Electron Dynamics of Light Harvesting Systems

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University College London

erc

Science and Technology Facilities Council

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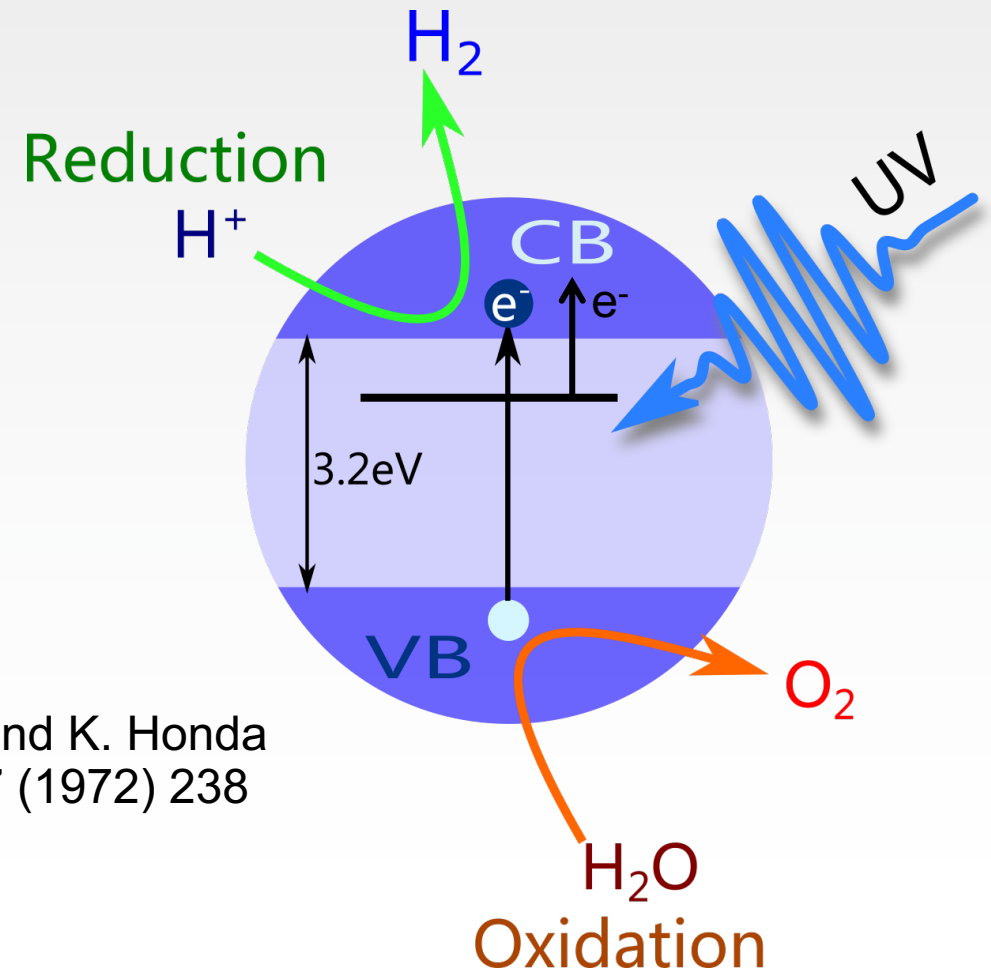
Alexander von Humboldt Stiftung/Foundation

LCN LONDON CENTRE FOR NANOTECHNOLOGY

Input from solar radiation ~10^8 GW

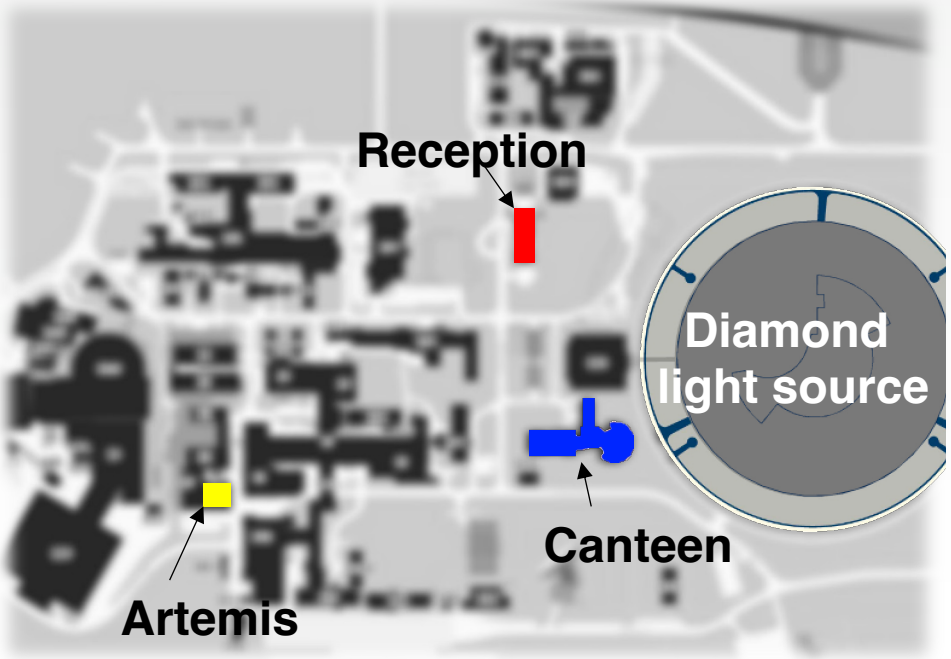
Photocatalytic water splitting on TiO_2:

