Transition Metal Surfaces

Pt 5d^9

Two strongly bound interstitial electrons between three atoms.

Methyl prefers to be directly above a Pt atom.

Ethyl prefers bridging sites.

H prefers cap sites.

Localized covalent bond can form w/ unpaired d spin of the metal.

O₂ resonance stabilized 2 center, 5 e⁻ bonds.

If we bond to one of the oxygen, we lose most of the resonance.
H₂O₂  \[ \text{O} - \text{O} \]  lose an additional 14 kcal/mol of resonance.

Forming O₃:

0-0 σ bond is about 47 kcal/mol. But we lose 57 kcal/mol of resonance in the O₂.

Net bond -10 kcal/mol, no bond.

Actually, net bond is 25 kcal/mol. New π bonding is 35 kcal/mol.

Unpaired electron on the new O interacts with the π system.

Consider charge transfer

Now we can form a π bond.
\[ \text{Singlet state} \]

Extra resonance stabilization from quencher contribution.

Triplet state - no resonance, no \( \pi \) bonds. There are two three electron bonds.

\[
\text{With } 3 \text{ } \pi \text{ bonds and } 6 \text{ } \sigma \text{ electrons in the } \pi \text{ system, the state is } 1.2 \text{ eV above the ground state.}
\]

\( \sigma \) bond is worth about 39 kcal/mol, less than a usual O-O bond because of strain due to 60° bond angle.

**Impurities in semiconductors**

\[
\begin{align*}
\text{IP} &= 13 \text{ eV} \\
\text{DE} &= 9 \text{ eV to 1st excited state.}
\end{align*}
\]

MO's -

\[
\begin{bmatrix}
\sigma & \sigma \\
\sigma & \sigma
\end{bmatrix}
\rightarrow
\begin{bmatrix}
\sigma & - \\
\sigma & \sigma
\end{bmatrix}
\rightarrow
\begin{bmatrix}
\text{LUMO} \\
\text{HOMO}
\end{bmatrix}
\]

\( \sim 13 \text{ eV} \)
In an infinite solid, we have a continuum of levels below the HOMO and above the LUMO.

\[ \begin{align*}
\text{C} &: \text{Si} & \text{Ge} & \text{Sn} \\
\text{LUMO} &: -0.5 \text{ eV} & -4.0 \text{ eV} & \\
\text{HOMO} &: -6 \text{ eV} & -5.1 \text{ eV} &
\end{align*} \]

\[ \Delta E = 5.5 \text{ eV} \quad 1.1 \text{ eV} \quad 0.7 \text{ eV} \quad 0.2 \text{ eV} \]

As we go down the column,

For diamond,

\[ \begin{align*}
\text{HOMO} &: 6 \text{ eV} \\
\text{LUMO} &: 5.5 \text{ eV} \\
\end{align*} \]

\[ \text{IP} = 6 \text{ eV} \quad \text{Greater distribution of + charge lowers IP.} \]

\[ \Delta E = 6 \text{ eV} \quad \text{1st excited state.} \]
We replace one Si with P. Now we have an extra e⁻. This will lower the ionization potential. IP: 4.05 eV. After ionization, a covalent bond can form.

\[
\text{Si} \quad \text{P} \quad \text{Si} \\
\text{Si} \quad \text{Si} \quad \text{Si}
\]

To ionize this bond and have an e⁻ somewhere in the conduction band is only .05 eV.

At room temperature, we have no e⁻'s in the conduction band. A 1.1 eV barrier to having any e⁻'s there. If we have a P atom, we can have an e⁻ in the conduction band.

Al impurity - This will raise the IP. The electron affinity is more important. We can add an e⁻ to this bond.

EA: 5.03 eV.
Impurities make it easy to change the insulator to a conductor.

Donor impurity

\[ E_{\text{donor}} = -7.03 \text{ eV} \]

Acceptor impurity

\[ E_{\text{acceptor}} = -5.1 \text{ eV} \]