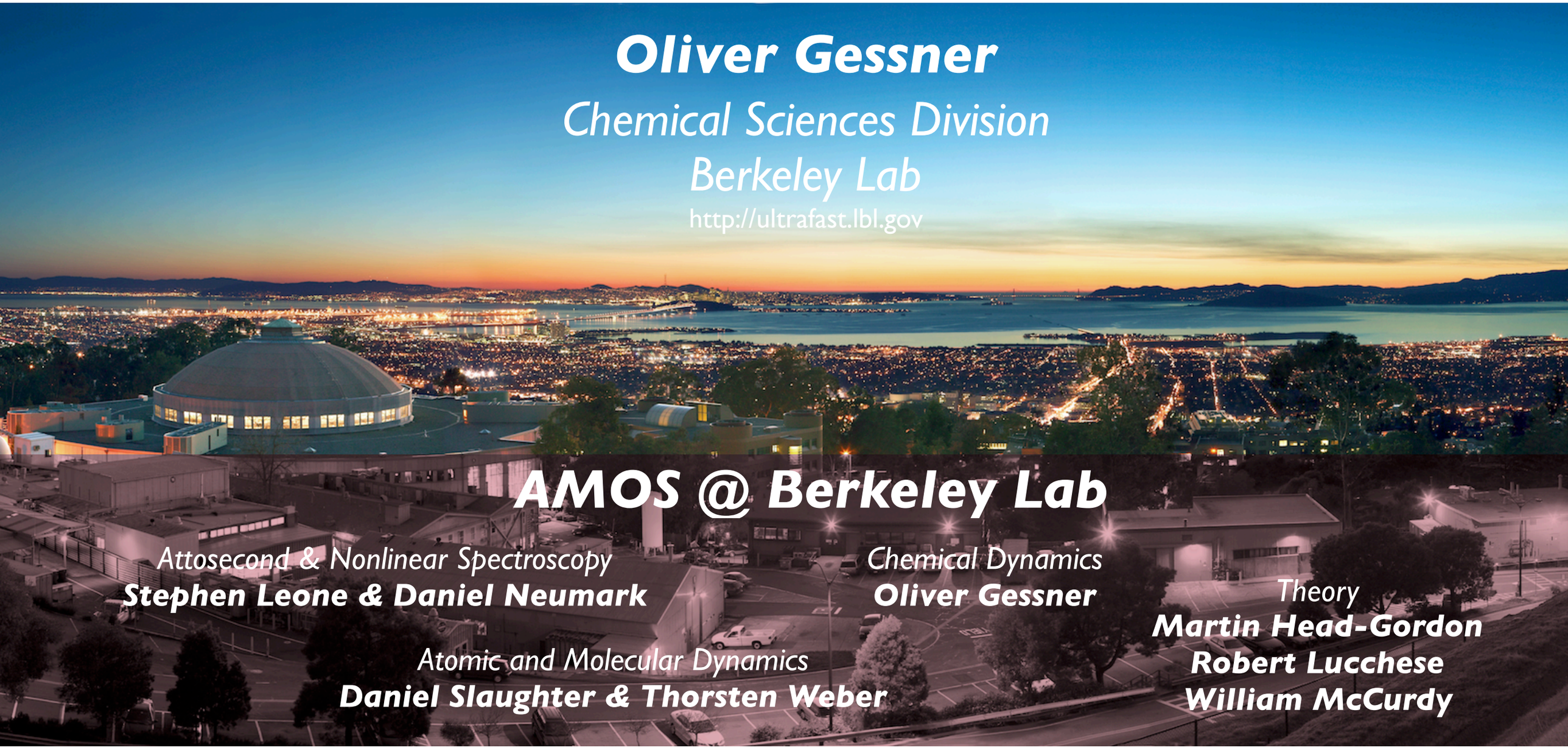
Ultrafast X-ray Studies of Chemical and Interfacial Dynamics

Oliver Gessner

Chemical Sciences Division

Berkeley Lab

http://ultrafast.lbl.gov



AMOS @ Berkeley Lab

Attosecond & Nonlinear Spectroscopy
Stephen Leone & Daniel Neumark

Chemical Dynamics
Oliver Gessner

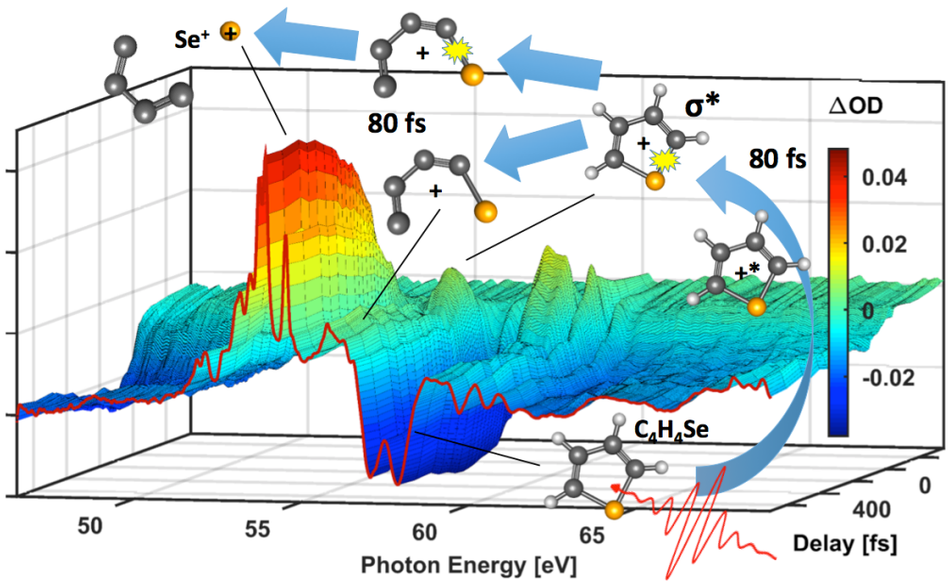
Theory
Martin Head-Gordon
Robert Lucchese
William McCurdy

Atomic and Molecular Dynamics
Daniel Slaughter & Thorsten Weber

U.S. DEPARTMENT OF ENERGY

AMOS @ Berkeley Lab – Chemical Dynamics Group

Photodynamics in Organic Molecules



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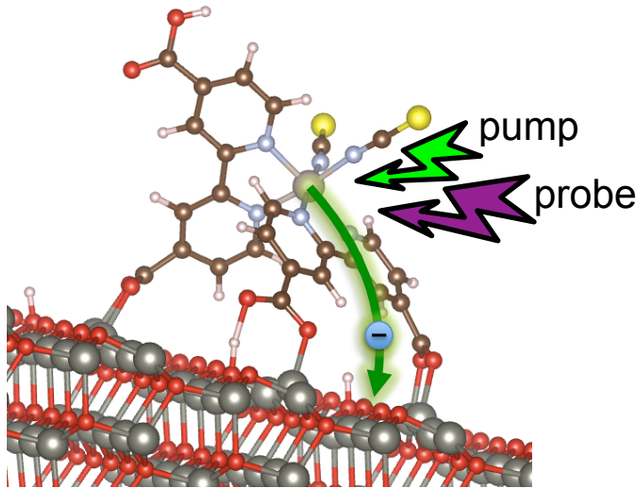
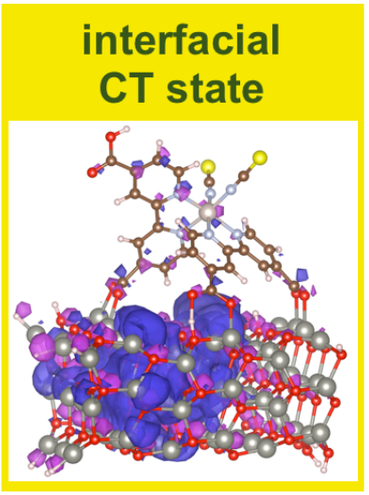
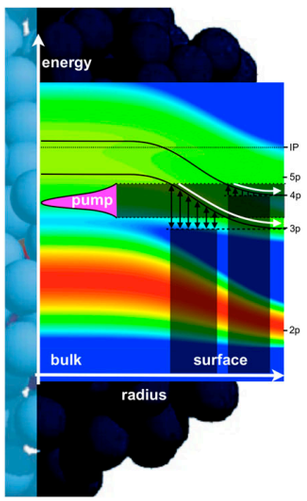
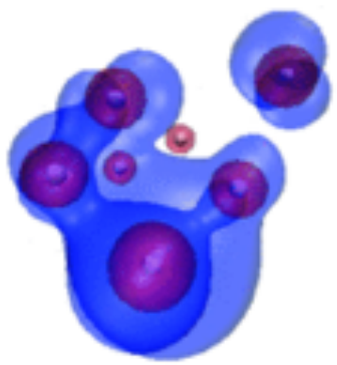
Interfacial Charge Transfer Dynamics

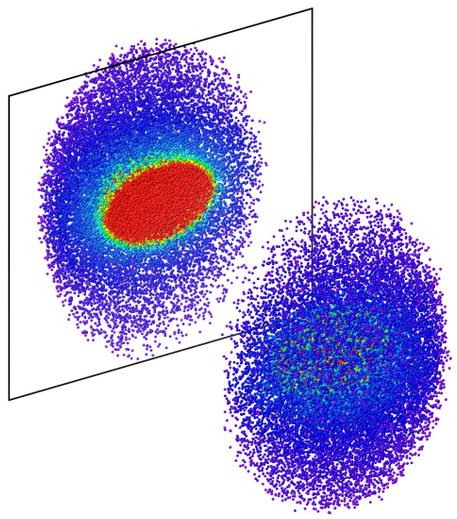




Coupled Electron-Nuclear Dynamics in Large Clusters







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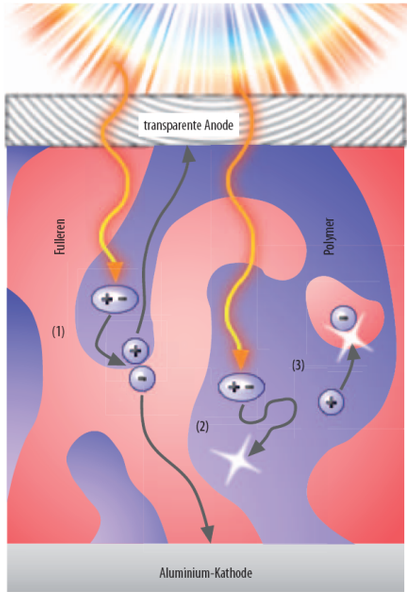
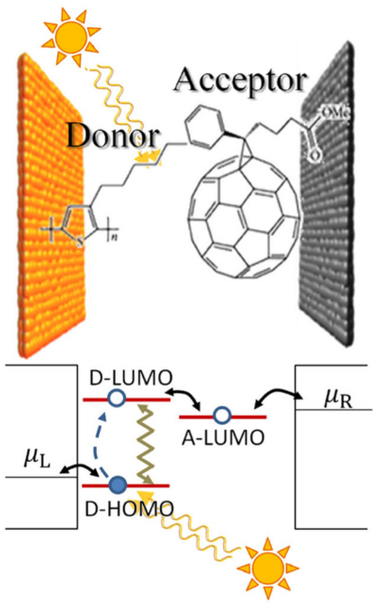
Bernando *et al*., Phys. Rev. B **95**, 064510 (2017)





Siefermann *et al*., J. Phys. Chem. Lett. **5**, 2753 (2014)
Arion *et al*., Appl. Phys. Lett. **106**, 121602 (2015)
Neppl and O.G., J. Electron Spectrosc. Relat. Phenom. **200**, 64 (2015)
O.G. and M. Gühr, Acc. Chem. Res. **49**, 138 (2016)
Neppl *et al*., Faraday Discuss. **194**, 659 (2016)
Roth *et al*., Phys. Rev. B **99**, 020303(R) (2019)
Mahl *et al*., Faraday Discuss., *Accepted Manuscript* (2019)

AMOS @ Berkeley Lab – Chemical Dynamics Group

Current Team

Johannes Mahl

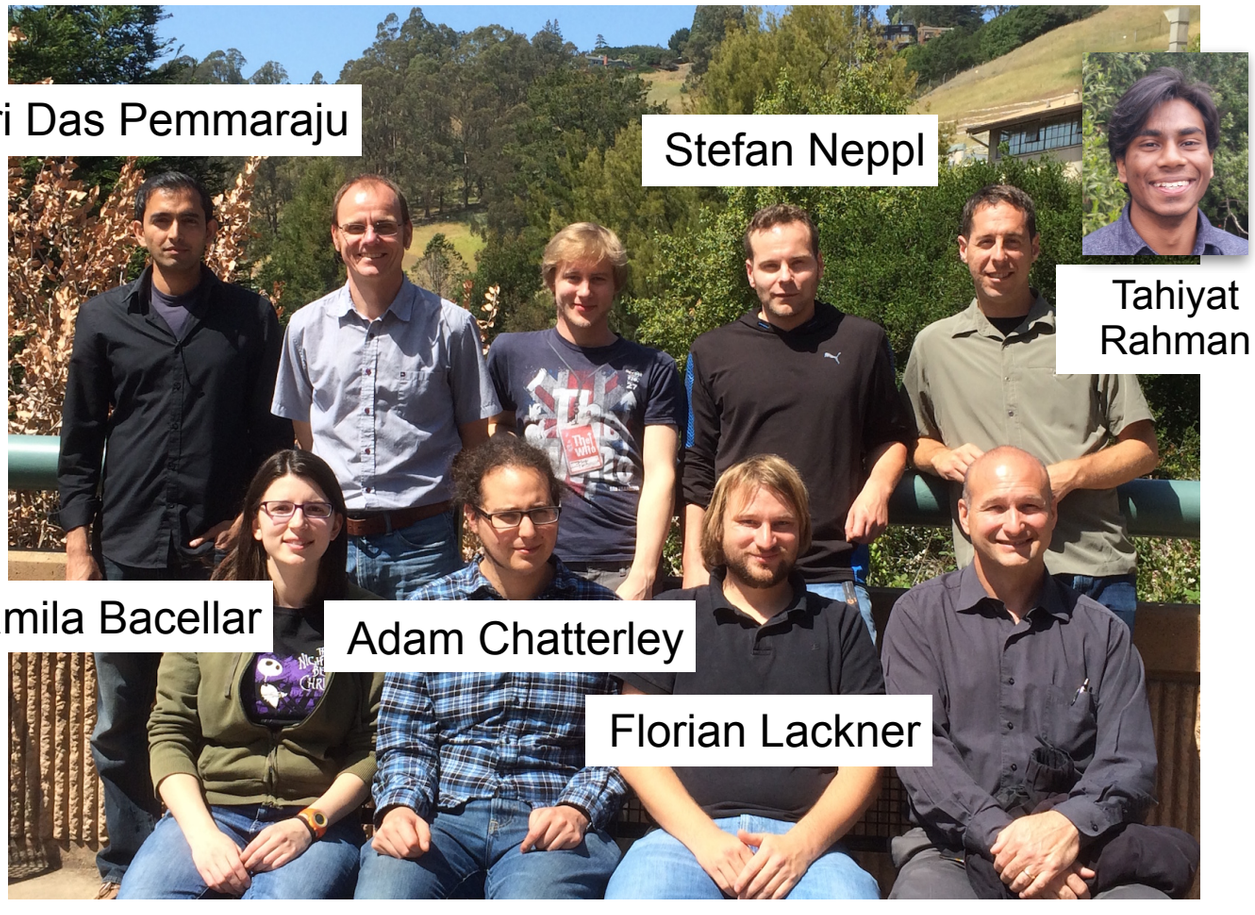
Catherine Saladrigas

Benjamin Toulson

Mario Borgwardt

Felix Brausse

Alumni



Collaborators

Friedrich Roth

Wolfgang Eberhardt

David Prendergast, *LBNL*
Das Pemmaraju, *SLAC*
Nils Huse, *U Hamburg*
Hendrik Bluhm, *FHI Berlin*
Andrey Shavorskiy, *Max Lab*
Serguei Molodtsov, *European XFEL*
Wilfried Wurth, *U Hamburg*
Lukas Wenthaus, *DESY*
Steffen Palutke, *DESY*
Adrian Benz, *DESY*
Giuseppe Mercurio, *XFEL*
Günther Brenner, *FLASH*
Siarhei Dziarzhytski, *FLASH*
Jinghua Guo, *LBNL*
Wanli Yang, *LBNL*

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Lawrence Berkeley National Laboratory

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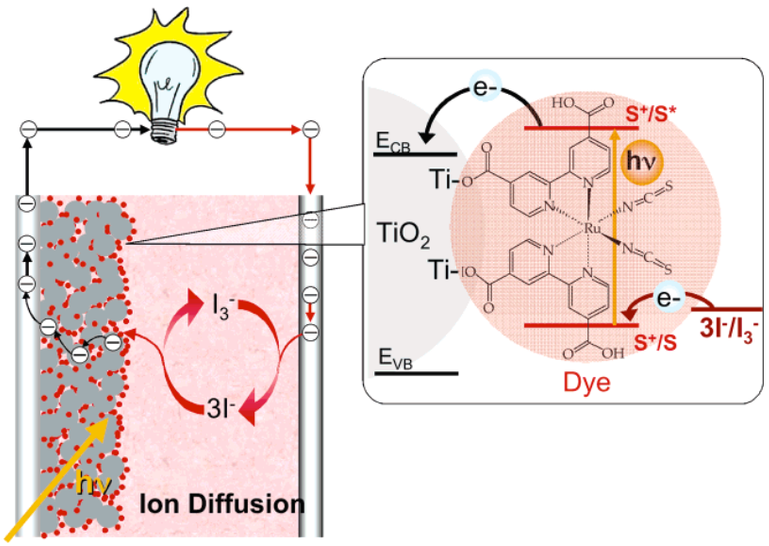
Alexander von Humboldt
Stiftung/Foundation

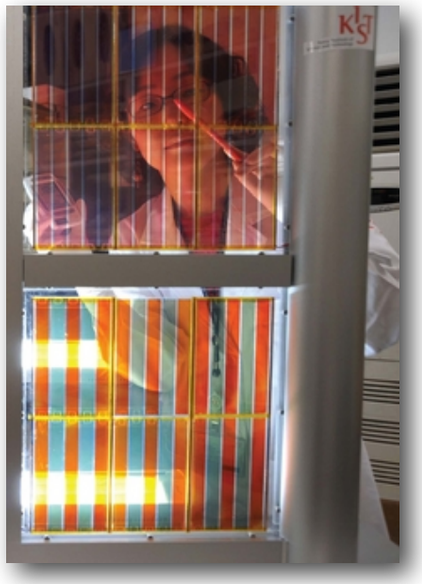
FWF
Der Wissenschaftsfonds.