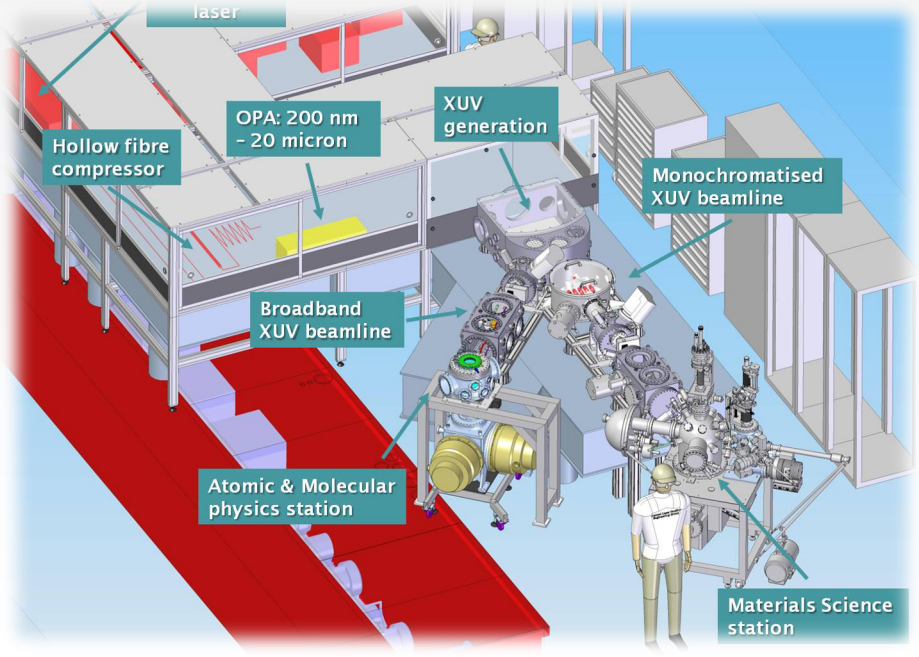


A. Fujishima and K. Honda
Nature **37** (1972) 238

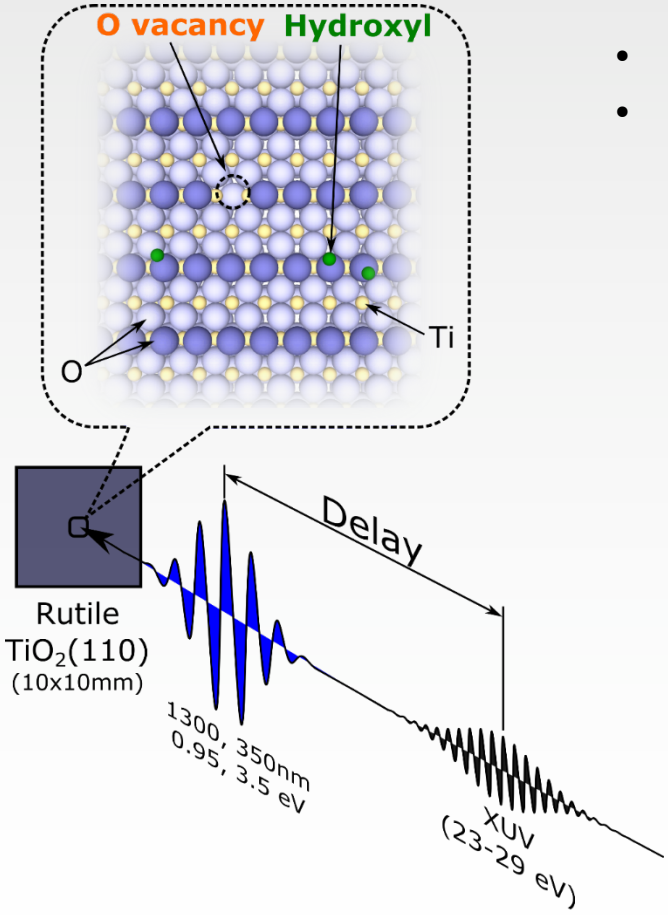
Artemis lab, Central Laser Facility, STFC

- XUV: ~30 fs, **10 - 100 eV**, 10^8 photons/pulse
- IR-UV: ~40 fs, **15 µm – 235 nm**
- Repetition rate : **1 kHz**
- Condensed matter physics & Atomic/molecular physics stations

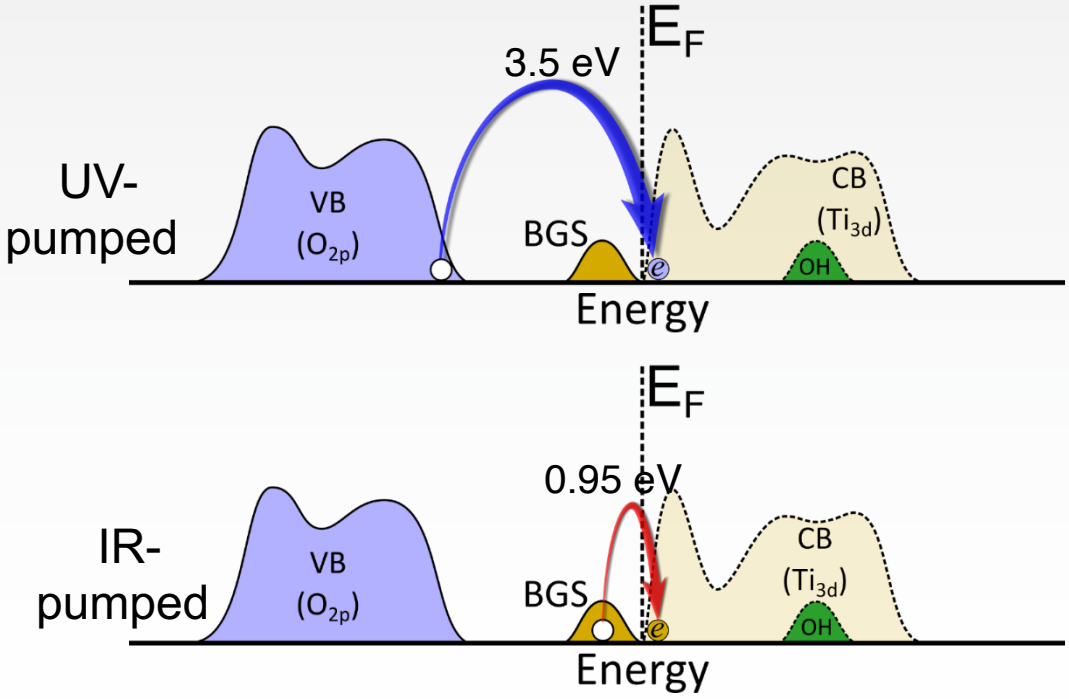




IR/UV-pump XUV-probe measurements on rutile TiO_2



- The dynamics of hot electrons and holes in VB, BGS.
- UV/IR excitation induced VB changes.



Y. Zhang, D.T. Payne, C.L. Pang, C. Cacho, R.T. Chapman, E. Springate, H.H. Fielding, G. Thornton, J. Phys. Chem. Lett. 10 5265 (2019)

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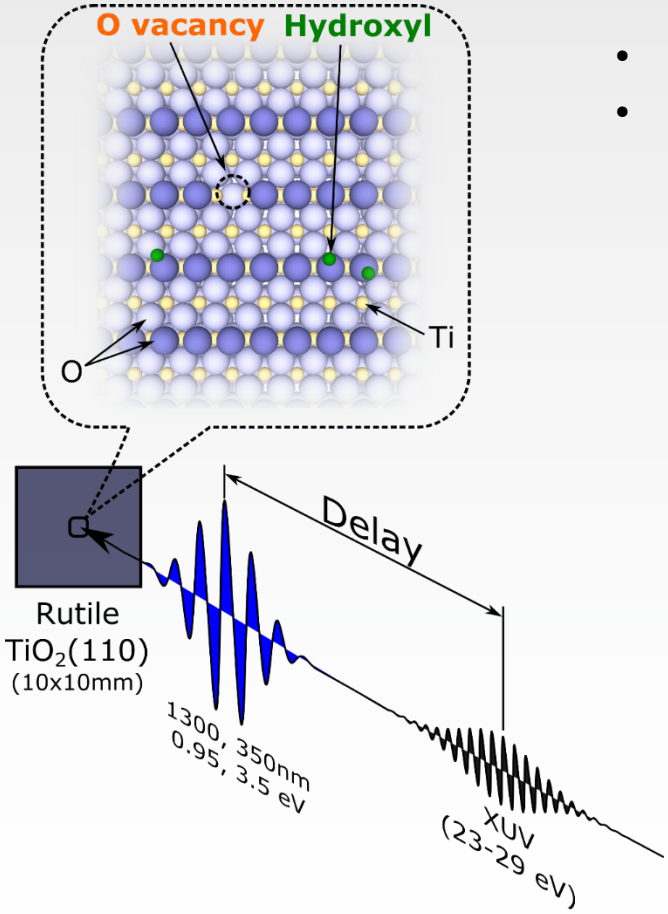

