Why Is Pt So Unique

A Chemical Physics Approach

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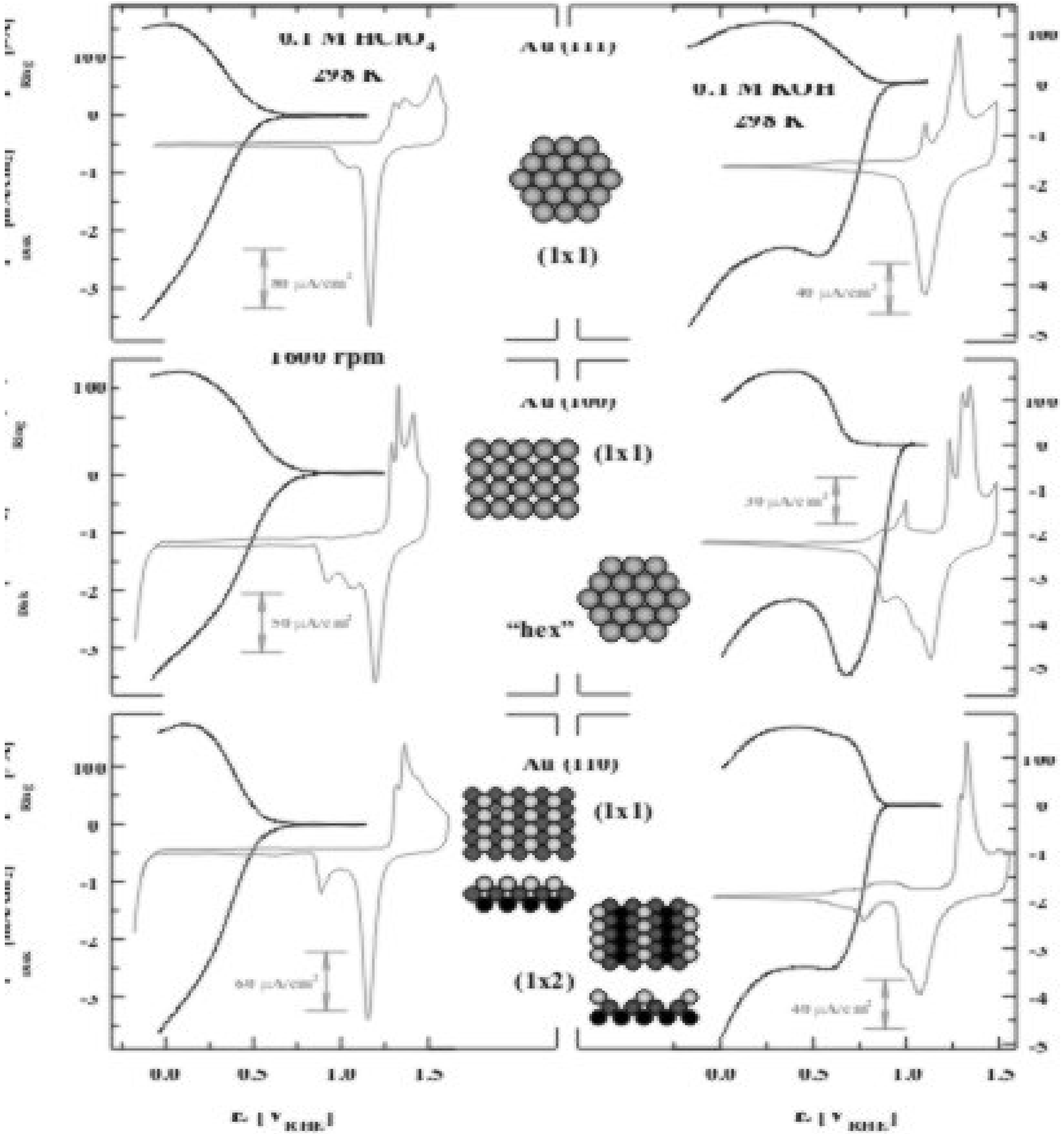
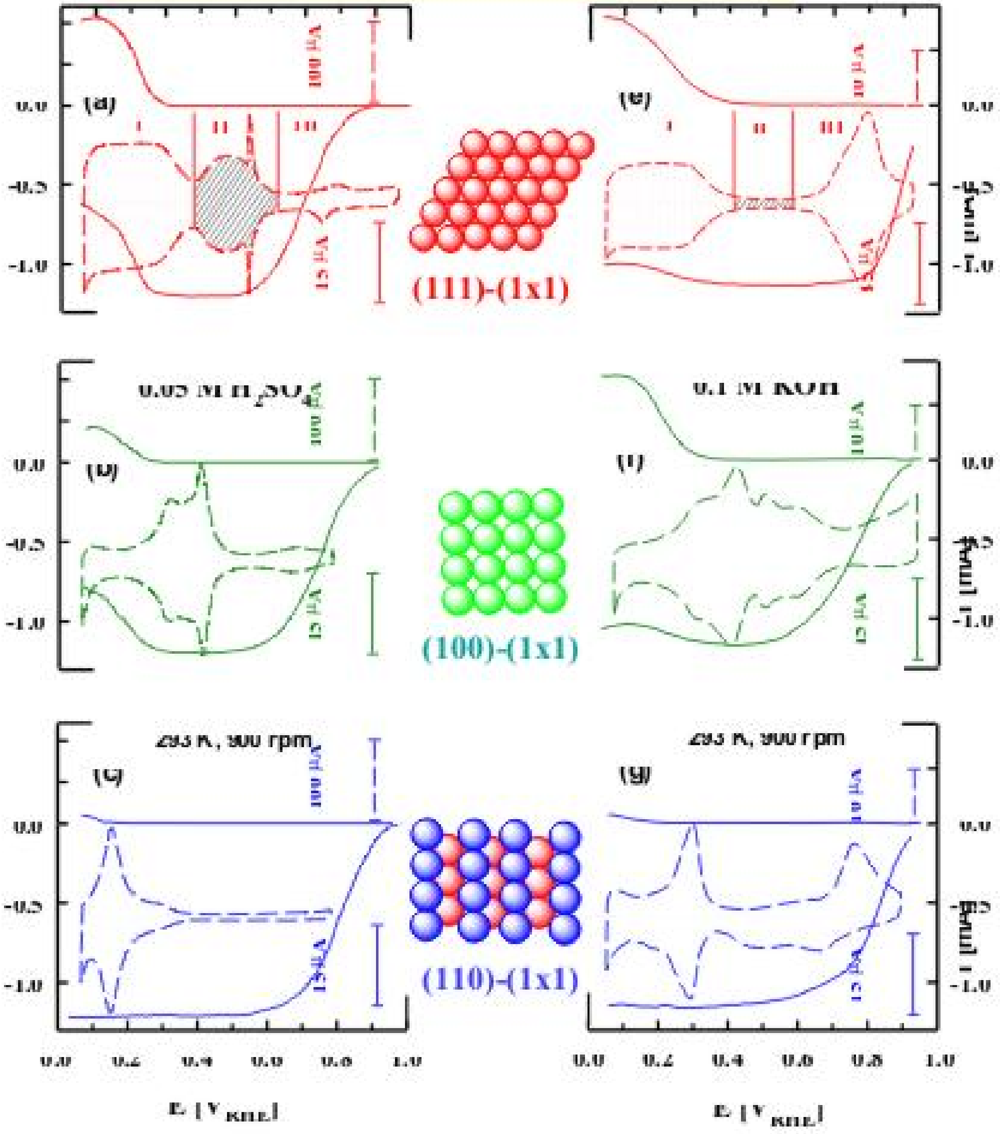
Outline

