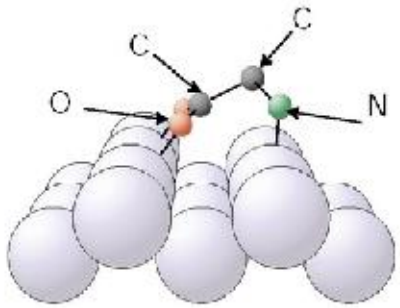
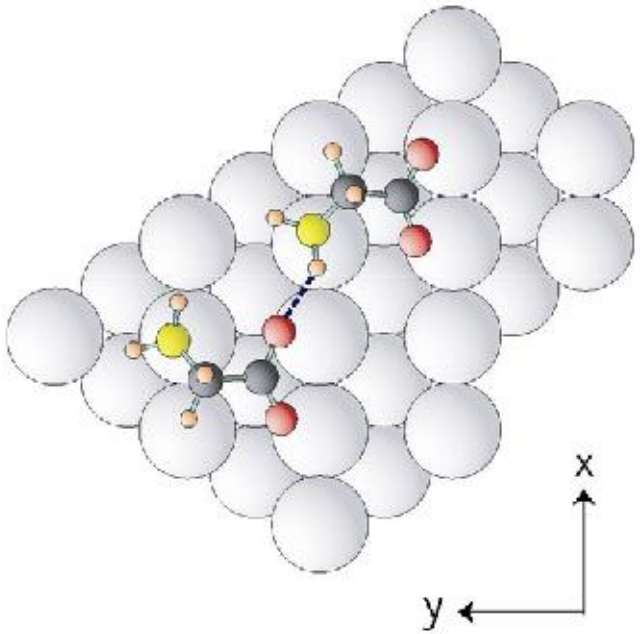
X-ray Photoelectron and Absorption Spectroscopy Investigations on Molecule Surface Interactions¶

SARP KAYA

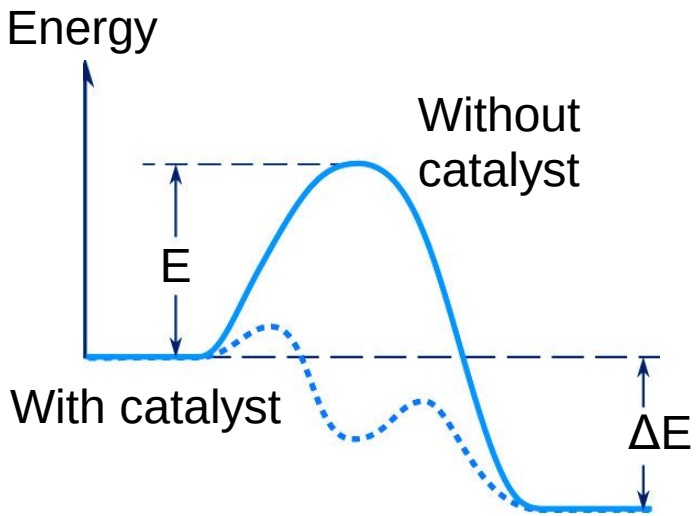
Department of Chemistry, Koç University, Istanbul, Türkiye
KUHyTech - Koç University Hydrogen Technologies Center

Surface Chemical Bond





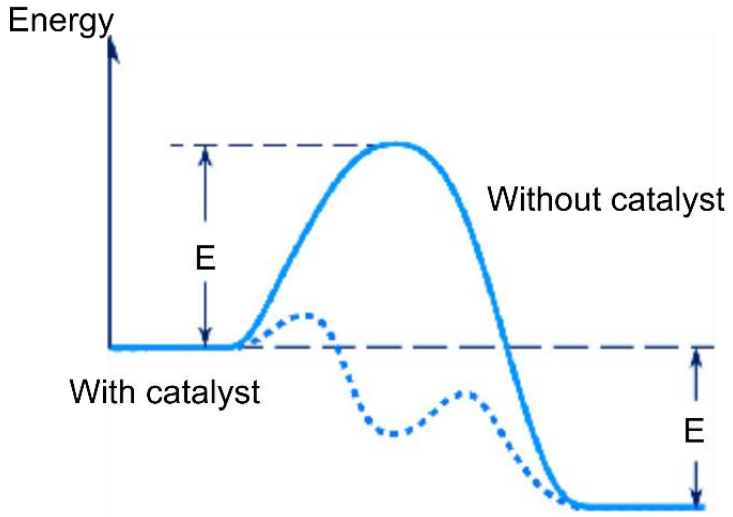
How can we understand the nature of the chemical bonding between surfaces and adsorbates?



Elementary steps of catalytic conversion

- Molecular adsorption
- Dissociation
- Surface reaction
- Desorption

$A+B \rightarrow AB$



$A+* \rightarrow A*$

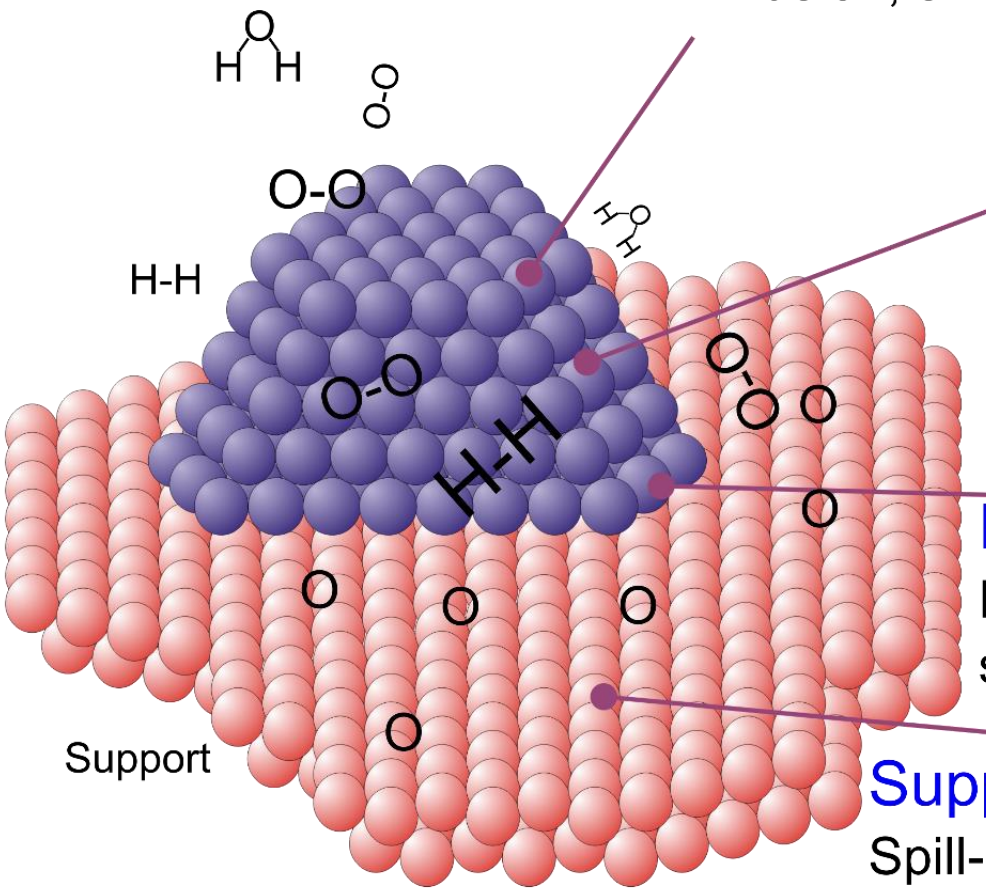
$A*+B \rightarrow BA*$

$BA* \rightarrow AB+*$

Ertl, Nobel Lecture, 2007

What determines catalytic activity?

Adsorption
Desorption
Dissociation



Transport effects

Diffusion, sintering

Geometric effects

Facets, edges, corners, strain, defects, size

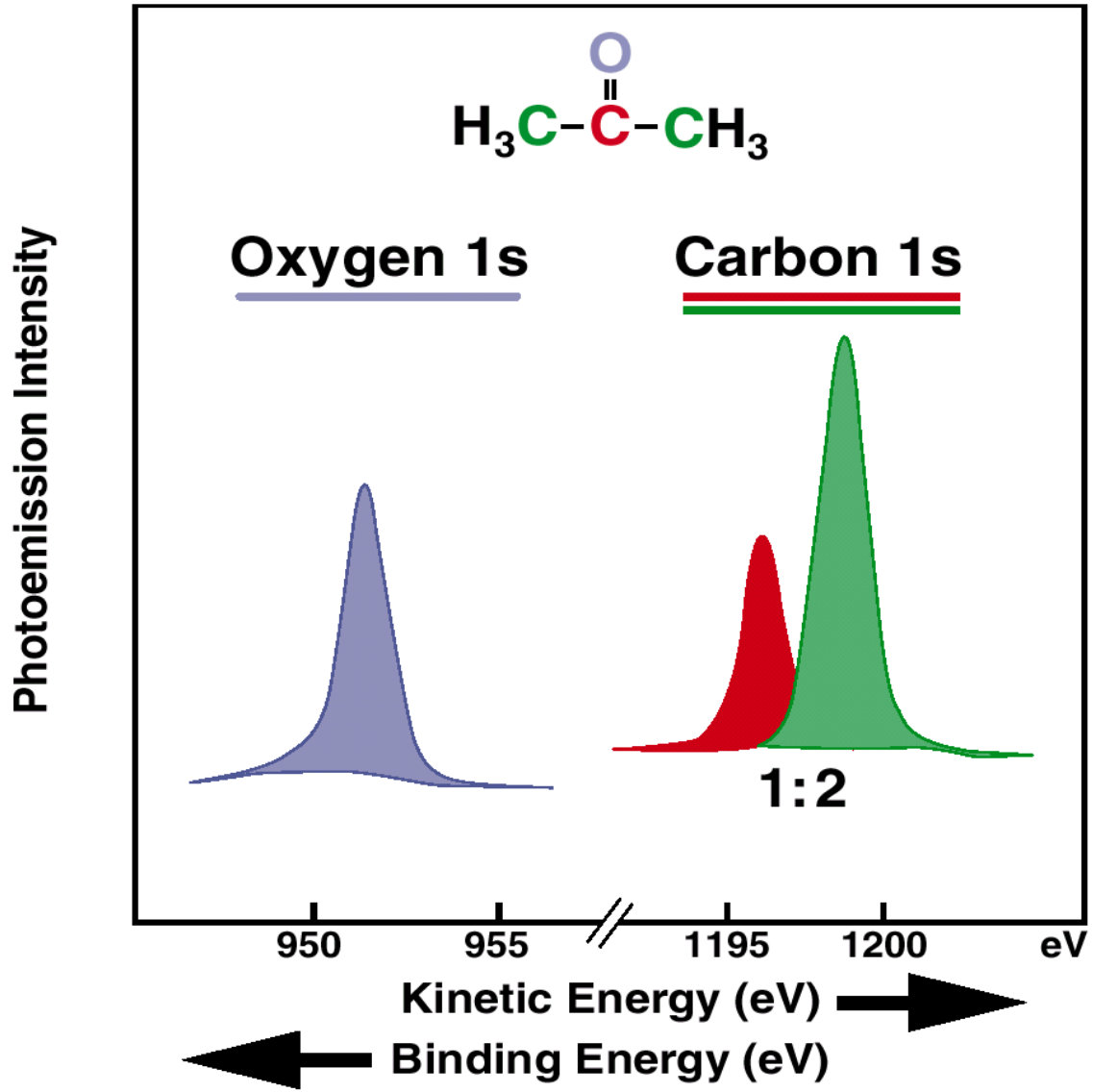
Electronic effects

Electron confinement, support interaction

Support effects

Spill-over, diffusion, reaction

Chemical Shifts



Provides information about

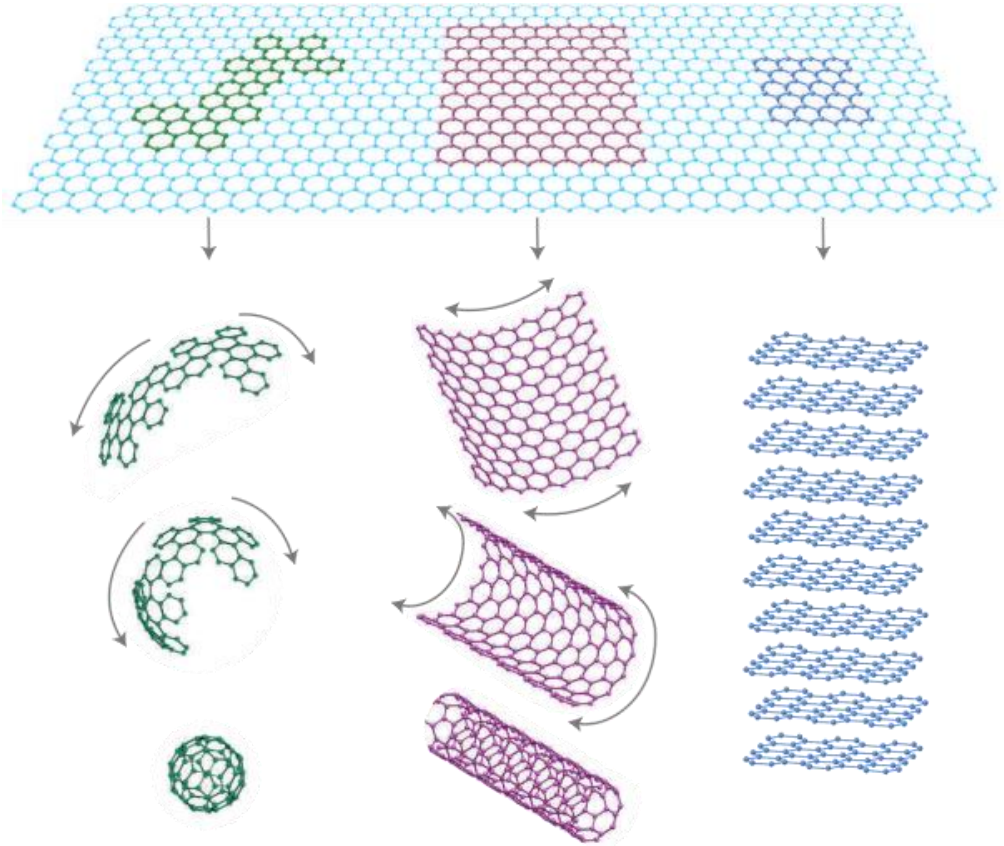
- Kind of atom
- Number of atoms
- Chemical shift

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

Applications of sp^2 carbon

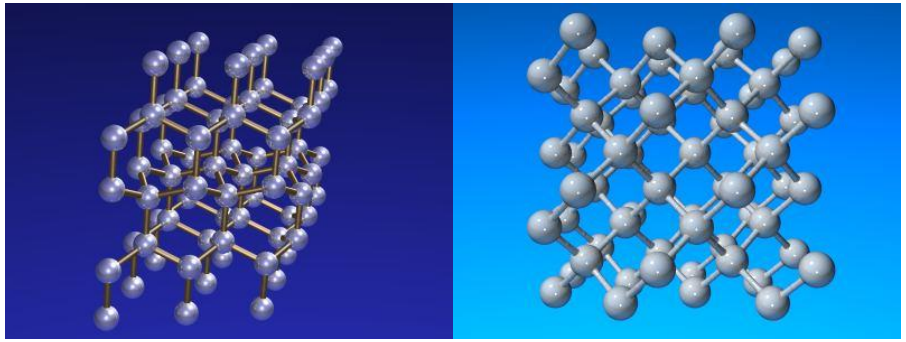
sp^2 hybridization

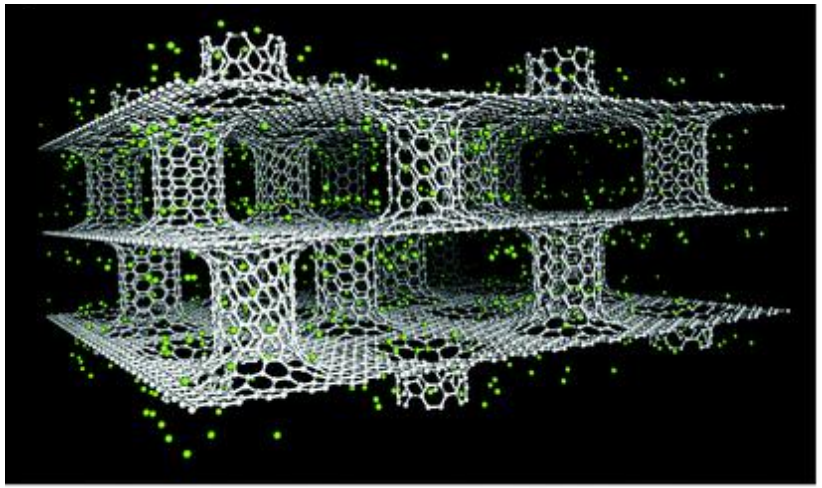
Graphene sheet, carbon nanotube (CNT)



sp^3 hybridization

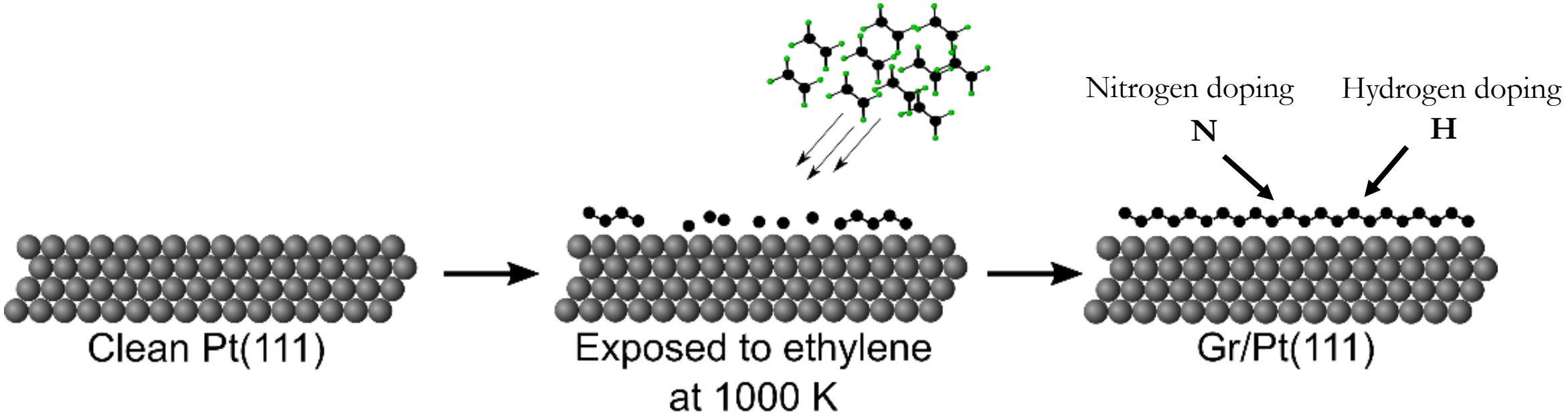
Diamond

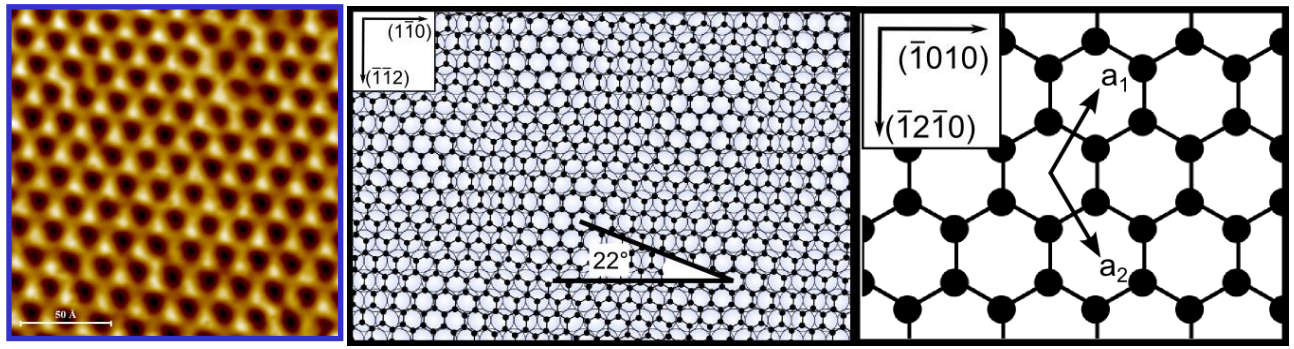




Graphene on metal surfaces

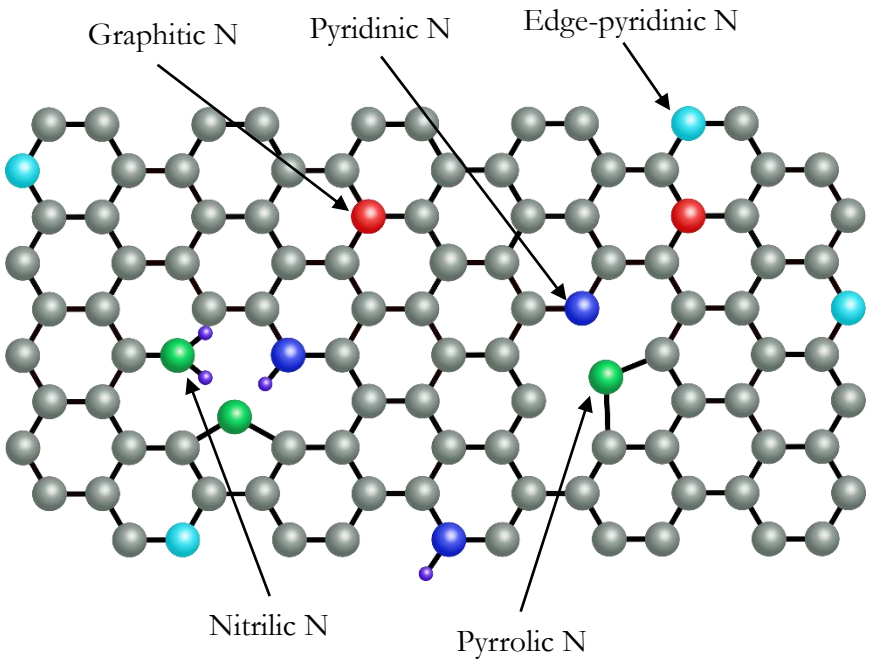
Single layer graphene grown on Pt(111)



