Science with TXPES: X-ray Photoelectron Spectroscopy (XPS) on Catalytically Active Surfaces

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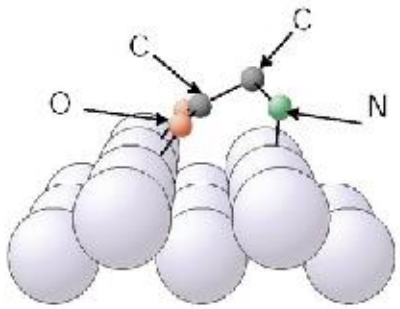
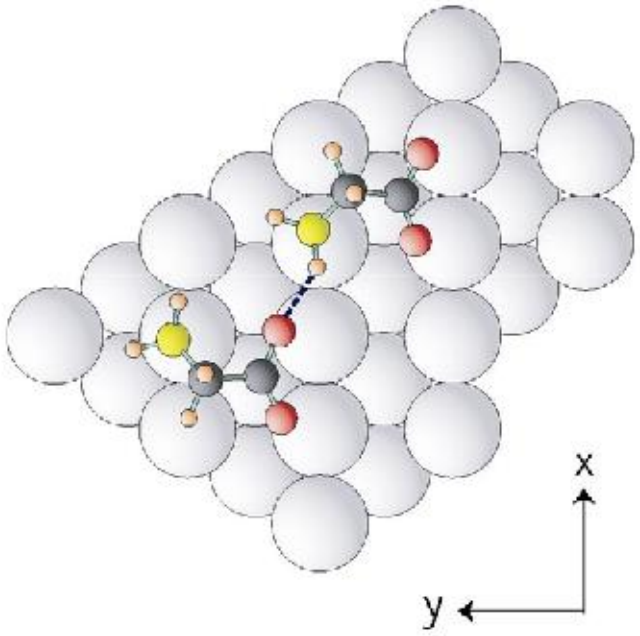
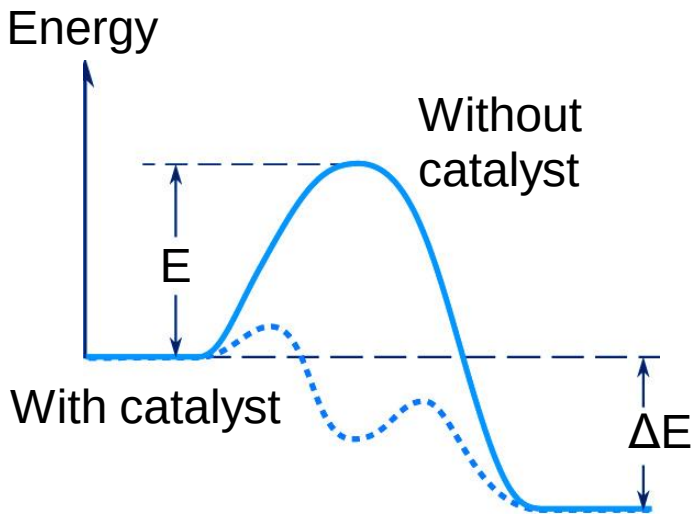
Surface Chemical Bond

How can we understand the nature of the chemical bonding between surfaces and adsorbates?



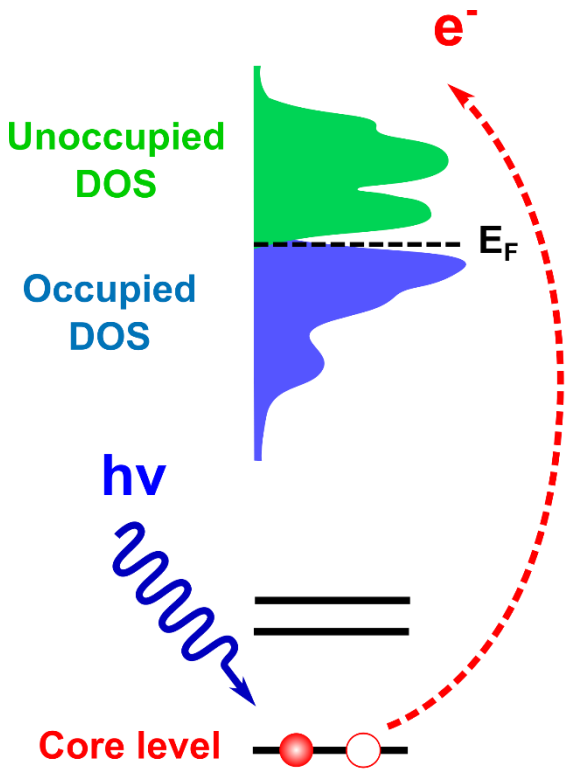




Elementary steps of catalytic conversion

- Molecular adsorption
- Dissociation
- Surface reaction
- Desorption

XPS Measurements (solid samples)



Ionization

X-ray Photoelectron Spectroscopy (XPS)

Energy balance

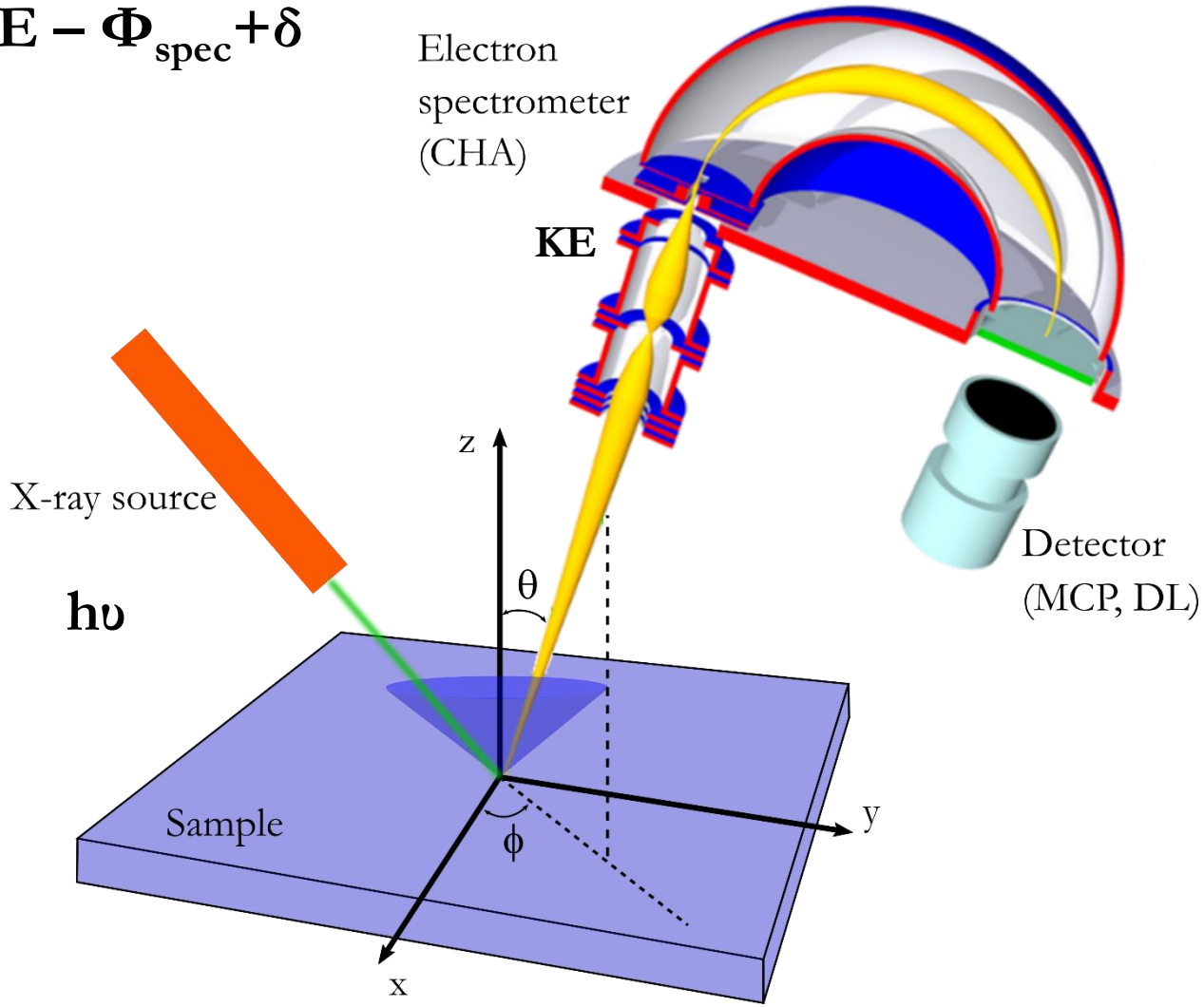
$$BE = h\upsilon - KE - \Phi_{spec} + \delta$$

$h\upsilon$ = excitation x-ray energy (fixed energy)

Φ_{spec} = electron spectrometer work function

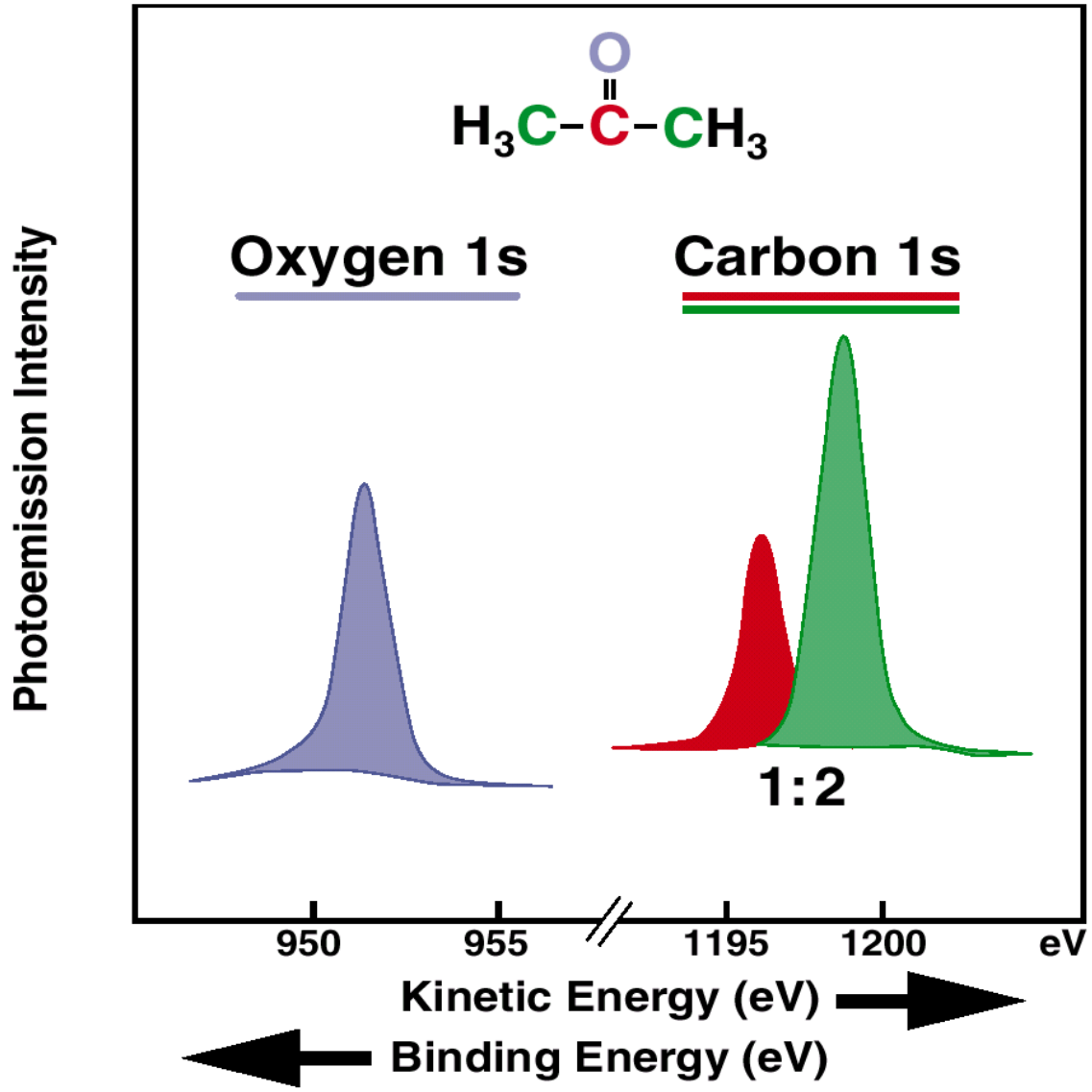
δ = net surface charge

•Reference of BE (zero BE) is the Fermi-level of the sample (and of the spectrometer)