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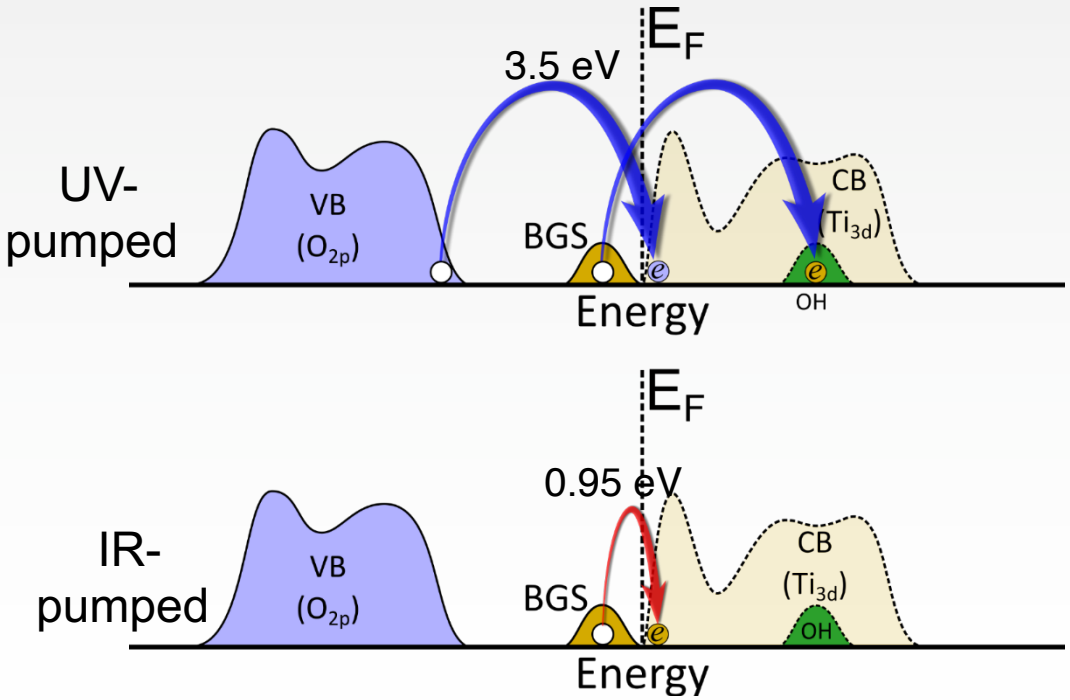

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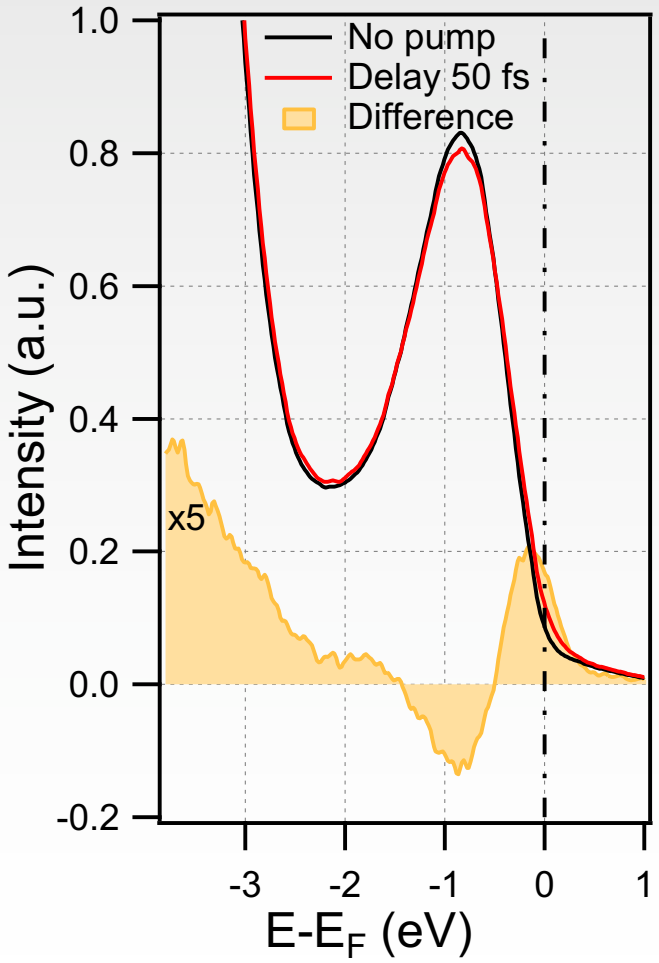
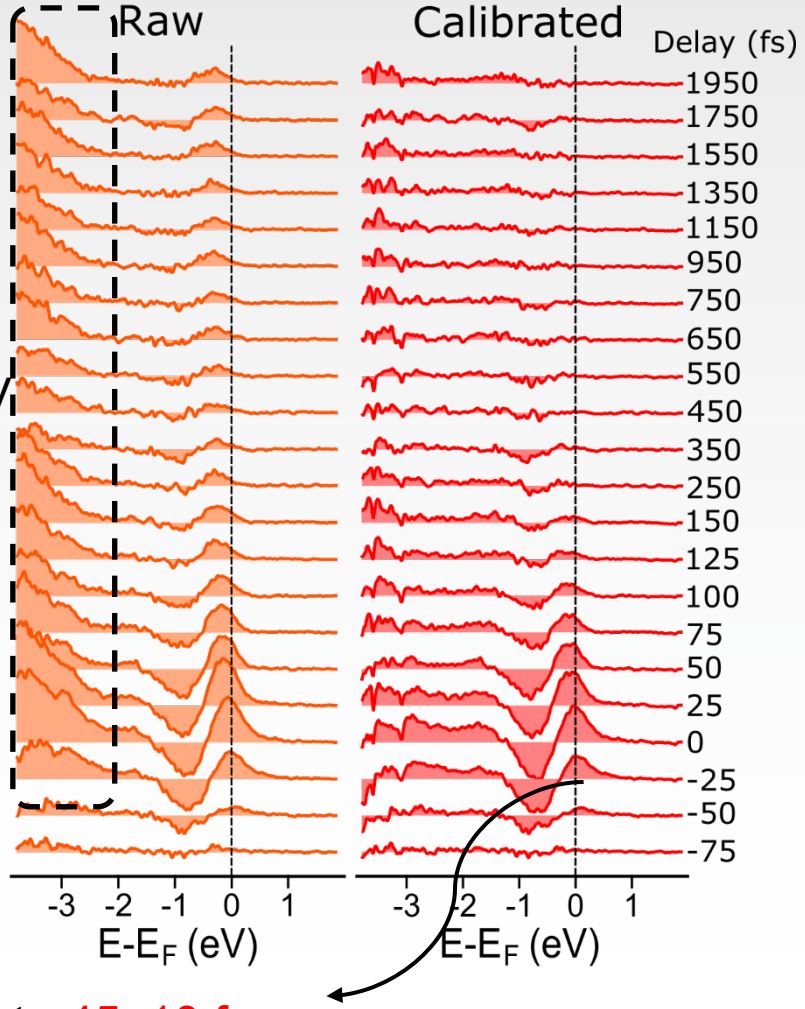
IR-pump XUV-probe measurements

