

# FUNDAMENTALS OF SOLAR LIGHT HARVESTING: ULTRAFAST X-RAY INSIGHTS INTO INTERFACIAL ELECTRON DYNAMICS

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U.S. DEPARTMENT OF  
**ENERGY**



# AMOS Program @ Berkeley Lab

## Experiment



Oliver Gessner (PI)



Stephen Leone



Daniel Neumark



Daniel Slaughter



Thorsten Weber



William McCurdy



Robert Lucchese

## Theory



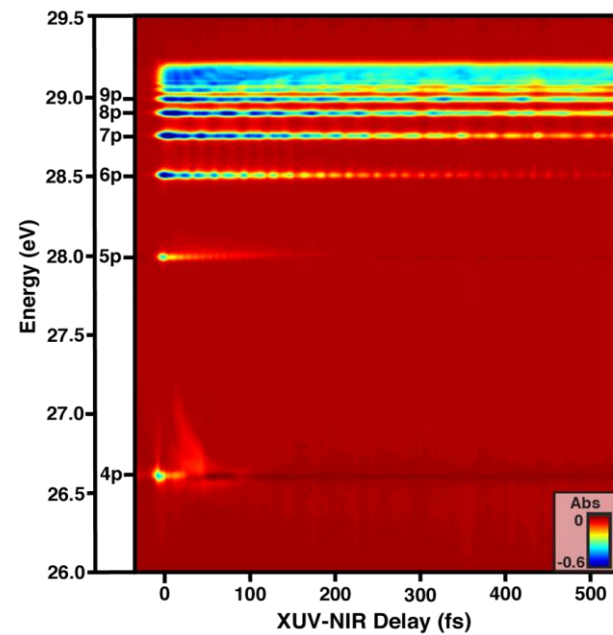
Martin Head-Gordon



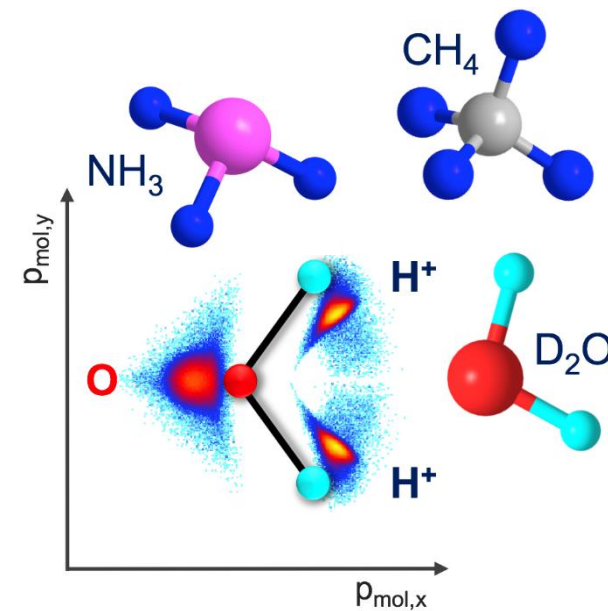
Jin Qian



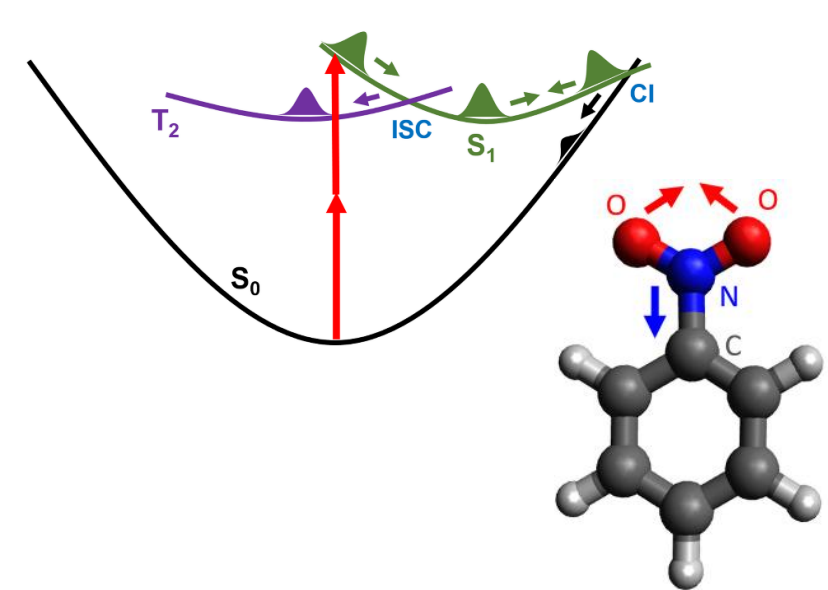
Thomas Rescigno (Contributor)



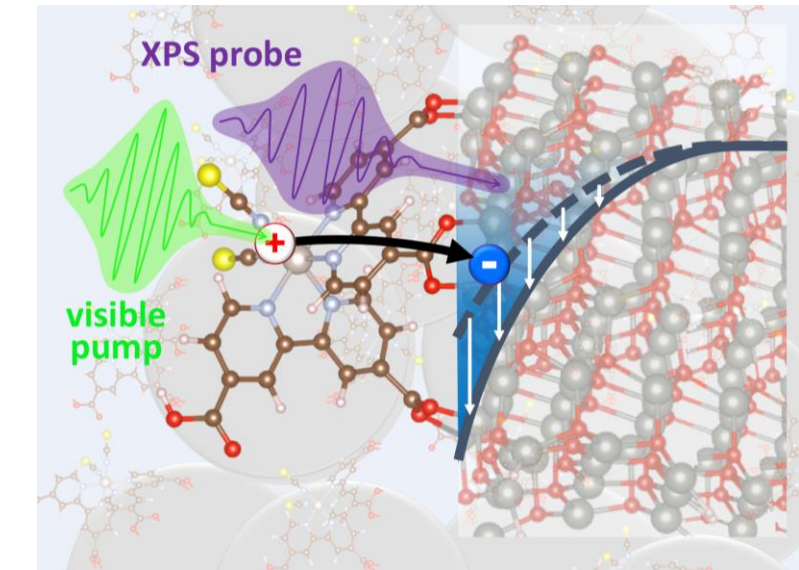
Attosecond electron dynamics in atoms and molecules



Molecular ionization & dissociation dynamics



Neutral excited state dynamics in isolated and solvated molecules



Photoinduced interfacial charge transfer dynamics

### Timescales (s)

atto – femto

femto – pico

femto – nano+



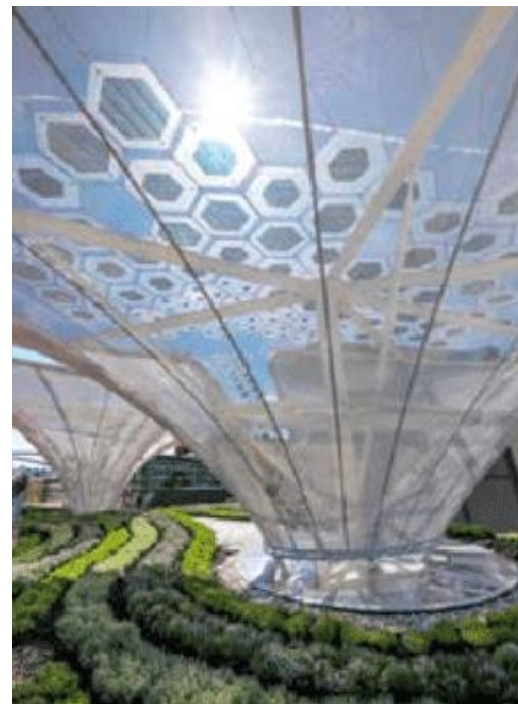
# Renewable Energy Technologies and Interfacial Dynamics

## Molecule-Semiconductor Interfaces



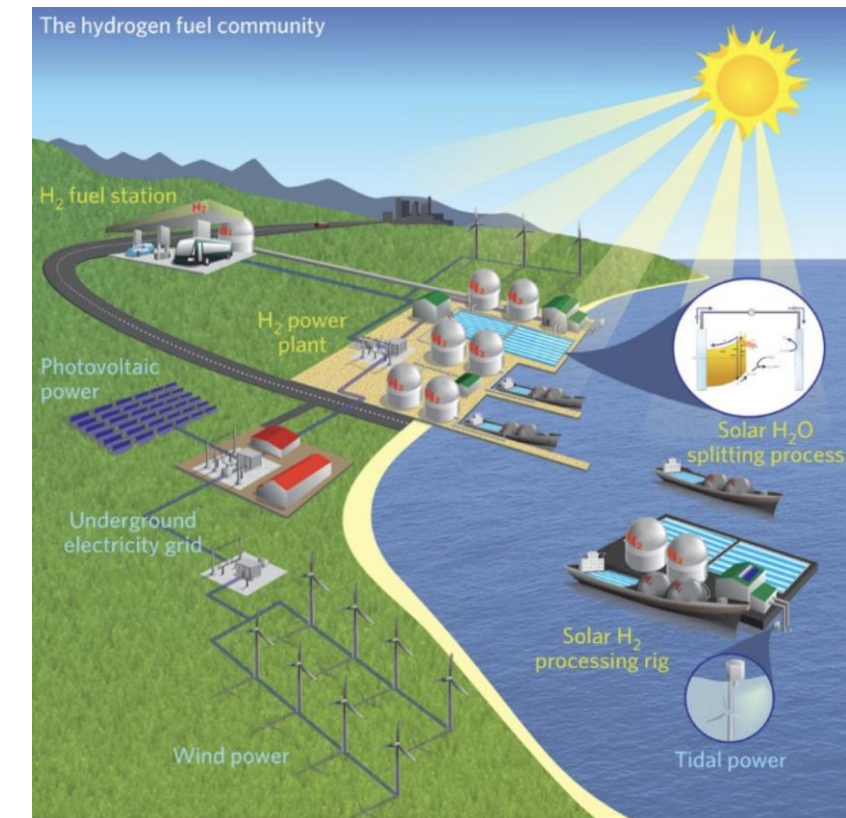
Dye-Sensitized Solar Cell Windows, SwissTech convention center at EPFL

## Organic Semiconductors

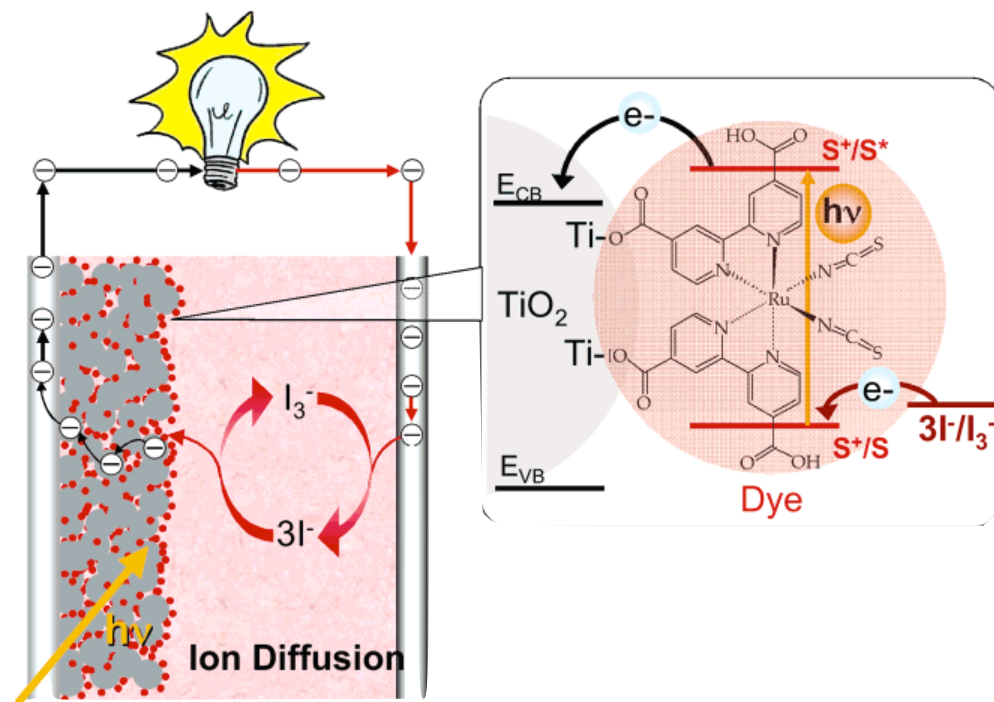


OPV integrated solar trees of German Pavilion Expo 2015

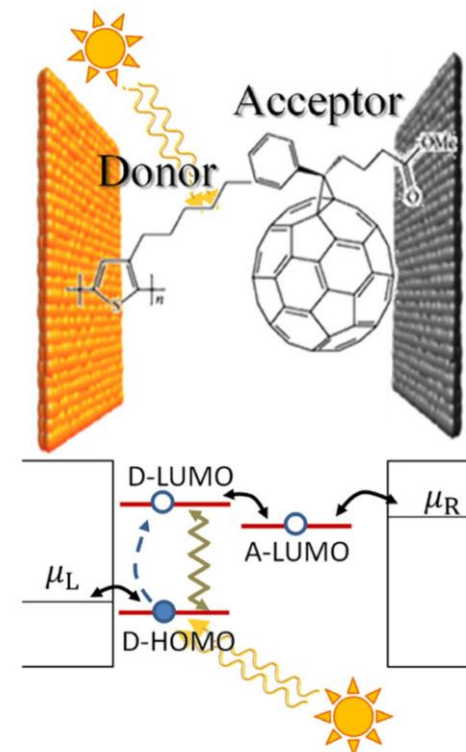
## Nanostructure Enabled Catalysis



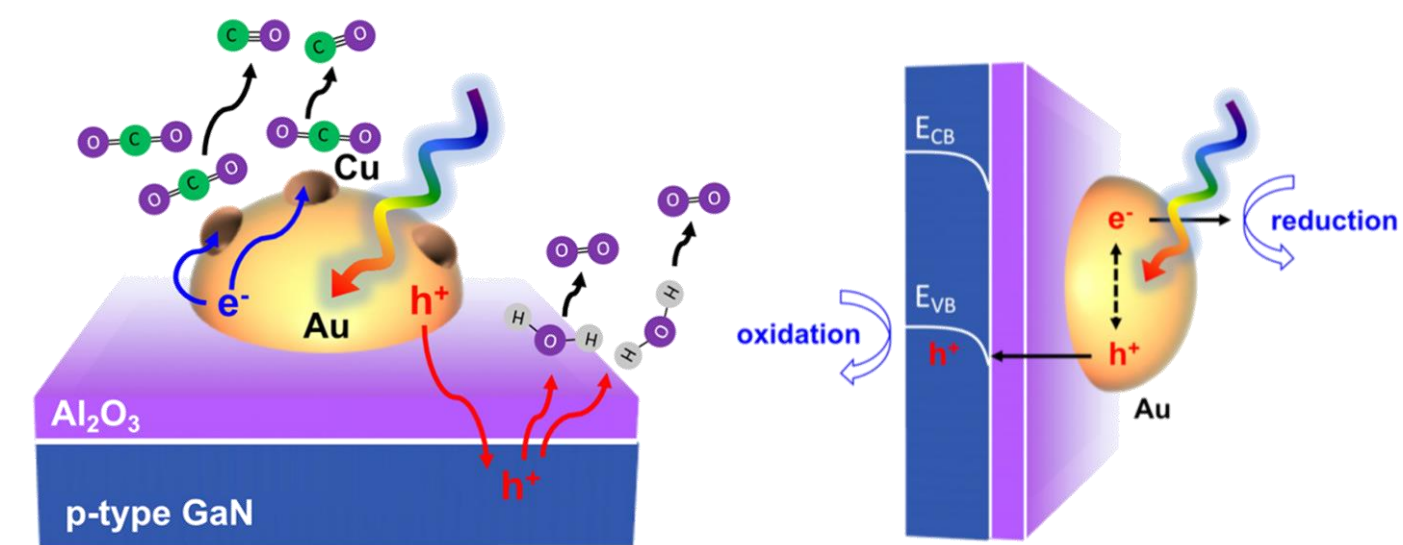
Y. Tachibana, L. Vayssieres, and J. R. Durrant, Nat Photon **6**, 511 (2012)