Light Sources in the World

Chemical Shifts



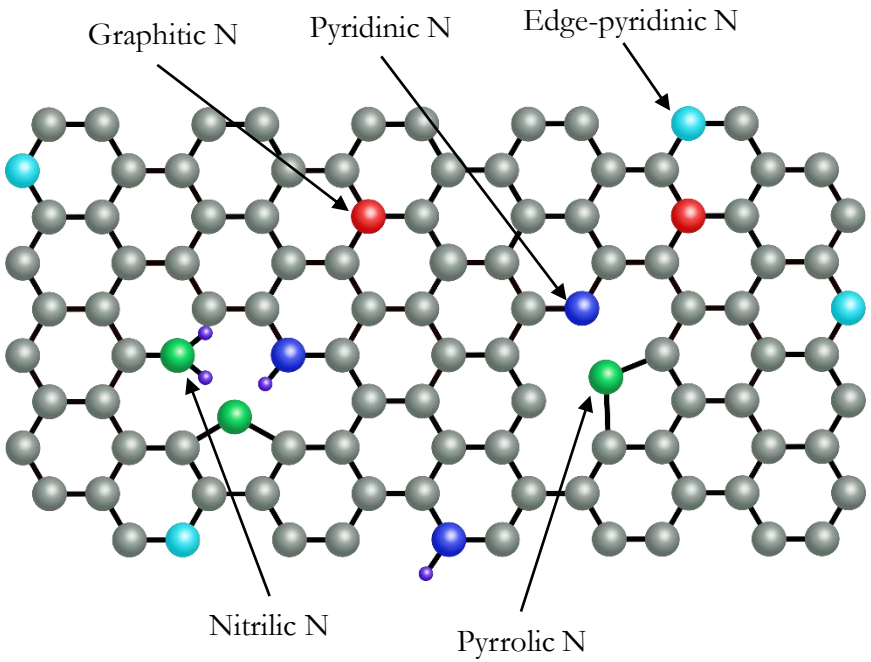
Provides information about

- Kind of atom
- Number of atoms
- Chemical shift

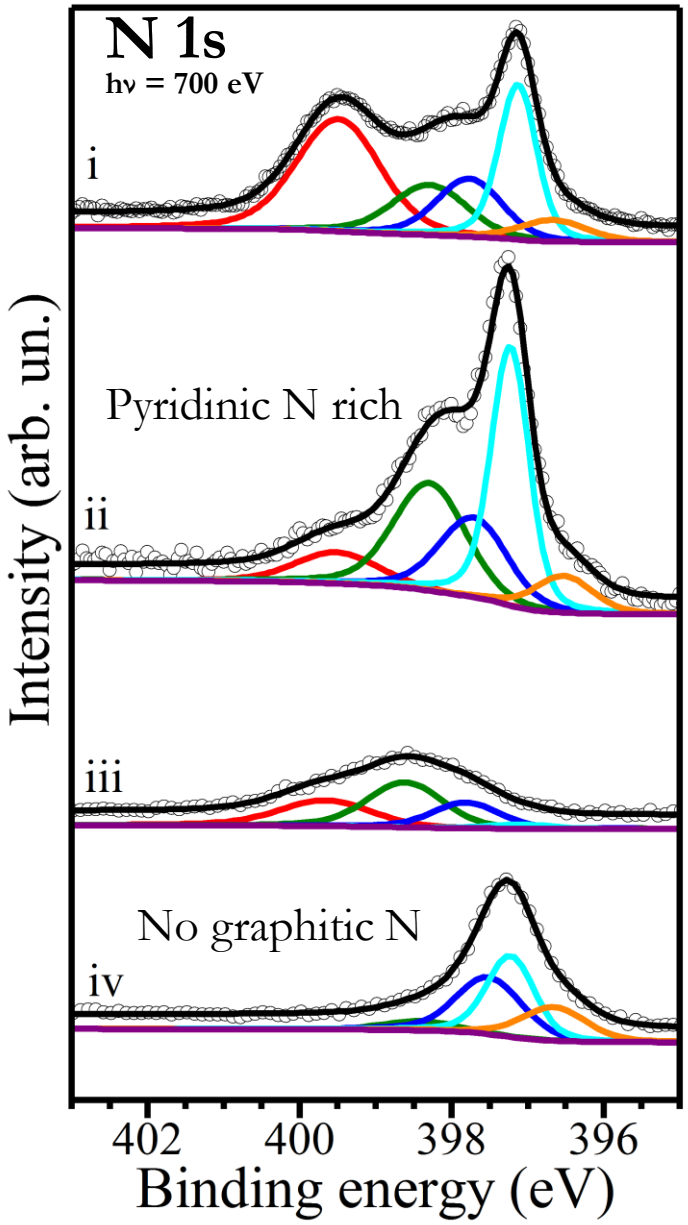
(Siegbahn et al.) Lab x-ray source: Resolution = ~ 0.5 eV (mono)

Chemical Shift: Nitrogen Doped Graphene

Different Nitrogen groups in N-doped Graphene: Ideal metal-free electrode material



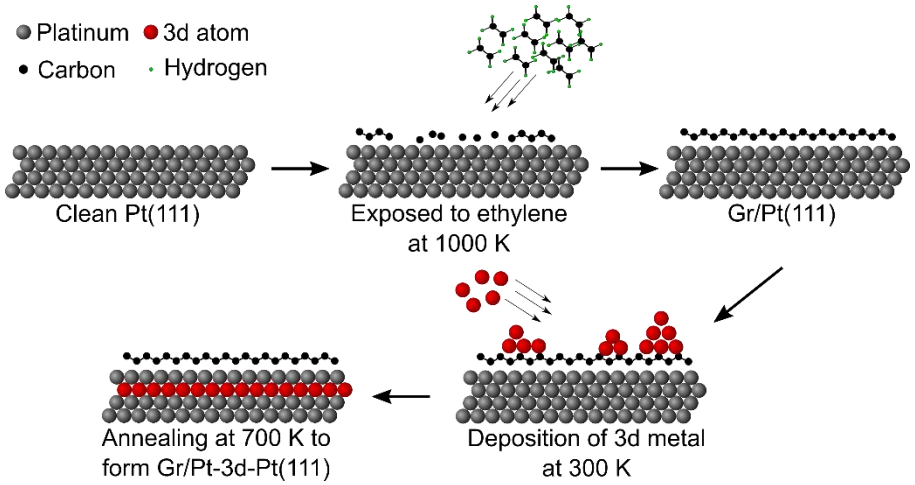
Graphitic N (n-type)
Pyridinic N (p-type) → Lewis basicity (electron donor)



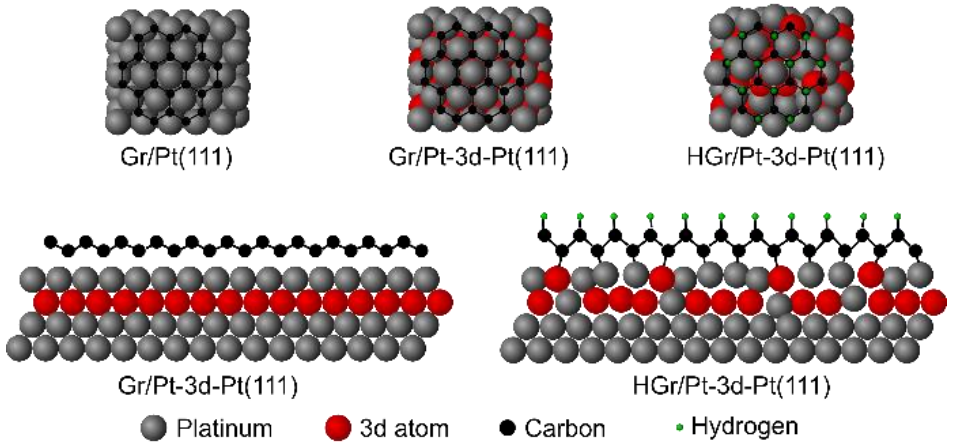
Appl. Surf. Sci., 495, 143518 (2019)

Hydrogenation of Single Layer Graphene on Subsurface Alloys

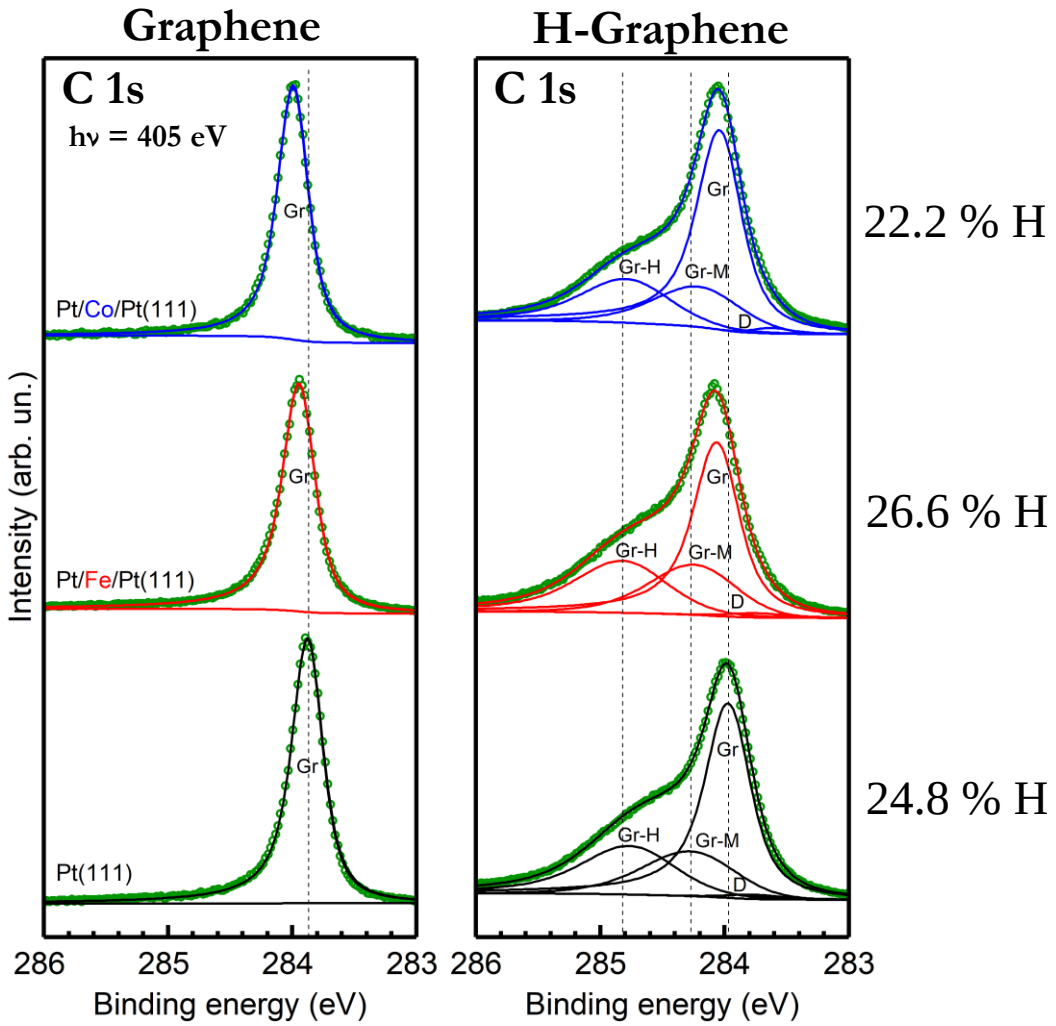
Fe and Co subsurface alloys on Pt(111)



Hydrogenation of graphene grown on subsurface alloys on Pt(111)



Carbon 170, 636 (2020)

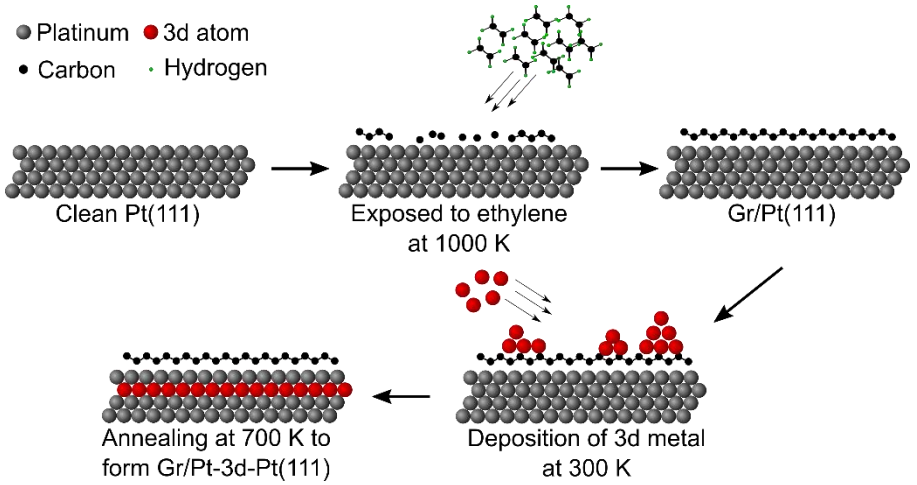


Peak shift: a measure of graphene surface interaction

H coverage can be quantified

Hydrogenation of Single Layer Graphene on Subsurface Alloys

Fe and Co subsurface alloys on Pt(111)



