The Great Electron Escape: Measuring Through-Space Charge Transfer in Metal-Molecule Interfaces

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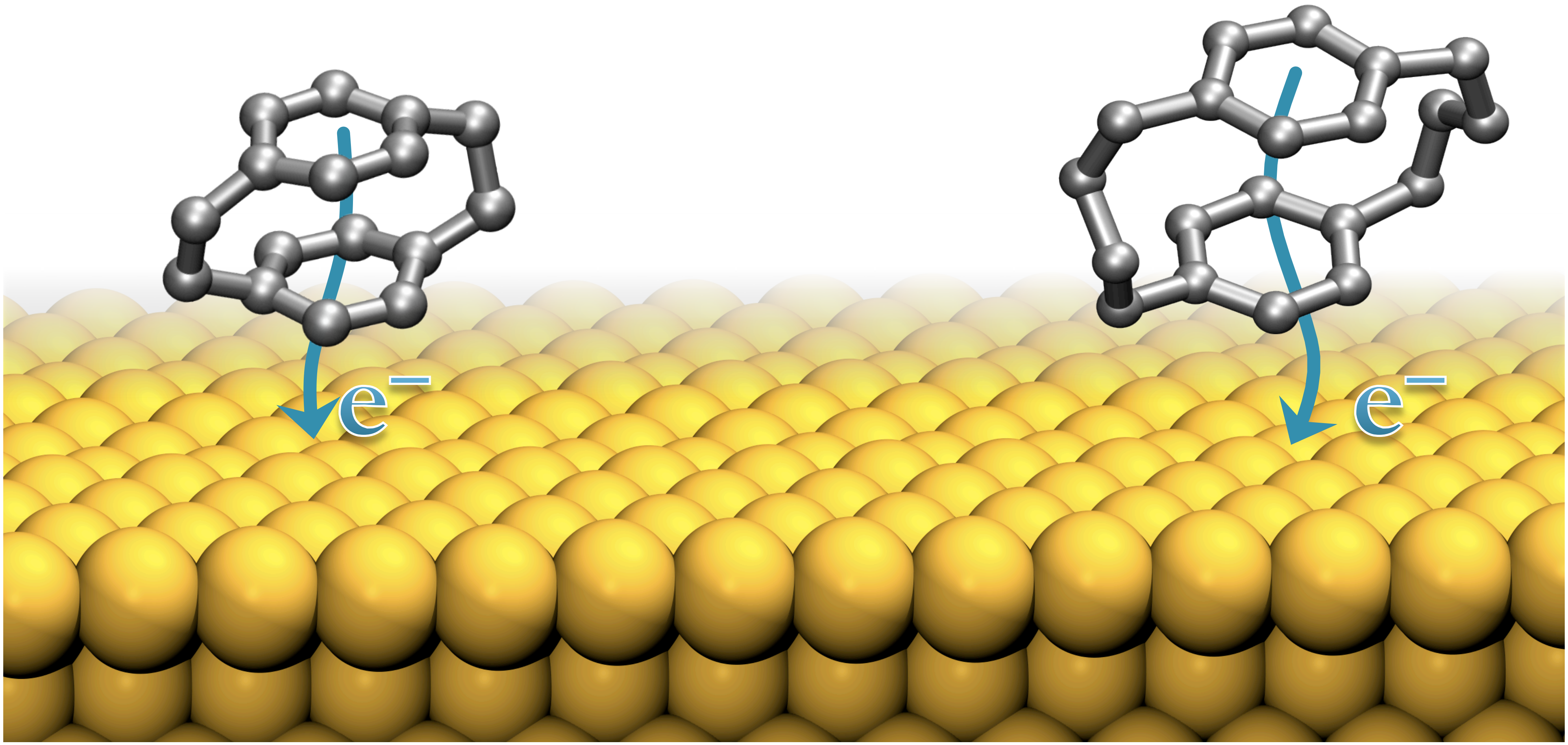
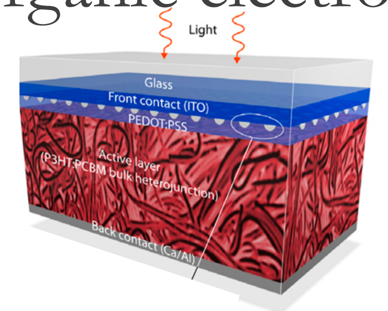
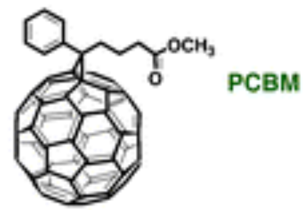
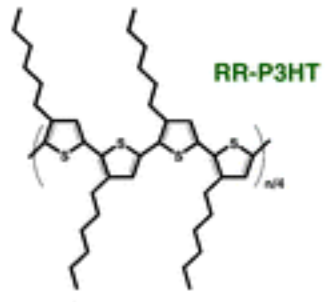


Motivation

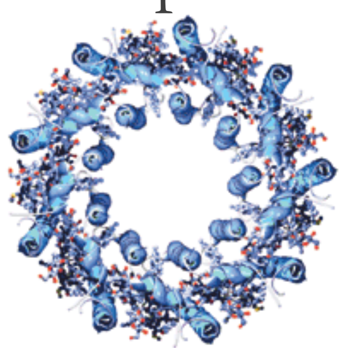
- Through-space charge transport is important in:
  - Organic electronics/photovoltaics