U.S. DEPARTMENT OF ENERGY

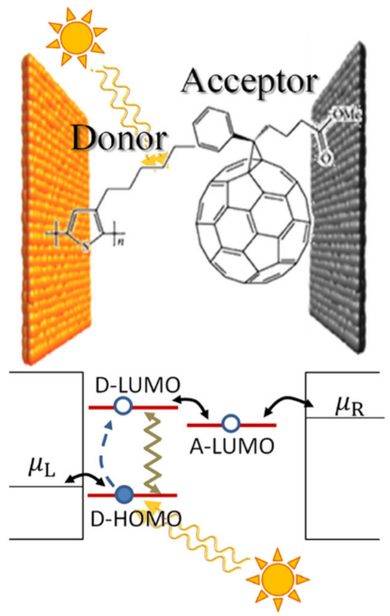
Renewable Energy Technologies and Interfacial Chemistry

Charge Transfer at Molecule-Semiconductor Interfaces

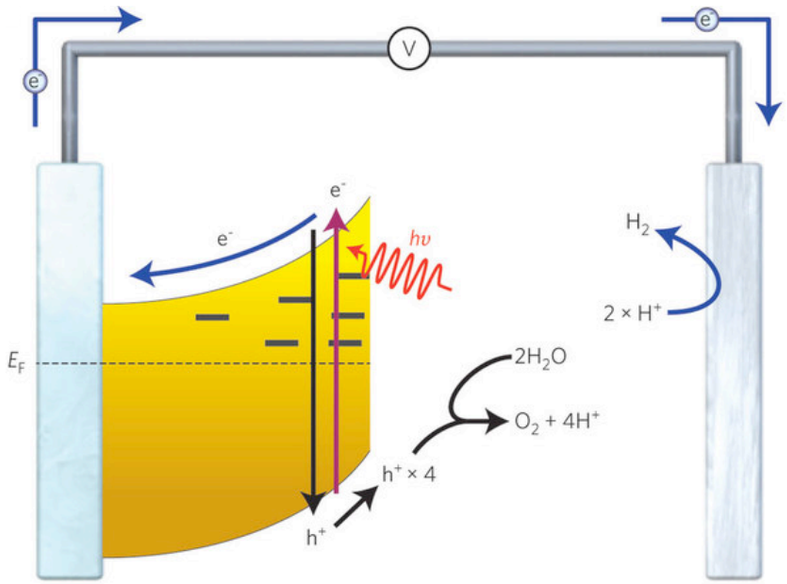




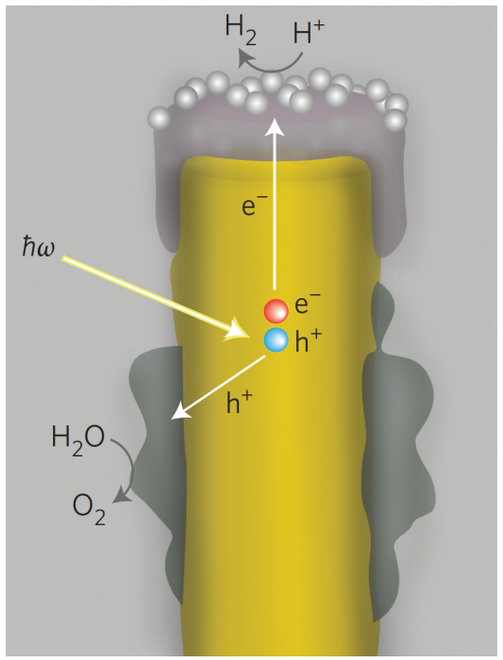
Charge Migration in Organic Semiconductors

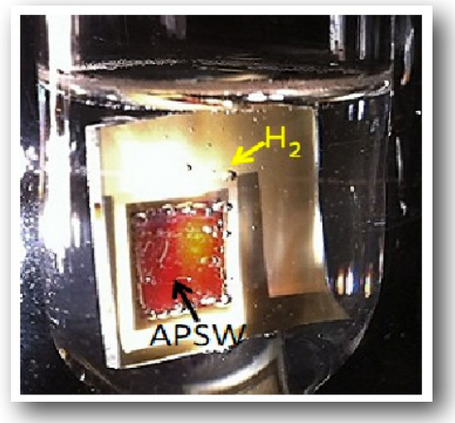


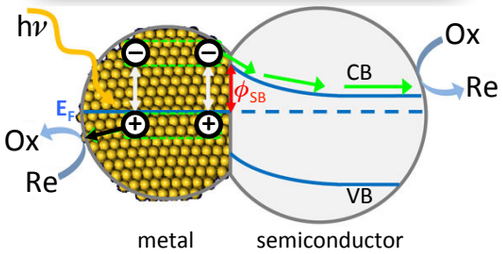
Water Splitting at Semiconductor-Liquid Interfaces



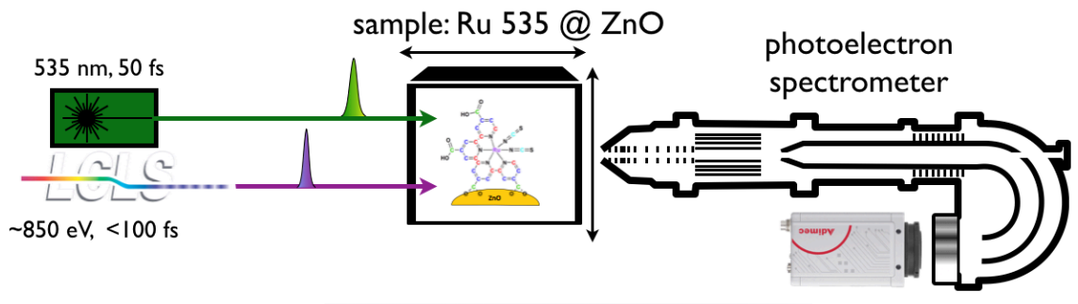
Plasmon Enabled Photochemistry

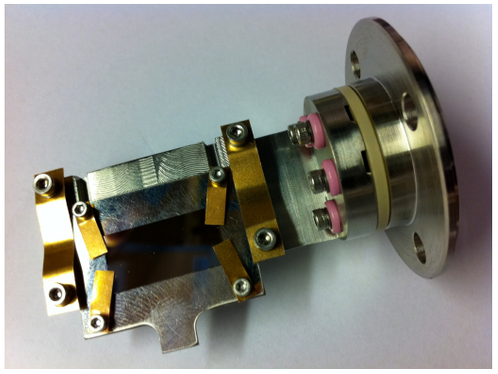


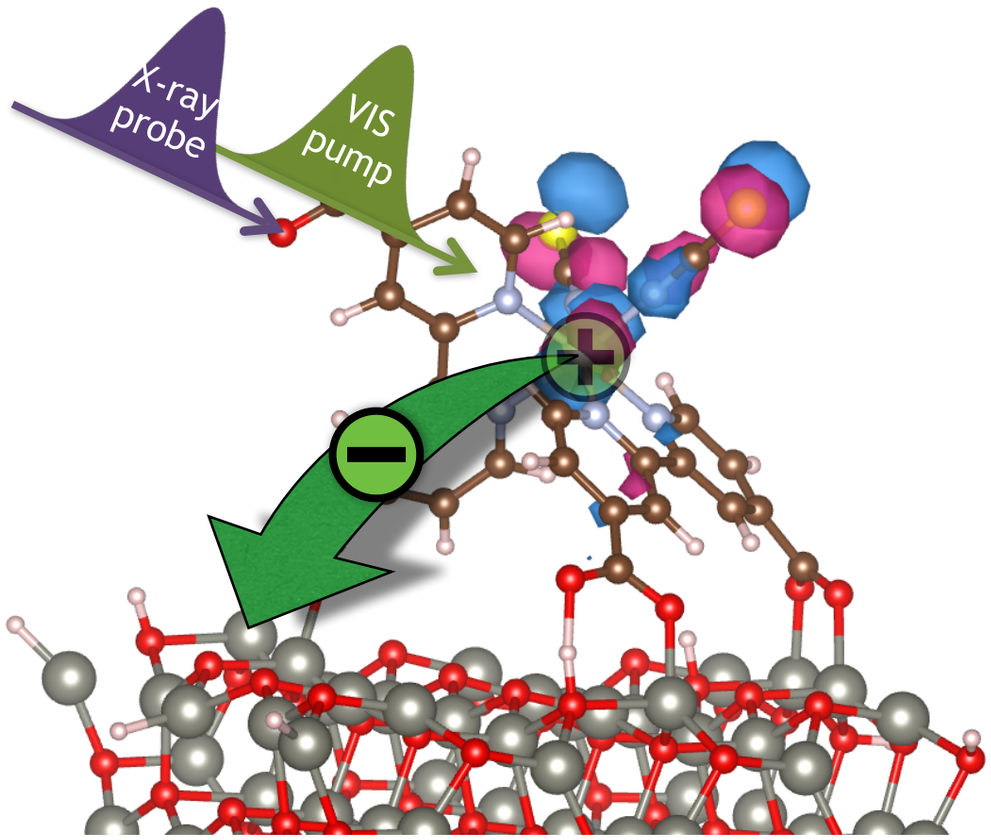


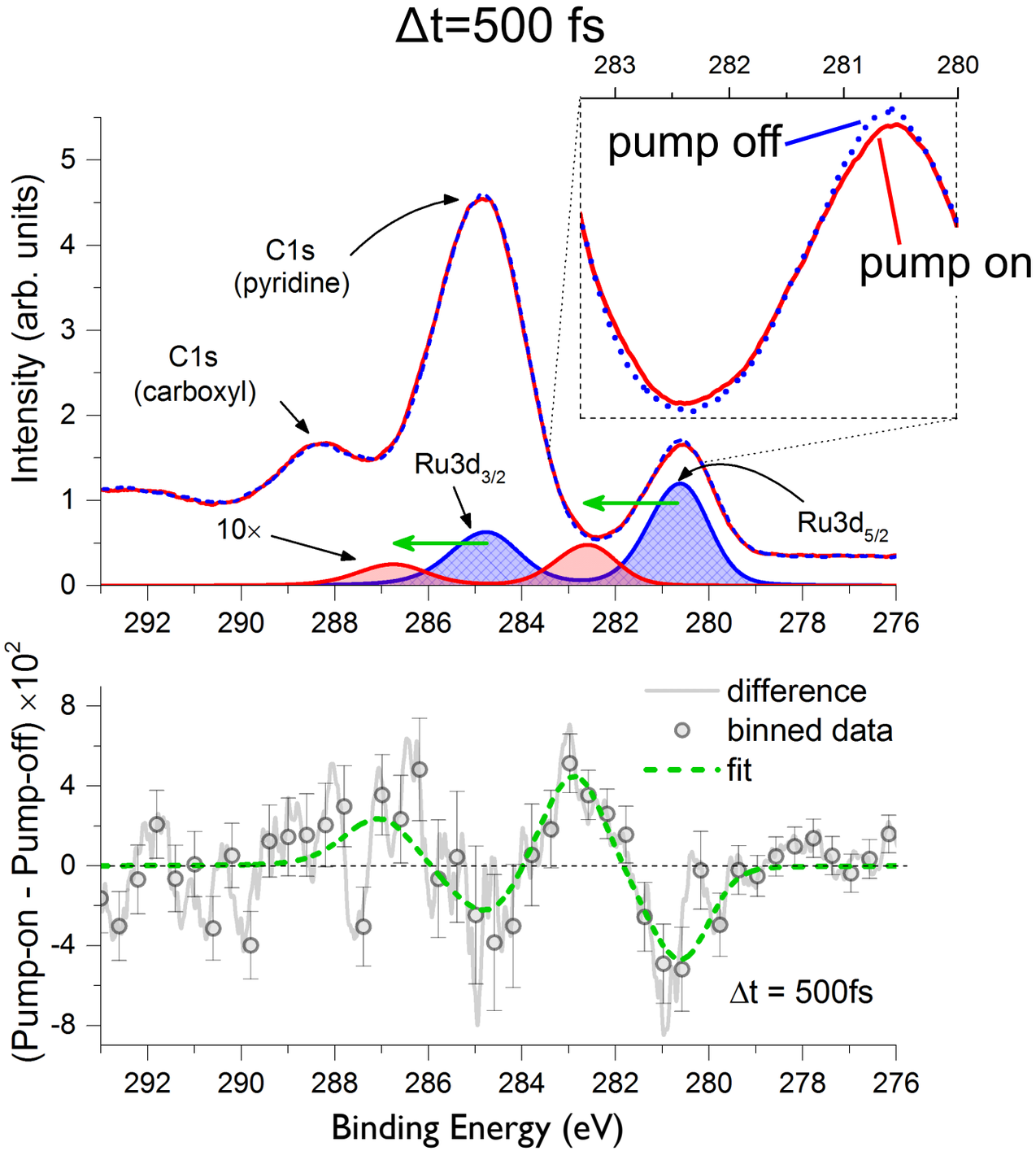


Femtosecond Atomic-Scale Perspective of Interfacial Charge Transfer



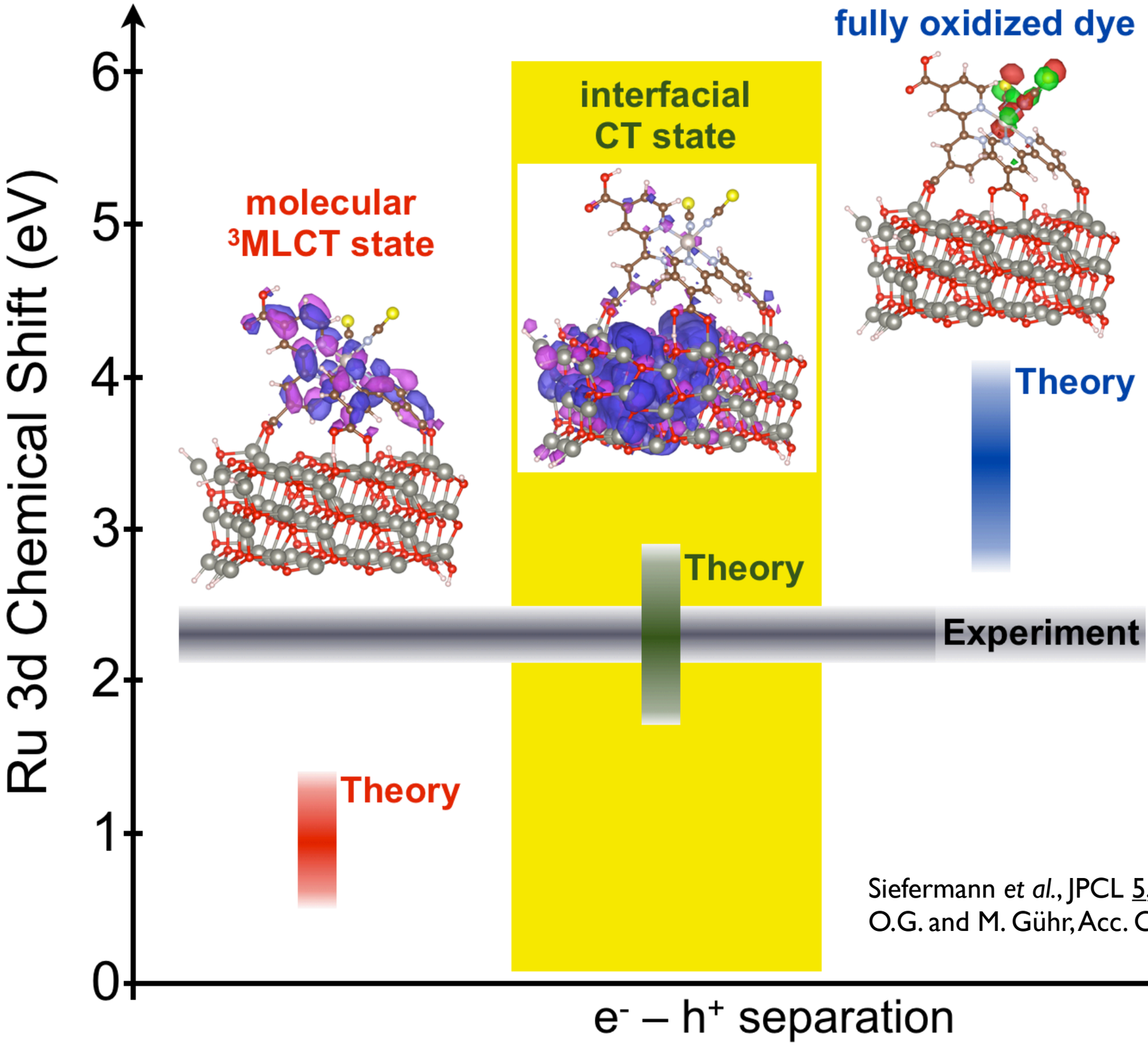






Siefermann *et al.*, JPCL 5, 2753 (2014)
O.G. and M. Gühr, Acc. Chem. Res. 49, 138 (2016)