M. Grätzel, J. Photochem. Photobiol. A-Chem. **164**, 3 (2004)



S. Ajsaka *et al.*, Sci. Rep. **5**, 8312 (2015)



R. Li *et al.*, ACS Energy Lett. **6**, 1849 (2021)



# Time-Resolved Experiments - Seeing How They Run

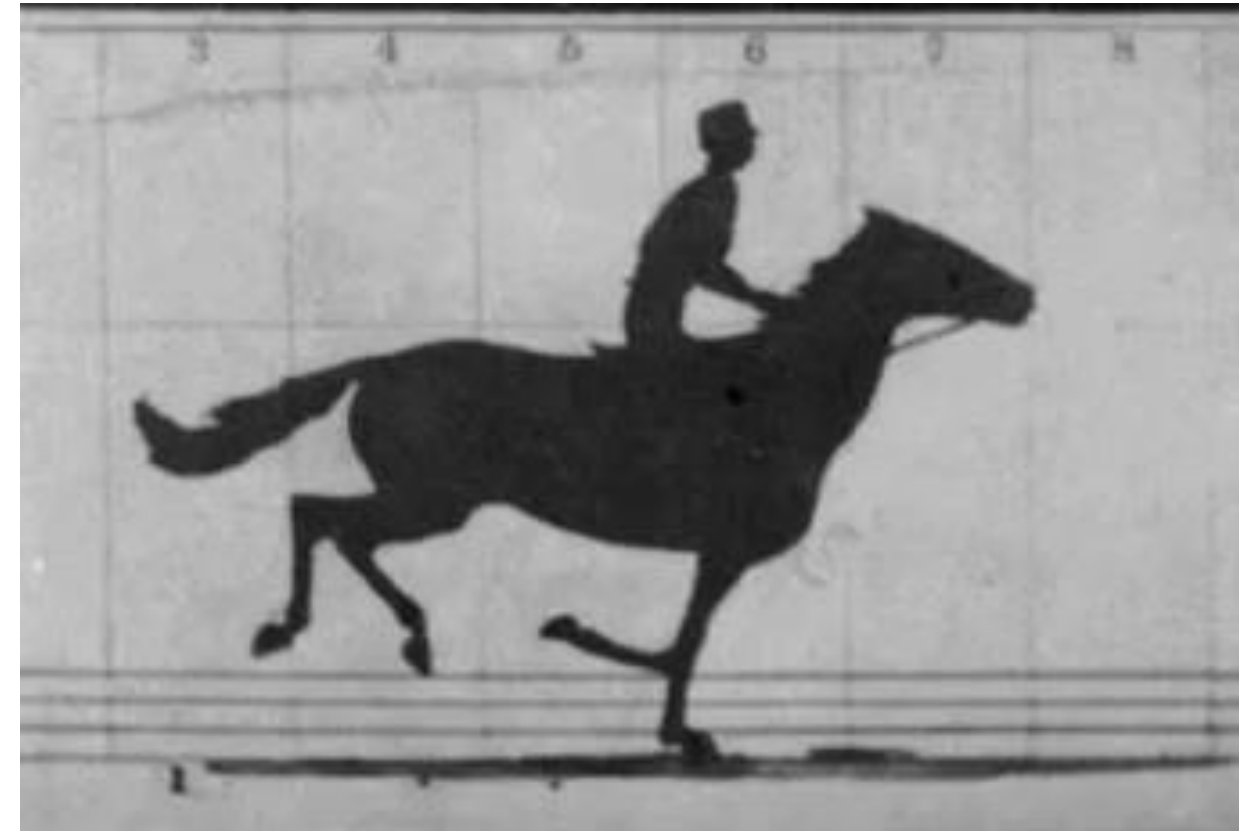


Henry Thomas Alken (1785 – 1851)

# Time-Resolved Experiments - Seeing How They Run



Henry Thomas Alken (1785 – 1851)



Eadweard Muybridge (1878)





# Time-Resolved Experiments - Seeing How They Run



Henry Thomas Alken (1785 – 1851)

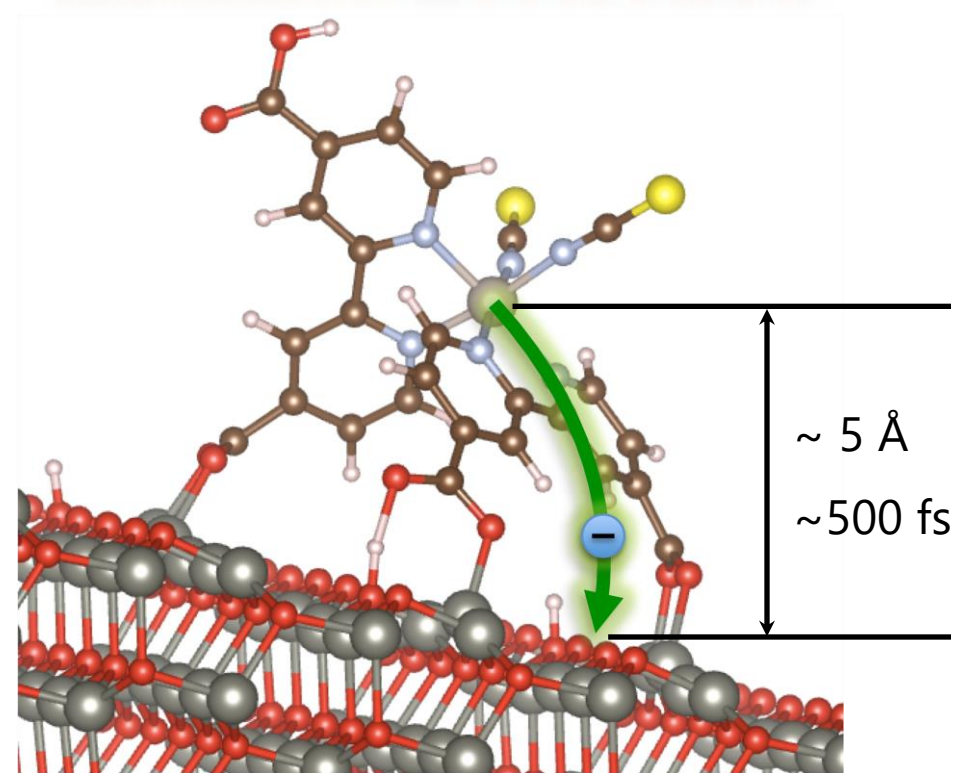


Eadweard Muybridge (1878)

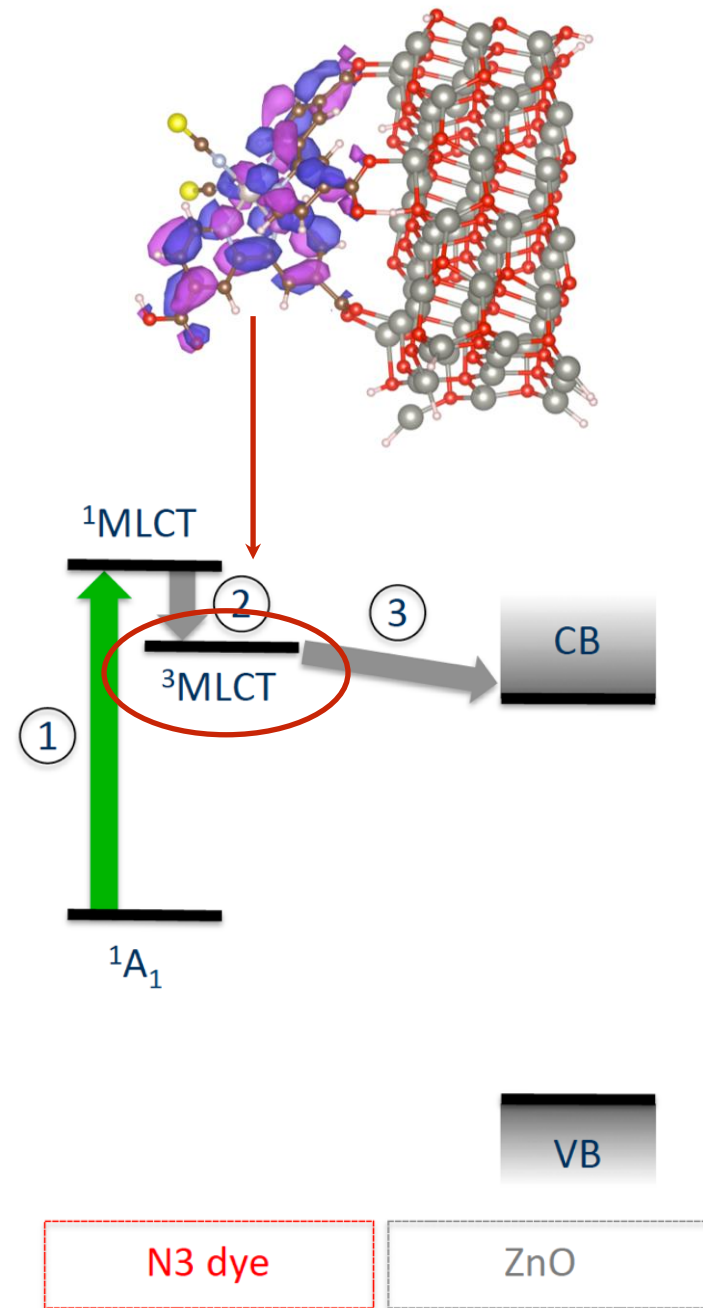


# Competing Models for Ru535-ZnO Charge Injection

## Catching Electrons off Work

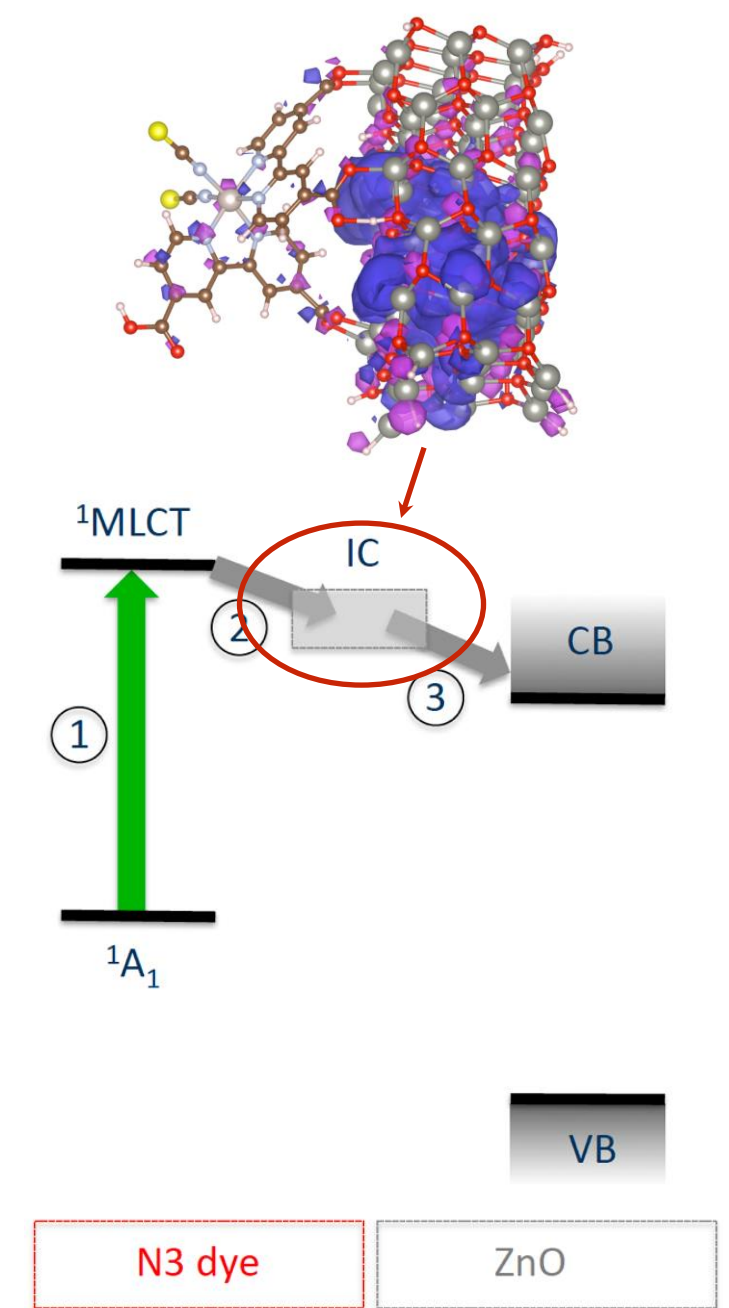


## Biphasic Injection Model



Kallioinen *et al.*, JPC-B 106, 4396 (2002)  
Anderson *et al.*, JPC B 107, 14414 (2003)  
Benkö *et al.*, JPC-B 108, 2862 (2004)  
Anderson and Lian, Annu. Rev. Phys. Chem. 56, 491 (2005)

## Interfacial Exciplex Model

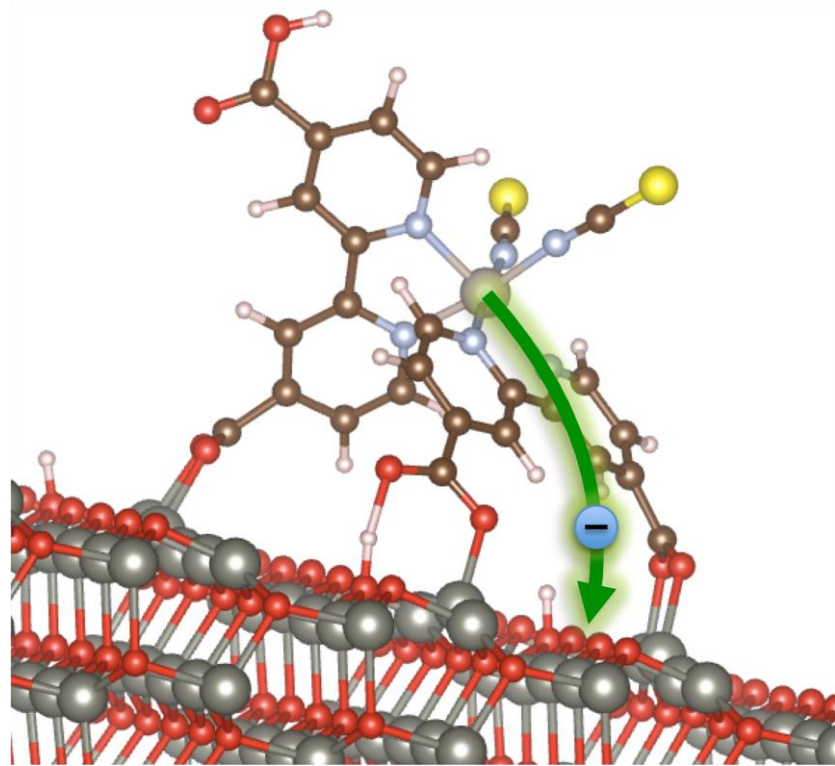


Furube *et al.*, JPC-B 107, 4162 (2003)  
Kato *et al.*, Coord. Chem. Rev. 248, 1195 (2004)  
Němec *et al.*, PRL 104, 197401 (2010)  
Tiwana *et al.*, ACS Nano 5, 5158 (2011)



