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External Chemical Reactivity of Fullerenes and Nanotubes

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ABSTRACT

The external chemical reactivity of graphene sheet, fullerenes and carbon nanotubes has been investigated. The total reaction energy is analyzed with several contributing terms and formulated as a function of the pyramidal angles of C atoms. We have determined the parameters for the formulae from ab initio simulation of graphene. We have applied them to predict hydrogenation energy of several nanotubes and C₆₀, and demonstrated that the predicted total reaction energies are very close to the results of total energy pseudo-potential density functional theory calculations. This analysis can be used to predict the reaction energy and local bonding configuration of a reactant with diverse fullerenes and nanotubes within 0.1 eV accuracy.

INTRODUCTION

There has been much research interest in carbon nanotubes and fullerenes since the discovery of C₆₀ [1]. They have been considered as promising materials for nanotechnology applications, such as biochemical and gas sensors [2] and molecular transistor [3]. From the recent studies on possible nanodevice applications, it has been recognized that the surface functionalization of nanotubes and fullerenes would play an important role for nanodevice development. In order to functionalize nanotubes and fullerenes, the chemical reactivity of carbon atoms need to be understood with a quantitative accuracy.

Generally, the chemical reactivity on the external surface of a fullerene or a nanotube is characterized by local bonding configuration of carbon atoms, more specifically, pyramidalization (θ_p) of C atoms as illustrated in Fig. 1 [4, 5]. Since the surface of a fullerene or a nanotube is curved, it is natural to have pyramidalized C atoms as shown in Fig. 1. Pyramidalization changes the hybridization of atomic orbitals at the C atom so that the π orbital contains different portion of s and p orbitals leading to different chemical reactivity. For example, graphite has planar structure ($\theta_p = 0$) corresponding to sp^2 for σ bonds and p for π bond. However, fullerenes and nanotubes have the hybrid bonding orbitals between sp^2 to sp^3 . Because of this hybridization, fullerenes and nanotubes are known to be more reactive than graphite. The degree of pyramidalization (θ_p) is defined by the angle between σ bond and π orbital and named as pyramidal angle (Fig. 1).

When a C atom interacts with an external chemical reactant, several processes occur simultaneously: orbital hybrid changing toward sp^3 , π bond breaking, and reaction between free π orbital and external reactant. In order to quantify the analysis of the chemical reactivity, we divide a reaction into several contributing parts: (a) straining of surface C atom, which is changing the hybrid of atomic orbital of C atom, (b) breaking of π bond and binding with external reactant, and (c) local relaxation of neighbor C atoms. We name several energy terms

following each contributing part, such as, "strain energy" for (a), "binding energy" for (b), and "local relaxation energy" for (c). To elucidate these terms, we will use a hydrogen atom as a point probe to measure binding energy. We have analyzed and formulated these energies in terms of pyramidal angles. And we have applied them to graphene sheet, several nanotubes, and C_{60} fullerene. We have chosen graphene sheet as a representative system for large fullerenes and nanotubes. We have chosen several nanotubes with different radii such that the pyramidal angles are between those of graphene sheet and C_{60} . In the analysis, we have calculated the energy parameters for our formulae from graphene sheet data. These parameters and the energy expressions are used to predict the interaction energies of nanotubes and C_{60} . The accuracy of the prediction is tested by comparing to full ab initio simulations.

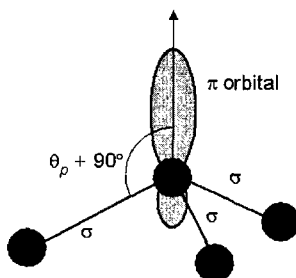


Figure 1. Pyramidal angle (θ_p) is defined by the angle between π orbital and σ bond minus 90° .

COMPUTATIONAL DETAILS

All the results in this work are calculated using total energy pseudo-potential density functional theory (DFT) method [6, 7], and a supercell approximation is used to simulate the periodic systems. In order to minimize the interactions between the repeated images, we include 5 Å vacuum separating the neighboring images. Kohn-Sham single-electron wave functions are expanded by 50,000 plane waves for C_{60} , and between 10,000 and 36,000 for nanotubes depending on their diameters, and 18,000 for graphite, corresponding to 40 Ry cut-off energy. We use single k -point for C_{60} , because it is a molecule. For a graphene sheet and nanotubes, k -point convergence was tested and it is confirmed that a single k -point sampling for graphene sheet and four k -point for nanotubes are enough for the convergence. During geometry optimizations, the atomic positions were relaxed until the forces became smaller than 0.05 eV/Å.