Pump: λ = 1300 nm, 0.95 eV, 4 mW, Probe: 20.9 eV



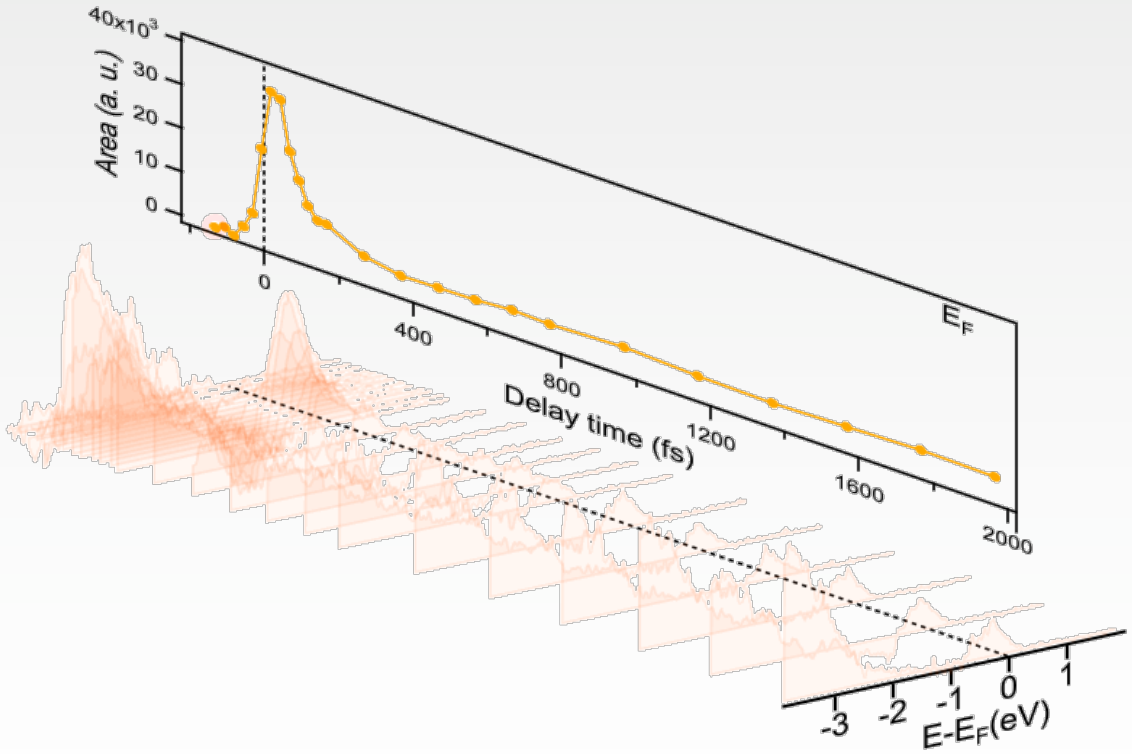
SPV
10 meV
max



- Hot electron lifetime of about ~45±10 fs
- Surface Photo-Voltage effect lasts longer than 2 ps

IR-pump XUV-probe measurements—hot electrons

Pump: λ = 1300 nm, 0.95 eV, 4 mW, Probe: 20.9 eV



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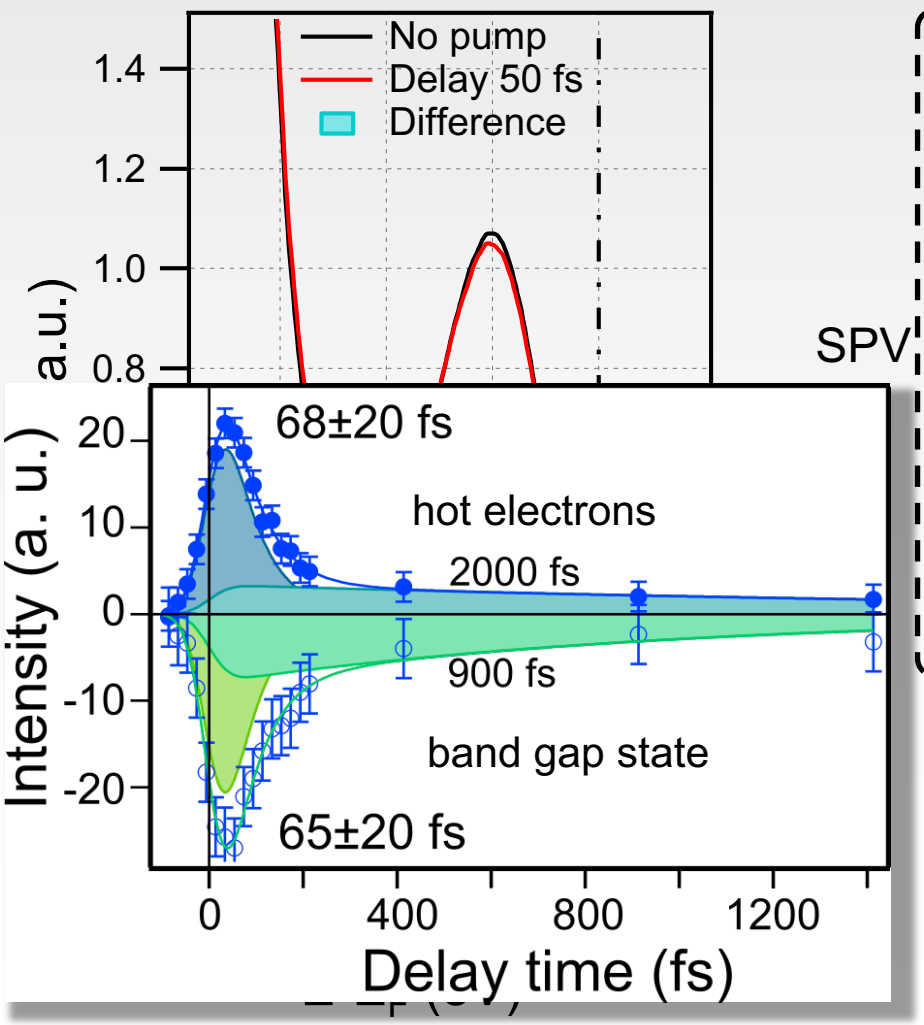
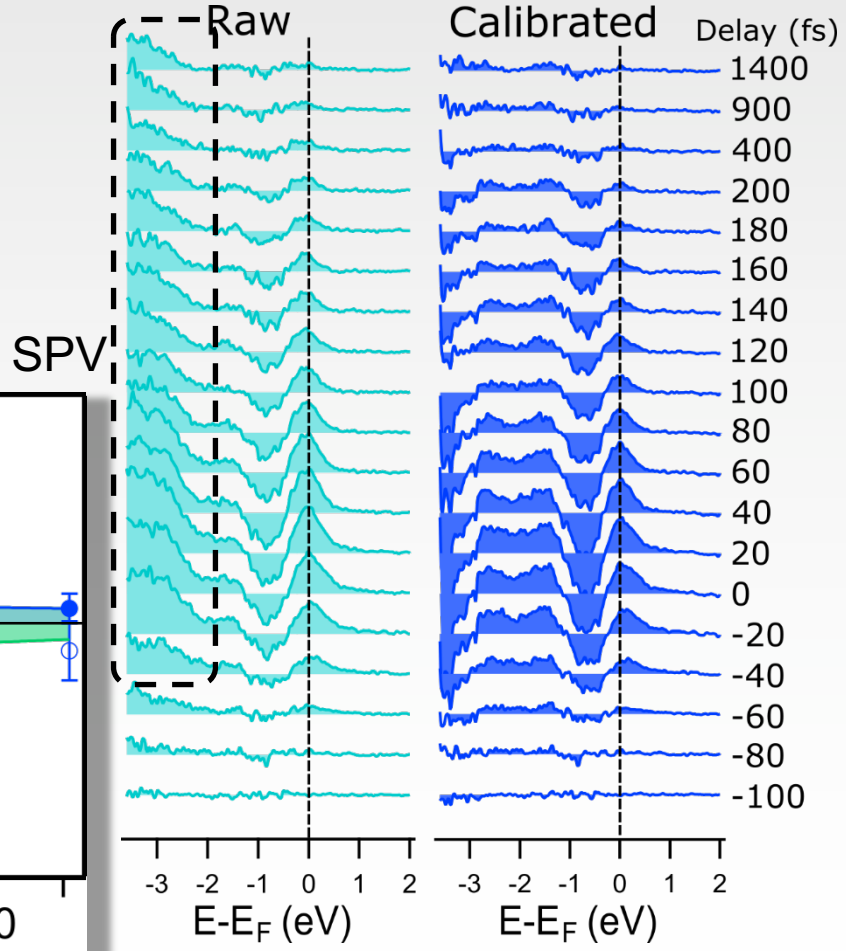
UV-pump XUV-probe measurements

