The UNIVERSITY of OKLAHOMA

Plasmonic Phase Transition and Chemical Transformation

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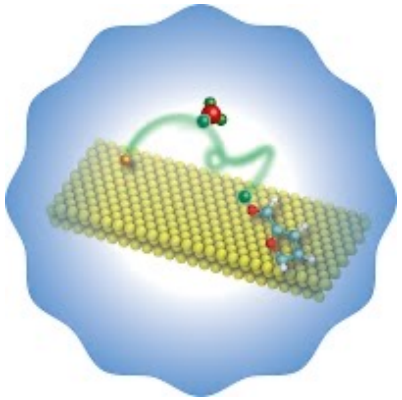
Lawrence Livermore National Laboratory, January 18, 2024

Interfacial engineering for controllable energy & molecular transformation

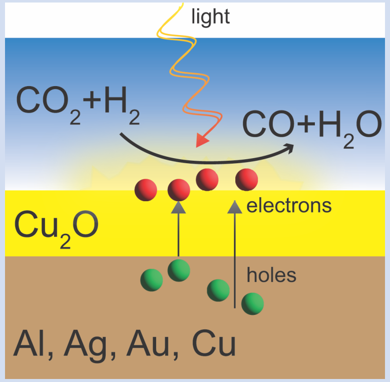
Approaches: DFT, GW, ΔSCF, AIMD, DPMD

Liquid-phase catalysis



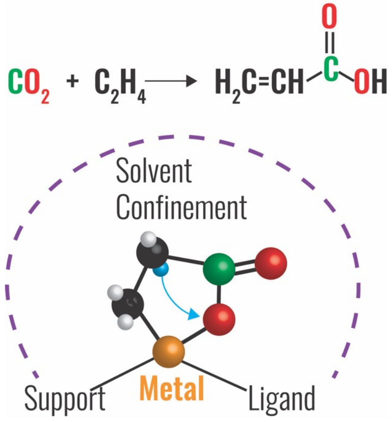
Proton shuttling
Remote polarization
Confinement
Dielectric screening

Non-equilibrium non-thermal catalysis



Charge transfer
Energy transfer
Defect engineering
Interfacial engineering

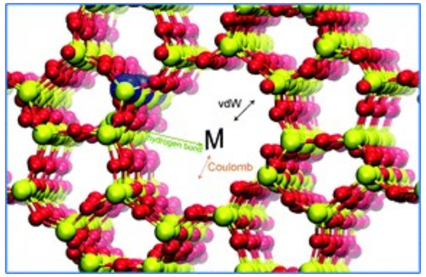
Active sites design



Coordination
Charge localization
Local confinement

CO_2 conversion
plastic recycling
methane pyrolysis

Fundamentals in acid catalysis



Batteries/PV

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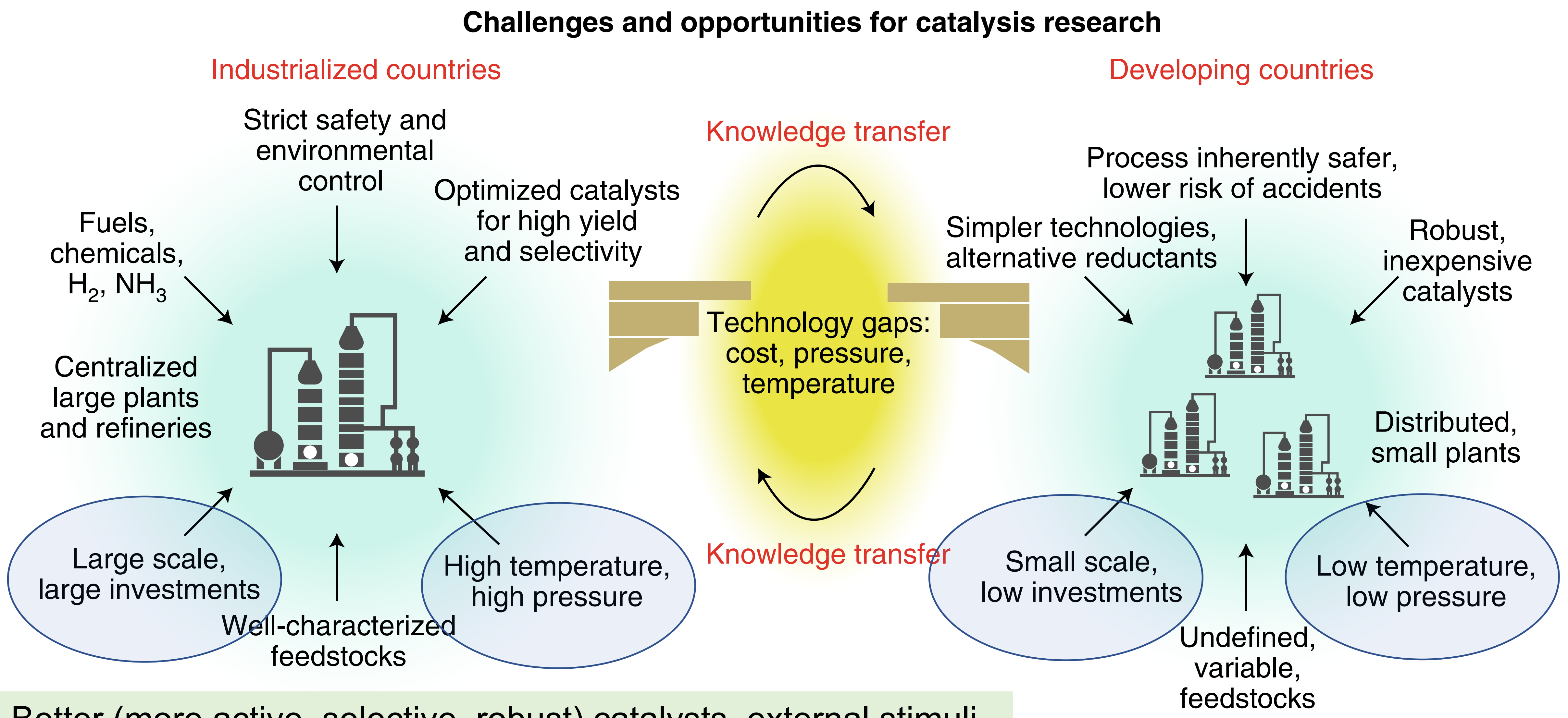
Distributed manufacturing: Renewal feedstock and energy

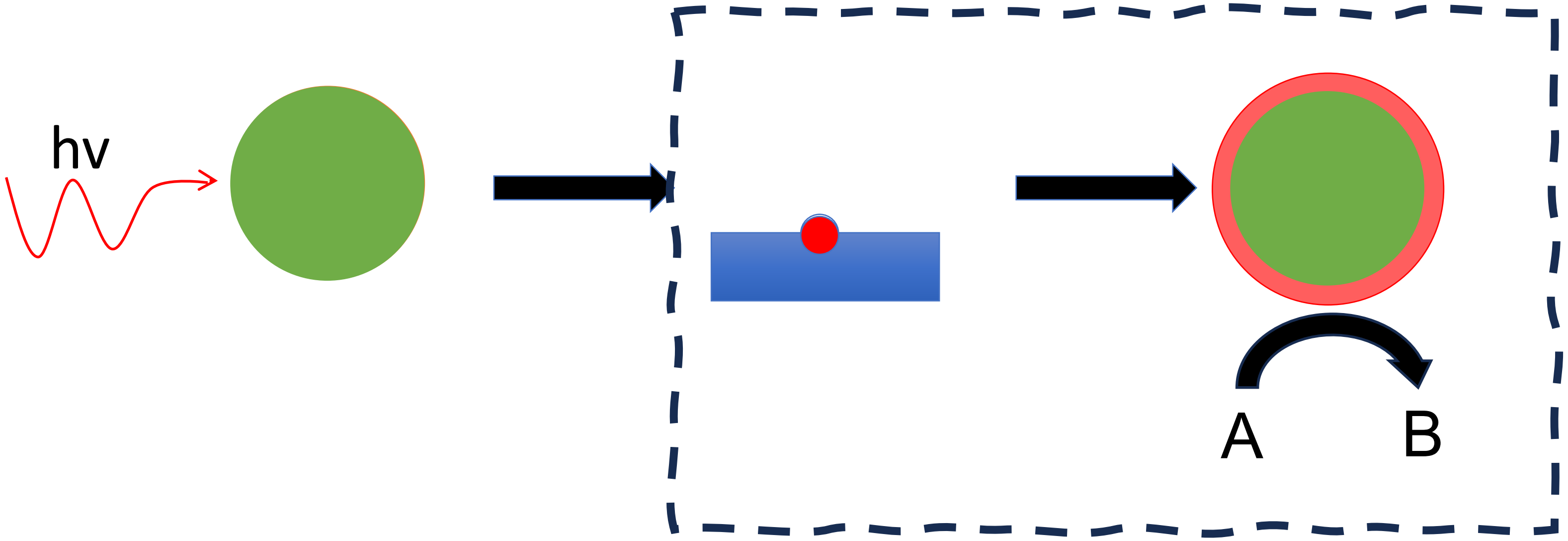


Better (more active, selective, robust) catalysts, external stimuli

D. E. Resasco, B. Wang, D. Sabatini, *Nat. Catal.*, 1, 731-735 (2018)

localized surface plasmon drives chemical transformation

“Labors of the Months”
(Norwich, England, ca. 1480).



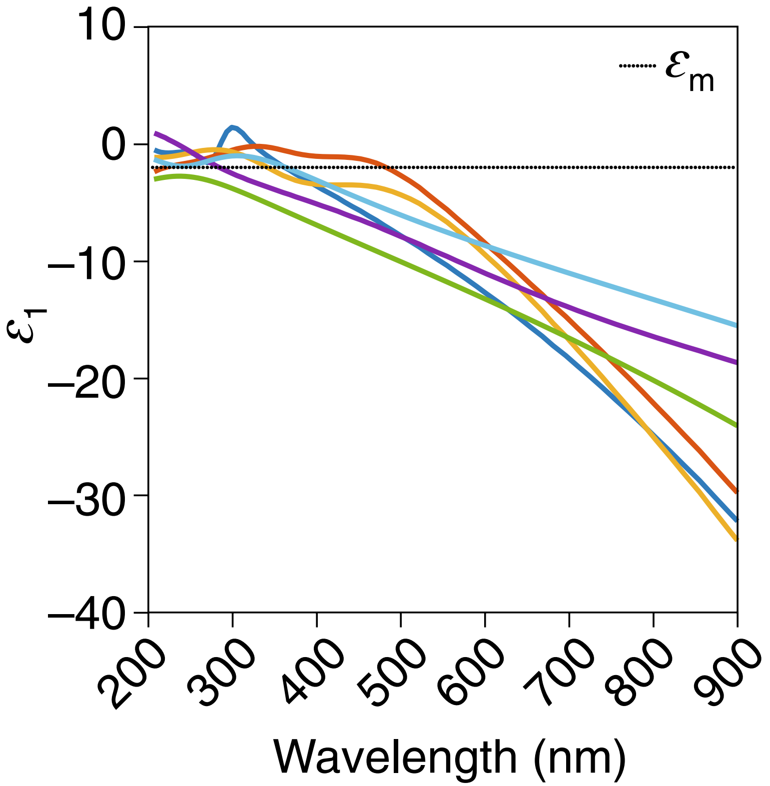
Questions:
Interfacial charge/energy transfer – where to where?
How it couples with molecular reaction?
Is it just activity, how about selectivity?
Can we control such charge/energy transfer and reactions?