- A brief history of electrode kinetics
- Reaction pathway for oxygen reduction
- Effect of pH
- Systematic trends across Periodic Table
- One electron makes a big difference
    - d^9s^1 versus $d^{10}s^1$
- Pt at the top of the Volcano Curve

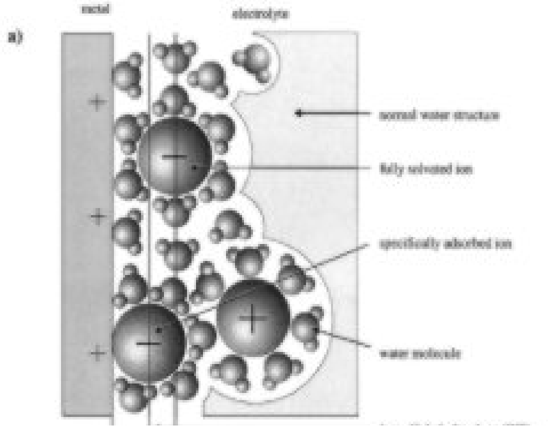


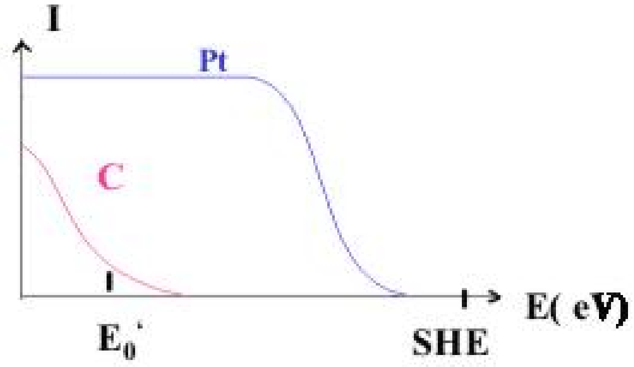
0.1 M HClO$_4$
298 K
Au (111)
0.1 M KOH
298 K
(1x1)
80 μA/cm²
40 μA/cm²
1600 rpm
Au (100)
(1x1)
"hex"
50 μA/cm²
30 μA/cm²
Au (110)
(1x1)
(1x2)
60 μA/cm²
40 μA/cm²
100
0
-1
-2
-3
-4
-5
0.0
0.5
1.0
1.5
E [V$_{RHE}$]

ORR Kinetics on Pt(hkl)



Mechanism of the ORR at metal electrodes





Addition of first electron needed to break O-O bond

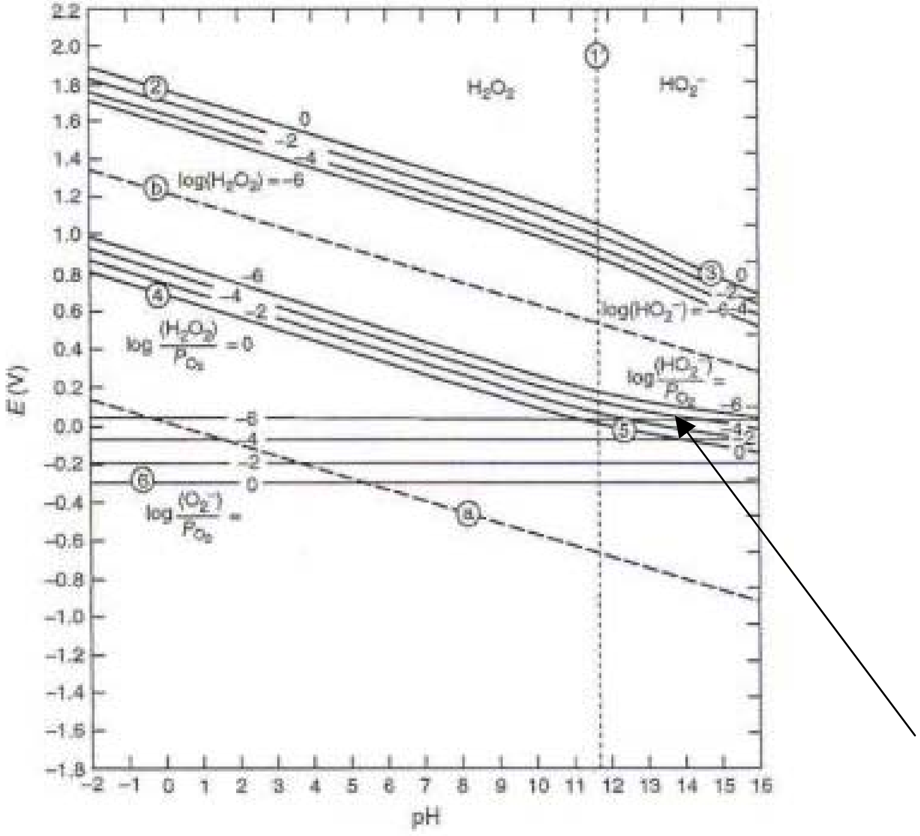
Rate limiting step in electrochemical reduction of O_2 is 1st electron transfer