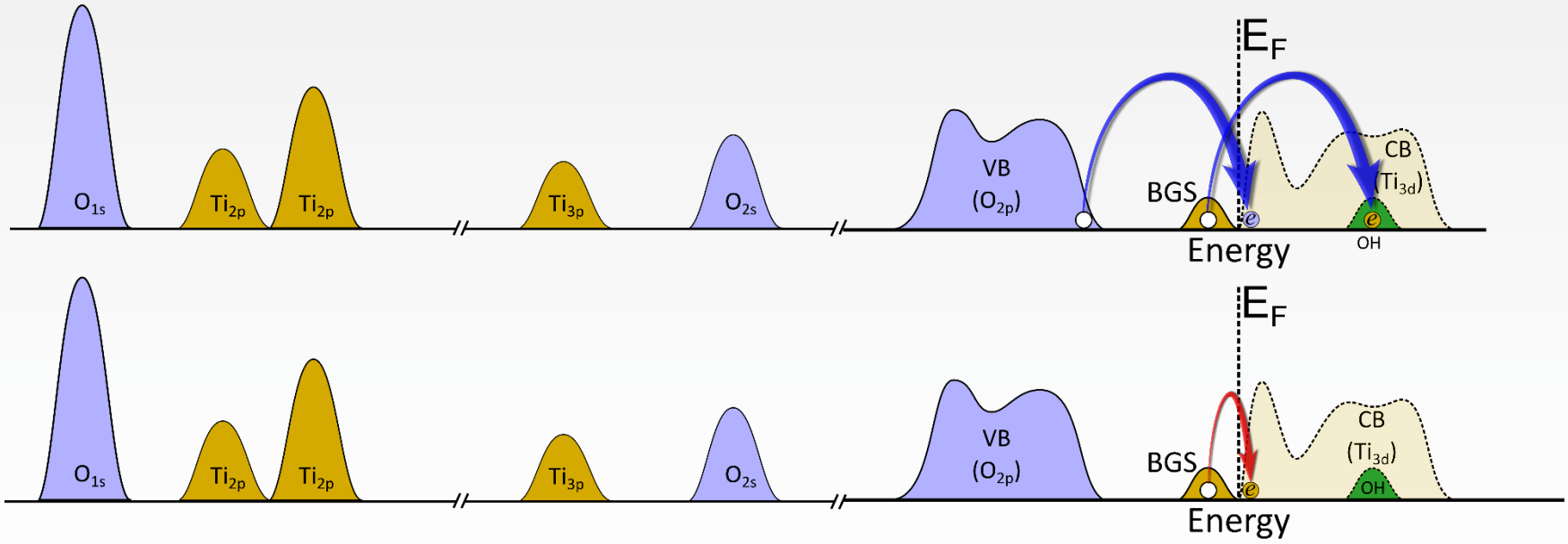
Pump: λ = 350 nm, 3.5 eV, 1 mW, Probe: 30.4 eV