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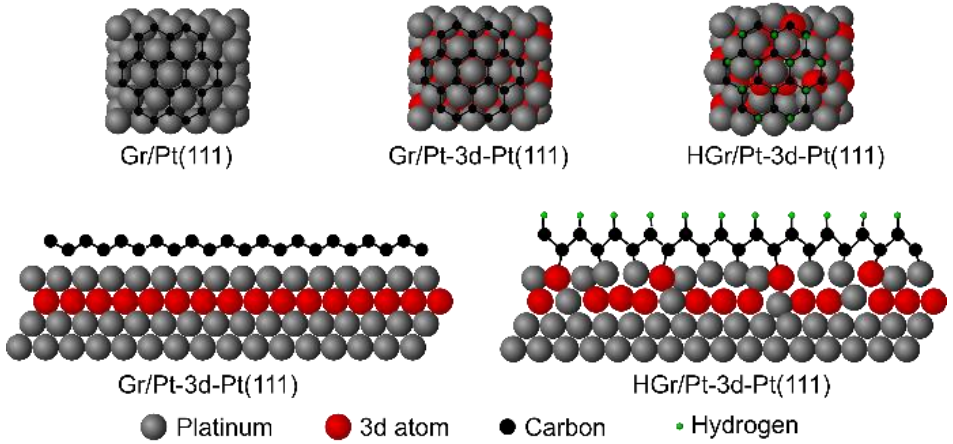
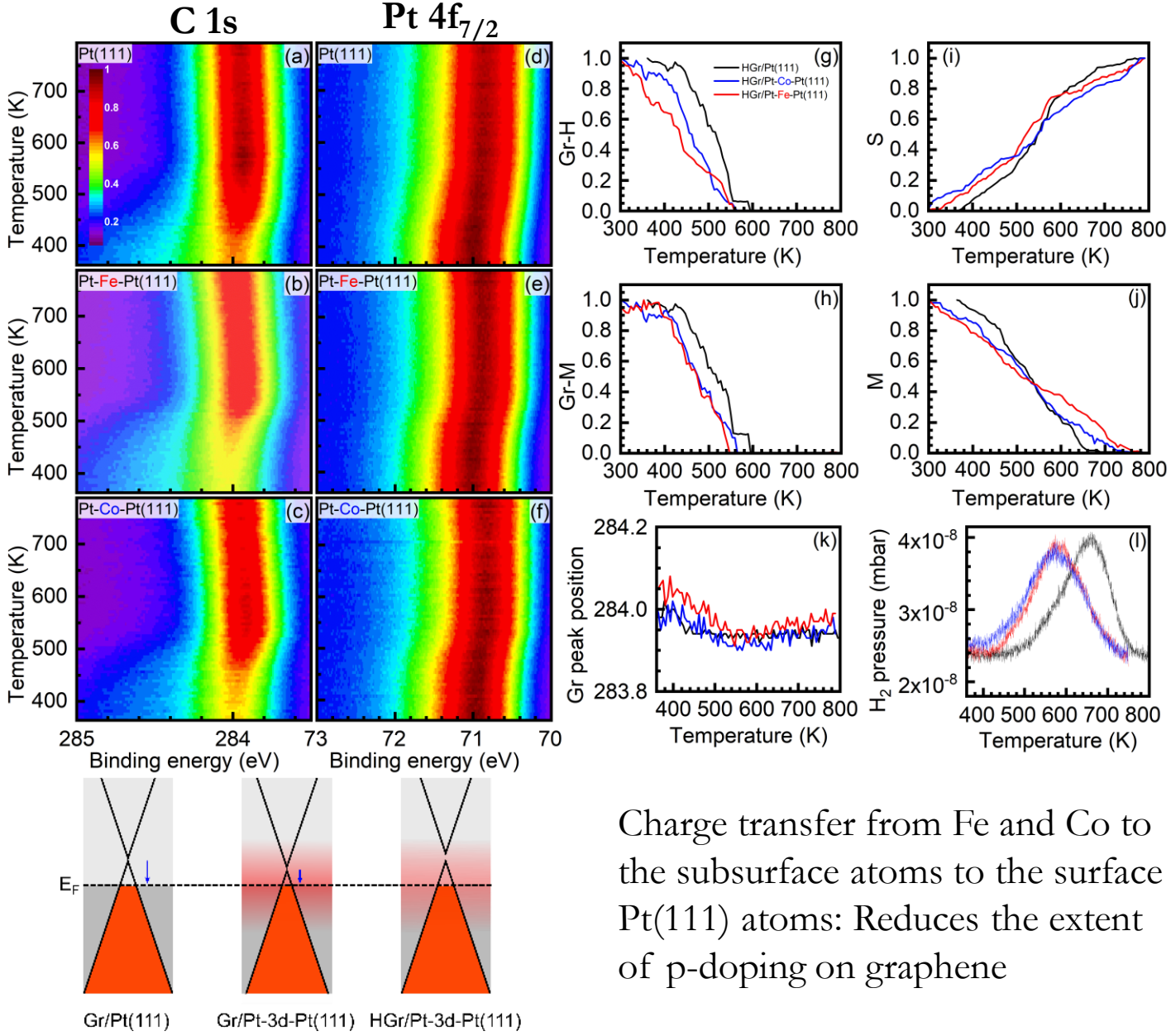
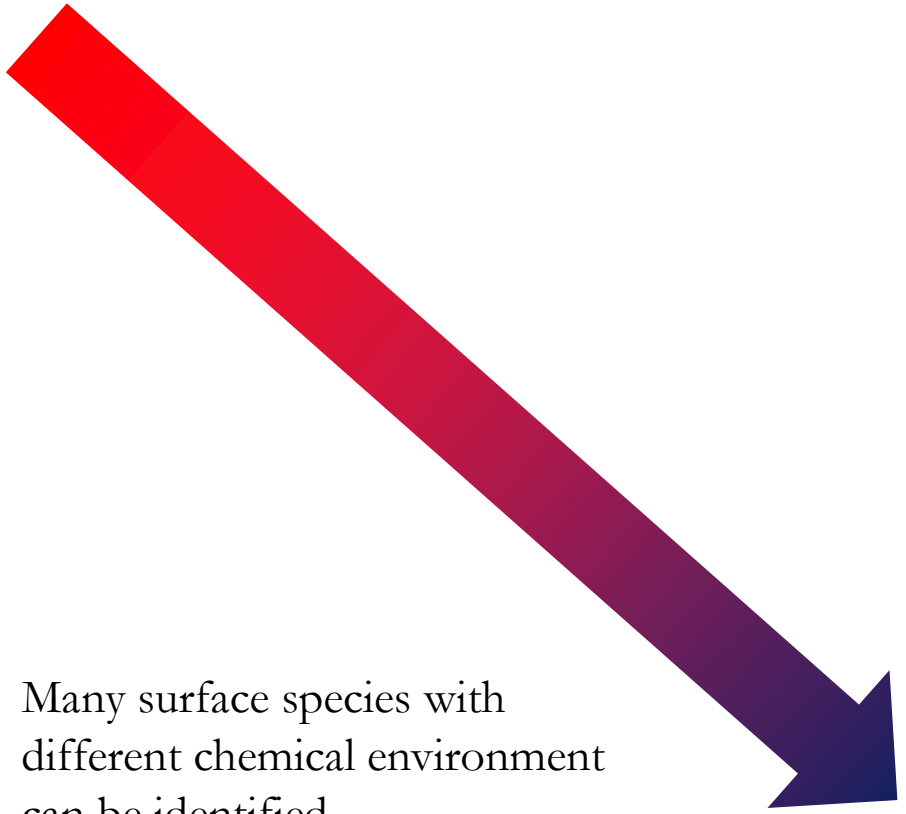


Carbon 170, 636 (2020)

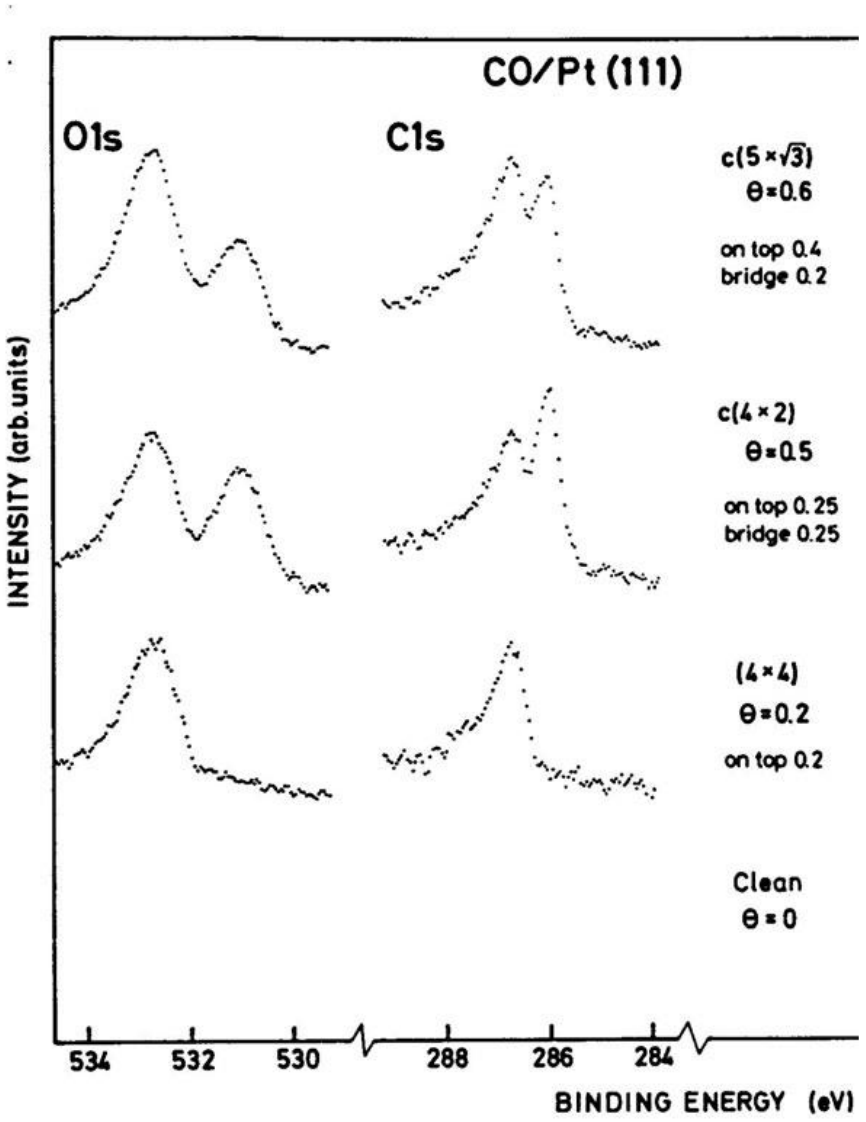


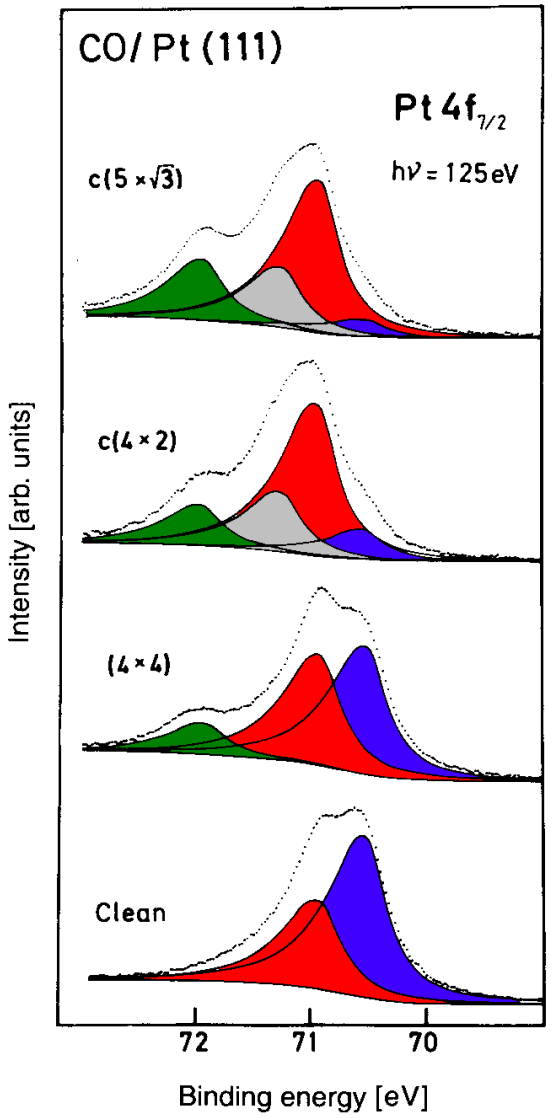
Charge transfer from Fe and Co to the subsurface atoms to the surface Pt(111) atoms: Reduces the extent of p-doping on graphene

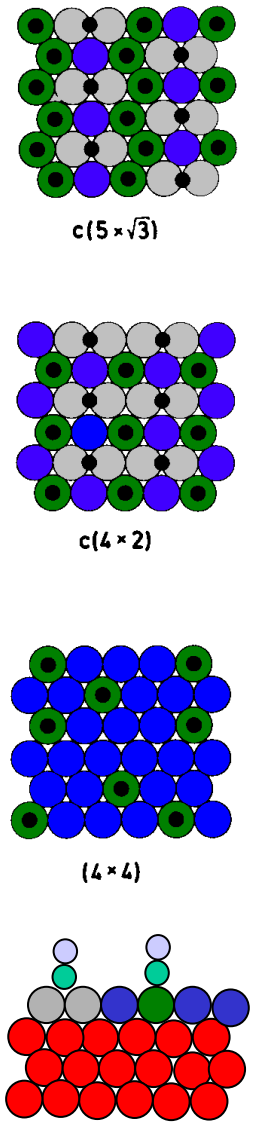
Chemical State of Carbon in Various Functional groups

C 1s binding energy									
Functional group	284	285	286	287	288	289	290	291	292
C=C C-(C,H,S,Si) C-N C-O C-Cl C=O CHF N-C=O O-C-O CO_3 CF_2									

XPS is structure sensitive: CO on Pt(111)

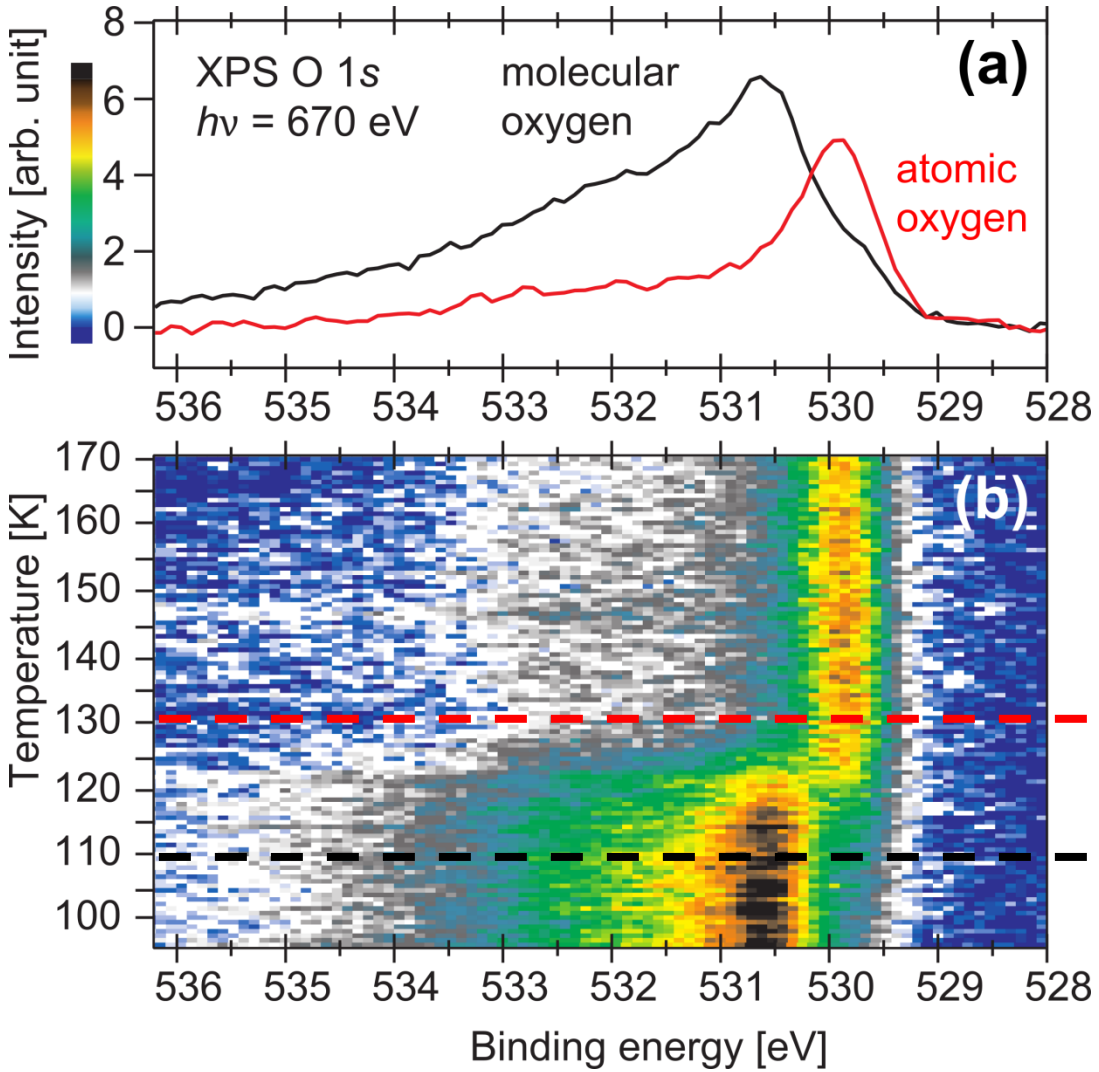


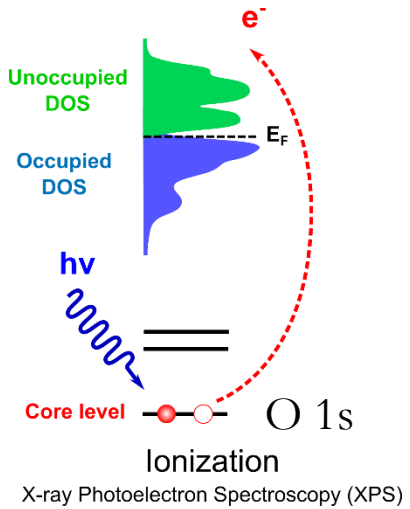




Surface Science, 315, L983 (1994)