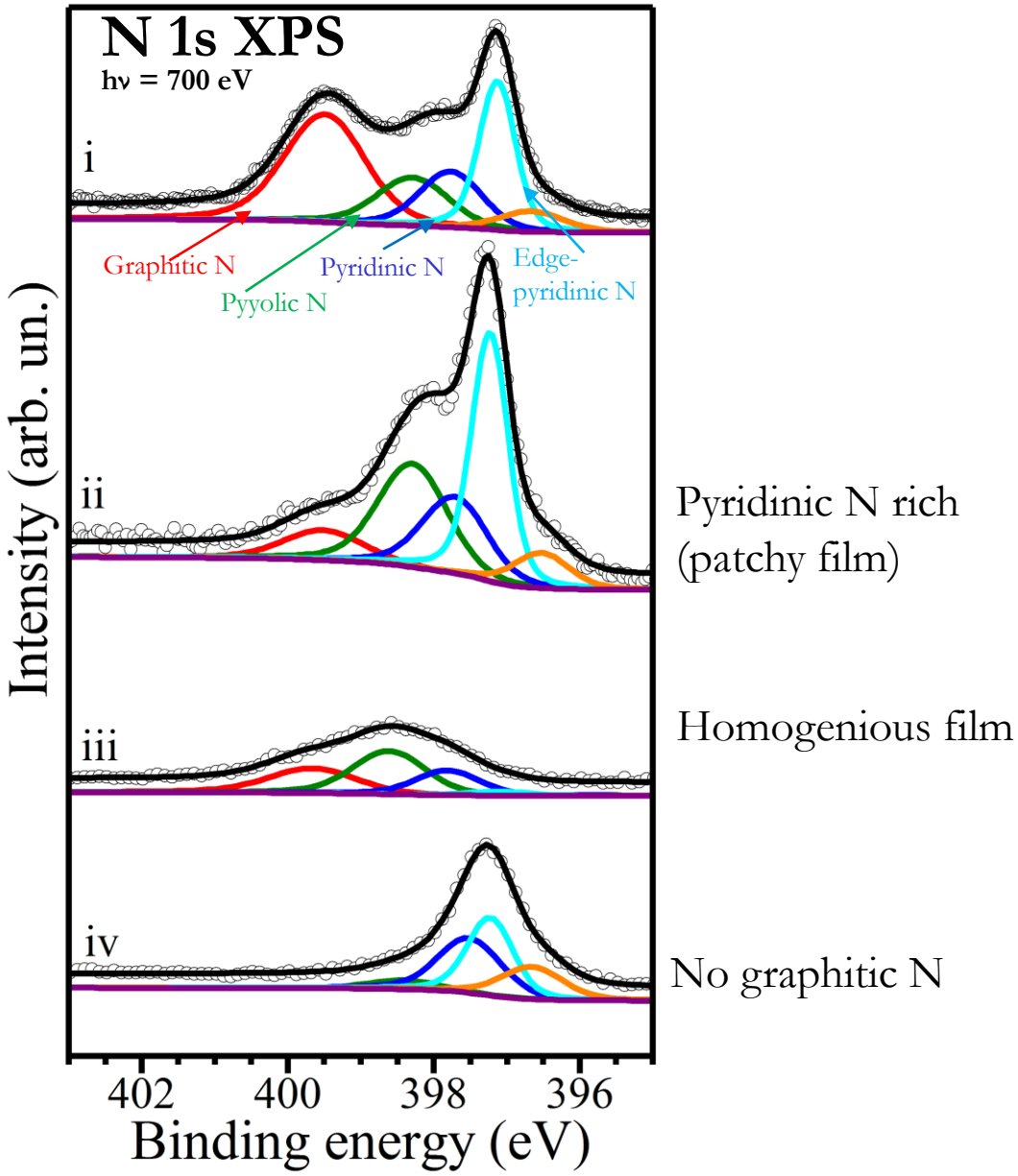


Chemical Shift: Nitrogen Doped Graphene

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



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



Pyridinic N rich (patchy film)

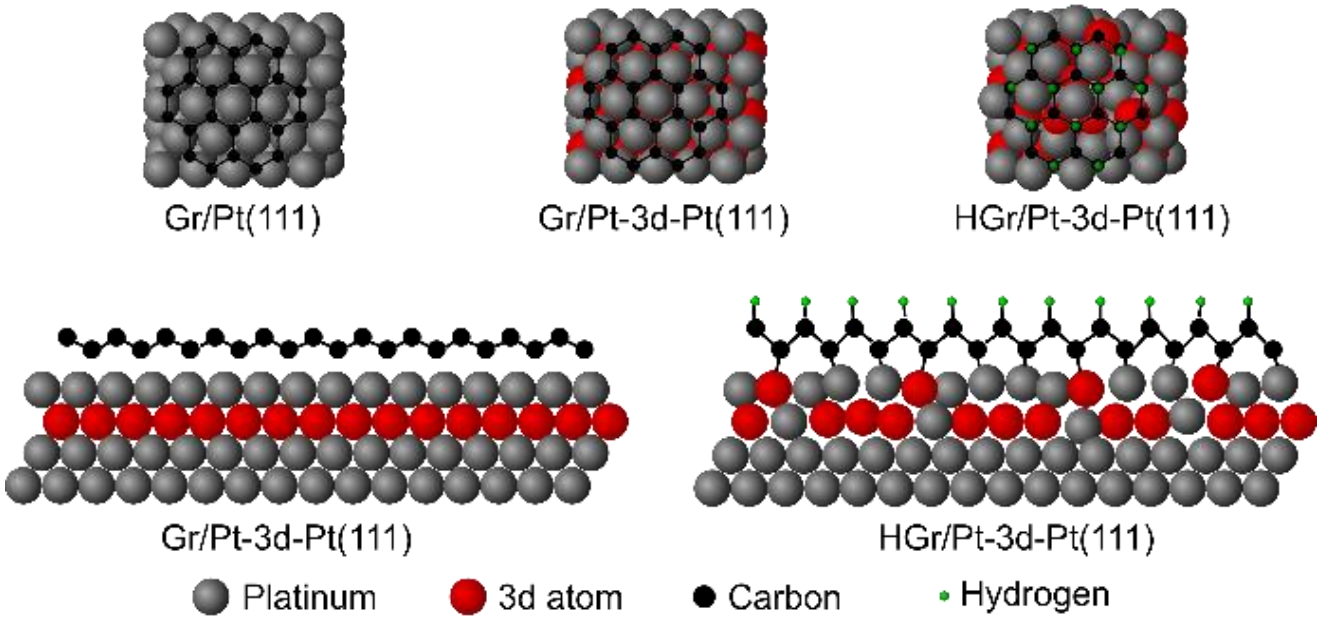
Homogenious film

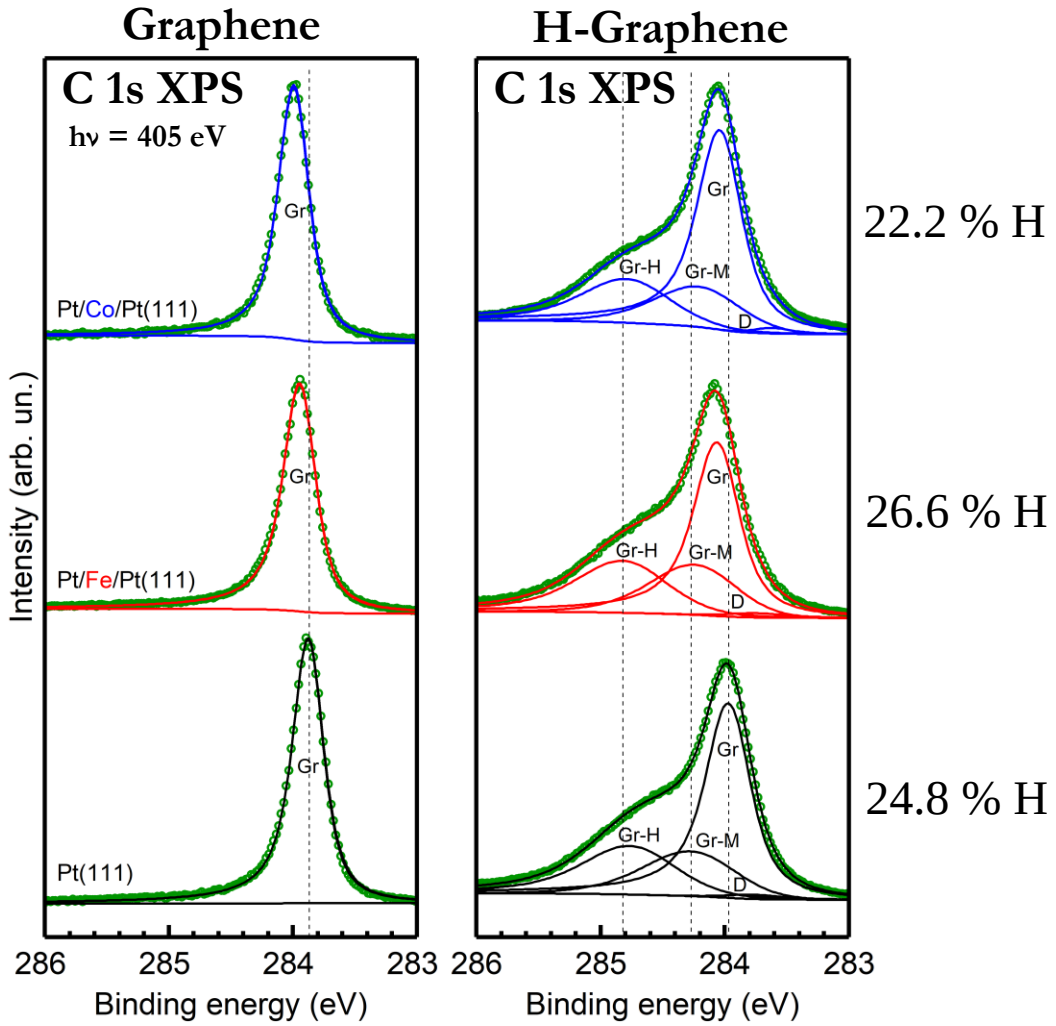
No graphitic N

Materials Today Chemistry, 38, 102081 (2024)
Appl. Surf. Sci., 495, 143518 (2019)

Chemical shift: Hydrogenation of Single Layer Graphene on Subsurface Alloys

Hydrogenation of graphene grown on Fe and Co subsurface alloys on Pt(111)





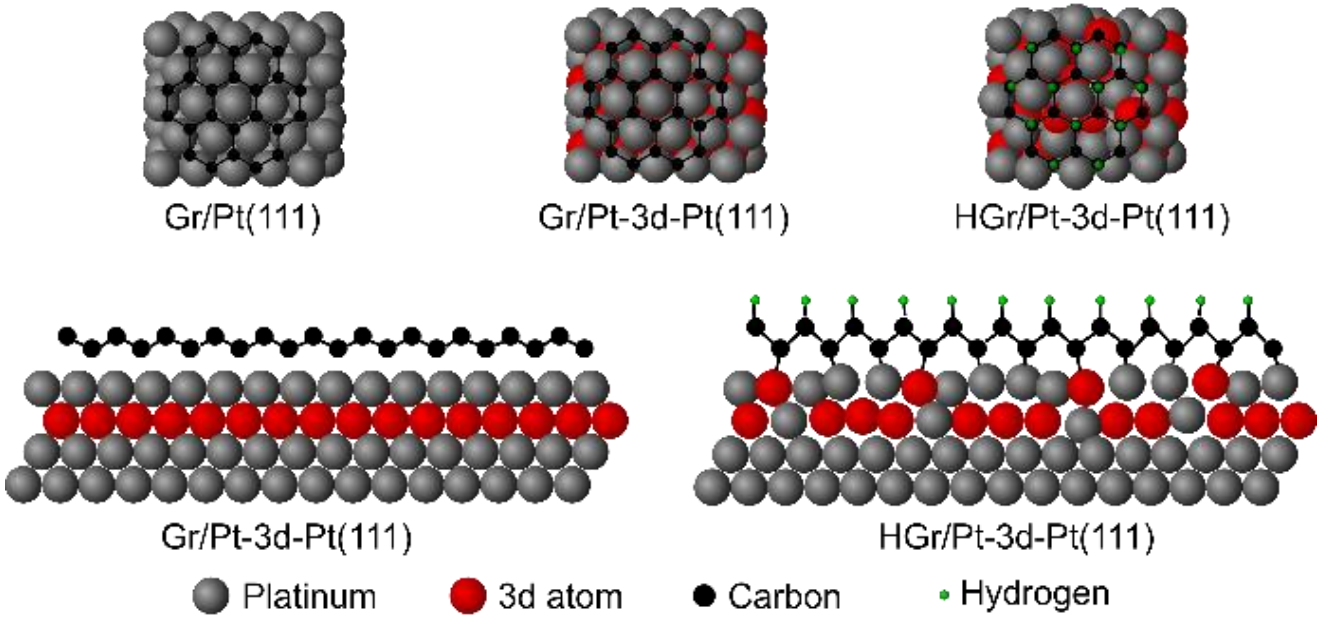
Peak shift: a measure of graphene surface interaction

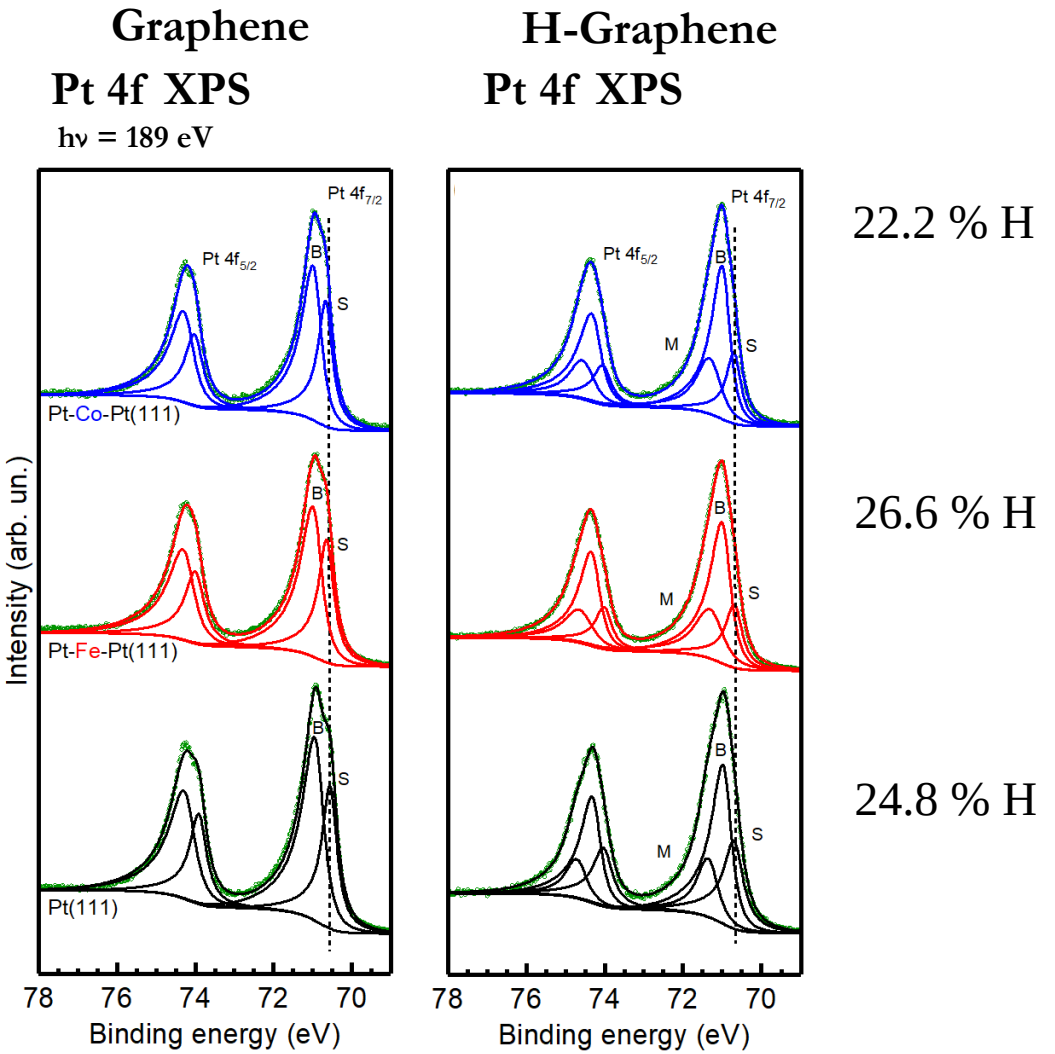
H coverage can be quantified

Carbon, 170, 636 (2020)

Chemical shift: Hydrogenation of Single Layer Graphene on Subsurface Alloys

Hydrogenation of graphene grown on Fe and Co subsurface alloys on Pt(111)



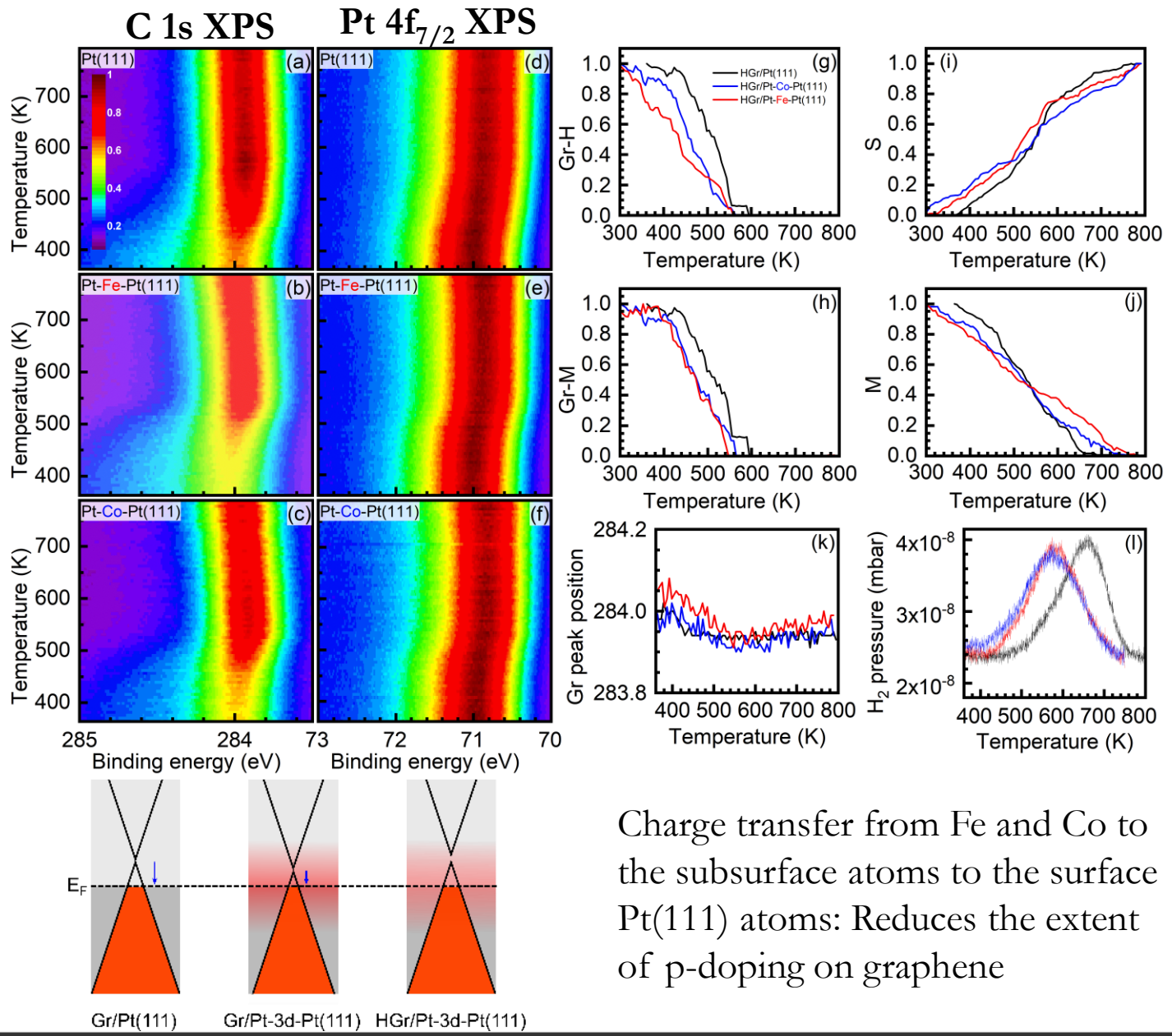


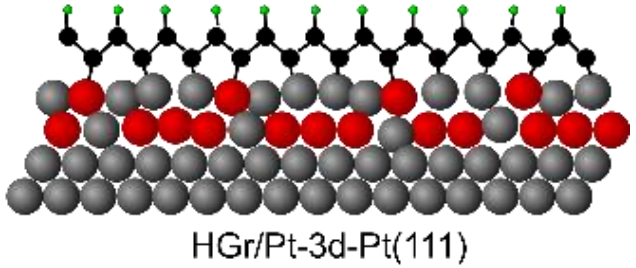
S peak shift: a measure of graphene surface interaction