# Competing Models for Ru535-ZnO Charge Injection

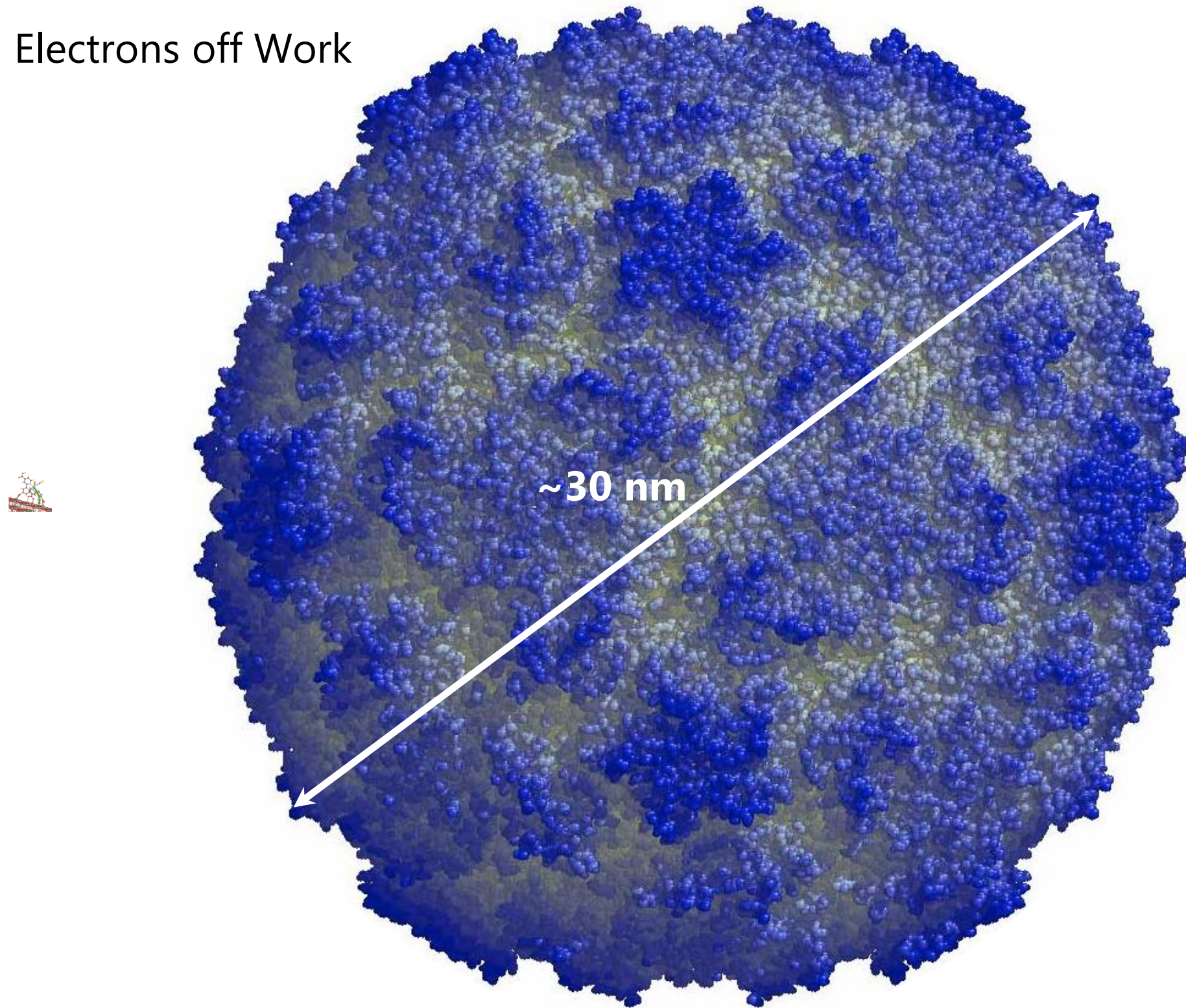
Catching Electrons off Work





# Competing Models for Ru535-ZnO Charge Injection

Catching Electrons off Work



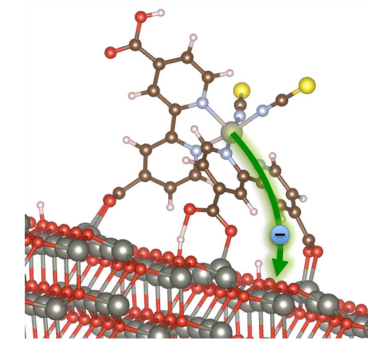
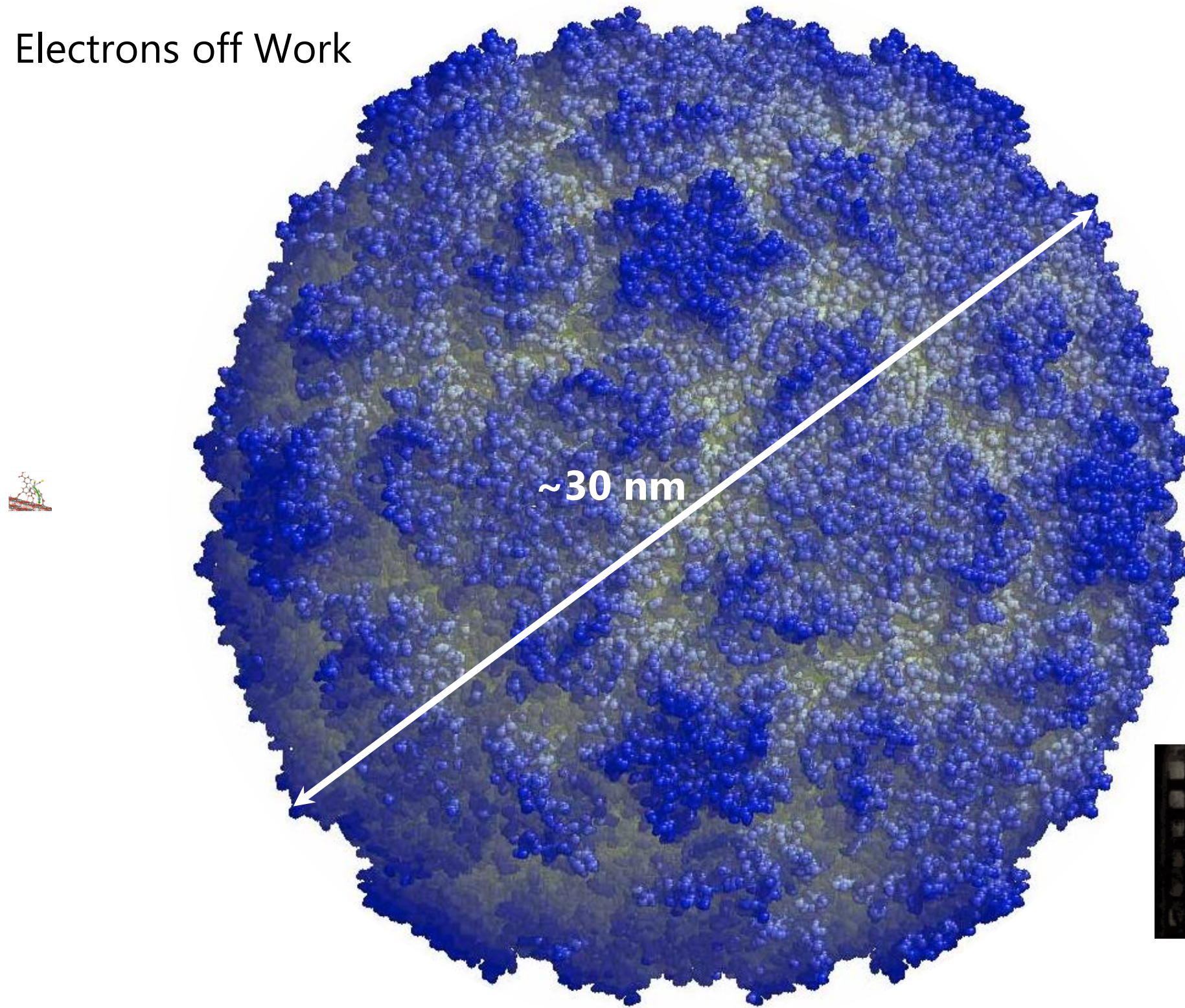
Human Rhinovirus



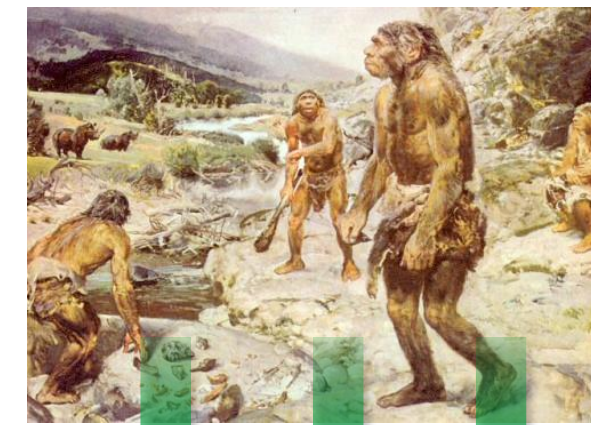
# Competing Models for Ru535-ZnO Charge Injection

Catching Electrons off Work

500 fs : 1s  $\approx$  1s : 63,000 yrs



$\approx$



Human Rhinovirus



# Competing Models for Ru535-ZnO Charge Injection

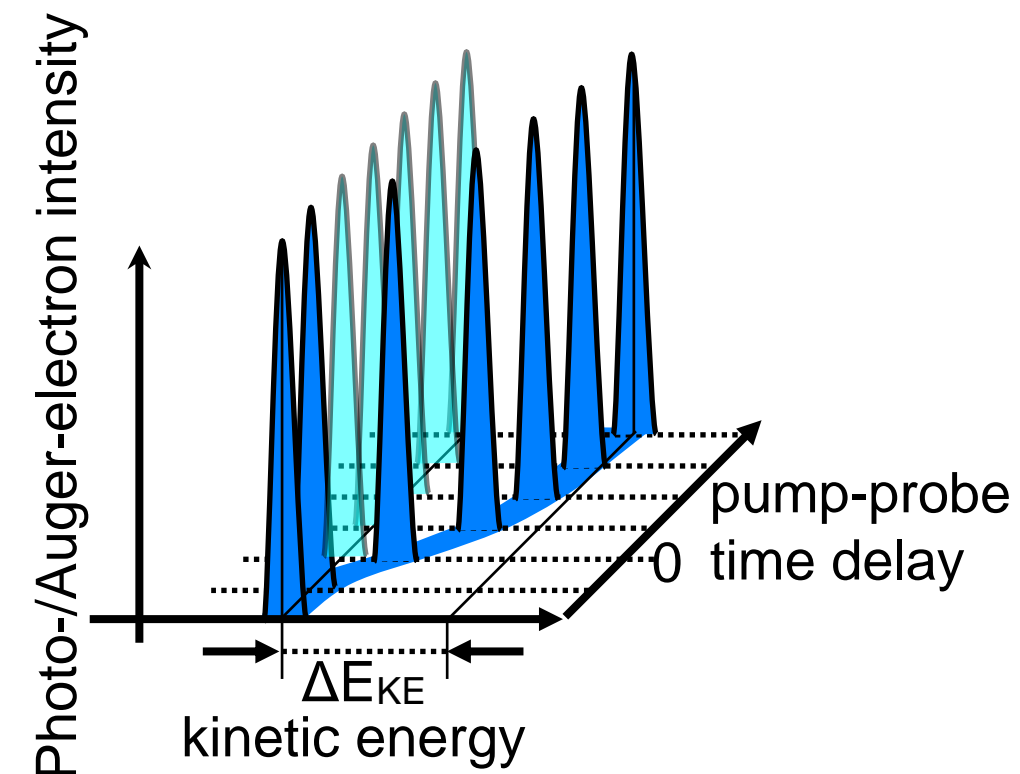
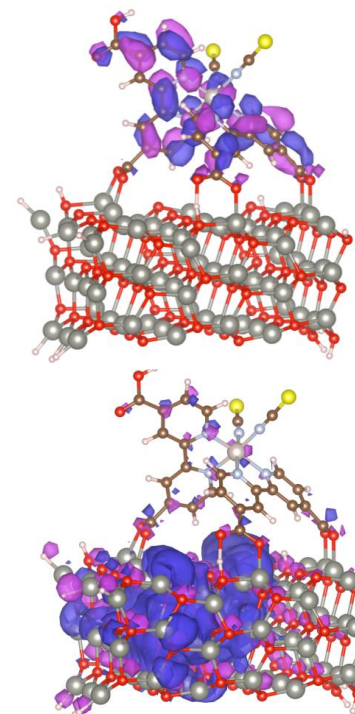
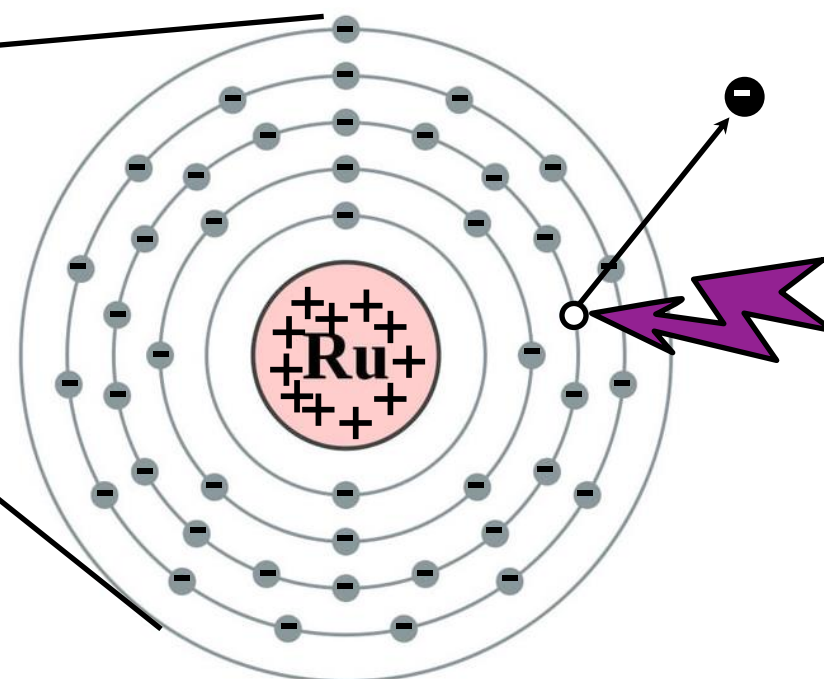
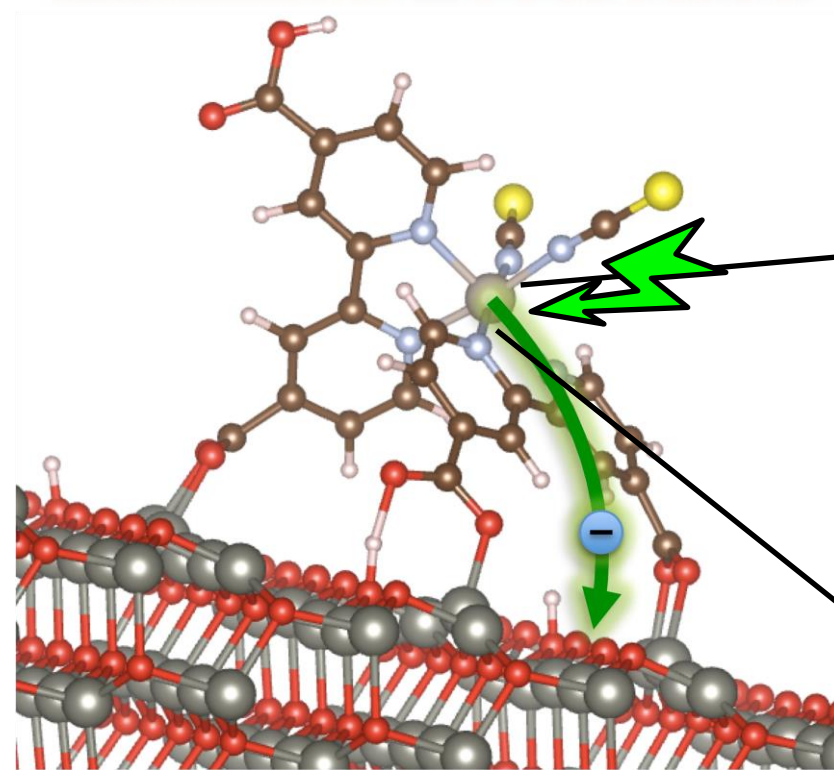
Catching Electrons off Work