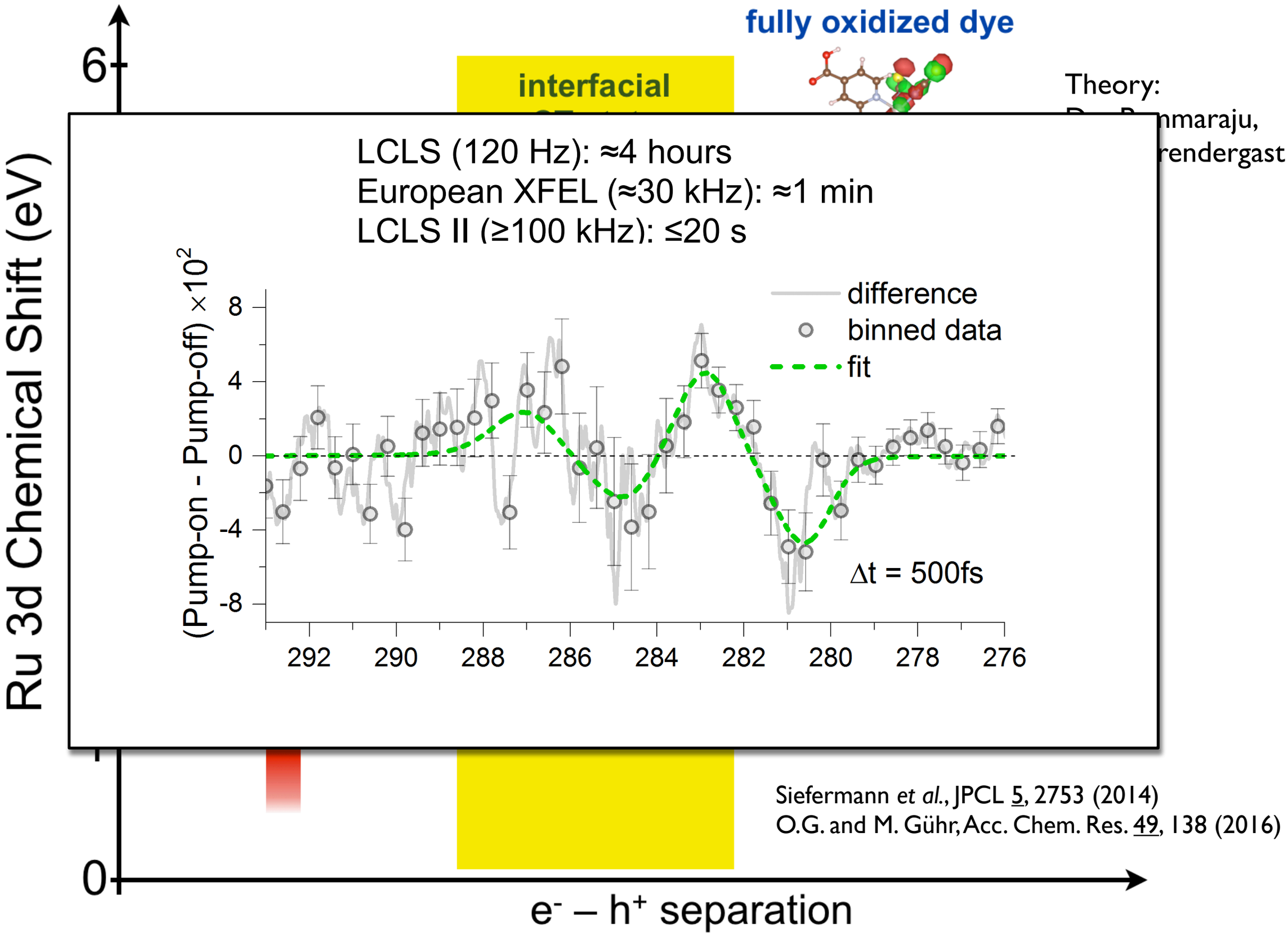
Transient Electronic Configuration 500 fs after Excitation



Theory:
Das Pemmaraju,
David Prendergast

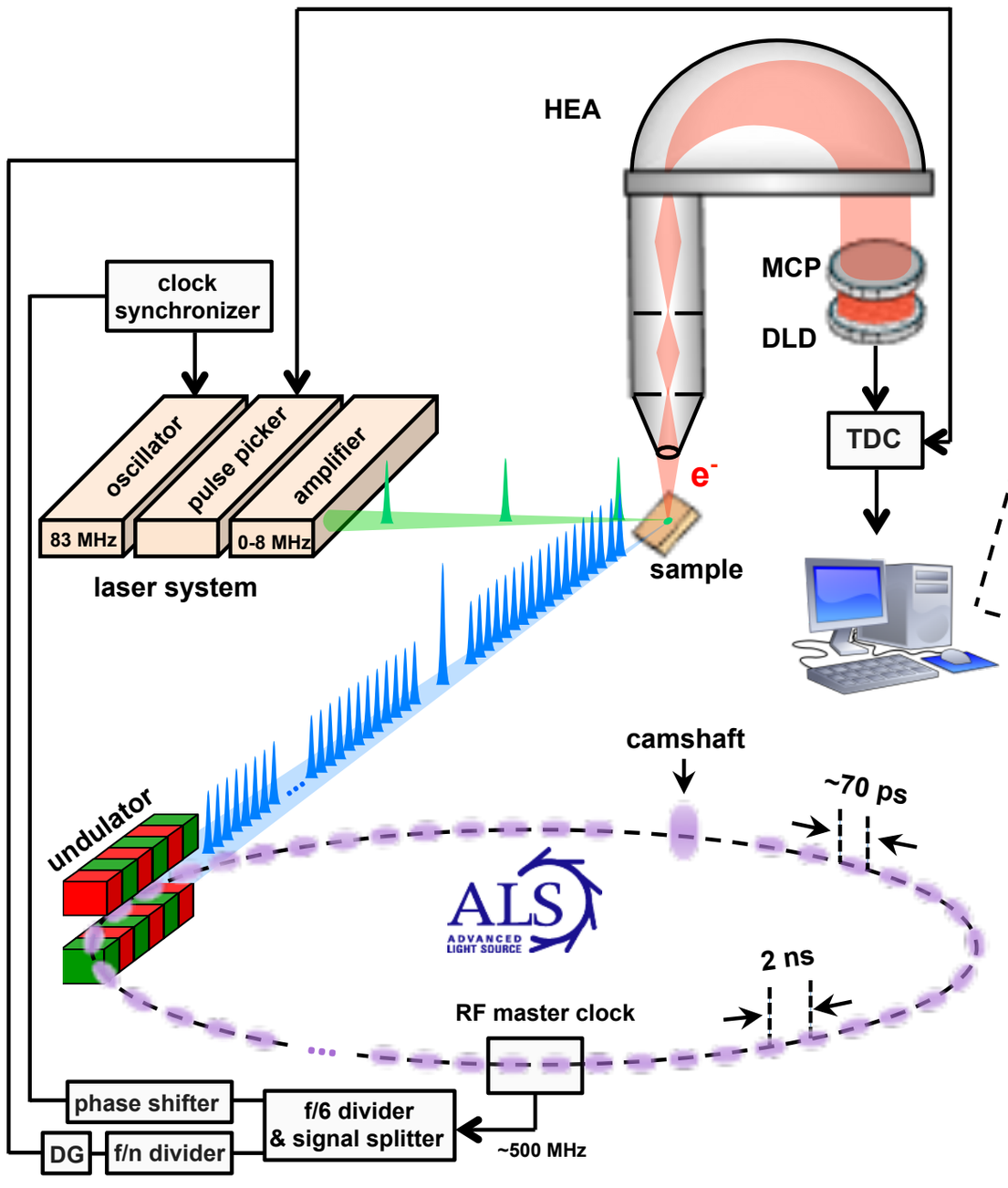
Siefermann *et al.*, JPCL 5, 2753 (2014)
O.G. and M. Gühr, Acc. Chem. Res. 49, 138 (2016)

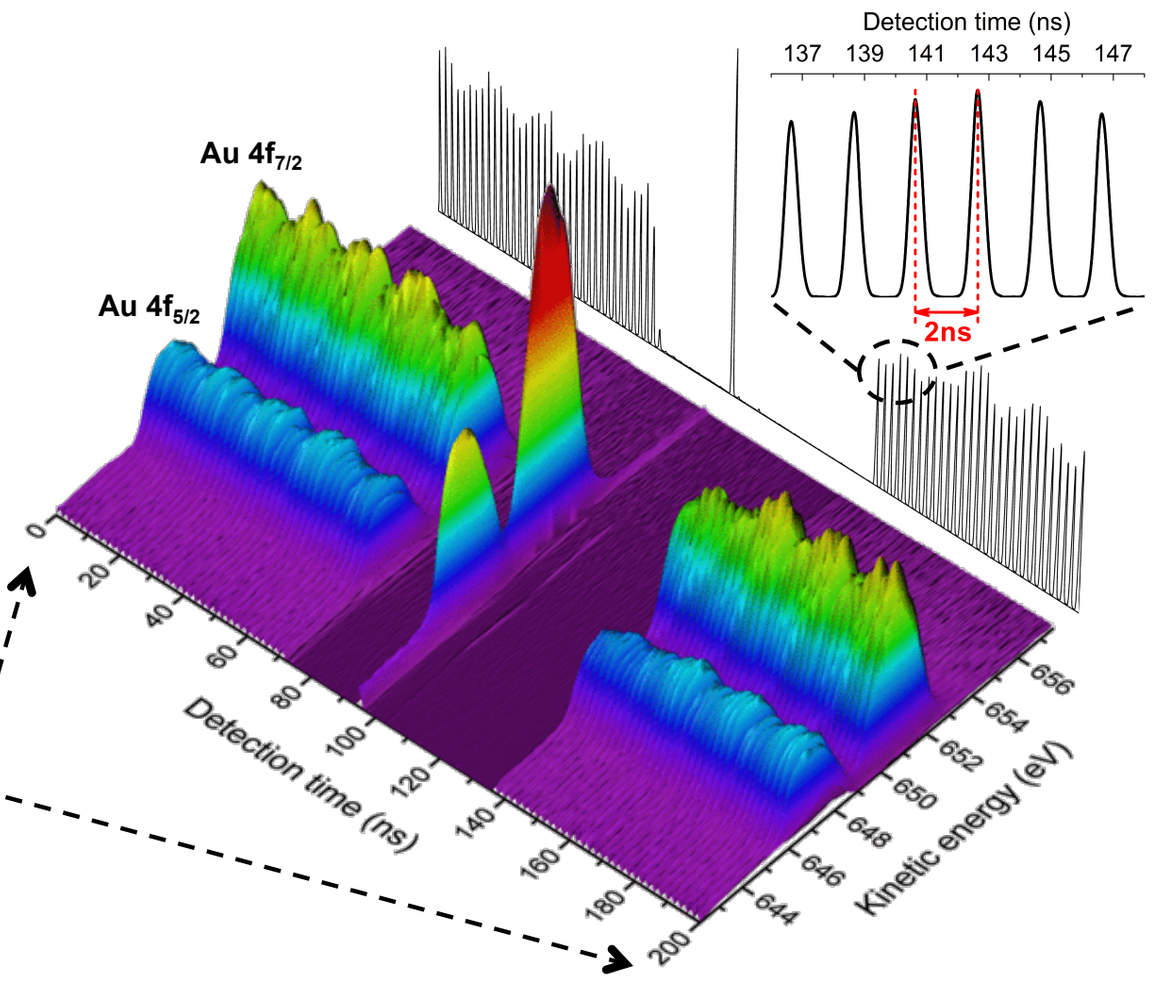
Transient Electronic Configuration 500 fs after Excitation



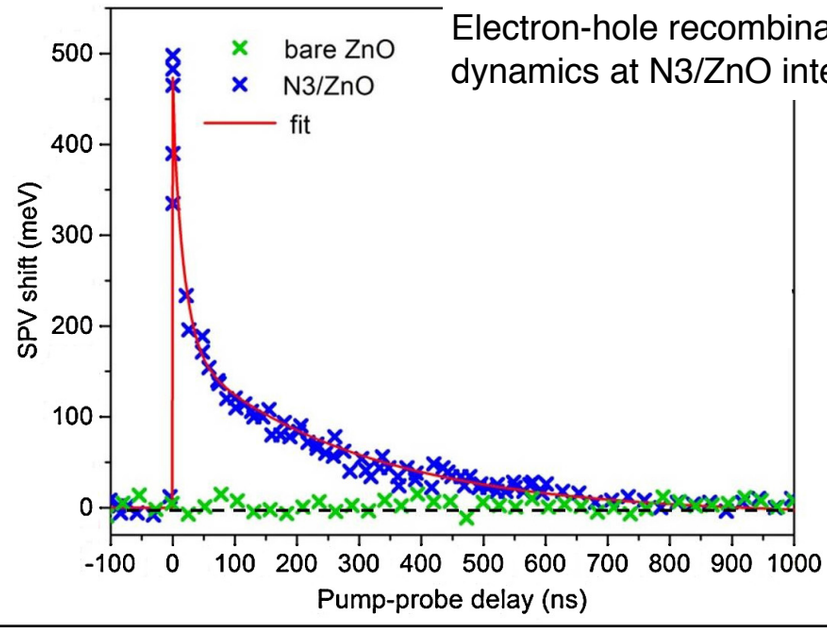
Siefermann *et al.*, JPCL 5, 2753 (2014)
O.G. and M. Gühr, Acc. Chem. Res. 49, 138 (2016)

