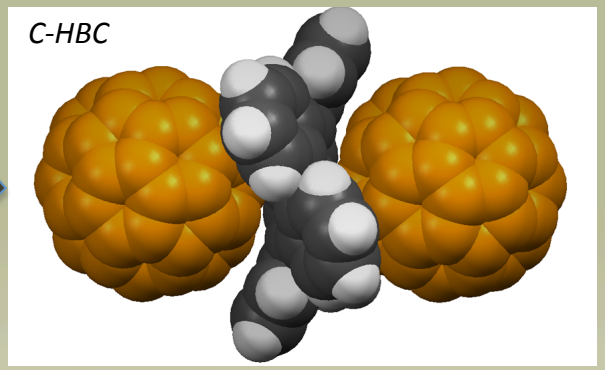
Shape matched C_{60} / c-HBC vs C_{60} / f-HBC

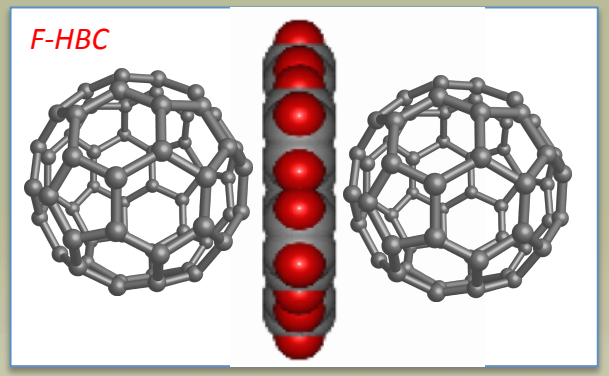
10-times increase in energy conversion (0.55% vs. 0.03% solar, 3.4% vs 0.03% UVLED; U_{OC}, J_{SC} -> EQE)

N.J.Tremblay et al., ChemPhysChem 2010, A.C. Whalley et al., Chem. Sci., 2011

"Flat" vs. "contorted" HBC/C_{60} assembly

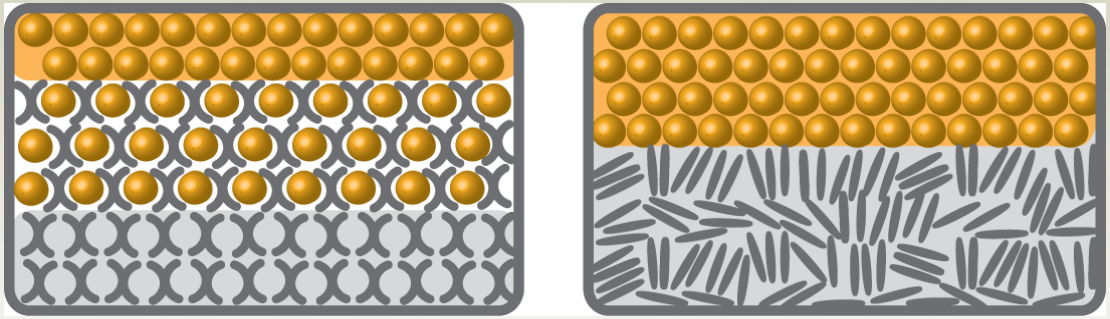
c-HBC/C_{60} 10x higher efficiency than f-HBC/C_{60}





Faster CT and exciton break-up in c-HBC/C_{60} junction ?