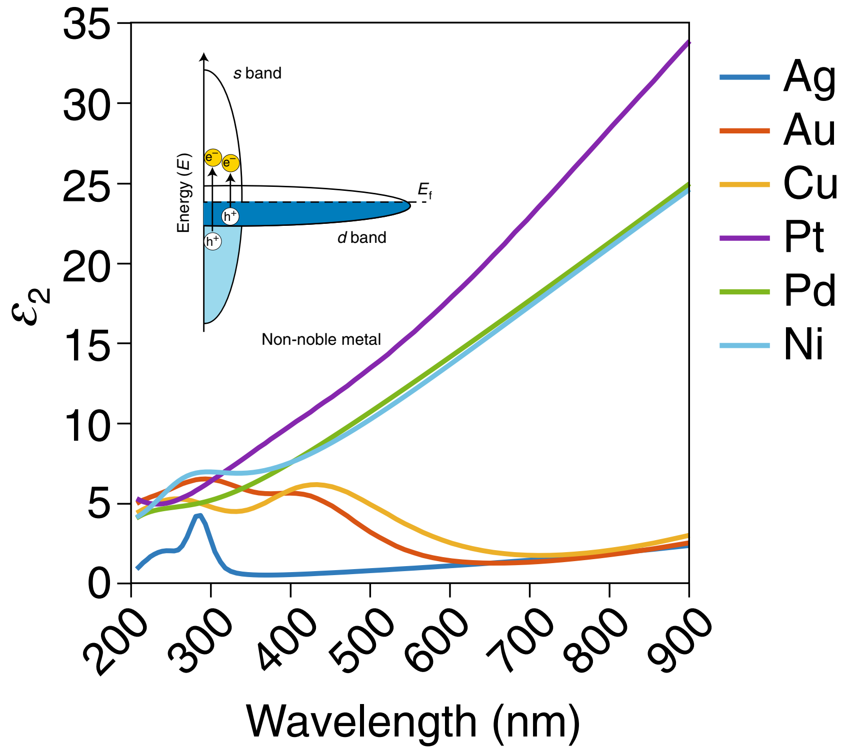
ALL-Optically Controlled Activation and Targeted Excitation (ALLOCATE)

A little bit more details

$$\sigma_{\mathrm{ext}} \sim \frac{\varepsilon_2}{[\varepsilon_1 + 2\varepsilon_{\mathrm{m}}]^2 + \varepsilon_2^2}$$

The extinction cross section approximated using, using the Mie theory, assuming spherical nanoparticles





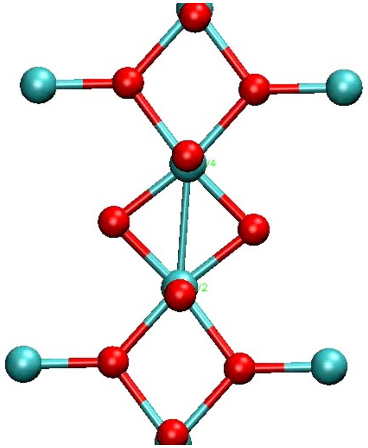
$$\varepsilon_1 \approx -2\varepsilon_{\mathrm{m}}$$

ε_2 small at the photon wavelength

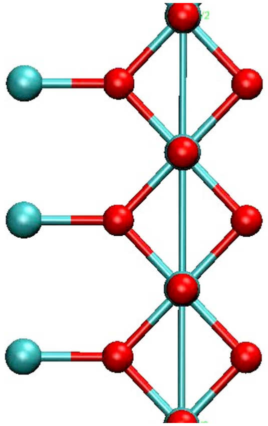
Ag, Au and Cu exhibit LSPR in the visible range. These metals are typically regarded as the plasmonic metals.

Aslam et al., *Nat. Catal.*, (2018)

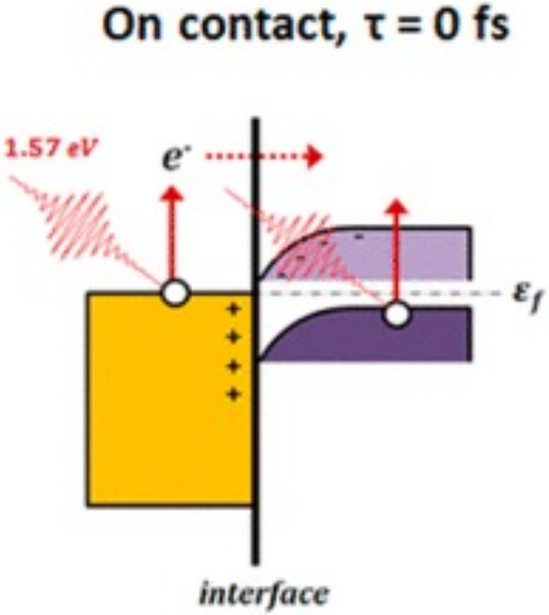
Plasmon-induced ultrafast phase transition of VO_2

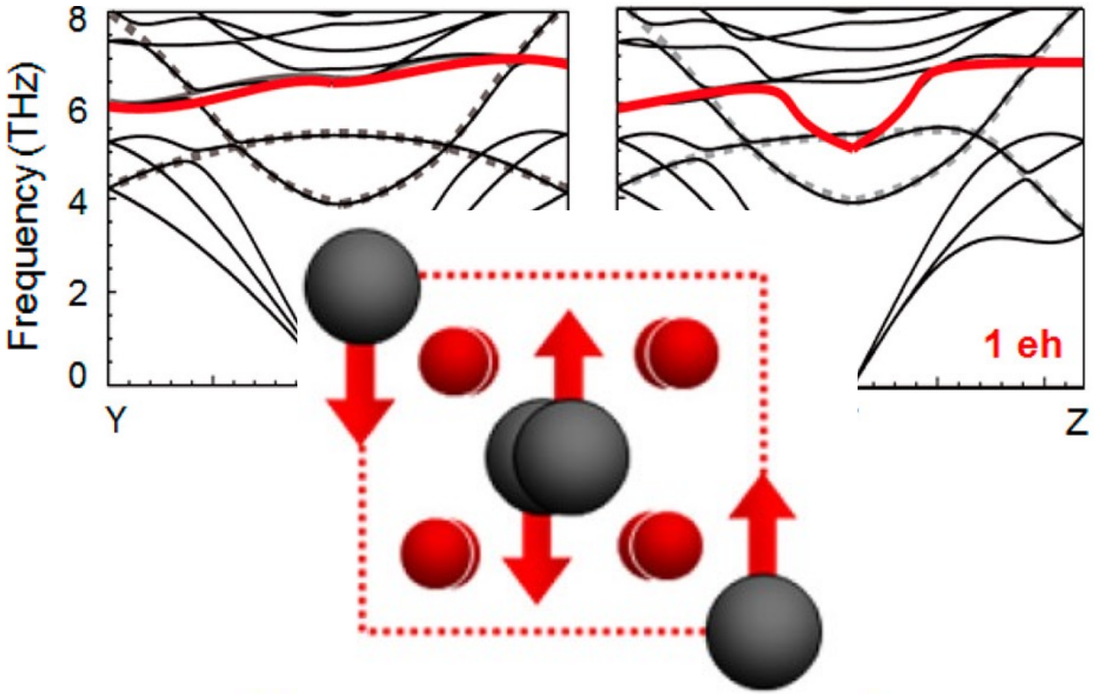


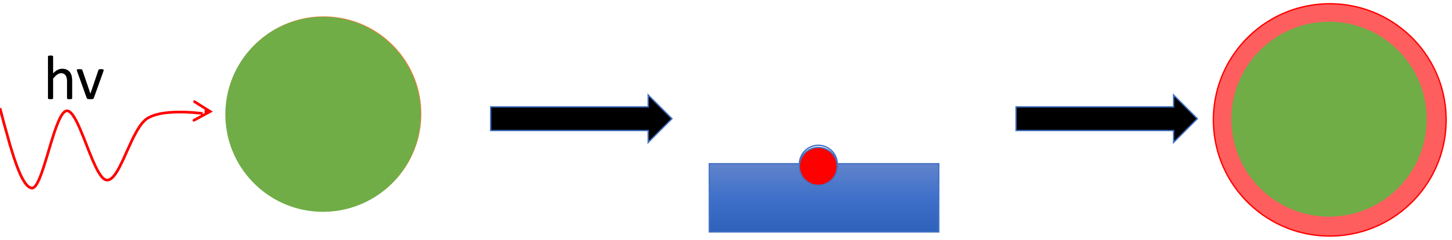
Monoclinic
Insulating

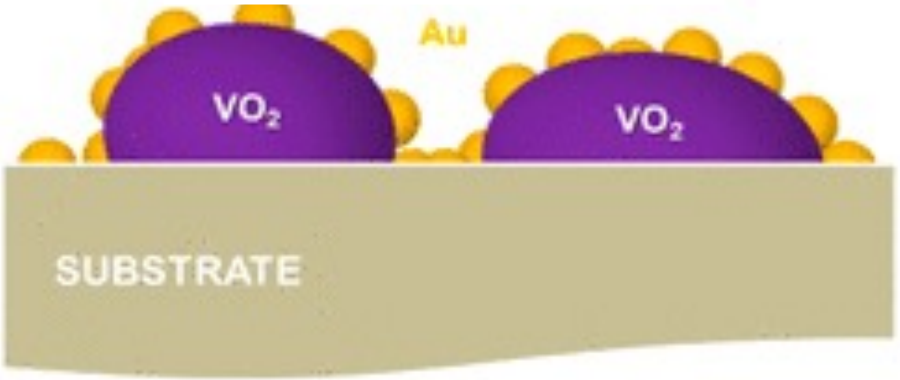


Rutile
Metallic



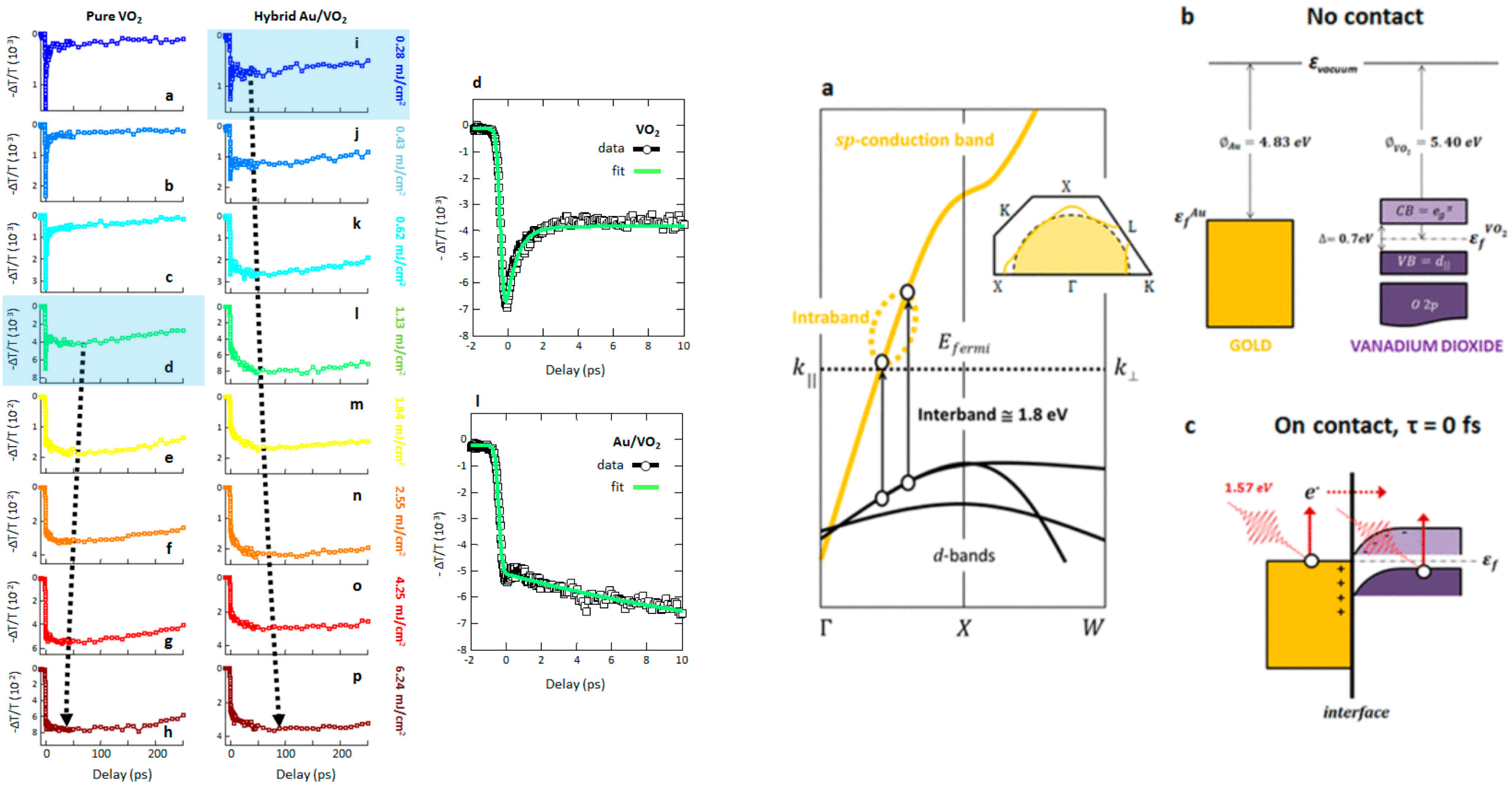






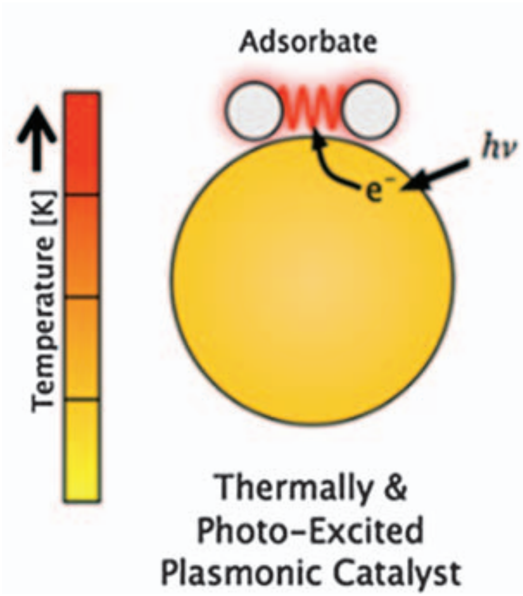
K. Appavoo, B. Wang, N. Brady, M. Seo, J. Nag, R. Prasankumar, D. Hilton, S. Pantelides, R. Haglund, ***Nano Lett.*** 14, 1127 (2014)