$O_2 + 1\,e^- \rightarrow (O_2{}^-)_{sol}$ Outer Sphere **(E_0'=-0.3 V)**
$O_2 + 1\,e^- \rightarrow (O_2{}^-)_{ads}$ Inner Sphere **($E_0' + \Delta G_{ad}/F$)**

$O_2{}^-$ adsorption strength related to the electronic properties of the electrode material

Establish general trends across Periodic Table using quantum chemical modeling

Origin of the pH Effect



$$\mathbf{O_{2,ad} + e^- \rightarrow \bullet O^-_{2,ad}} \quad \textbf{(rds)}$$

Because H^+ does not occur in the rds, the rate of this reaction step will not depend on pH. But if we define the electrode potential using the rhe scale, then the *overpotential* will be pH dependent and thus the polarization curve will shift with pH

$$I = k\ F\ C_{O2} \exp\left(\beta F \eta / RT\right)$$

$$\eta = E - 0.059\text{pH} - E_o[(O_2/O_2^-)_{ad}]$$

Note that at pH = 14 only weak adsorption of O_2^- is needed to have reduction in the potential region (rhe) of interest

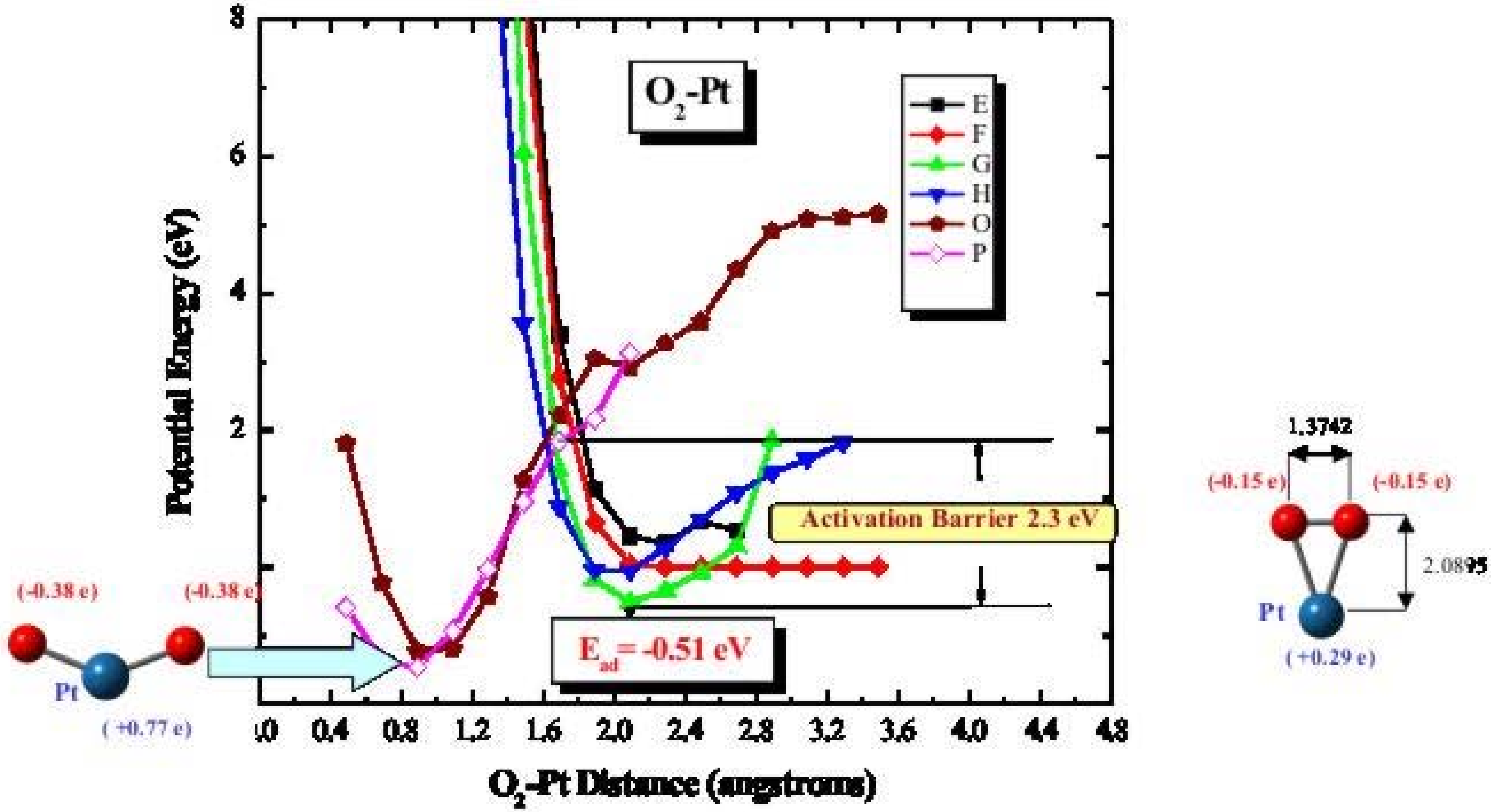
Quantum Chemical Modeling Approach

Calculate the interaction of molecular oxygen and the superoxide radical anion (O_2^-) with a single metal atom using DFT (B3LYP) LANL2DZ/6-31+G(d)