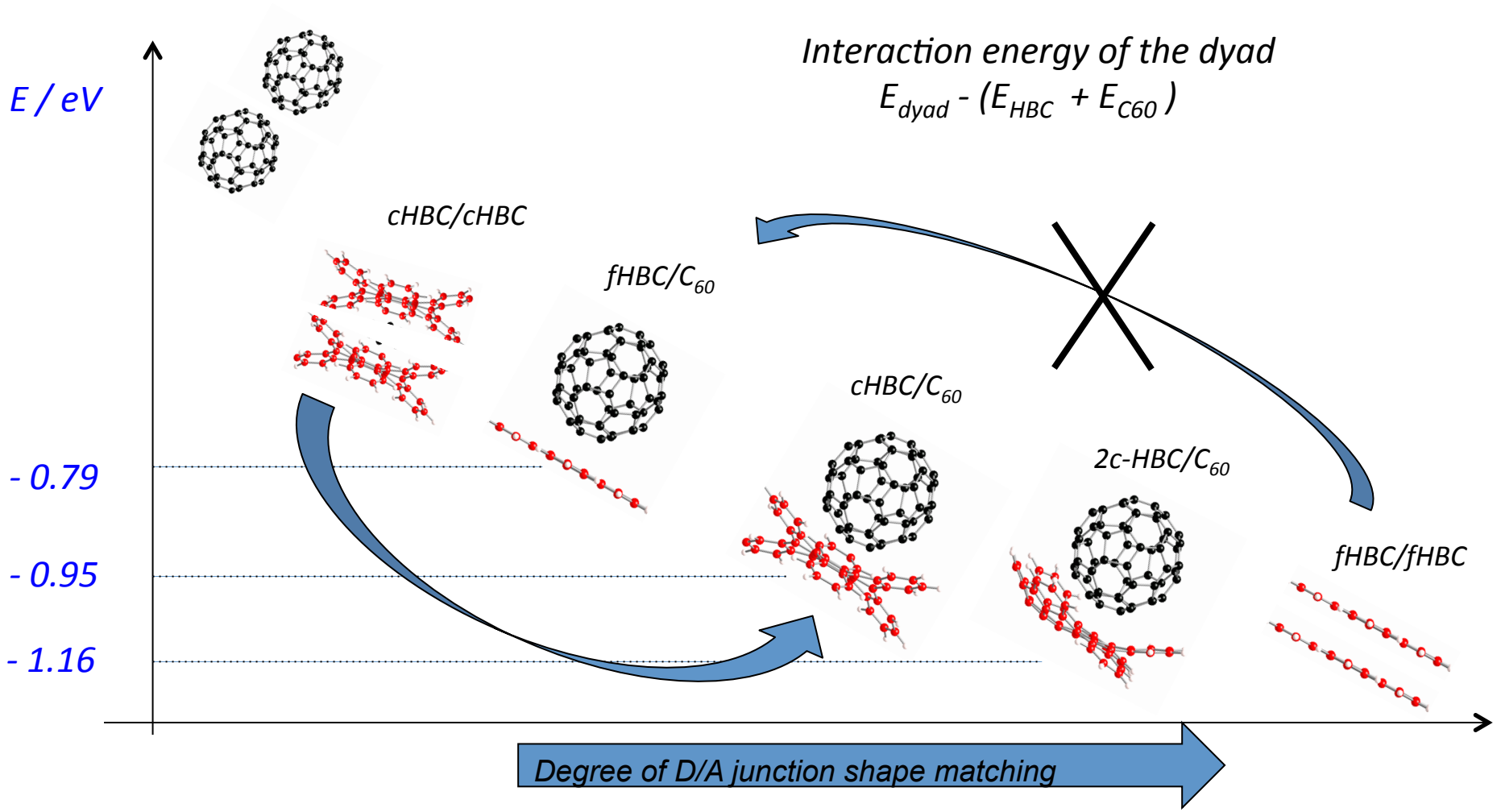
OR



Schiros *et al.* in preparation.

Supramolecular assembly drives higher efficiency OPV ?

DFT calculations



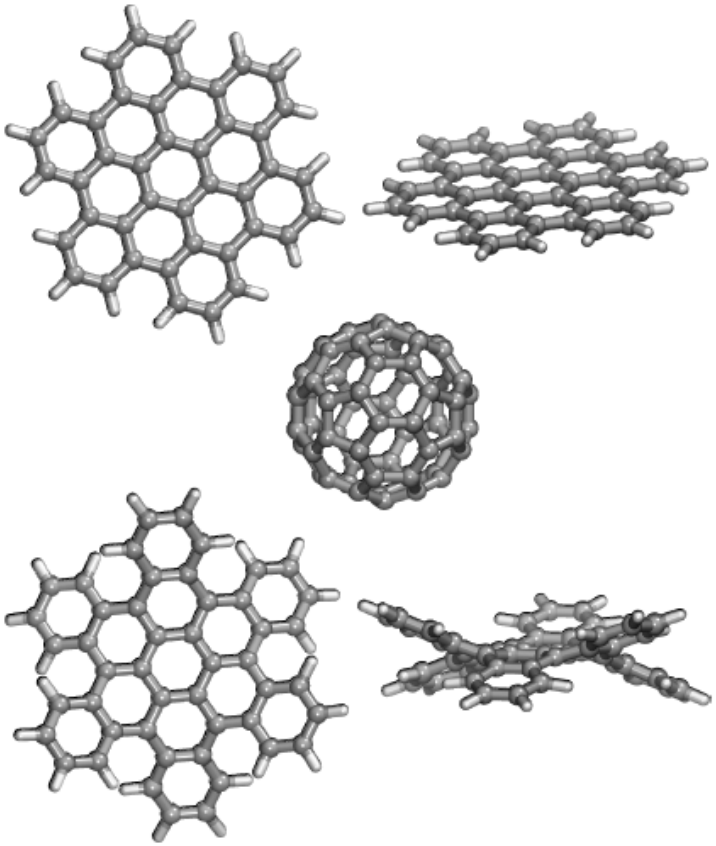
Intermixing morphology favoured for shape matched pairs ?

Perhaps exciton break-up is faster for shape matched dyads ?

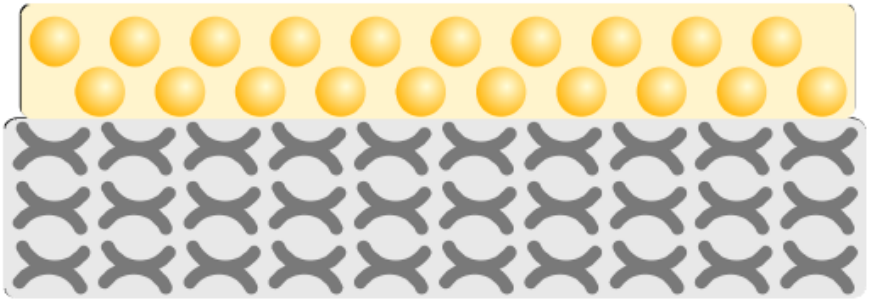
T. Schiros et al., Advanced Energy Materials (2013)

Interfacial CT in a Donor-Acceptor Assembly

- Flat HBC (f-HBC) a planar molecule and contorted HBC (c-HBC) is doubly concave with different degrees of shape matching to C60



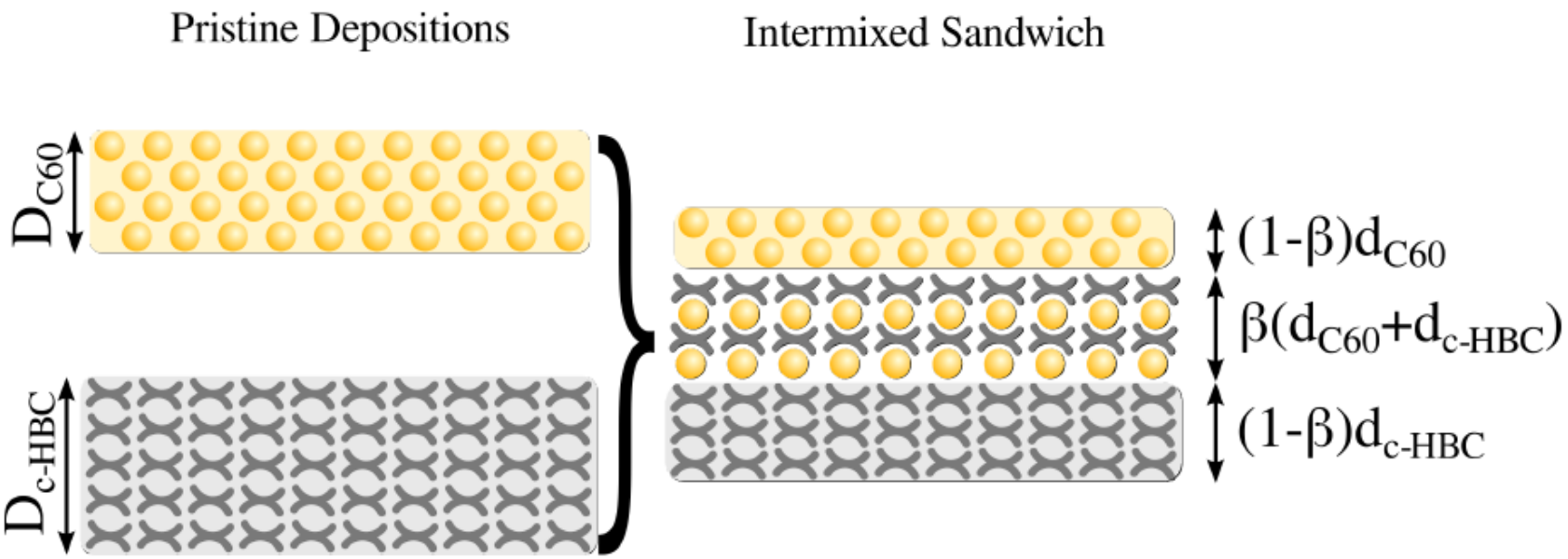
- **Idea**: prepare hetero-organic sandwich layers (C60 on-top of HBC)