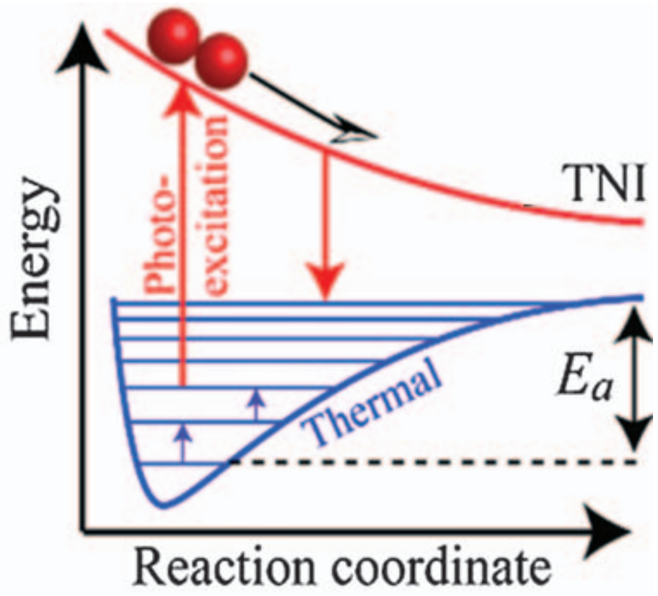
Plasmon-induced ultrafast phase transition of VO_2

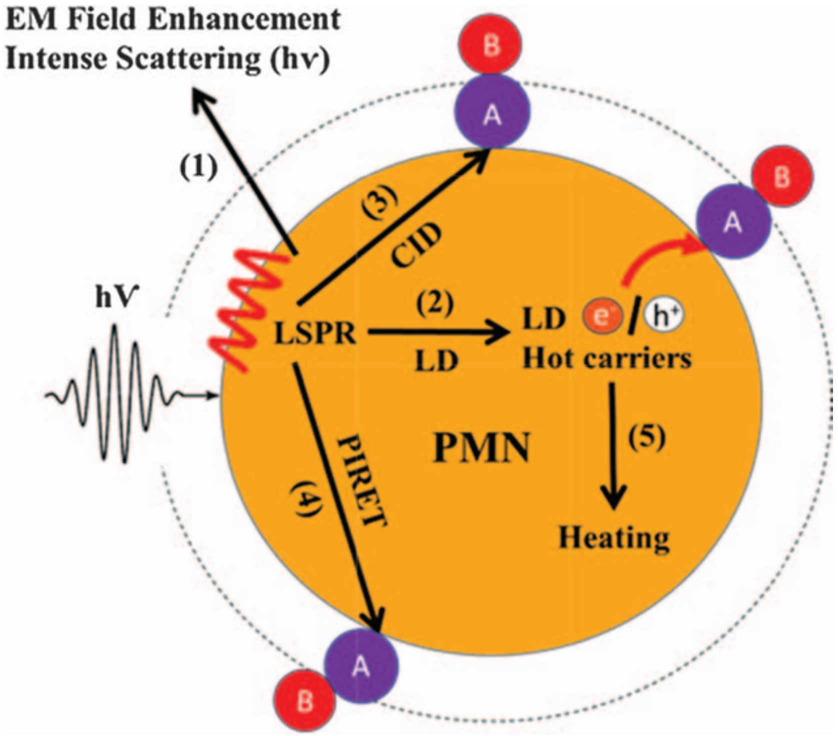


Plasmonic Photocatalysis

Many different interfacial dynamics to dissipate the energy

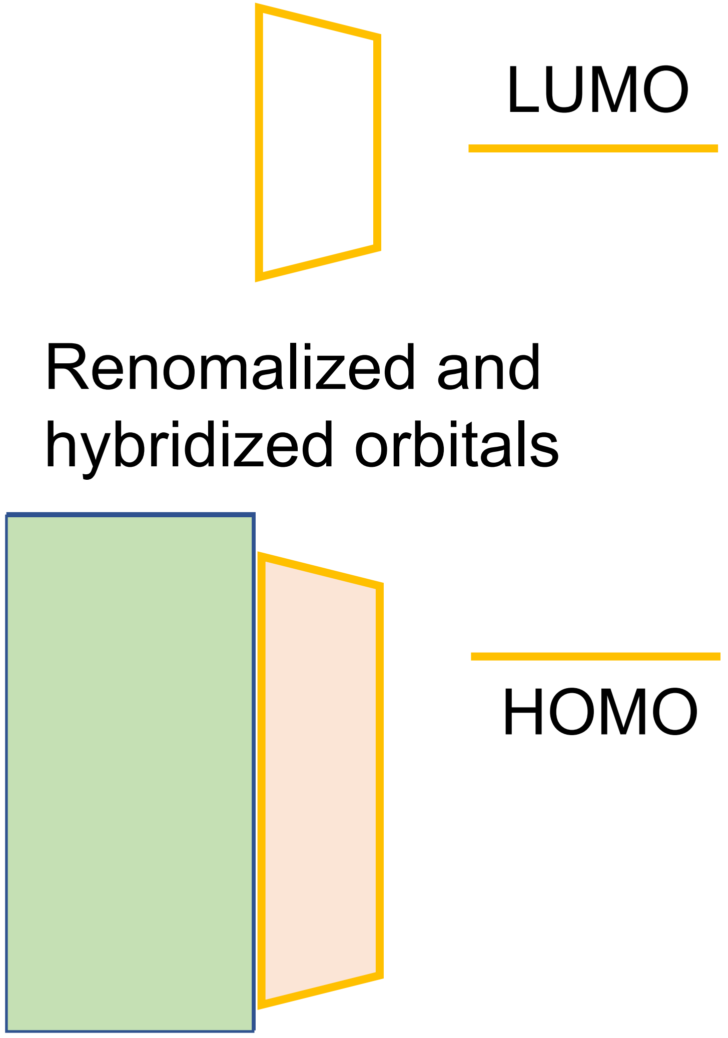


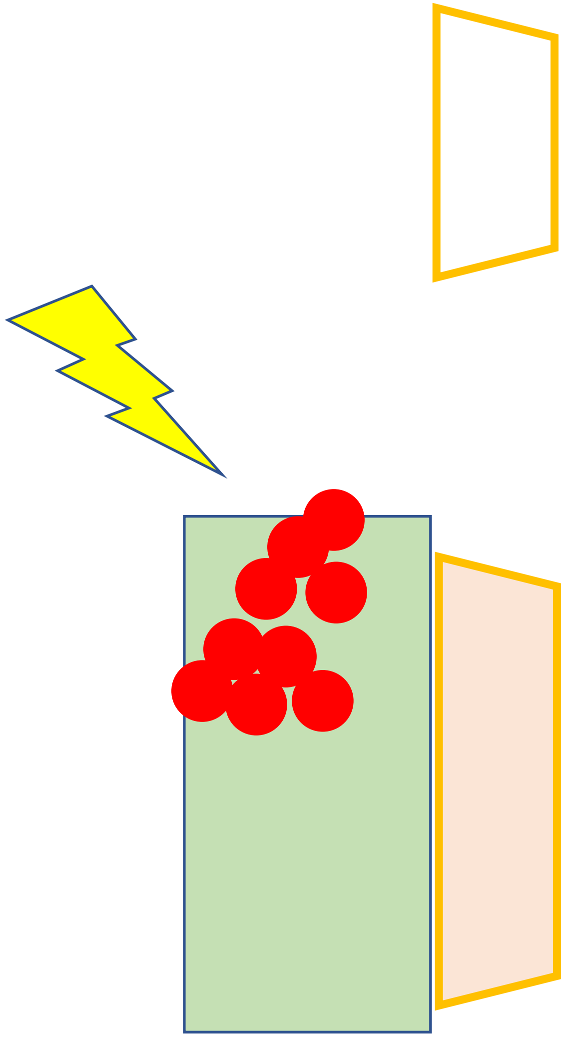




S. B. Ramakrishnan, F. Mohammadparast, A. P. Dadgar, T. Mou, T. Le, B. Wang, P. K. Jain, M. Andiappan, ***Adv. Opt. Mater.*** 9(22), 2101128 (2021)

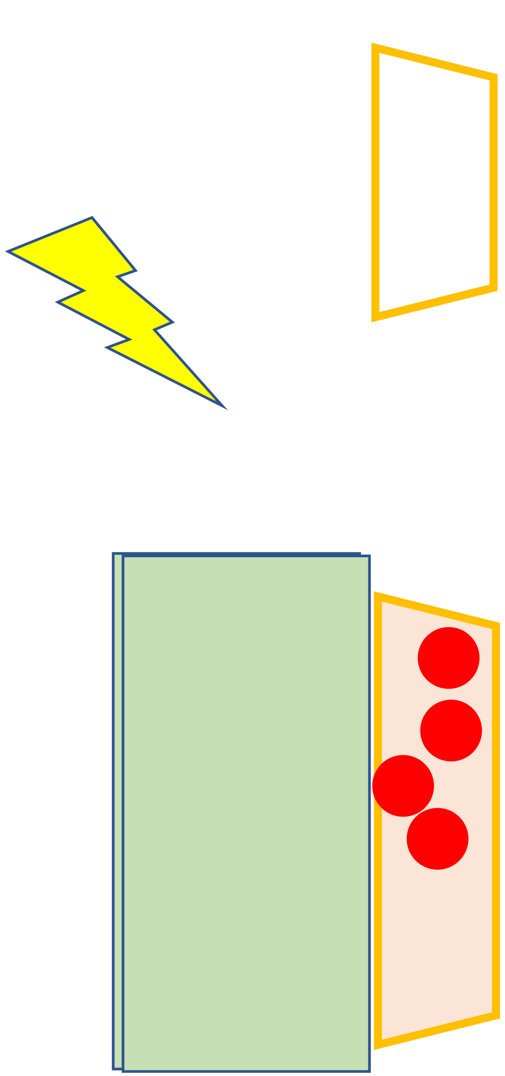
Mechanisms for Interfacial charge and energy transfer