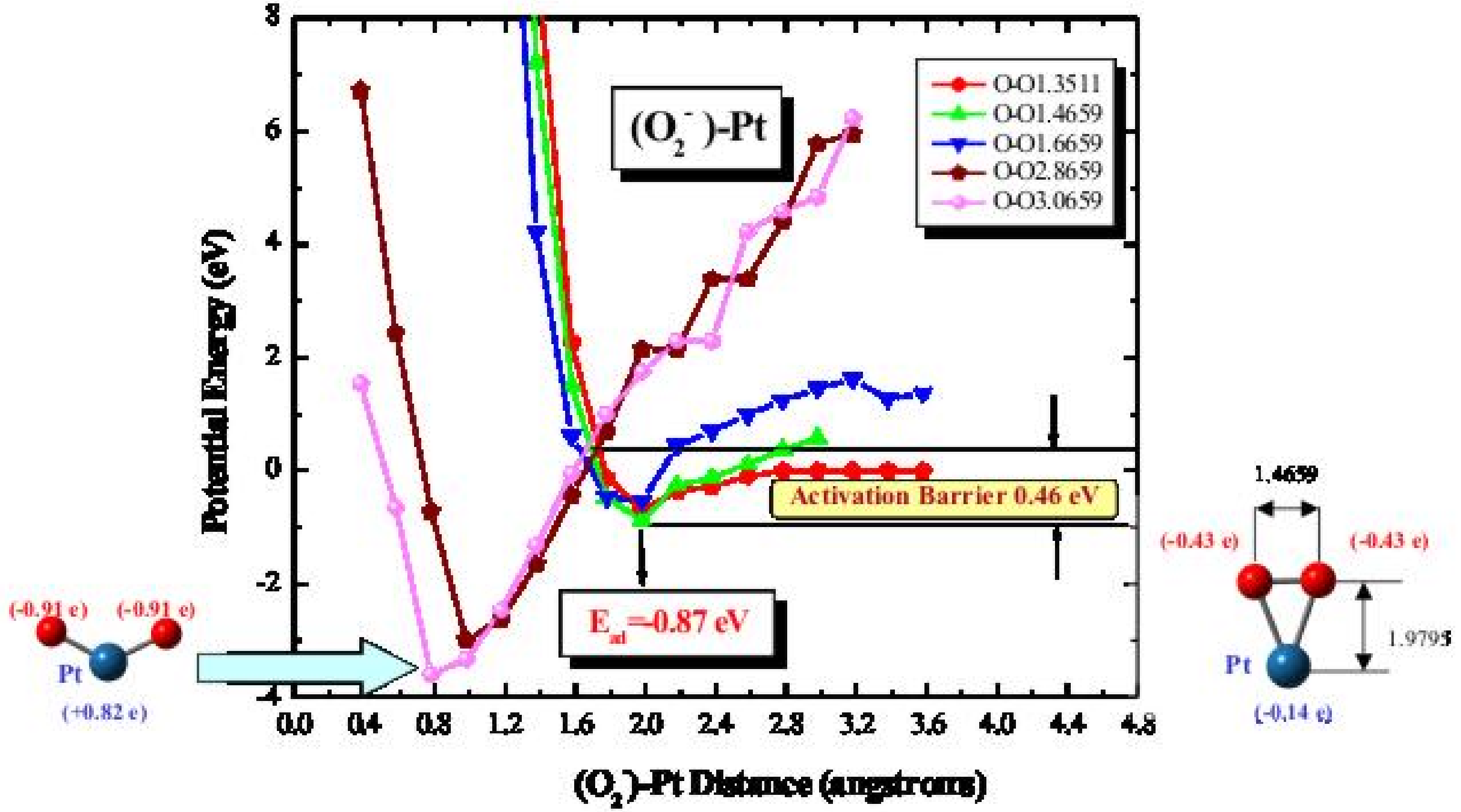
Obtain the Potential Energy Surface (PES) as a function of (O_2^-) distance above the metal atom and the O-O bond extension

Examine the molecular orbital character at various adsorption configurations and plot the correlation diagrams using Hartree-Fock (HF) LANL2DZ/6-31+G(d)