H coverage can be quantified

Carbon 170, 636 (2020)

Chemical shift: Hydrogenation of Single Layer Graphene on Subsurface Alloys

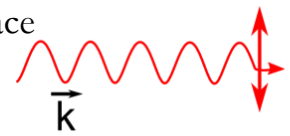


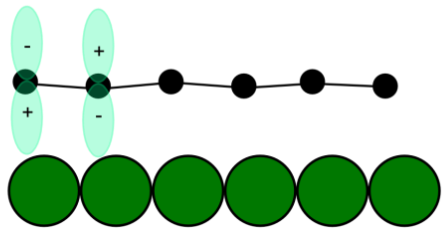


Charge transfer from Fe and Co to the subsurface atoms to the surface Pt(111) atoms: Reduces the extent of p-doping on graphene

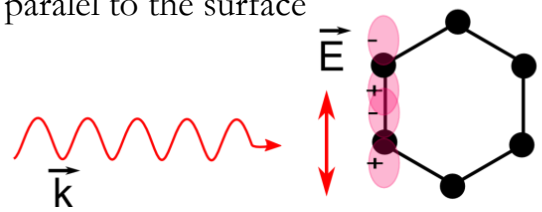
Polarization: Single Layer Graphene on Pt(111)

Polarization vector is perpendicular to the surface

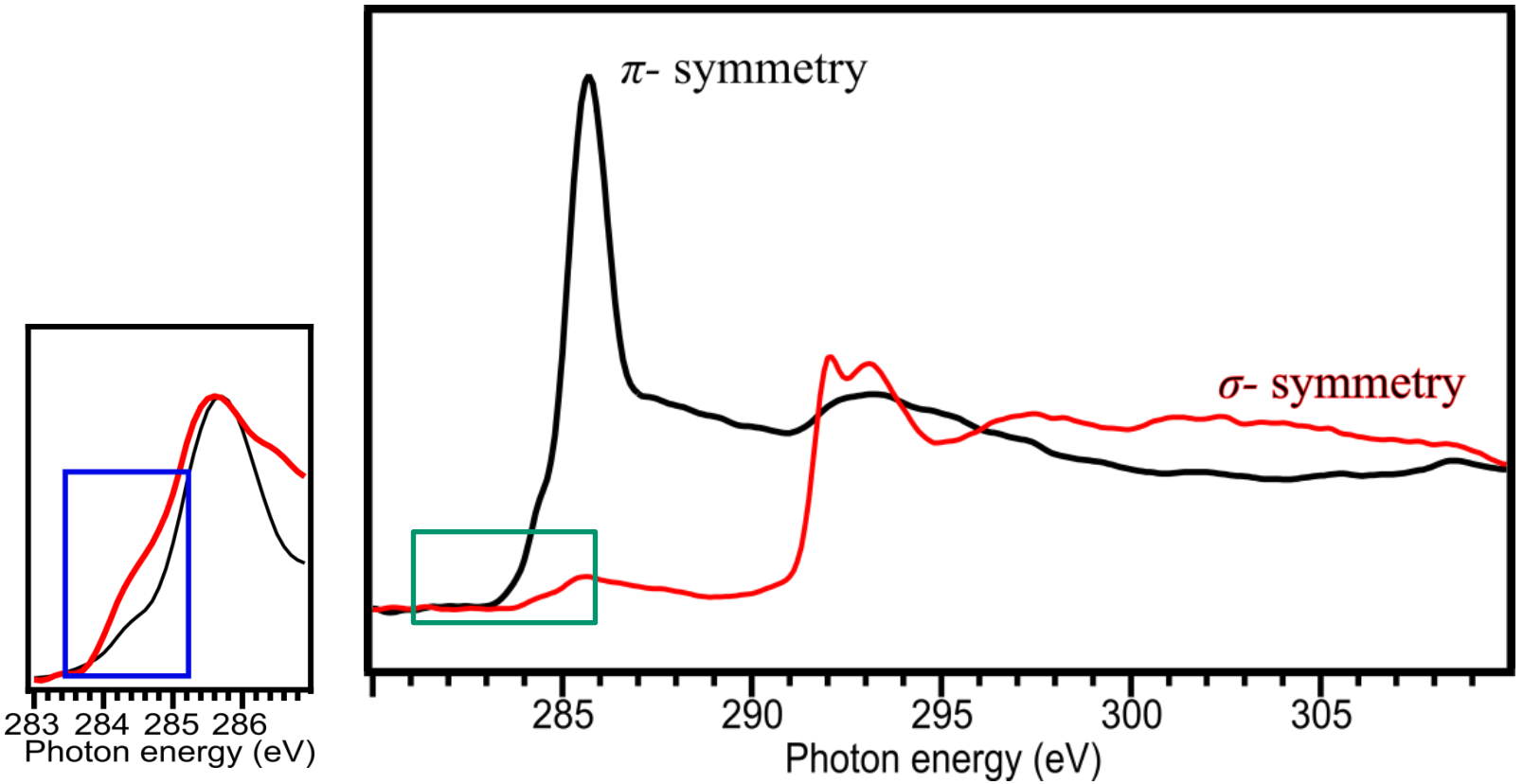




Polarization vector is paralel to the surface



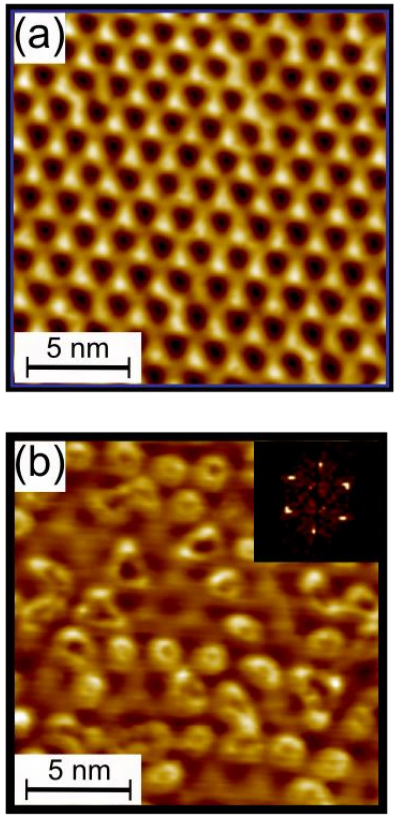
Symmetry resolved measurements: C K-edge XAS



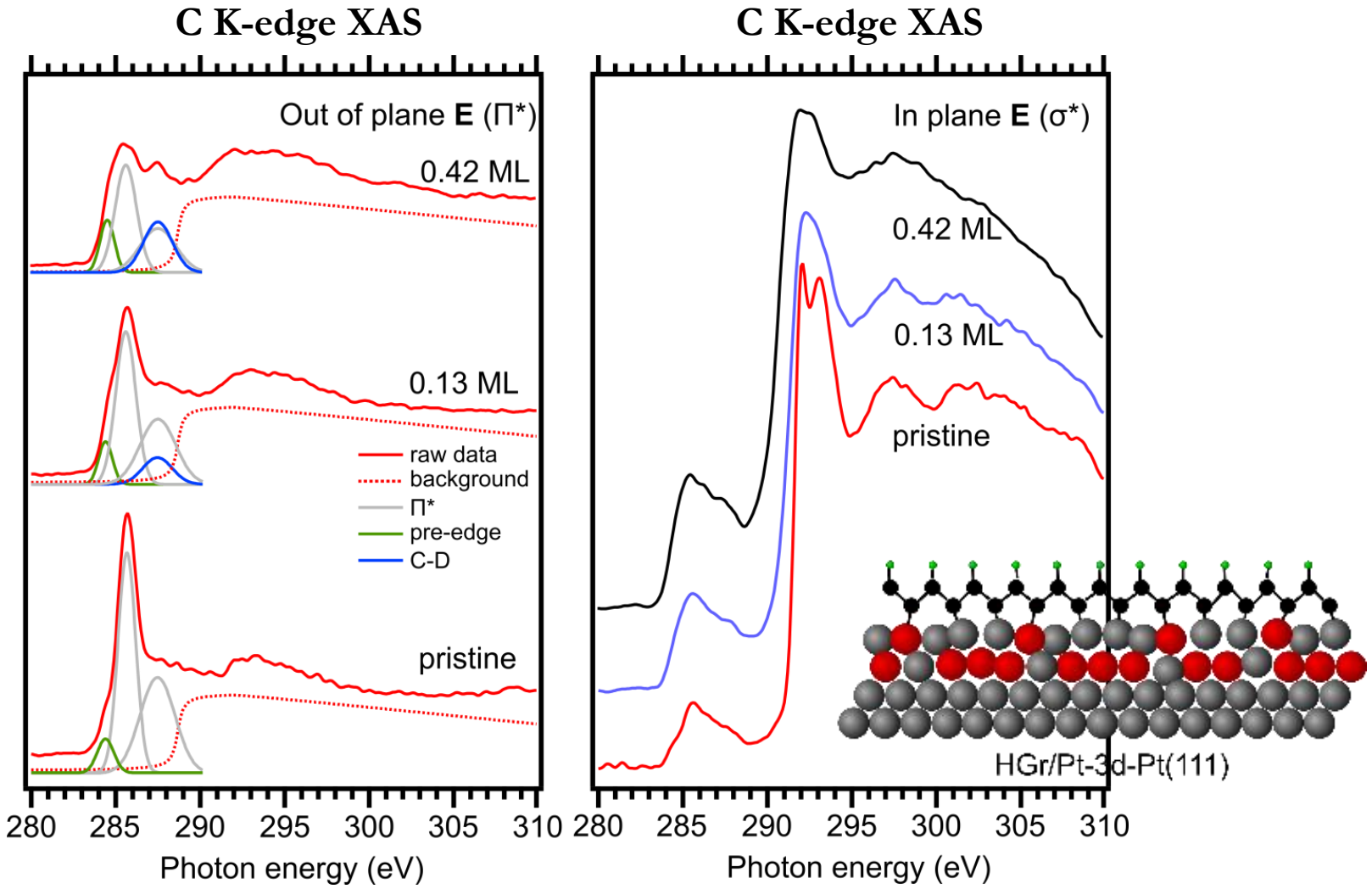
Symmetry forbidden π^* resonance in σ symmetry XAS.
Attributed to rippling of graphene – Moiré lattice.

Polarization: Hydrogenation of Single Layer Graphene on Pt(111)

STM

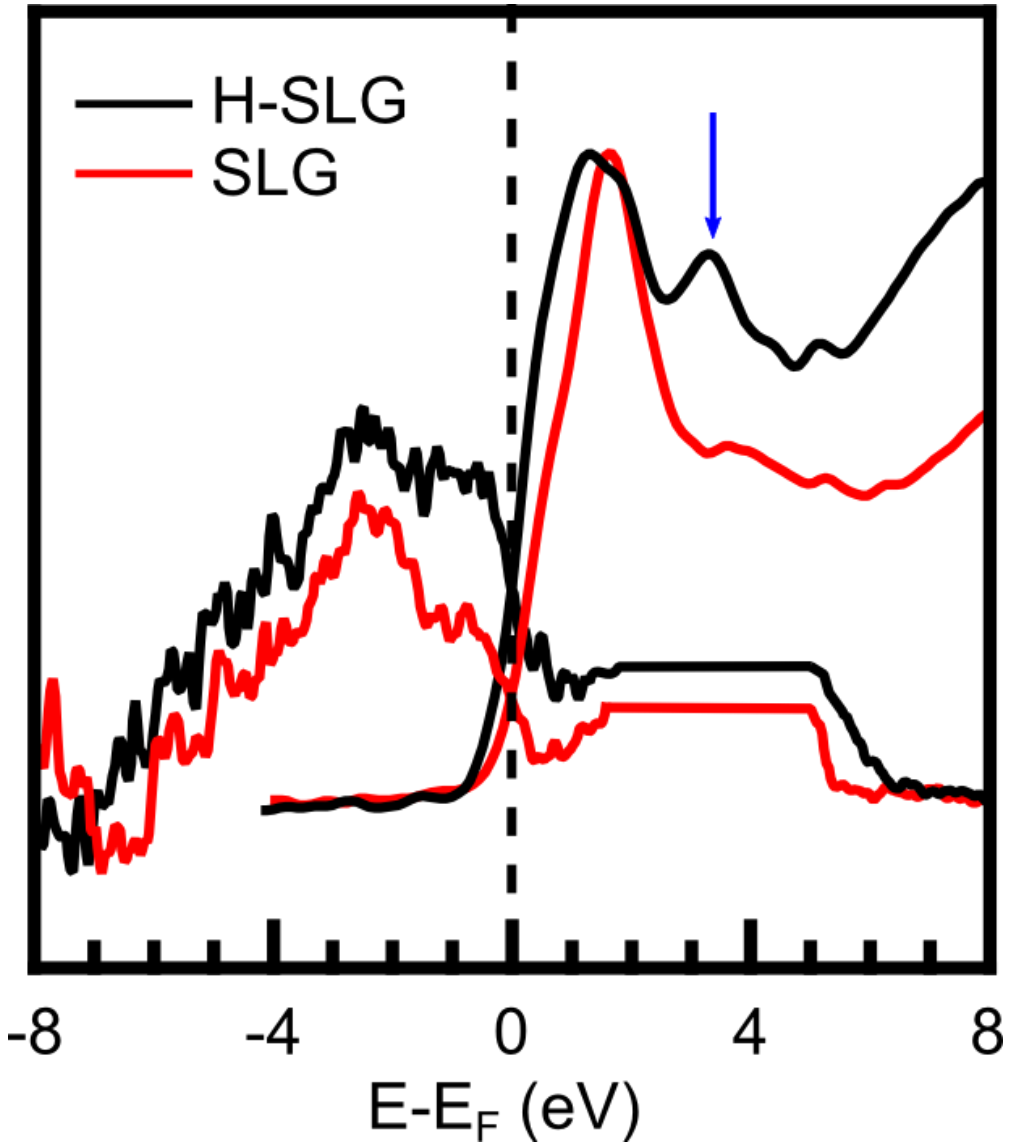


STM indicates preferential 'quantum dot type' hydrogenation

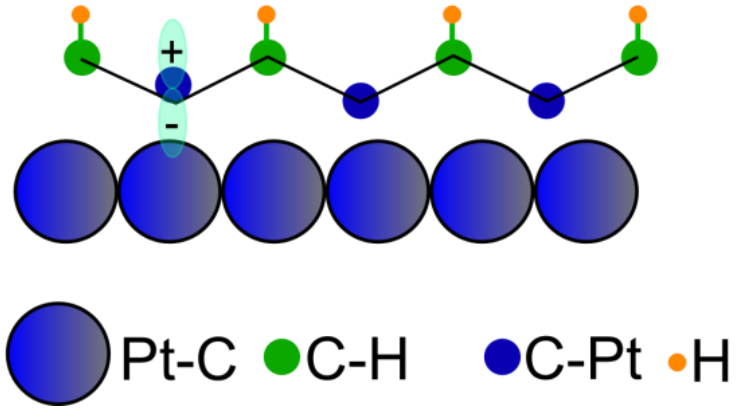


Broadening of excitonic peak.
Appearance of C-H feature.
Enhanced corrugation of SLG after hydrogenation.

Polarization and chemical shift: Hydrogenation of Single Layer Graphene on Pt(111)



π orbital interaction with Pt states

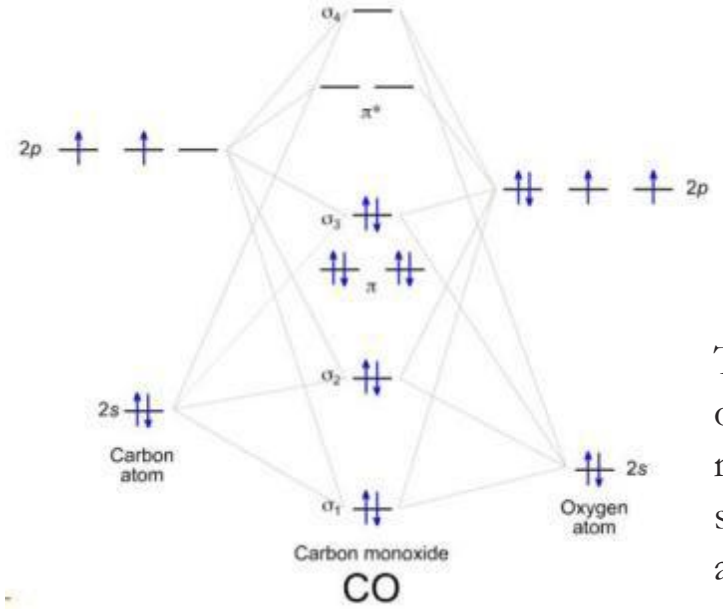


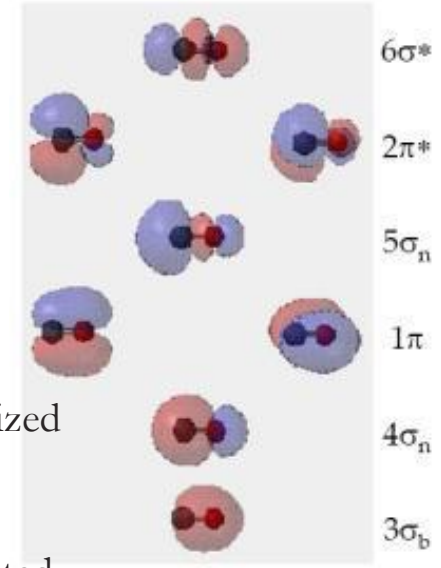
Excitation energy ($h\nu_{in}$) ~ 287.5 eV, we excite the C-H resonance, we observe more emission close to E_F for HSLG than SLG

Phys. Rev. Lett., 111, 085503 (2013)
Phys. Rev. B, 86, 075417 (2012)

The Blyholder Model of Chemisorption of CO

CO as a model adsorbate

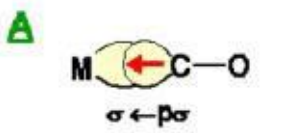


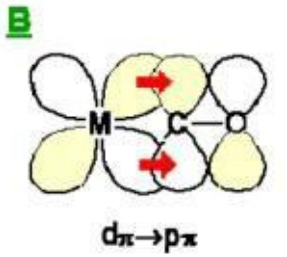


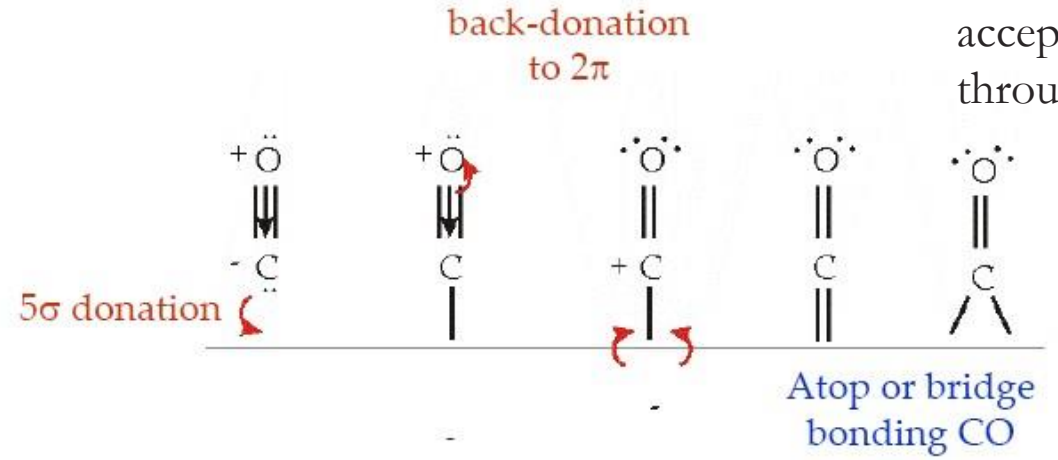
The 5σ orbital is localized on the C end of the molecule. The 2π* is symmetrically distributed along the molecular axis.