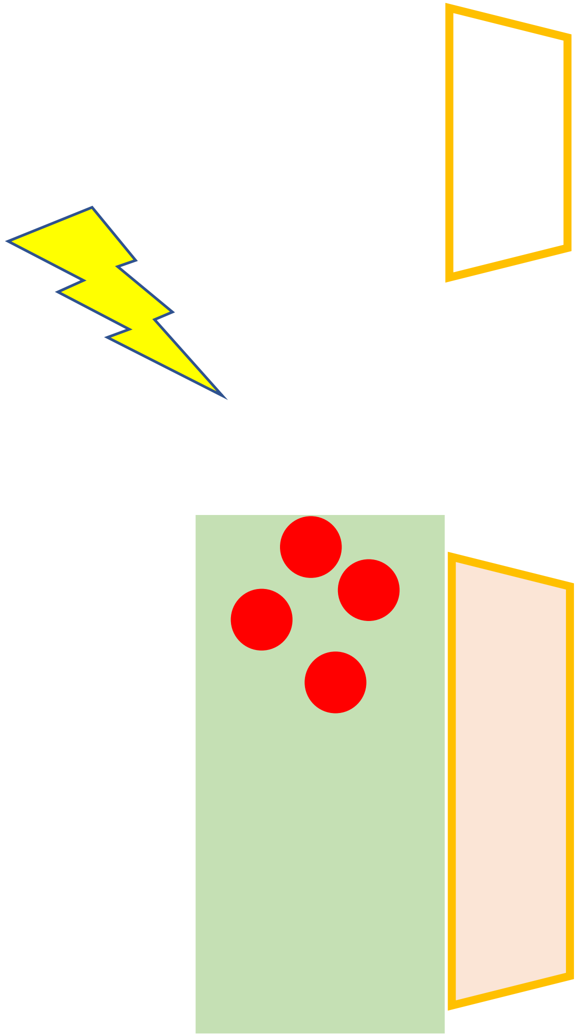


Generation of hot electrons in the metal

Mechanisms for Interfacial charge and energy transfer



Resonant energy transfer



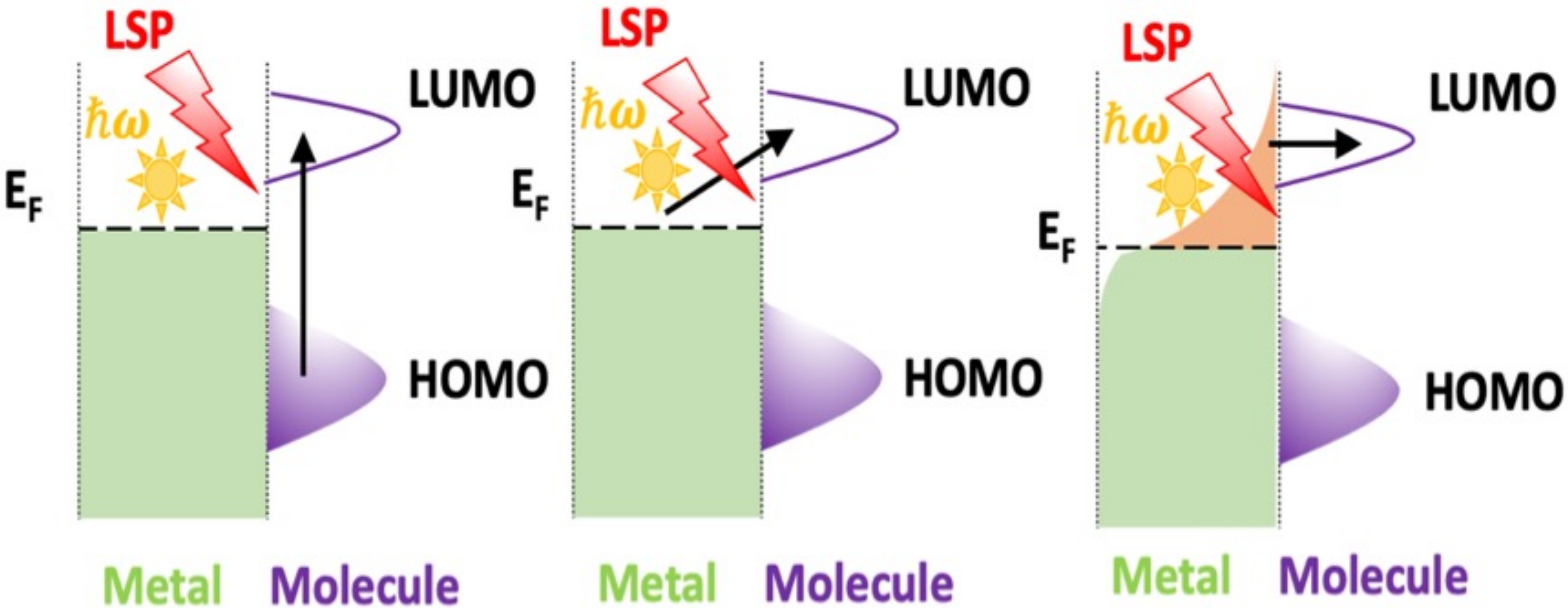
Direct interfacial charge transfer

Different ways of interfacial charge transfer and energy excitation

Direct intramolecular excitation

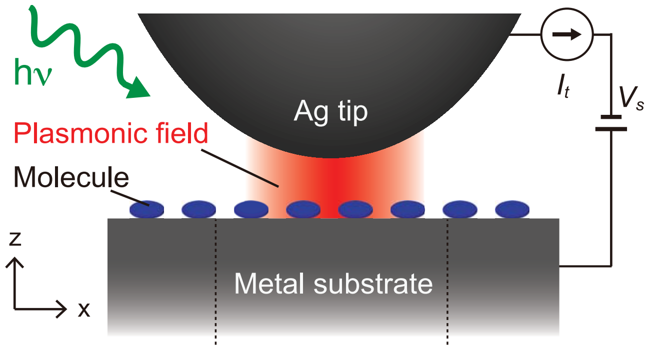
Direct interfacial charge transfer

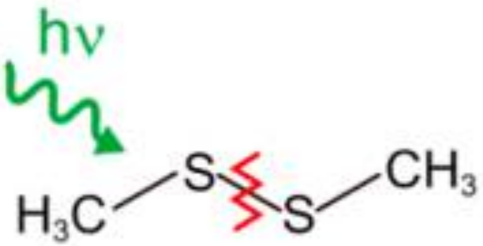
Hot electron mechanism

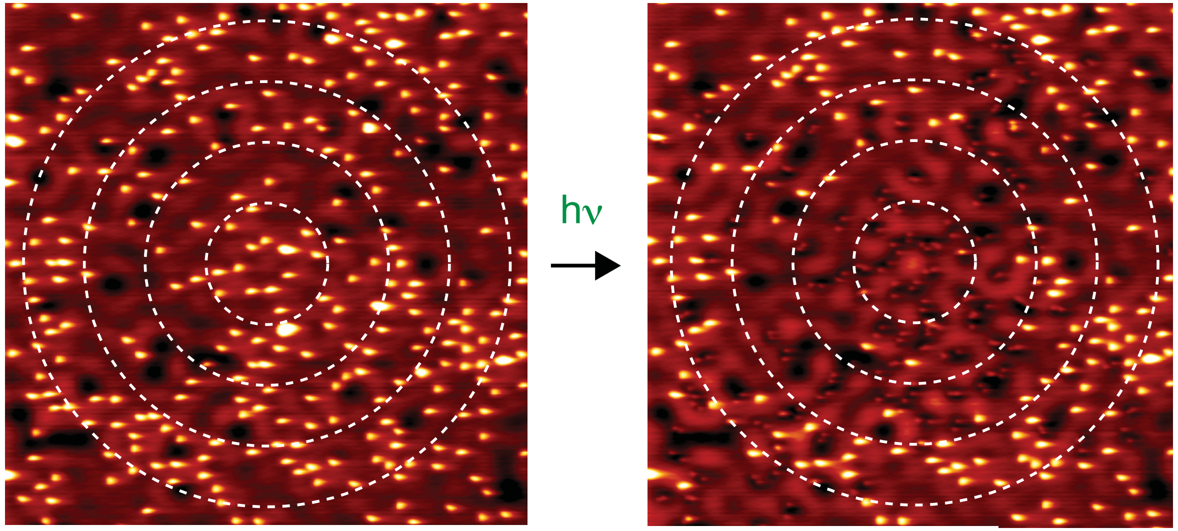


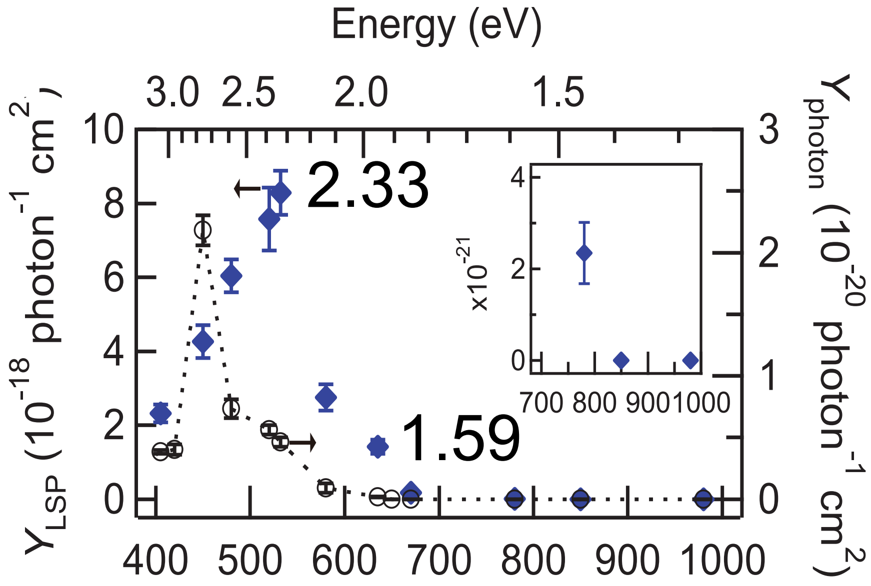
Benchmark study

a. Relatively simple reaction
b. Report activation or excitation energy
c. Performed on well-defined surfaces
d. Ideally no coverage and entropy effects