130 kHz pump / 500 MHz probe
Picosecond Time-Resolved XPS @ ALS





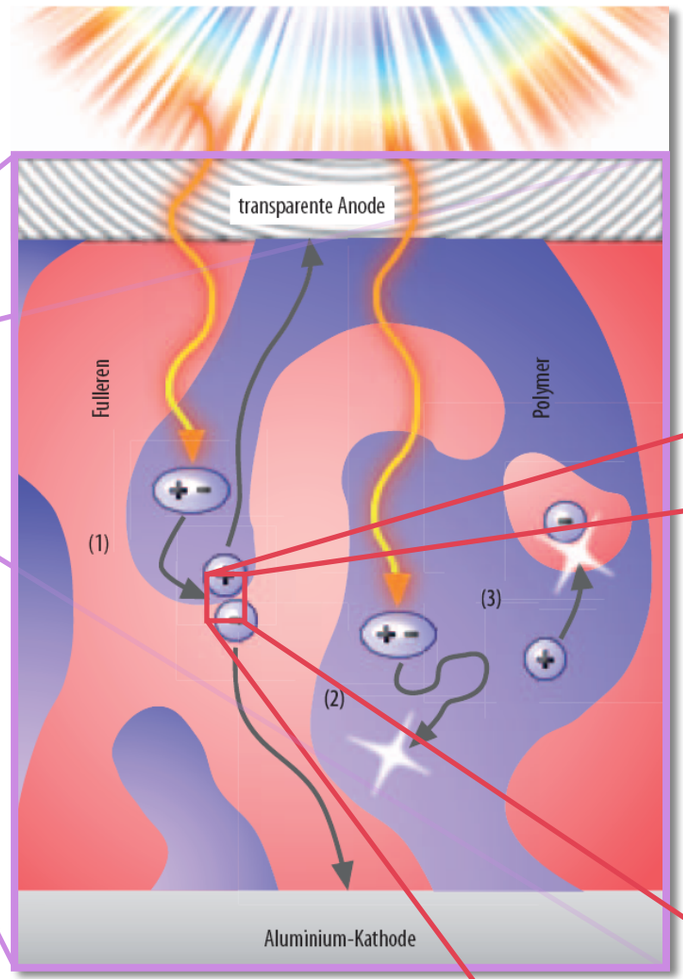
Electron-hole recombination dynamics at N3/ZnO interface

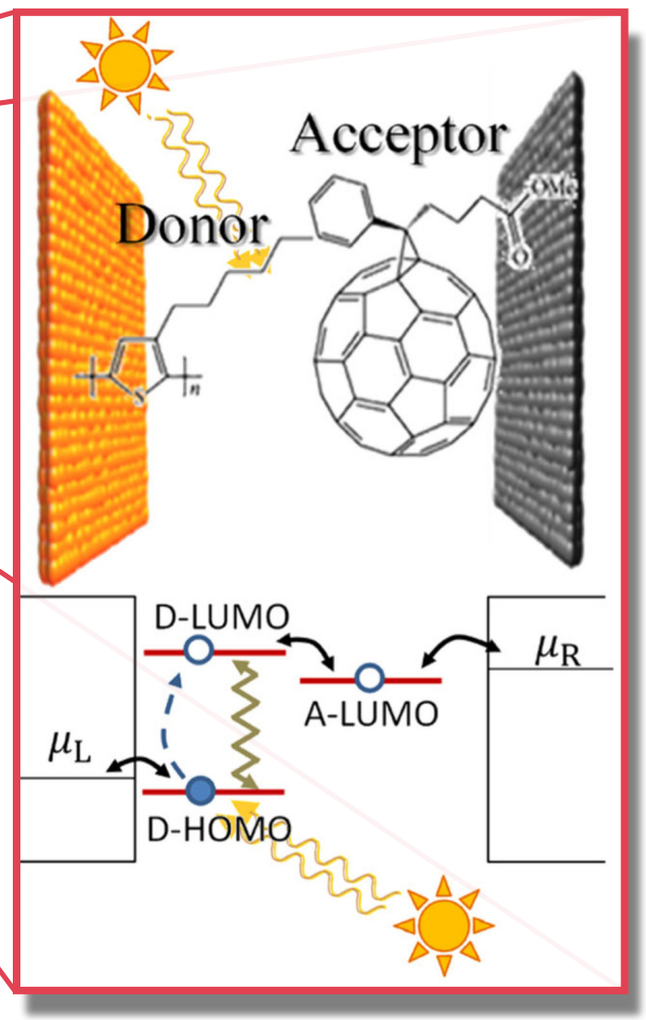


A. Shavorskiy *et al.*, RSI 85, 093102 (2014)
S. Neppl *et al.*, Faraday Discuss. 171, 219 (2014)
S. Neppl and O.G., J. Electron Spectrosc. Relat. Phenom. 200, 64 (2015)

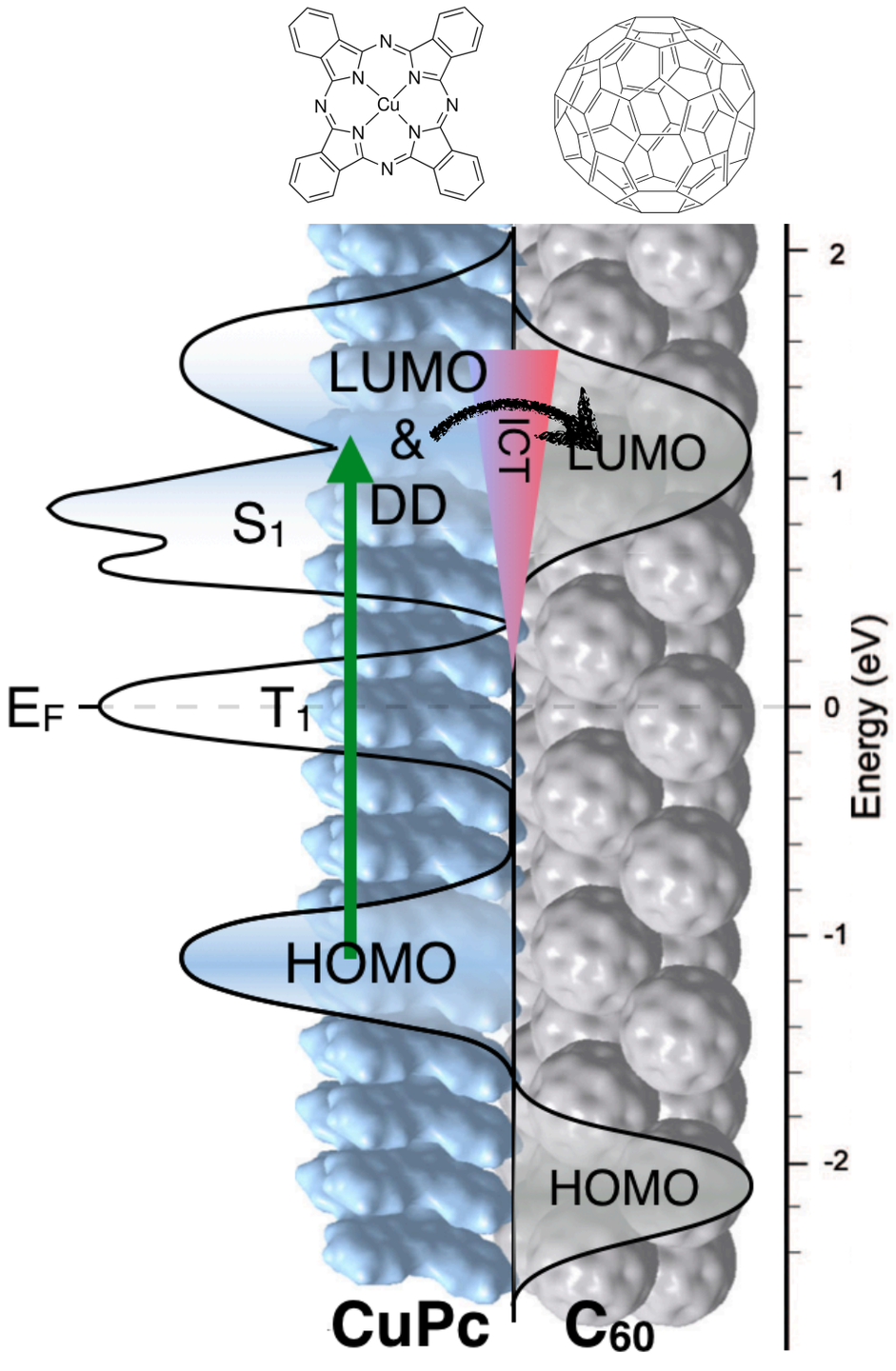
Charge Transfer Dynamics in Organic Donor-Acceptor Blends

with Wolfgang Eberhardt, Friedrich Roth



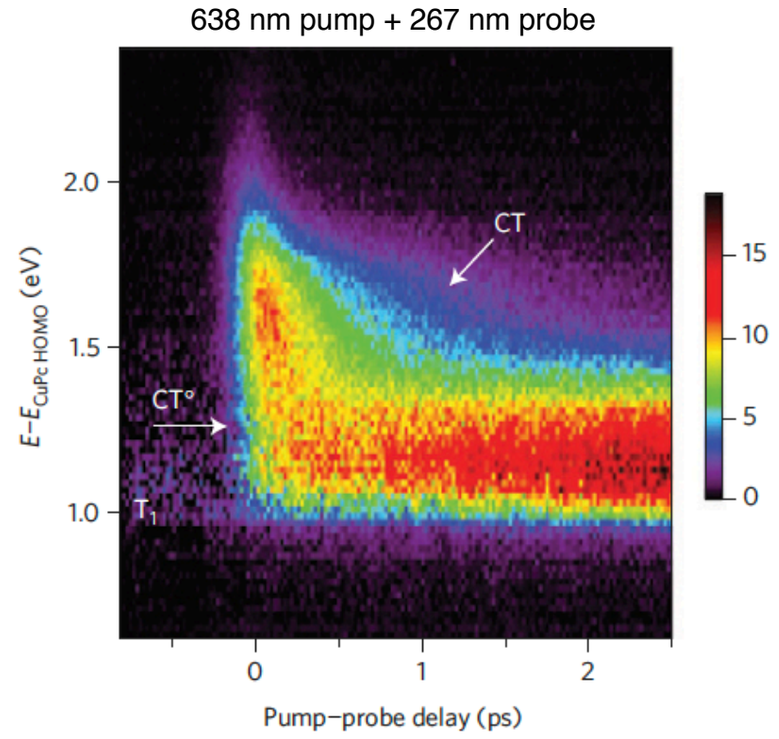


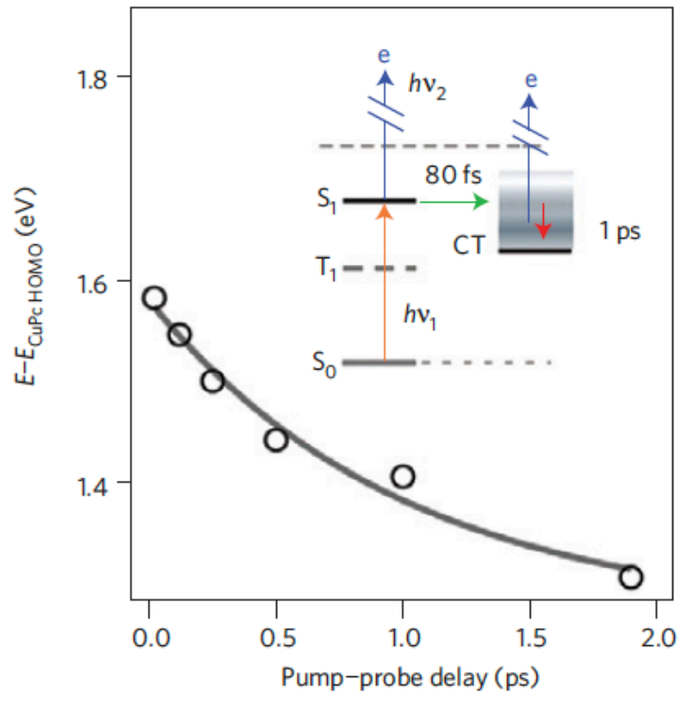
Charge Transfer Dynamics in Donor-Acceptor Blends



Dutton, Robey *et al.*, PRB (2010), JPCC (2012), JPCC (2013)
Zhu *et al.*, Acc. Chem. Res. (2009), Nat. Mat. (2013)

TR-2PPE of C_{60} (1 ML) on CuPc (25 nm)

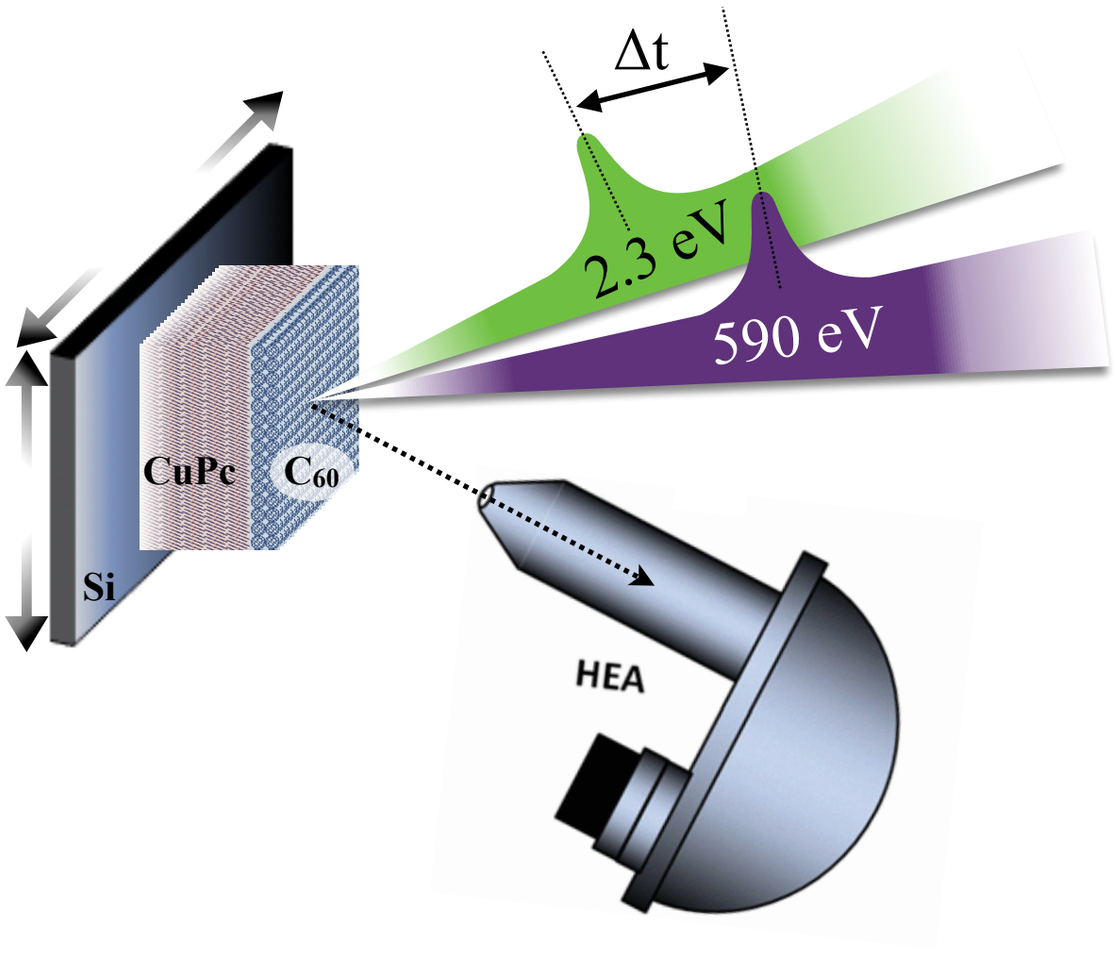




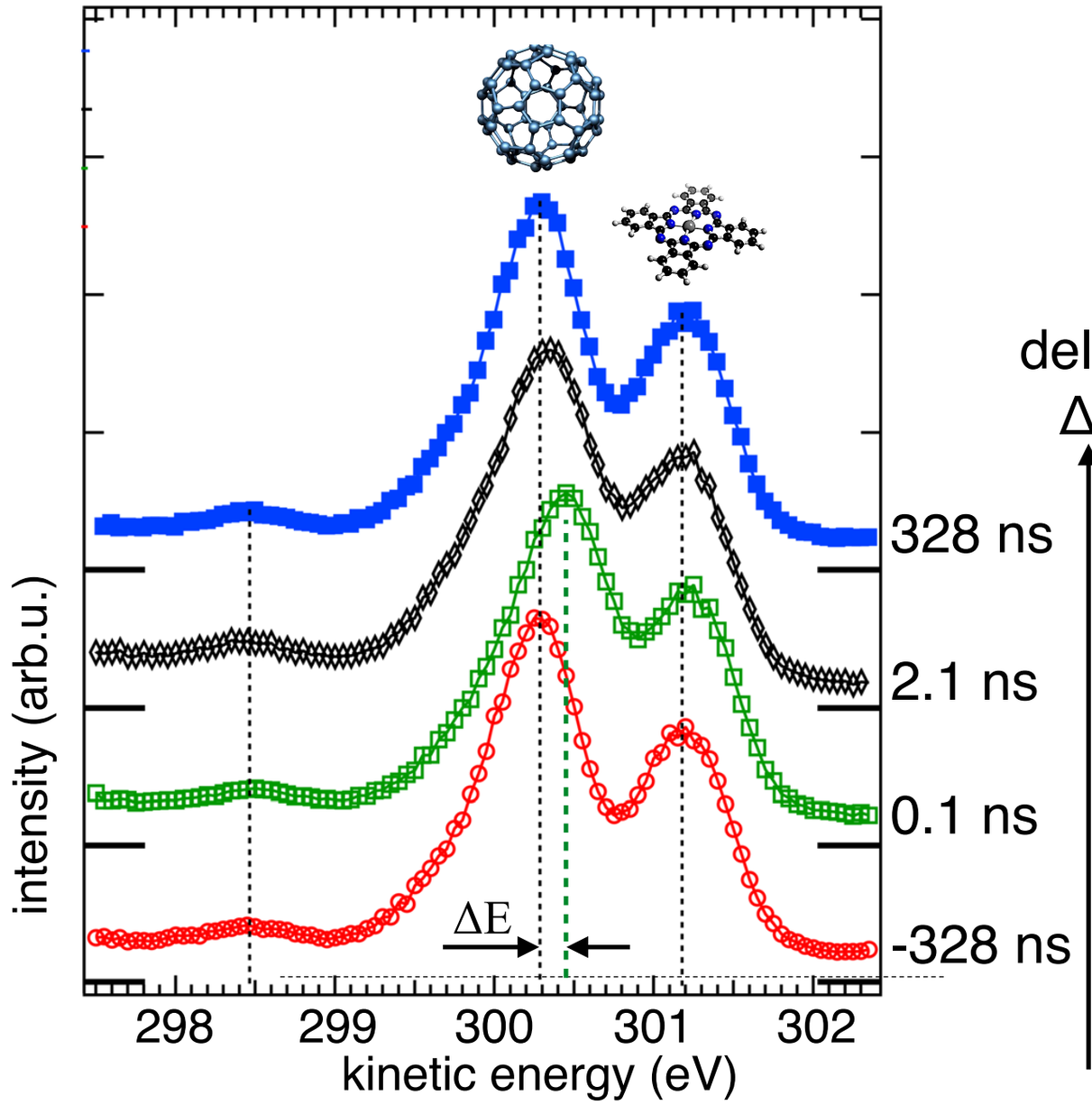
Zhu *et al.*, Nat. Mat. (2013)