- MO of gas-phase CO
- The wavefunction changes sign in going from the region shown by different color

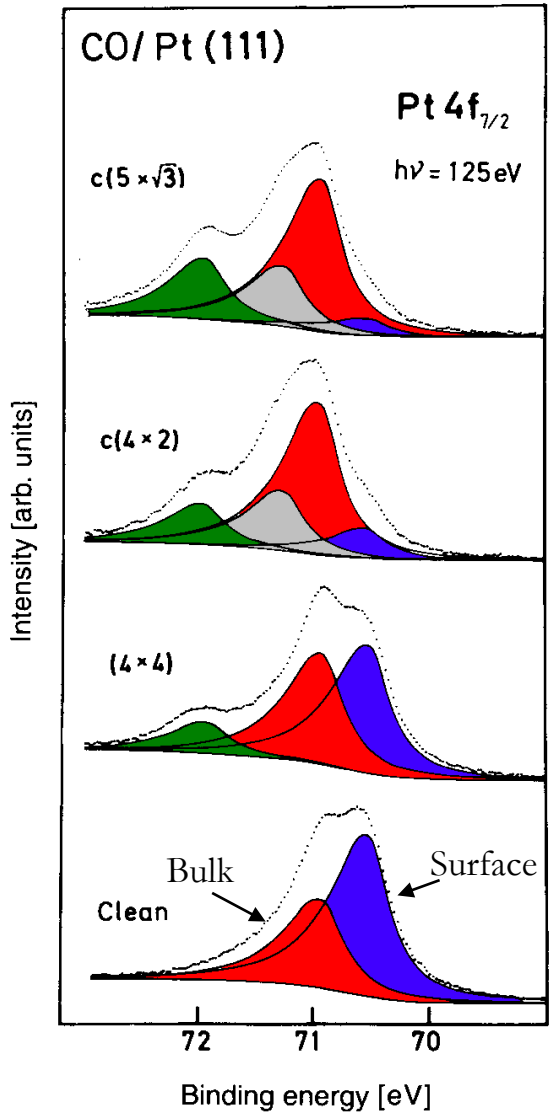
5σ orbital is completely occupied as it lies below the Fermi energy. It interacts strongly with the metallic electronic states. Effectively, the electron density of the 5σ orbital is donated to the metal and new hybrid electronic states are formed (donation)
The 2π* is partially occupied. The 2π* orbital accepts electron density from the metal through a process known as backdonation.

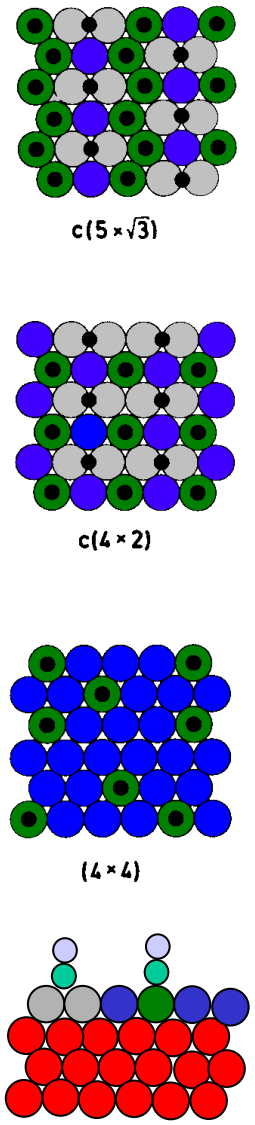


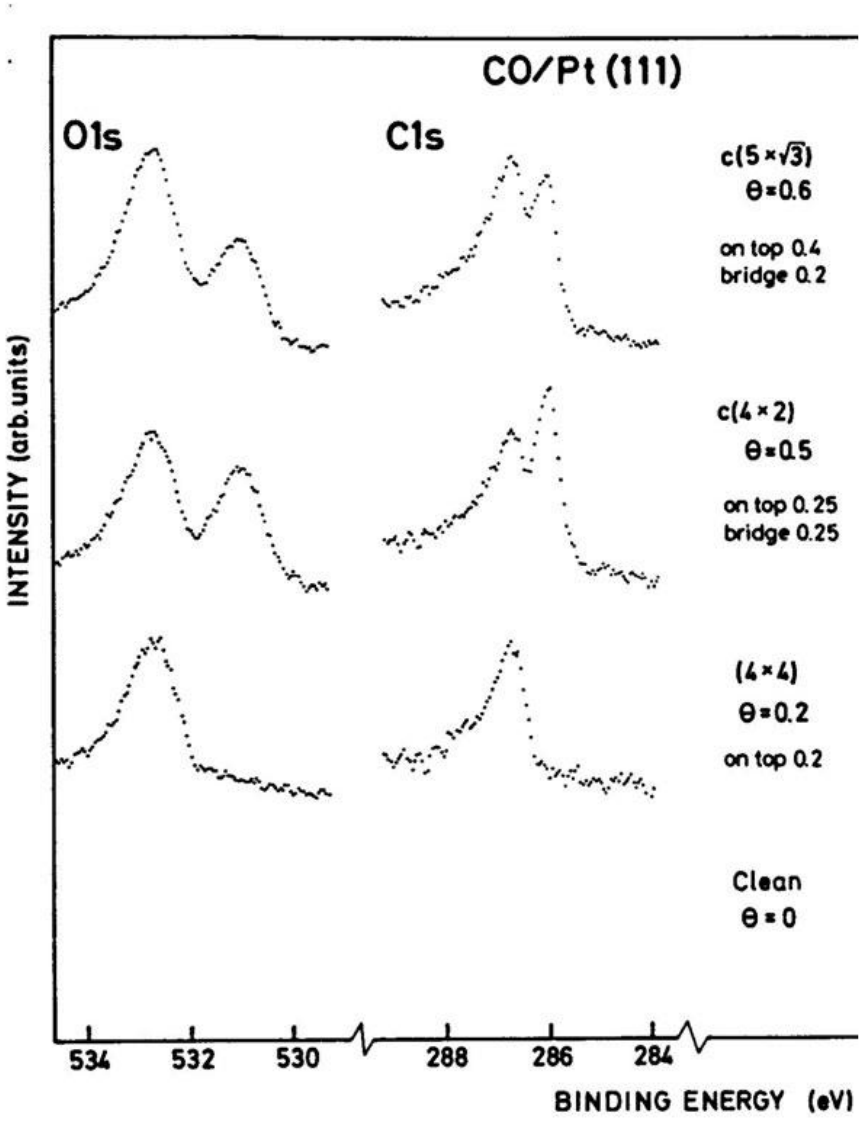




XPS is structure sensitive: CO on Pt(111)



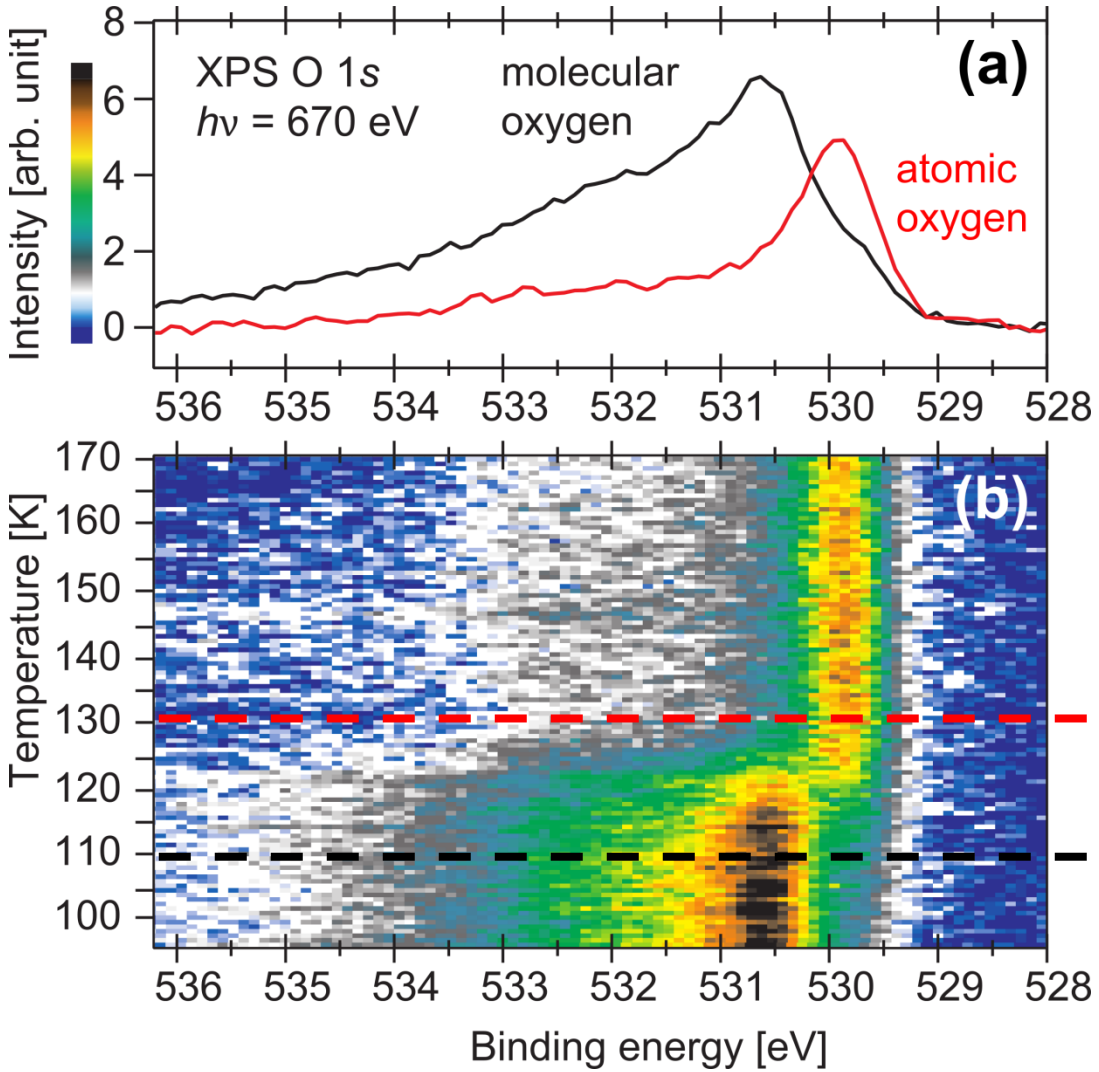


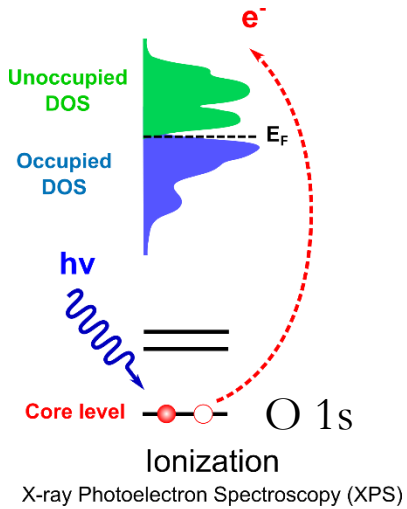


Surface Science, 315, L983 (1994)

O_2 dissociation on Pt(111)

TP-XPS of a partial O_2 adlayer





0.20 ML
atomic oxygen

Completion ~ 130 K

Onset ~ 110 K

0.40 ML
molecular oxygen

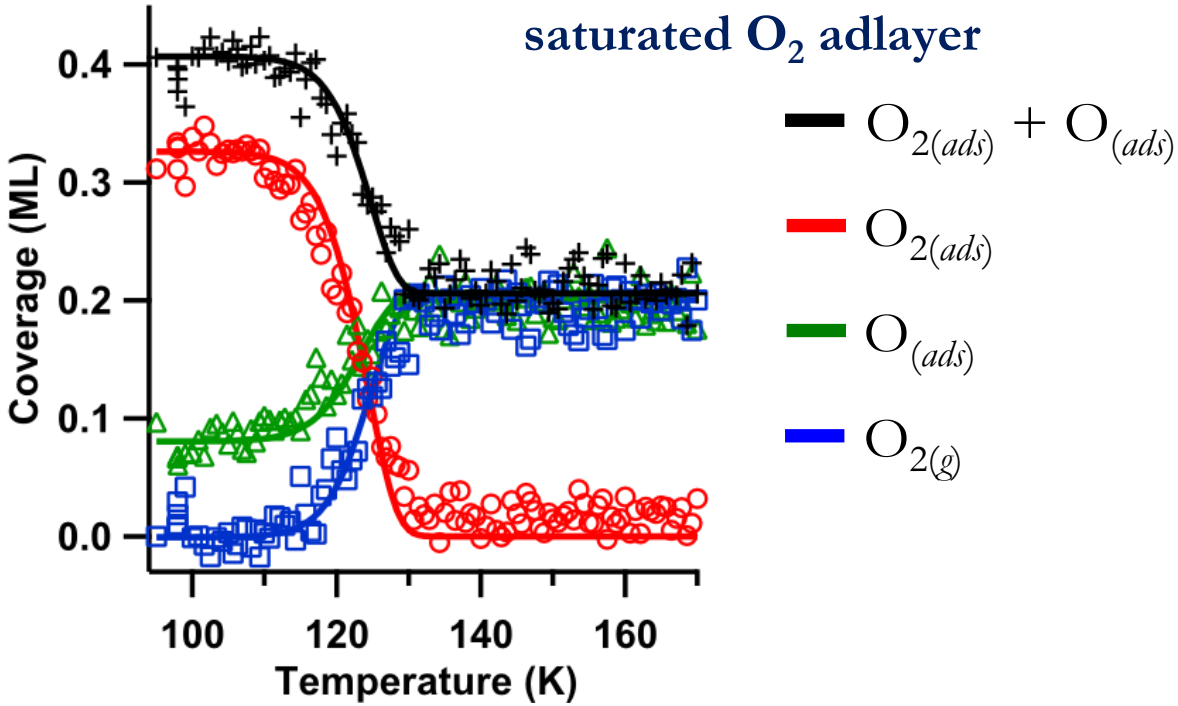
J. Chem. Phys., *133*, 224701 (2010)

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

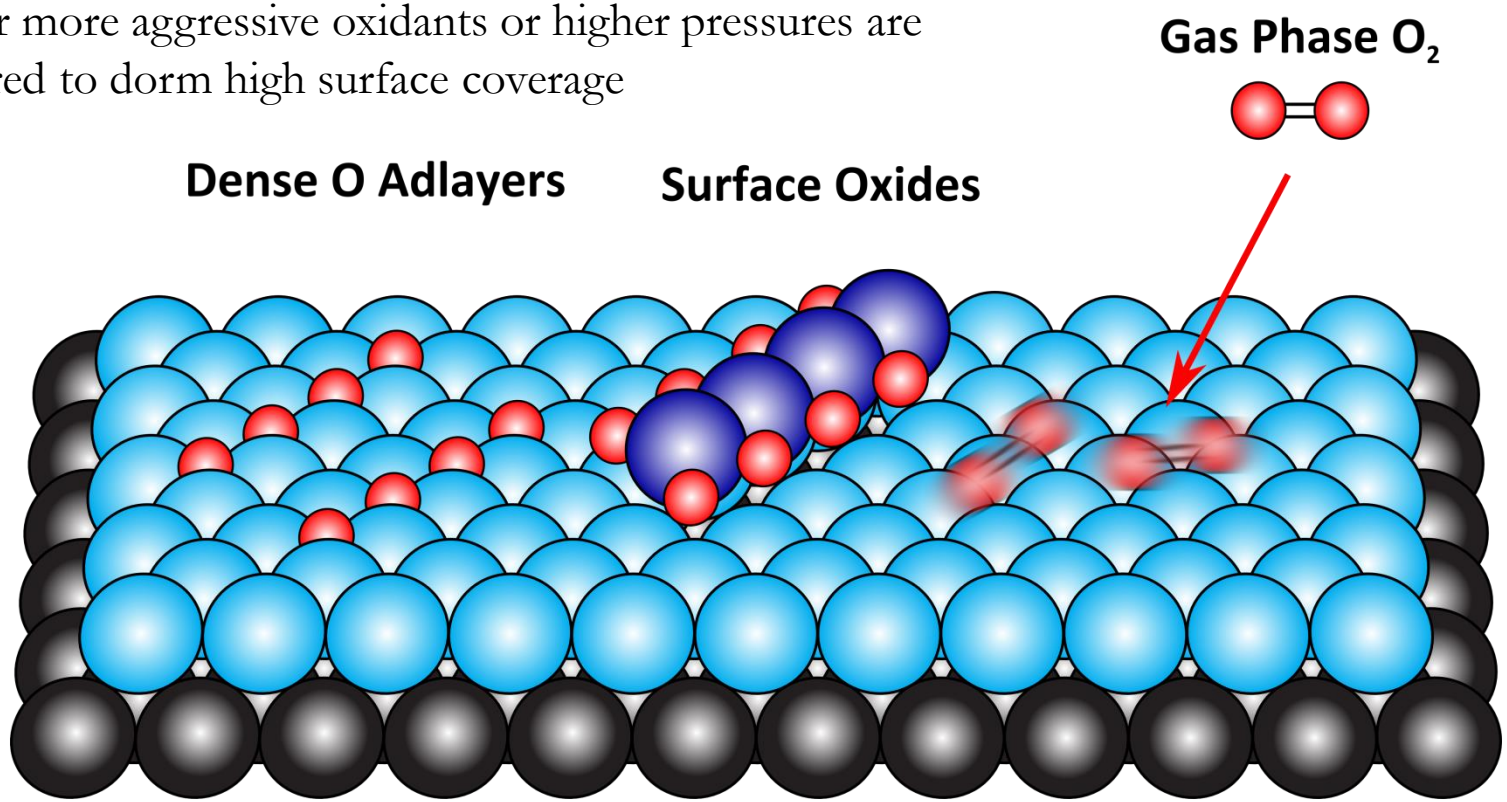


	Constrained	Floating
Dissociation $O_{2(ads)} + Pt \rightarrow 2O_{(ads)}$	$\nu_{diss} = 10^{11}$–10^{13} s^{-1}	$E_{diss} \sim 0.32 \pm 0.03$ eV
Desorption $O_{2(ads)} \rightarrow O_{2(g)} + Pt$	$\nu_{des} = 10^{13}$ s^{-1}	$E_{des} \sim 0.37 \pm 0.01$ eV

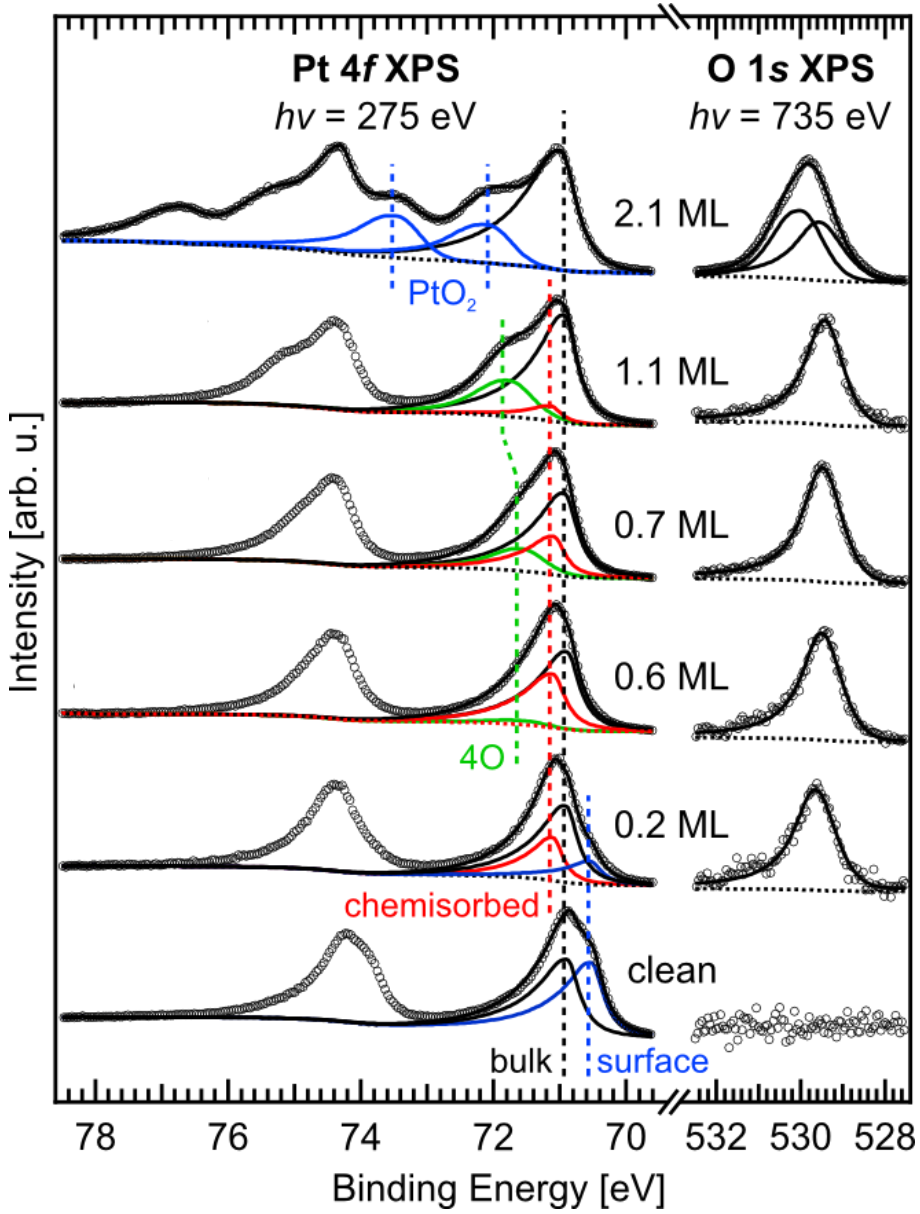
Adlayers and Oxides

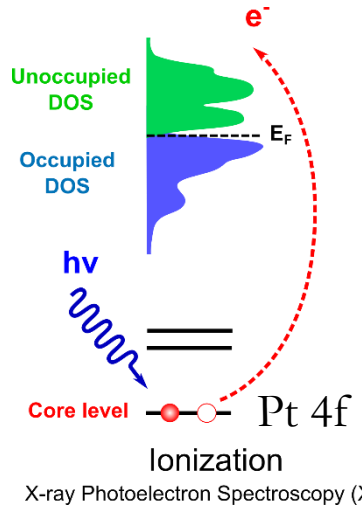
Near-ambient O_2 pressures are needed to generate $\theta > 0.25$ ML