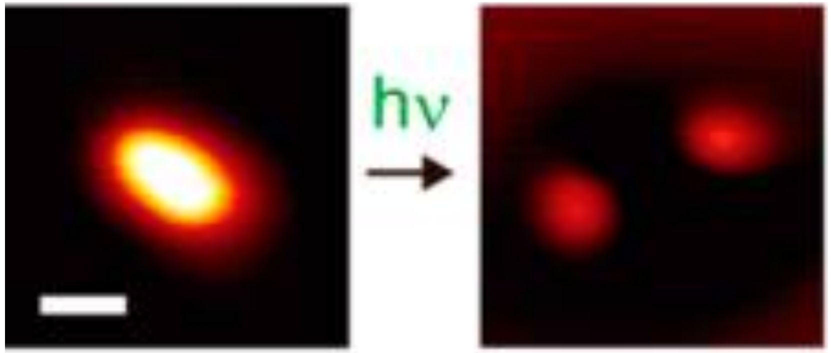






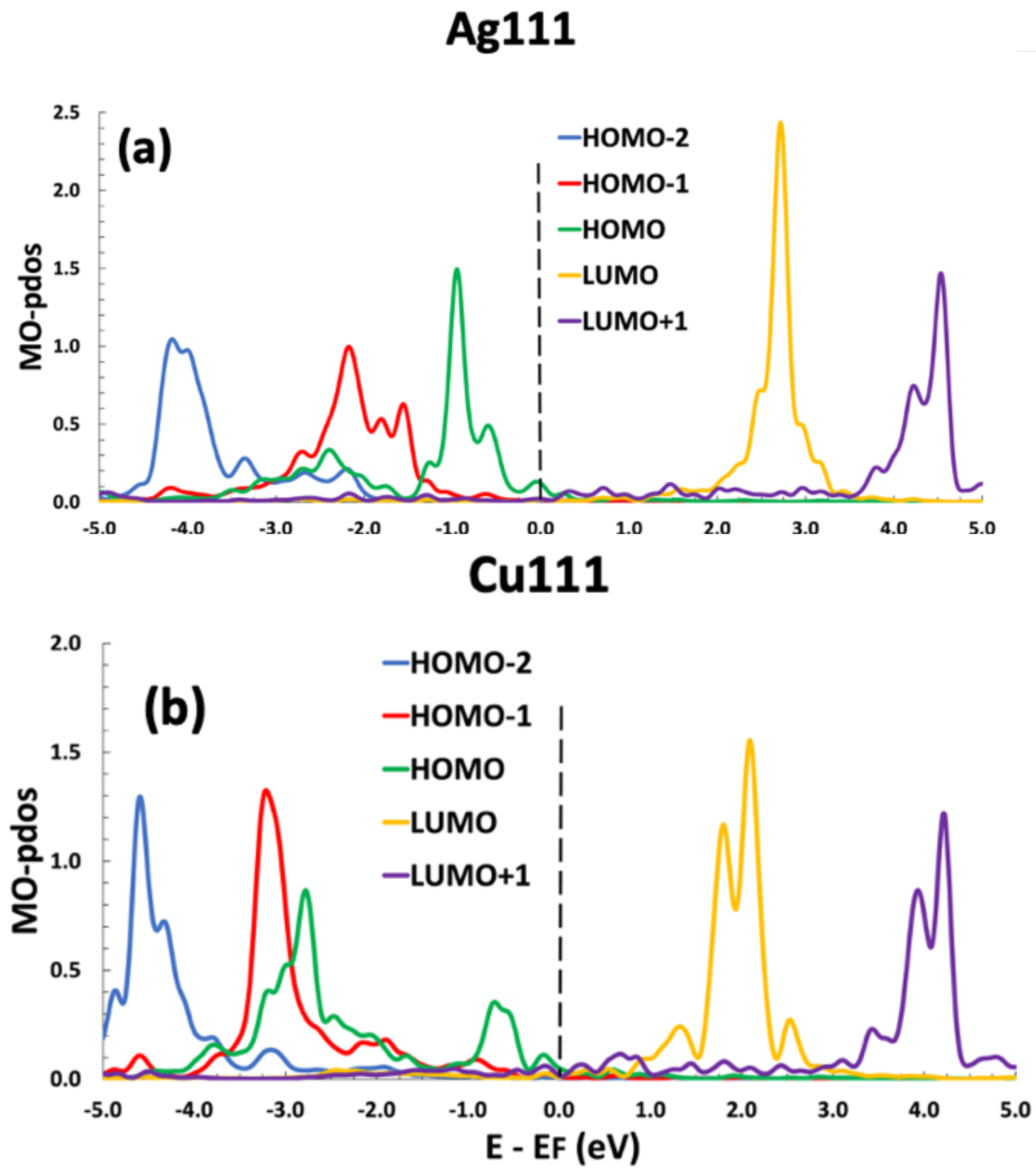


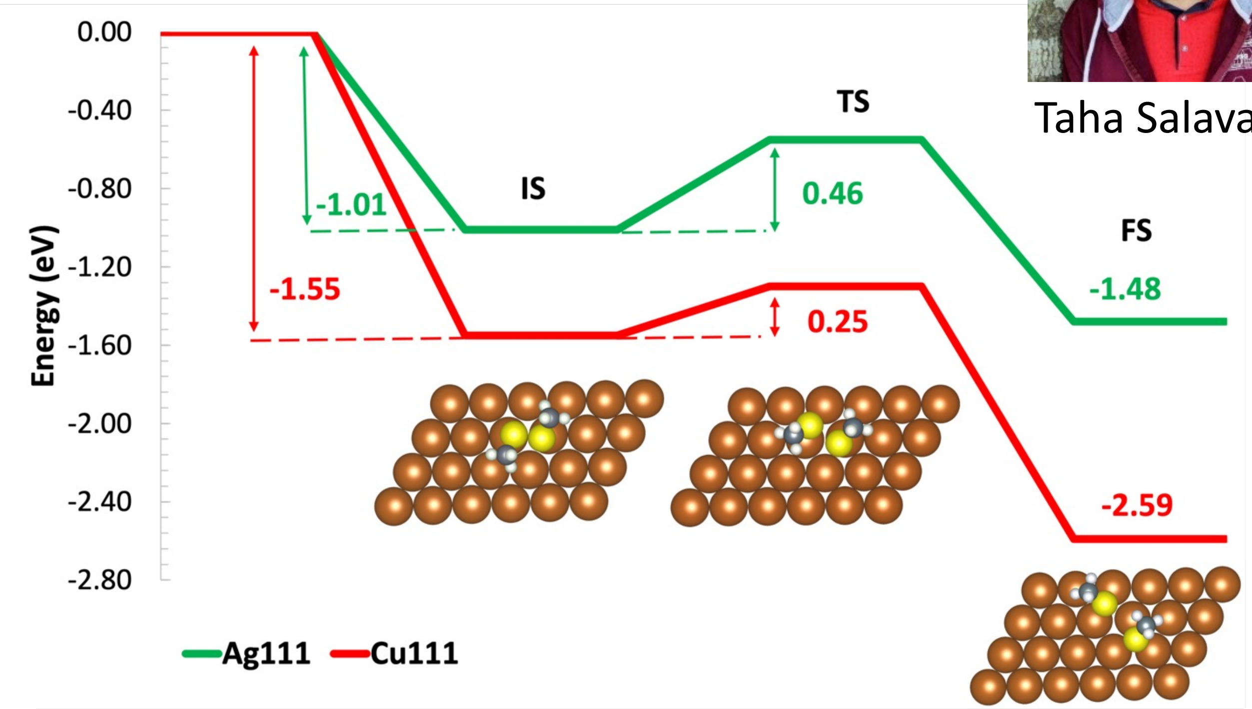
5 K, over Cu(111) and Ag(111), UHV
Kazuma et al. Science 2018



Ag: Maximum Yield E: 2.33; Threshold E: **1.59**
Cu: Maximum Yield E: 1.85; Threshold E: **1.27**

Electronic structure calculations (VASP)

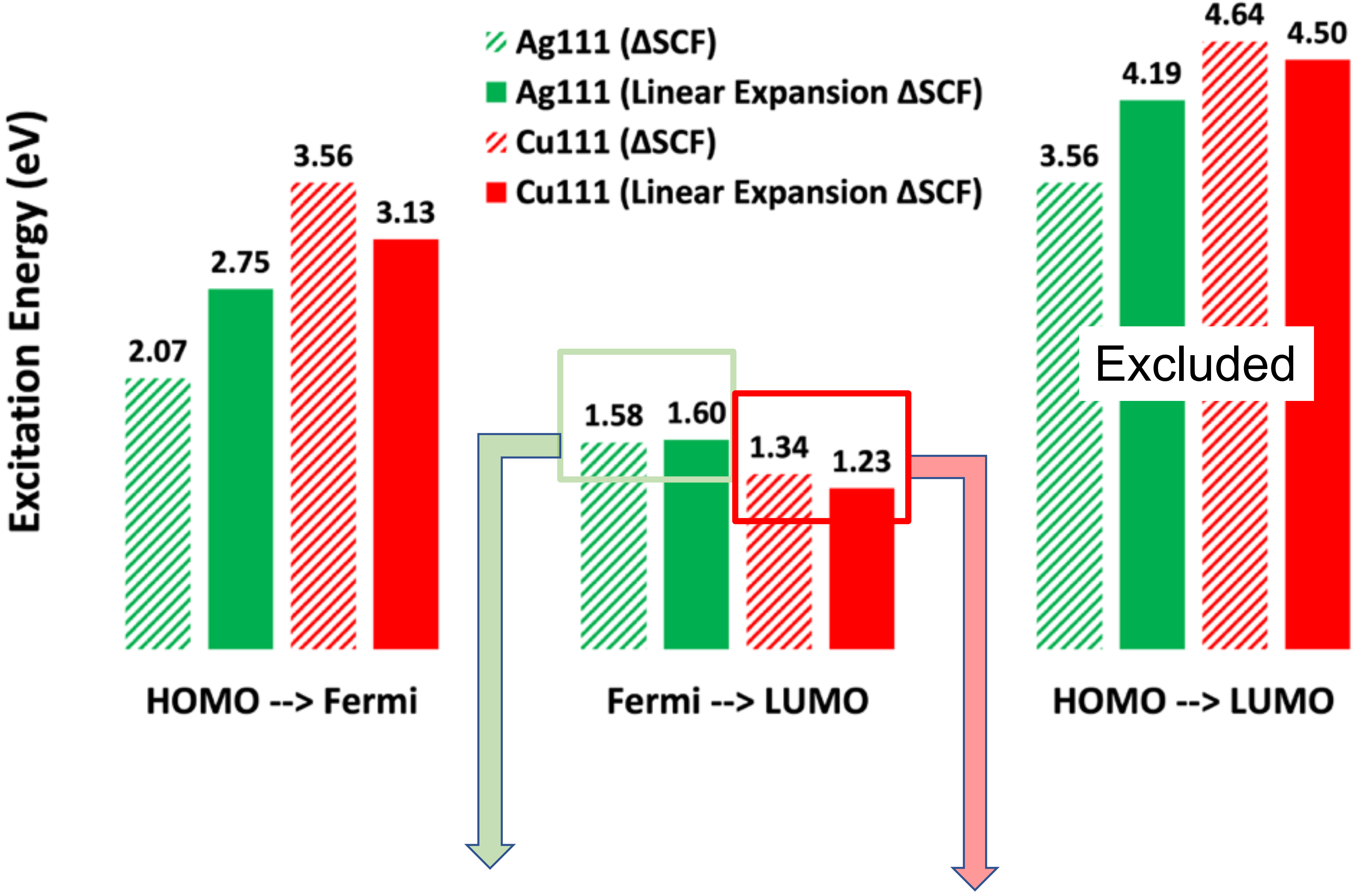


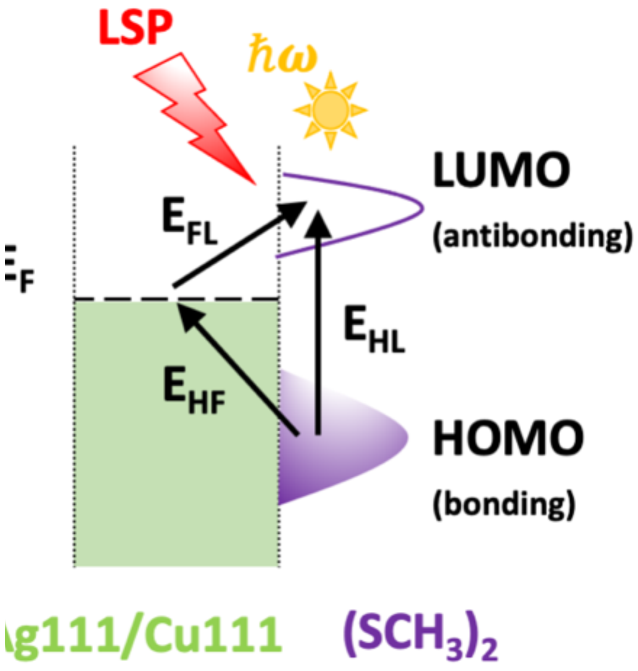


Taha Salavati-fard

Stronger mol. Interaction with Cu than Ag
More broadened (delocalized) states on Cu
LUMO more localized than HOMO
Lower activation barrier on Cu

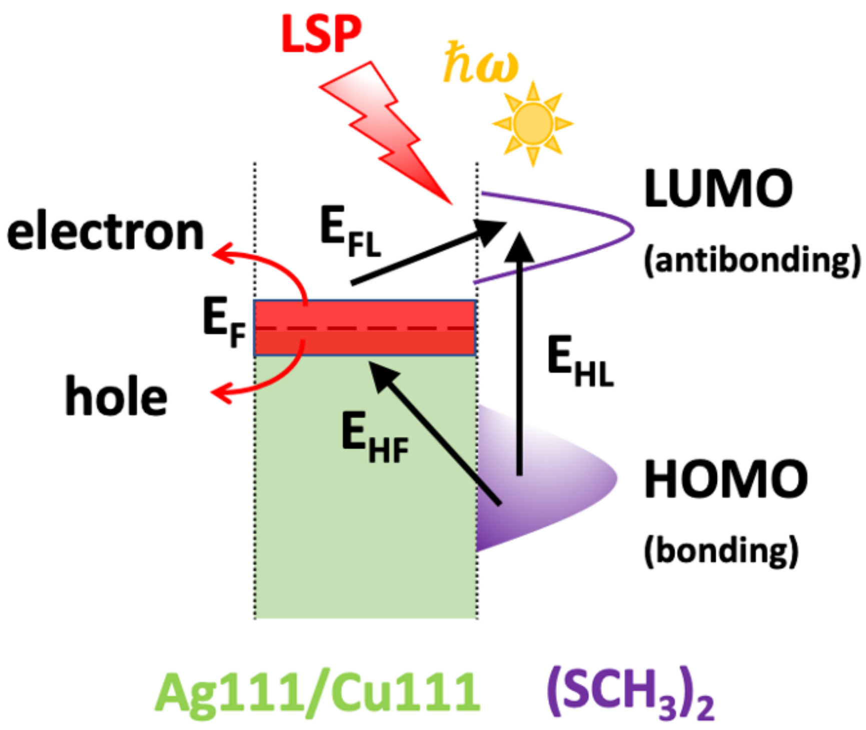
Delta SCF benchmark (GPAW)





Ag: Threshold E: 1.59 eV; Cu: Threshold E: 1.27 eV

Take home message I



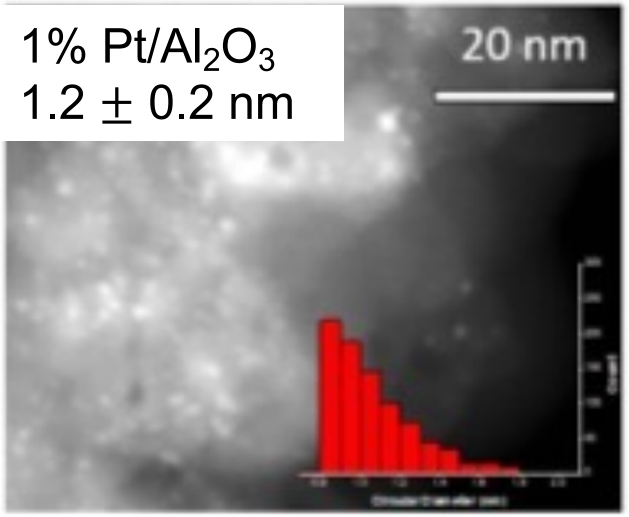
Calculated excitation energy from linear expansion delta SCF method agrees with experiments.

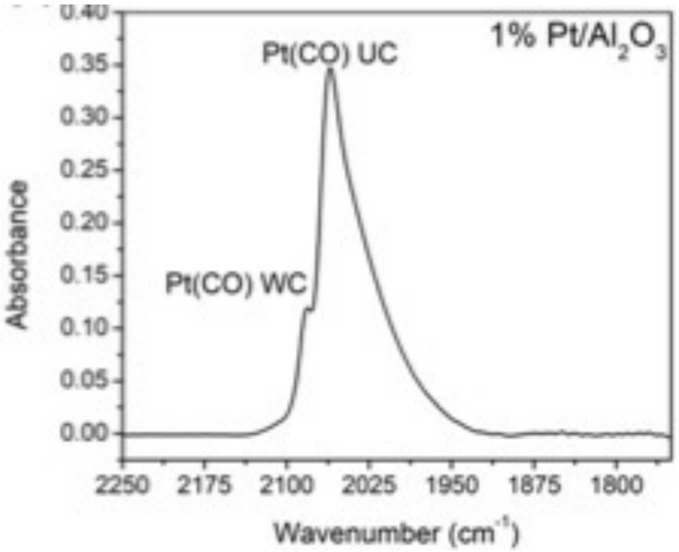
Interfacial charge transfer may explain the experimental observation.