Transient XPS of Electron Dynamics in Planar Heterojunctions

Vis. pump / X-ray probe experiment



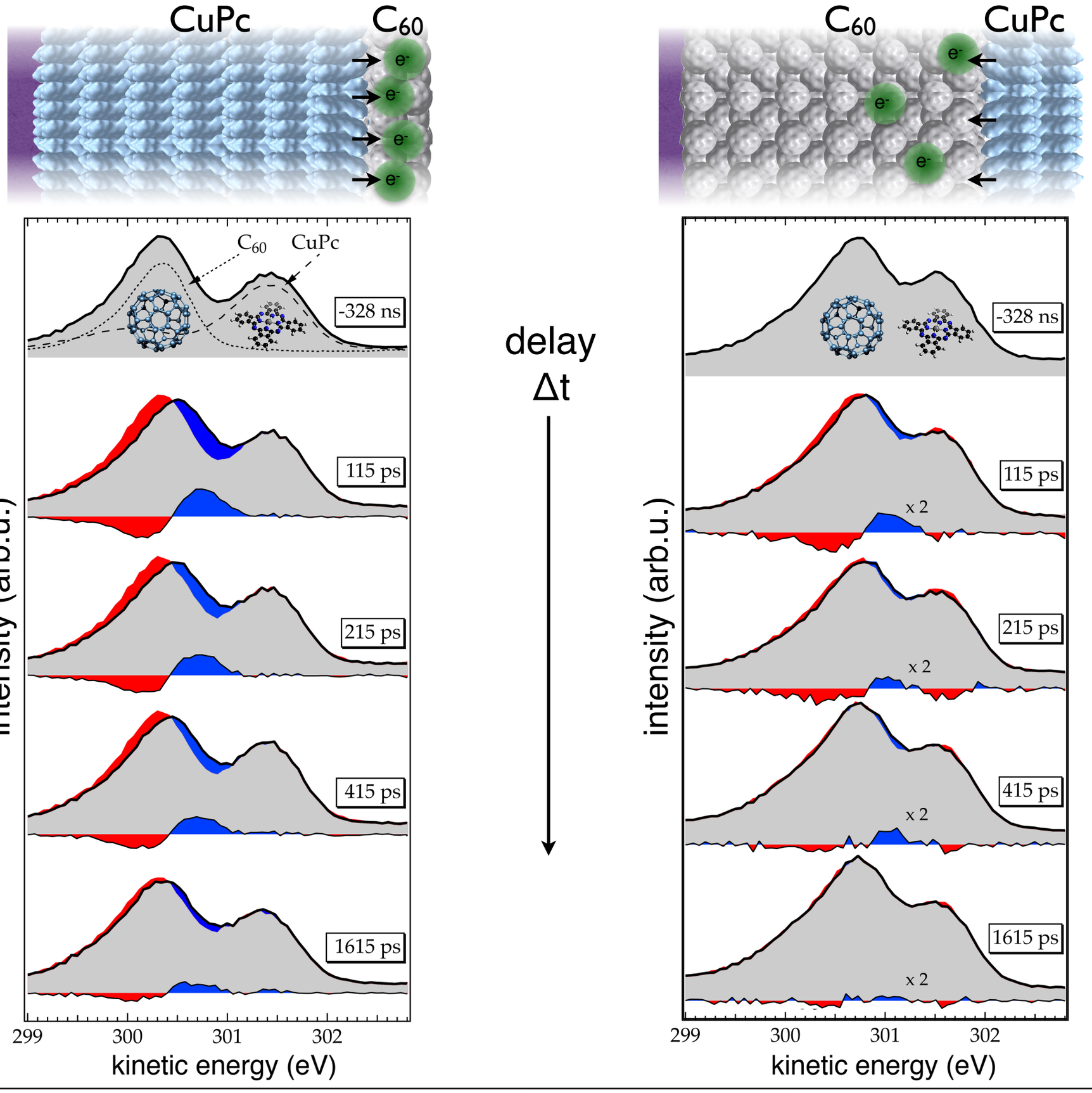
Picosecond Time-Resolved C1s^{-1} Spectrum



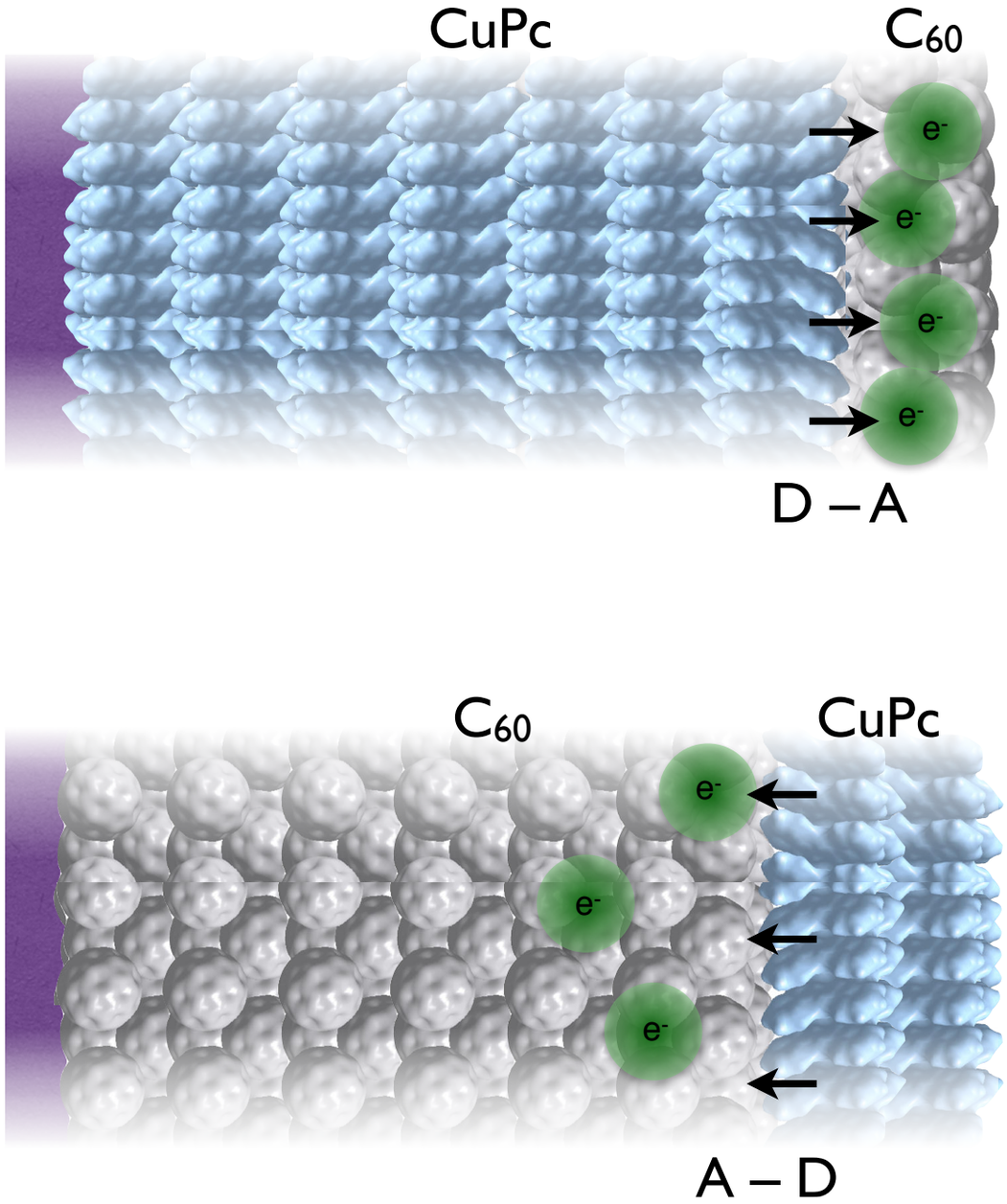
Arion *et al.*, Appl. Phys. Lett. **106**, 121602 (2015)

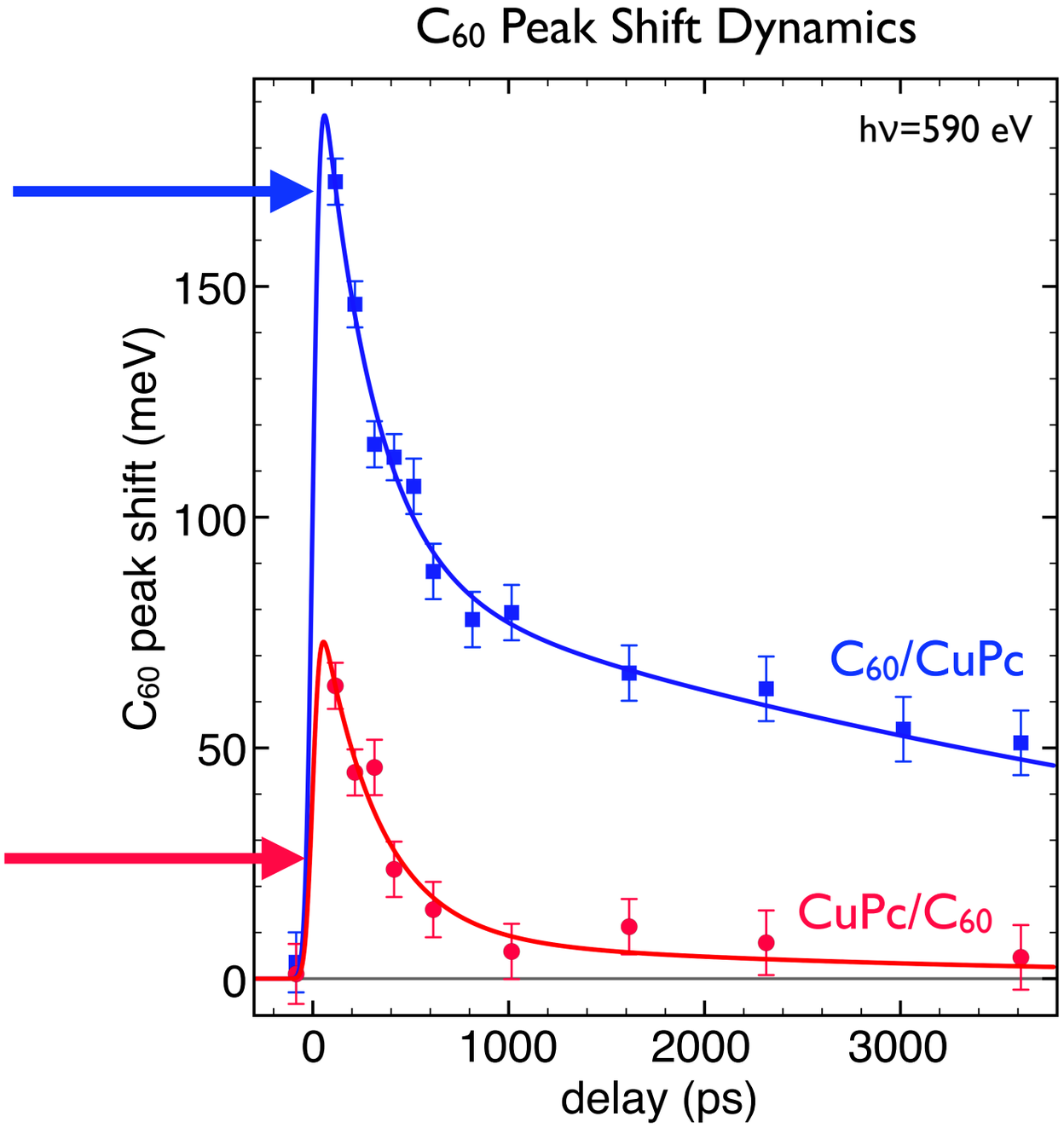
Transient XPS of Electron Dynamics in Planar Heterojunctions

Roth *et al.*, Phys. Rev. B **99**, 020303(R) (2019)