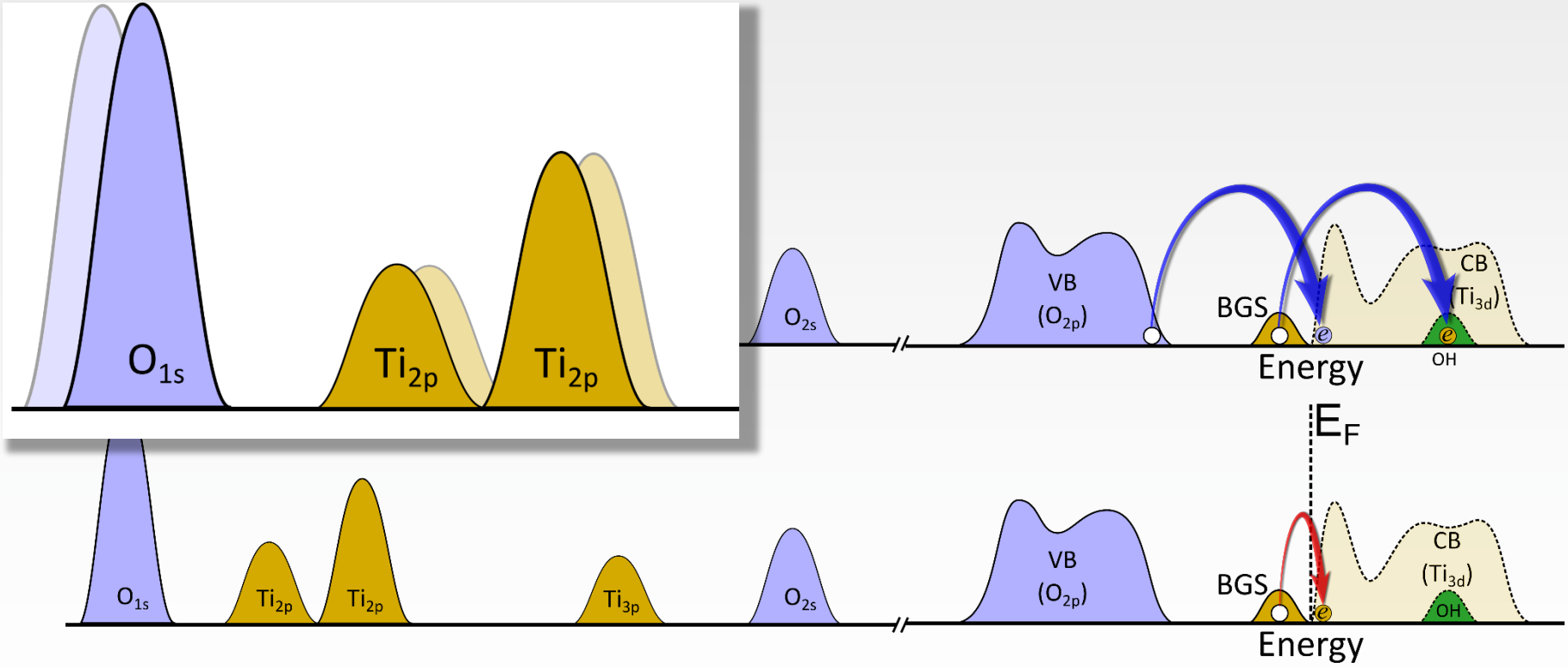


- Longer time decay points to BGS-mediated recombination

X-FEL--IR/UV Pump →chemical state surface sensitive Tr-PES experiments

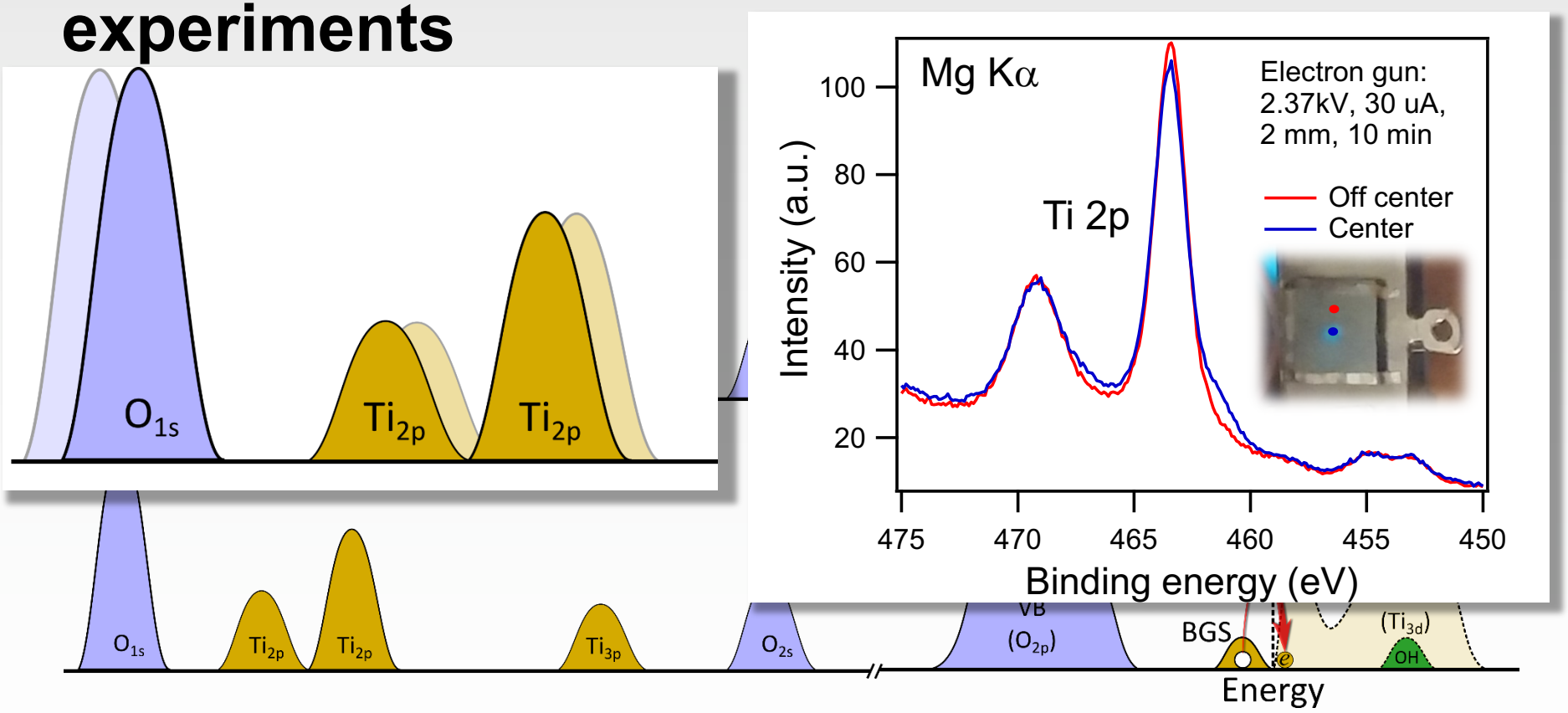


IR/UV Pump, surface sensitive X-ray probe experiments



Time dependent dissipation, formation of adsorbate intermediates

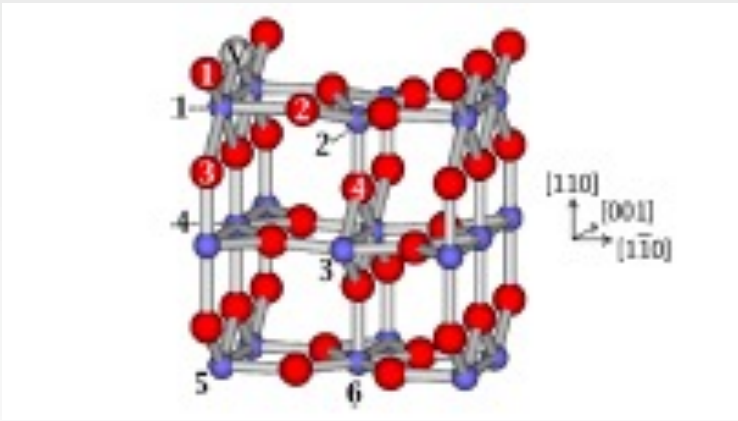
IR/UV Pump, surface sensitive X-ray probe experiments