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



Oxide Formation on the Pt(111) Surface



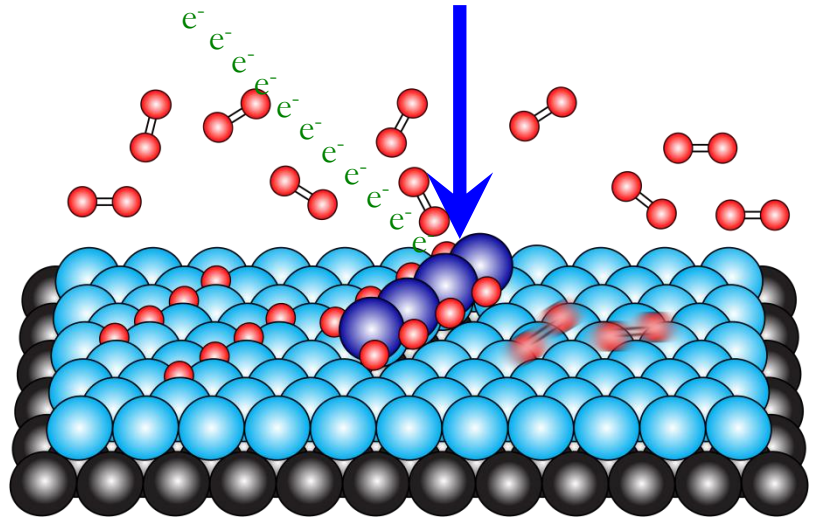


X-ray Photoelectron Spectroscopy (XPS)

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

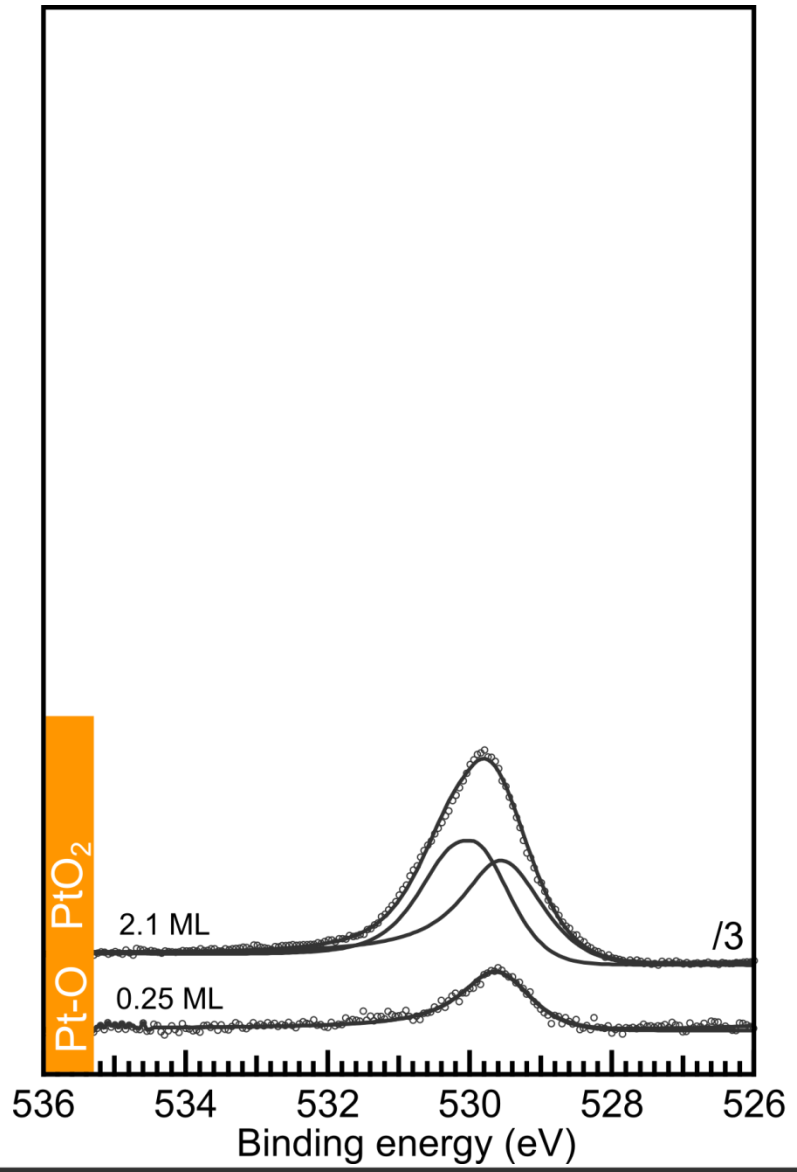
Pt 4*f*/O 1*s* XPS **$h\nu$ = 275 or 735 eV**

K.E. ~ 200 eV normal incidence



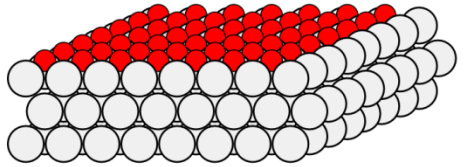
Phys. Rev. Lett. 107, 195502 (2011).

Oxygen Species on the Pt(111) Surface



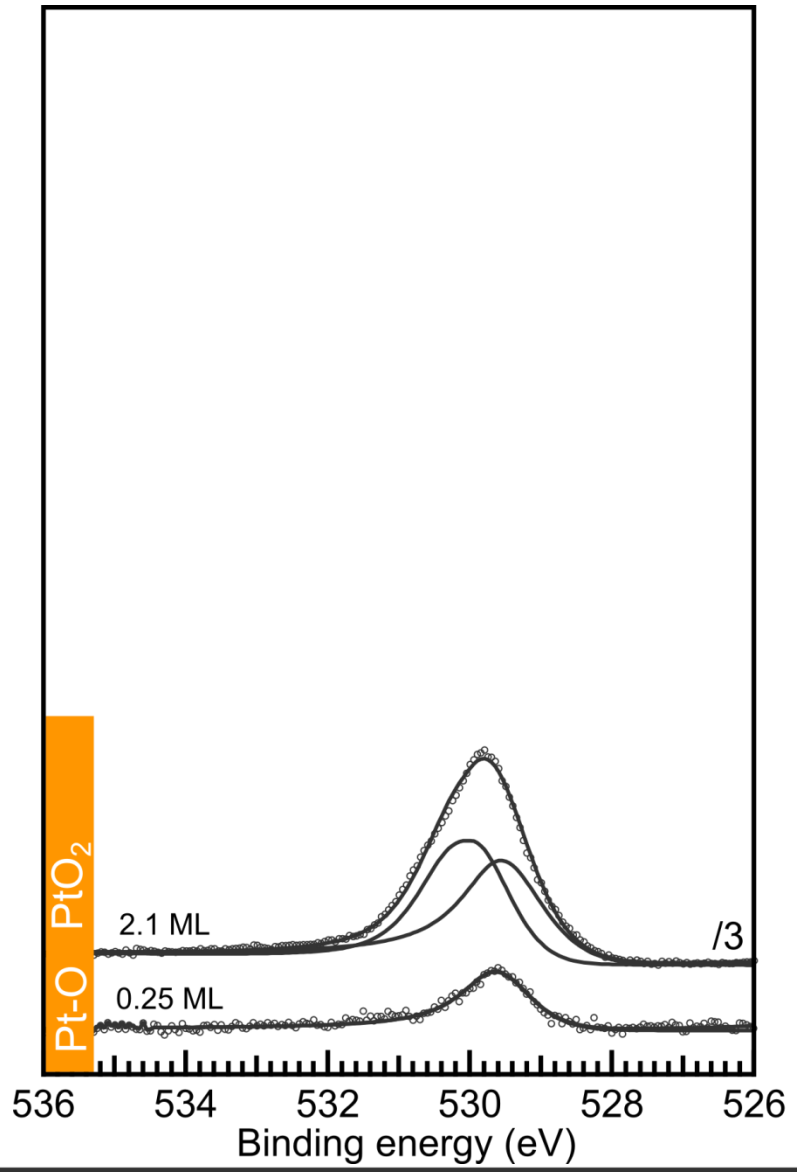
Various adsorbate species can be stabilized on Pt(111) under high temperature and pressure conditions.

UHV



Chemisorbed O surface oxide

Oxygen Species on the Pt(111) Surface



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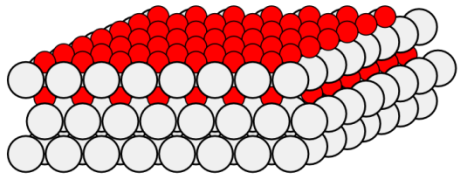

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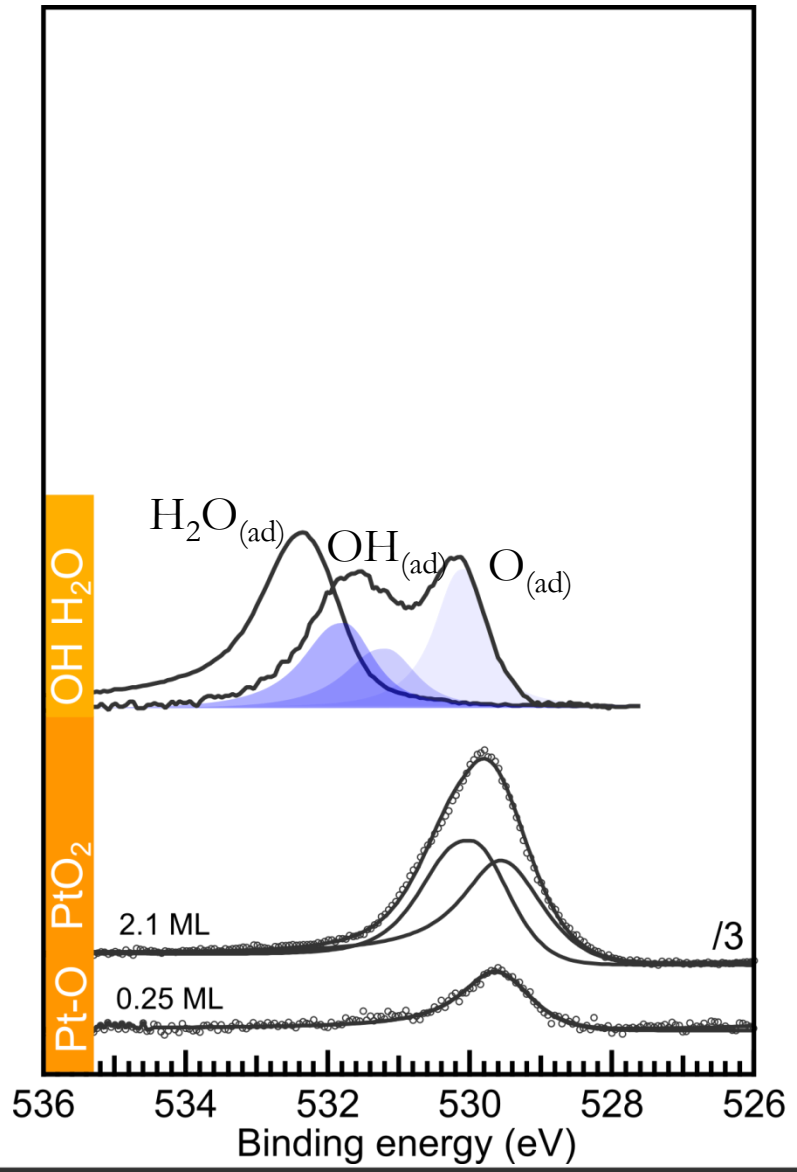

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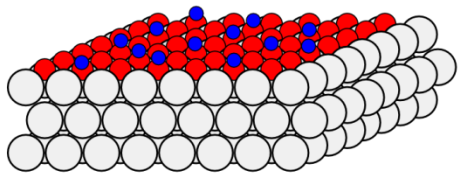
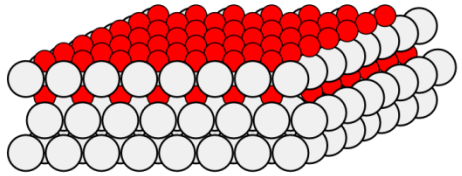


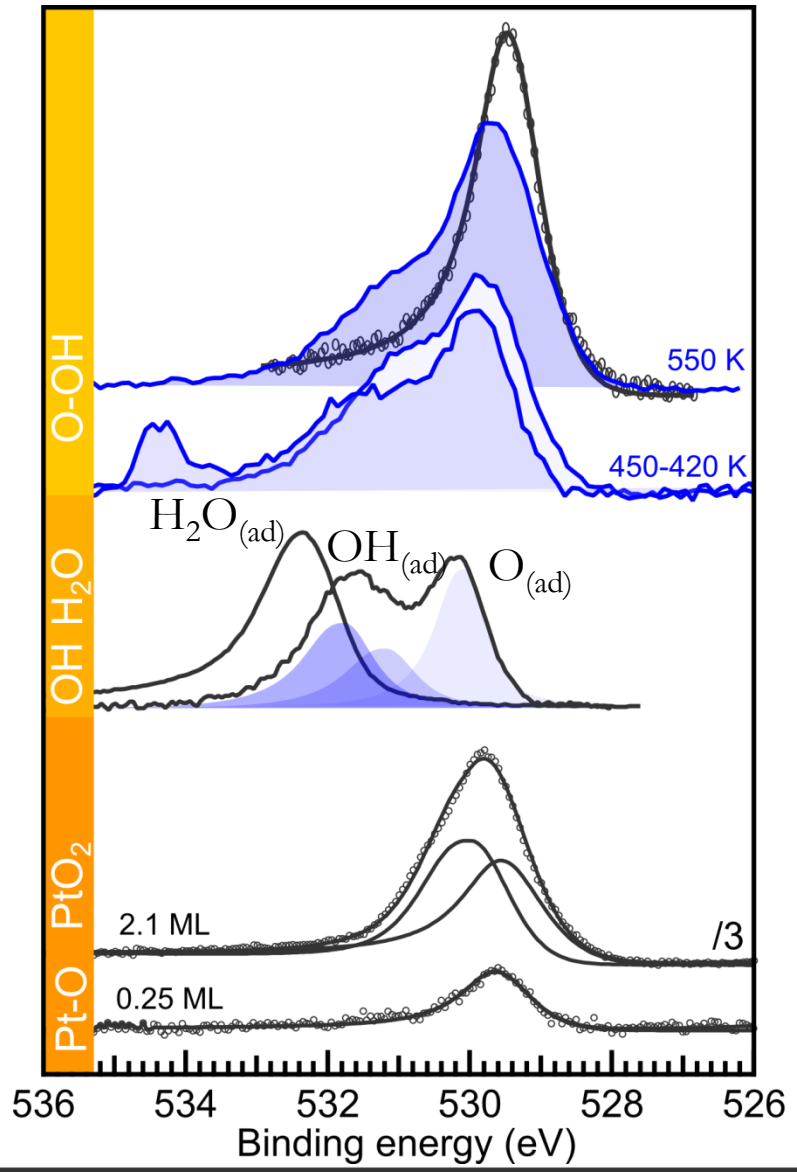
Chemisorbed
O-OH biphase

UHV



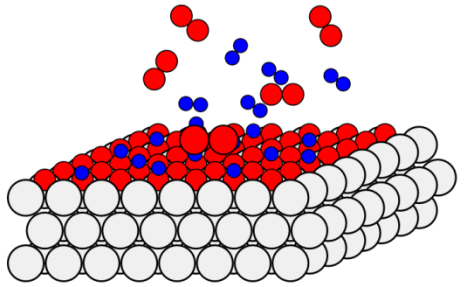
Chemisorbed O
surface oxide

Oxygen Species on the Pt(111) Surface

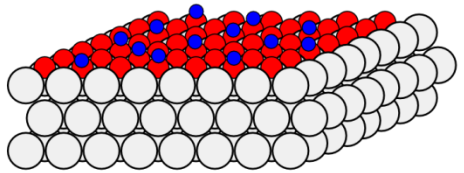


Various adsorbate species can be stabilized on Pt(111) under high temperature and pressure conditions.

Ambient

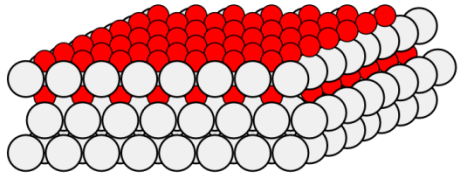


$O\text{-}OH\text{-}H_2O$



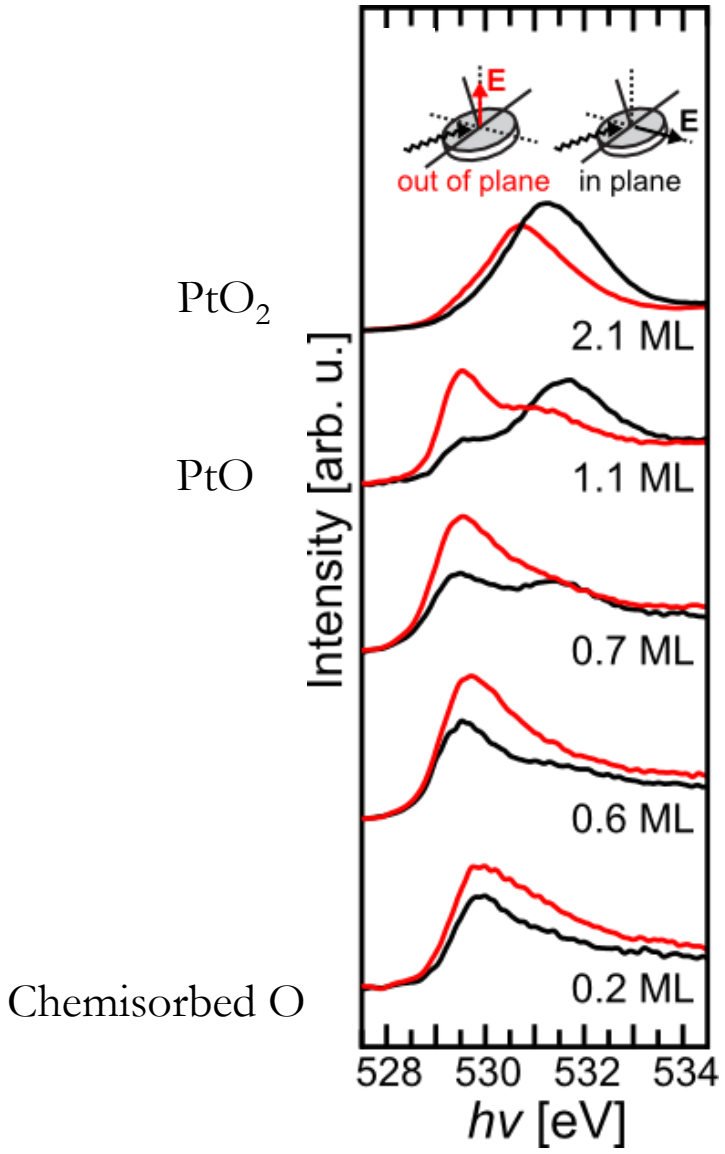
Chemisorbed
O-OH biphase

UHV



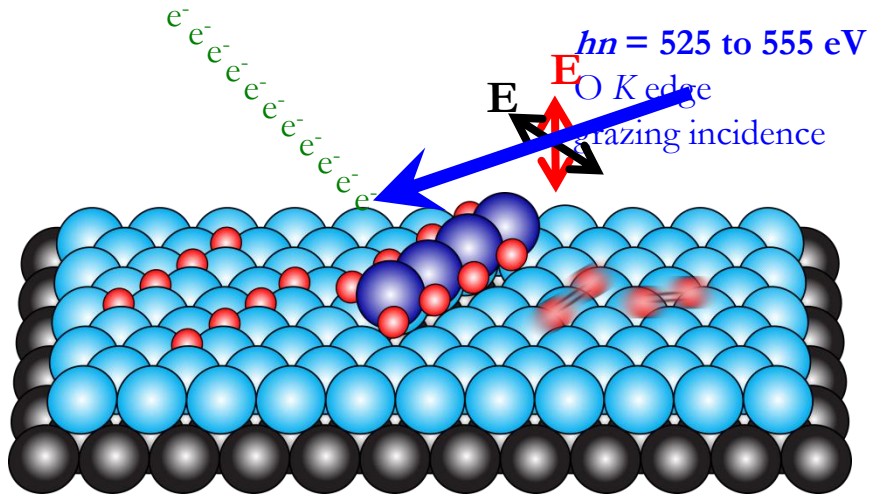
Chemisorbed O
surface oxide

Oxygen Species on the Pt(111) Surface

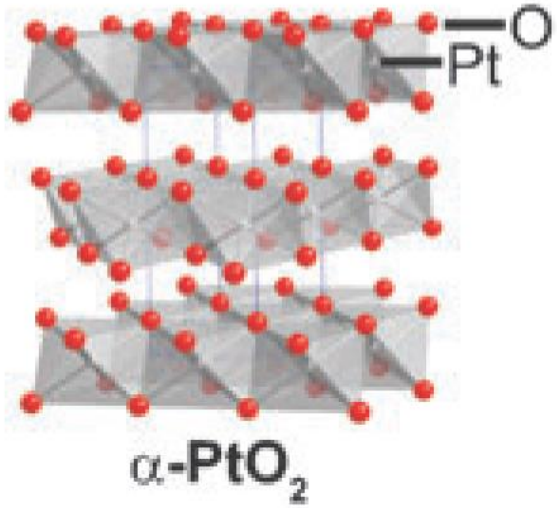


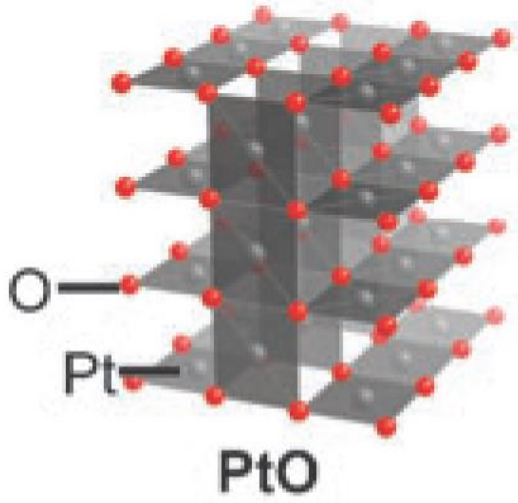
O K-edge XAS: Signatures of high-coverage oxygen layers