- Measure interfacial CT with RPES-CHC using pure films as reference
- **New**: Take into account possible intermixing at the interface

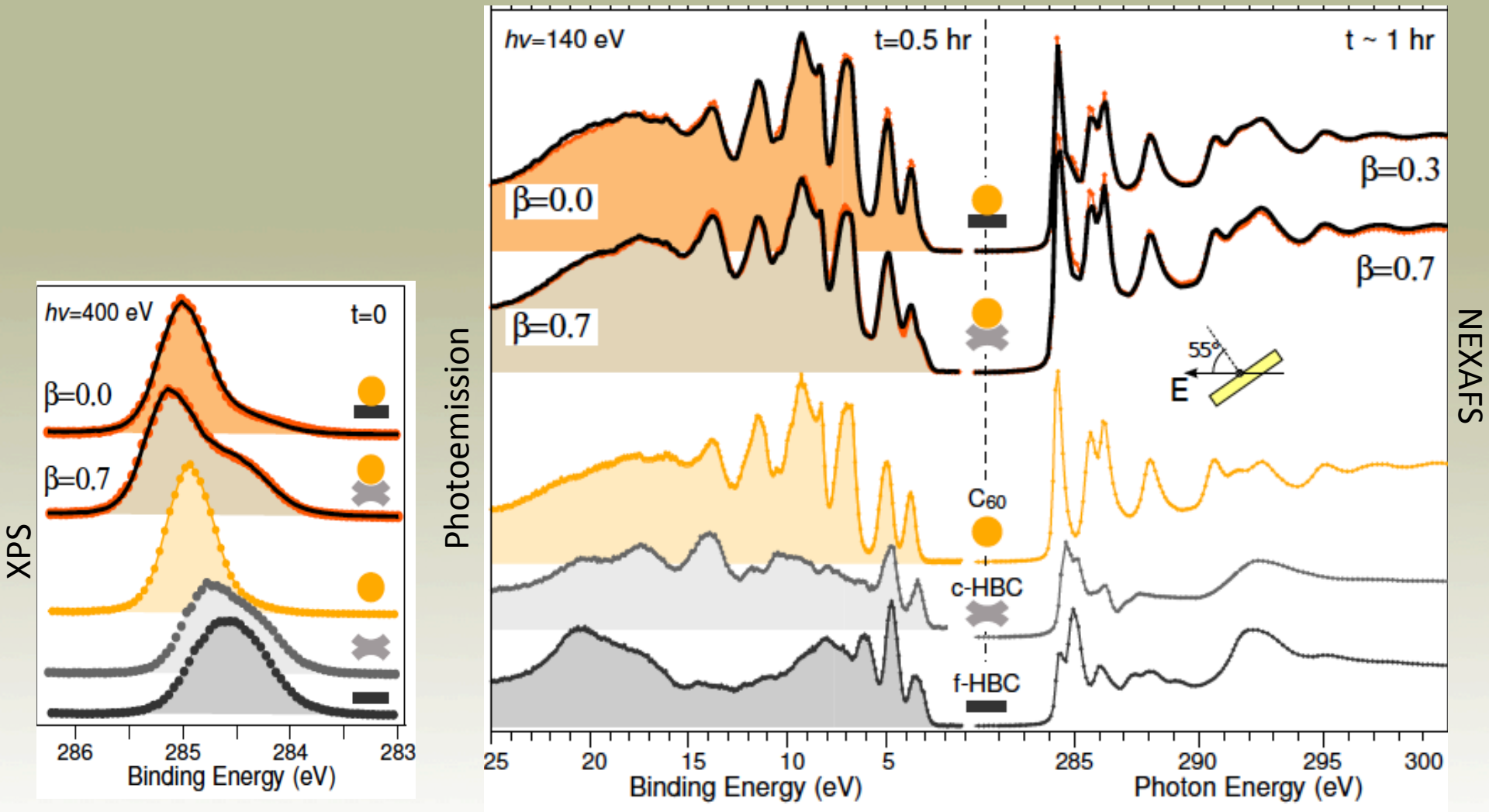
Intermixing Model

- Start from single phase layers with different thickness
  - Use a superposition of single phase spectra to model the sandwich
- Parameter β measures the amount of intermixing in the sandwich:



- Take into account X-ray absorption and electron scattering

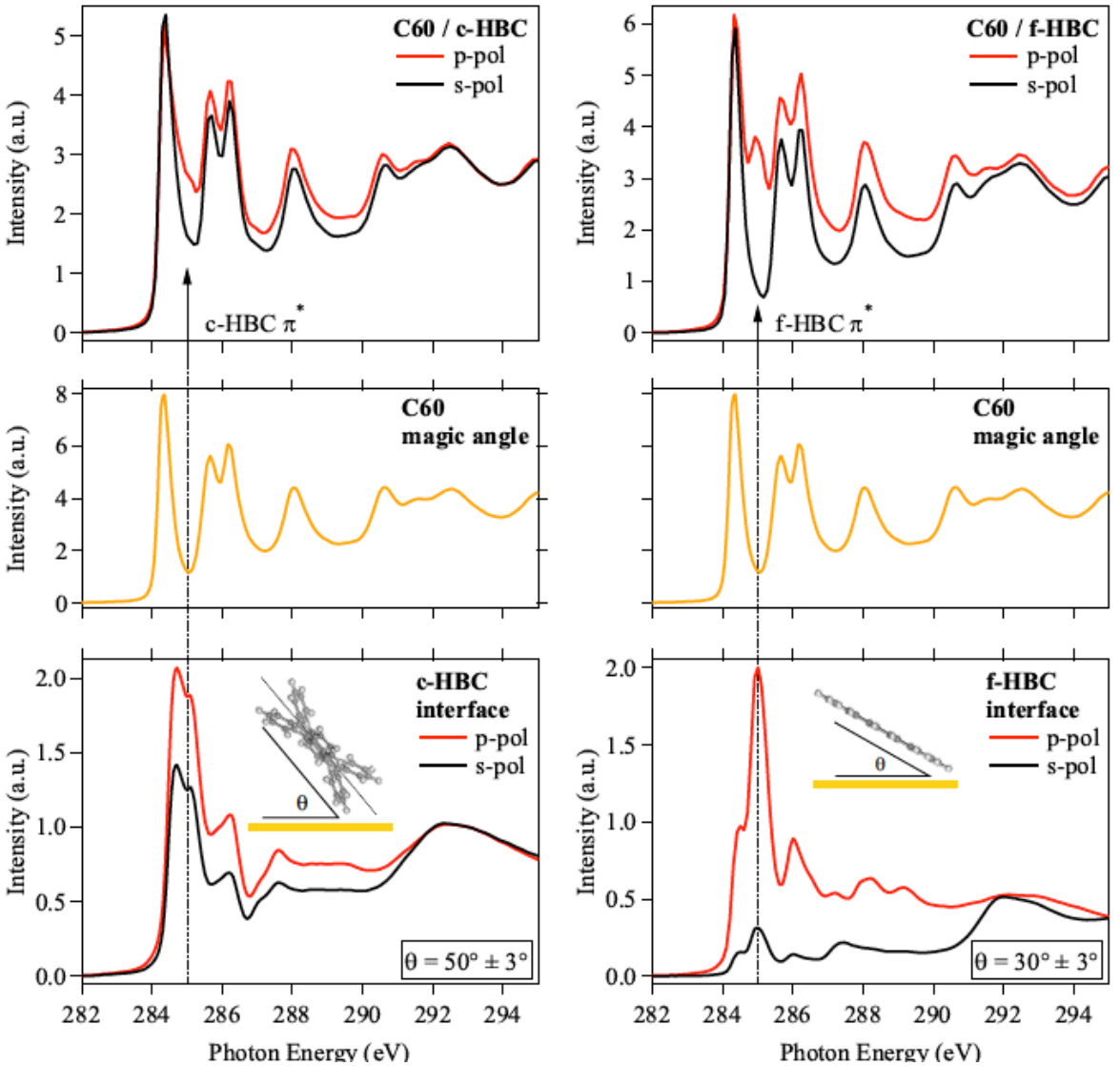
Experimental results – β from fit



β = 0.7 ± 0.1 (C_{60} / c-HBC) and **β = 0.15 ± 0.15** (C_{60} / f-HBC)

Molecular Orientation from NEXAFS Dichroism

- In the intermixed region we use the β-model to decompose into C60 and HBC components
- C60 NEXAFS shows no polarization dependence
- Molecular orientation changes from 25° to 50° in c-HBC and 14° to 30° in f-HBC/C60 interface



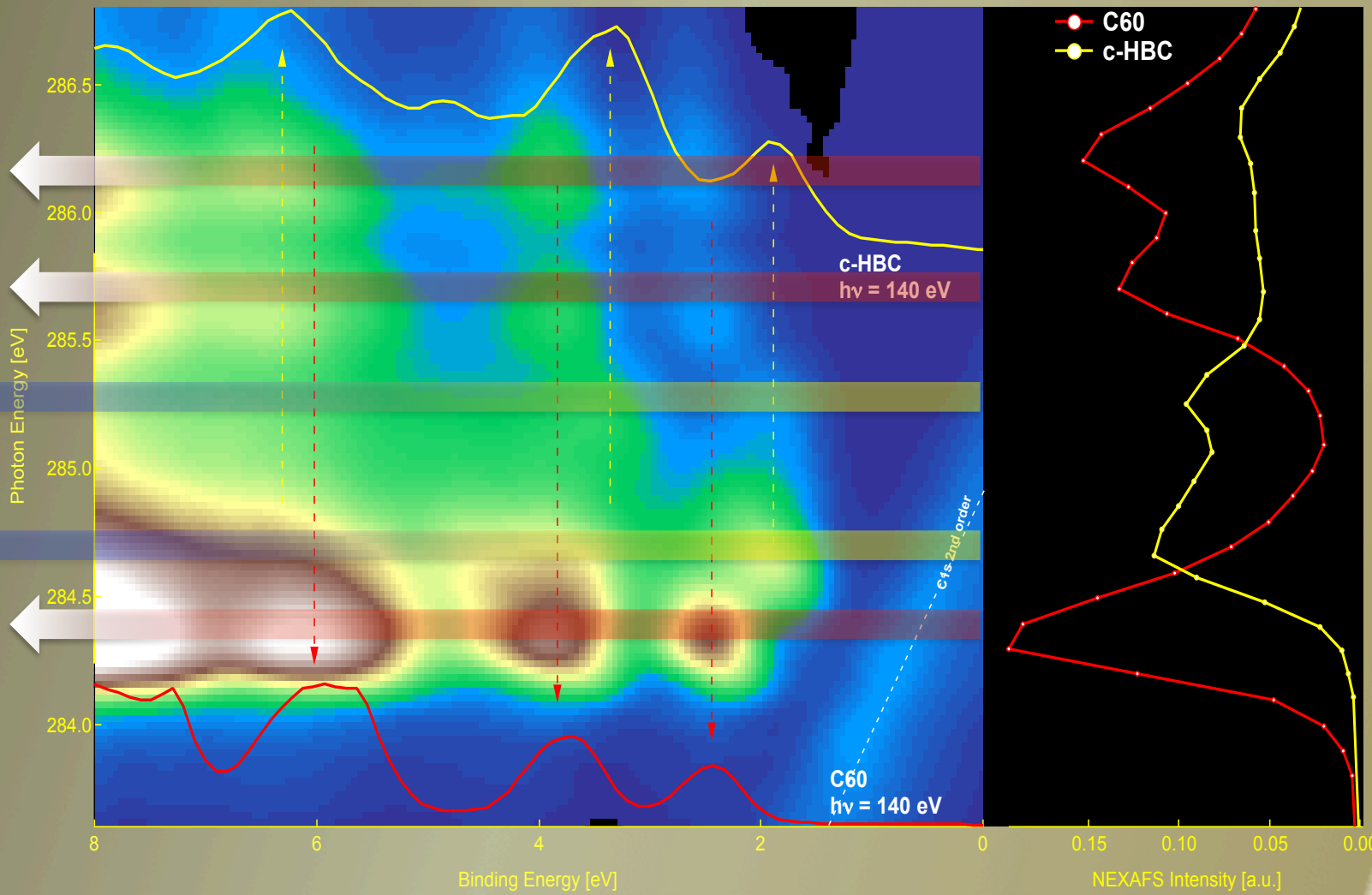
"Core Hole Clock" of HBC/C_{60} interface