O_2 dissociation on Pt(111)





0.20 ML
atomic oxygen

Completion ~ 130 K

Onset ~ 110 K

0.40 ML
molecular oxygen

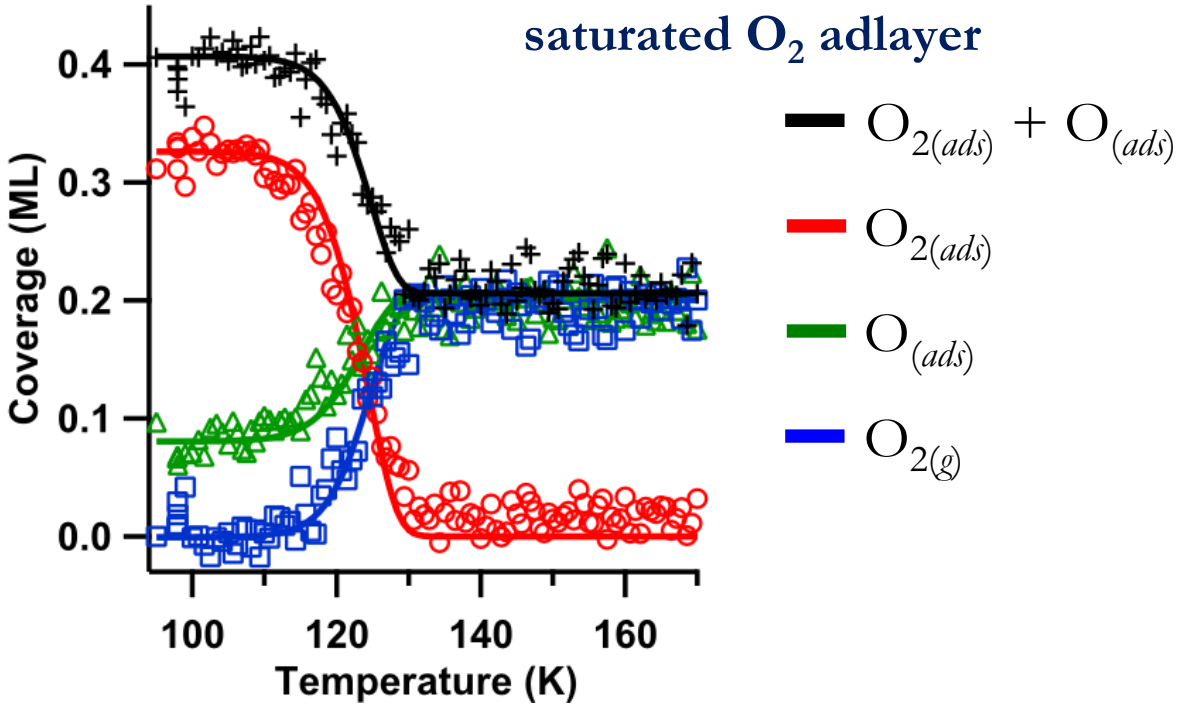
J. Chem. Phys., *133*, 224701 (2010)

Temperature ramp ~ 0.1 K/s = 0.7 K/sweep

O_2 dissociation on Pt(111)

Desorption and dissociation are competing

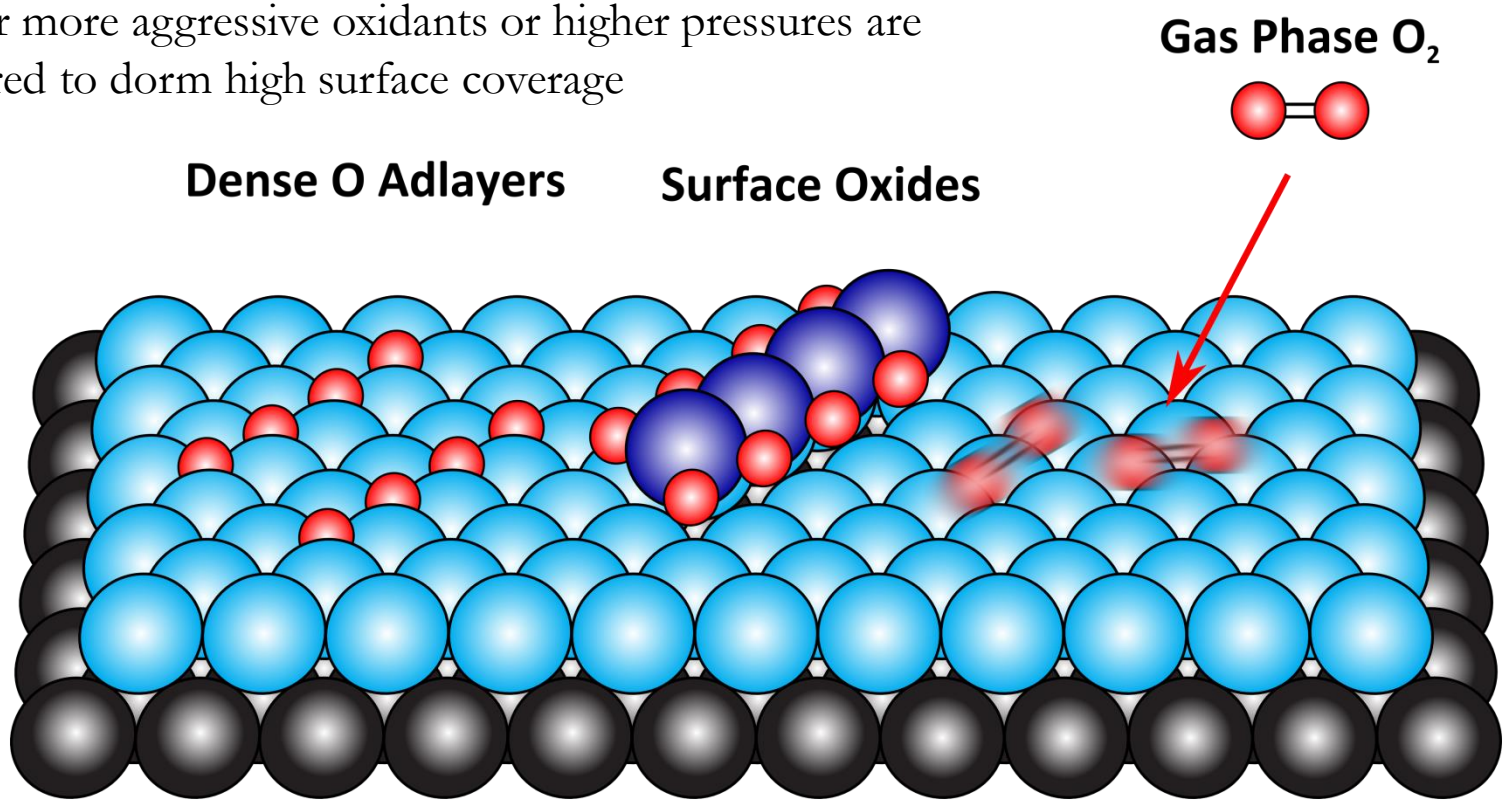
Mean-field simulations of a saturated O_2 adlayer



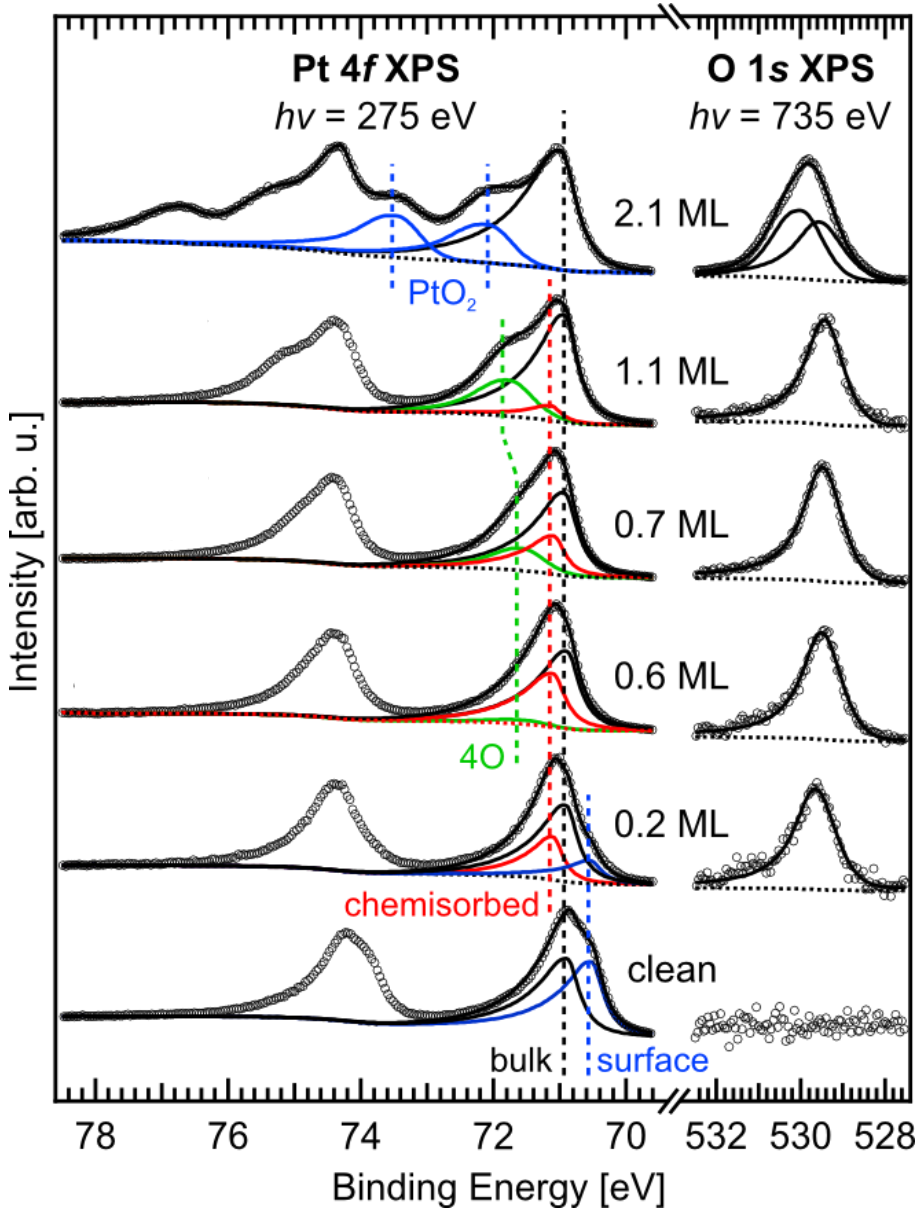
	Constrained	Floating
Dissociation $O_{2(ads)} + Pt \rightarrow 2O_{(ads)}$	$\nu_{diss} = 10^{11}$–10^{13} s^{-1}	$E_{diss} \sim 0.32 \pm 0.03$ eV
Desorption $O_{2(ads)} \rightarrow O_{2(g)} + Pt$	$\nu_{des} = 10^{13}$ s^{-1}	$E_{des} \sim 0.37 \pm 0.01$ eV

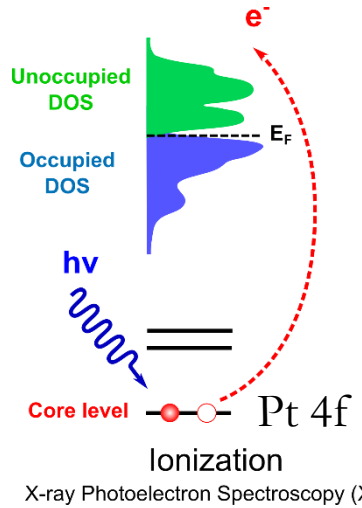
Adlayers and Oxides

Either more aggressive oxidants or higher pressures are required to dorm high surface coverage



Oxide Formation on Platinum Surface



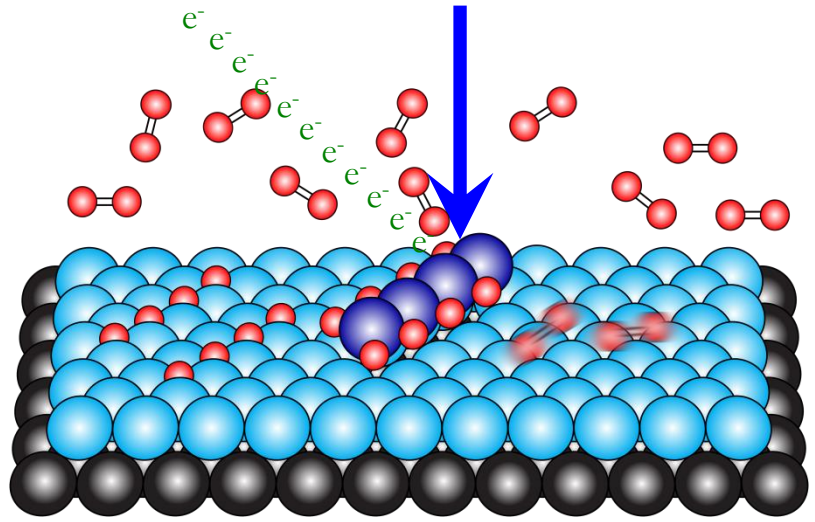


X-ray Photoelectron Spectroscopy (XPS)

Surface oxide formation and transformation to the Pt bulk oxide on Pt(111) in ambient conditions.