O(*KVV*) Auger electrons
K.E. ~ 500 eV

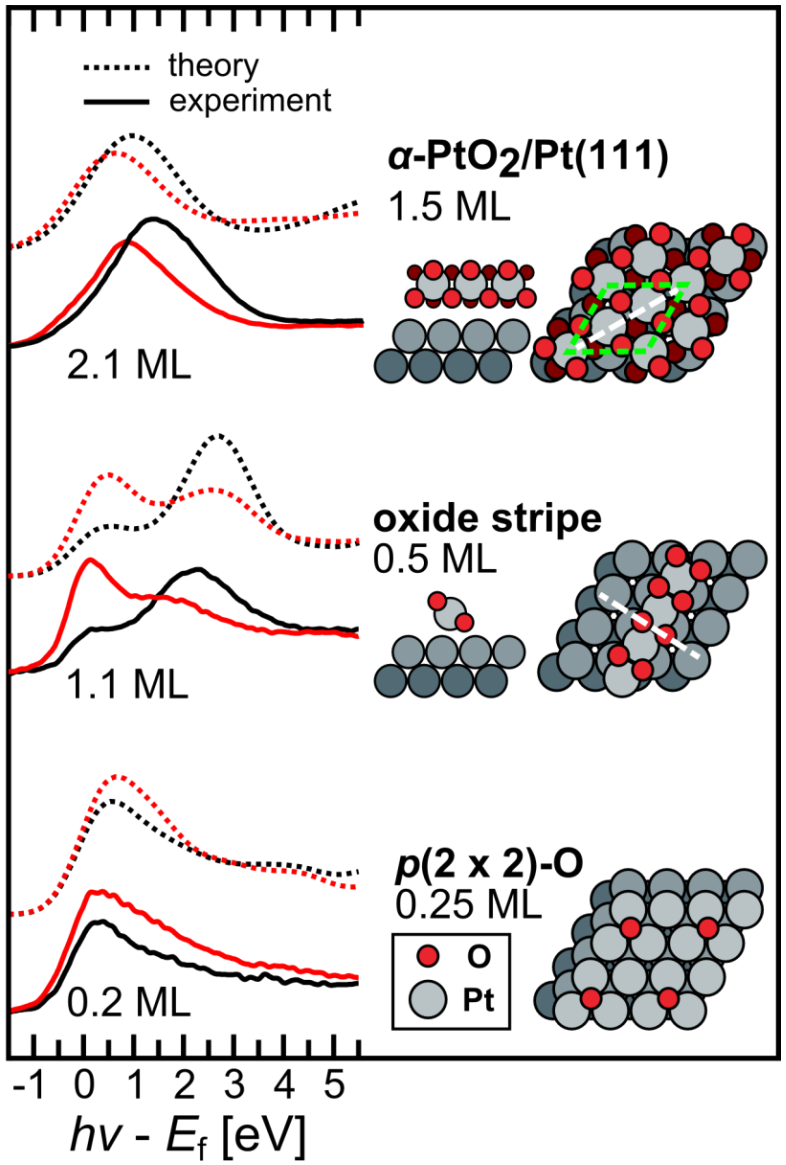


Oxygen Species on the Pt(111) Surface





bulk PtO_x phases



Experimental spectra

- Binding-energy scale determined from O 1*s* XPS

Theoretical spectra

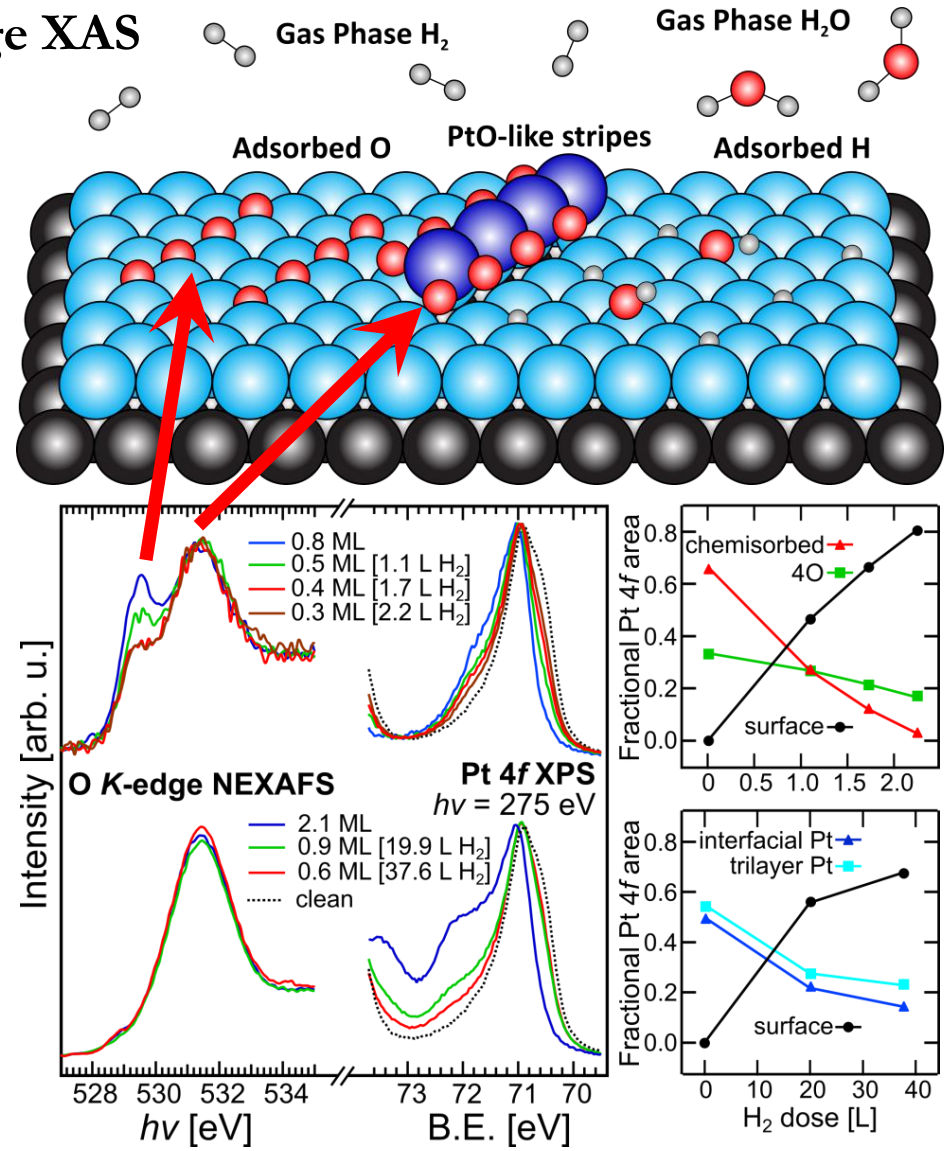
- Half-core-hole transition-potential approach in GPAW
- Multiple scattering simulations using FEFF qualitatively similar

Reactivity of Chemisorbed O, PtO (4O-Pt), and PtO_2 towards H_2

Pt 4*f* XPS and in-plane O *K*-edge XAS

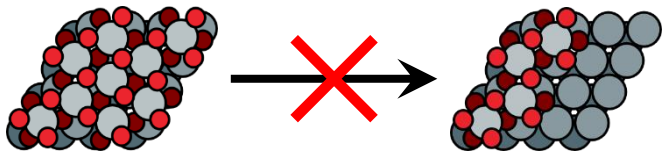
ex situ after dosing

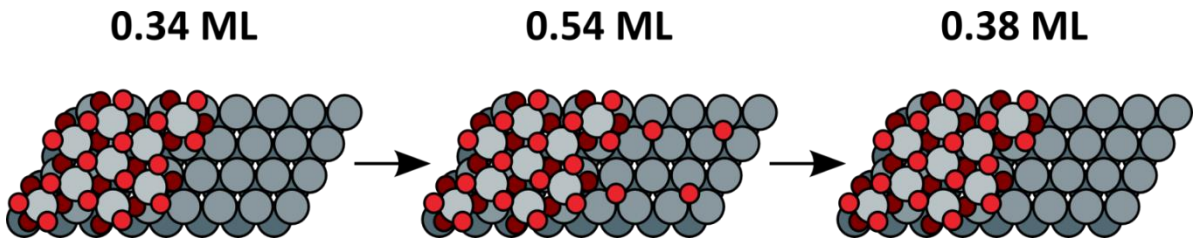
2×10^{-8} Torr H_2 at 300 K



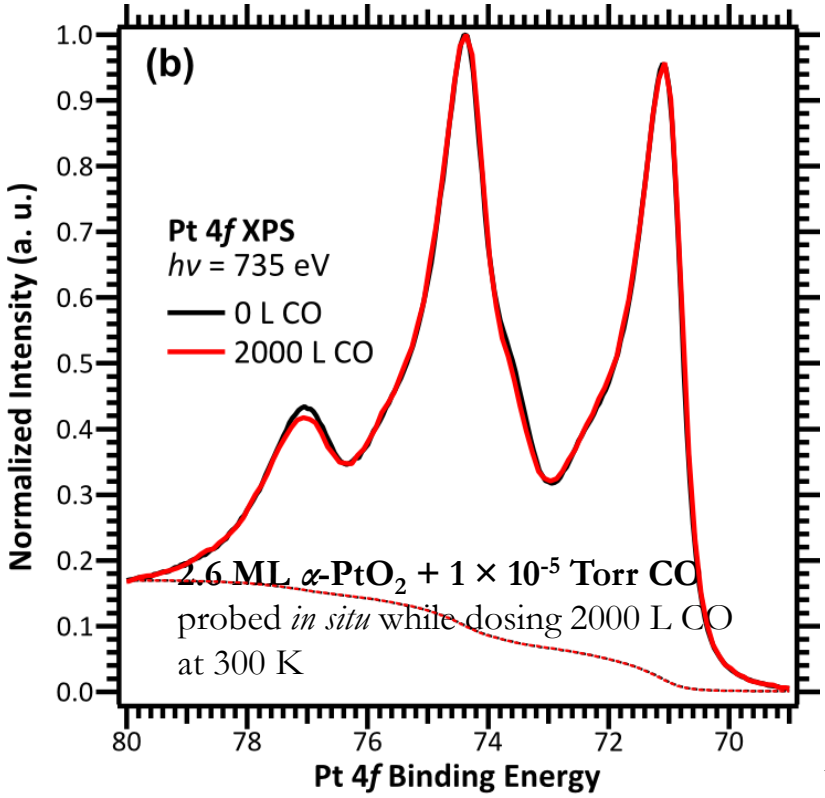
Phys. Rev. Lett. 2011, 107, 195502.

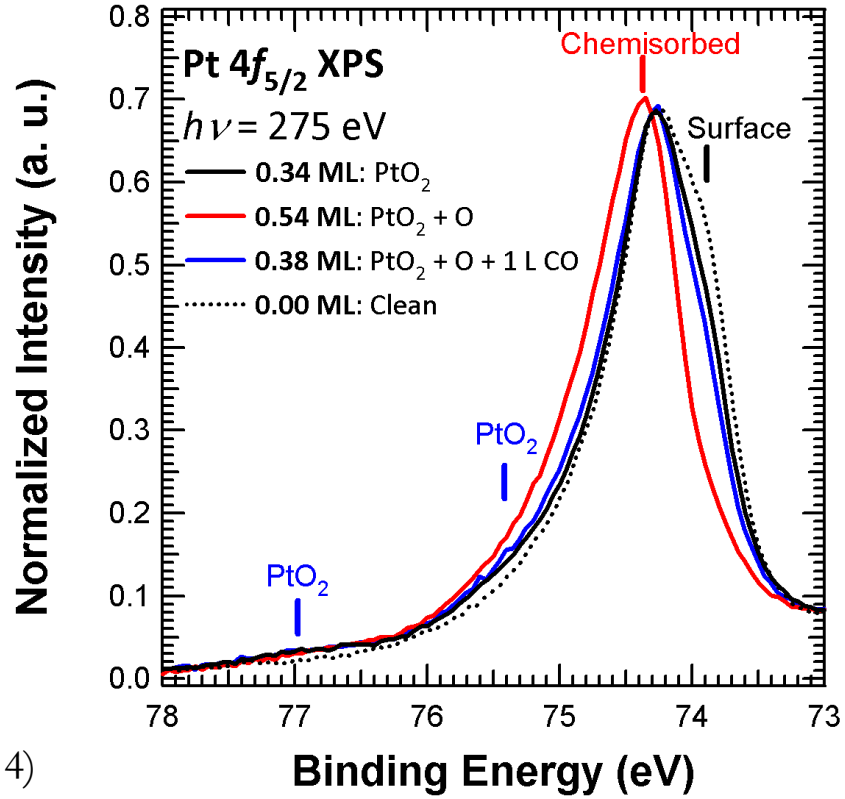
Reactivity of Chemisorbed O, PtO (4O-Pt), and PtO_2 towards CO





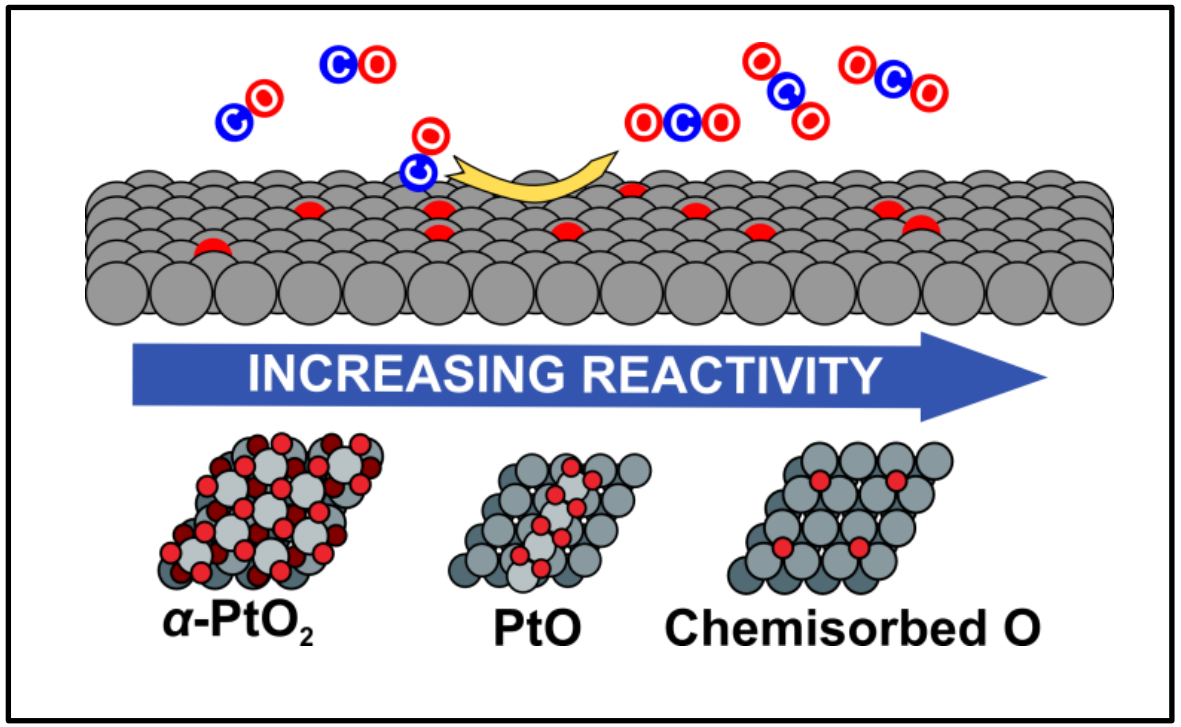
O 1s and Pt 4f: Thick α-PtO_2 films are inert to CO



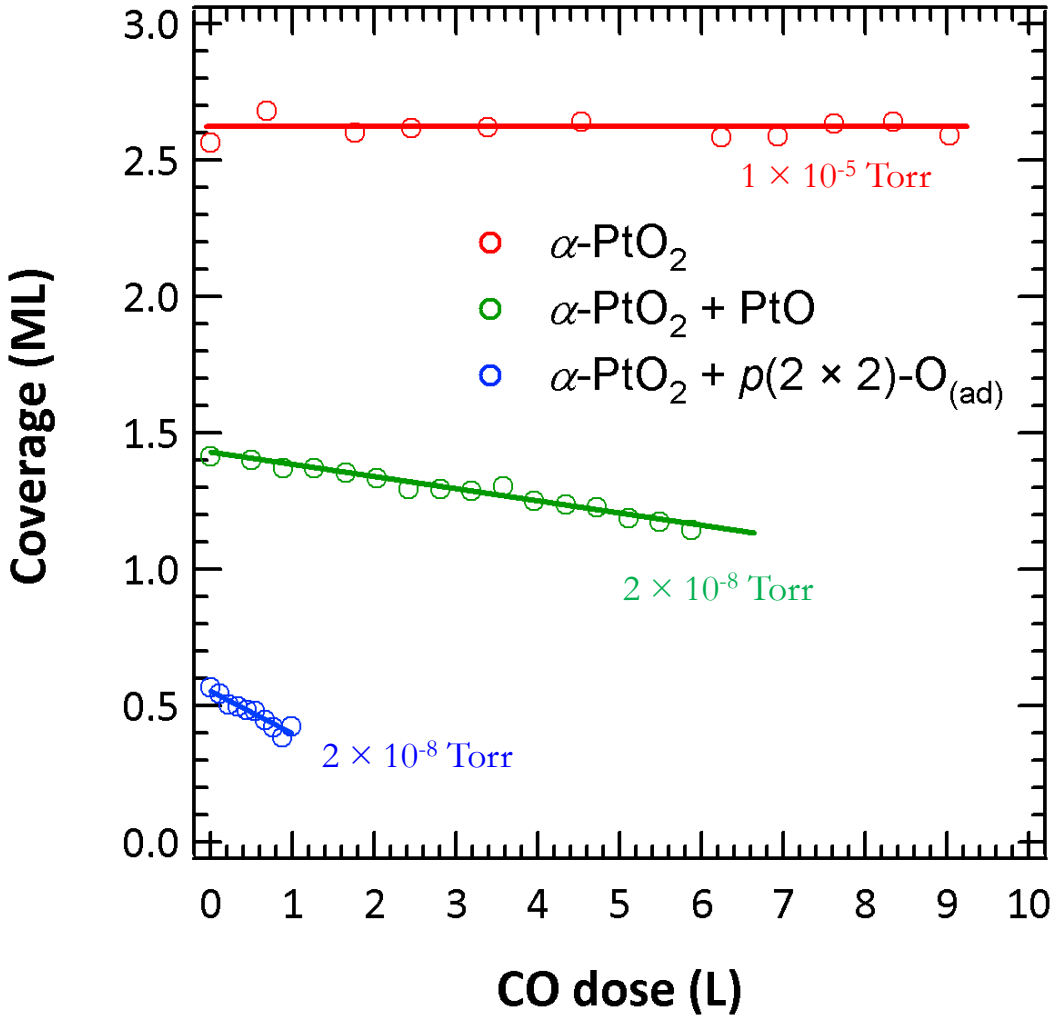


J. Am. Chem. Soc., 136, 6340 (2014)

Reactivity of Chemisorbed O, PtO (4O-Pt), and PtO_2 towards CO



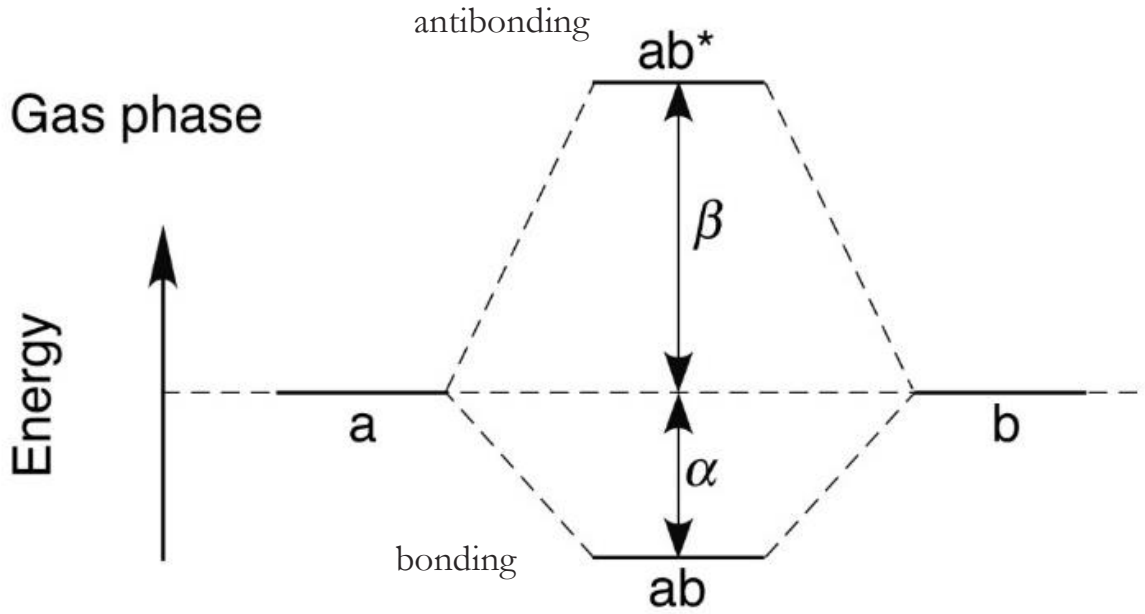
Adsorbed O domains are more active than α-PtO_2 trilayers