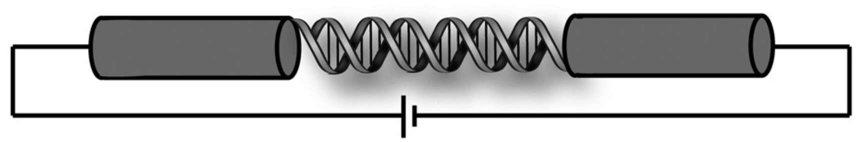






  - Biocomplexes (eg. Chromophores), Molecular wires



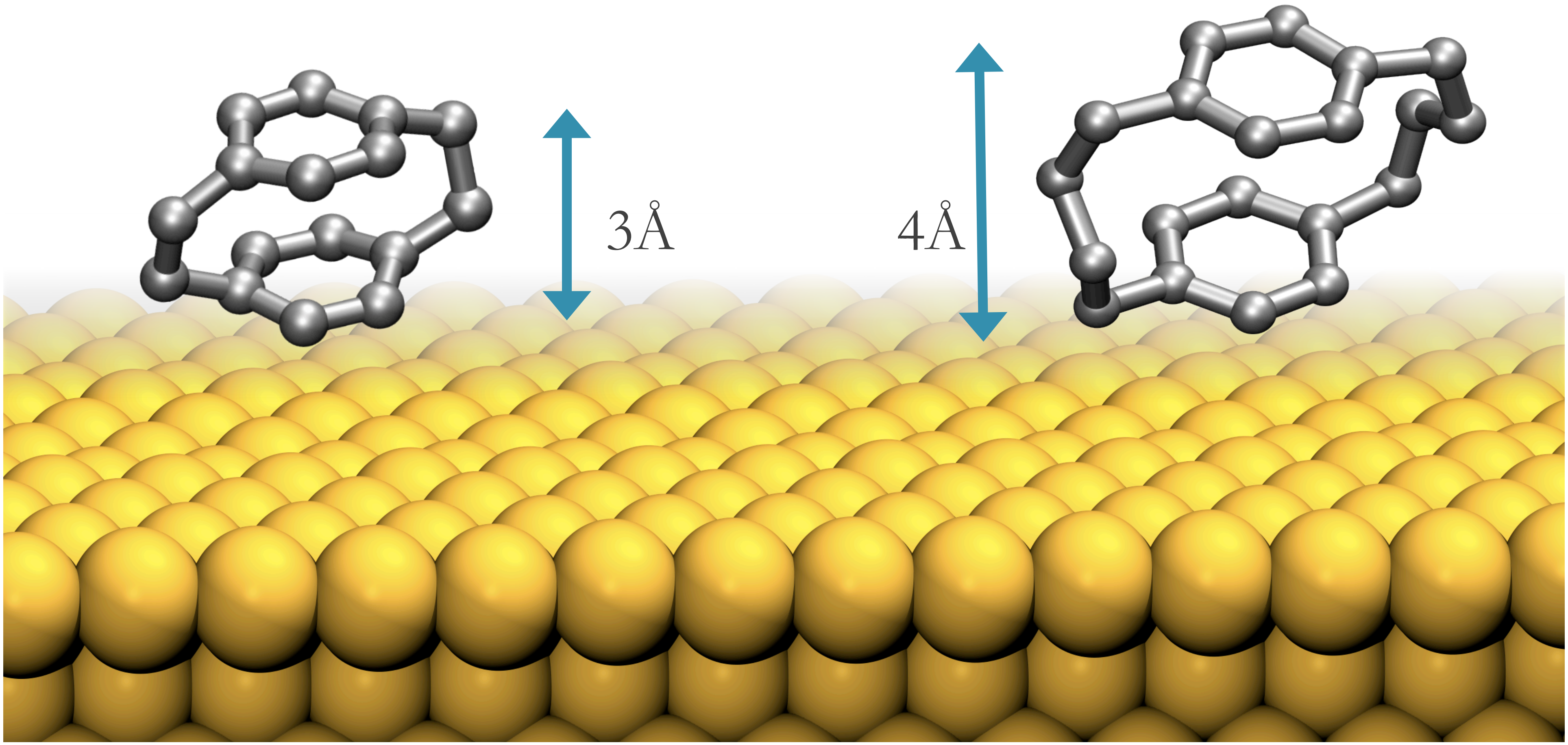


  - Multilayer Graphene devices, molecular electronics, nonlinear optical phenomena…

Molecular systems

[2,2]Paracyclophane (22PCP) // Au(111)

[4,4]Paracyclophane (44PCP) //Au(111)



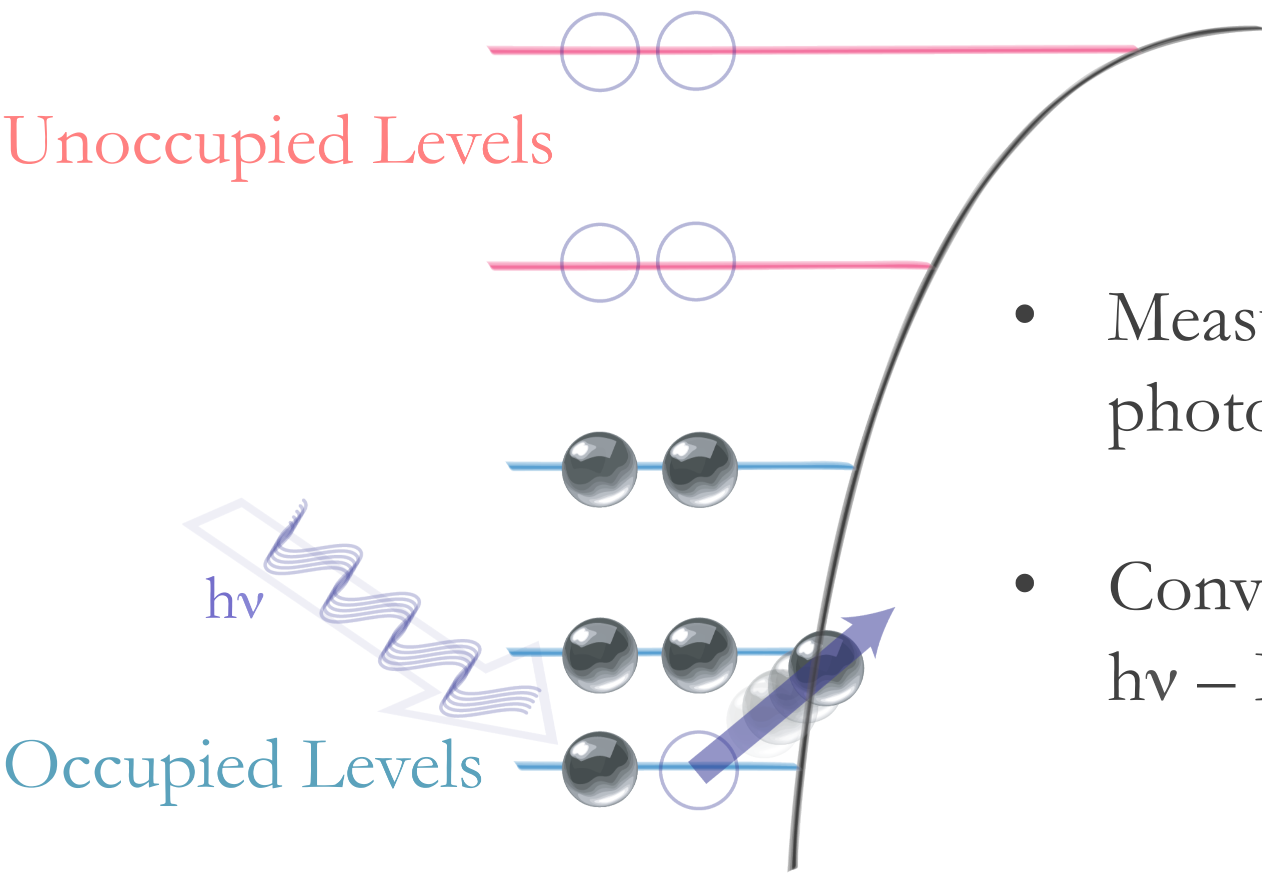
Experimental Techniques

- X-Ray Photoemission Spectroscopy (XPS)
- Near-Edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS)

- Resonant Photoemission Spectroscopy (ResPES)

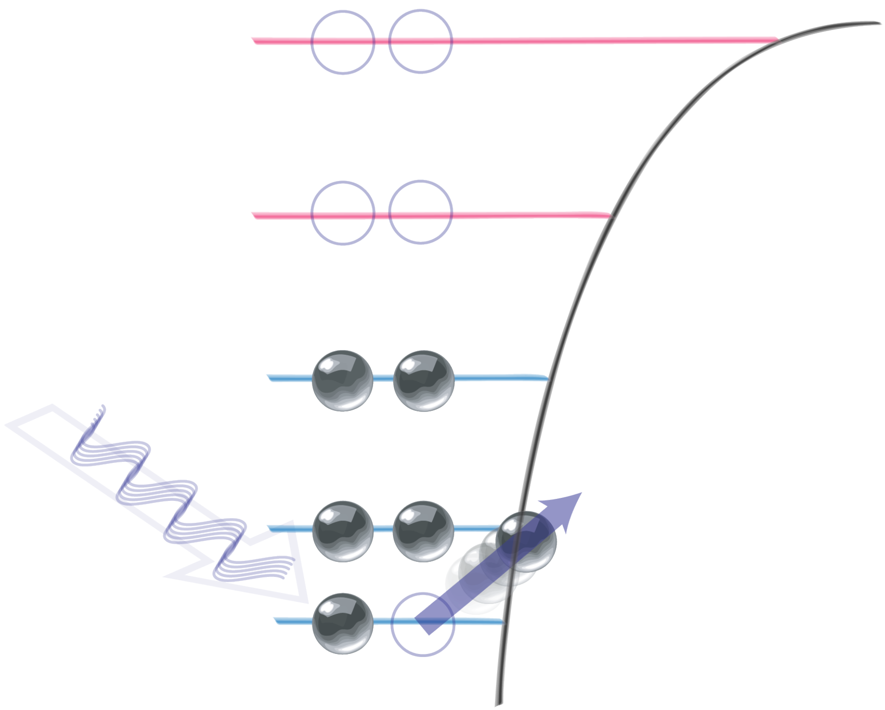
X-Ray Photoemission Spectroscopy (XPS)