The initial values of the pyramidal angles θ_0 of graphene sheet, C nanotubes, and C_{60} used in this work are listed in Table I. When we compute the strain energy, we fix all the C atoms and move one C atom, on which the reaction will occur, normal to the surface in order to increase pyramidal angle artificially. We calculate the total energy of the strained structure and get the strain energy of given structure from the difference of total energies between the strained structure and the initial structure. In order to understand strain energy dependency on pyramidal angle, we have computed a set of strain energy with different pyramidal angles.

We have calculated the binding energy of H atom for each strained structure. We have introduced an H atom above the strained C atom structure generated in the previous analysis and

calculated hydrogenation energy to compare the chemical reactivity difference induced by pyramidal angle change. During the calculation of binding energies, we keep the C atoms fixed to maintain the artificially produced pyramidal angle and atomic hybrid, and relax the position of the introduced H atom. We have also simulated fully relaxed hydrogenation energy to compare with our predictions. We relax C atoms up to the third nearest neighbors for graphene sheet, up to the first nearest neighbors for nanotubes, and all the C atoms for C₆₀ fullerene during the full relaxation simulations.

Table I. Initial Pyramidal Angles (θ_0) of graphene sheet, several nanotubes, and C₆₀ (rad.)

	θ_0		θ_0
Graphite	0.000	(10,0) Nanotube	0.090
(15,0) Nanotube	0.059	(8,0) Nanotube	0.113
(12,0) Nanotube	0.075	C ₆₀	0.202

RESULTS and DISCUSSION

When we strain one C atom, the pyramidal angle and the bond length of the pulled C atom are changed. So, we have divided strain energy into two terms, bending energy and bond stretching energy. We have analyzed those terms by force constant models and described as quadratic function of pyramidal angle (θ_p) changes from the initial equilibrium pyramidal angle (θ_0) and bond length (a) changes from the initial equilibrium bond length (a_0), respectively. When C atom is pyramidalized as shown in Fig. 1, the bottom triangle is consist of neighboring three C atoms. Because the triangle of bottom pyramid is not changed during the straining and the strained C atom is pulled up normal to the triangle, $a \cos(\theta_p)$ remains a constant and bond length (a) can be replaced by a function of pyramidal angle (θ_p) as shown in equation (1). Due to three bonds in strained C atom, there are factors of three in equation (1). Since nanotubes and fullerenes are graphite-like materials, we develop the scheme for graphene sheet and apply it for the other carbon materials with averaged bond lengths and averaged pyramidal angles due to C₃ symmetry in graphene sheet.

$$E_{strain} = \frac{3}{2} k_{bending} (\theta_p - \theta_0)^2 + \frac{3}{2} k_{stretching} a_0^2 \left(\frac{\cos(\theta_0)}{\cos(\theta_p)} - 1 \right)^2 \quad (1)$$

DFT simulation of strain energy for graphene sheet, (10, 0) nanotube, and C₆₀ is shown in Fig. 2. We fit the DFT simulation data for graphene sheet to equation (1) and determine the spring constants: 10.70 eV/rad² for $k_{bending}$ and 7.44 eV/Å² for $k_{stretching}$. In Figure 2, we plot the predicted strain energy curves for (10,0) nanotube and C₆₀ and these curves show a good agreement with the DFT simulation results.

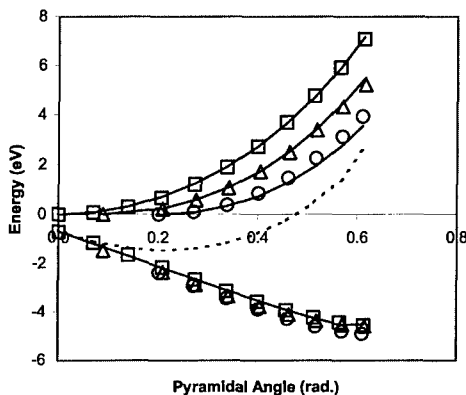


Figure 2. DFT simulation results for strain energy and binding energy. Strain energy is always positive and shown as top three set of data and binding energy is shown as bottom three set of data. We use *square* for graphene sheet, *triangle* for (10,0) nanotube, and *circle* for C₆₀. The solid line for graphene is a fitting to the equations, and the solid lines for the nanotube and C₆₀ are predictions from the equations. The dotted line is the sum of strain energy and binding energy for graphene sheet.