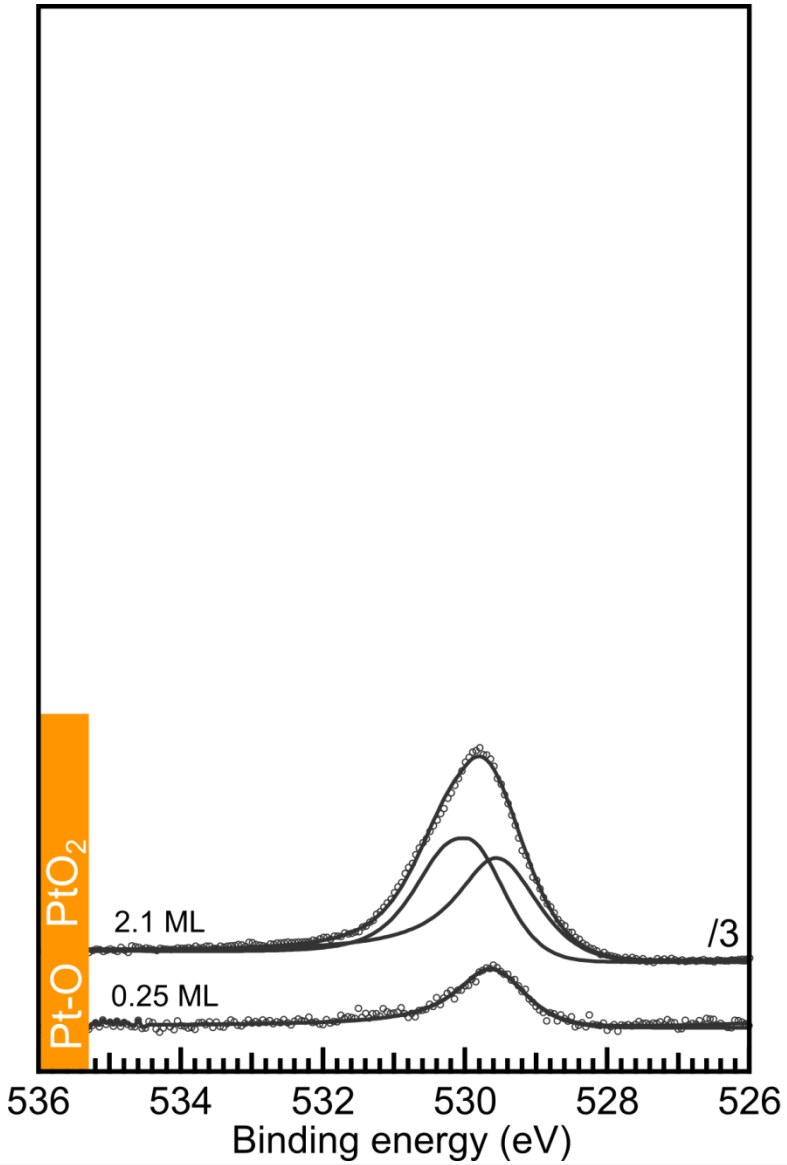
Pt 4*f*/O 1*s* XPS **$h\nu$ = 275 or 735 eV**

K.E. ~ 200 eV normal incidence



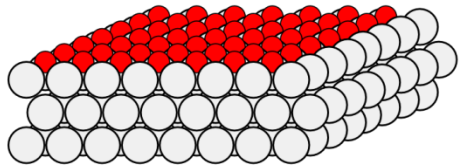
Phys. Rev. Lett. 107, 195502 (2011).

Species on Platinum



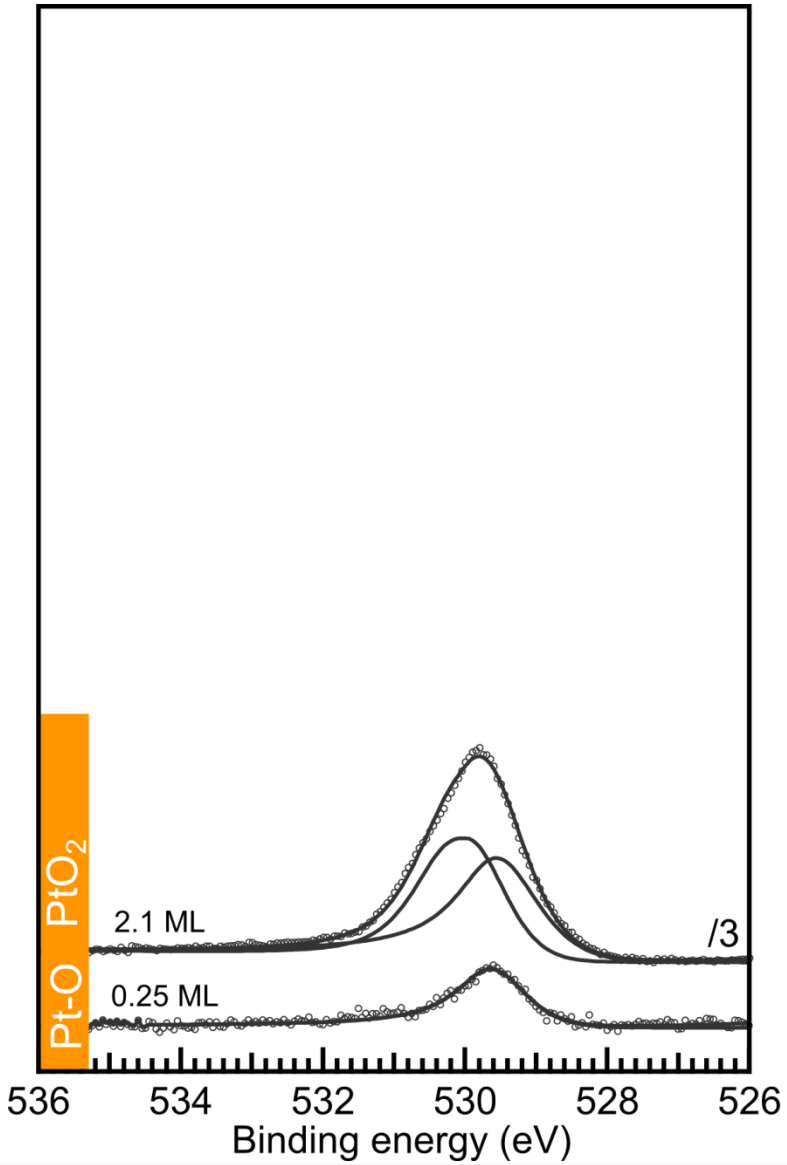
Various adsorbate species can be stabilized on Pt(111) under high temperature and pressure conditions.

UHV



Chemisorbed O surface oxide

Species on Platinum



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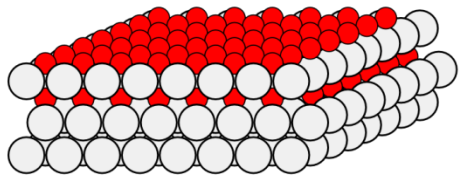
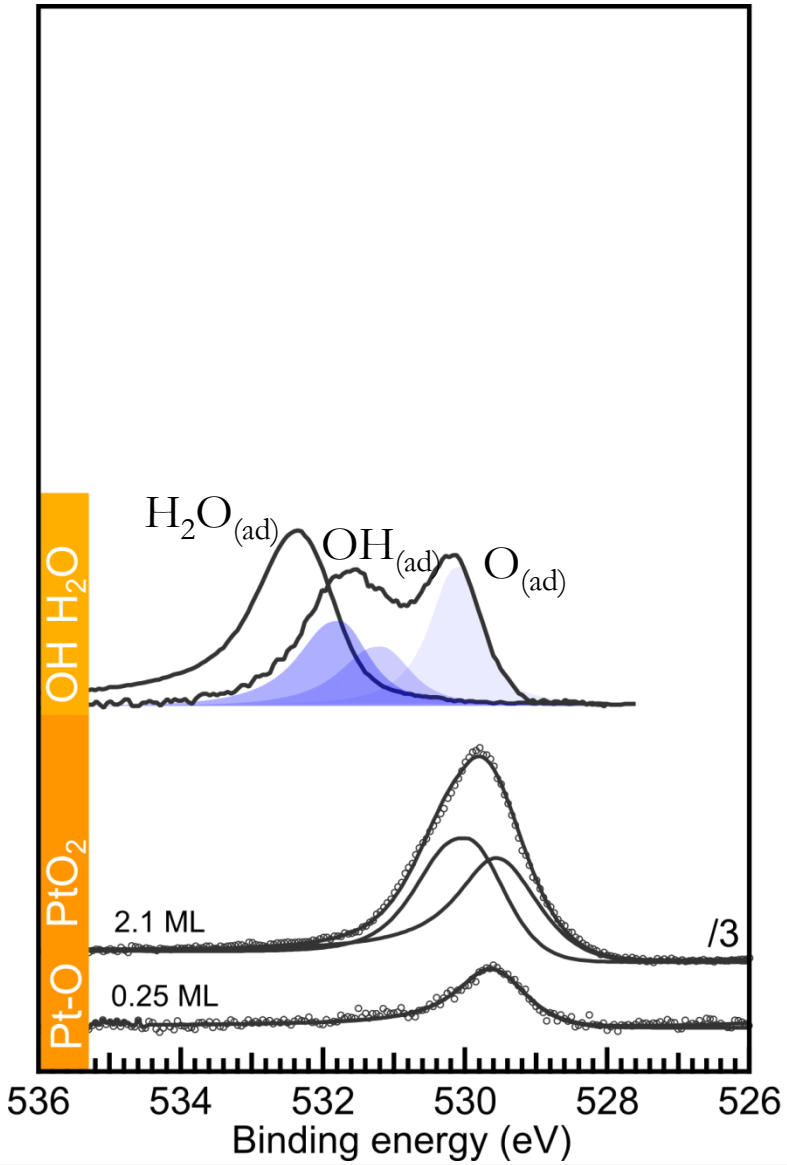


Chemisorbed O surface oxide

Species on Platinum



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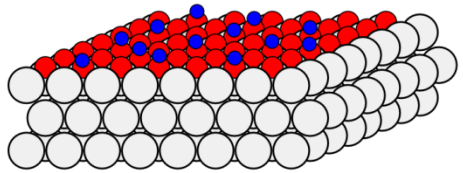
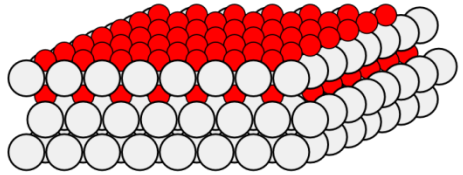


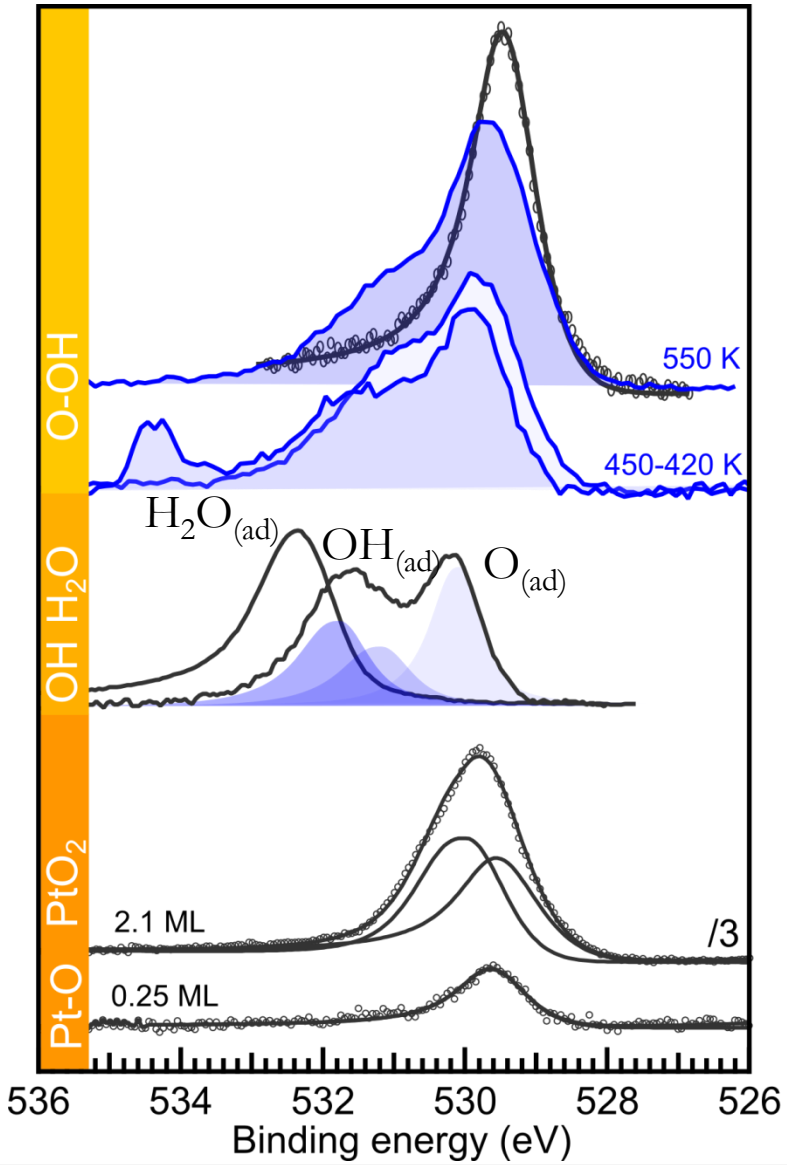
Chemisorbed
O-OH biphase

UHV



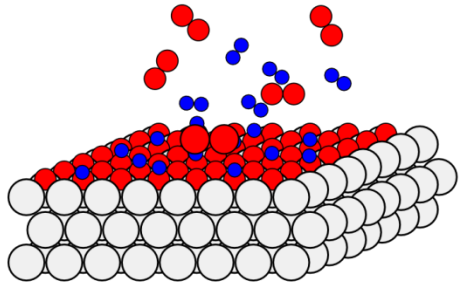
Chemisorbed O
surface oxide

Species on Platinum

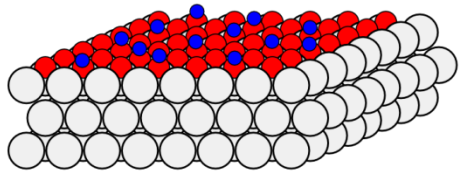


Various adsorbate species can be stabilized on Pt(111) under high temperature and pressure conditions.