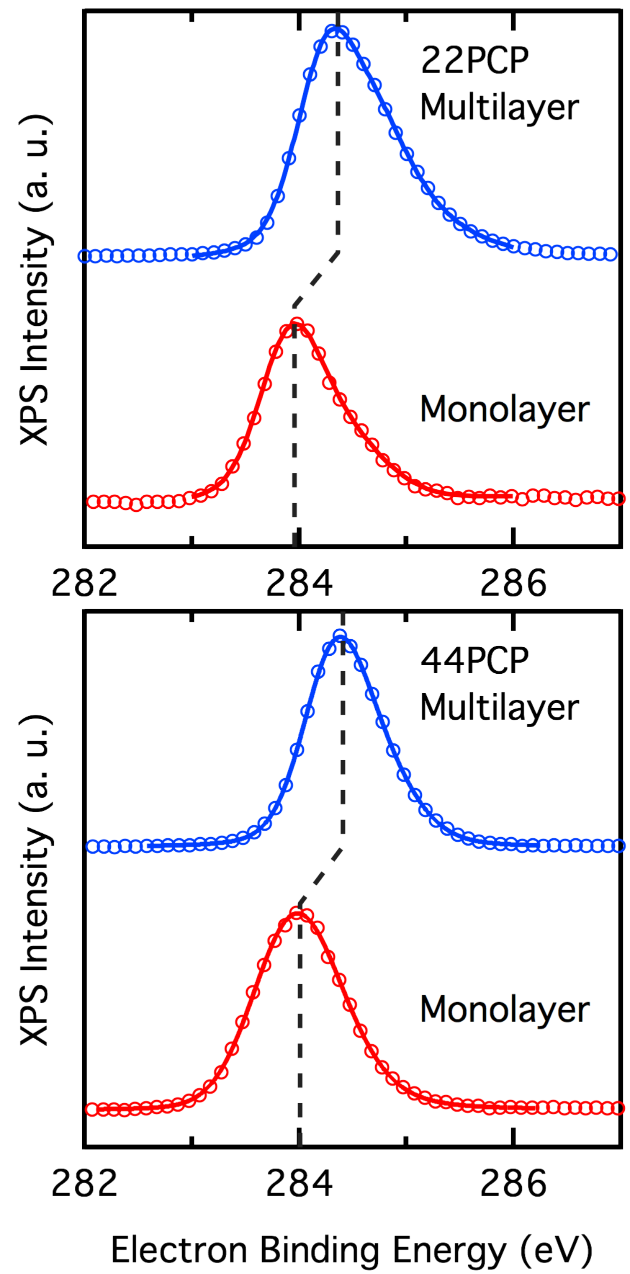
LIGHT IN ⟶ ELECTRONS OUT



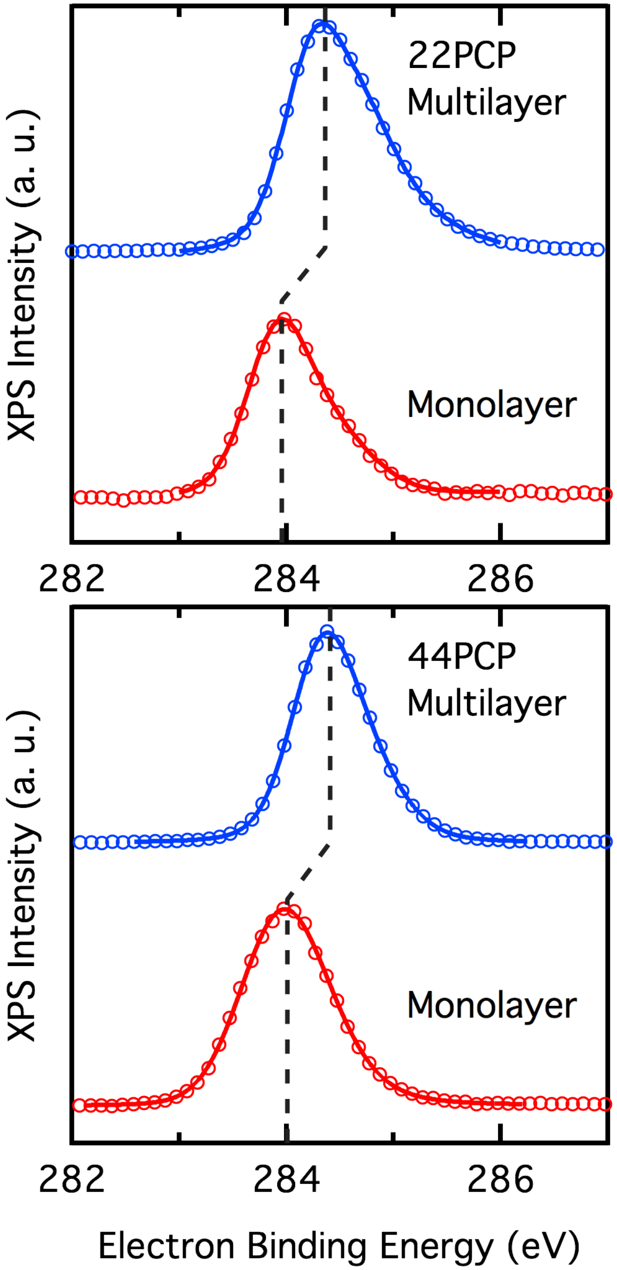
- Measure $E_{kinetic}$ of photoelectrons
- Convert to $E_{binding}$ via $h\nu - E_{kinetic} = E_{binding}$

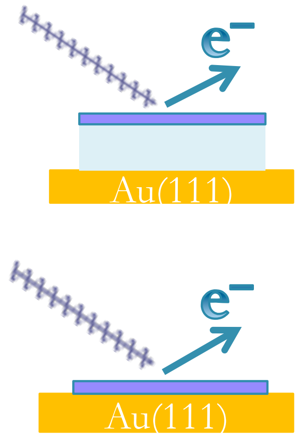
Film Morphology (XPS)





Film Morphology (XPS)