J. Am. Chem. Soc., 136, 6340 (2014)

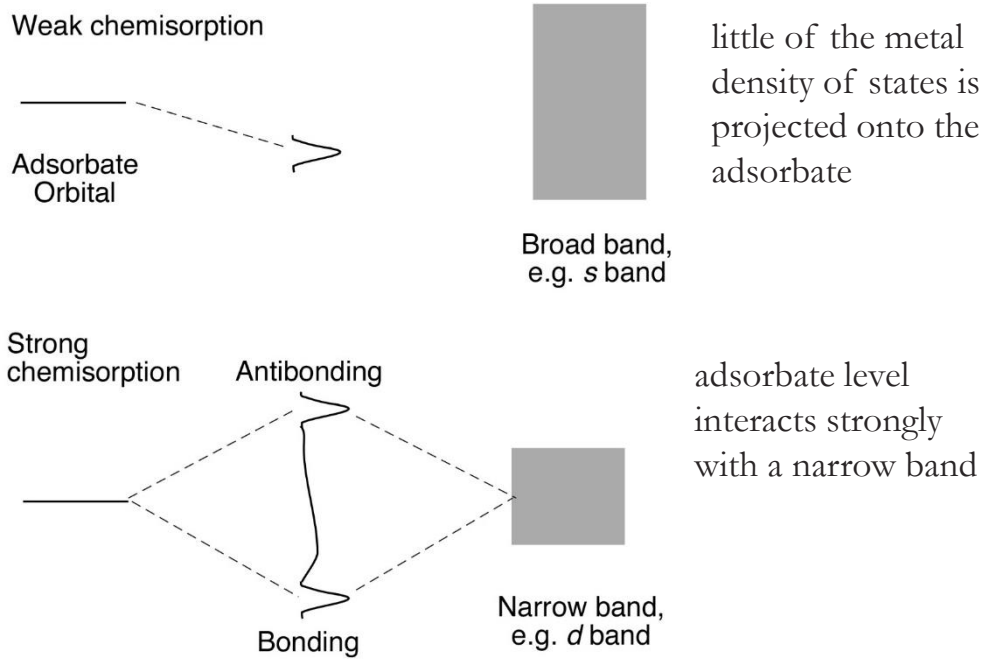
Theoretical Treatment of Chemisorption

LCAO: linear combination of atomic orbitals



The antibonding state is generally more antibonding than the bonding state is bonding, $\beta > a$. Consequently, if *ab* and *ab** are both fully occupied, not only is the bond order zero, the overall interaction is repulsive.

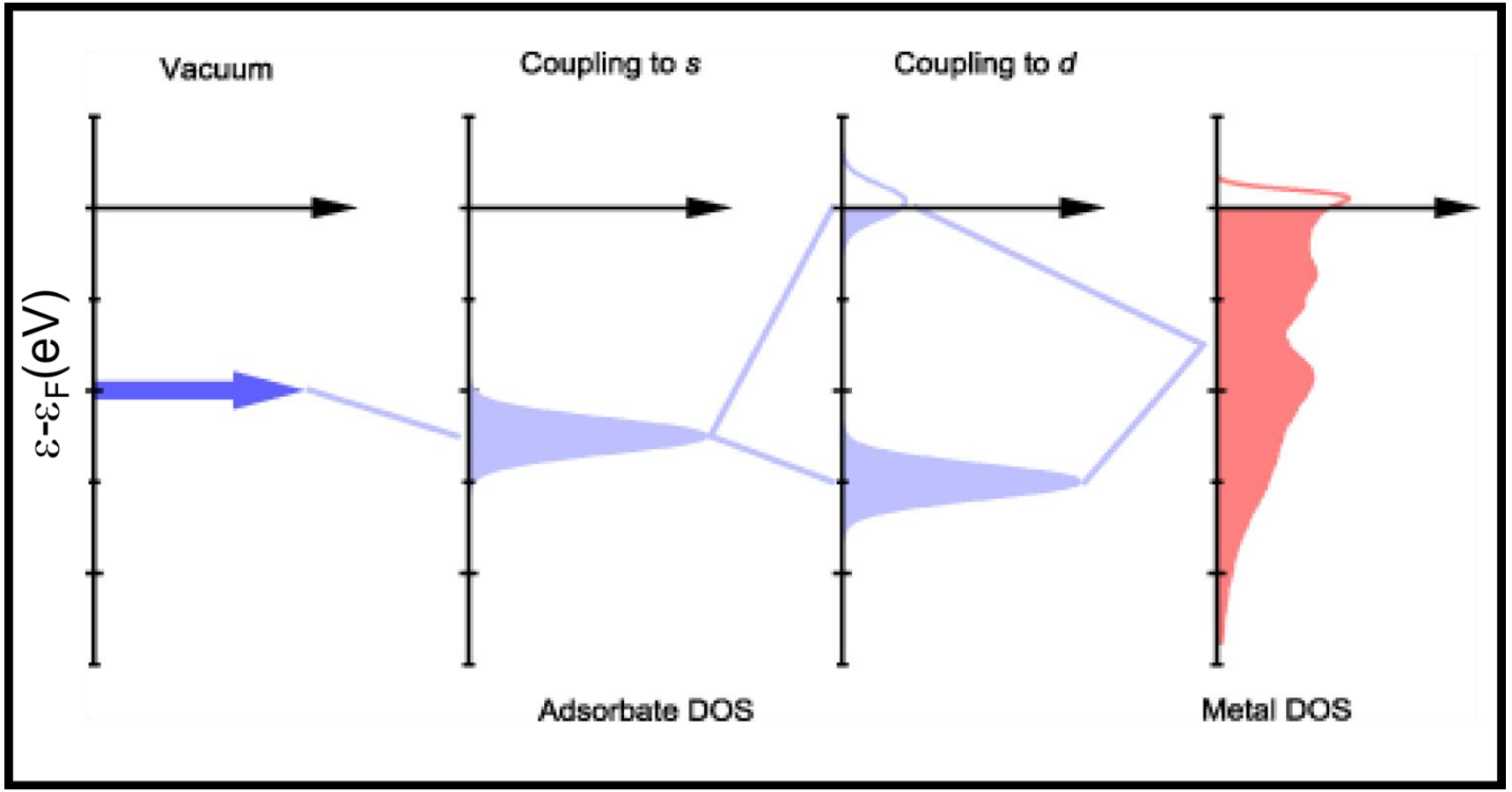
Chemisorption



The Anderson-Grimley-Newns approach: the types of electronic states that arise after chemisorption depend not only upon the electronic structure of the substrate and adsorbate but also the coupling strength between the adsorbate and the substrate. The adsorbate levels may end up either inside or outside the metal band.

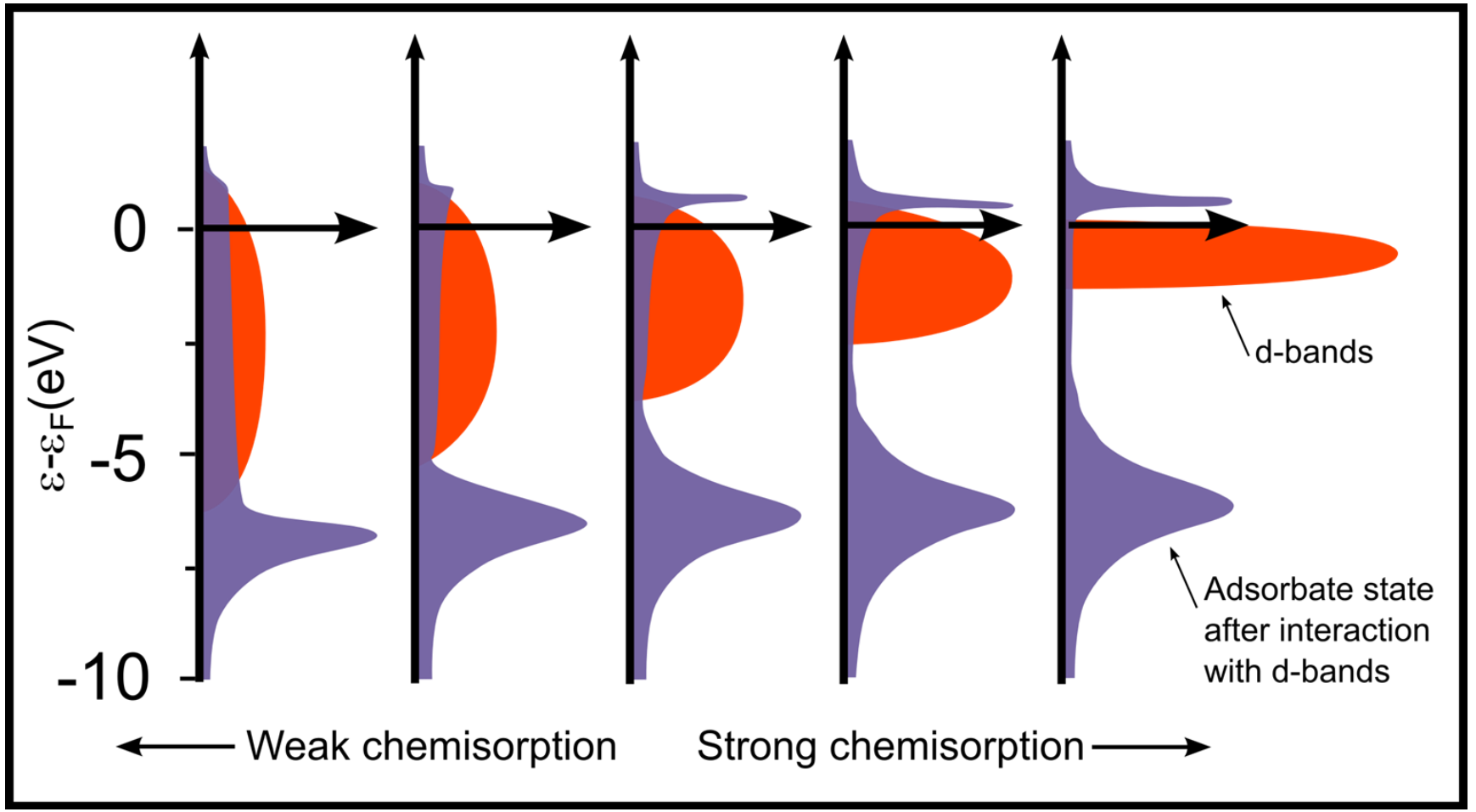
Change in local electronic structure at an atom upon adsorption on a simple metal

Sharp gas phase atomic states are broadened and shifted down due to interactions with the metal



d-band center

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

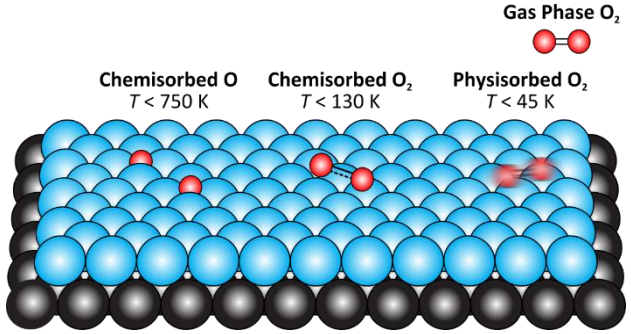


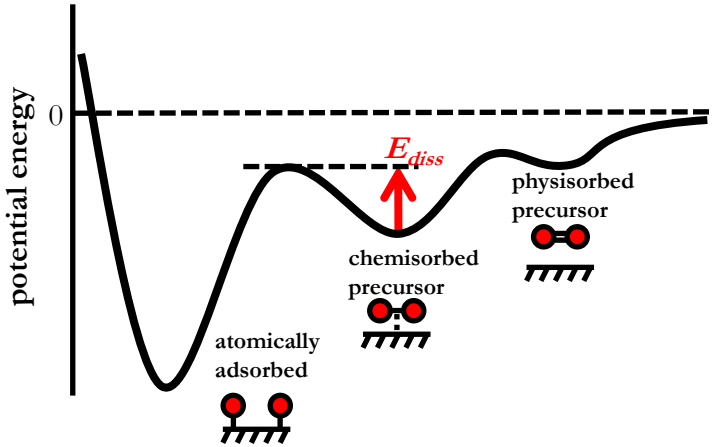
Hammer and Nørskov

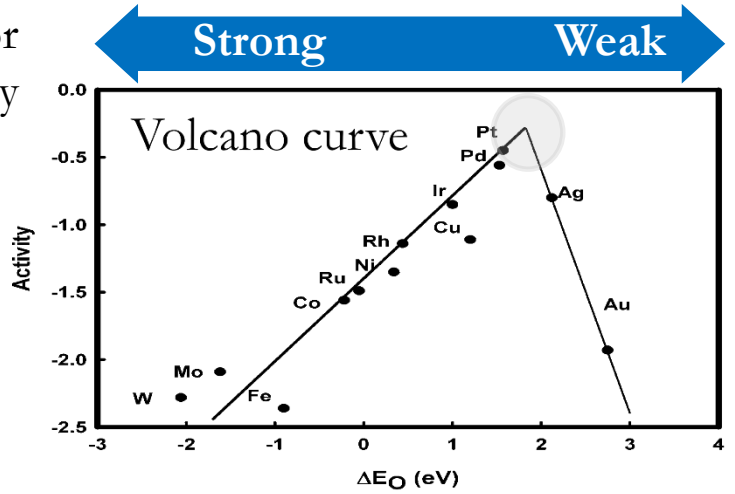
Scaling Relationships

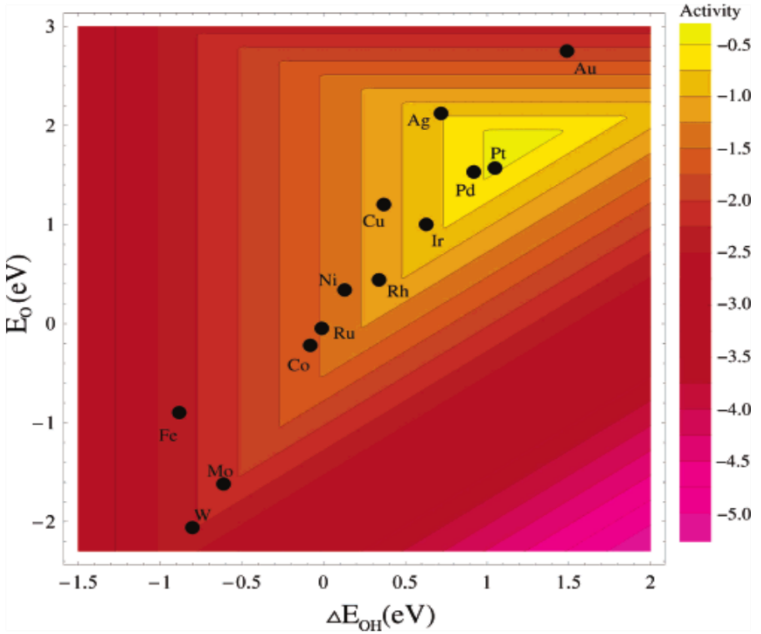
Trends in catalytic activity are also valid for adsorption binding energy

Example: oxygen adsorption



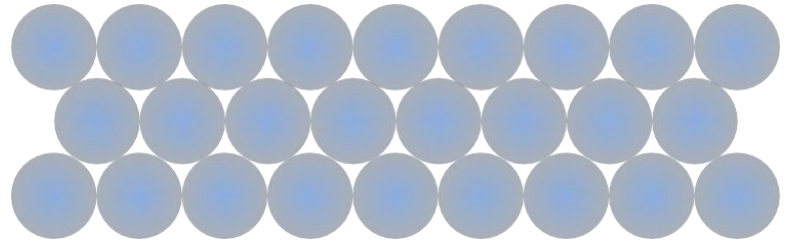




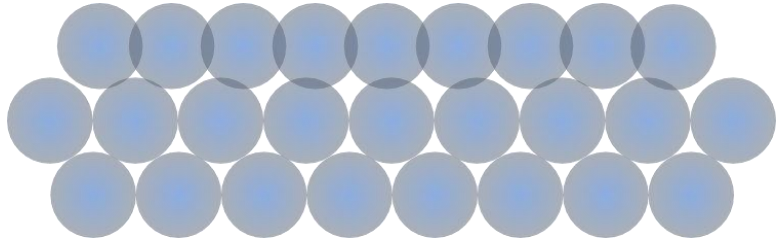


Strain and Ligand Effects

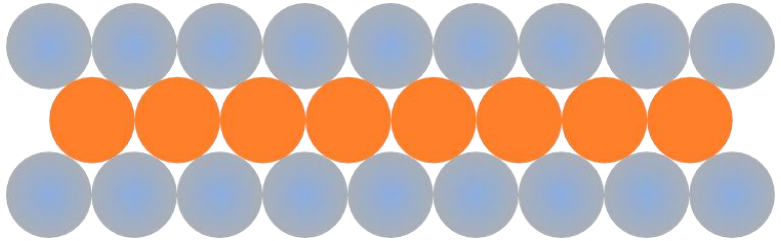
Strain and ligand effects modify the electronic structure of the catalytically active materials