Ambient

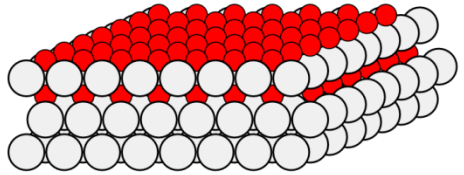


O-OH-H_2O



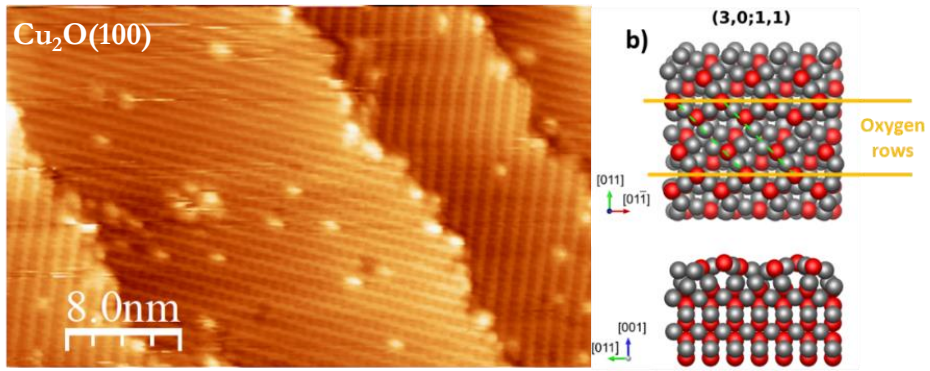
Chemisorbed O-OH biphase

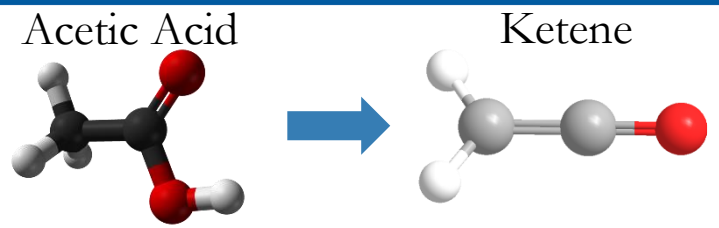
UHV

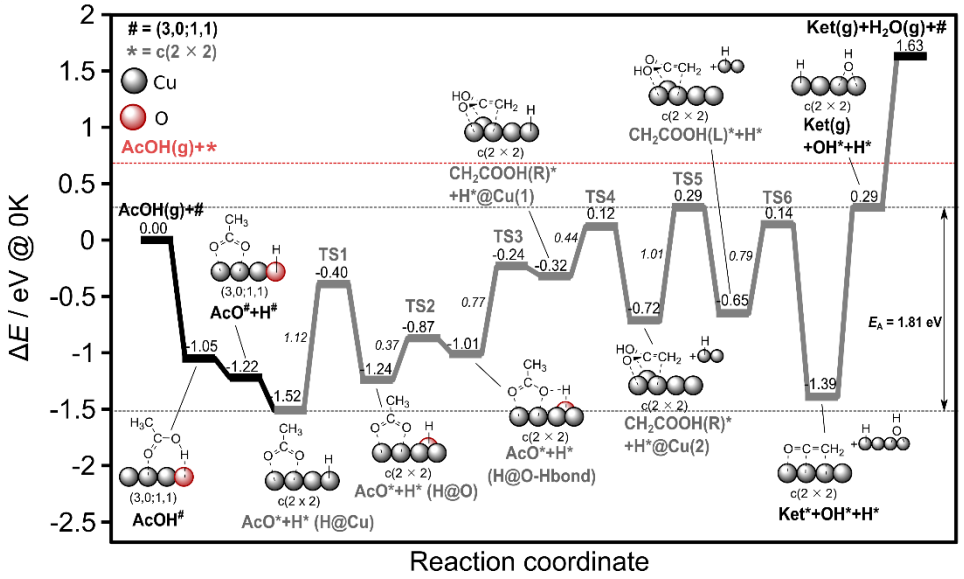


Chemisorbed O surface oxide

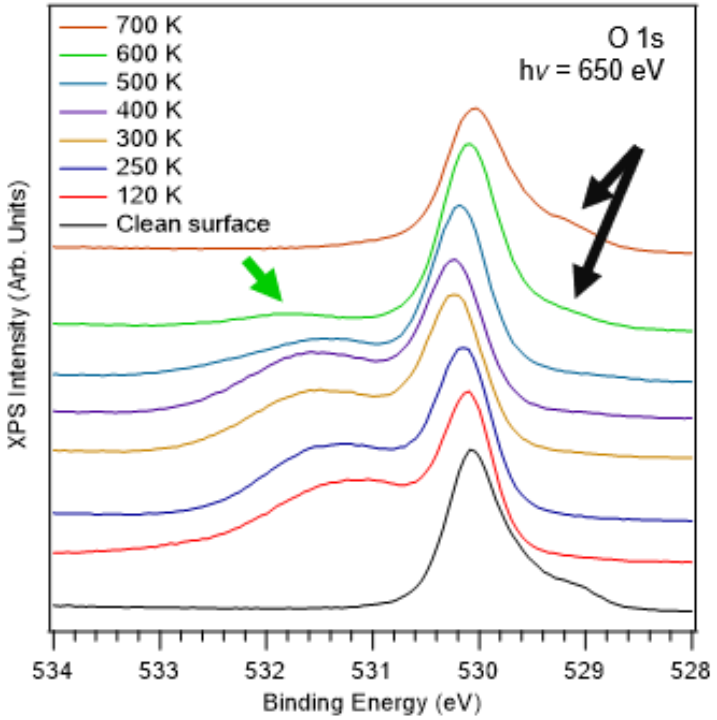
Chemical Conversion: Acetic Acid Conversion to Ketene on $Cu_2O(100)$



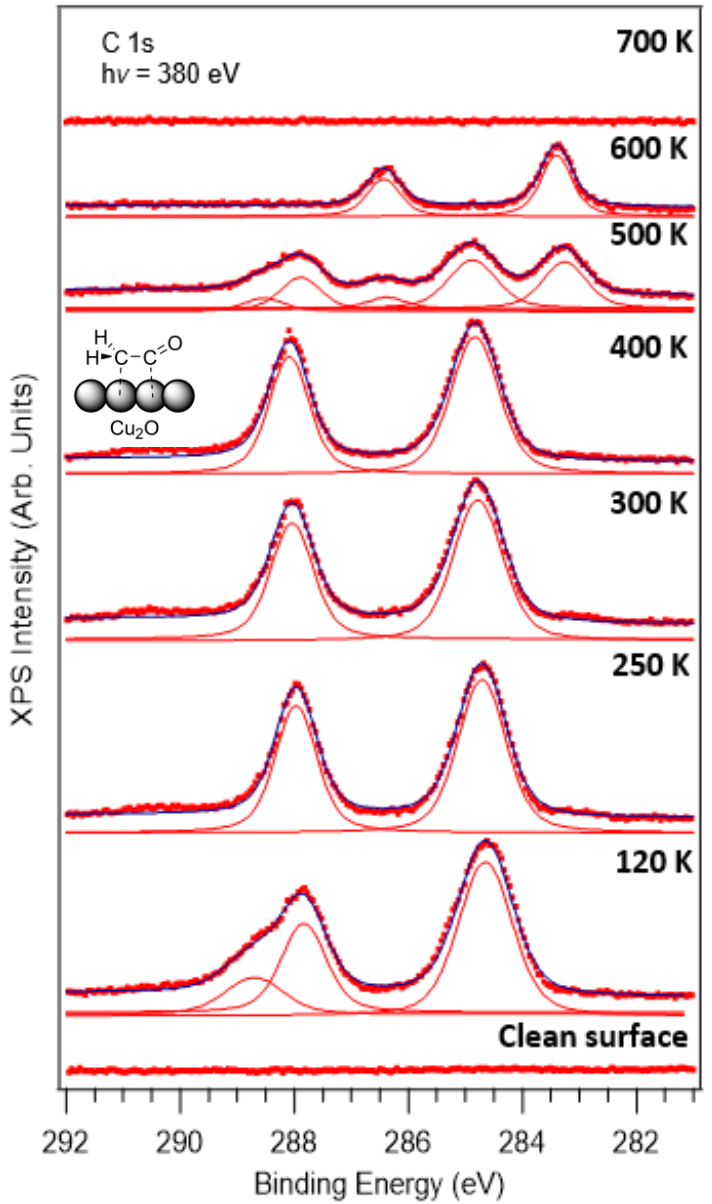




Mechanism of acetic acid conversion to ketene over $Cu_2O(100)$

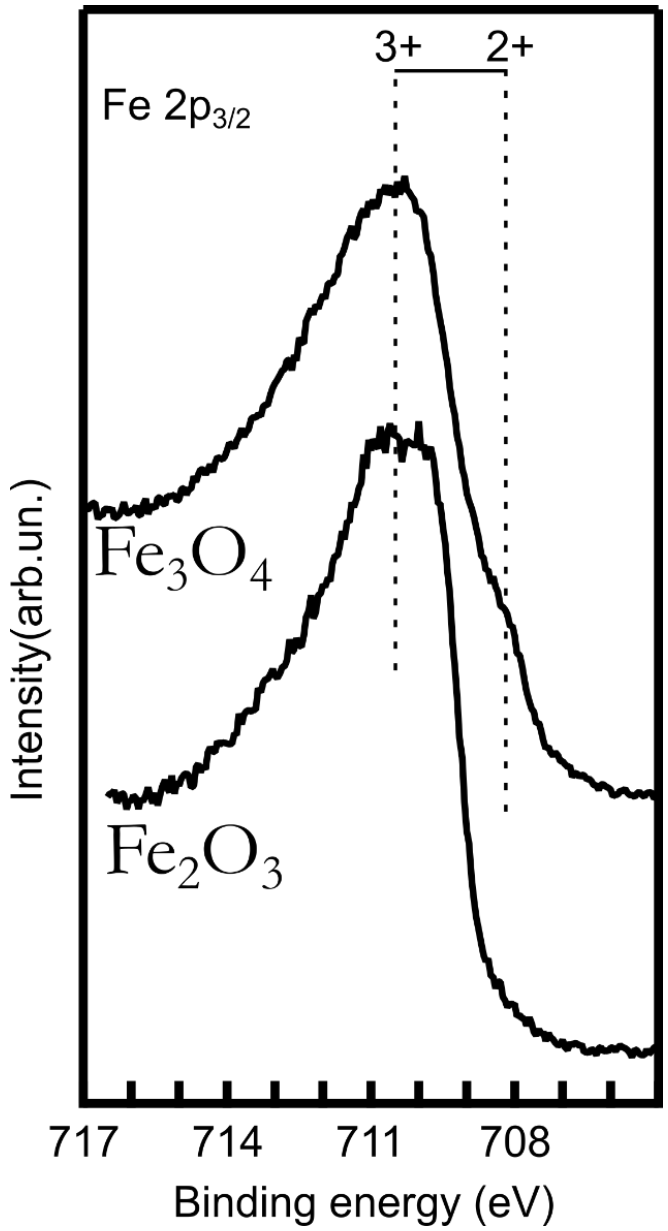


Reaction intermediate binds via all C and O atoms to Cu surface sites



Journal of Catalysis, 402, 154 (2021)