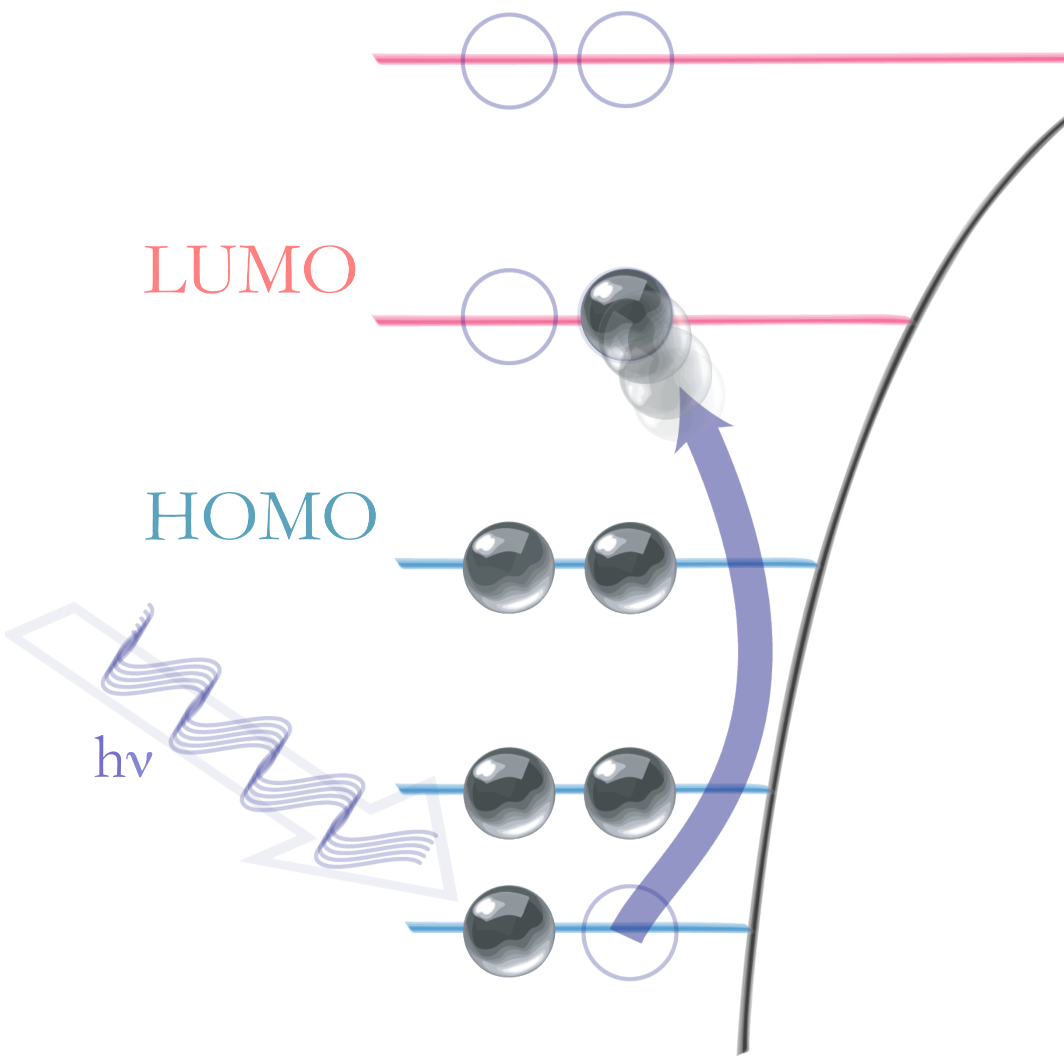


- XPS for Monolayer looks like multilayer, except for 'screening' shift. Both molecules adsorb weakly

- Similar $E_{binding}$, similar shape. Both molecules have similar adsorption energies

Near Edge X-Ray Absorption Fine Structure (NEXAFS)

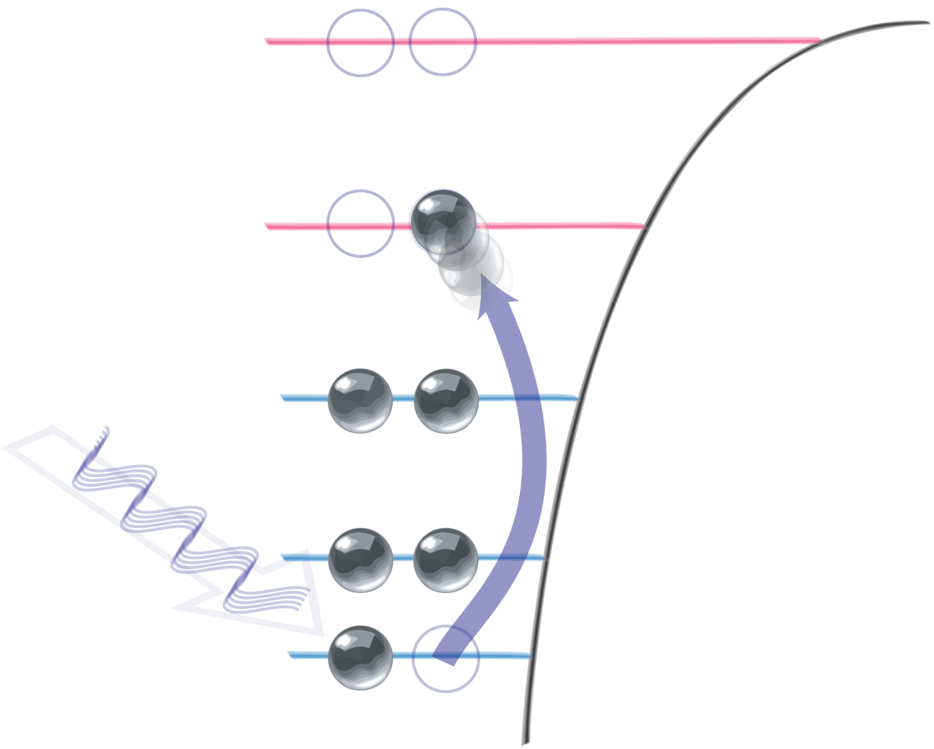
LIGHT IN → EXCITATION/DECAY → ELECTRONS OUT

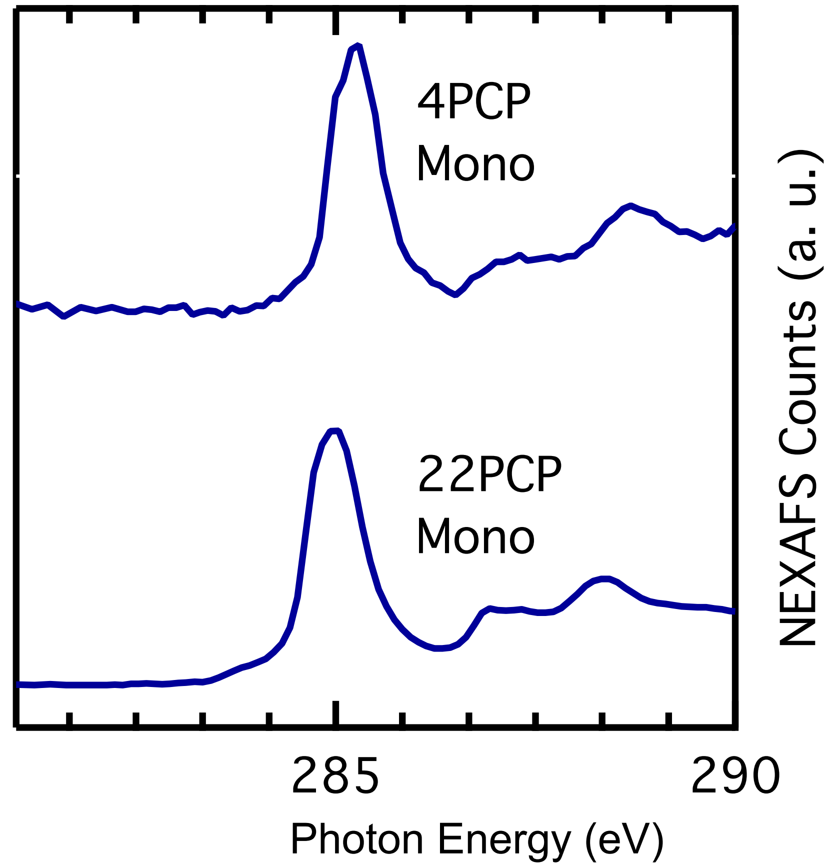


- Scan photon energy across C1s→ LUMO transition
- Count all photoelectrons coming out
- Multiple decay processes, no $E_{kinetic}$ information