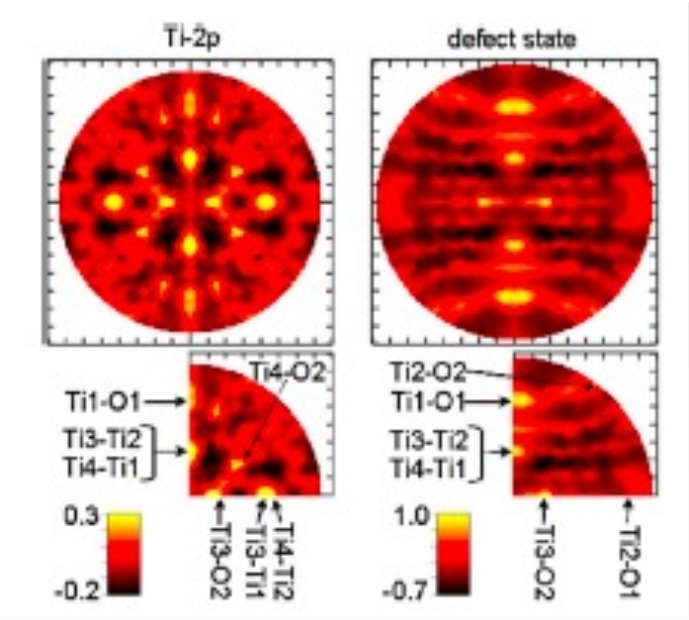


PRL 100, 055501 (2008) PHYSICAL REVIEW LETTERS week ending 8 FEBRUARY 2008

Defect States at the TiO_2(110) Surface Probed by Resonant Photoelectron Diffraction

P. Krüger,[1] S. Bourgeois,[1] B. Domenichini,[1] H. Magnan,[2] D. Chandesris,[3] P. Le Fèvre,[3] A. M. Flank,[3] J. Jupille,[4] L. Floreano,[5] A. Cossaro,[5] A. Verdini,[5] and A. Morgante[5,6]



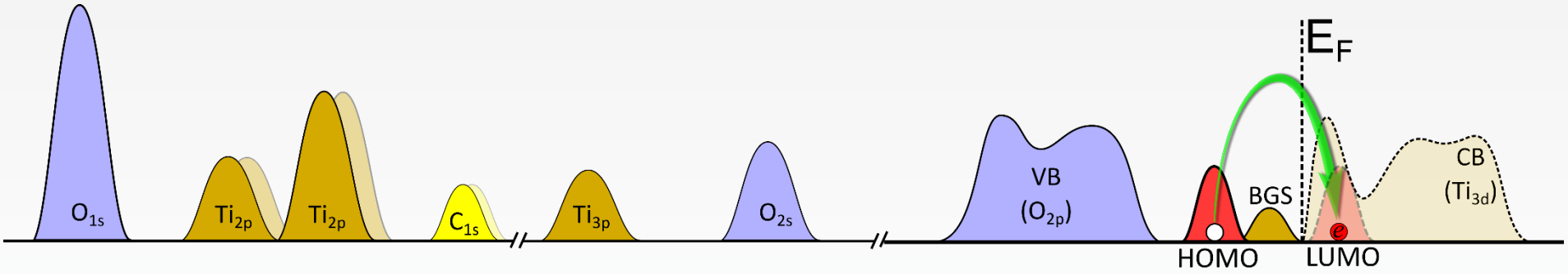


Ti 2p --> 3d resonant photoemission

300 K: BGS (polarons) delocalised over several in-plane and subsurface Ti atoms

XFEL pump probe—time and spatially dependent dissipation/recombination processes

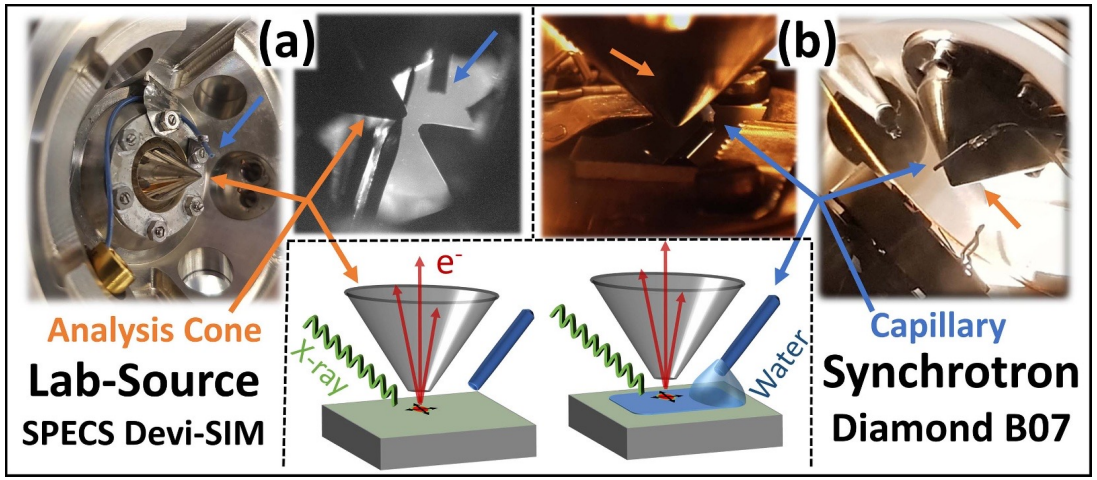
IR/UV Pump, X-ray probe experiments on dye sensitized metal oxides



- **HOMO-LUMO excitation induced chemical shift.**
- **Element specified charge transfer to metal oxide dynamics.**

Ambient pressure photoemission end station

electron dynamics of photoelectocatalysis at solid/liquid interfaces



C. Byrne, K.M. Zahra, S. Dhaliwal, D.C. Grinter, K. Roy, W.Q. Garzon, G. Held, G. Thornton, A.S. Walton, J. Phys. D Appl. Phys. **54** 194001 (2021)

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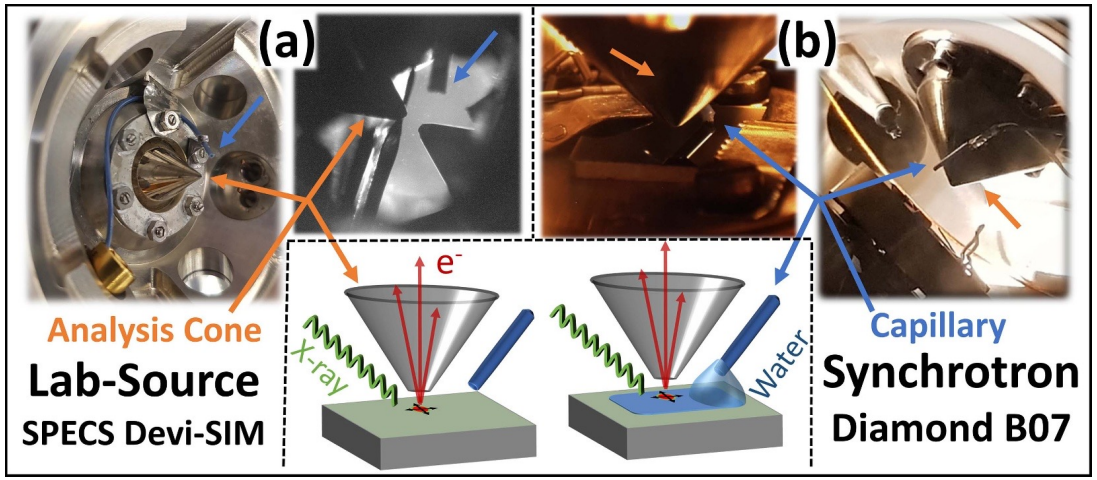