Strain

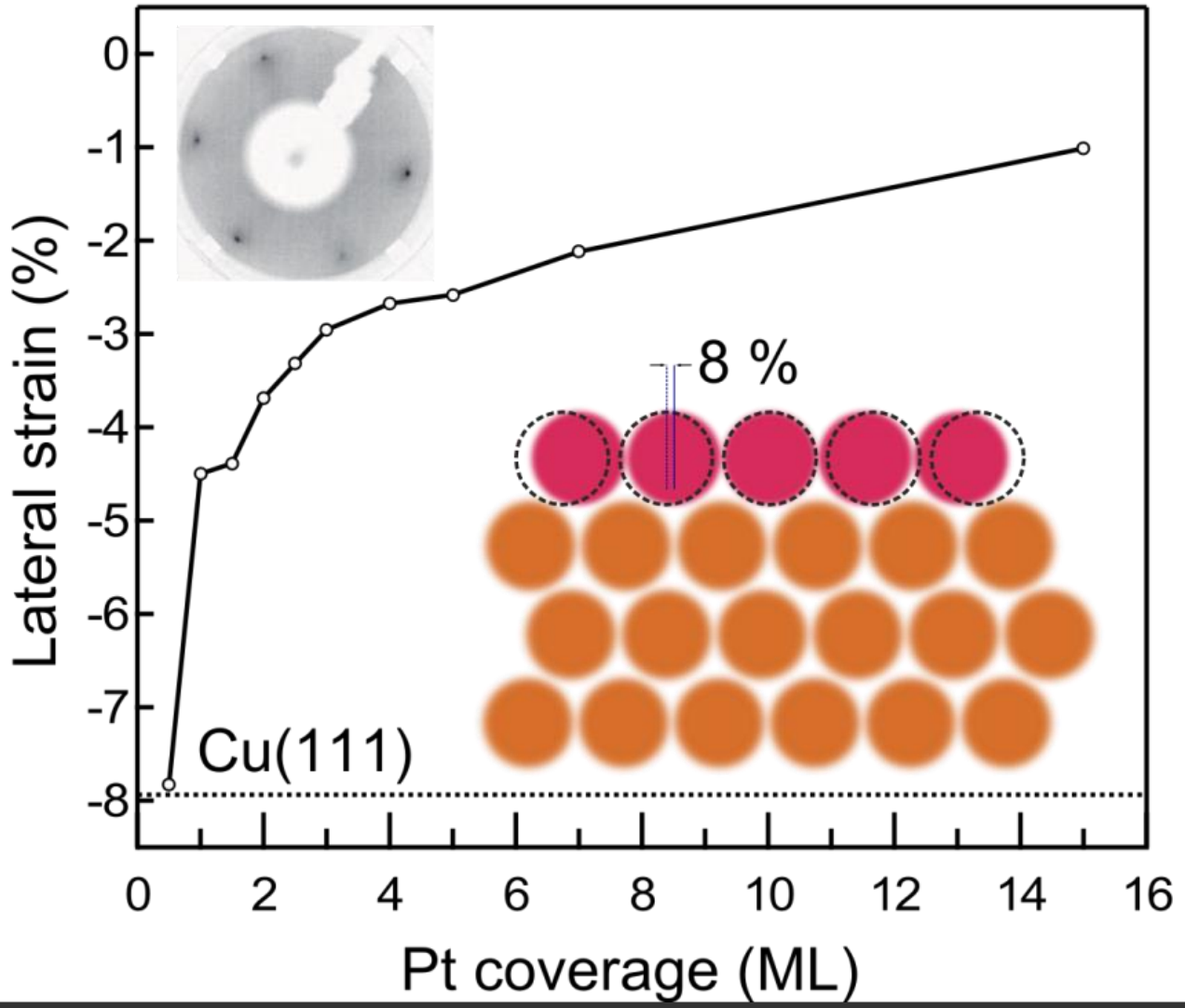


Ligand



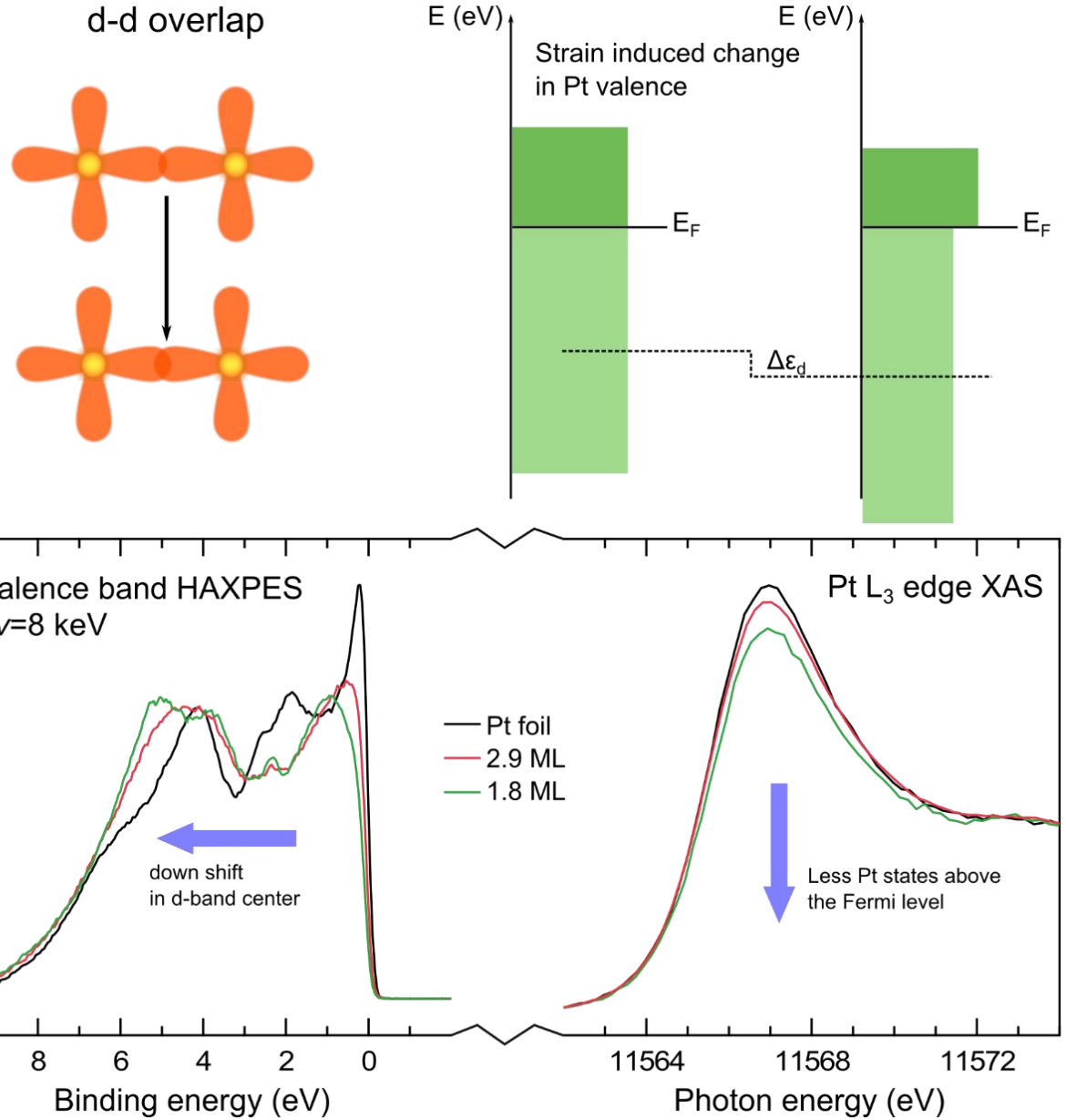
Compressive strain: Pt on Cu(111)

Coverage dependent compressive strain on Pt shell



On the Cu(111) surface, Pt overlayers are compressed due to lattice mismatch, however, this compressive strain is relaxed with increasing the thickness of the Pt overlayer

d-band Center

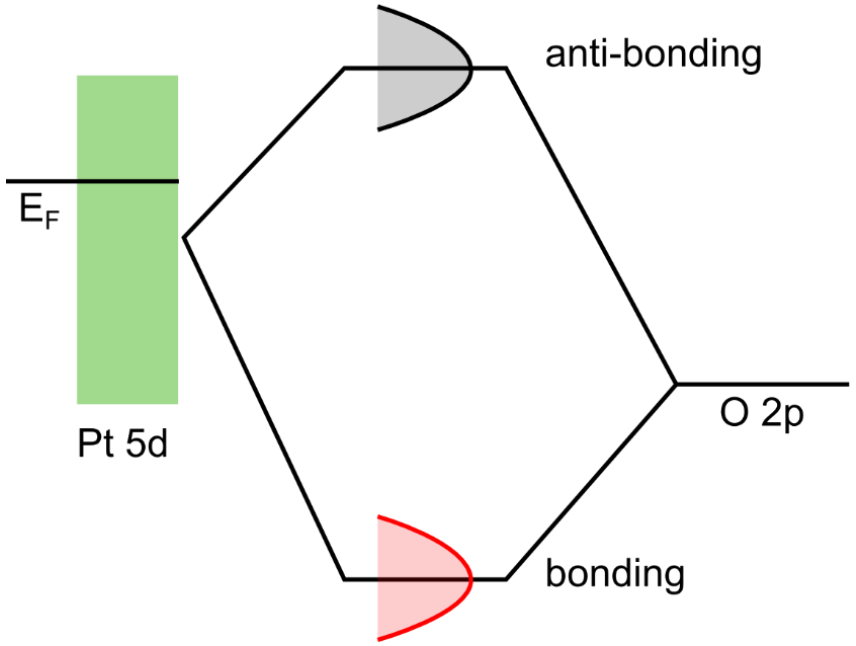


Strain induced change in the overlap between d-states leading to a change in the d-band width.

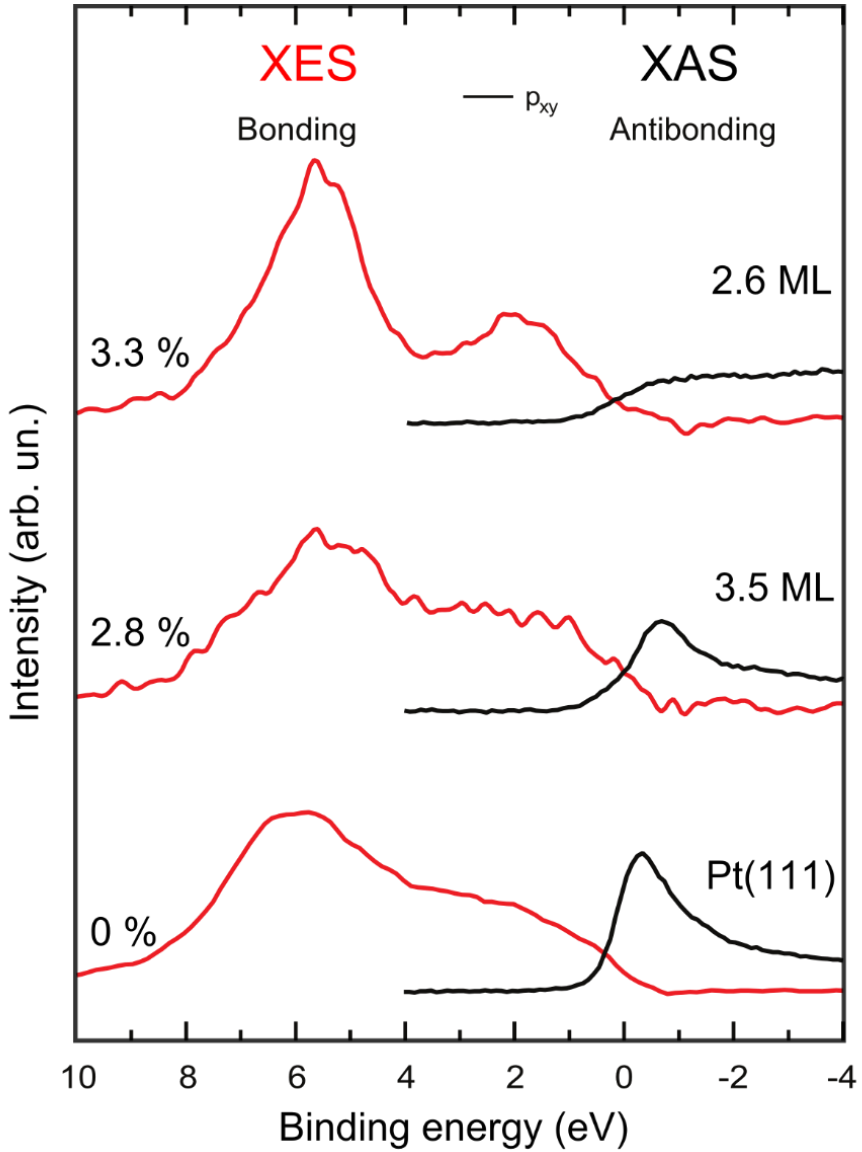
Change in the d-DOS, shift of the d-band center can be probed by spectroscopy.

Electronic Structure on Chemisorbed Oxygen on Compressed Pt on Cu(111)

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



O K-edge XAS and XES

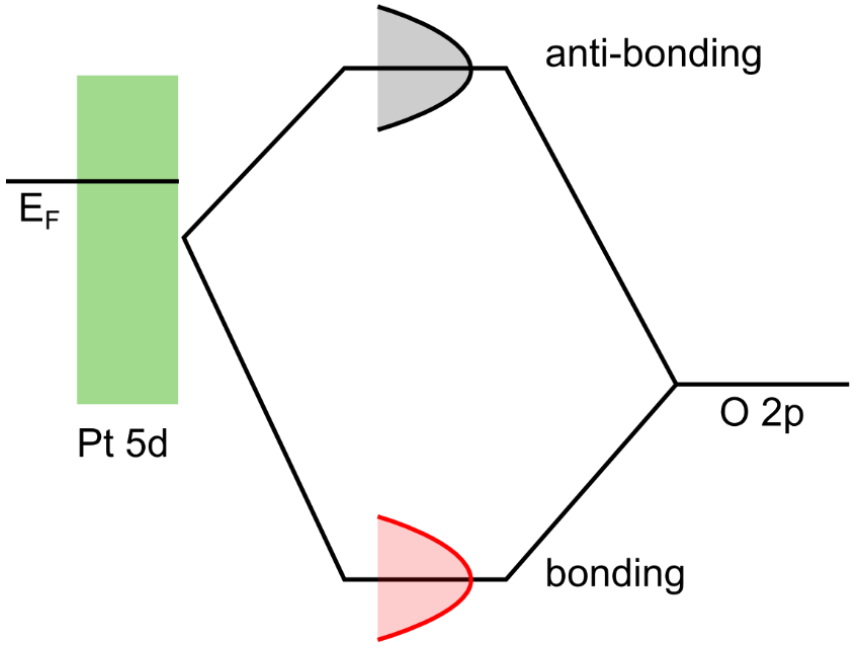
Compressive strain

No strain

Nat. Chem. 2, 454–460 (2010)

Electronic Structure on Chemisorbed Oxygen on Compressed Pt on Cu(111)

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



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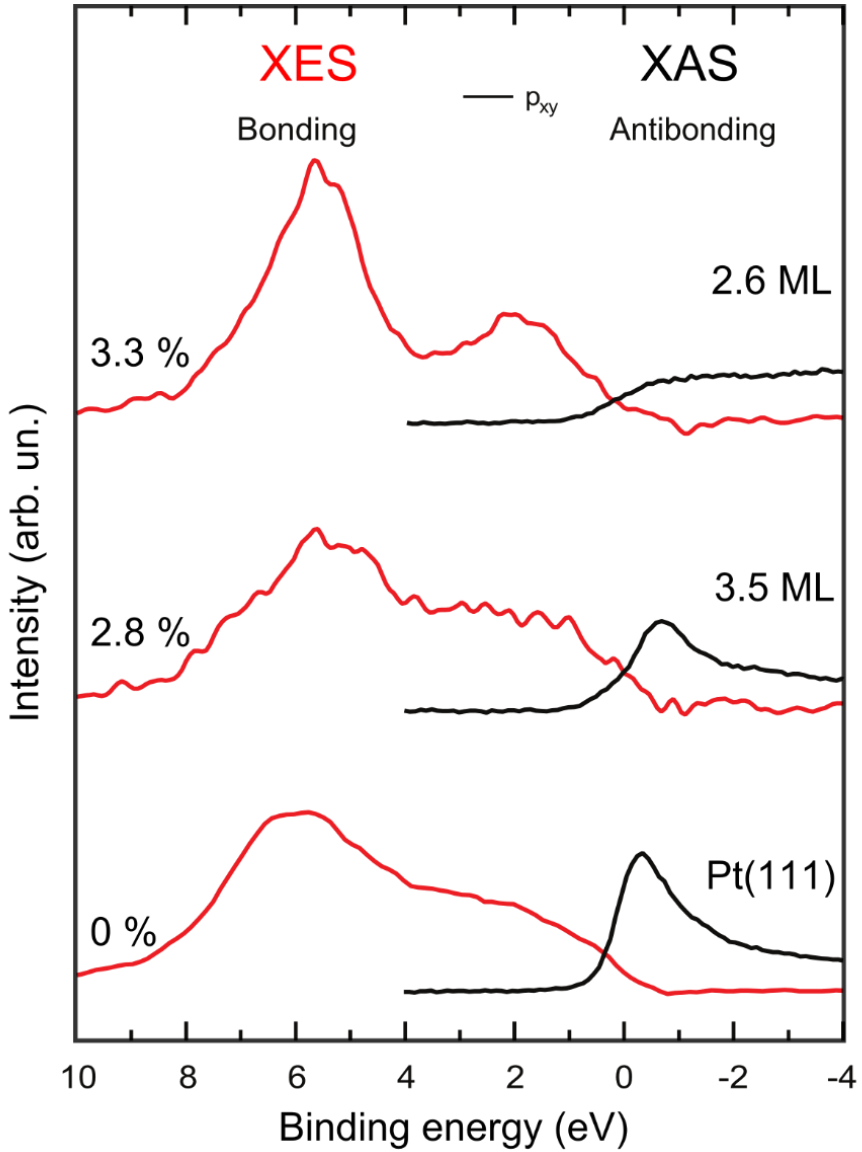


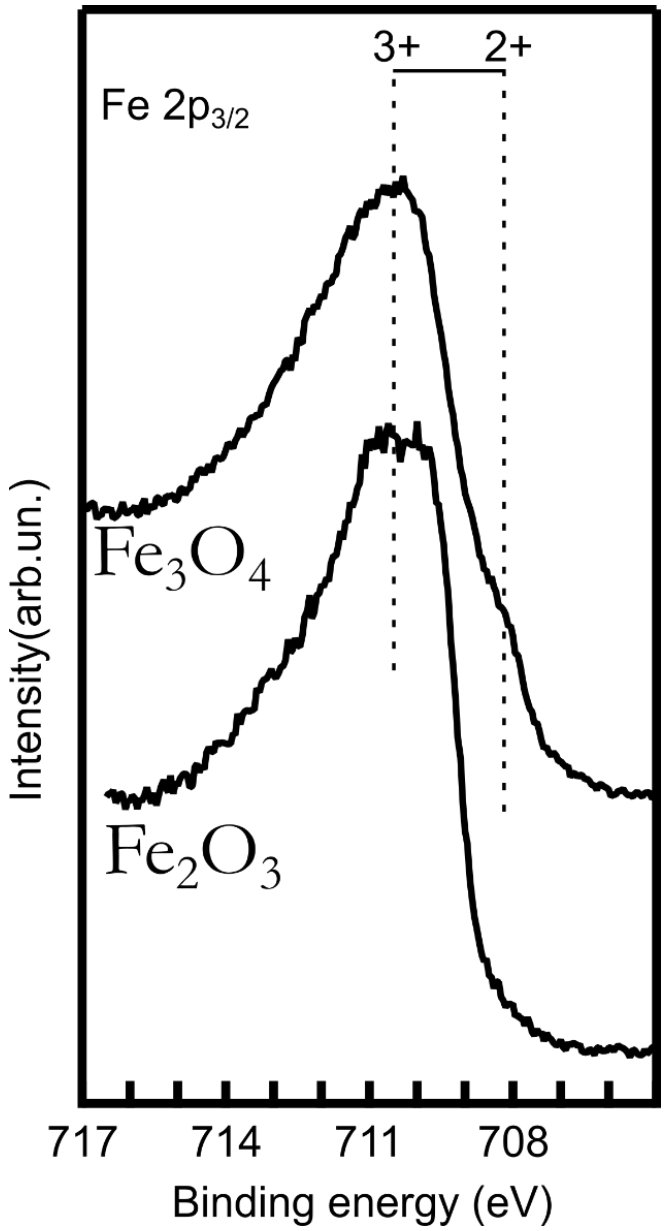
O K-edge XAS and XES

Compressive strain

No strain

Nat. Chem. 2, 454–460 (2010)

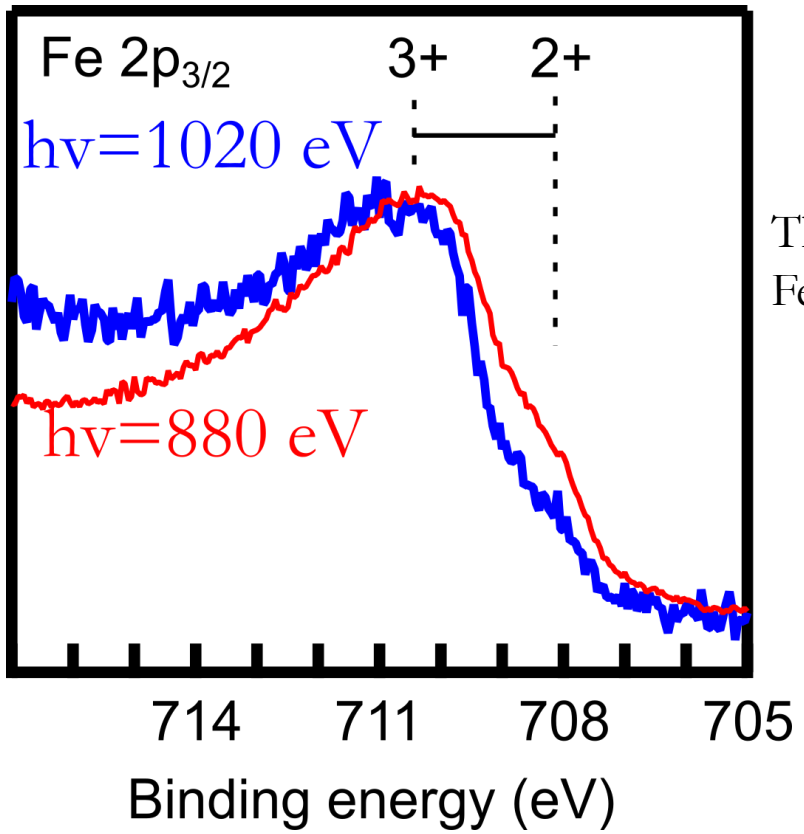
Identifying the Surface: Photon Energy



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

~711 eV ? 100-200 eV

Fe_3O_4



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

Summary

If you need to identify

- Surface elemental composition
- Chemical states
- Surface electronic structure

All you need is XPS and XAS

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)

Graduate students

Amin Mohammadpour
Fatih Uçar
Mert Can Korkutan
Janset Otuzoğlu
Başak Ataş
Ela Ayral

Postdoctoral fellows

Hamaneh Zarenezhad
Shervin Daneshvarasl

Undergraduate students

Eğin İrem Haznedar
Azra Şekercioğlu
Alp Eren Başaran
Esra Altuntaş
Ali Eren Ekşi

Collaborators

Alphan Sennaroglu / Koç Univ.
Can Erkey / Koç Univ.
Hirohito Ogasawara / SLAC
Dennis Nordlund / SLAC
Andreas Stierle / DESY
Jonas Weissenrieder/KTH
Federica Bondino / Elettra
Ferdi Karadaş / Bilkent Univ.
Önder Metin / Koç Univ.
Adem Tekin / ITU
Emre Erdem / Sabancı Univ.
Julia Wiktor / Chalmers University of Technology

Thank you

KOÇ UNIVERSITY KUHyTech KUTEM

sarpkayaLAB.ku.edu.tr **sarpkaya@ku.edu.tr**