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Curvature Dependent Reactivity of Fullerenes and Nanotubes

Example: Hydrogenation of Fullerenes and Nanotubes

- External Surface: Nucleophilic
- Internal Surface: Electrophilic
- Chemical reactivity is a function of the curvature of fullerene.

Dependence on Pyramidalization Angle?

- The Chemical Reactivity of Fullerene
- Pyramidalization
- Between $sp^2$ and $sp^3$
- Pyramidal angle ($\theta$) = $\theta_{sp^2} - \theta_{sp^3}$

Three Examples of Surfaces

- Graphite (0.00)
- (10,0) Nanotube (0.99)
- $C_{60}$ (0.22)
Example: Reaction on Surfaces

- Hydrogenation of graphene sheet and Fullerenes

\[ E = -4.50 \text{ eV} \]
\[ \theta_1 = 12.95^\circ (0.226) \]
\[ \theta_2 = 20.56^\circ (0.359) \]
\[ \theta_3 = 0.0^\circ (0.0) \]
\[ \theta_4 = 7^\circ (0.22) \]

- Chemical reactivity difference = Strain energy difference ?

External Chemical Reaction on Fullerene

- Total reaction energy
  1. Straining the bonds. (+ \( \Delta E \))
  2. Breaking \( \pi \) bonds. (+ \( \Delta E \))
  3. Reacting with external reactant (X) in given structure. (- \( \Delta E \))
  4. Global relaxations (- \( \Delta E \))

Strain Energy Contribution to Reaction

- Fix all the carbon atoms, pull only one carbon up and calculate the energy difference

\[ E_{\text{strain}} = \sqrt{\tan(\theta_4)} \quad E_{\text{total}} = \sqrt{\tan(\theta_4) + \sqrt{1 - 2 \tan^2(\theta_4)}} \quad E_{\text{shift}} = \sqrt{\tan(\theta_4) + \sqrt{1 - 2 \tan^2(\theta_4)}} \]

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- The relation with the pyramidal angle (\( \theta_4 \))

\[ E_{\text{energy}} = \sqrt{\tan(\theta_4)} \quad E_{\text{total}} = \sqrt{\tan(\theta_4) + \sqrt{1 - 2 \tan^2(\theta_4)}} \quad E_{\text{shift}} = \sqrt{\tan(\theta_4) + \sqrt{1 - 2 \tan^2(\theta_4)}} \]

- Binding energy with external reactant X

Where \( E_\text{ex} \) and \( E_\text{ex} \) depends only on external reactant X.
**Binding Energy Dependence on Pyramidal Angle**

- Hydrogen is used as the point probe.

- \[ E_1 = 5.34 \text{ eV} \]
- \[ E_2 = 1.71 \text{ eV} \]
- \[ \Delta E_{\text{pyramidal}} = 0.1 \text{ eV} - 0.3 \text{ eV} \]
- Independent of \( \theta_p \)
- Almost linear in small \( \theta_p \)

**Total Reaction Energy Estimation**

- Total reaction energy = Minimum (strain energy + binding energy)
- Small Errors (\(-0.1 \text{ eV}\)) from ignoring global relaxation

**Formation Energy Comparison with Full Relaxation Results**

<table>
<thead>
<tr>
<th>Pyramidal Angle (( \theta_p ))</th>
<th>Total Reaction Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial Value</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.000</td>
</tr>
<tr>
<td>Nanotube</td>
<td>0.091</td>
</tr>
<tr>
<td>C_60</td>
<td>0.202</td>
</tr>
</tbody>
</table>

*The forces are relaxed up to the first nearest neighbors*

**External Chemical Reactivity (Conclusions?)**

- \( \theta_p \) (initial pyramidal angle)
  - Strain Energy curve shift \( \theta_p \)
  - Binding Energy curve shift \(-0.3 \text{ eV}\)
- Binding Energy curve - almost linear
  - \( \theta_p = \theta_{p1} + \theta_{p2} - \delta \) (stiffness change)
- Total reaction energy changing by \( \theta_p \)
  - Strain energy effect \(-0.3 \text{ eV}\)
  - Binding energy effect \(- \theta_p E_1 \text{ eV}\)

**Internal Reaction**

- Less Reactive than External Reaction \(-\) Less Electron Density
- Total reaction energy
  1. Straining the bonds (\(+\Delta E\))
  2. Breaking x bonds (\(+\Delta E\))
  3. Reacting with external reactant (X) in given structure (\(-\Delta E\))
  4. Global relaxations (\(-\Delta E\))
  5. Weak bonds with neighbor carbon atoms (\(-\Delta E\))

Same as External Chemical Reaction

Difference from External Reaction
Internal Chemical Reactivity

The portion of \( \pi \) state decreases (+ \( \Delta E \))

- As \( \theta \) increases, \( \pi \) bond breaking energy decreases (- \( \Delta E \))
- Global Interaction increases (- \( \Delta E \))

- Two negative effect and one positive effect combined.

Hard to estimate reaction energy
Quantum Computer

- Solid state quantum computer can be designed by $^{31}$P atoms in bulk Si [1].
- Remaining Problems: Placing of a $^{31}$P atom, Diffusion of a $^{31}$P atom
- $^{31}$P @ Bucky Onion: Possible self-ordering, Preventing diffusion of $^{31}$P


P @ the Center of C$_{60}$

- Full Relaxation
- Binding Energy: Center = 0.99 eV, (6,6) Bond = 0.81 eV
- Diffusion Barrier: Center = Bond = 0.33 eV

H @ C$_3$D$_{60}$

- No meta-stable site and Diffusion Barrier = 1.17 eV

Conclusions

- The external reaction energy is determined by a competition of strain energy and binding energy.
- We can estimate external reaction energy up to 0.1 eV error, which is from global relaxation.
- External Chemical Reactivity is enhanced by binding energy difference due to initial pyramidal angle.
- Inner Chemical Reactivity is enhanced by Global Interactions.
- Possible candidates for Quantum Computer: $^{31}$P @ C$_{60}$ and H @ C$_3$D$_{60}$
Future Work

- We are going to test more examples on external chemical reactivity.
- We will continue to work on the reactivity of the multi-bonds reactions and non-covalent bond reactions.
- We need more systematic study on internal chemical reactivity.
- Since we found the way to encapsulate P and H, we will work on self-ordering of endo-fullerene for quantum computer application.
- As another candidate for quantum computer, we are looking into compressed bucky onion, which has diamond core structure.