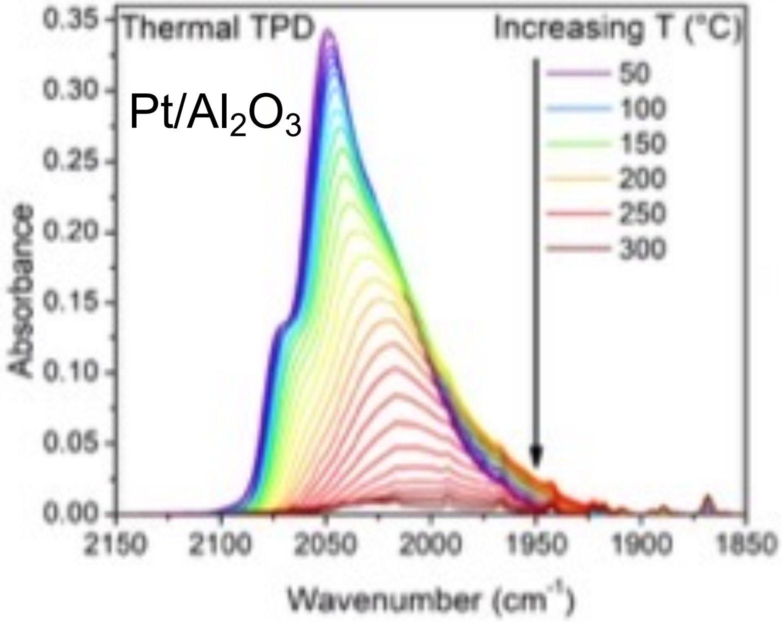
Since Fermi-LUMO dominates, one can think about changing the Fermi level (work function) or the molecular frontier orbitals (e.g., by solvent).