Sandwich film C_{60}/HBC/Au compared to pristine films of C_{60} and HBC.

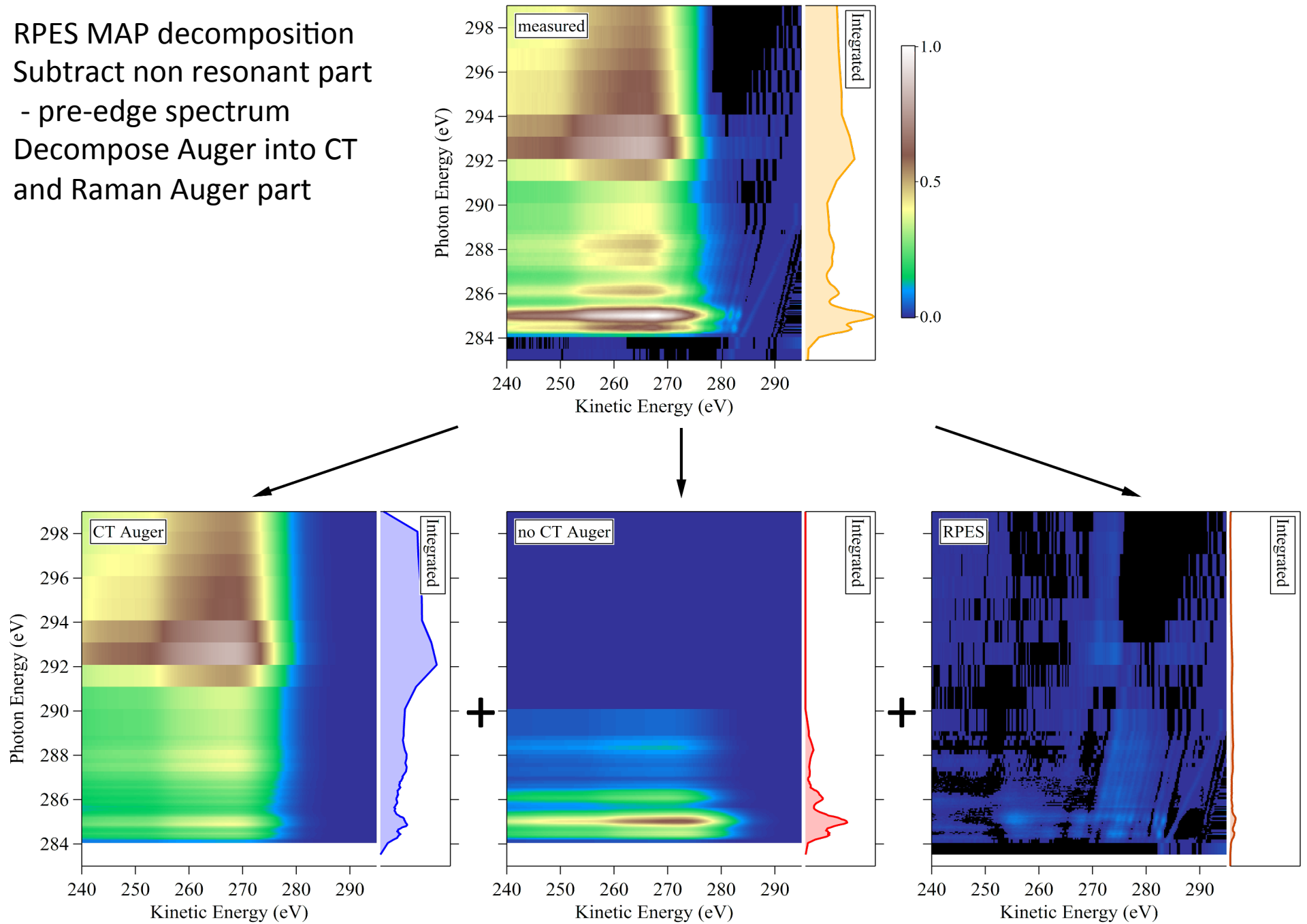
? Quenching of C_{60} RPES

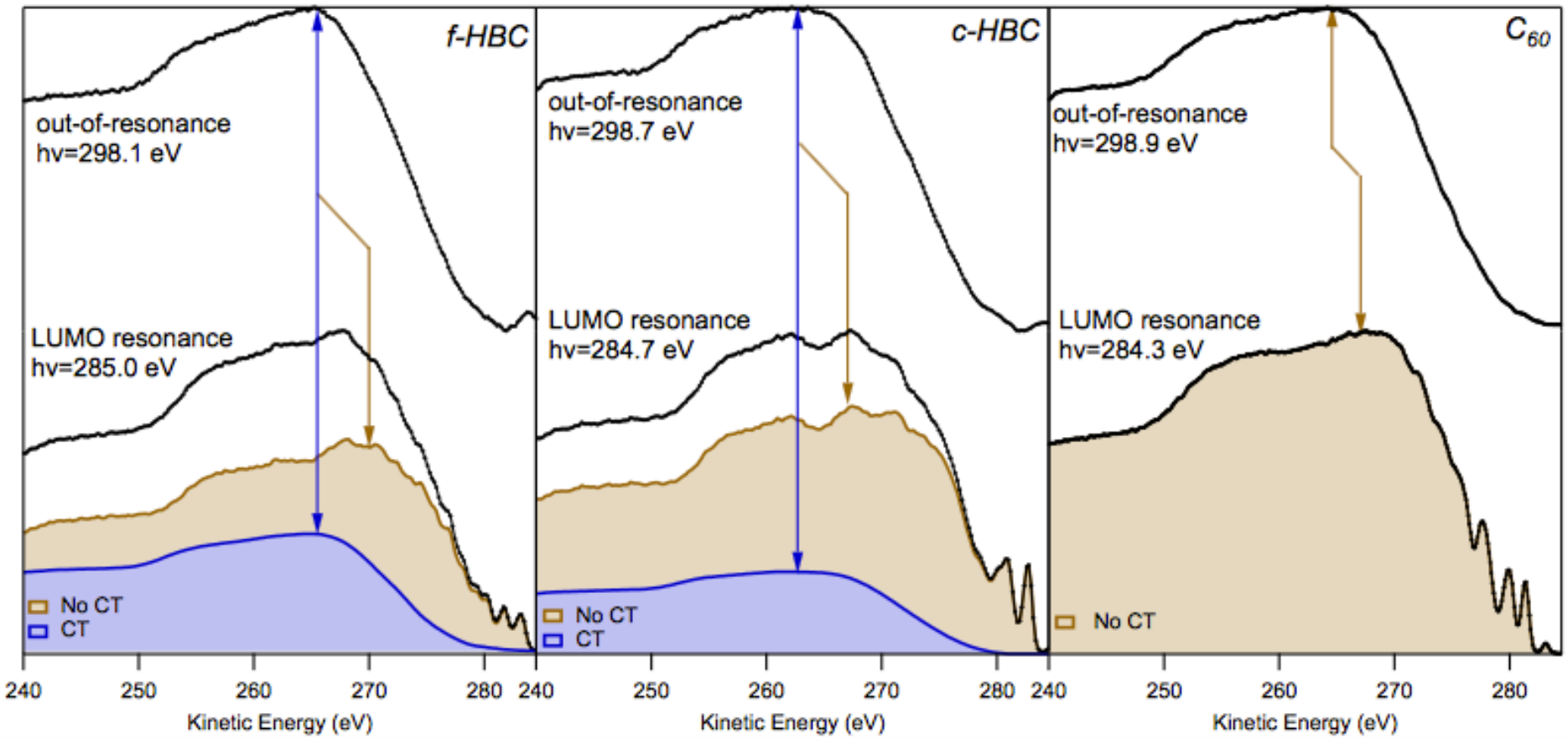
? Quenching of HBC RPES