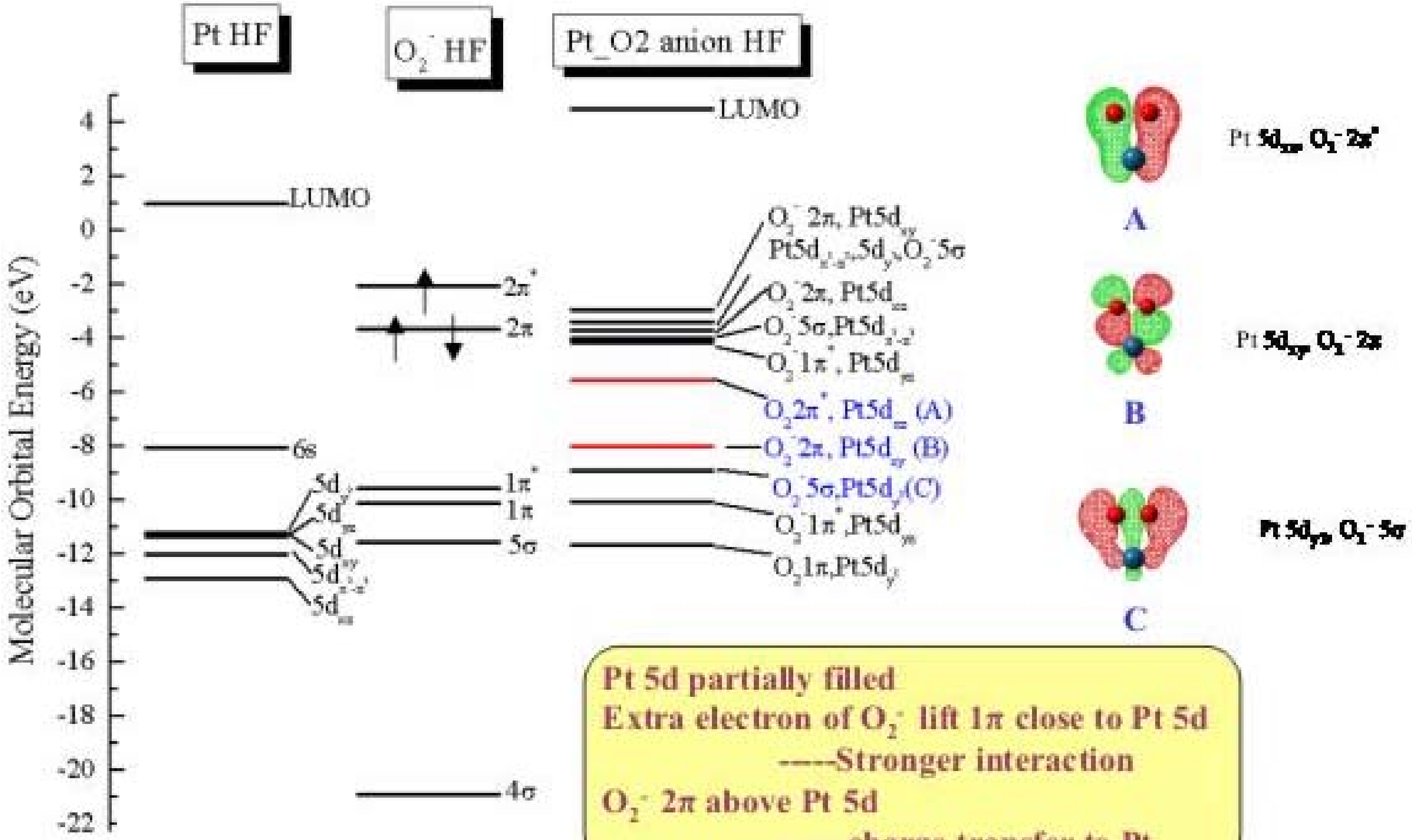
O_2 –Pt Potential Energy Curves vs. O-O bond length