Trick 1: Ultrafast Stroboscope



Trick 1I: A Local Observer – Inner-shell Photoelectron Spectroscopy





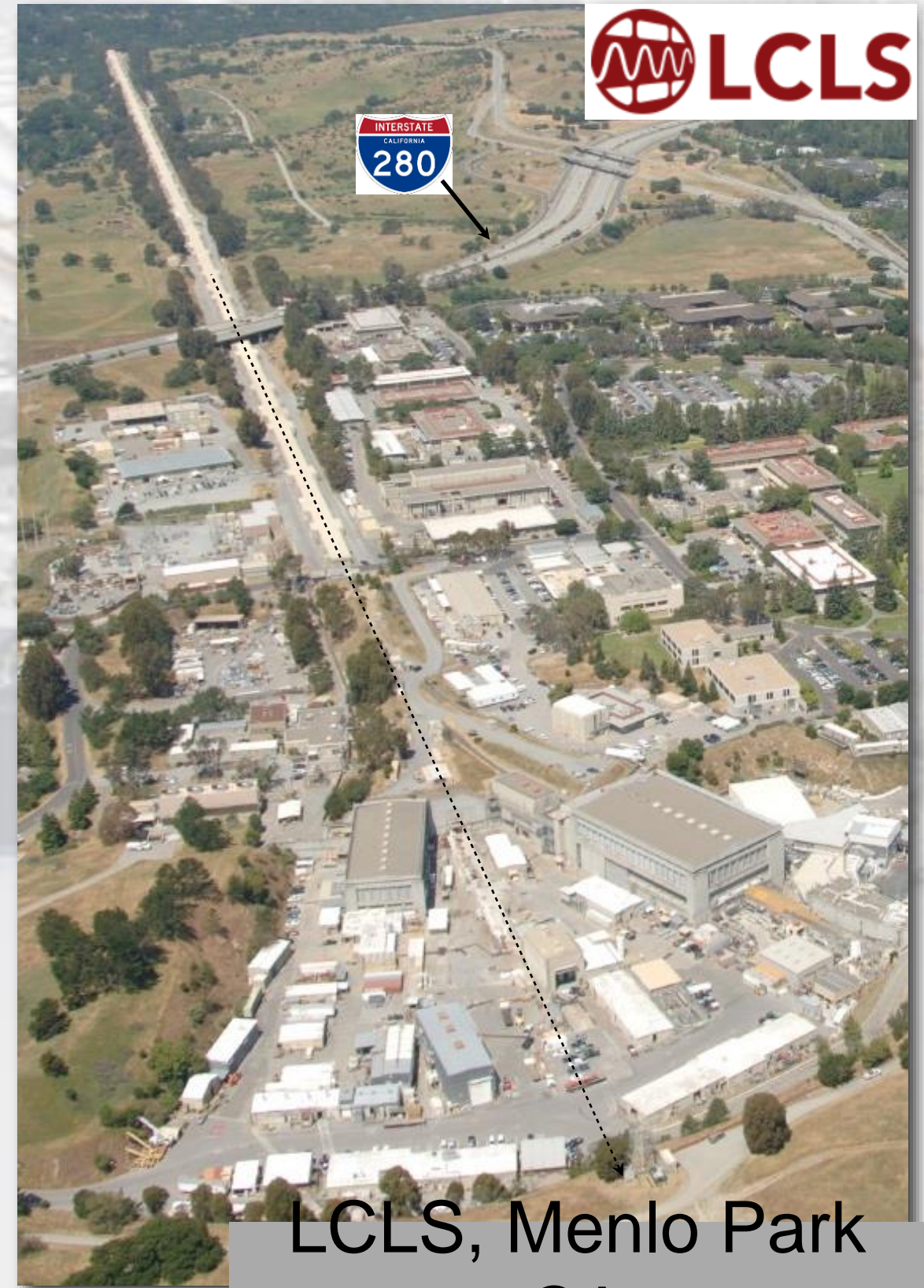
# We Need a Really Big Laser...



1964



LCLS Undulator Hall  
2012



LCLS, Menlo Park  
CA



# We Need a Really Big Laser...

# ...and a Really Big Team!



1964

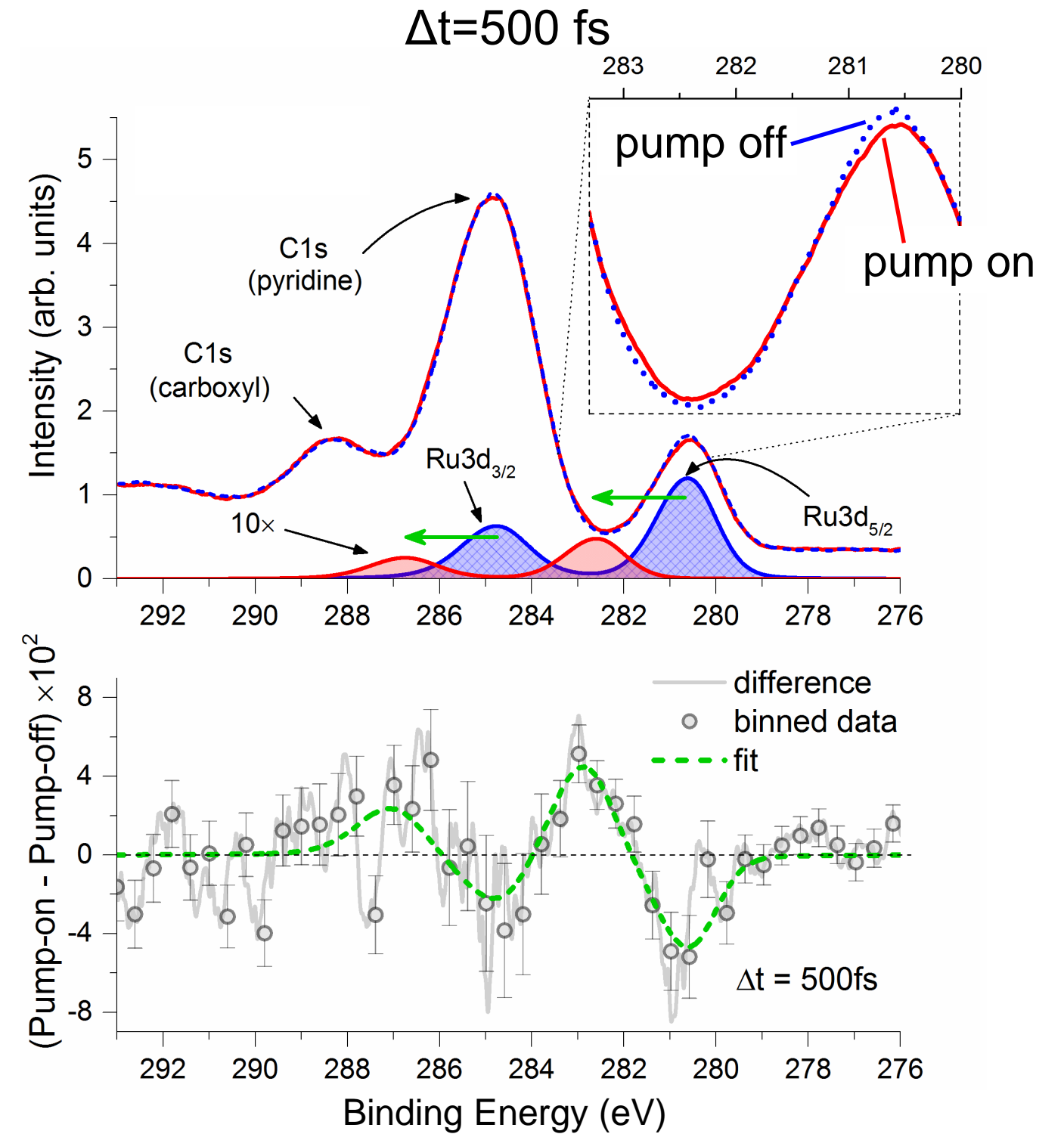
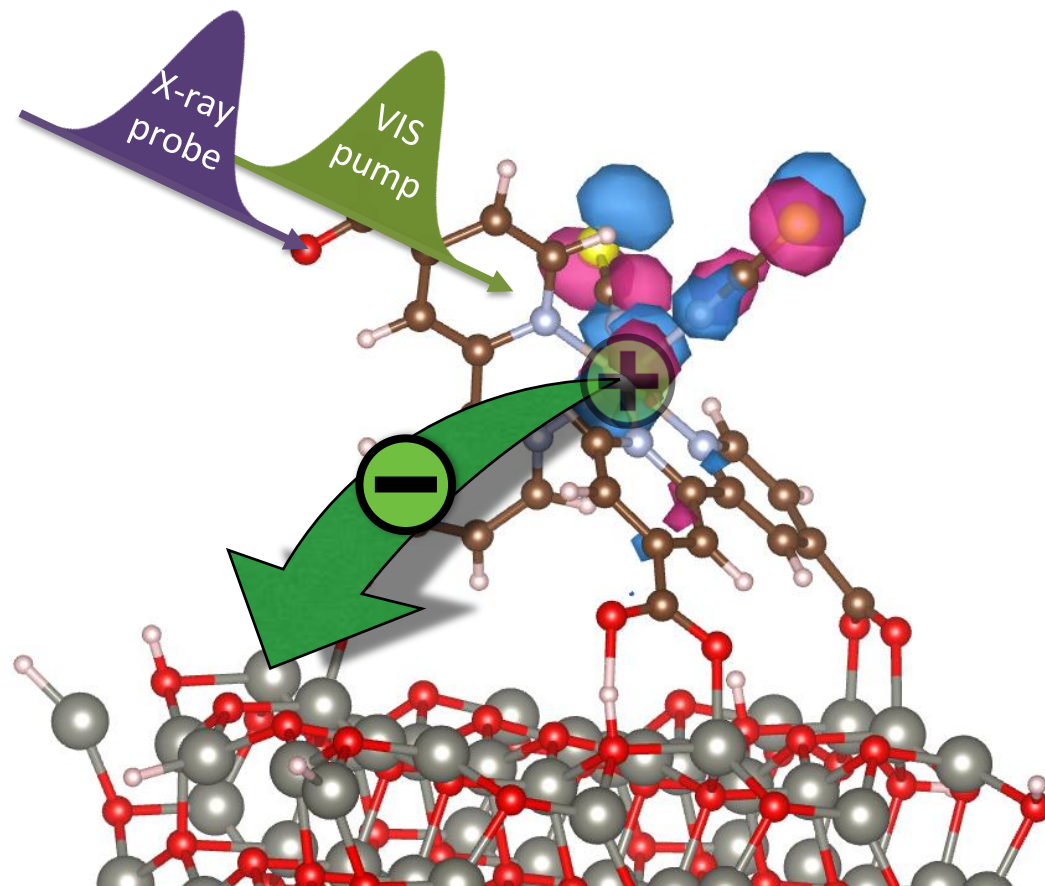
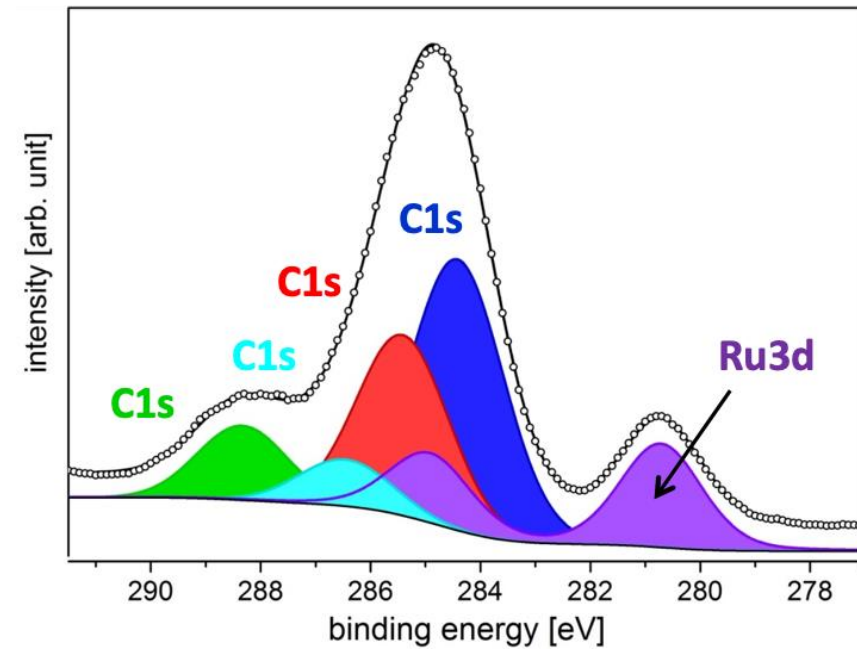
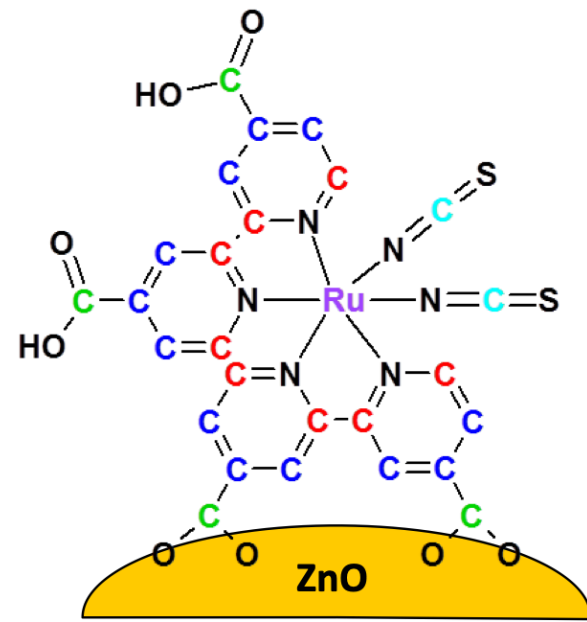