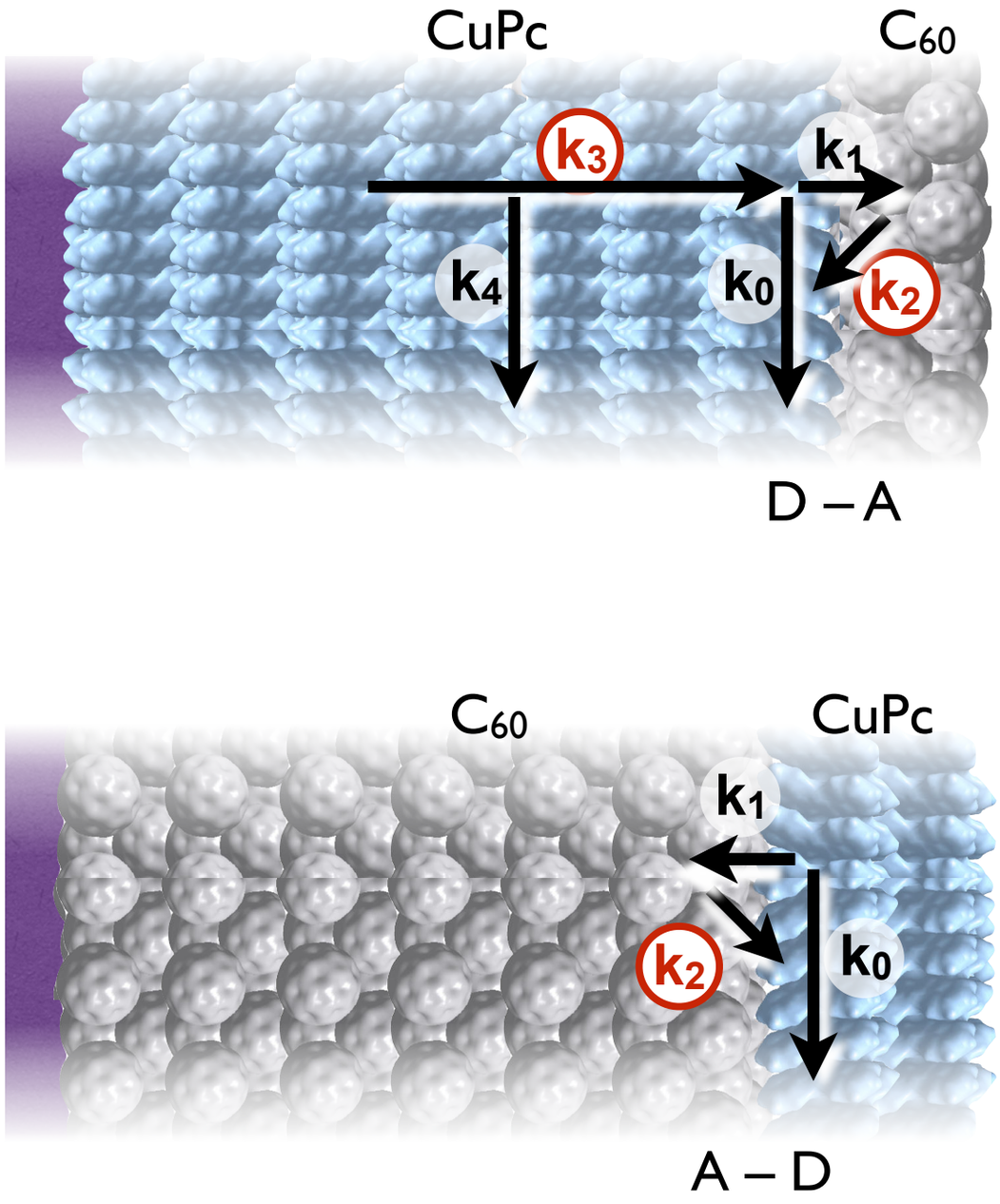


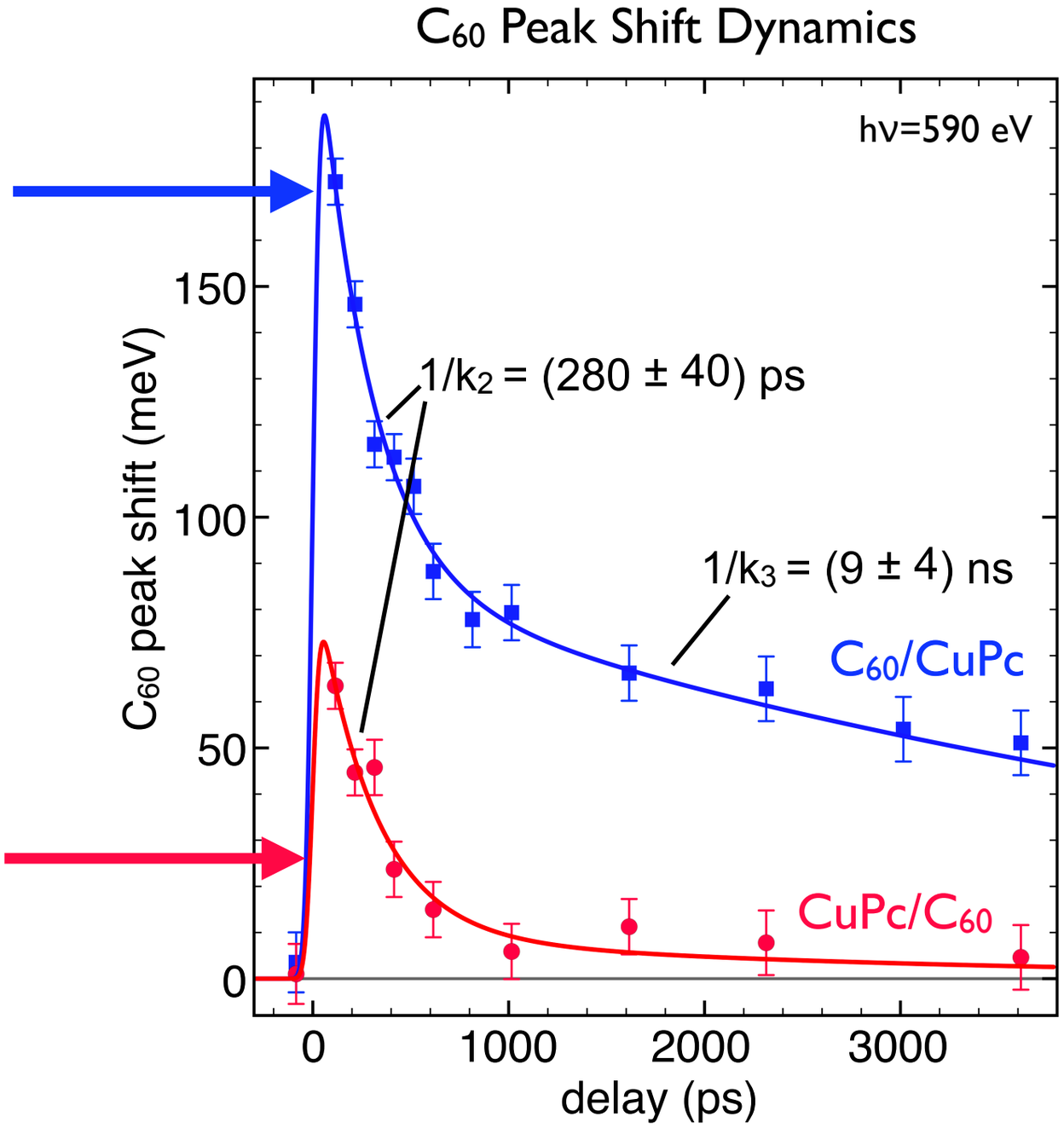
Transient XPS of Electron Dynamics in Donor-Acceptor Bi-Layers