T. Salavati-fard, B. Wang, *ACS Catal.* 12, 12869 (2022)

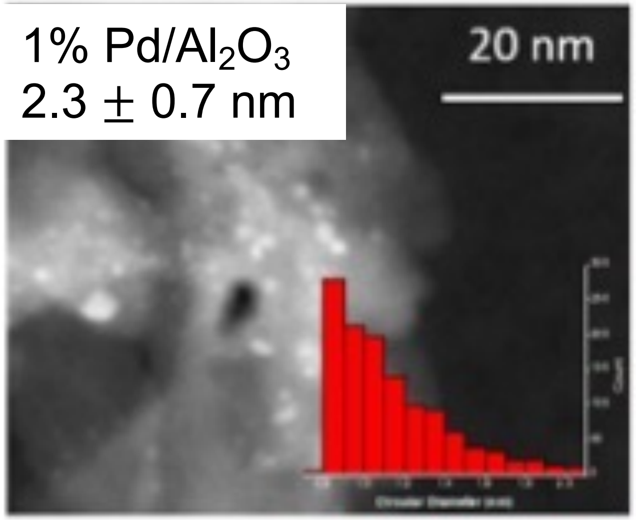
Thermal CO desorption from Pt and Pd

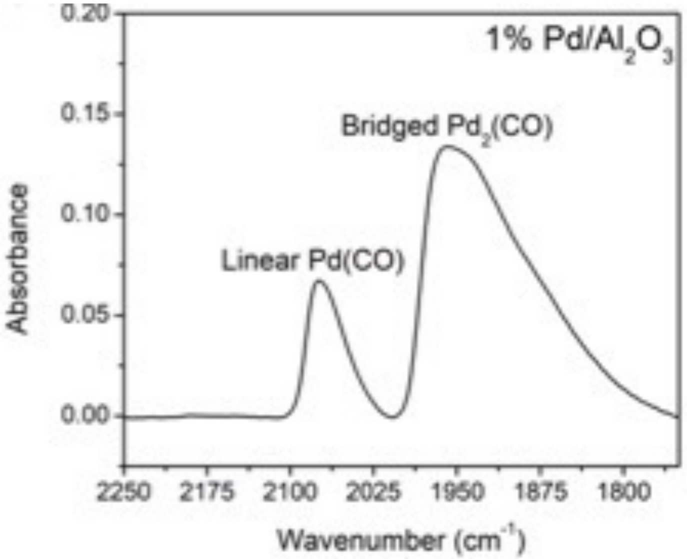


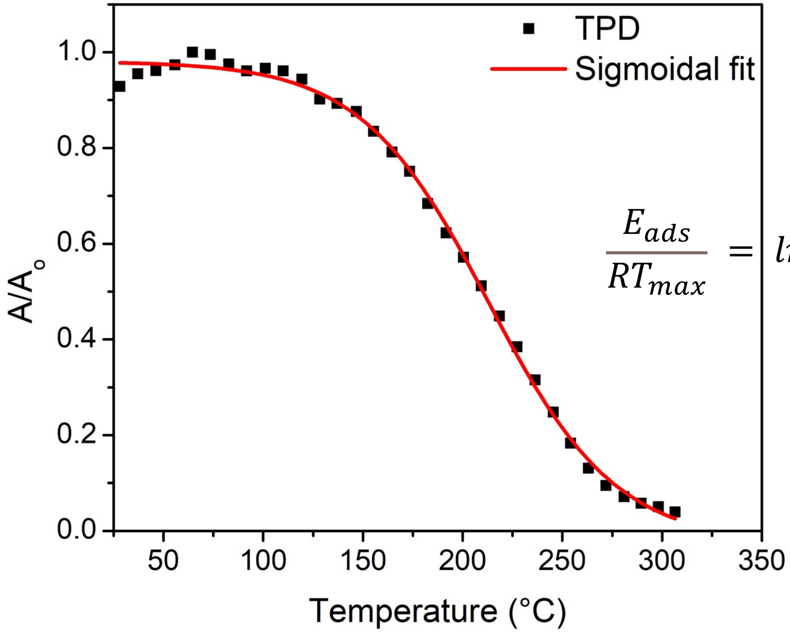




Isabel Barraza
UCSB

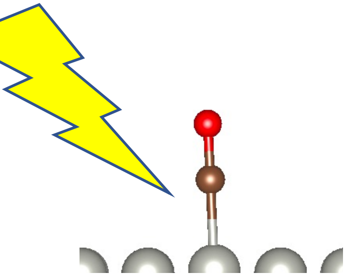


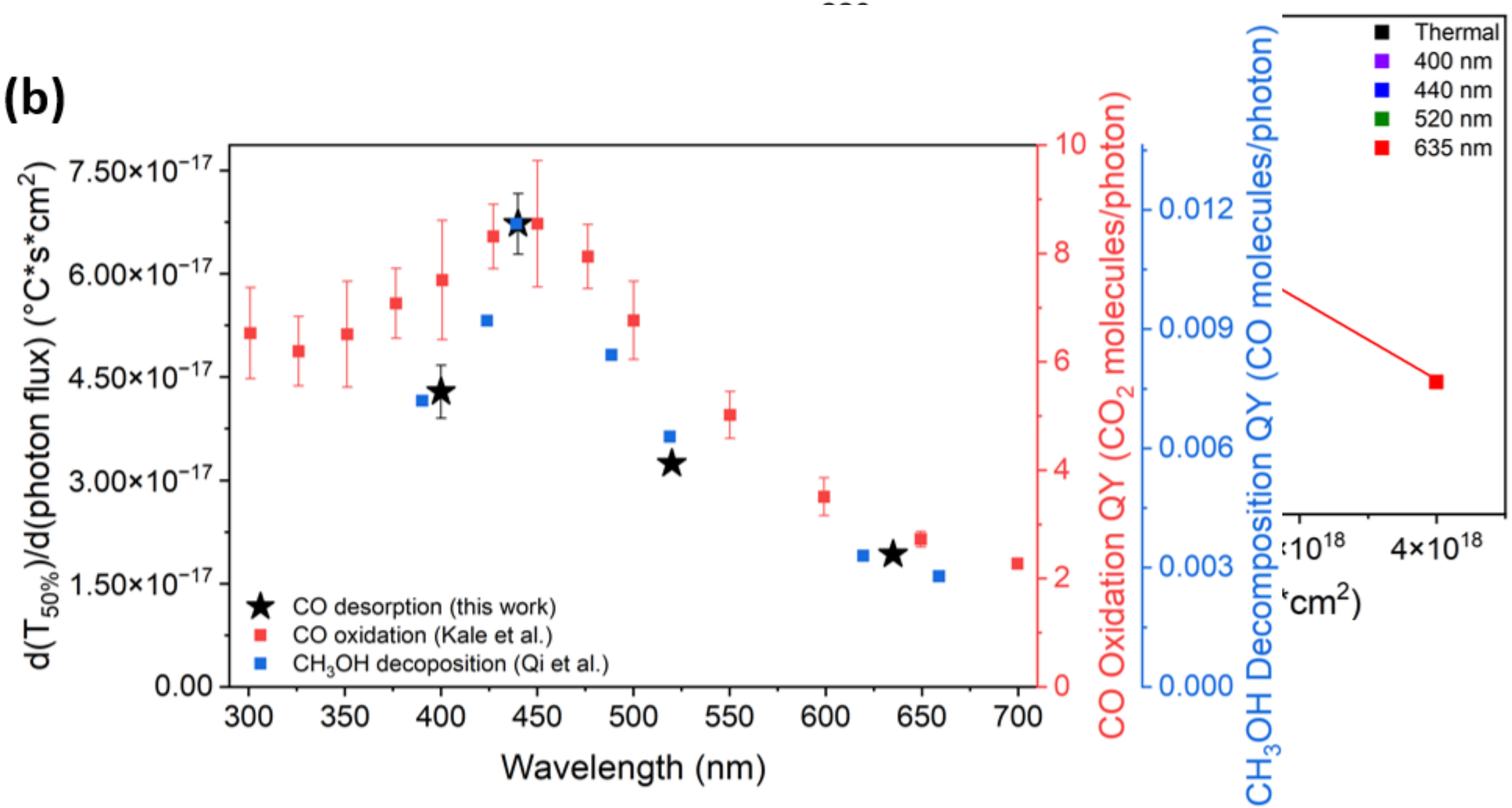




$$\frac{E_{ads}}{RT_{max}} = ln\left(\frac{\nu T_{max}}{\beta}\right) - 3.46$$

Non-thermal plasmonic CO desorption from Pt

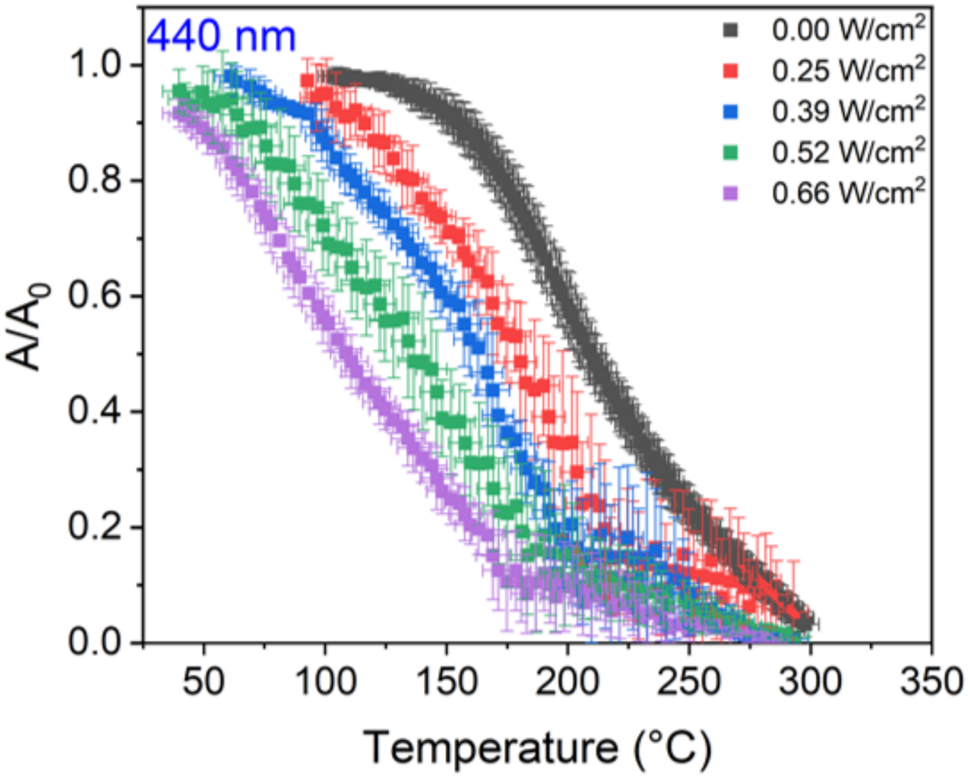




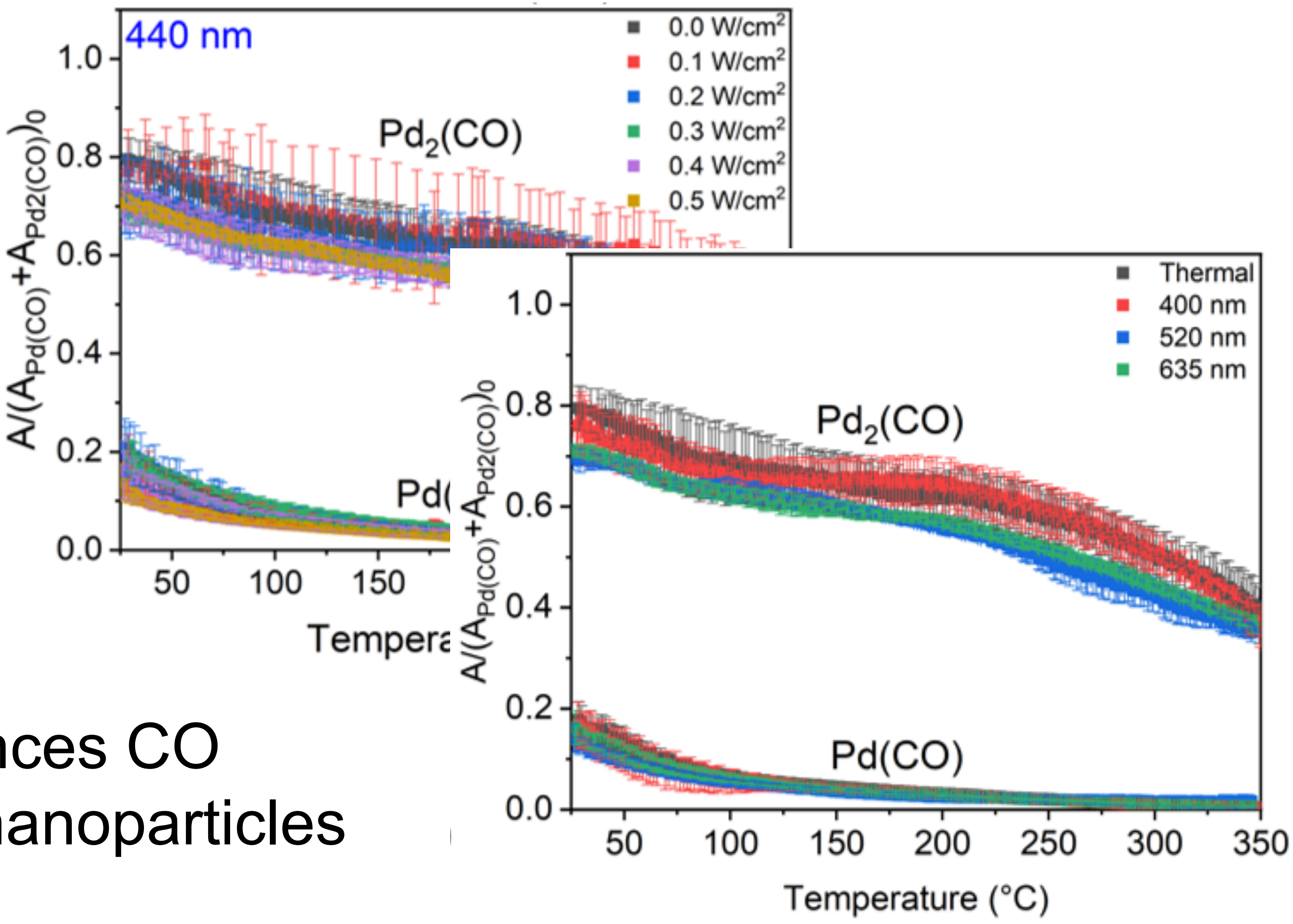
CO is the most abundant surface intermediate and CO desorption is a kinetically relevant step that limits reaction rates.

Compare non-thermal plasmonic CO desorption from Pt and Pd

Pt/Al_2O_3

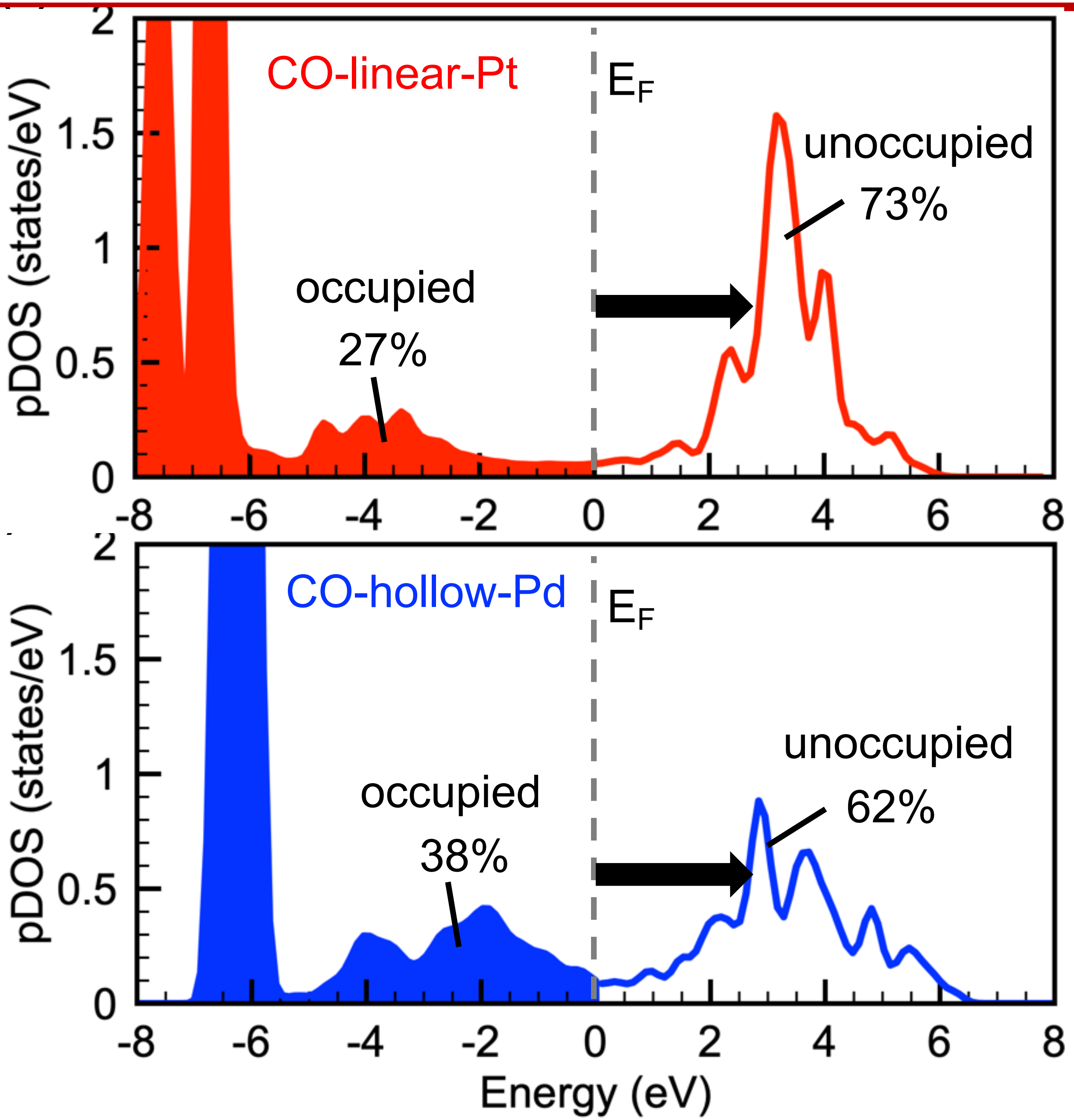


Pd/Al_2O_3

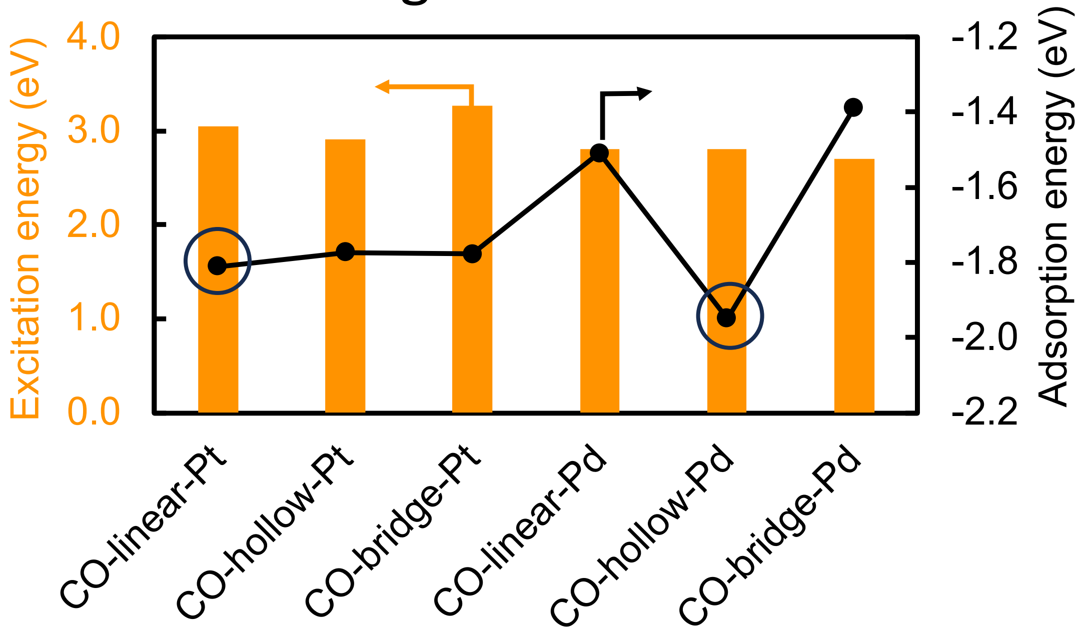


Photons irradiation influences CO desorption rates from Pt nanoparticles but not Pd nanoparticles?

Excitation energy calculations



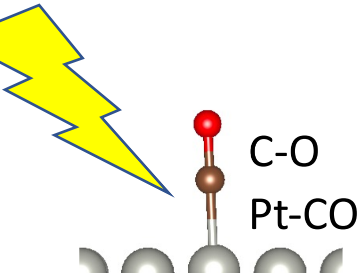
(i) Excitation energy not sensitive to ads configuration

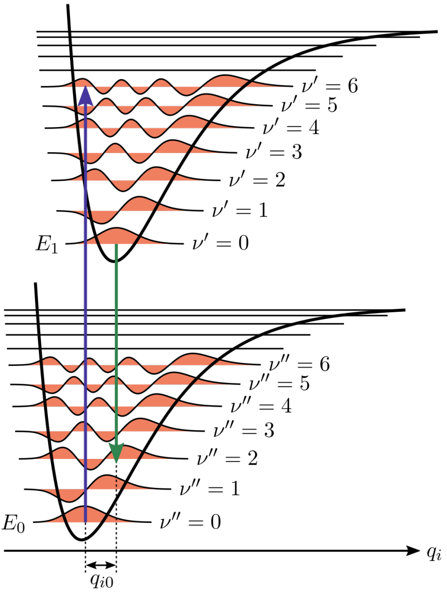


(ii) Excitation energy 2.8-3.0 eV agrees with experimental values 440 nm (2.82 eV)

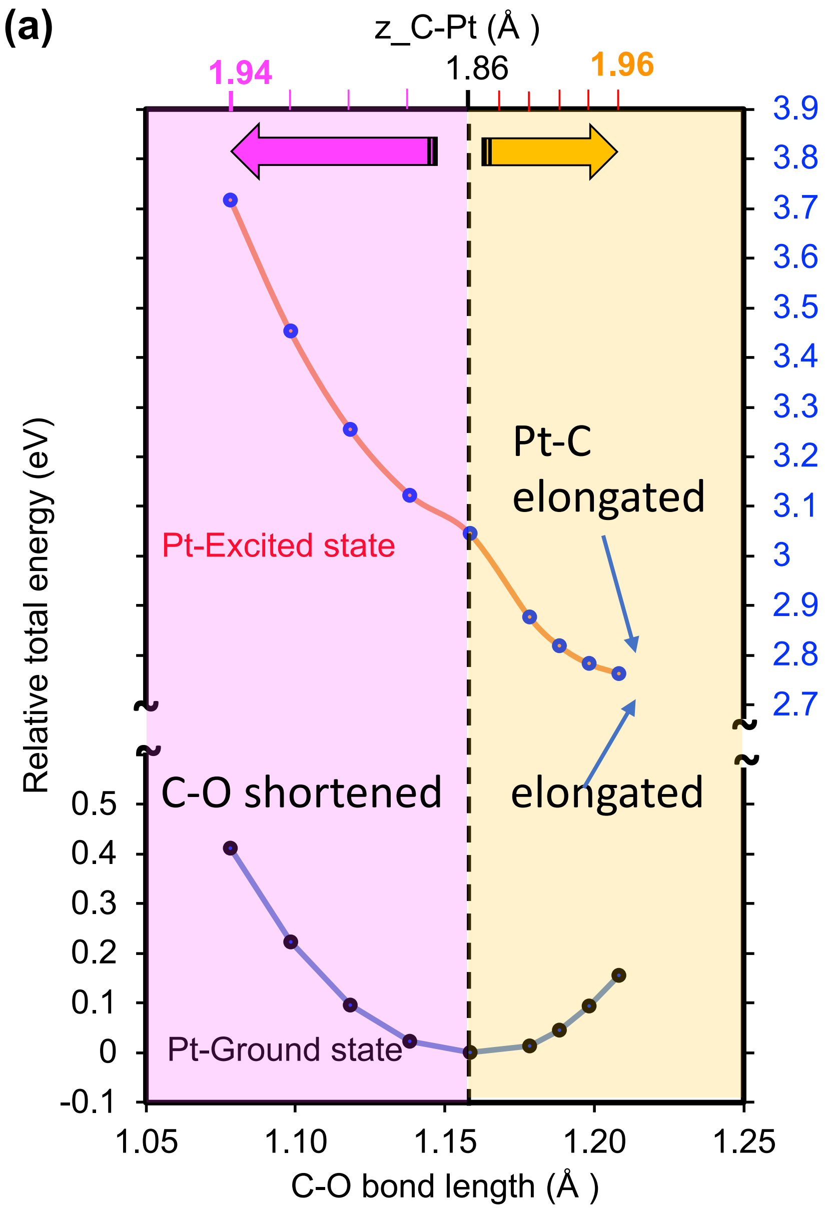
(iii) More localized, unoccupied empty LUMO on Pt