LCLS Undulator Hall  
2012





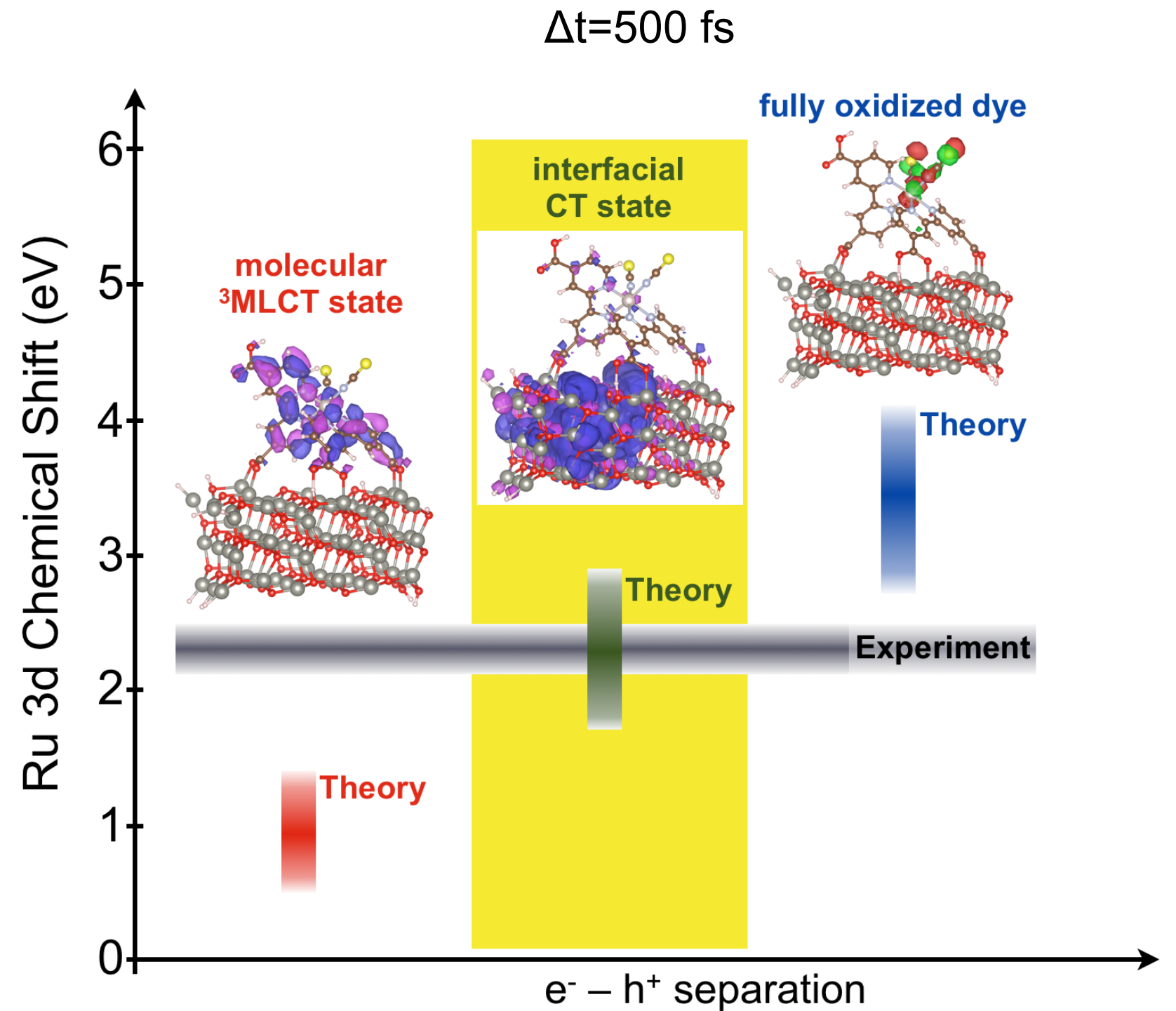
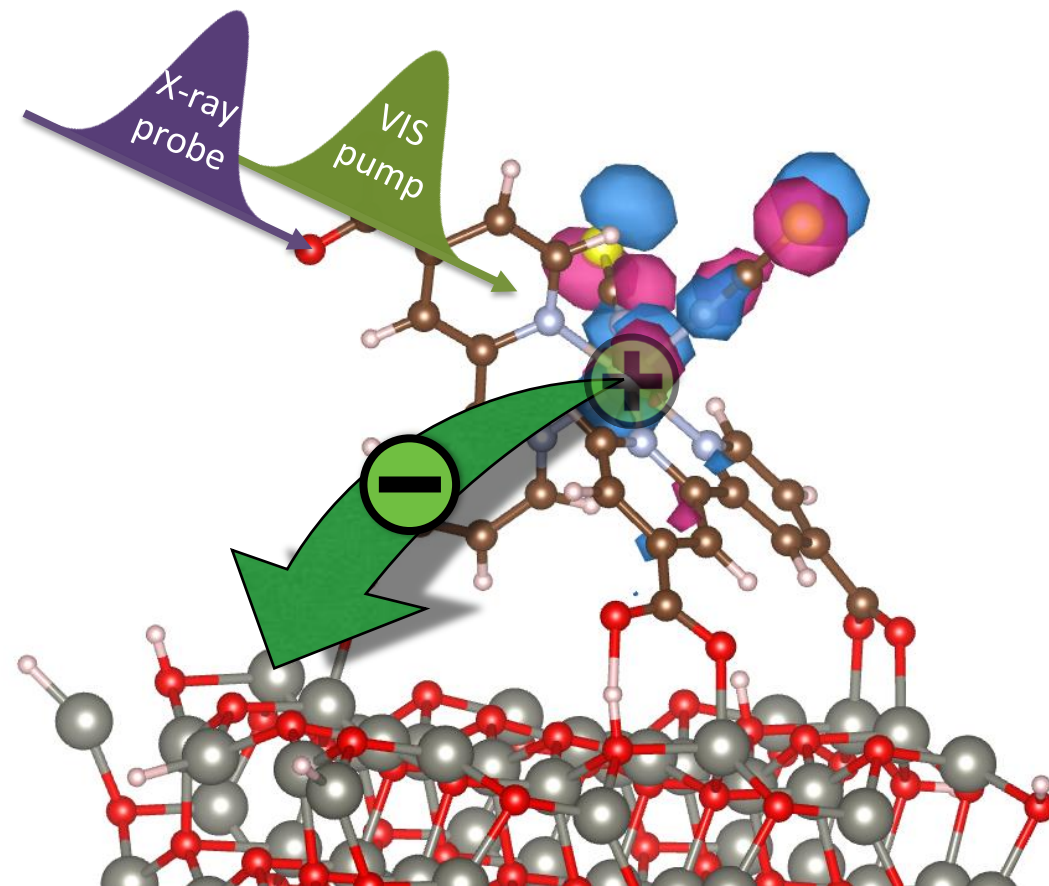
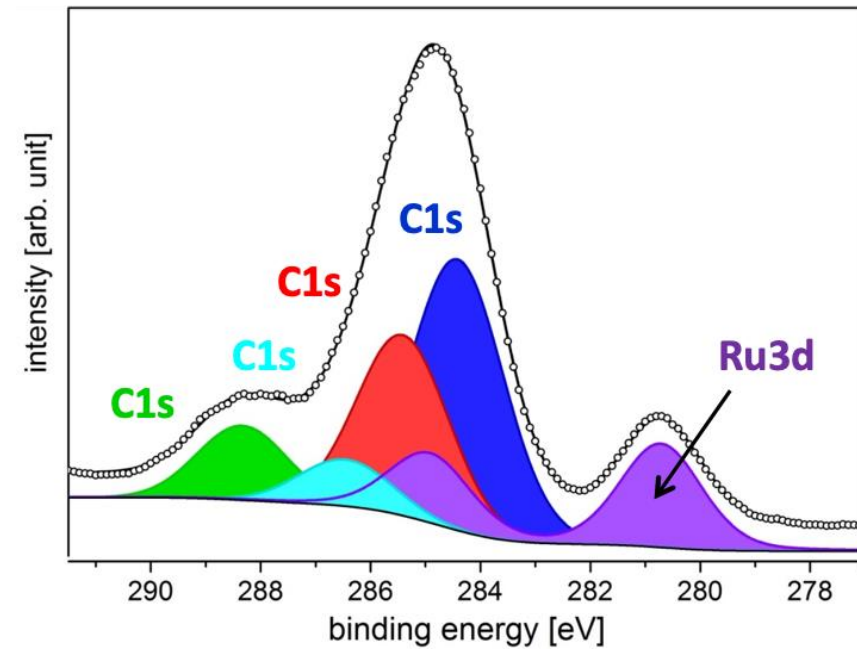
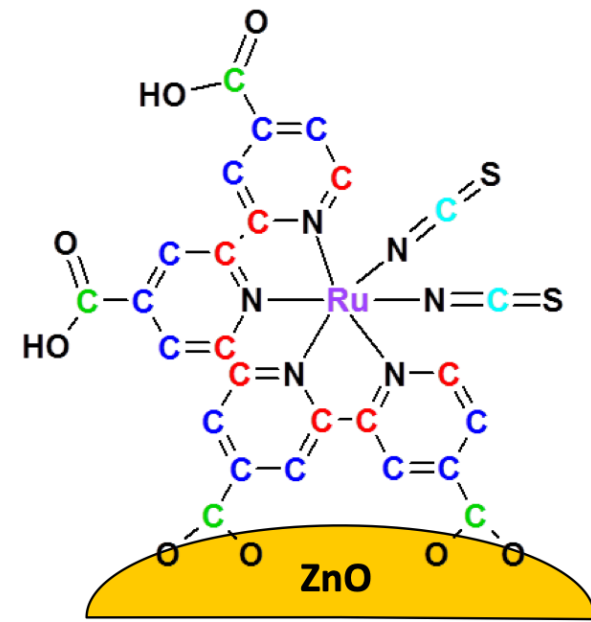
# Femtosecond Atomic-Scale Perspective of Interfacial Charge Transfer