? Quenching of C_{60} RPES



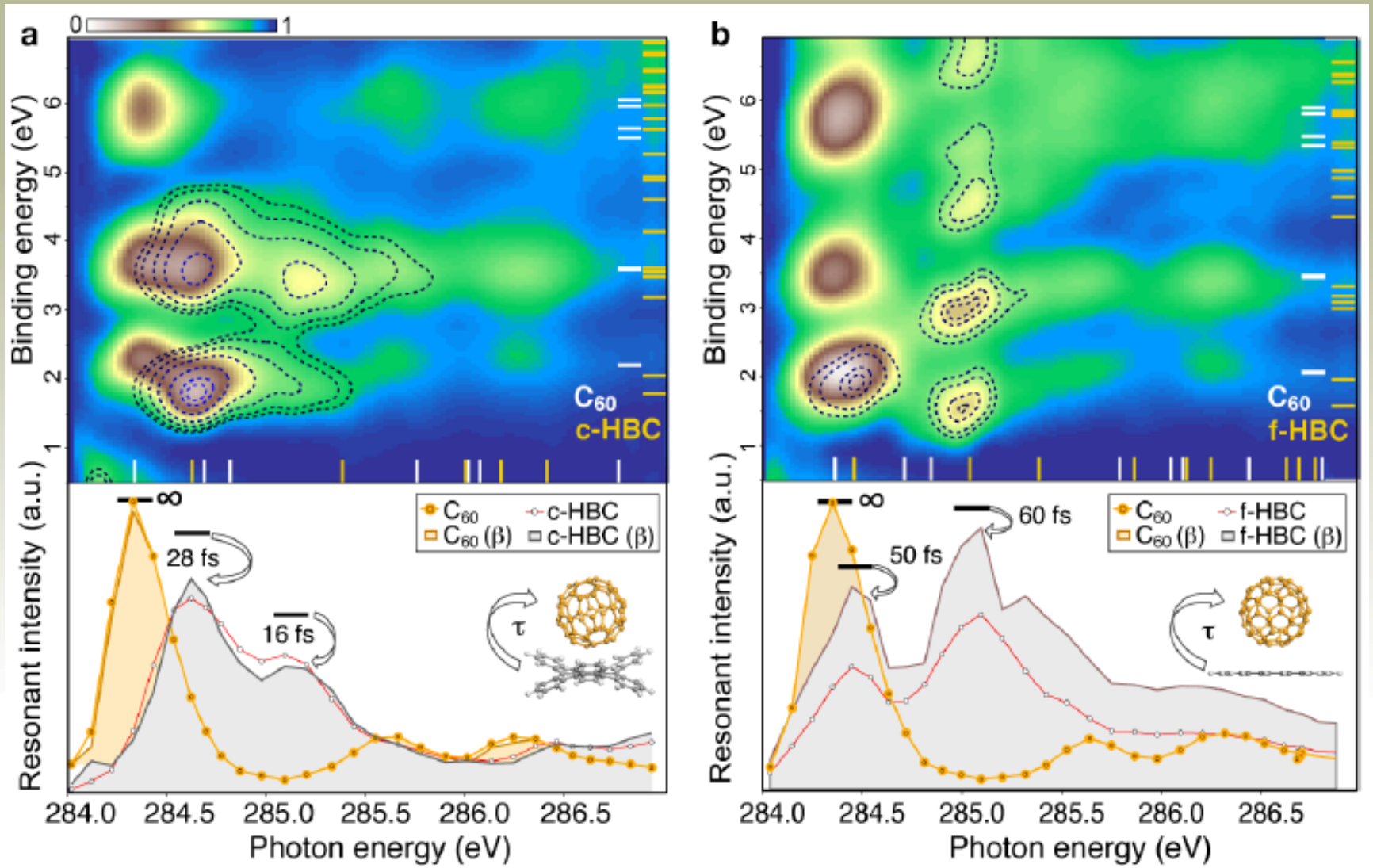
RPES MAP decomposition
Subtract non resonant part
- pre-edge spectrum
Decompose Auger into CT and Raman Auger part