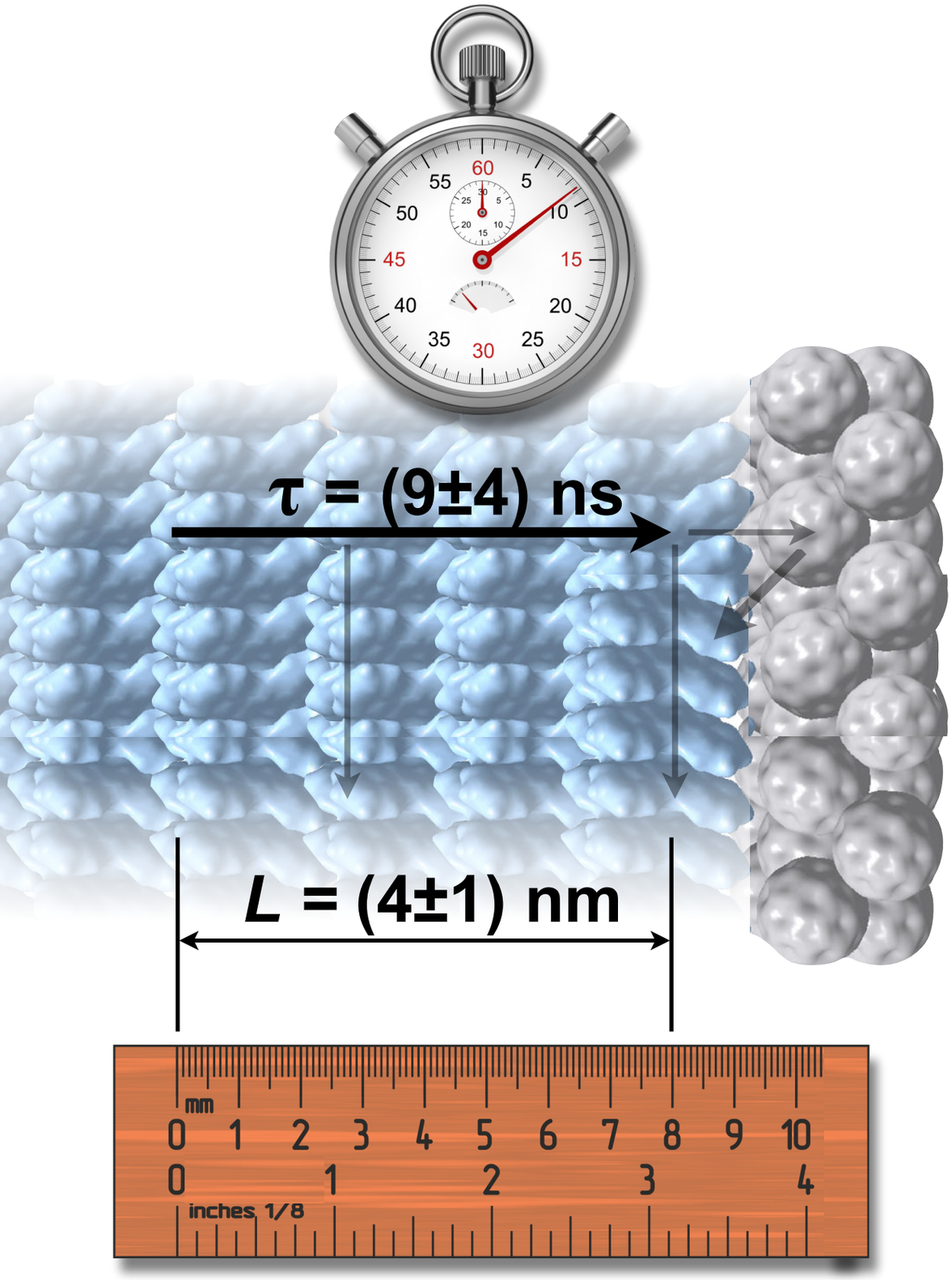


Transient XPS of Electron Dynamics in Donor-Acceptor Bi-Layers

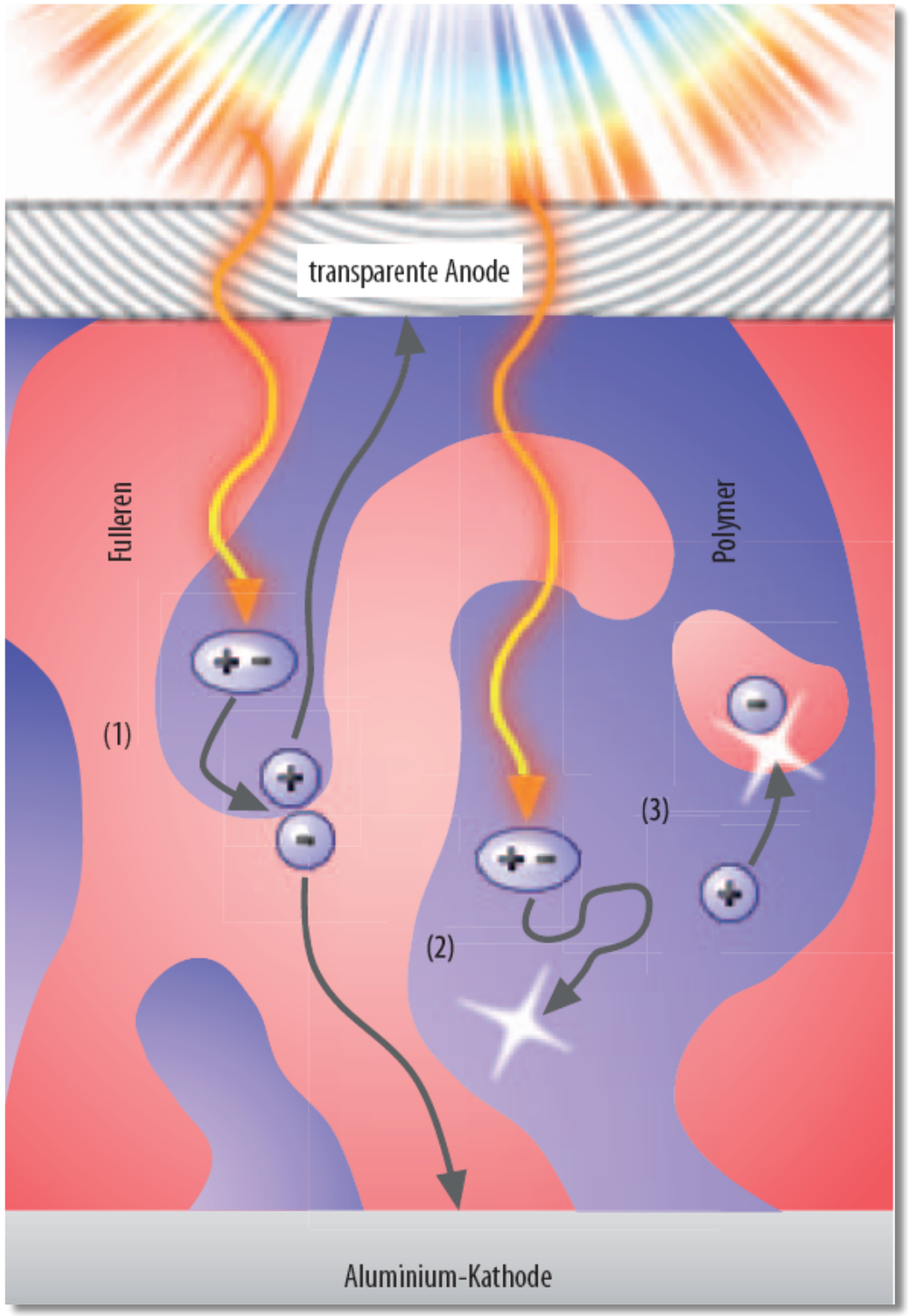




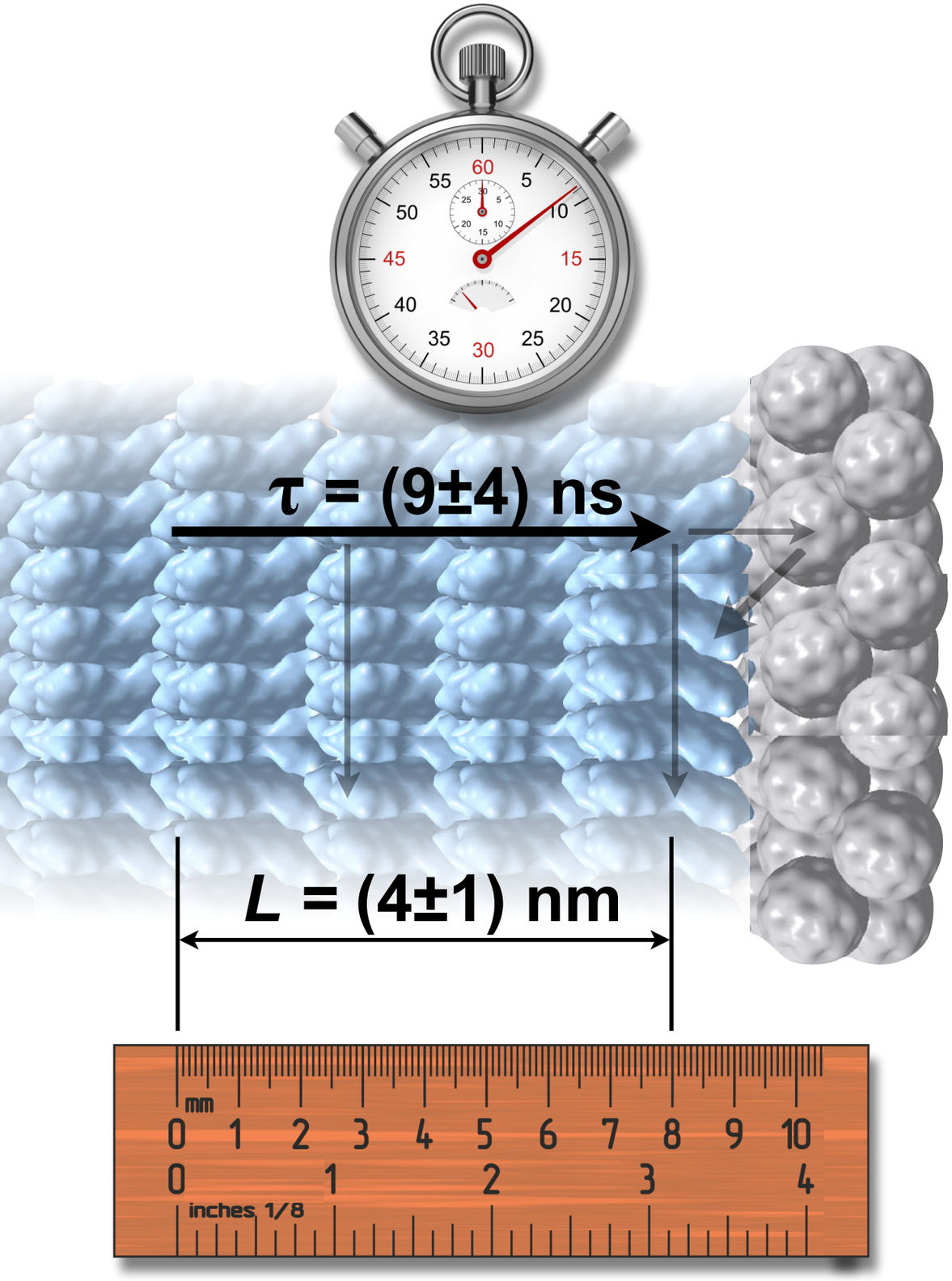
Exciton Diffusion Dynamics



Exciton Diffusion: $L^2 = D \times \tau$



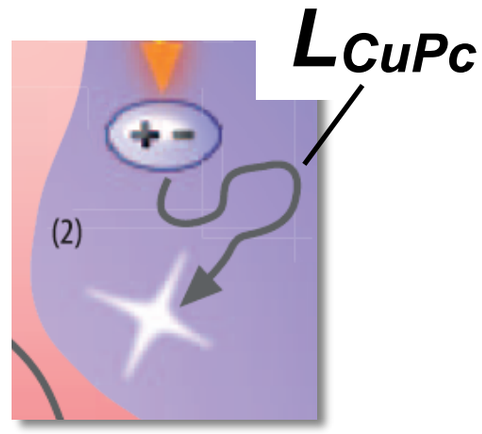
Exciton Diffusion Dynamics



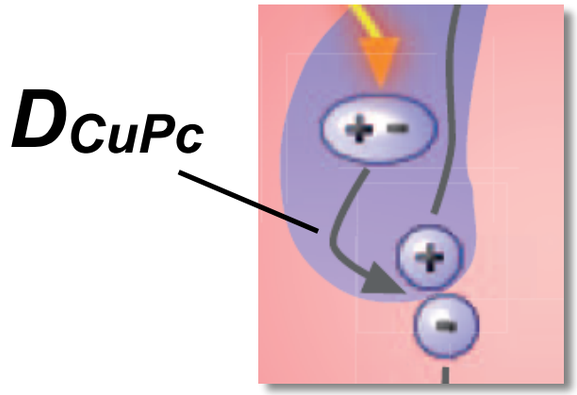
Diffusion Length

L_{CuPc} = (8 ± 3) nm

Literature: ~5 - 70 nm



"Dark" Triplet Exciton Diffusivity

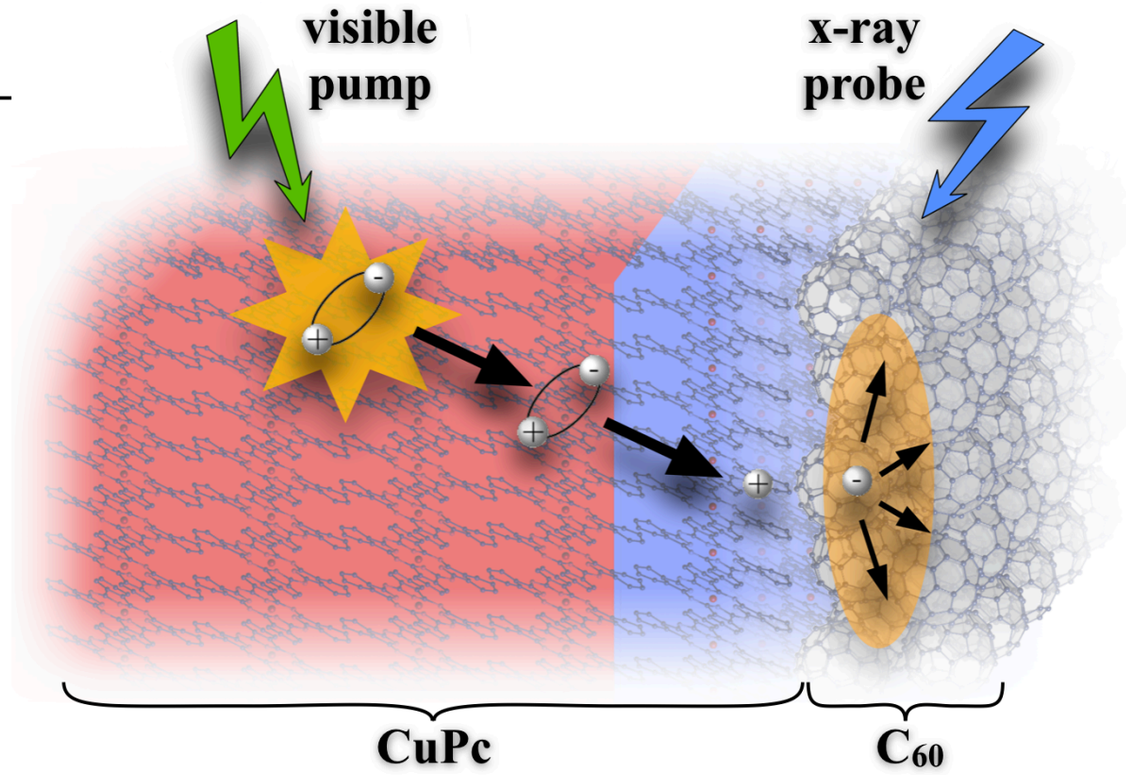


D_{CuPc} = (1.8 ± 1.2) x 10^{-5} cm^2/s

Literature (indirect):

D_{CuPc}~1 - 540 x 10^{-5} cm^2/s

Singlet vs Triplet Exciton Charge Generation



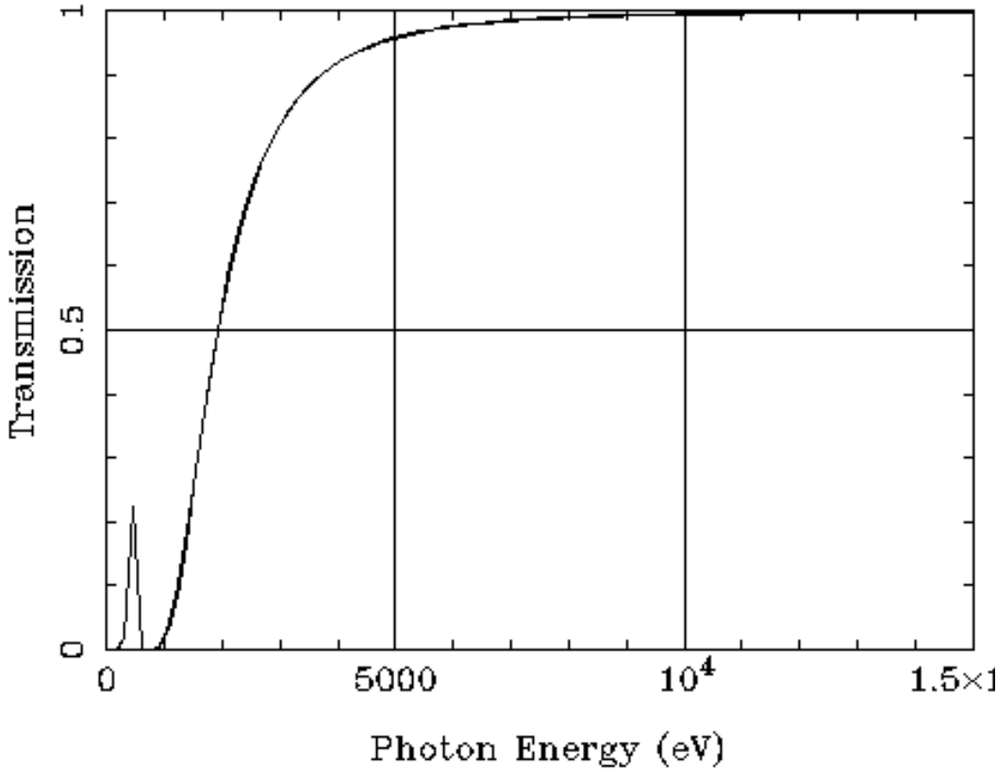
$$\frac{\#\text{Charges (Triplets)}}{\#\text{Charges (Singlets)}} \approx 10\ !!!$$

Roth et al., Phys. Rev. B **99**, 020303(R) (2019)

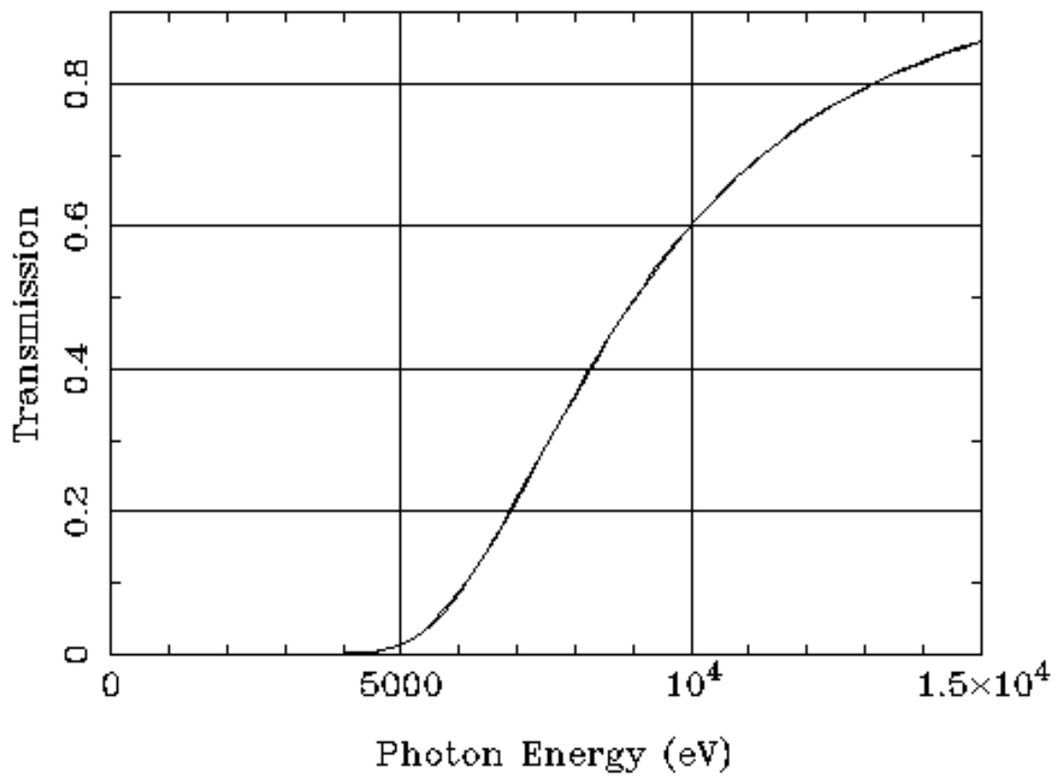
In situ / operando Studies Enabled by Hard X-rays

X-ray Transmission

10 μm of water



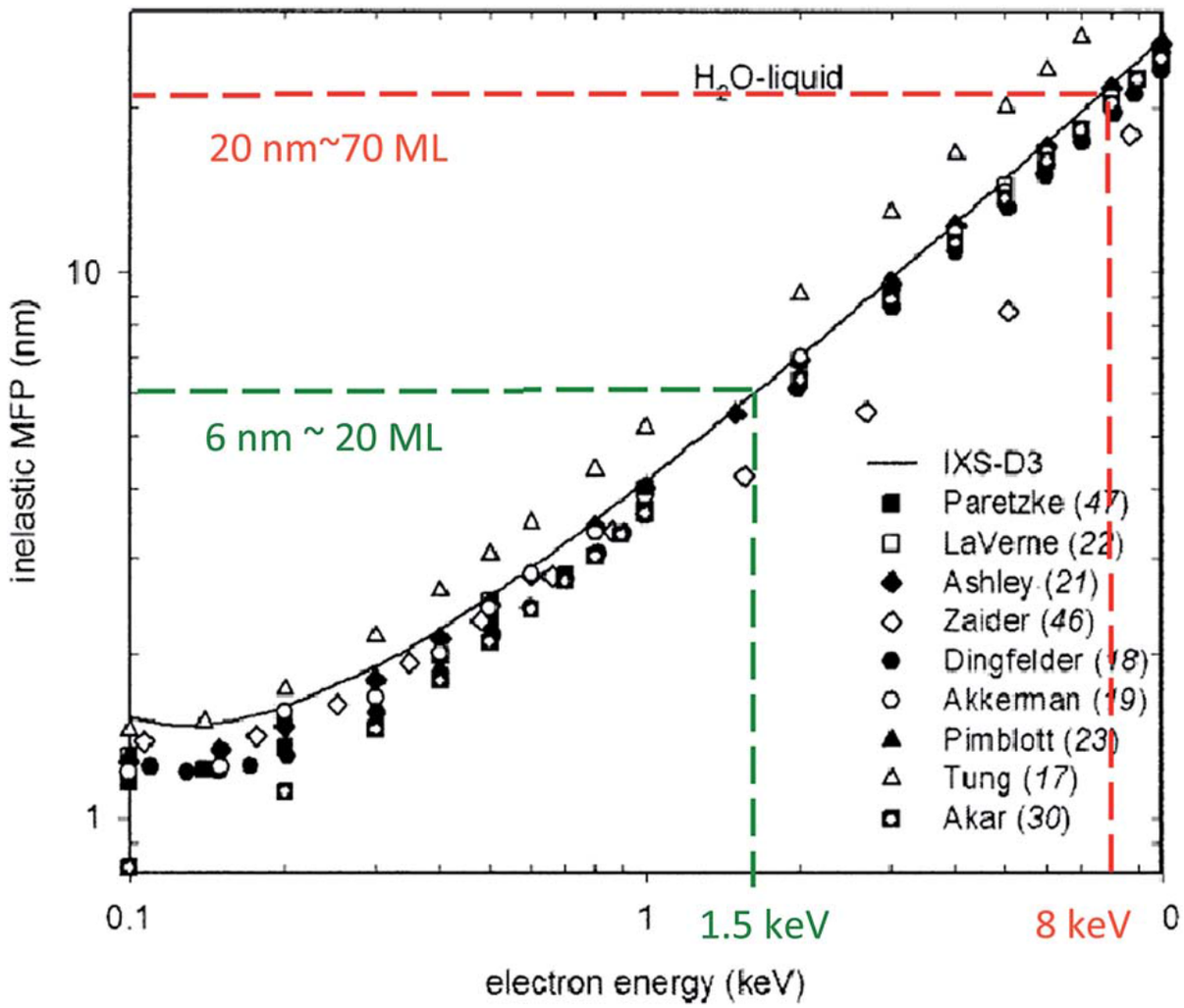
1 mm of water



source: CXRO calculator, http://henke.lbl.gov/optical_constants/

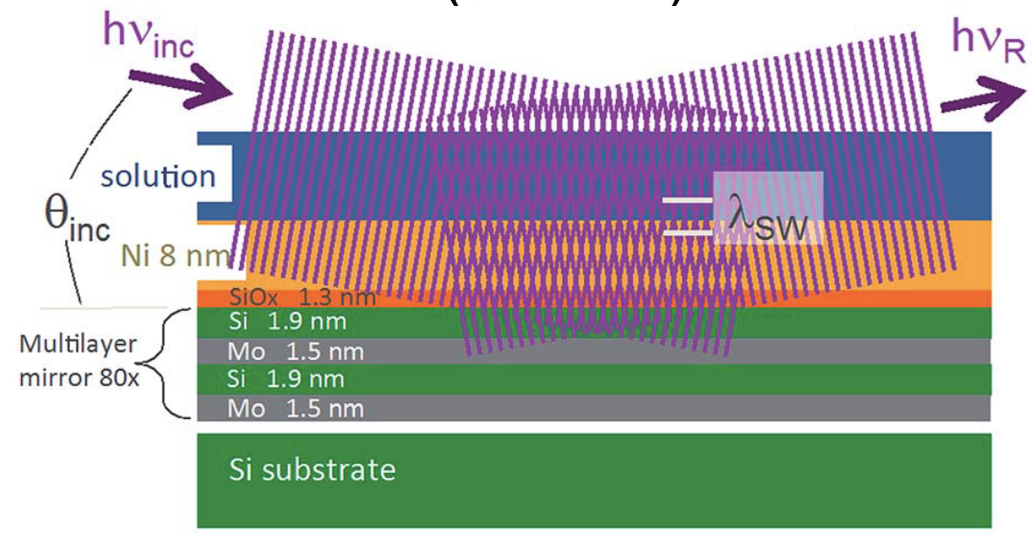
In situ / operando Studies Enabled by Hard X-rays

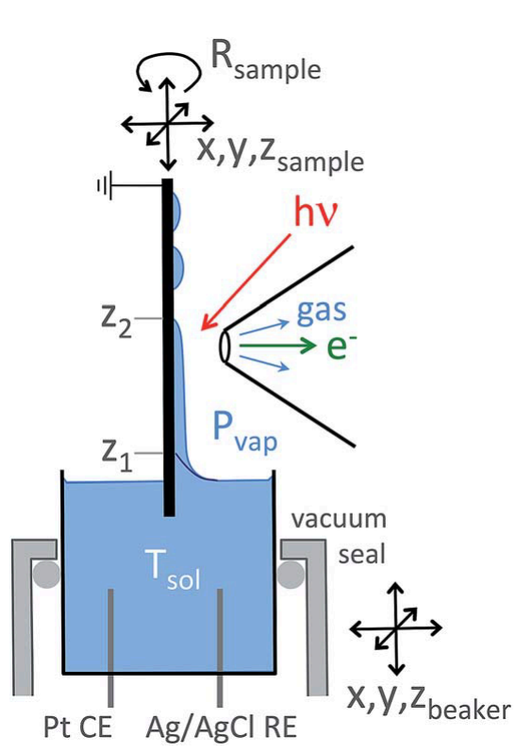
Electron Inelastic Mean Free Path In Water