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



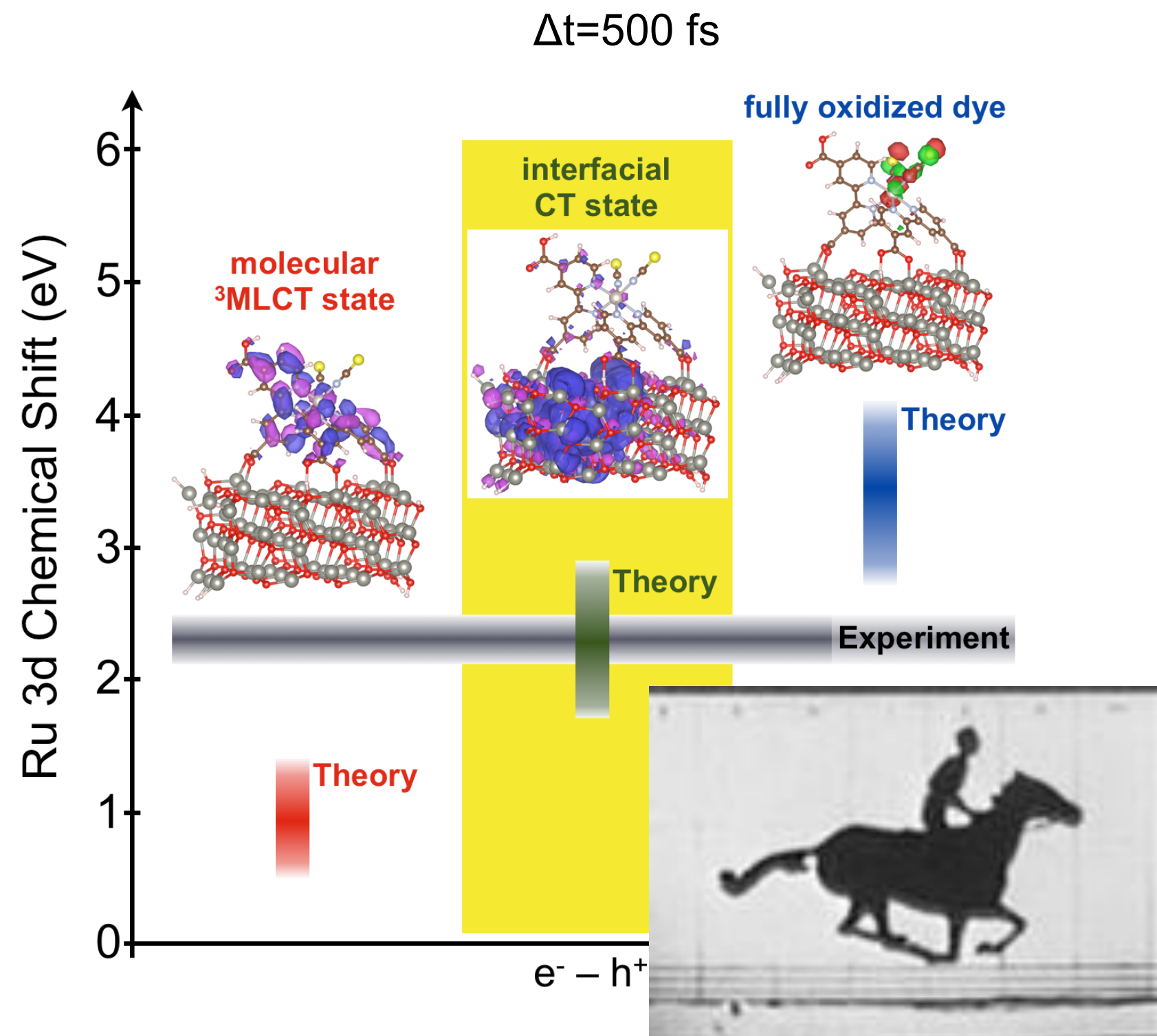
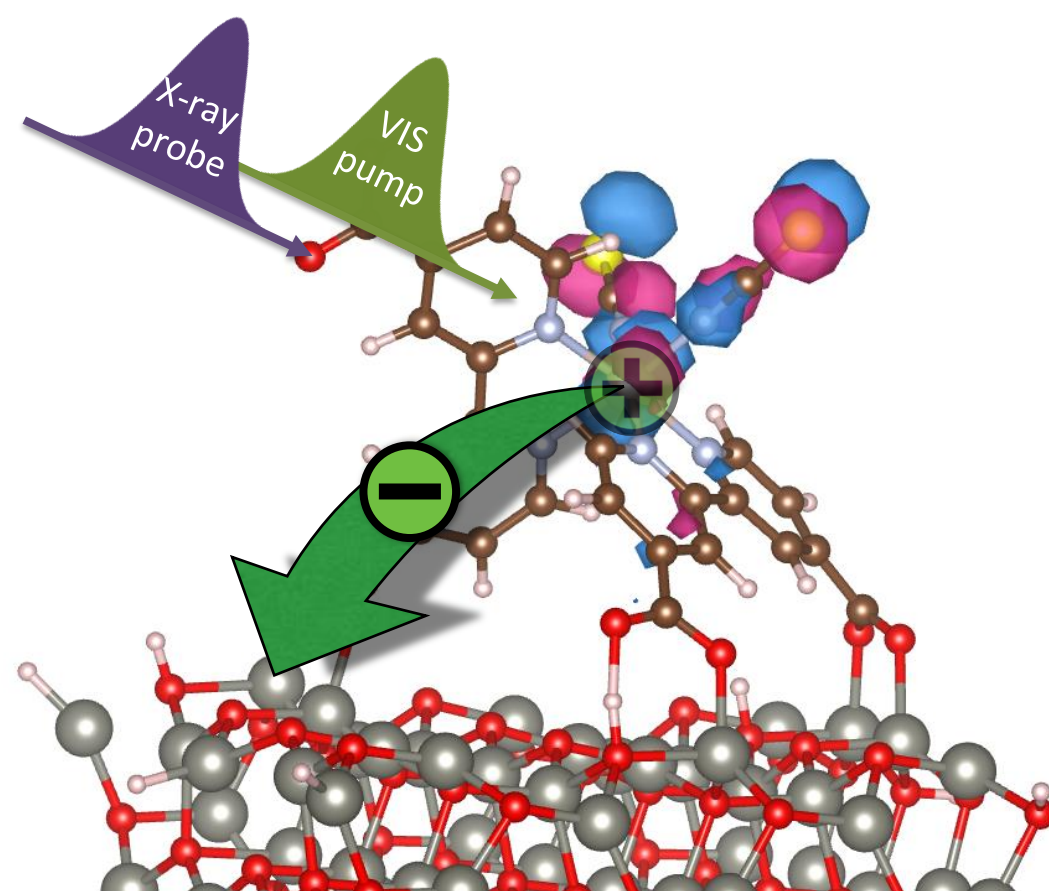
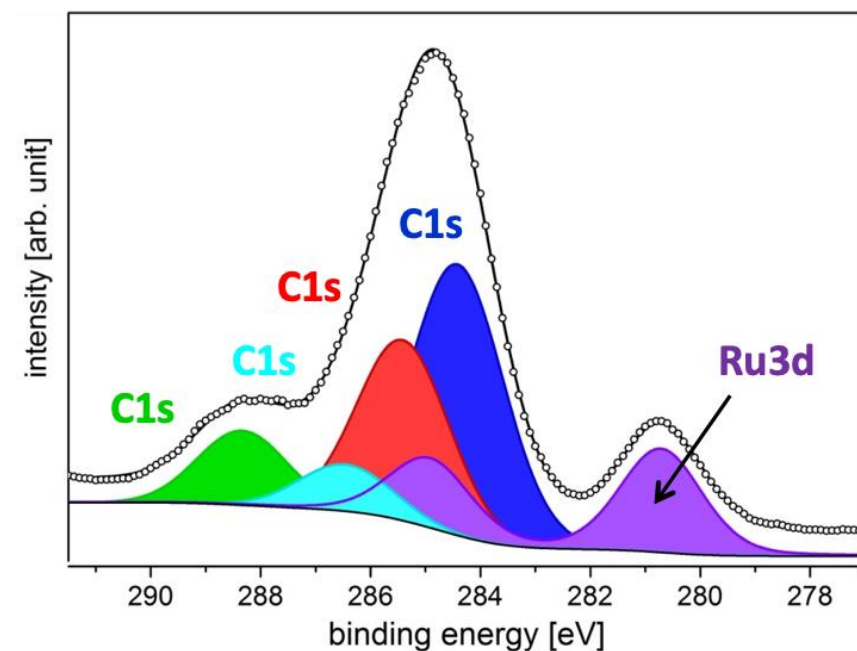
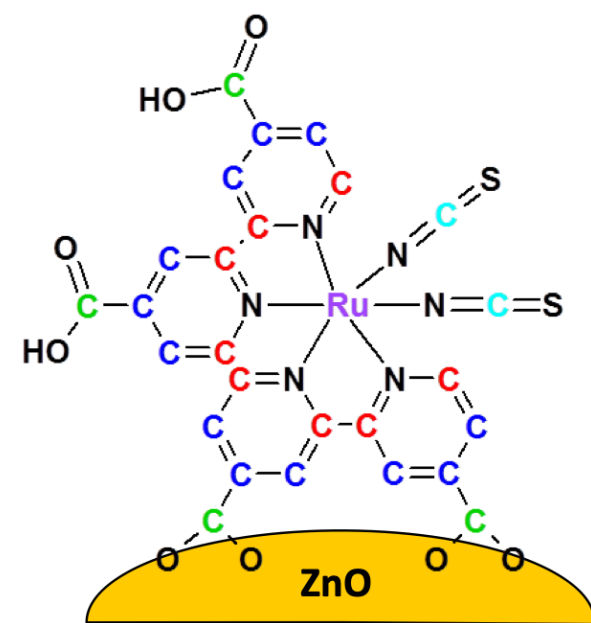
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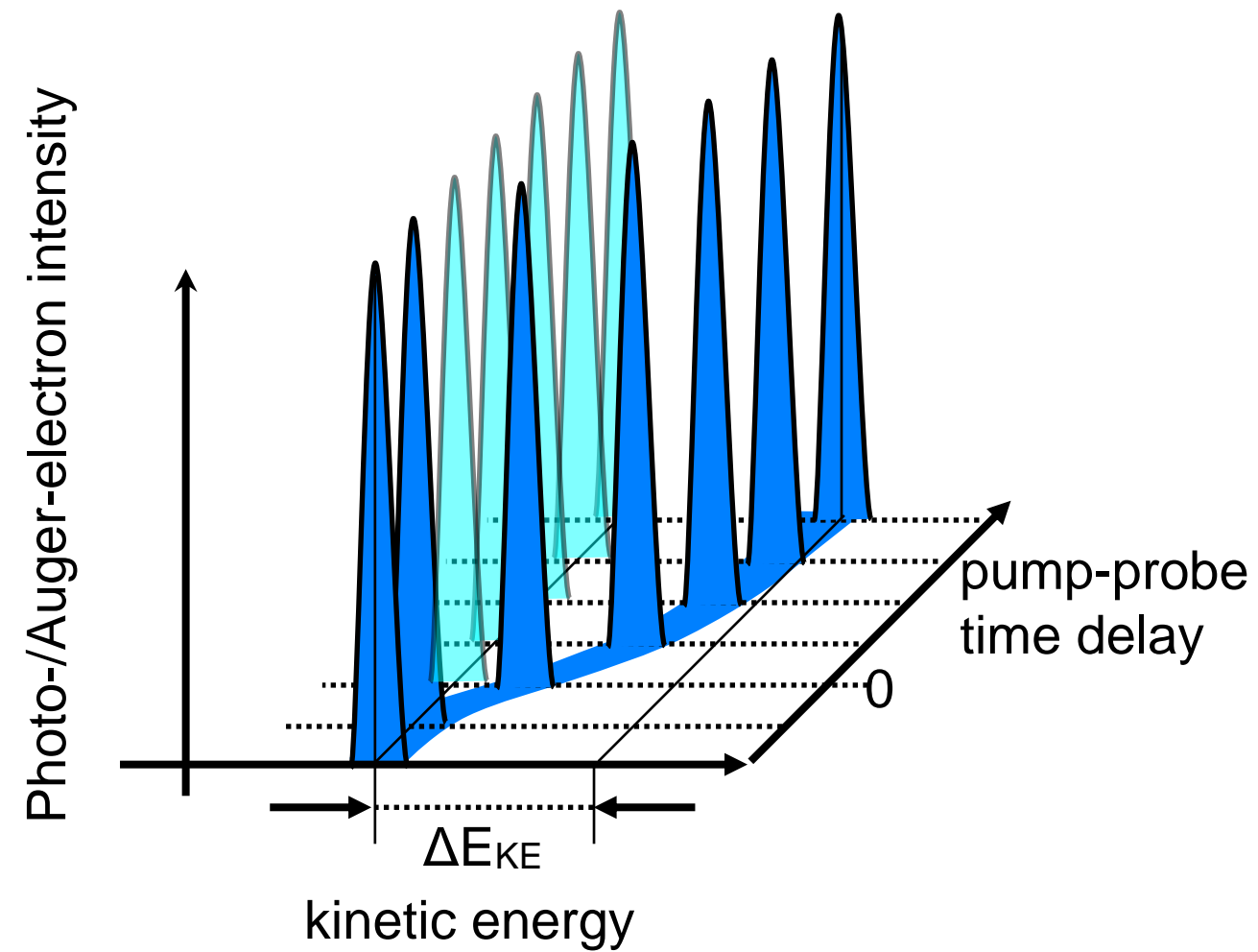


Siefermann, O.G., *et al.*, *JPCCL* **5**, 2753 (2014)  
 O.G. and M. Gühr, *Acc. Chem. Res.* **49**, 138 (2016)

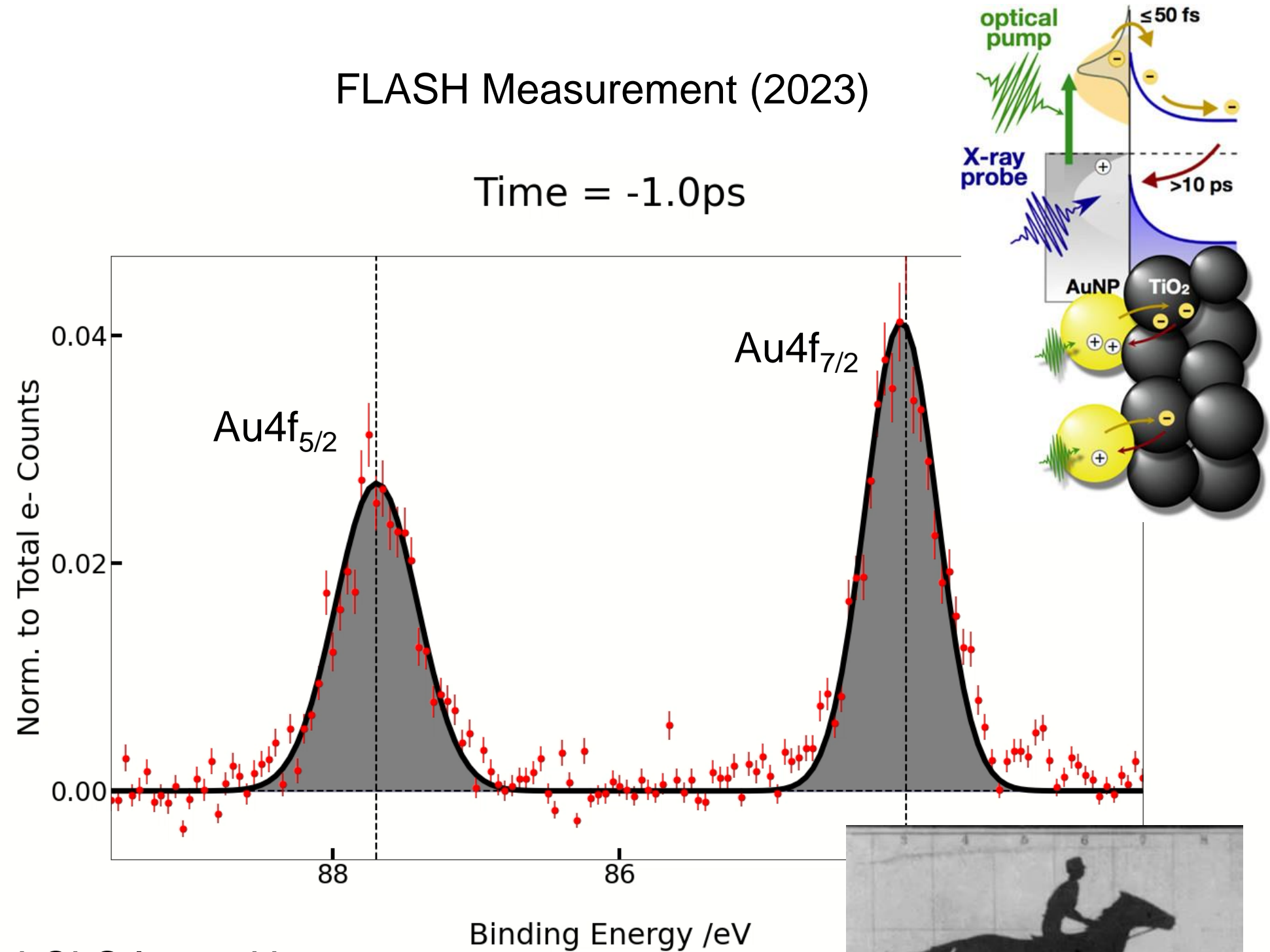


# Time-Resolved XPS of Interfacial Dynamics— From Concept to Reality

TRXPS Concept (2012)



FLASH Measurement (2023)