Binding energy is composed of two different contributions, π bond breaking and reaction between external reactant and free π state. We use π bond breaking energy of graphene sheet as a reference and represent π bond breaking energy of other material based on π bond breaking energy of graphene sheet and the difference, which is shown in equation (2), where E_{shift} is the energy difference.

$$E_{\pi} = E_{graphite} + E_{shift} \quad (2)$$

For the reaction of free π state, we use POVA (π Orbital Vector Analysis) [8], which assigns one s and three p orbitals to three σ bonds and determine π state from the rest. Equation (3) shows π state in terms of the s and p orbitals derived from POVA. When an external reactant is introduced to the π state expressed in equation (3), the energy for the reaction with an external reactant (x) will be expressed by $\langle s|H|x\rangle$ and $\langle p|H|x\rangle$ using proper Hamiltonian H . The binding energy is the sum of π bond breaking energy in equation (2) and the energy for the reaction of free π state. And the binding energy will be expressed as equation (4), where E_{sx} and E_{px} are $\langle s|H|x\rangle$ and $\langle p|H|x\rangle$, respectively.

$$|\pi\rangle = \sqrt{2} \tan(\theta_p) |s\rangle + \sqrt{1 - 2 \tan^2(\theta_p)} |p\rangle \quad (3)$$

$$E_{binding} = \sqrt{2} \tan(\theta_p) E_{sx} + \sqrt{1 - 2 \tan^2(\theta_p)} E_{px} + E_{graphite} + E_{shift} \quad (4)$$

DFT simulation results of binding energy are also summarized in Fig. 2. We fit the graphene sheet data to equation (4) to get the parameters: -5.24 eV, -1.55 eV, and 0.87 eV for E_{sx} , E_{px} and $E_{graphite}$, respectively. The fitted binding energy curve is drawn in Fig. 2 as solid curve connecting square data points. From a comparison between this curve and other DFT data in Fig. 2, we can see that a small energy shift, around -0.2 eV ~ -0.3 eV, is needed for (10,0) nanotube and C_{60} to match the binding energy curve of graphene sheet. In equation (4), the first two terms depends only on the pyramidal angle (θ_p), and the third term is a constant. The only possible energy difference for different structured materials is coming from the last term, E_{shift} . As shown in Fig. 2, E_{shift} is not affected very much by the initial pyramidal angle, and we choose -0.2 eV as E_{shift} for other nanotube systems.

Total reaction energy is obtained as the sum of strain energy, binding energy, and local relaxation energy, as describe above. First, we try to estimate the total reaction energy using only strain energy and binding energy, which are represented by equations (1) and (4) respectively. As an example, we determine the total reaction energy of graphene sheet from the minimum of the sum of strain energy and binding energy from Fig. 1. We compare the total reaction energy from full relaxed result and get 0.16 eV of energy difference, which is the local relaxation energy.

Finally, we now predict the total reaction energy of an H atom on different nanotubes and C_{60} . We approximate that the local relaxation energy does not strongly depend on the initial structure and use the value of graphene sheet, -0.16 eV, for other nanotubes and C_{60} . Therefore, we determine the total reaction energy, especially hydrogenation energy for this case, from equation (1) for strain energy, equation (4) for binding energy, and -0.16 eV for local relaxation energy. The predicted total reaction energy results are summarized in Fig. 3 as square date points. In Figure 3, we compare the predicted data with the DFT calculations with full relaxation (circle data points). Figure 3 shows that we can predict hydrogenation energy of fullerenes and nanotubes within 0.1 eV errors compared to the full DFT simulations.

CONCLUSIONS

We have shown that the total reaction energy can be divided into three energy terms, strain energy, binding energy, and local relaxation energy. We also have shown that those energy terms can be formulated and that the total reaction energy of different carbon based materials can be predicted from four energy parameters, E_{sx} , E_{px} , $E_{graphite}$, and local relaxation energy. The parameters E_{sx} and E_{px} depend on the external reactants (x), and $E_{graphite}$ and local relaxation energy do not depend on the reactants. Therefore, once an external reactant is chosen, we can determine E_{sx} and E_{px} from DFT calculations of its reaction with the graphite. From these energy parameters, we can predict the total reaction energies and binding configurations of the reactants on diverse fullerenes and nanotubes. This analysis is based on local configurations of carbon atoms so that one can apply this method to predict local deformation effects in diverse carbon nanostructres without performing full DFT simulations.

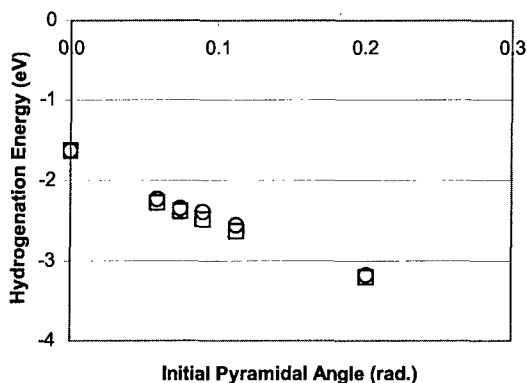


Figure 3. Hydrogenation energies of graphene sheet, various nanotubes, and C_{60} . Circles are DFT simulation data with full relaxations, and squares are the predicted values from our analysis. Data points represent from left to right, graphene sheet, and four different sizes of nanotubes listed above, and C_{60} .

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