Near Edge X-Ray Absorption Fine Structure (NEXAFS)

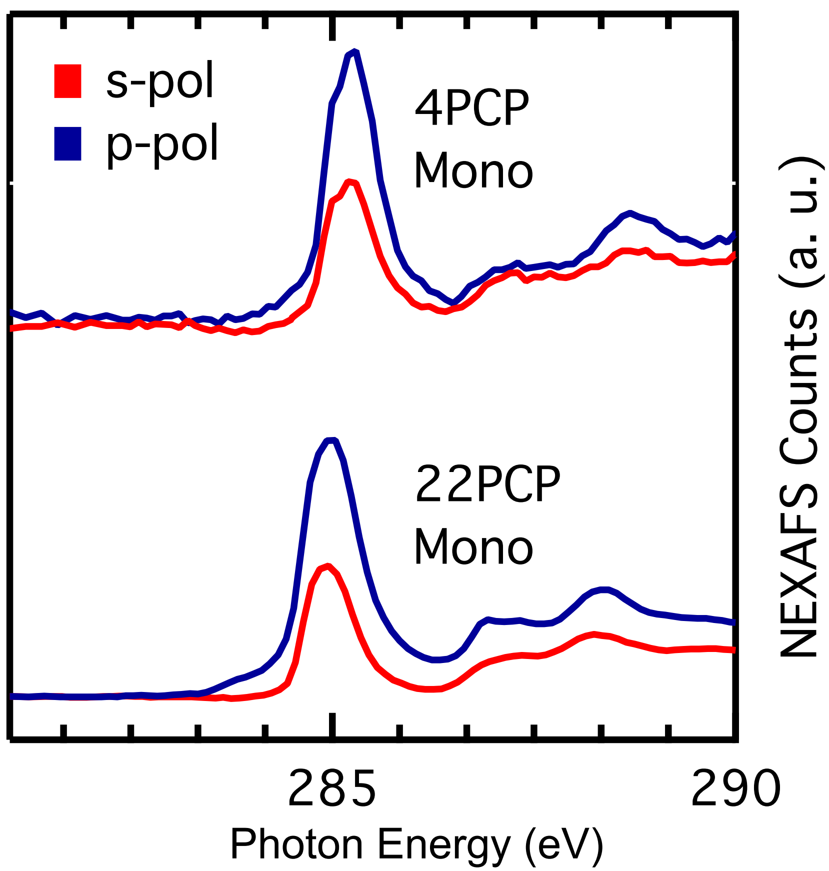
LIGHT IN ⟶ EXCITATION/DECAY ⟶ ELECTRONS OUT

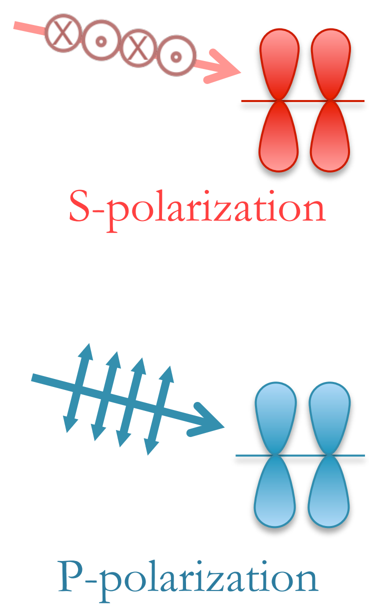




Near Edge X-Ray Absorption Fine Structure (NEXAFS)

LIGHT IN ⟶ EXCITATION/DECAY ⟶ ELECTRONS OUT





- Ratio of peak heights gives us tilt angle
- 22PCP ~ 47°
- 44PCP ~ 45°

Experimental Techniques

- X-Ray Photoemission Spectroscopy (XPS)
- Near-Edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS)

- 22PCP and 44PCP adsorb very similarly on Au(111) and therefore can be compared.

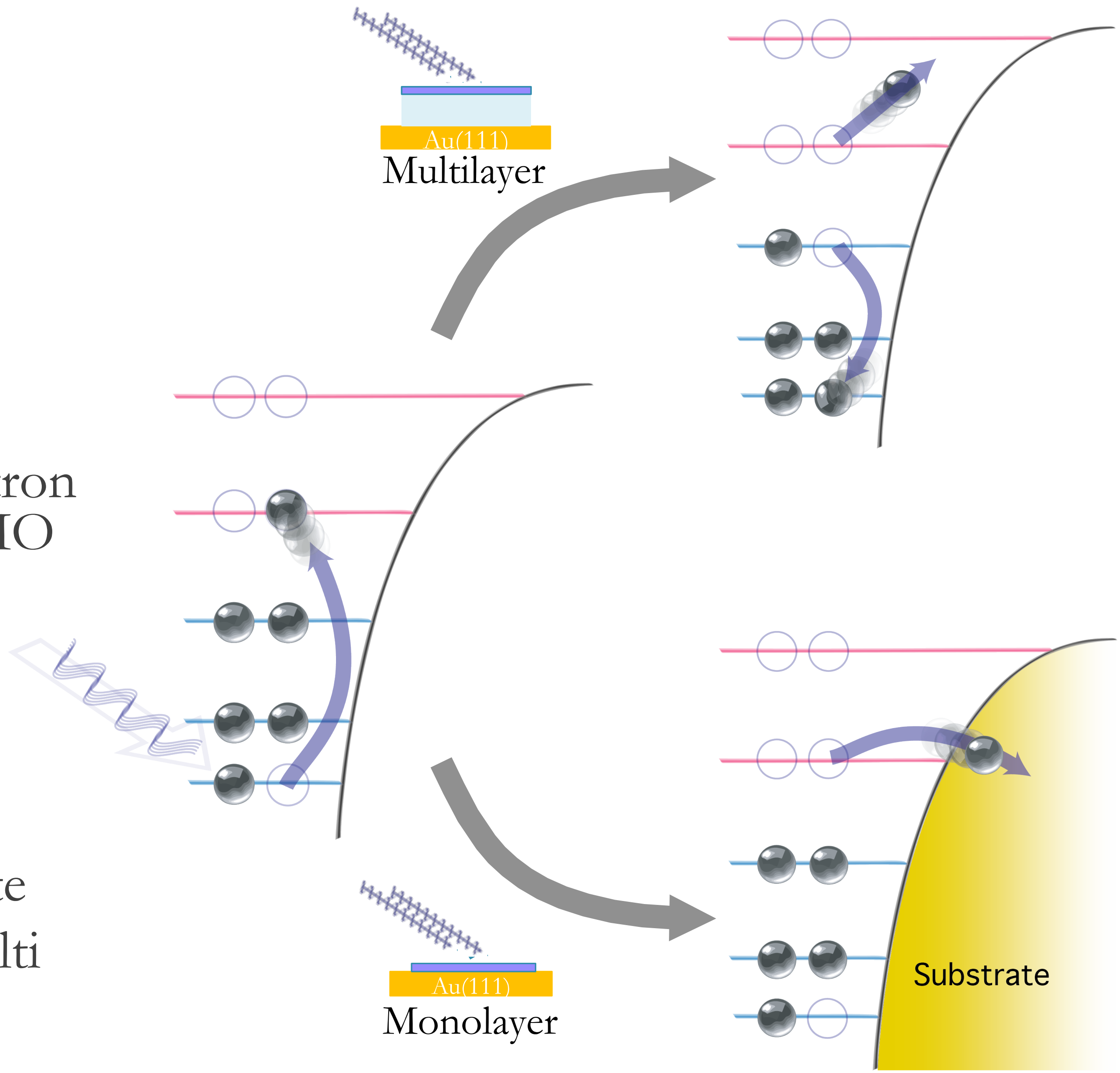
- Such ‘tunable’ systems are difficult to find!