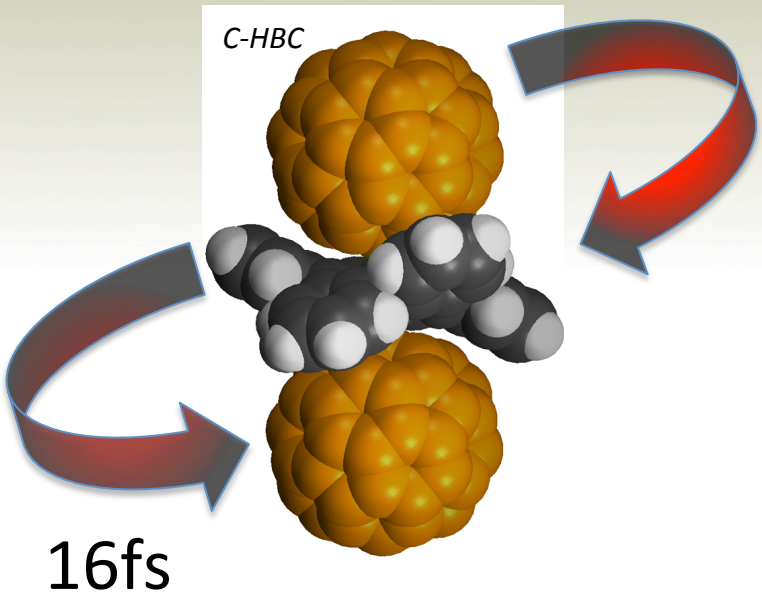
T.Schiros et al., Advanced Energy Materials (2013)

Using β-model with best fit Participator channel quenching



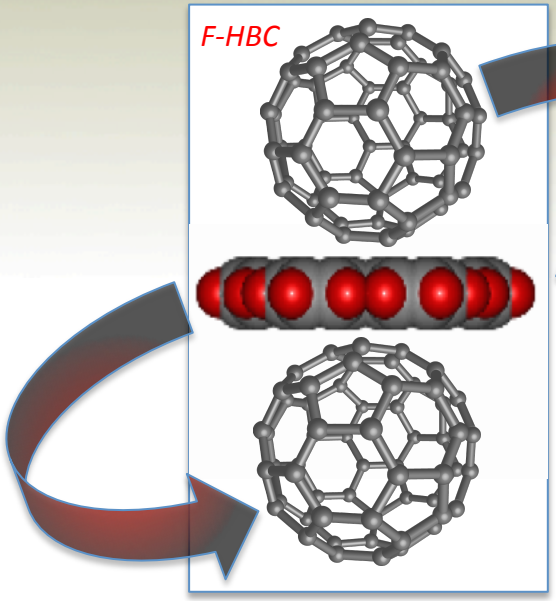
T. Schiros et al., Advanced Energy Materials (2013)

$$\tau_{CT} = \tau_{core} \frac{P_{no\,CT}}{P_{CT}} = \frac{I_{coupled}}{I_{Iso} - I_{coupled}}$$



16fs

∞



60fs

∞

D/A assemblies : Fast , highly directional CT from HBC to C_{60} ?

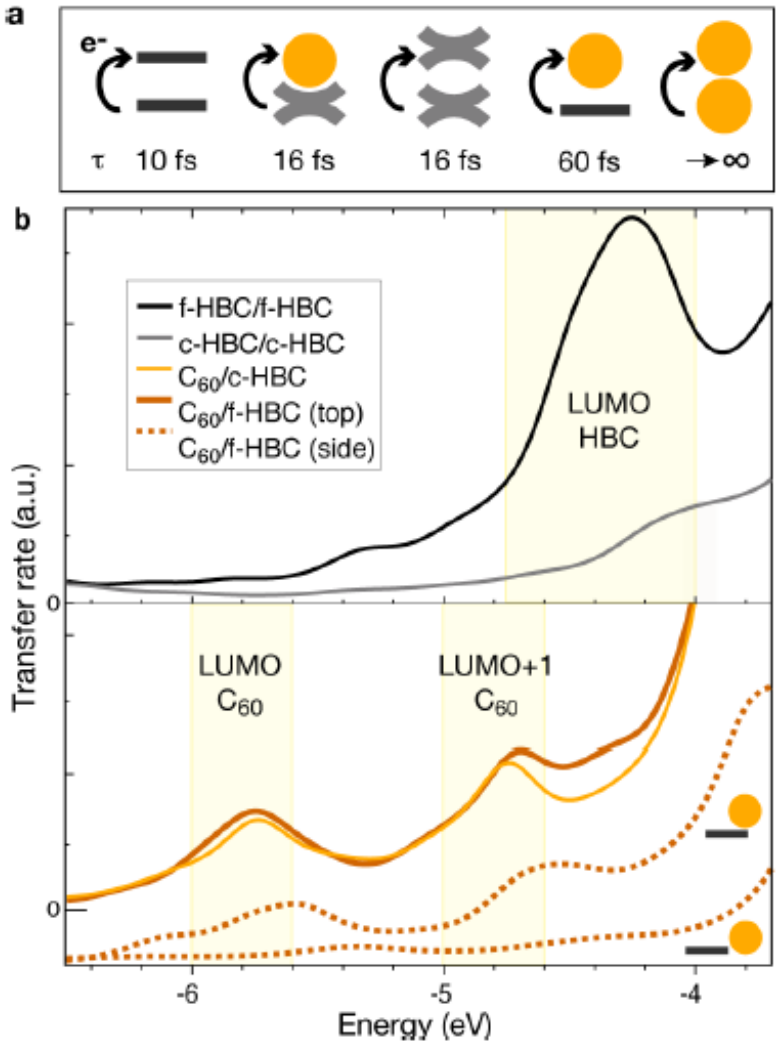
Interfacial CT in a Donor-Acceptor Assembly