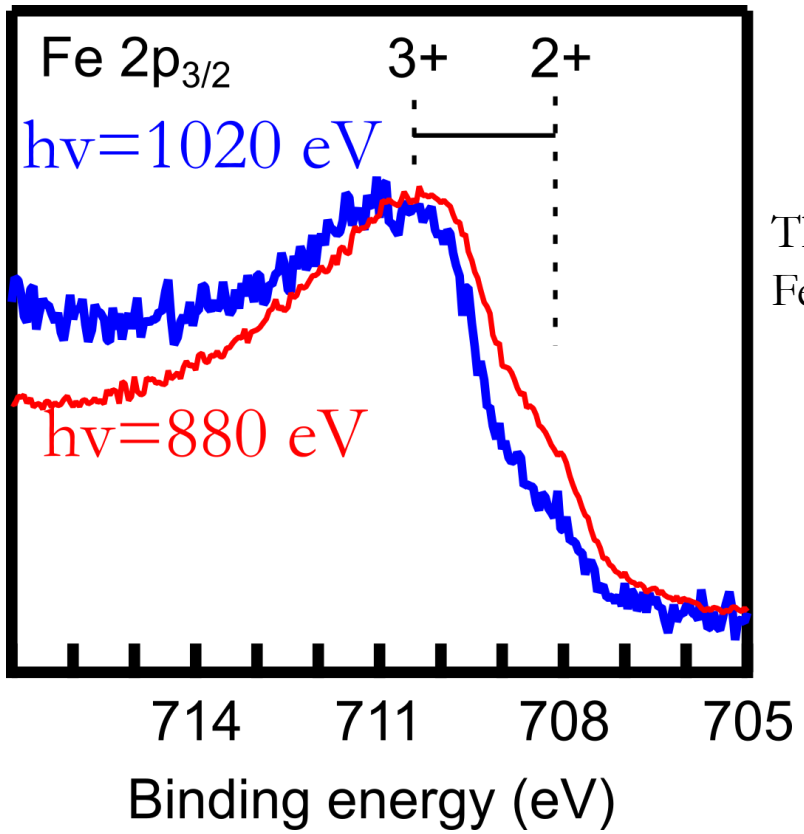
Identifying the Surface: Photon Energy



$$BE = h\upsilon - KE - \Phi_{spec} + \delta$$

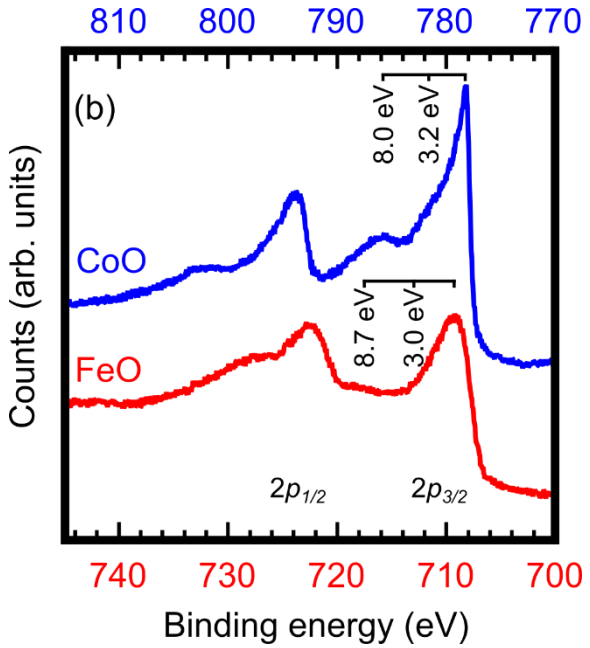
~711 eV ? 100-200 eV

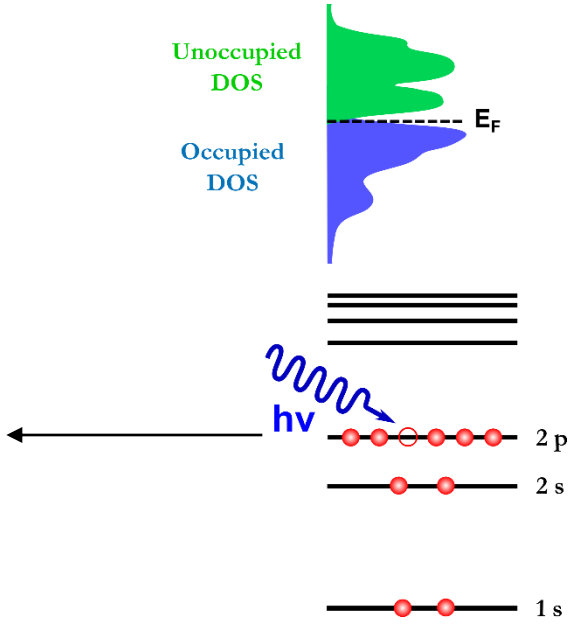
Fe_3O_4

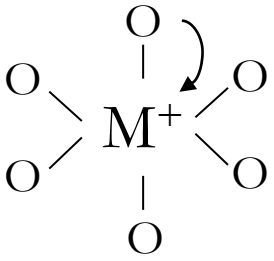


The surface of Fe_3O_4 is Fe^{2+} rich

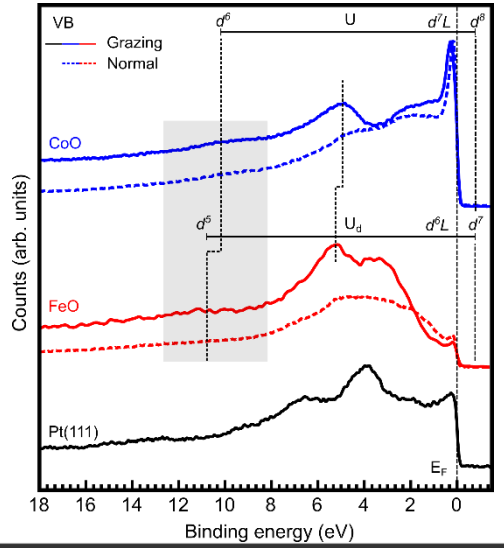
Satellites, more





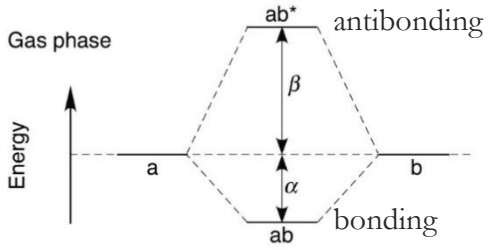


Ligand to metal charge transfer

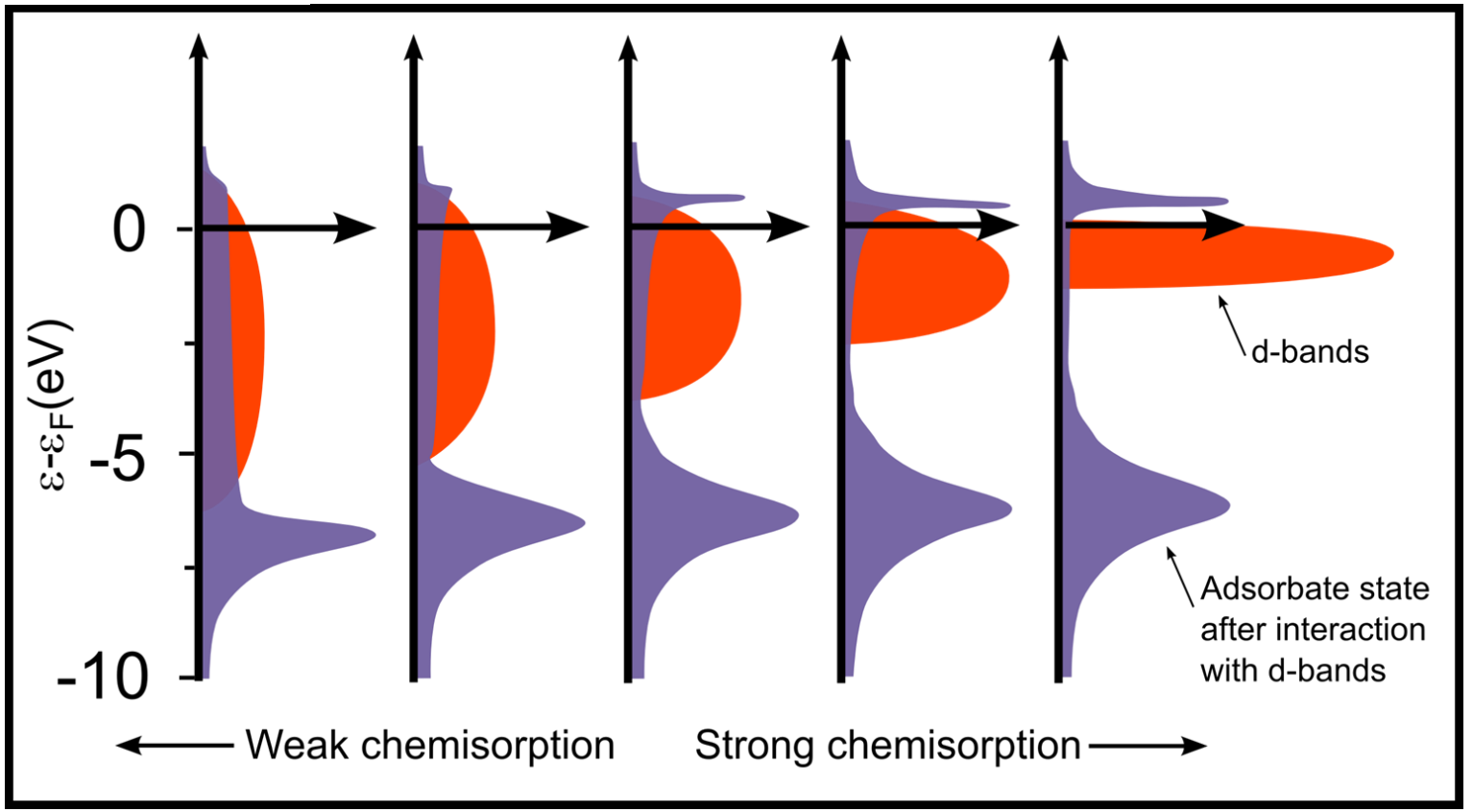


The final state of the photoemission process contains a core hole which is coupled with the partially filled TM 3*d* states, giving rise to mainline broadening and satellite features in XPS spectra depending on the particular overlap between core levels and the valence states.

d-band center



Position of the d-band center determines the strength of the adsorbate-metal bonding

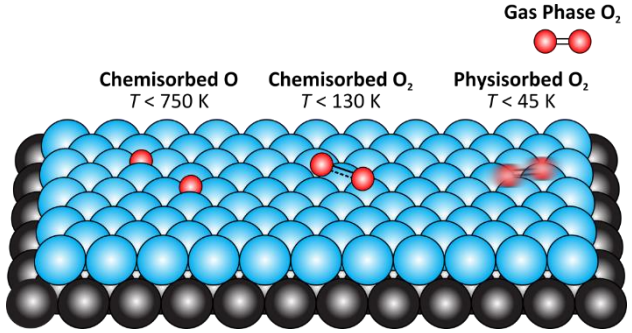


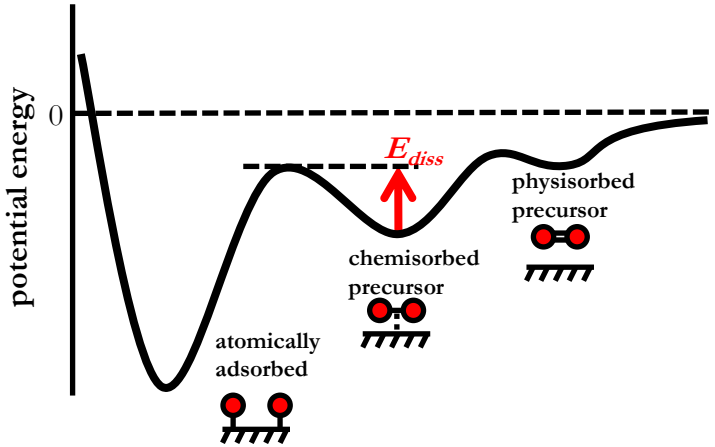
Hammer and Nørskov

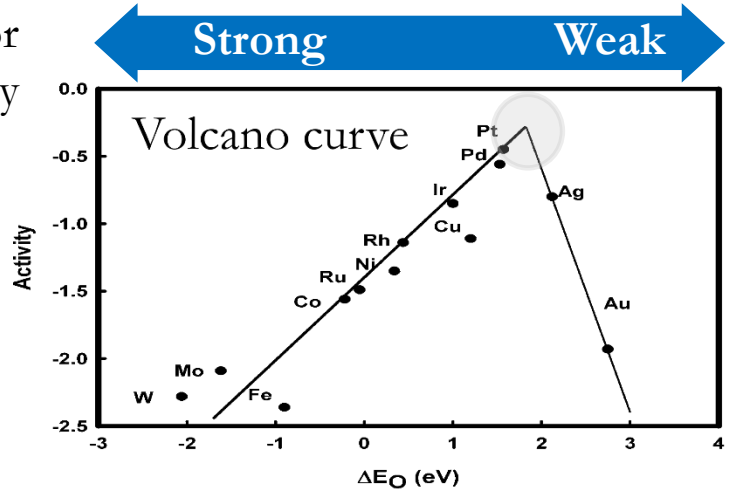
Scaling Relationships

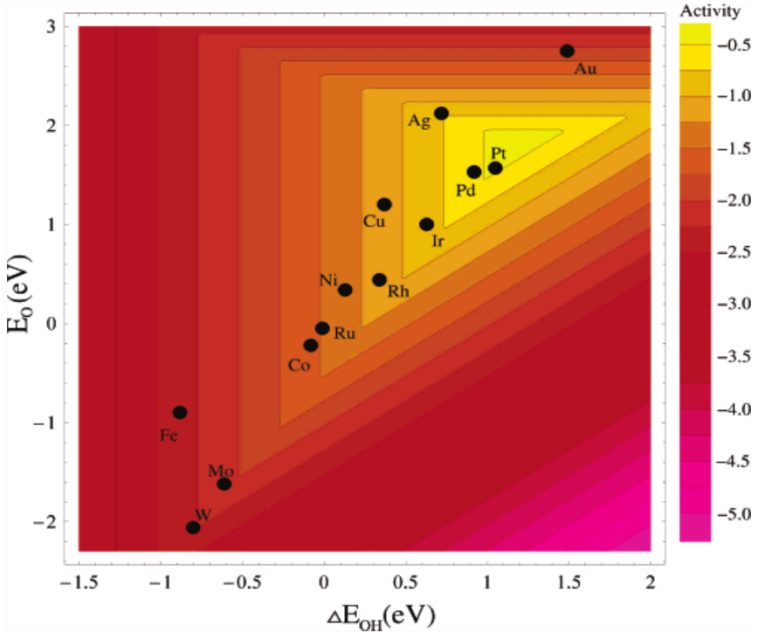
Trends in catalytic activity are also valid for adsorption binding energy

Example: oxygen adsorption



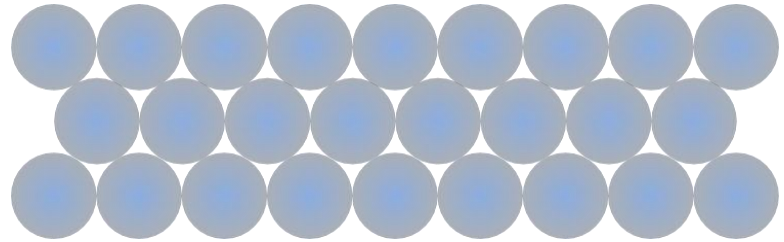




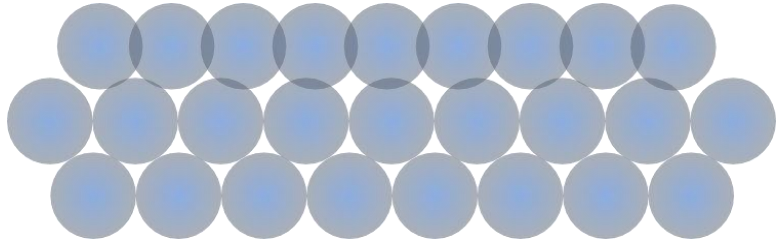


Strain and Ligand Effects

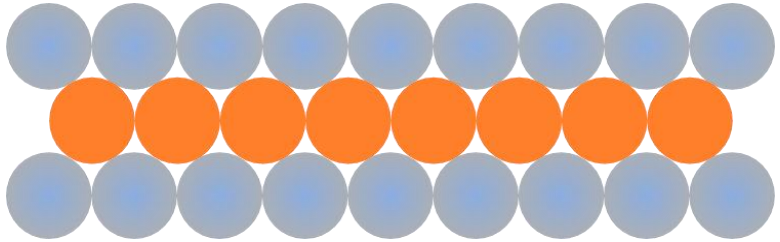
Strain and ligand effects modify the electronic structure of the catalytically active materials