(O_2 $^-$)–Pt Potential Energy Curves vs. O-O bond length

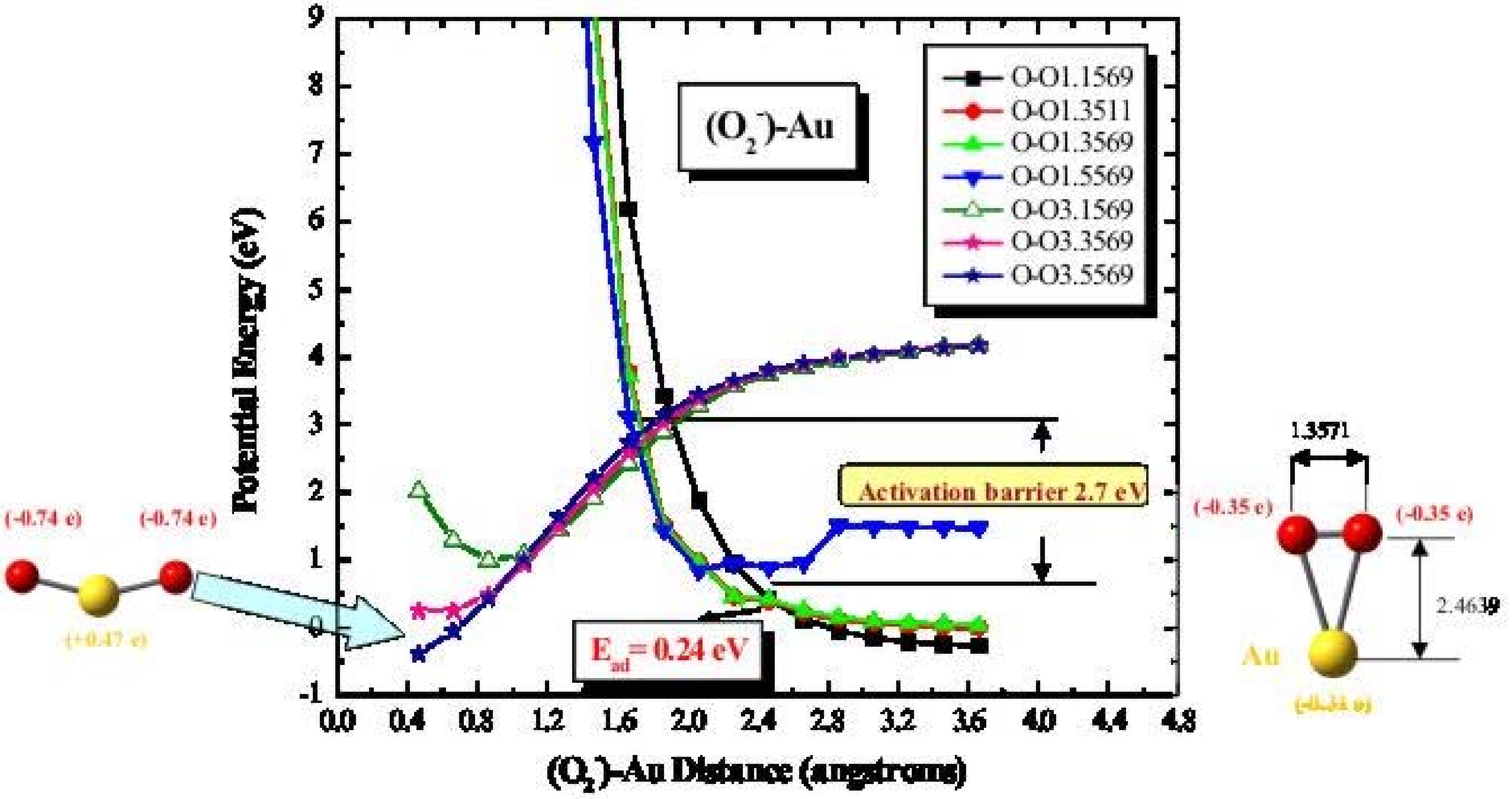


Correlation Diagram of the Molecular Orbitals of (O_2^-)-Pt □

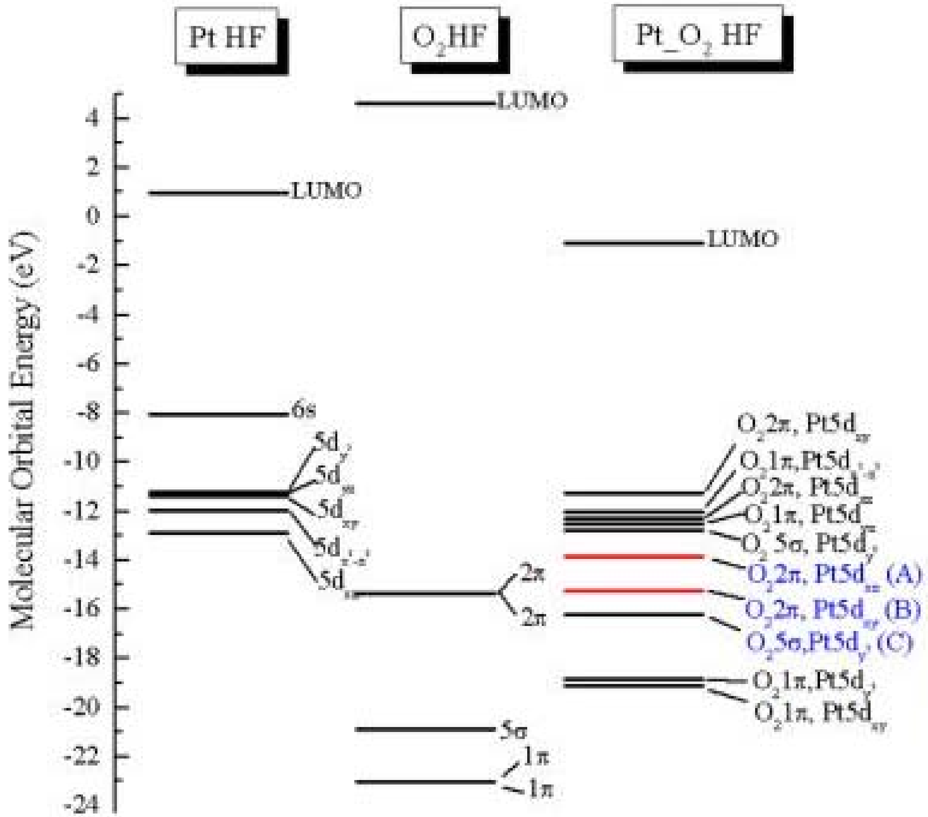


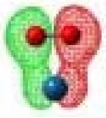
Pt 5d partially filled
Extra electron of O_2^- lift 1π close to Pt 5d
-----Stronger interaction
O_2^- 2π above Pt 5d
------charge transfer to Pt

(O_2^-)–Au Potential Energy Curves vs. O-O bond length



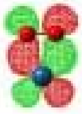
Correlation Diagram of the Molecular Orbitals of (O_2)-Pt□