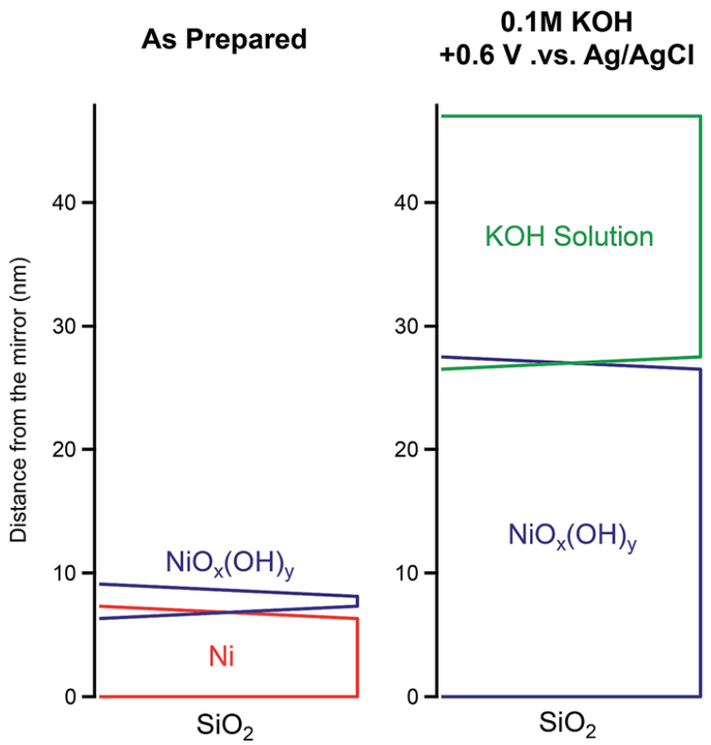


Karslıoğlu *et al.*, Faraday Discuss. **180**, 35 (2015)
Emfietzoglou and Nikjoo, Radiat. Res. **167**, 110 (2007)

In-Operando Standing Wave Ambient Pressure Photoemission (SWAPPS)



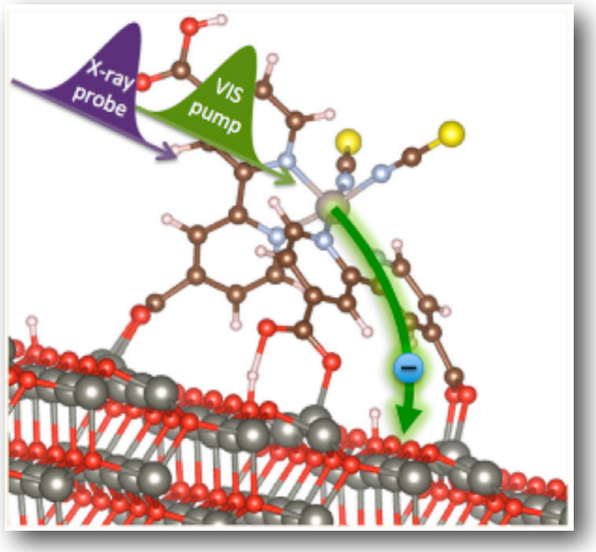


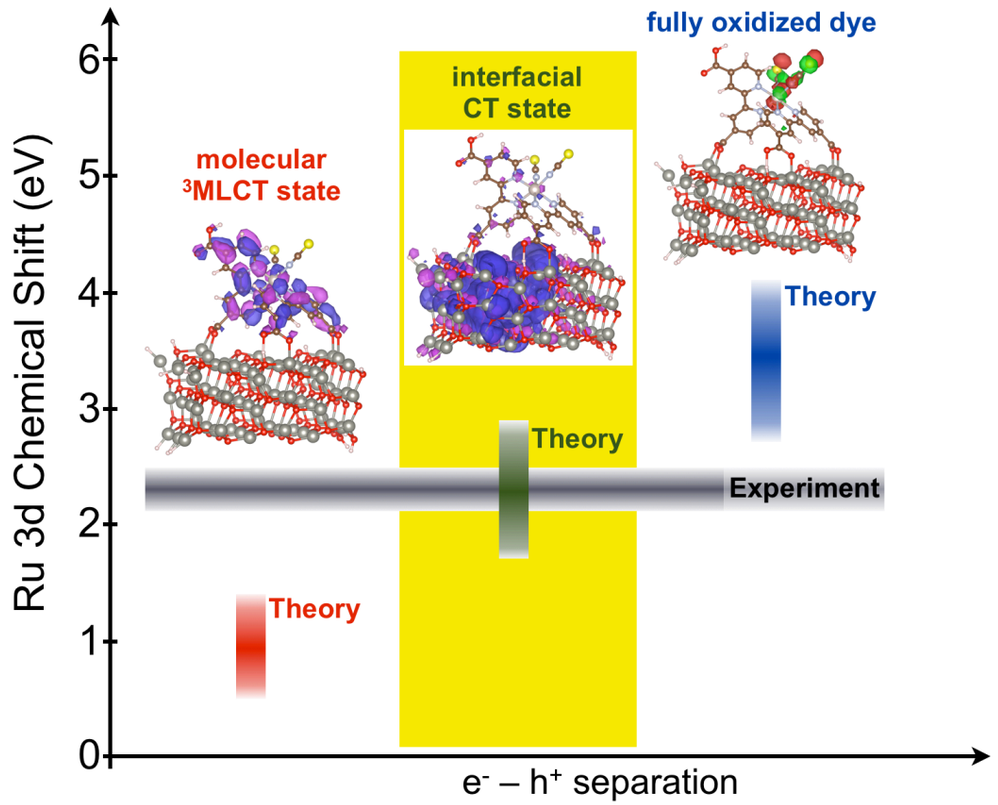


Karslıoğlu *et al.*, Faraday Discuss. **180**, 35 (2015)
Nemšák *et al.*, Nat Commun **5**, 5441 (2014)

Summary

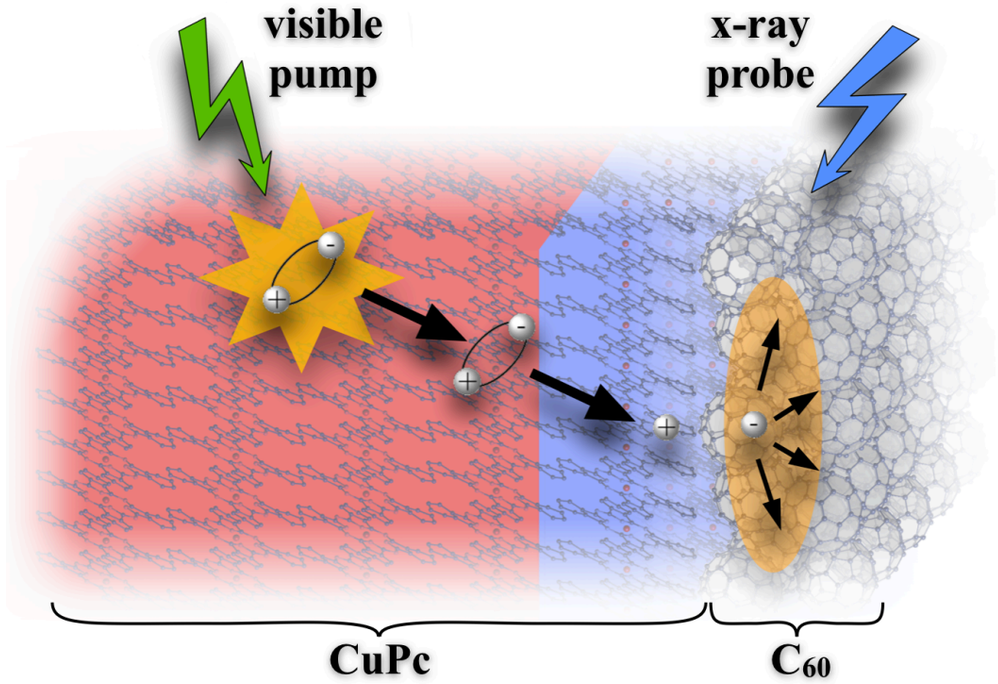
Interfacial Charge Transfer in N3/ZnO

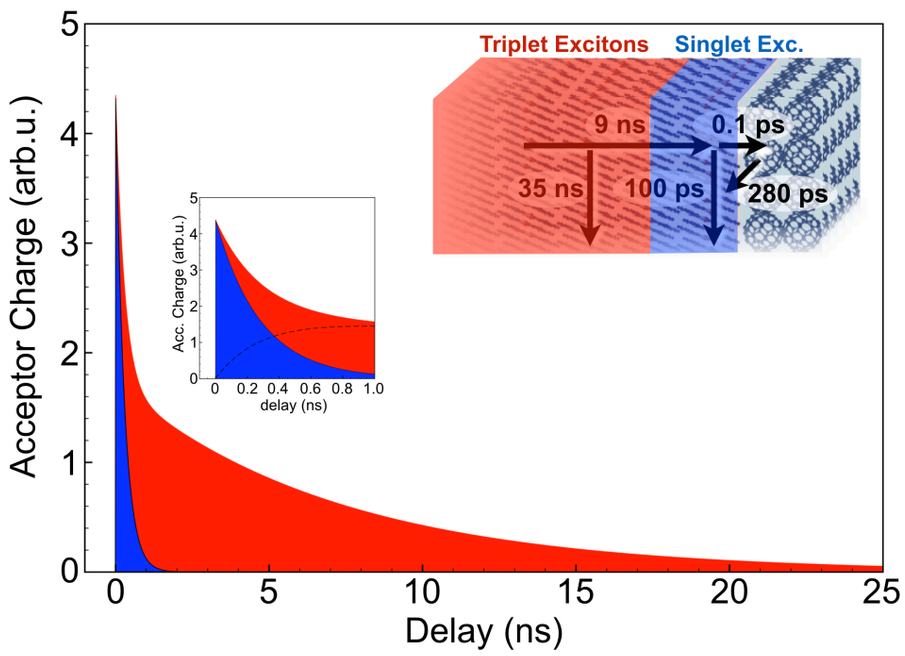




Siefermann *et al.*, JPCL 5, 2753 (2014)
S. Neppl and O.G., J. Electron Spectrosc. Relat. Phenom. **200**, 64 (2015)
O.G. and M. Gühr, Acc. Chem. Res. 49, 138 (2016)

Bulk and Interfacial Dynamics in $CuPc/C_{60}$

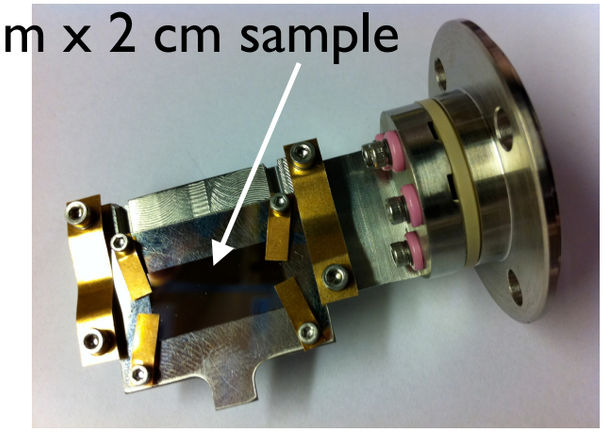




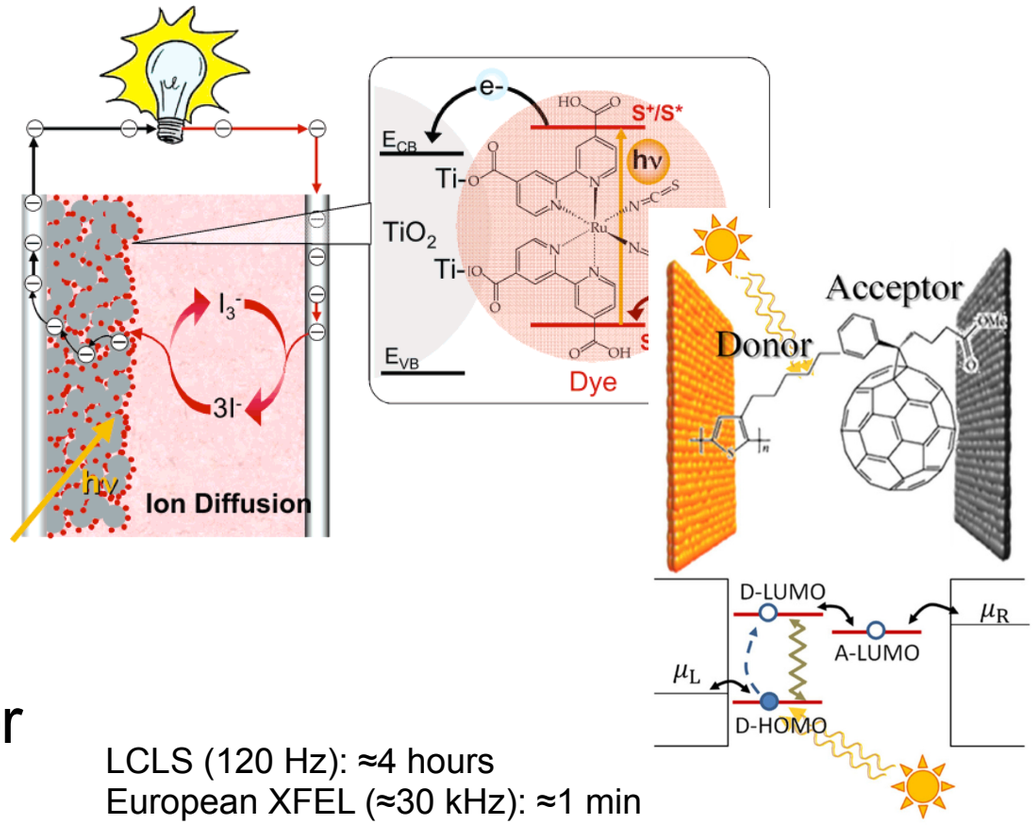
Arion *et al.*, Appl. Phys. Lett. **106**, 121602 (2015)
Roth et al., Phys. Rev. B **99**, 020303(R) (2019)

Figure of Merit:
Information / Photon / Sample Damage Rate

("photon-hungry" is not always best choice)

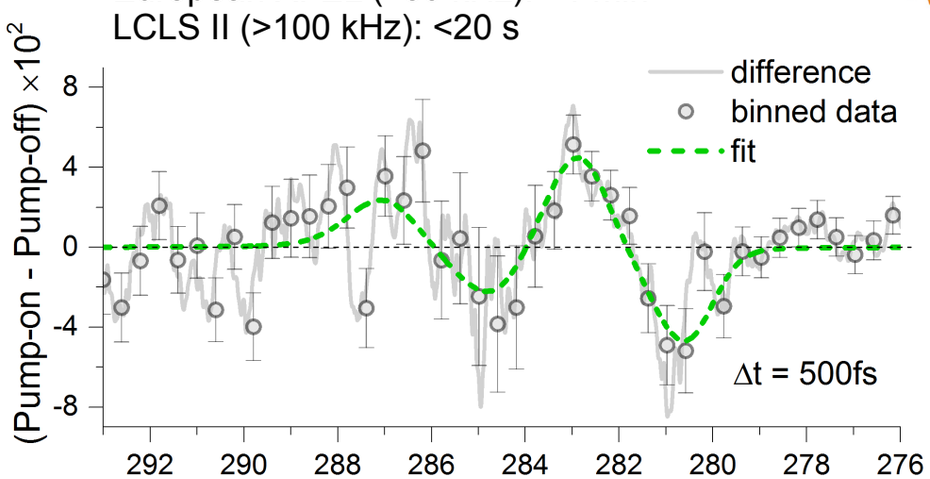


- **What is to be measured?**
  - –Surface and interfacial electronic & chemical dynamics during (photo-)electrochemical reactions



- **Advanced method, instrument, or approach**
  - –trXPS, trAPPES, trSWAPPS
  - –Needed: NAP/AP HE-XPS setup w/ DLD detector
  - –Existing: MHz setups @ synchrotrons, e.g. >100kHz laser / 500 MHz X-ray setup @ ALS
  - –Detector problem solved!
  - –Rep. rate as high as possible.
  - –Monochromator.

LCLS (120 Hz): ≈4 hours
European XFEL (≈30 kHz): ≈1 min
LCLS II (>100 kHz): <20 s



Current, Former, and Future Chemical Dynamicists…

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