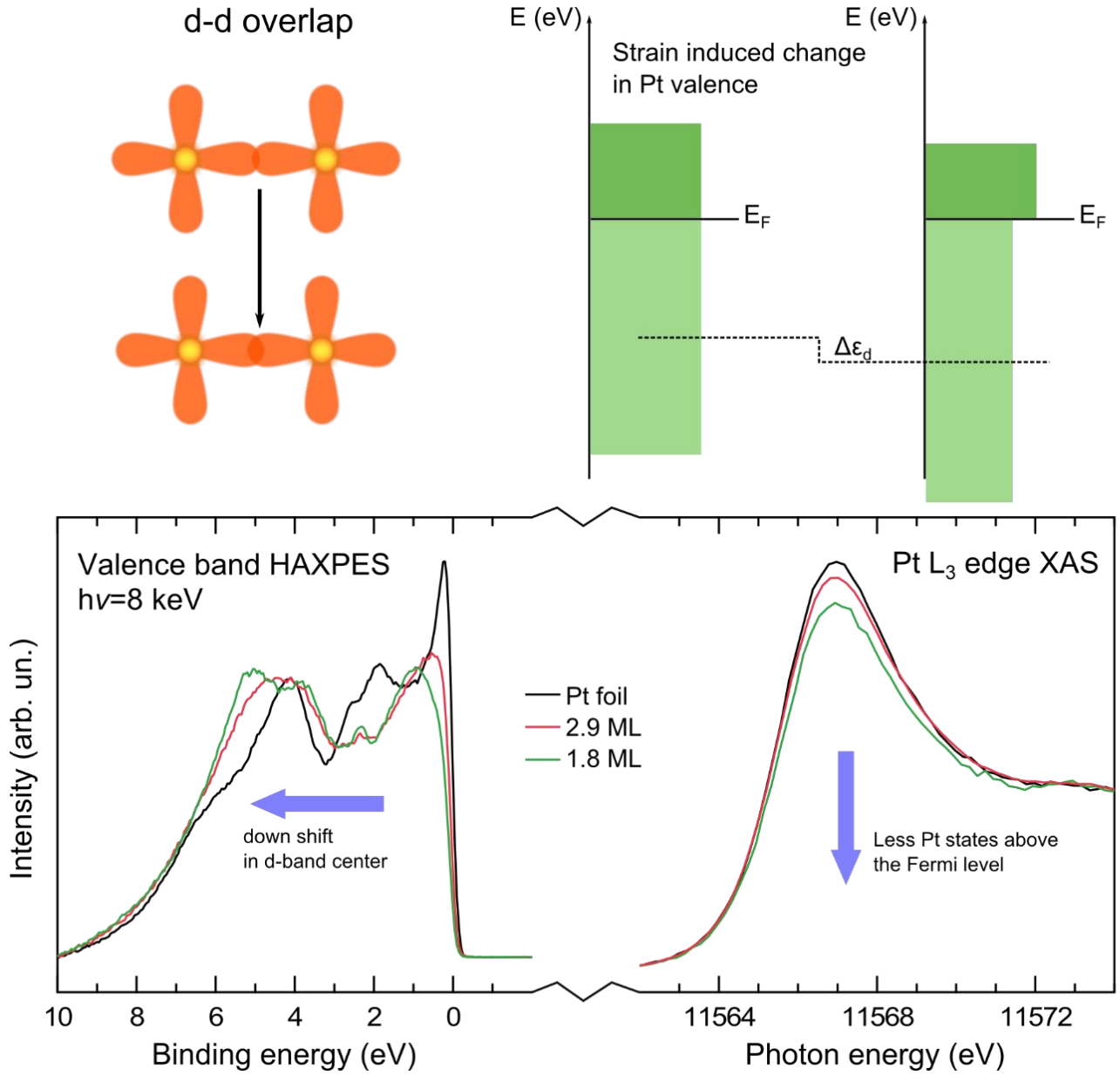
Strain



Ligand



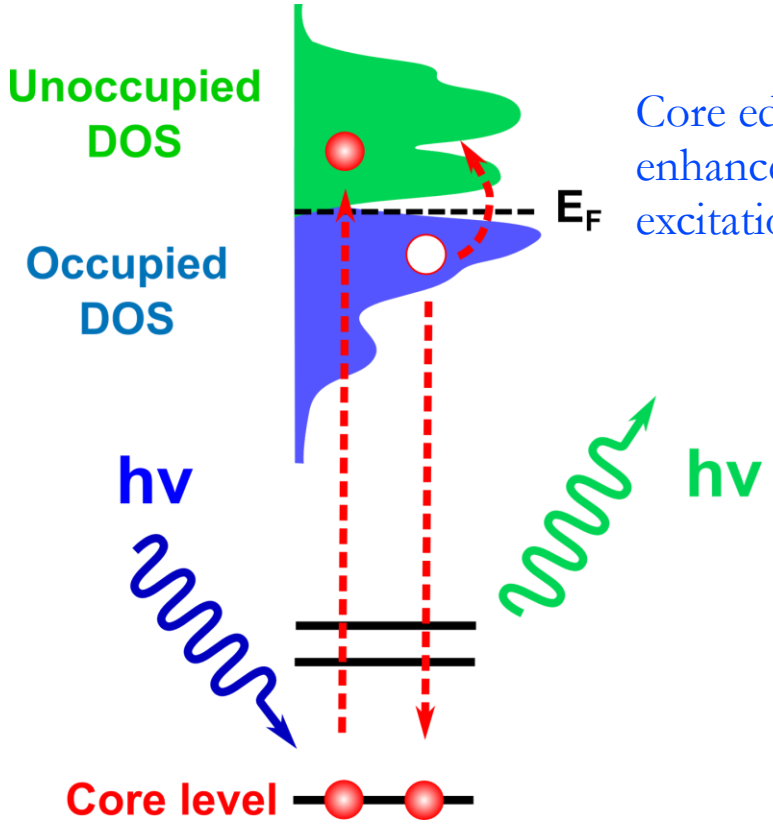
d-band Center



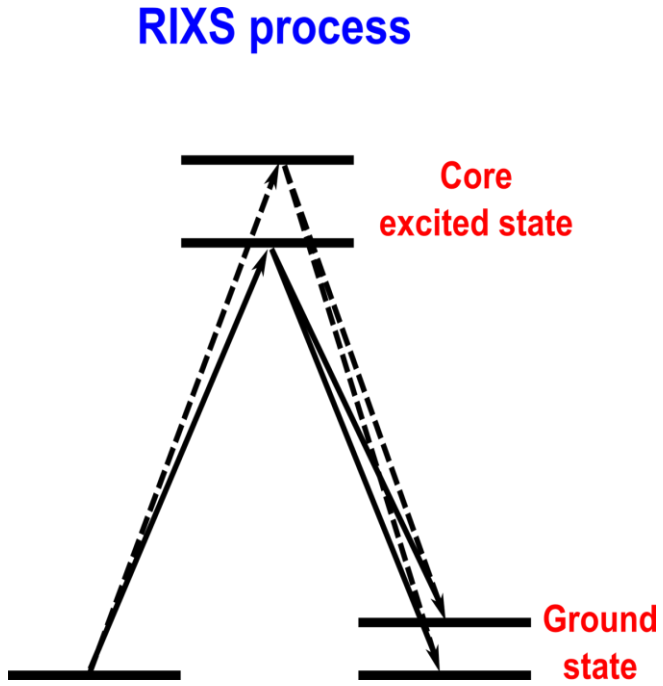
Strain induced change in the overlap between d-states leading to a change in the d-band width.

Change in the d-DOS, shift of the d-band center can be probed by spectroscopy.

X-ray Absorption and Emission Spectroscopy (XAS-XES)



Core edge resonance enhanced valence band excitation



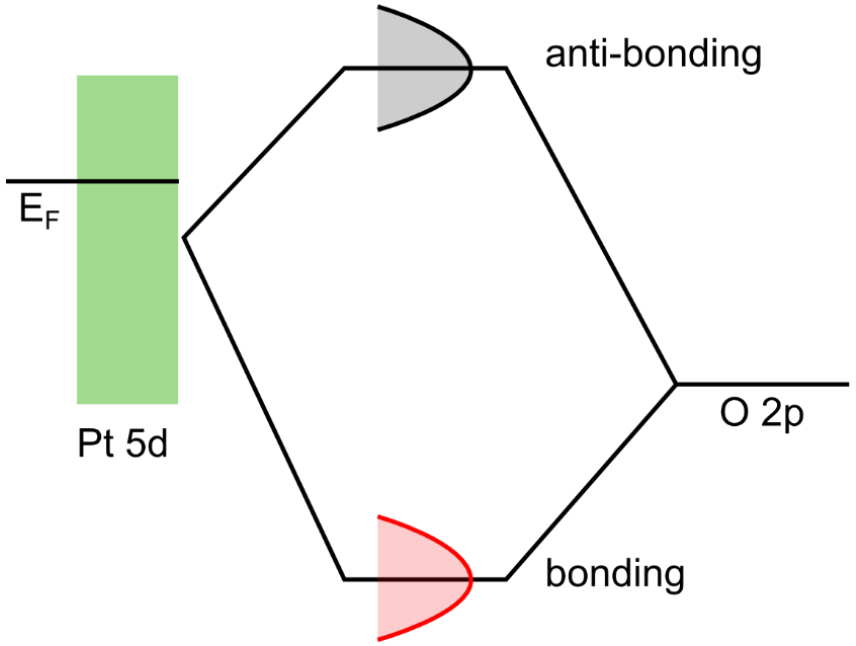
Kremers-Heisenberg formula

$$F(v,v') = \sum_f \left| \sum_m \frac{\langle f \mid r \mid m \rangle \langle m \mid r \mid i \rangle}{E_i + v - E_m - \Gamma_m} \right|^2 \delta\left(E_i + v - E_f - v'\right)$$

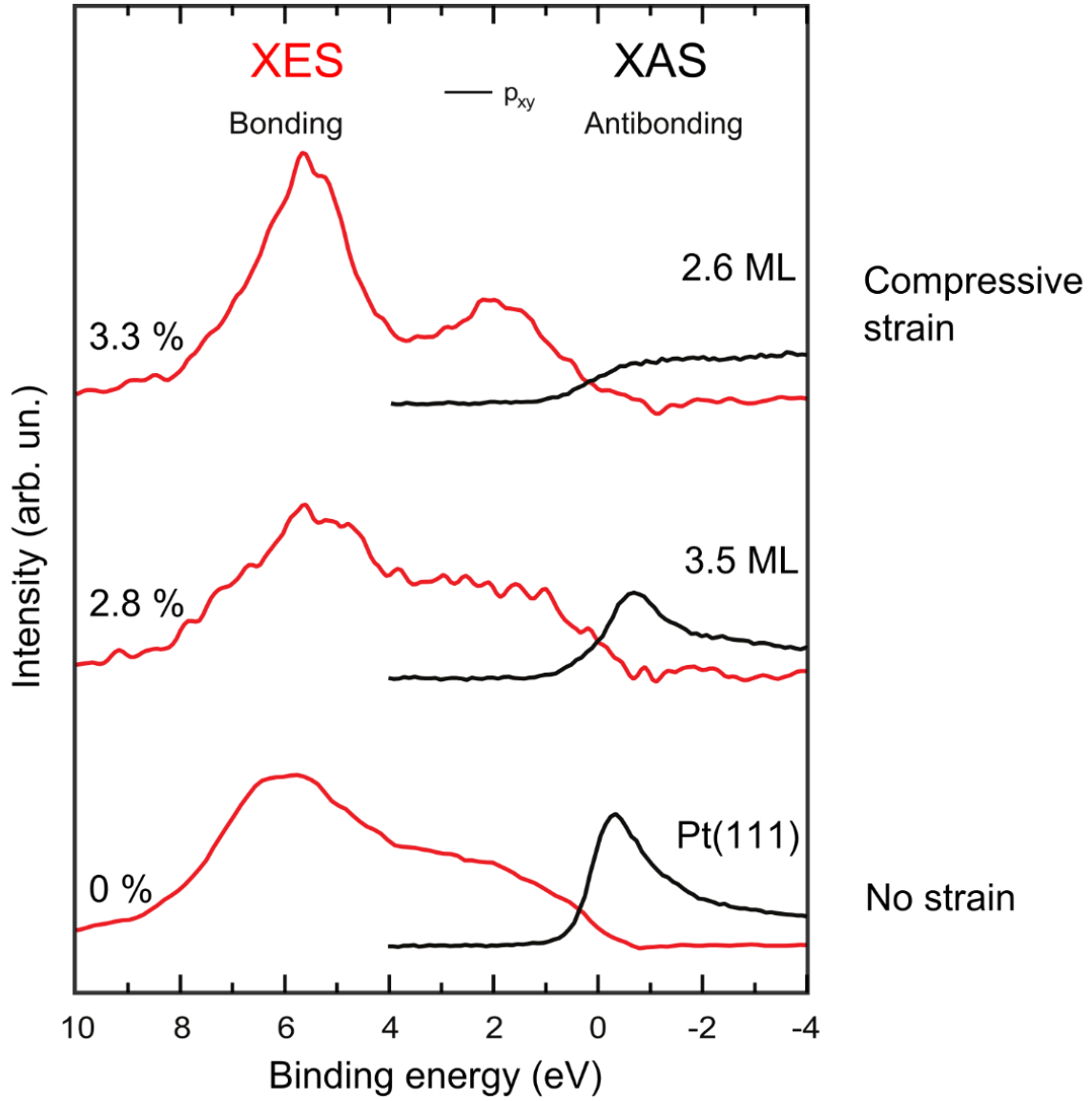
- Atom specific
- Symmetry selection (band structure)
- Polarizarion dependence
- Dynamics
- In-situ characterization

Electronic Structure

The anti-bonding states of oxygen atoms are populated due to induced strain in the Pt films.



Populated antibonding states:
Weak Pt-O chemical bond



Nat. Chem. 2, 454–460 (2010)

Summary

If you need to identify

- Surface elemental composition
- Chemical states

All you need is XPS ❤

But the technique also offers

- ARPES (UPS): complete band structure
- Ambient pressure XPS: XPS in gas or liquid environment
- Photoelectron diffraction (XPD): Periodicity of the surface
- Photoemission microscopy: spectral imaging
- Time-resolved XPS, ARTOF (Time of flight)