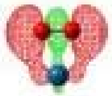
O_2 2π, **Pt 5d_{xz}**

A



O_2 2π, **Pt 5d_{xy}**

B



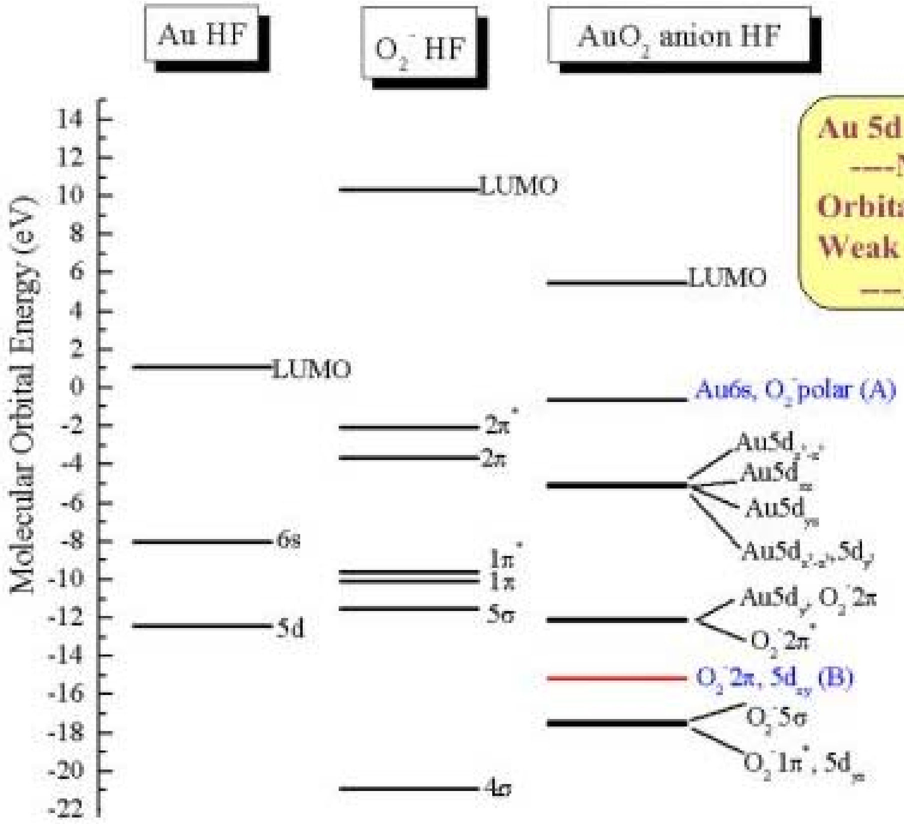
O_1 **5σ, Pt 5d_{y^2}**

C

Pt 5d levels above O_2 2π
Charge transfer from Pt to O_2

O_2 1π level lower than Pt 5d levels
Weaker interaction between Pt and O_2

Correlation Diagram of Molecular Orbitals of $(O_2^{\,-})$-Au□



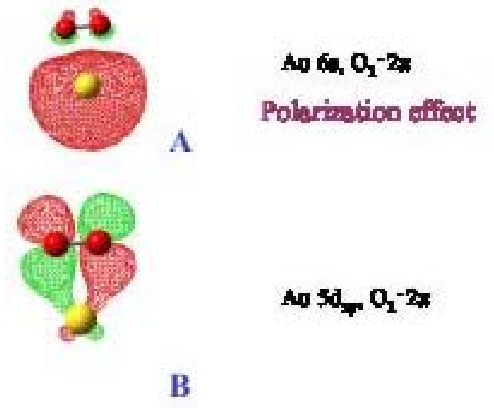
Au 5d completely filled

----No charge transfer between Pt and (O_2^-)

Orbital with different symmetry do not interact

Weak Interaction due to polarization

---Au6s and (O_2^-) π levels



Au 6s, $O_2^-2\pi$

Polarization effect

Au $5d_{xy}$, $O_2^-2\pi$

Conclusions from Quantum Chemical Modeling

The strength of interaction of O_2 and O_2^- with metals is uniquely related to their electronic structure

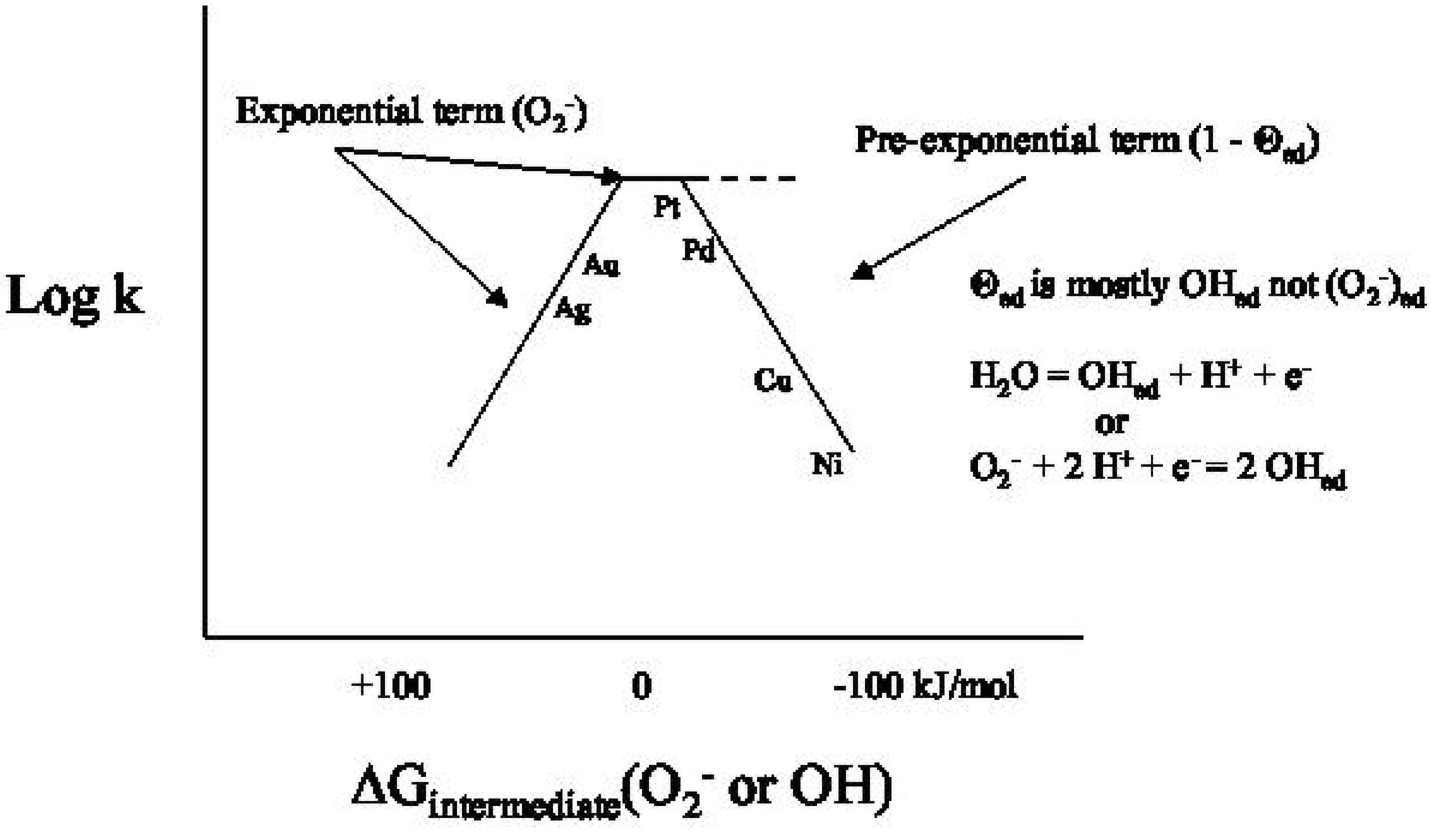
d^9s^1 Metal - O_2^- interaction much stronger than $d^{10}s^1$ Metal - O_2 interaction
(d^9s^1)- O_2^- >> $(d^{10}s^1)$ - O_2^-