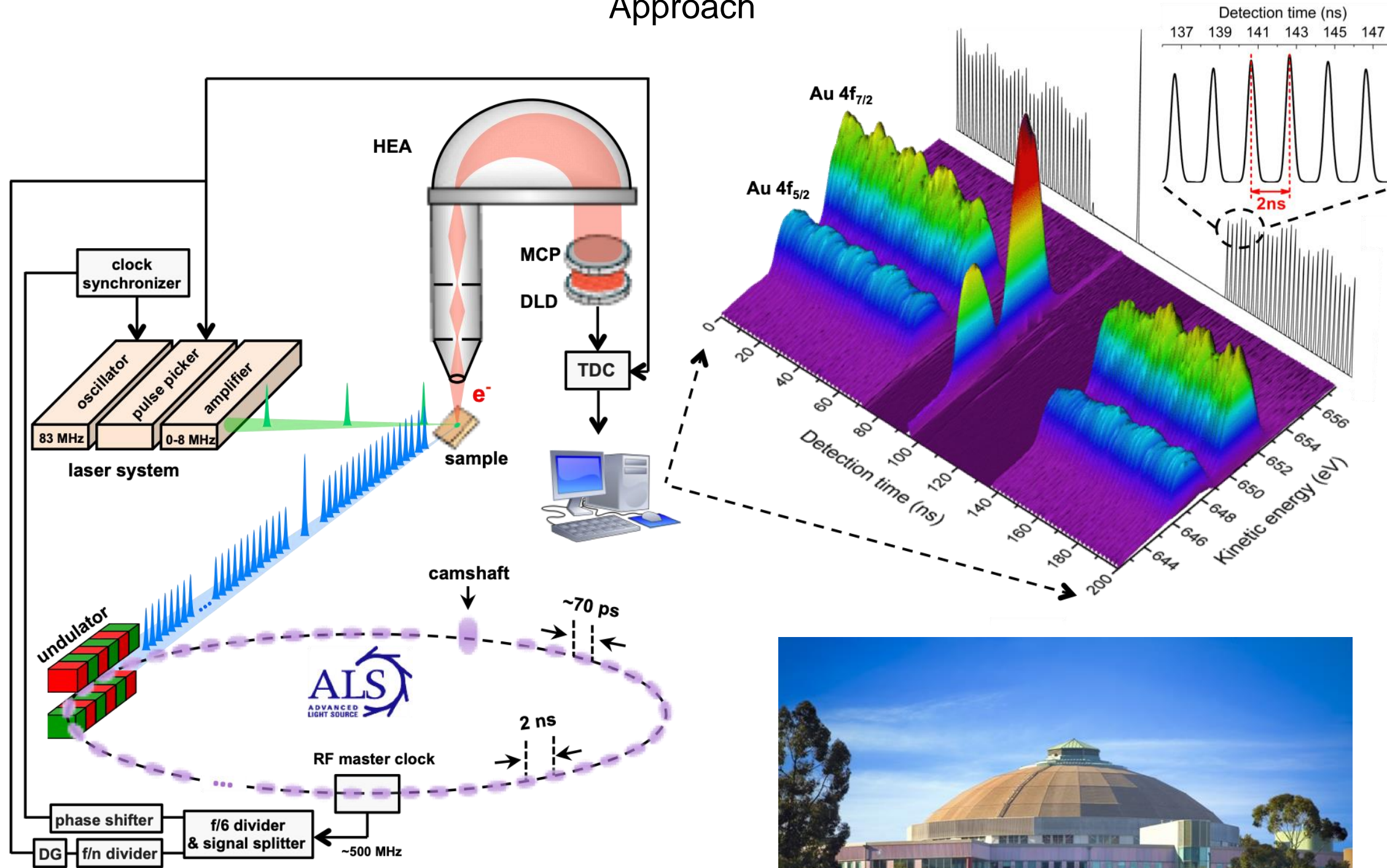


LCLS I: 120 Hz  
 FLASH: 4 kHz  
 LCLS II (2025+): 100+ kHz

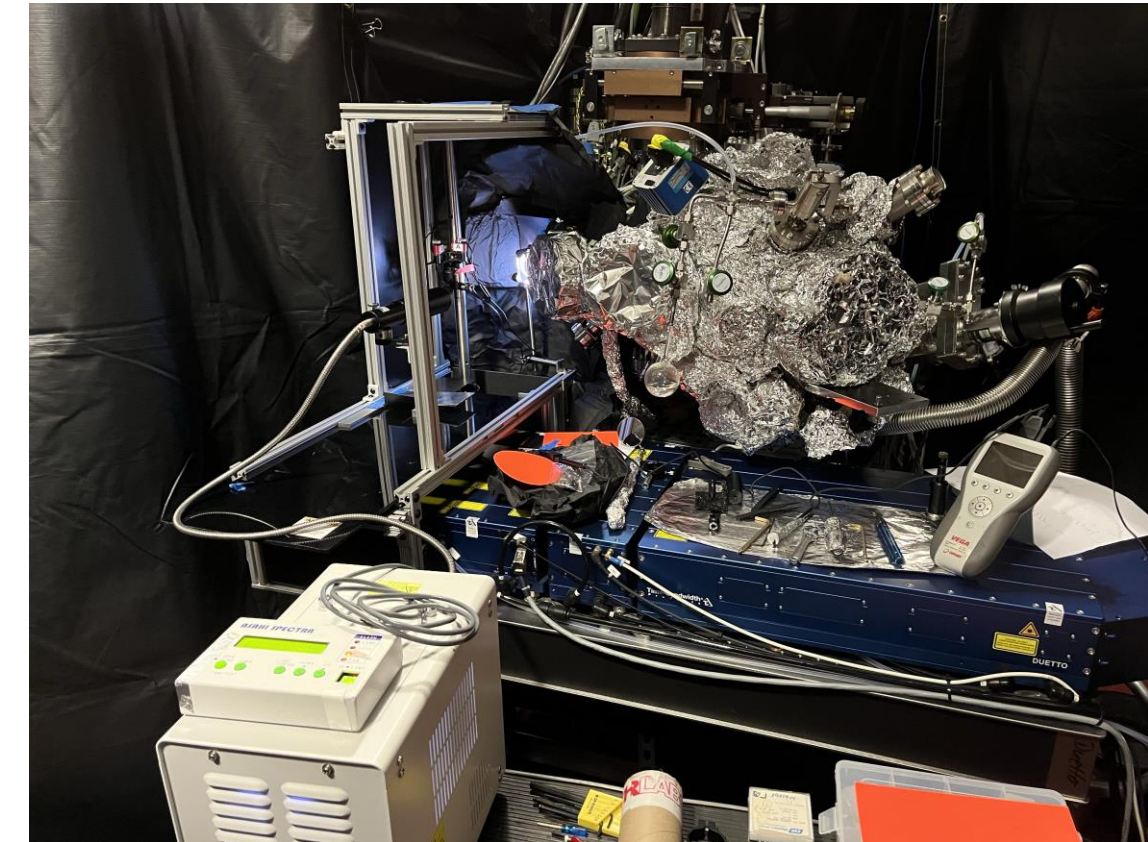


# Picosecond Time-Resolved XPS @ ALS – An Ultrafast Electron Stroboscope

~127 kHz Pump / ~3-500 MHz Probe Time-Tagging Approach



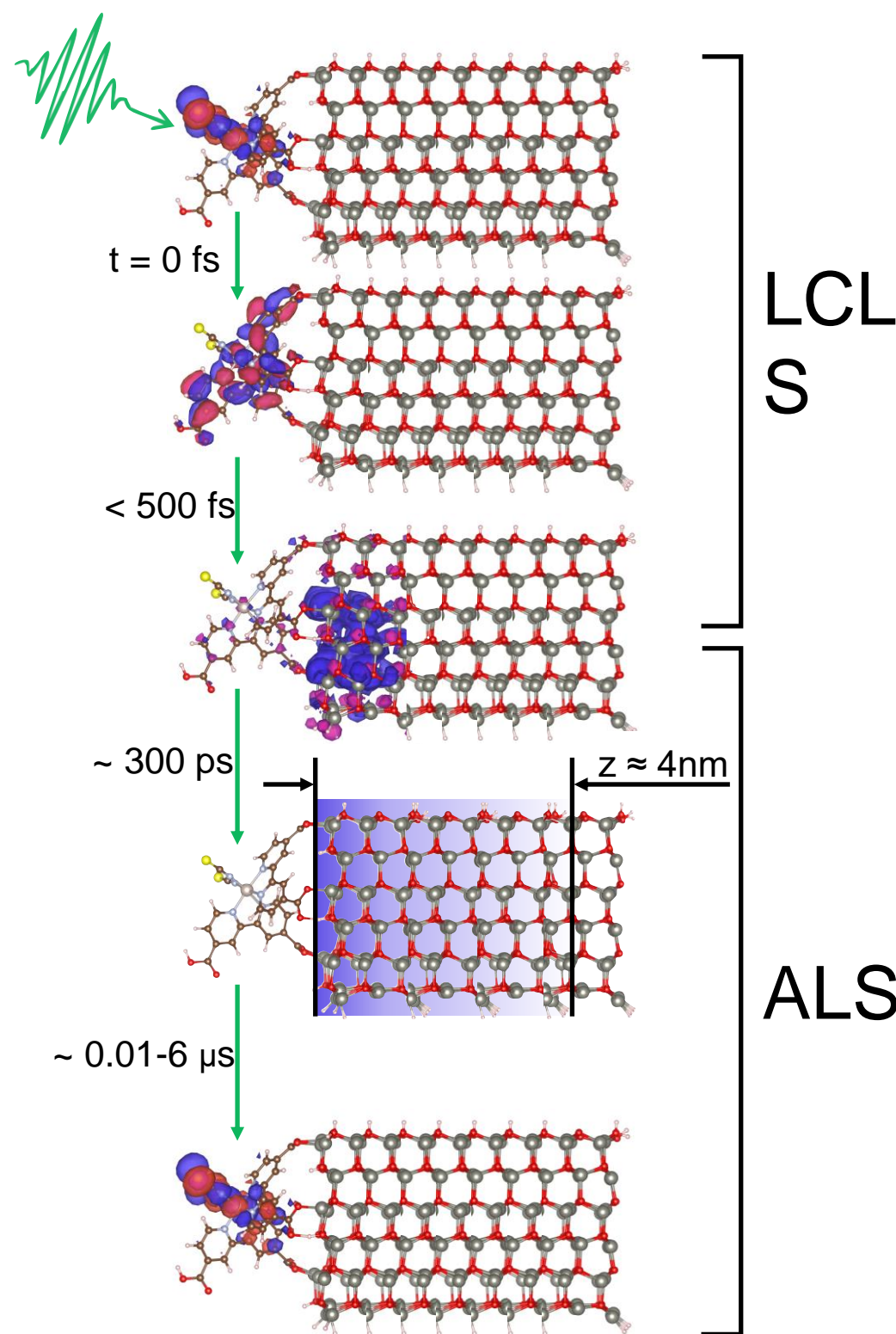
Mobile TRXPS Setup @ ALS BL 11.0.2



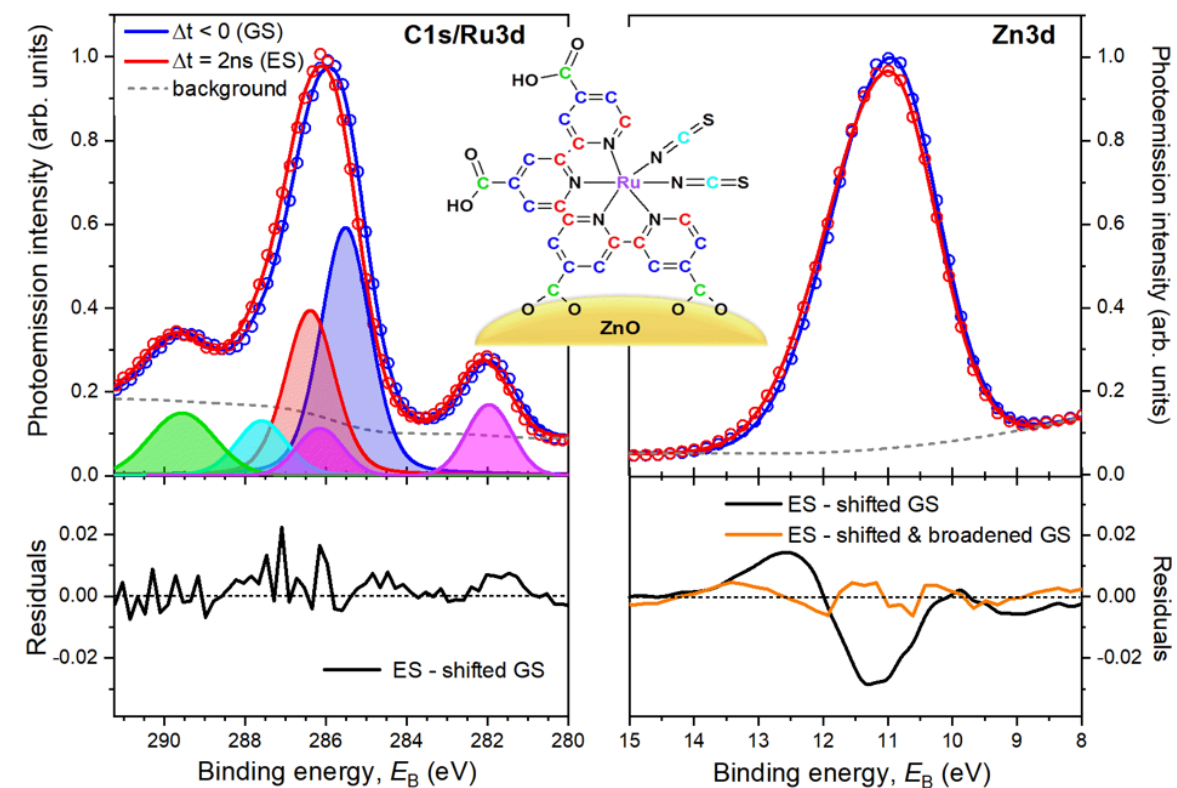
A. Shavorskiy, O.G., *et al.*, RSI **85**, 093102 (2014)  
 S. Neopl, O.G., *et al.*, Faraday Discuss. **171**, 219 (2014)  
 S. Neopl and O.G., J. Electron Spectrosc. Relat. Phenom. **200**, 64 (2015)



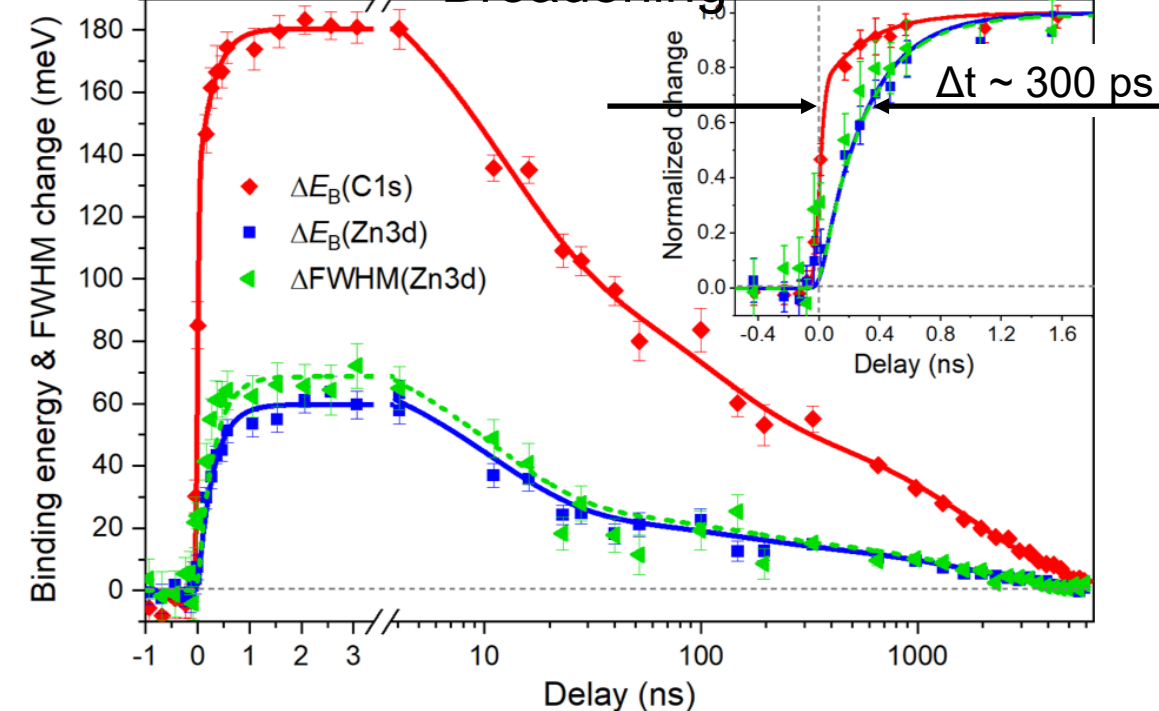
# Interfacial Charge Transfer Dynamics Across >5 Orders of Magnitude in Time



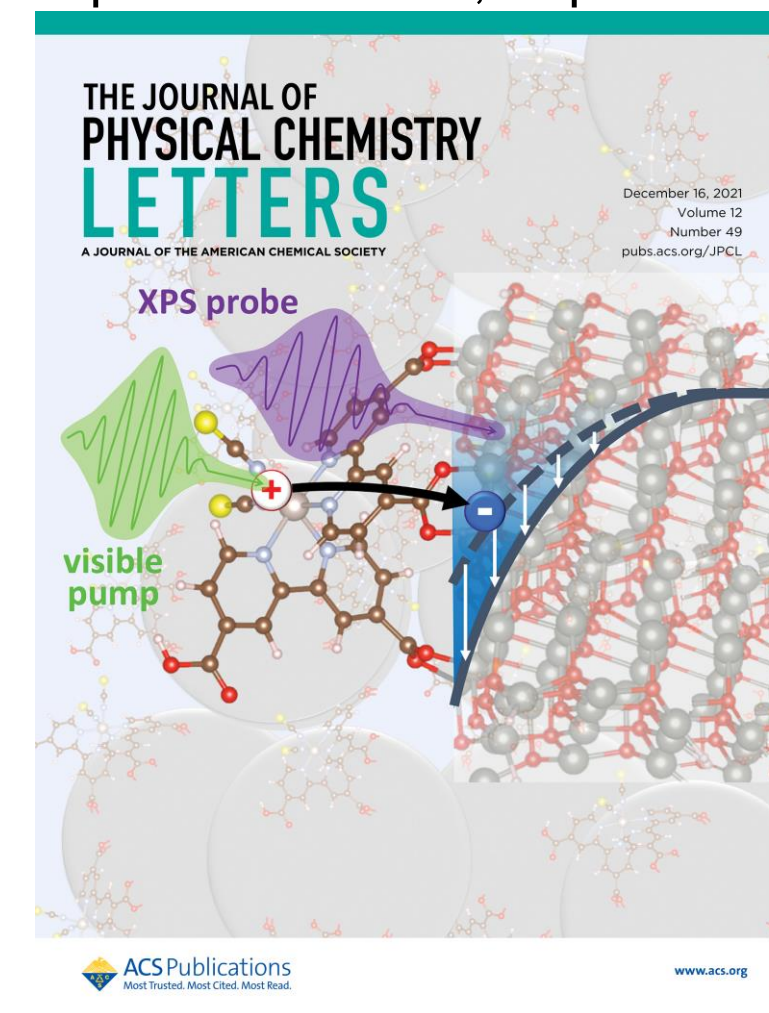
TRXPS Responses Differ on Two Sides of the Interface