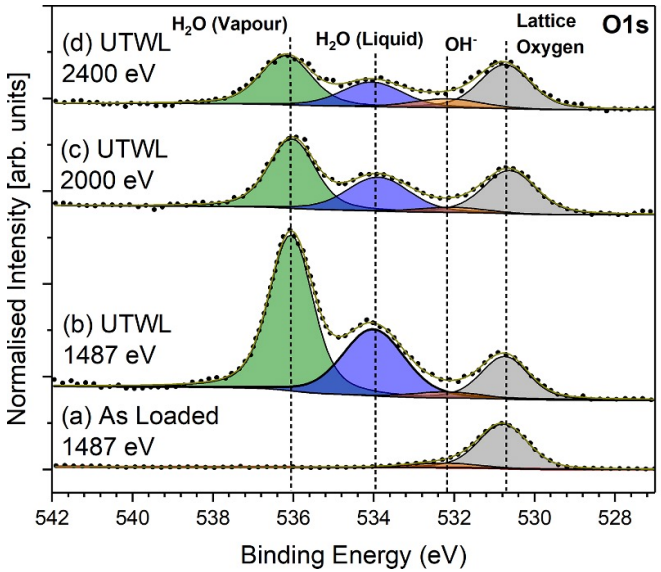

10 nm ultrathin layer

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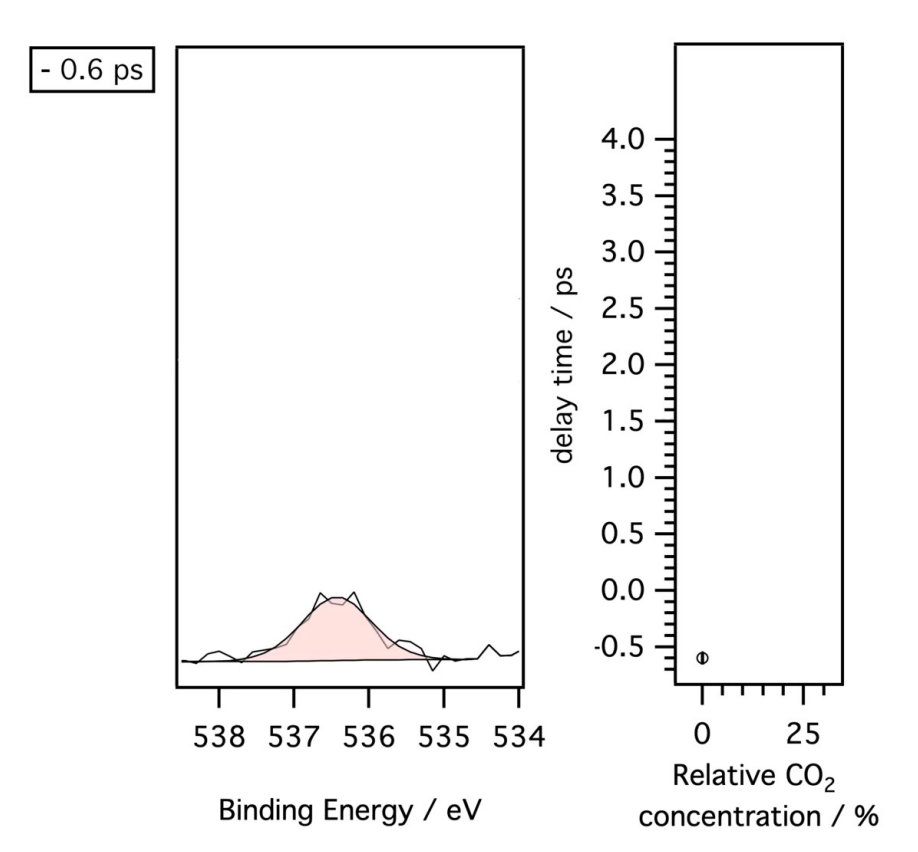
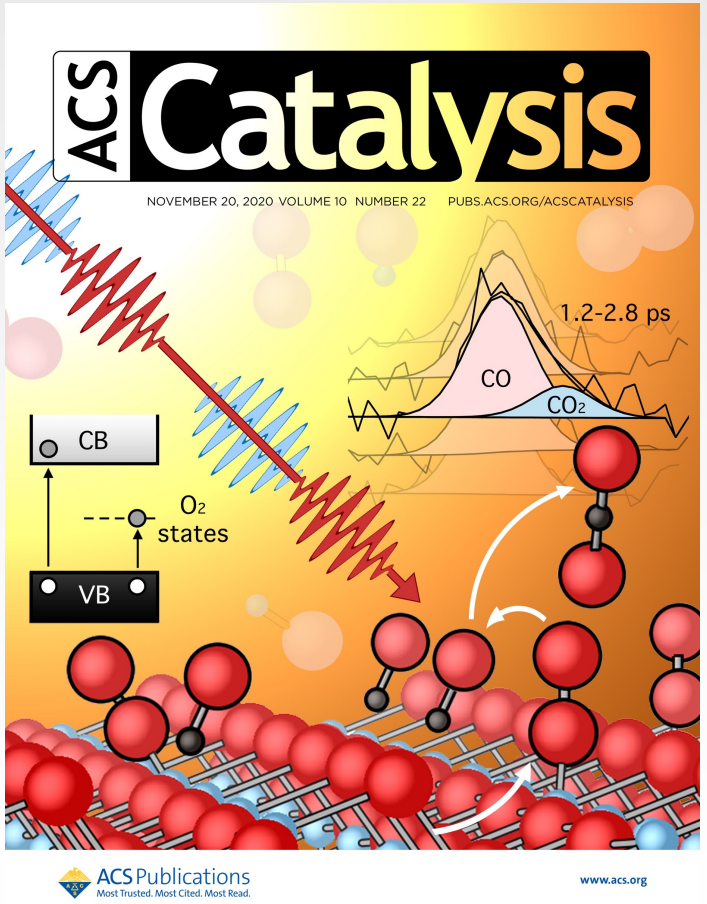
Time resolved XPS with free electron lasers



C 1s (hv=647 eV) of surface CO to CO_2 after UV/Vis pulse excites O_2 via anatase TiO_2

Recorded using FLASH



Noei et al, ACS Catal 10 13650 (2020)

Time Resolved Photoemission Light Harvesting SXP

Future Prospects:

- TR-ARPES of conduction band/LUMO states
- C,N,O core level photoemission to investigate intermediate species in water chemistry, photodegradation on transition metal oxides
- Time resolved photoelectron diffraction to follow electron dissipation following pump pulse
- DSSC, hybrid perovskites-- element-specific recombination paths and charge transfer to electron and hole collectors
- Tender X-ray (3 keV) measurements of photoelectrochemistry, photovoltaics, photodegradation at liquid/solid interfaces