- Complex **C**, constituted by two weakly interacting subunits **A** and **B**
- Transfer Integral defined as

$$\mathbf{TI}_{\alpha\beta} = \langle\alpha|H_C|\beta\rangle = \sum_{\gamma}\langle\alpha|\gamma\rangle\varepsilon_C\langle\gamma|\beta\rangle$$

- $\langle\alpha|\gamma\rangle$, $\langle\beta|\gamma\rangle$ are the projections of each subsystem onto the full system **C**
- a measure of the coupling between states α of **A** and β of **B** when the two units are brought together to form **C**
- Transfer rate is then given by

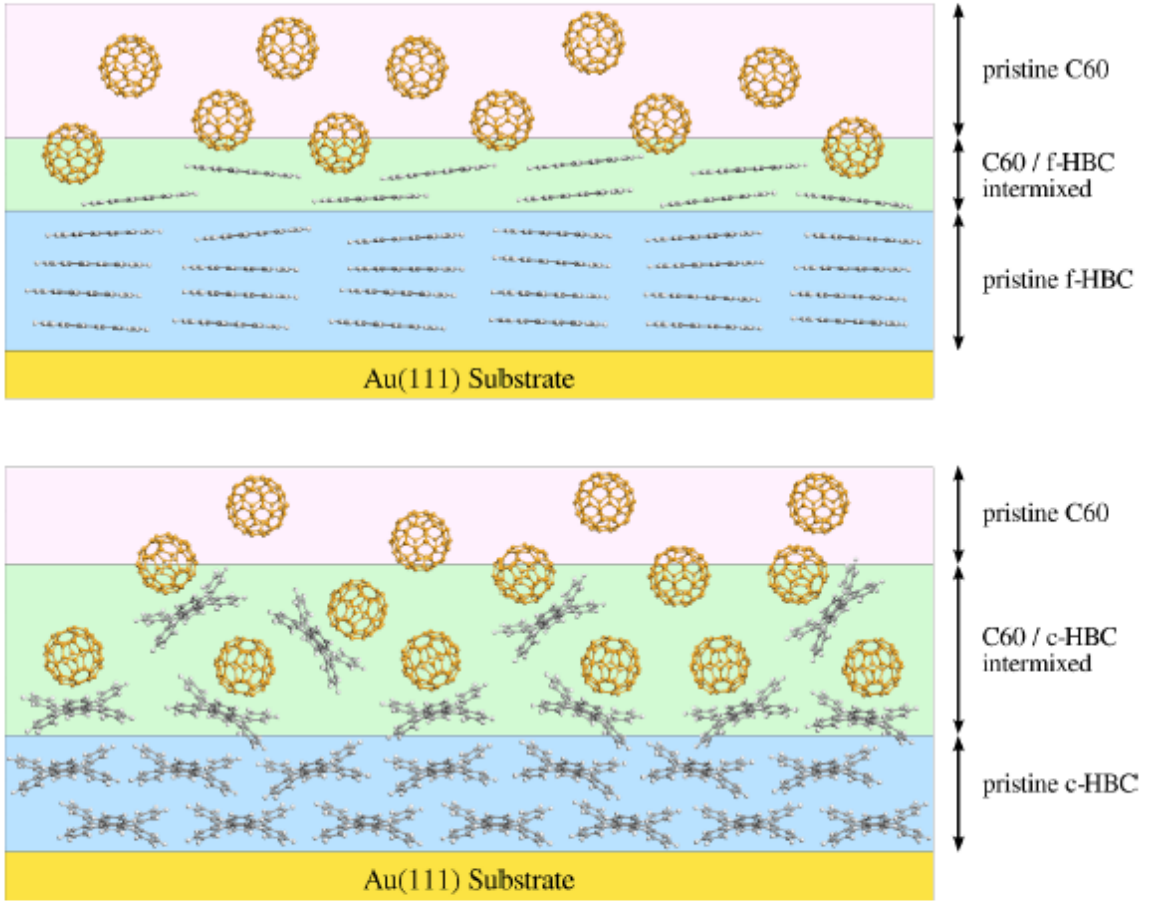
$$\Gamma_\alpha(\omega) = \sum_{\beta}|\mathbf{TI}_{\alpha\beta}|^2\delta(\omega-\varepsilon_\beta)$$



Results – C60/HBC

C60/c-HBC interface:

- Better intermixing ($\beta = 0.7$ vs. $\beta = 0.3$) – larger active volume
- Faster CT (2-3×) – higher exciton dissociation rate
- Consistent with OPV device scale efficiency (0.55% vs. 0.07% VIS) (3.36% vs. 0.03% UV) Tremblay et al. (2010)



T.Schiros et al., Advanced Energy Materials (2013)

Univerza v Ljubljani

Acknowledgements

[Physics Dept., Ljubljana University](#)

Dr. Gregor Kladnik

[Columbia Applied Physics & Chemistry](#)

Prof. Latha Venkataraman

Dr.Arunabh Batra

Dr.Masha Kamenetska

Prof. Colin Nuckolls

Dr. Jeffrey S. Meisner

[CNR Modena , Italy](#)

Dr.Andrea Ferretti

Dr.Deborah Prezzi

Prof.Elisa Molinari

[ALOISA beamline, IOM CNR](#)

Dr.Albano Cossaro

Dr.Luca Floreano

Dr.Alberto Verdini

Dr.Martina Dell'Angela

Prof. Alberto Morgante

Dr. M.Coreno (GAPH)

Dr.M.DeSimone

UC Berkeley & Molecular Foundry

Prof. Jeffrey Neaton

[Dip.chimica, Trieste University](#)

Dr.Gabriele Balducci

Dr. Mauro Stener,

Michele Romeo

Prof.Giovanna Fronzoni

[Columbia Applied Physics](#)

Prof. John Kymissis

Dr.Theanne Schiros

Prof. Alon Gorodetsky

Prof.J.Yardley

Thank you.