Transient Peak Shifts and Broadening



Possible ZnO Bottleneck: Electron nanoconfinement in defect-rich surface region of nanoporous network, traps abundant



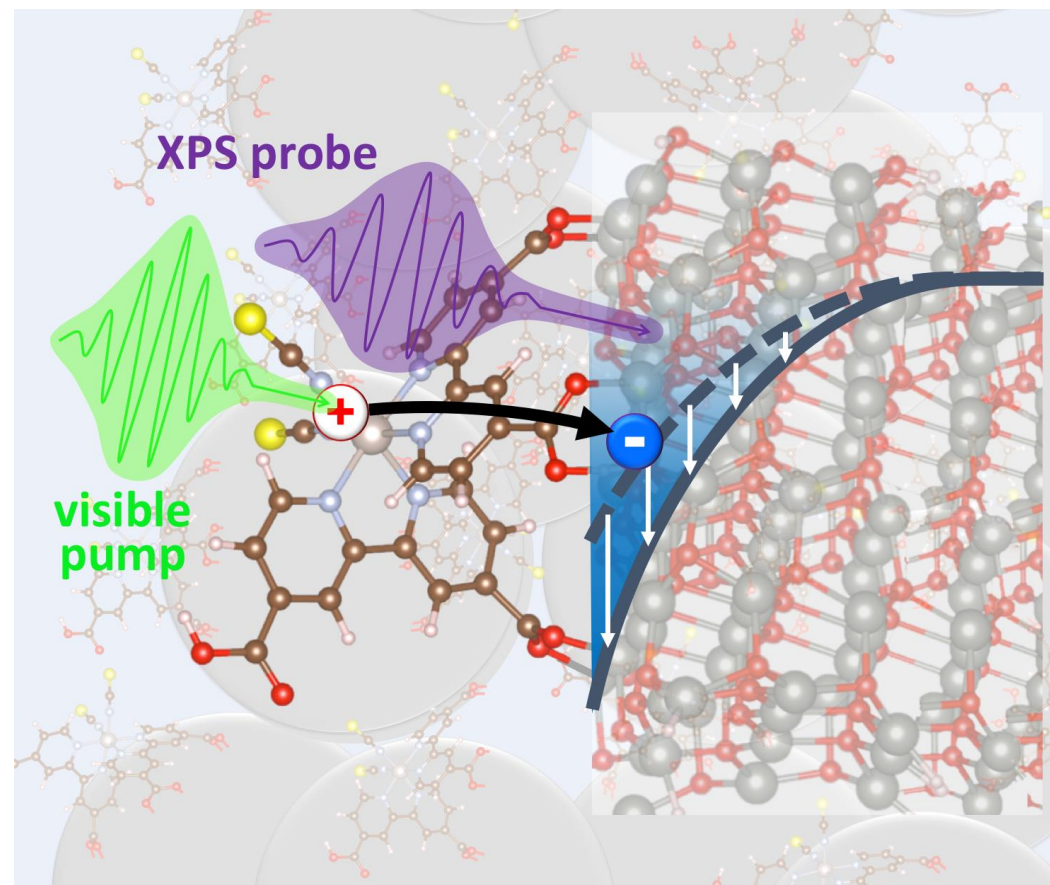
S. Nepll, J. Mahl, O.G., *et al.*, J. Phys. Chem. Lett. **12**, 11951 (2021) ; ACS Appl. Nano Mater. **4**, 12213 (2021)



# Renewable Energy Technologies and Interfacial Dynamics

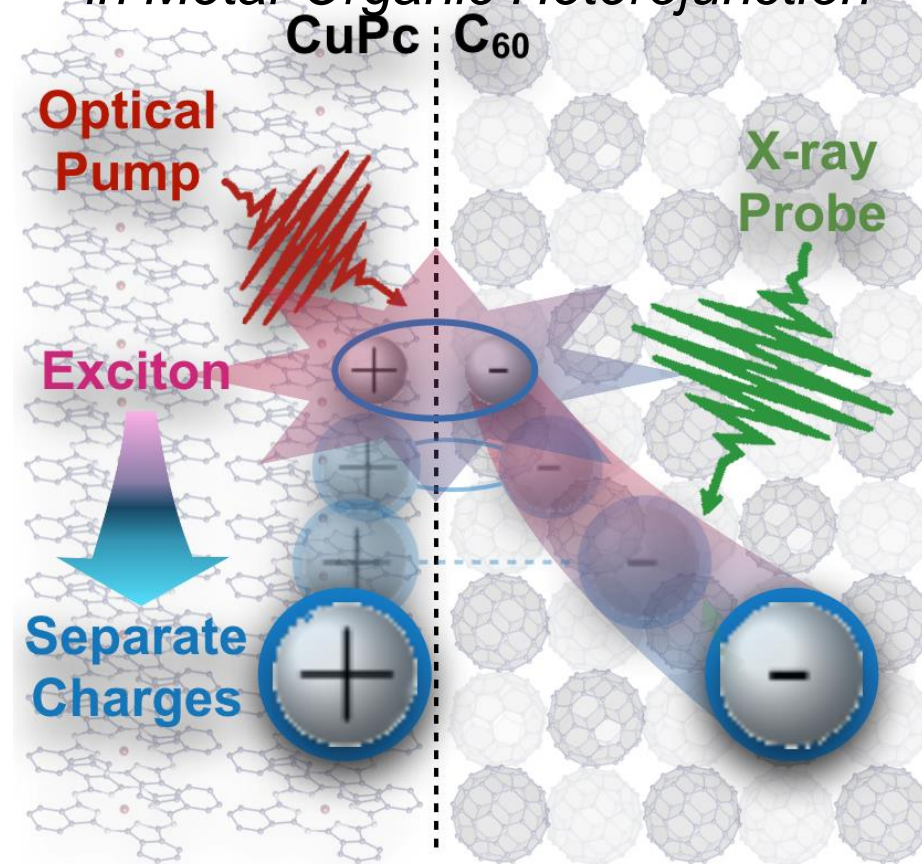
## Molecule-Semiconductor Interfaces

### Decoding the Lifecycle of Photogenerated Charges



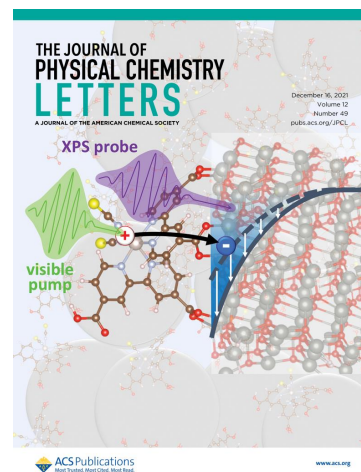
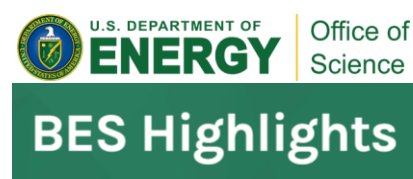
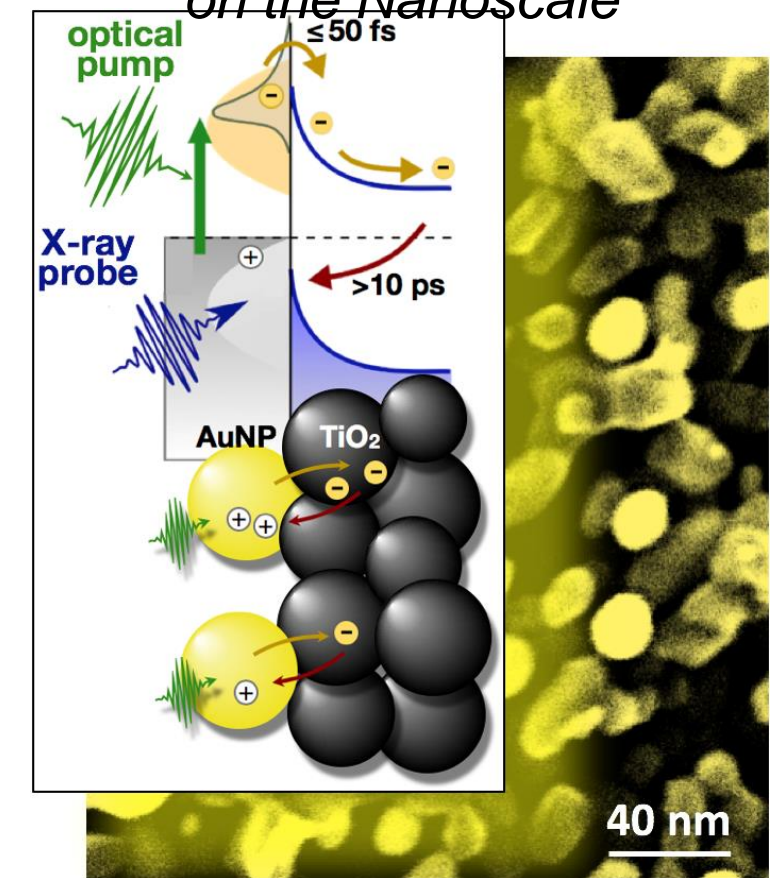
## Organic Semiconductors

### New Path for Light-to-Charge Conversion in Metal-Organic Heterojunction



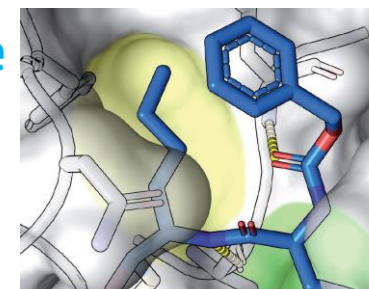
## Nanostructure Enabled Catalysis

### Observing Electrons Harvesting Light on the Nanoscale



New pathway to harnessing the sun for a clean energy future

Ultrafast X-ray measurement provides important findings for the solar industry



PHOTON SCIENCE 2021



Scientists Capture Candid Snapshots of Electrons Harvesting Light at the Atomic Scale

S. Neppl, J. Mahl, F.M. Toma, O.G. *et al.*, J. Phys. Chem. Lett. **12**, 11951 (2021)

F. Roth, M. Borgwardt, W. Eberhardt, O.G., *et al.*, Nat. Commun. **12**, 1196 (2021)  
F. Roth, W. Eberhardt, O.G., *et al.*, Phys. Rev. B **99**, 020303(R) (2019)

M. Borgwardt, F. M. Toma, M. Blum, O.G., *et al.*, J. Phys. Chem. Lett. **11**, 5476 (2020)



# Collaborators - LCLS Experiment on Interfacial Charge Transfer



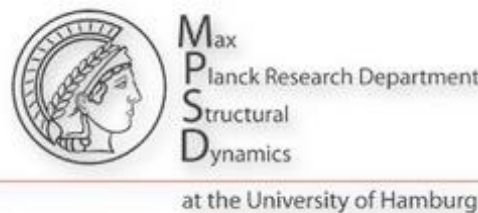
Lawrence Berkeley National  
Laboratory



University of California Berkeley



University of California Santa Cruz



Nils Huse



Martin Beye



Hirohito Ogasawara, Dennis Nordlund, Josh Turner, Bill Schlotter, Anders Nilsson, Oleg Krupin, Michael Holmes, Mike Minitti, Joseph Robinson, Marc Messerschmidt, Phil Heimann

Stefan Neppl, Katrin Siefertmann, Fabian Weise, Ming-Fu Lin, Camila Bacellar, Ali Belkacem, Thorsten Weber, Felix Sturm, Daniel Slaughter, Champak Khurmi, Travis Wright,  
Bob Schoenlein, Matthew Strader, Hana Cho, Robert Kaindl, Giacomo Coslovich, Das Pemmaraju, David Prendergast, Andrey Shavorskiy, Hendrik Bluhm, Jinghua Guo, Marcus Hertlein, Tolek Tyliszczak, and Oliver Gessner  
Amy Cordones, Josh Vura-Weis, Stephen Leone, Daniel Neumark



# Gessner Group & Collaborators

## Alumnae & Alumni



Johannes  
Mahl

Matthew  
Fraund

Catherine  
Saladrigas

Lida  
Kaphar

Chuying  
Huang

Ming-Fu  
Lin

## Gessner Group & Collaborators



Kin Fung  
Lai

Lars  
Hoffmann

Zach  
Donnellan

Angel  
Garcia

Marija  
Zoric

Sahan  
Perera

Amy  
Cordones-  
Hahn

## Alumni



Stefan  
Nepl



Mario  
Borgwardt



Felix  
Brausse

## Collaborators



Friedrich Roth  
TU Freiberg



Wolfgang Eberhardt  
CFEL



Moni Blum  
ALS & LBNL CSD

## Additional Collaborators

Francesca Toma, *LBNL*  
Lukas Wenthaus, *DESY*  
Nils Huse, *U Hamburg*

Serguei Molodtsov, *EuXFEL*  
Stephen Leone, *UCB/LBNL*  
Daniel Neumark, *UCB/LBNL*

Scott Cushing, *Caltech*  
Harry Atwater, *Caltech*  
Yvonne Joseph, *TU Freiberg*

Junko Yano, *LBNL*  
Michael Zürich, *UCB/LBNL*

## AMOS@LBNL Theory



Jin Qian



Early Career Research Program

DOE ECRP  
Awardee  
2023



# Some Measures of Impact of 2012 Early Career Research Program Award

## People

Camila Bacellar, *PSI, Villigen*  
 Mario Borgwardt, *BESTEC, Berlin*  
 Felix Brausse, *European XFEL, Hamburg*  
 Zachery Donnellan, *UC Berkeley*  
 Matthew Fraund, *Diablo Valley College*  
 Elham Ghanem, *Cal State – East Bay*  
 Lars Hoffmann, *UC Berkeley*  
 Chuying Huang, *Northwestern U*  
 Lida Kaphar, *California Department of Public Health*  
 Florian Lackner, *Styria State Government*  
 King-Fung Lai, *Berkeley Lab*  
 Melody Li, *UC Berkeley*  
 Ming-Fu Lin, *SLAC, Menlo Park*  
 Johannes Mahl, *Berkeley Lab*  
 Debadarshina Mishra, *Berkeley Lab*  
 Stefan Neppi, *PSI Villigen*  
 Sri Chaitanya Das Pemmeraju, *IBM, Menlo Park*  
 Sahan Perera, *Air Liquide*  
 Tahiyat Rahman, *U Washington*  
 Catherine Saladrigas, *CU Boulder*  
 Katrin Siefertmann, *Carl Zeiss, Oberkochen*  
 Benjamin Toulson, *KLA, Milpitas*  
 Fabian Weise, *ASML, Berlin*  
 Michael Ziemkiewicz, *BAE Systems, Boulder*

+ many, many more collaborating students, postdocs, PIs, ...

## Collaborations



## Funding



Alexander von Humboldt  
Stiftung/Foundation



## Career & Synergistic Activities

Elected Vice Chair of the APS Division of Chemical Physics (DCP) – 2023



Member, Committee on Atomic, Molecular and Optical Sciences (CAMOS), The National Academies of Sciences, Engineering, and Medicine – 2023



Leader of the LBNL AMOS Program – 2019

**Atomic, Molecular and Optical Sciences (AMOS)**



Journal of Physics B Editorial Board Member – 2019



Fellow of the American Physical Society – 2015