- Resonant Photoemission Spectroscopy (ResPES)

Measuring Charge Transfer time

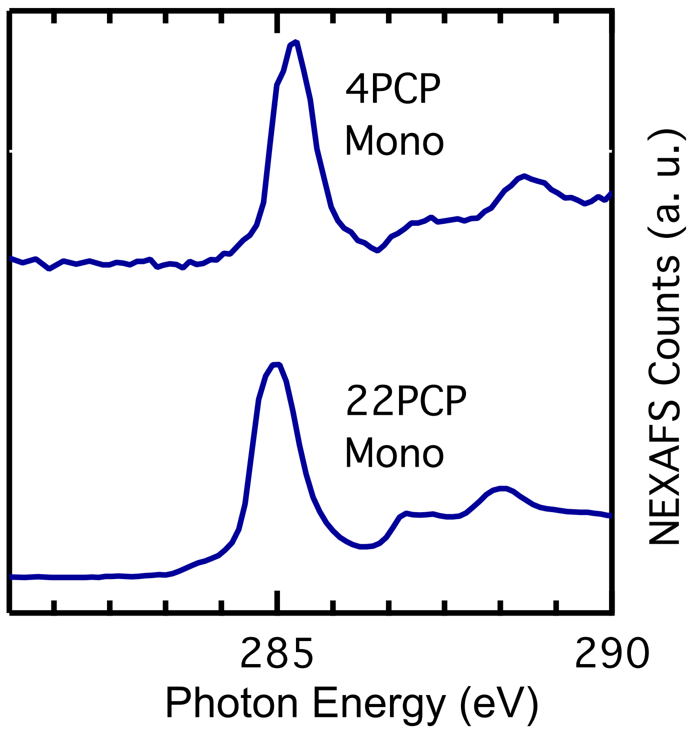
- Excite electron to LUMO (just like NEXAFS)
- Measure photoelectron intensity from LUMO electron decay

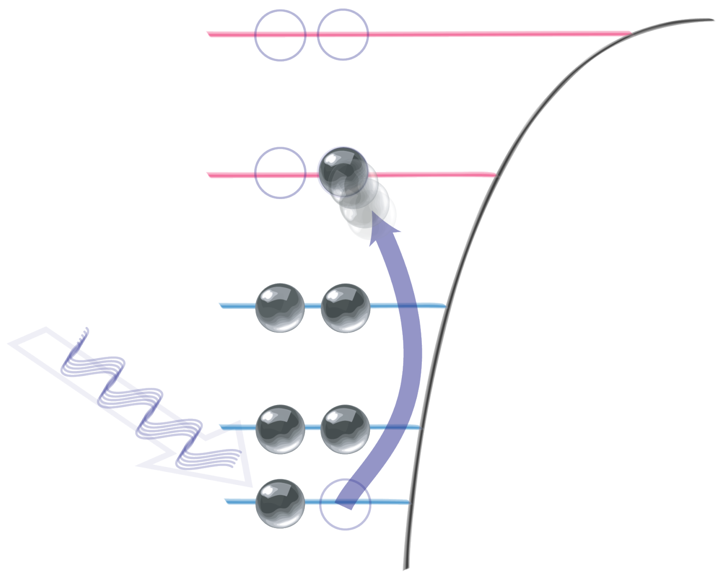
- Intensity from monolayer is lower, due to electrons escaping to substrate
- Ratio of mono/multi intensities gives CT time



Resonant Photoemission (ResPES)

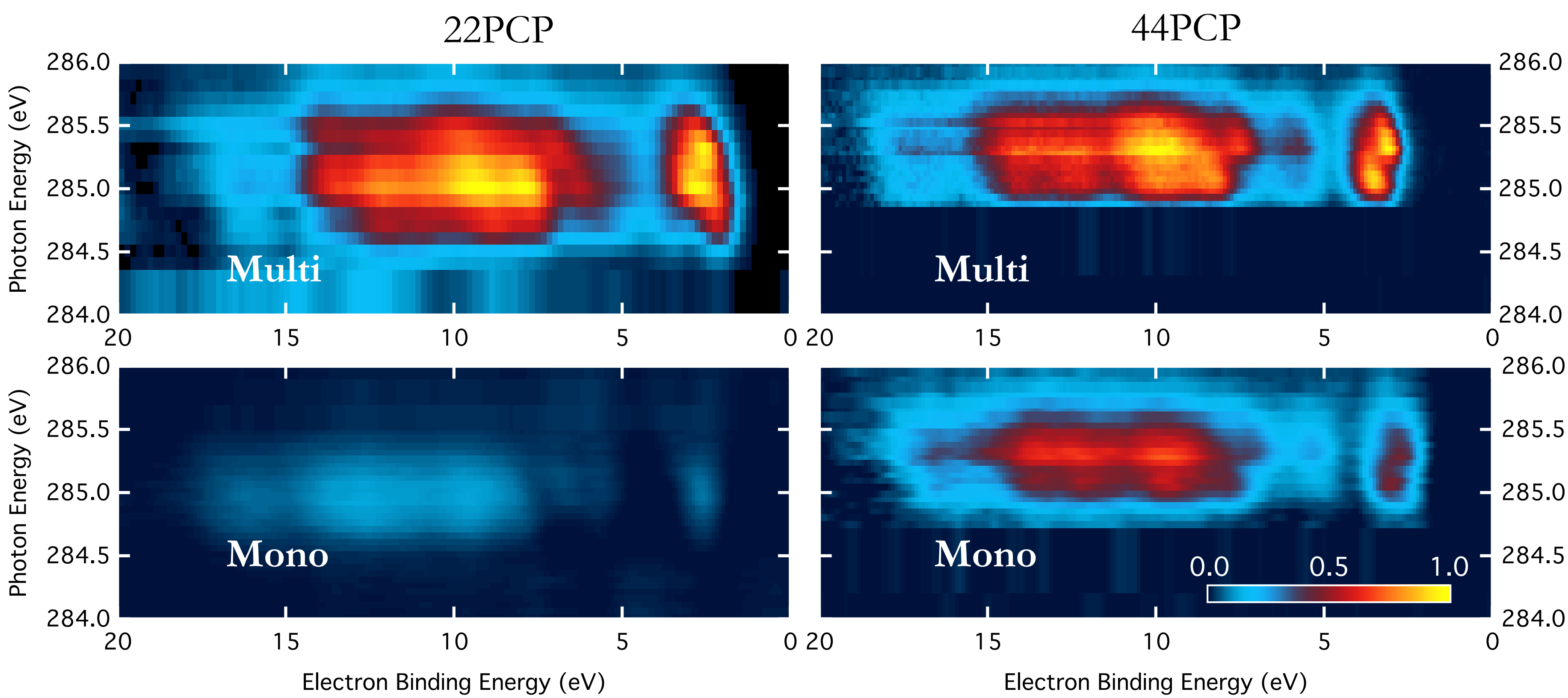
- Can we use NEXAFS signal for lifetime?
- Problem: NEXAFS loses all $E_{kinetic}$ information (multiple processes contribute to electron count)