d^9s^1 Metal - O_2^- interaction much stronger for 5d than 3d orbitals (relativistic effect)

$d^{9-n}s^1$ Metal - O_2^- interaction does not vary as much with n as the $d^{9-n}s^1$ Metal - O_2 interaction does (very strong with n>1)

Contribution of adsorption energy of intermediates to the kinetic rate of the ORR can be accurately captured by modern quantum chemical methods

The Volcano Relation in ORR Kinetics

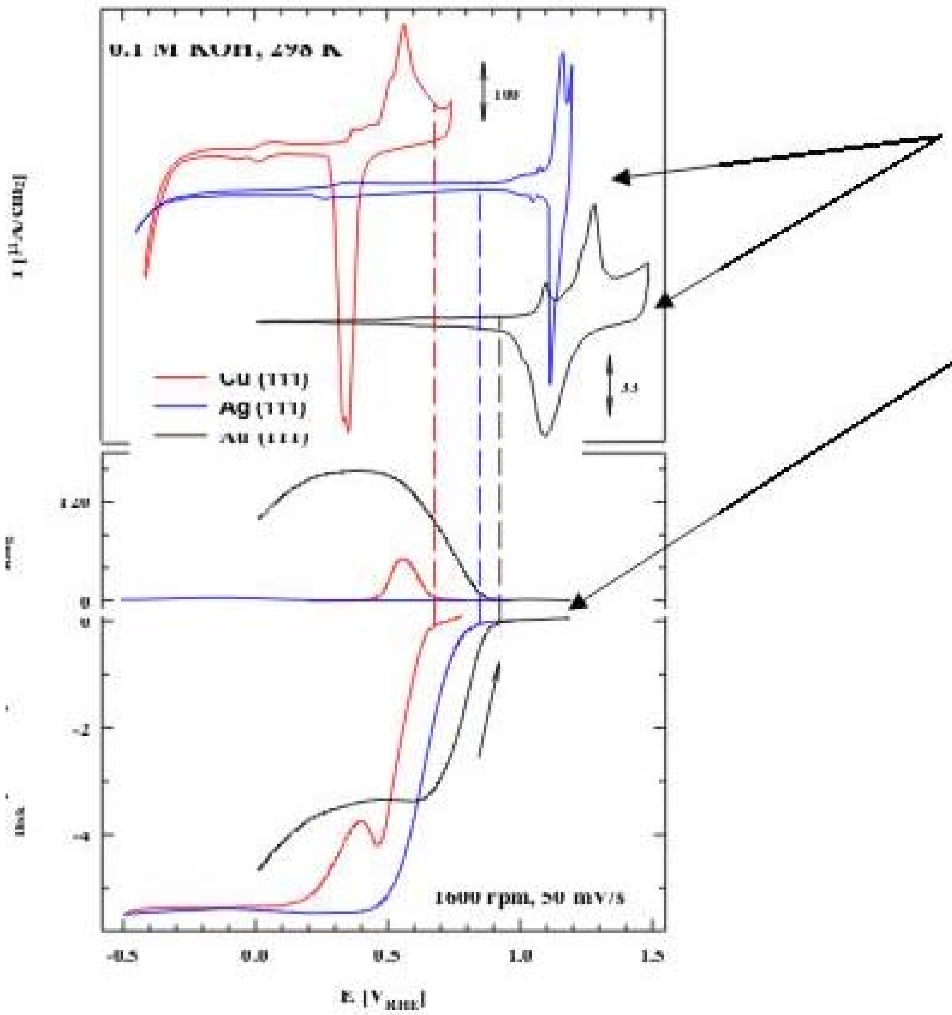


Θ_{ad} is mostly OH_{ad} not $(O_2^-)_{ad}$

$H_2O = OH_{ad} + H^+ + e^-$

or

$O_2^- + 2\,H^+ + e^- = 2\,OH_{ad}$



ORR on Ag and Au occurs entirely at low coverage By OH_{ad}

ORR on Cu affected by strong OH_{ad}

Pt at the Top of the Volcano

- Interaction of the electrode with O_2^- requires partially filled d-orbitals with large radial extent
  - Group 1B, 2B, 3B etc. metals have closed d-shells
  - Of Group VIII metals, d-orbitals in first row ($3d^{9-n}$) do not have sufficient radial extent
  - The $5d^{9-n}$ orbitals are the best for forming long bonds
- Interaction of the electrode with OH_{ad} must be relatively weak
  - Of the Group VII metals, Pt has the weakest interaction with OH_{ad}