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# Structure and Energetics of C<sub>60</sub>O: A Theoretical Study

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Equilibrium structure geometries and stability of the epoxide [6,6] and open [5,6] isomers of C<sub>60</sub>O as well as rearrangement paths between the two isomers were determined using the second-order Moller–Plesset perturbation theory (MP2) and hybrid density functional theory (DFT, B3LYP and B3PW91) methods. It is manifested that the geometrical parameters involved in oxygen binding in C<sub>60</sub>O and relative stability between the [6,6] and [5,6] isomer of C<sub>60</sub>O have a strong dependence on basis set and electron correlation treatment, and it is important to employ an appropriate basis set and correlation level to correctly predict the equilibrium geometries and stability of the [6,6] and [5,6] isomers of C<sub>60</sub>O. For large enough basis sets at proper correlated levels such as the MP2 and B3PW91 DFT methods, the [6,6] isomer is found to be more stable than the [5,6] isomer, in contrast to previous semiempirical and low-level *ab initio* studies. The stability of the [6,6] form over the [5,6] form also appears to be derived from the difference in vibrational motions between the two isomers. It is also found that there appears to exist only one transition state connecting the two isomers, and rearrangement from the [6,6] isomer to the [5,6] isomer occurs via this transition state in a single step, although the barrier height appears to be rather high. A comparison of the simulated IR absorption spectra of the [6,6] and [5,6] form at the B3PW91/cc-pVDZ level with the experimental spectrum of C<sub>60</sub>O appears to suggest the presence and near-isoenergeticity of the [6,6] and [5,6] isomer of C<sub>60</sub>O at low temperature, in accordance with the calculation results reported in this paper.

## I. Introduction

Since the discovery of buckminsterfullerene C<sub>60</sub> more than two decades ago, fullerene chemistry has grown into an important field in chemistry. Unlike graphite and diamond, which have an extended solid-state structure, fullerenes are stable molecules, soluble in various organic solvents. This allows for derivatization of fullerene using a variety of functional groups and manifestation of unique physical and chemical properties of fullerene derivatives thus produced. For example, it was known that some alkaline metal doped C<sub>60</sub> exhibit superconductivity even at the temperatures higher than 30 K,<sup>1,2</sup> and abrupt changes in magnetic susceptibility with temperature was also observed for many alkali-metal fullerenes,<sup>3–6</sup> which was explained, through theoretical calculations employing *ab initio* and DFT methods, in terms of spin-state transition between different crystalline phases existing in those fullerenes.<sup>7</sup> Monomer fullerenes can also be converted to dimers using nucleophiles such as cyanide or hydroxide in the solid-state reaction<sup>8</sup> and polymerized fullerenes with three-dimensional structures and hardness surpassing diamond could be produced under high pressure and high temperature conditions.<sup>9–11</sup> Furthermore, in addition to the common exohedral fullerene derivatives in which atoms or molecules are attached to the ring outside the fullerene cage, it has been shown that small atoms or molecules such as hydrogen could be inserted into the fullerene cage,<sup>12</sup> forming endohedral fullerene complexes with potential applications in the development of molecular electronic materials. Though not extensive, this exemplifies some of the diverse aspects of fullerene chemistry and importance of employing proper theoretical and experimental methods to understand the structures and properties of fullerene derivatives.

The simplest fullerene oxide, C<sub>60</sub>O, is an interesting chemical species. As a simple fullerene derivative, it can serve as a starting material for more complex fullerene oxides<sup>13,14</sup> and also serves as an important ingredient in the synthesis of various types of chemical compounds.<sup>13–22</sup> It also has an enhanced antioxidant activity<sup>23</sup> and much shorter lifetime in its triplet state compared to fullerene.<sup>24</sup> Interestingly, it was suggested from theoretical calculations that the oxygen atom could also be encapsulated inside the fullerene cage if it possesses enough energy to surmount both the bond formation of exohedral C<sub>60</sub>O and the potential barrier to endohedral O@C<sub>60</sub> complex, which was estimated to be about 89 kcal/mol at the B3LYP/3-21G level.<sup>25</sup> Since the first report on the synthesis of C<sub>60</sub>O by Creegan et al. in 1992,<sup>26</sup> the structure and stability of C<sub>60</sub>O has been the subject of many experimental<sup>24,27–30</sup> and theoretical<sup>13–37</sup> studies as the oxygen can bridge either to the carbon atoms adjoining two six-membered rings ([6,6] epoxide form) or one five- and one six-membered ring ([5,6] open form). Although it has been initially established from <sup>13</sup>C NMR and IR measurements<sup>26</sup> that C<sub>60</sub>O should be the epoxide C<sub>2v</sub> structure with an oxygen atom adjoining two six-membered rings; later experimental study using fullerene ozonide by Weisman et al.<sup>28</sup> confirmed that both the epoxide [6,6] and open (annulene-like) [5,6] isomeric form can be prepared, depending on how C<sub>60</sub>O is synthesized. For example, fullerene ozonide C<sub>60</sub>O<sub>3</sub> can be dissociated into either the [6,6] form (in the case of thermolysis) or the [5,6] form (in the case of photolysis).<sup>28</sup> However, it was found that the open [5,6] form spontaneously dimerizes to C<sub>120</sub>O<sub>2</sub> and it also transforms to epoxide form when irradiated.<sup>29</sup> This strongly suggests that the epoxide form is more stable than the oxido-annulene open form for C<sub>60</sub>O at room temperature.