- Solution: Take XPS scans ($E_{kinetic}$ preserving) across the C1s→LUMO NEXAFS Peak

Resonant Photoemission (ResPES)

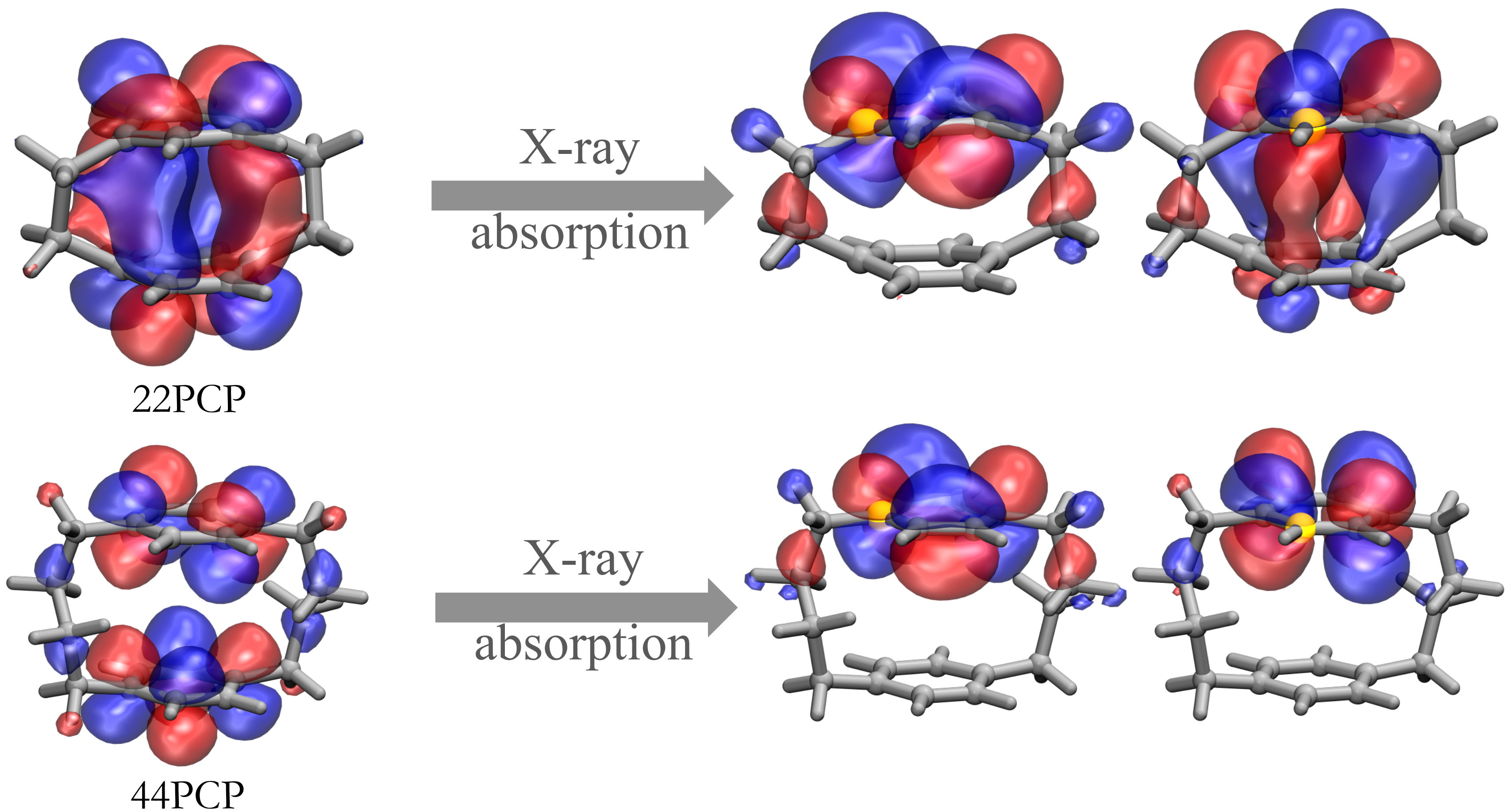


From these intensity ratios, and the lifetime of the C1s core-hole, we can calculate:

$$<\tau_{22}> = 1.4 \text{ fs and } <\tau_{44}> = 6.0 \text{ fs}$$

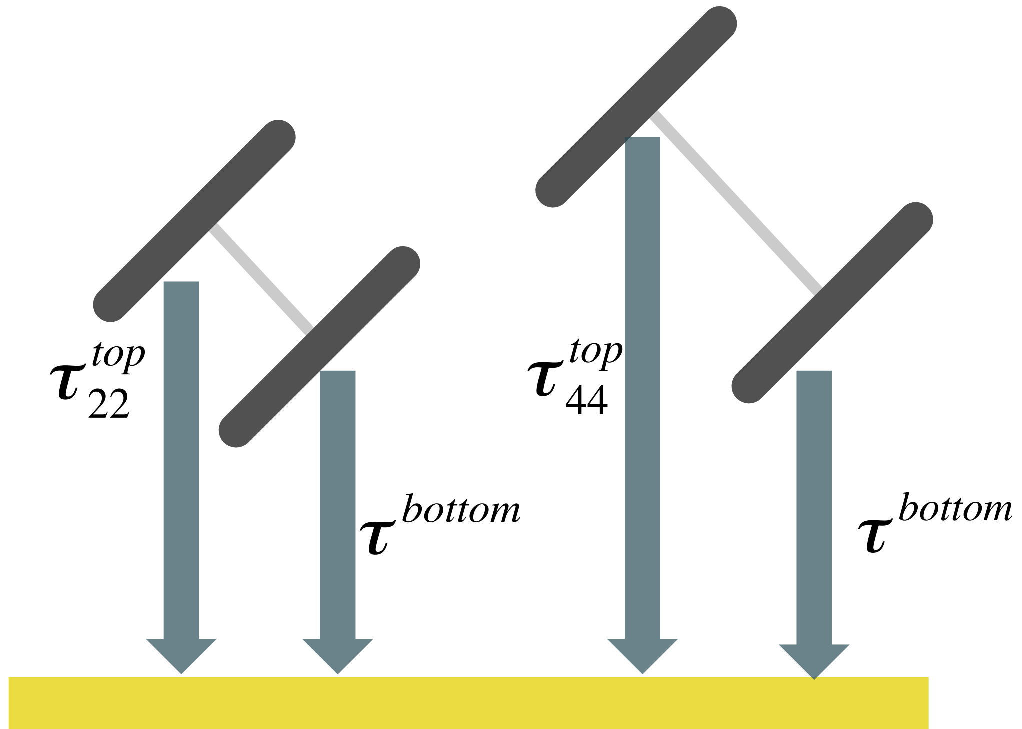
Beyond averaged charge transfer times

- We excite all carbons, at different distances from surface, does it make sense to quote averages?
- The excitation changes the LUMO wavefunction