How energetic electrons couple with the Pt/Pd-CO bonds

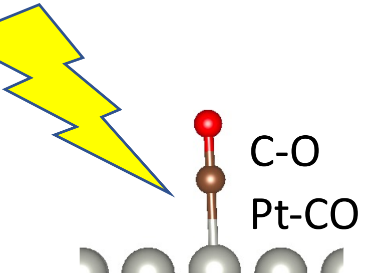




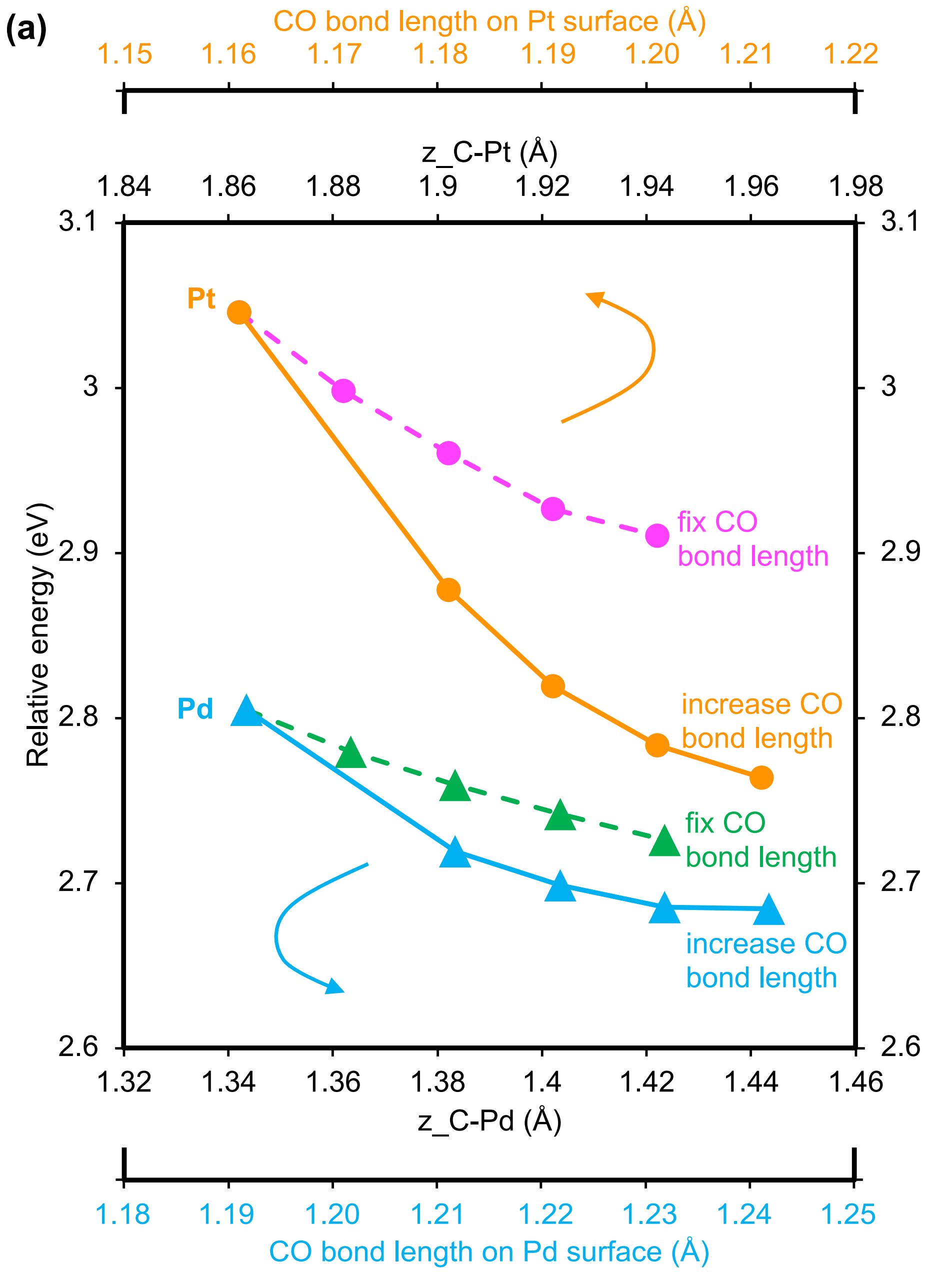
Franck–Condon principle
Taken from wikipedia

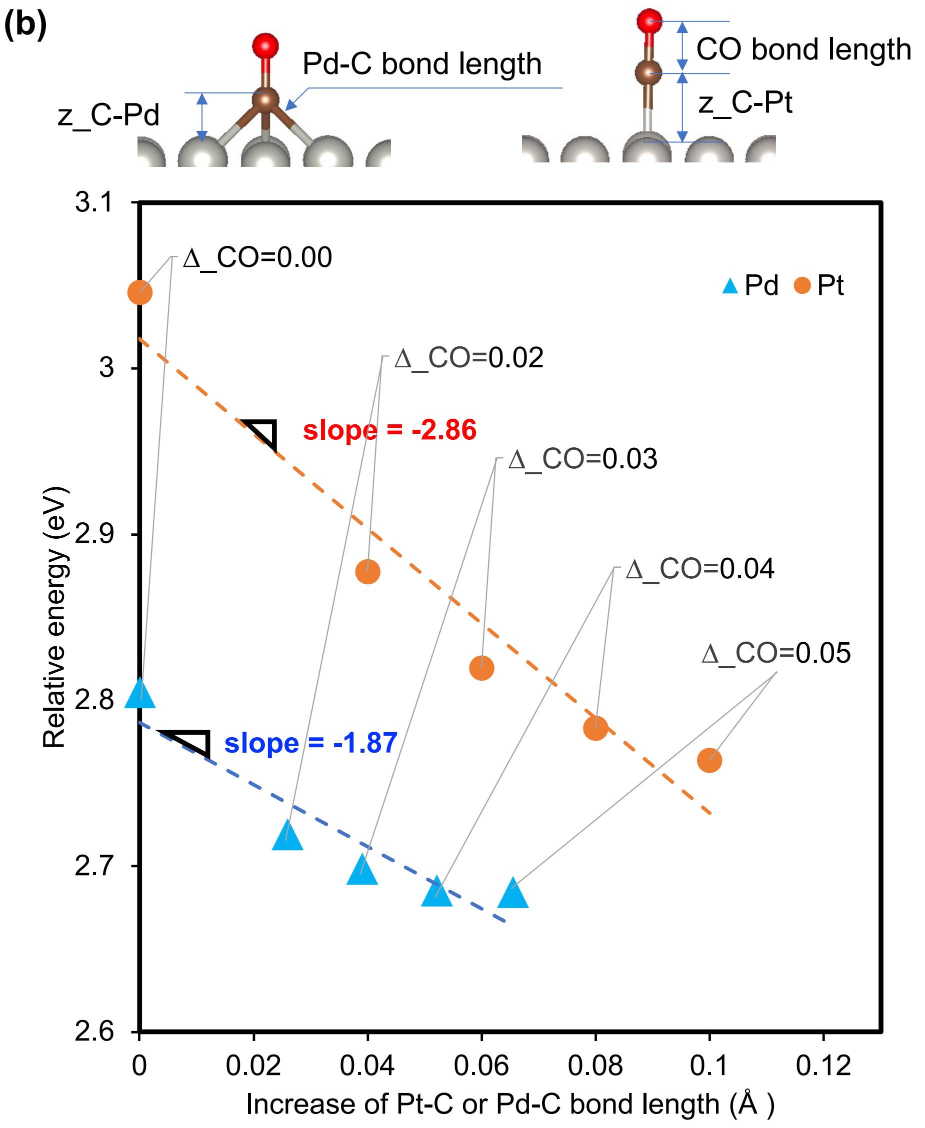


How energetic electrons couple with the Pt/Pd-CO bonds



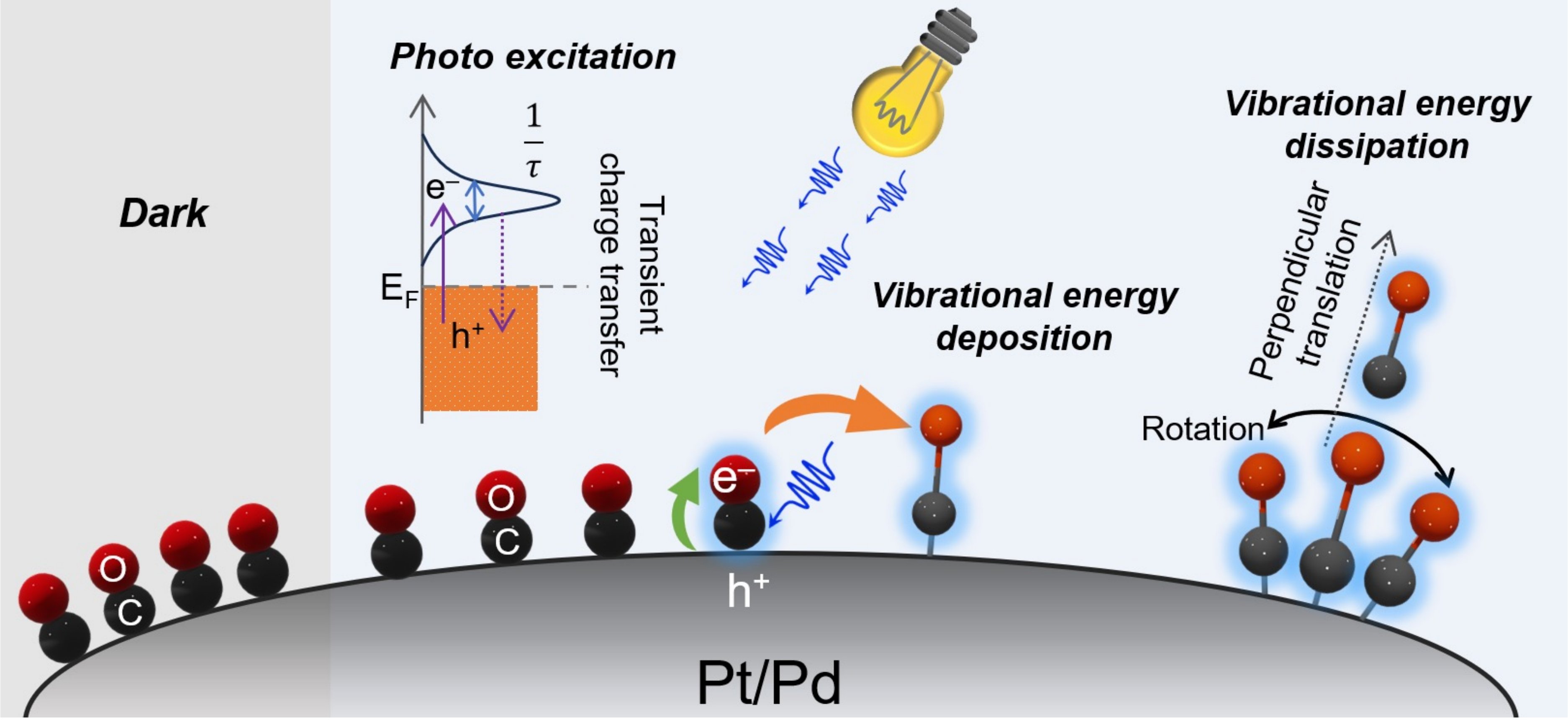
Coupling seems to be stronger for Pt-CO than Pd-CO, facilitating the desorption in the former case





Take home message II

Bond Selective Photochemistry at Metal Nanoparticle Surfaces



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ALUMNI

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