ABSTRACT OR SUPPORTING INFORMATION

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Curvature Dependent Reactivity
of Fullerenes and Nanotubes

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Curvature Dependent Reactivity

- Example: Hydrogenation of Fullerenes and Nanotubes

\[ \begin{align*}
\text{External Surface: Nucleophile} \\
\text{Internal Surface: Electrophile}
\end{align*} \]

- Chemical reactivity is a function of the curvature of fullerene.

Dependence on Pyramidalization Angle?

- The Chemical Reactivity of Fullurene ↔ The pyramidalization.
- Pyramidalization → Between sp³ and sp²
- Between sp³ and sp²
- Pyramidal angle \( \theta_p = \theta_m - \pi/2 \)

Three Examples of Surfaces

- Graphite (0.00)
- (10,0) Nanotube (0.09)
- C₆₀ (0.22)
Example: Reaction on Surfaces

- Hydrogenation of graphene sheet and Fullerenes

- H on Graphite
  - $E = -4.50 \text{ eV}$
  - $\theta_a = 12.95^\circ \pm 0.22^\circ$
  - $\theta_b = 20.56^\circ \pm 0.35^\circ$
  - $\theta_c = 7^\circ \pm 0.22^\circ$

- H on C$_6$

- Chemical reactivity difference = Strain energy difference

External Chemical Reaction on Fullerene

- Total reaction energy
  1. Straining the bonds $(\Delta E)$ → Strain Energy
  2. Breaking π bonds $(\Delta E)$ → Binding Energy
  3. Reacting with external reactant $(X)$ in given structure $(\Delta E)$

- 4. Global relaxations $(\Delta E)$ → Temporarily ignored

Strain Energy Contribution to Reaction

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

- 1. Elastic Strain Energy
- 2. Independent of External Reactant
- 3. $\theta_a$ shift
- 4. $\theta_a$ increase = stiffer

Need a new title for this slide

- The relation with the pyramidal angle $(\theta_i)$
  \[ |\phi| = \sqrt{2 \tan(\theta_i)} \]

- Binding energy with external reactant $X$
  \[ E_{\text{binding}} = \sqrt{2 \tan(\theta_i)} |E_x| + \sqrt{1 - 2 \tan^2(\theta_i)} E_x + E_{\text{vander}} (\theta_i) \]
  where $E_x = \langle x | \rho_x \rangle$ and $E_p = \langle x | \rho_p \rangle$

- $E_x$ and $E_p$ depends only on external reactant $X$. 
Binding Energy Dependence on Pyramidal Angle

- Hydrogen is used as the point probe.

1. \( E_\mu = -5.34 \text{ eV} \)
   \( E_\nu = -1.71 \text{ eV} \)

2. \( \Delta E_{\text{bonding}} = -0.1 \text{ eV} - 0.3 \text{ eV} \)

3. Independent of \( \theta_p \)

4. 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

<table>
<thead>
<tr>
<th>Pyramidal Angle (( \theta_p ))</th>
<th>Total Reaction Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Value</td>
<td>Estimated Value</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.000</td>
</tr>
<tr>
<td>Nanotube</td>
<td>0.091</td>
</tr>
<tr>
<td>C_{100}</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
  
  \( \theta_p = \theta_b + \theta_e - \delta \) (stiffness change)

- Total reaction energy changing by \( \theta_p \)
  
  Strain energy effect \( < 0.1 \text{ eV} \)
  
  Binding energy effect \( \theta_p E_\nu \text{ eV} \)

Internal Reaction

- Less Reactive than External Reaction \( \rightarrow \) 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 (\( - \Delta E \)) \( \rightarrow \) Difference from External Reaction
**C_{36} and C_{60}**

- Top Hexagon: B1 (1.44 Å)  
- B3 (1.44 Å)  
- B4 (1.43 Å)  
- Wall Hexagon: B2 (1.43 Å)

(5,5) Bond

**H @ C_{36} and H @ C_{60}**

<table>
<thead>
<tr>
<th>H on Carbon B</th>
<th>Initial ψ</th>
<th>Final ψ</th>
<th>Formation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>72.85</td>
<td>75.21</td>
<td>-1.28</td>
</tr>
<tr>
<td>C2</td>
<td>73.95</td>
<td>77.87</td>
<td>-1.54</td>
</tr>
<tr>
<td>C3</td>
<td>77.19</td>
<td>81.53</td>
<td>-1.40</td>
</tr>
<tr>
<td>Center</td>
<td></td>
<td></td>
<td>-0.46</td>
</tr>
<tr>
<td>Carbon</td>
<td>78.37</td>
<td>85.35</td>
<td>-1.23</td>
</tr>
<tr>
<td>Center</td>
<td></td>
<td></td>
<td>-0.43</td>
</tr>
</tbody>
</table>

**P @ C_{36} and P @ C_{60}**

<table>
<thead>
<tr>
<th>C_{36}</th>
<th>Formation Energy</th>
<th>Wall Hexagon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Hexagon</td>
<td>-0.27</td>
<td></td>
</tr>
<tr>
<td>Pentagon</td>
<td>-0.74</td>
<td></td>
</tr>
<tr>
<td>Wall Hexagon</td>
<td>-0.89</td>
<td></td>
</tr>
<tr>
<td>Bond 4</td>
<td>-0.80</td>
<td></td>
</tr>
<tr>
<td>Carbon 3</td>
<td>-0.85</td>
<td></td>
</tr>
<tr>
<td>(6,6) Bond</td>
<td>-0.81</td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>-0.99</td>
<td></td>
</tr>
</tbody>
</table>

- The other sites are unstable.

**Internal Chemical Reactivity**

- The portion of π state decreases (+ ΔE)
- As ψ increases, π bond breaking energy decreases (- ΔE)
- Global Interaction increases (- ΔE)
- Two negative effects 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


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

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

H @ C$_{60}$D$_{59}$

- 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$_{60}$D$_{59}$
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 an another candidate for quantum computer, we are looking into compressed bucky onion, which has diamond core structure.