CT from each Benzene ring

- Assumption: Bottom rings couple equally for 22PCP and 44PCP
- Assumption: CT from bottom rings must be at least as fast as from top rings

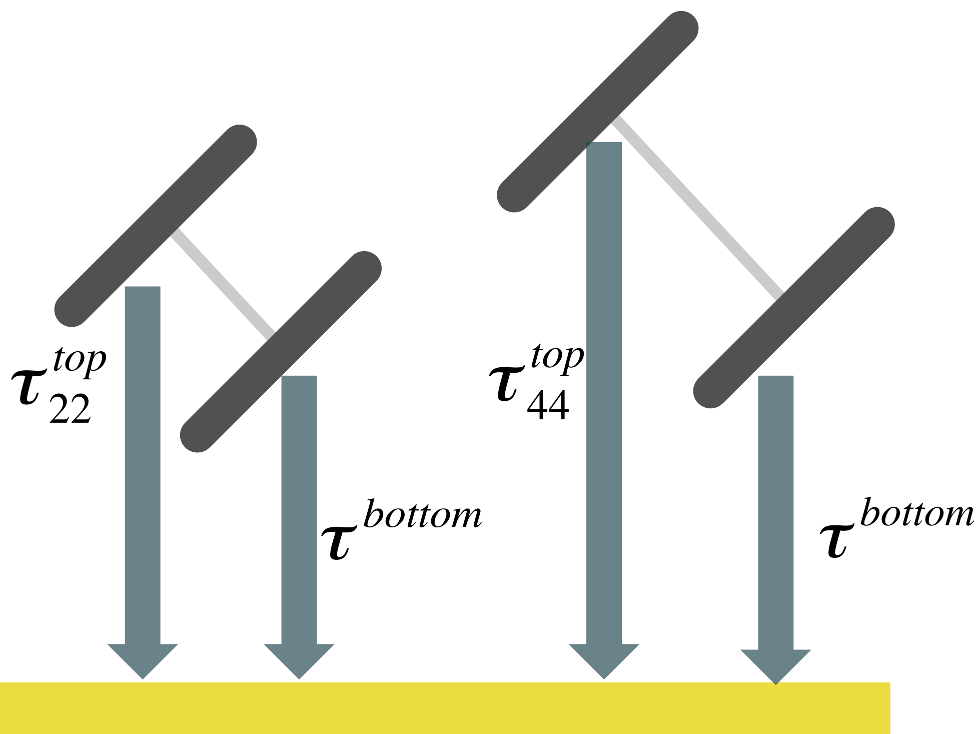


CT from each Benzene ring

$$\tau_{22}^{top} = 2.3 \pm 0.6\, fs \qquad \tau_{44}^{top} > 50\, fs$$

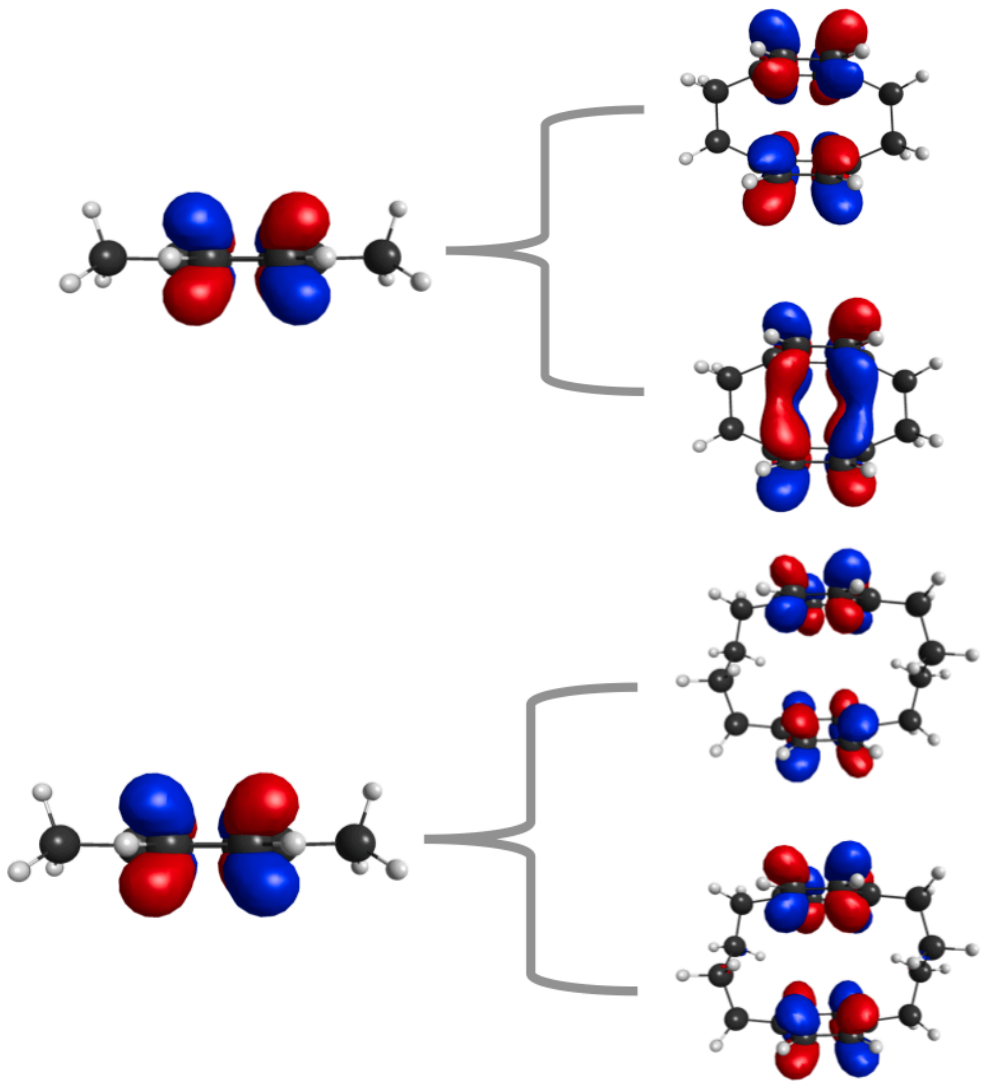
$$\tau^{bottom} = 0.7 \pm 0.3\, fs \qquad \tau^{bottom} = 0.7 \pm 0.3\, fs$$

22PCP is >20X faster



Do these CT times make sense?

- Compare to the theoretical inter-ring coupling:



$\Delta E_{22} = 1.3$ eV

$\Delta E_{44} = 0.21$ eV

$$\boxed{\frac{k_{22}}{k_{44}} \cong 40}$$

Conclusion

- We go beyond average CT times for molecule-metal junctions
  - First measurement of through-space CT time as a function of coupling
  - 20X faster CT from the top ring of 22PCP than 44PCP
- Generalizable to other monolayer or few-layer physisorbed molecular films

A. Batra, G. Kladnik, H. Vázquez, J.S. Meisner, L. Floreano, C. Nuckolls, D. Cvetko, A. Morgante, L. Venkataraman, *Quantifying Through-Space Charge Transfer Dynamics in π-Coupled Molecular Systems*, in review.

Acknowledgements

- ALOISA Beamline
  - Gregor Kladnik
  - Dr. Luca Floreano
  - Prof. Dean Cvetko
  - Prof. Alberto Morgante
- Columbia University/BNL
  - Dr. Mark Hybertsen
  - Dr. Hector Vázquez
  - Prof. Latha Venkataraman