Theoretically, although there have been several *ab initio* and semiempirical studies suggesting that the [5,6] isomer is slightly more stable than the [6,6] isomer<sup>30–33</sup> and rearrangement between

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**TABLE 1: Optimized Equilibrium Geometries of C<sub>60</sub>O Isomers<sup>a</sup>**

		[6.6]				[5.6]			
		3-21G	6-31G	cc-pVDZ	6-31G*	3-21G	6-31G	cc-pVDZ	6-31G*
HF	$R_{C-C}$	1.522	1.511	1.501	1.498	2.193	2.193	2.131	2.132
	$R_{C-O}$	1.457	1.447	1.390	1.392	1.398	1.390	1.361	1.362
	$\alpha_{C-O-C}$	63.0	63.1	65.4	65.1	103.3	104.2	103.1	103.0
	$R_{C-C}$	1.558	1.544	1.544	1.537	2.205	2.209	2.152	2.151
B3LYP	$R_{C-O}$	1.487	1.479	1.420	1.420	1.421	1.417	1.385	1.386
	$\alpha_{C-O-C}$	63.2	63.0	65.8	65.4	101.7	102.5	101.9	101.8
	$R_{C-C}$	1.553	1.540	1.538	1.534	2.188	2.192	2.130	2.131
	$R_{C-O}$	1.480	1.471	1.413	1.414	1.417	1.412	1.379	1.381
B3PW91	$\alpha_{C-O-C}$	63.2	63.2	66.0	65.7	101.1	101.9	101.1	101.1
	$R_{C-C}$	1.587	1.564	1.594	1.566	2.203	2.214	2.120	2.126
	$R_{C-O}$	1.512	1.518	1.420	1.428	1.444	1.443	1.390	1.392
	$\alpha_{C-O-C}$	63.3	62.0	68.3	66.5	99.4	100.2	99.4	99.5
MP2	$R_{C-C}$			1.596(1.546)				2.148(2.169)	
	$R_{C-O}$			1.405(1.420)				1.382(1.401)	
	$\alpha_{C-O-C}$			69.2(57.0)				102.2(101.9)	
	$R_{C-C}$								
MNDO (AM1) <sup>b</sup>	$R_{C-O}$								
	$\alpha_{C-O-C}$								
	$R_{C-C}$								
	$R_{C-O}$								

<sup>a</sup> Bond distances ( $R$ ) and angle ( $\alpha_{C-O-C}$ ) are in units of Ångstroms and degrees, respectively. <sup>b</sup> Values in parentheses correspond to the AM1 results from ref 33.

the two isomers involves two transition states and an intermediate state corresponding to local minimum,<sup>31,33</sup> it has to be noted that the methodologies employed for these studies could not account for the precise electron correlation or basis set effect on the equilibrium geometries and relative stability between the two isomers for this molecule, especially considering apparently small energy difference between the two isomers predicted from previous studies. Interestingly, a couple of molecular dynamics<sup>34,35</sup> and atomic force calculation<sup>36</sup> studies predicted the epoxide [6,6] form as the more stable species than the open [5,6] form. Therefore, in view of disagreement between various theoretical calculation results and experimental findings, it appears necessary to examine this molecule employing more sophisticated methods that should incorporate sufficient electron correlation treatment with large basis set effect as well as investigating vibrational and thermal contributions to the stability of the molecule. In this paper we systematically examine the effect of electron correlation and basis set as well as vibrational and thermal effect on the relative stability of the [6,6] and [5,6] isomers using abinitio Hartree–Fock (HF), density functional theory (DFT), and second-order Moller–Plesset perturbation theory (MP2) methods. We also simulate the infrared (IR) spectrum of the [6,6] and [5,6] forms from the results of vibrational frequency calculations and comparisons are made with the experimental IR spectrum of C<sub>60</sub>O for identification of the isomeric form contributing to the real spectrum of C<sub>60</sub>O.<sup>37</sup>

This paper is organized as follows. In the next section computational procedures are described in detail. In section III the results for the equilibrium structures, relative stability, and IR spectra of the two isomers of C<sub>60</sub>O as well as rearrangement pathway between them are presented and discussed. Concluding remarks are in section IV.

## II. Computational Details

In this work, the equilibrium structures of C<sub>60</sub>O for the epoxide [6,6] and the open [5,6] form were determined through full optimization of geometrical parameters without any constraint at different levels of electron correlation, which included the HF, hybrid DFT (B3LYP<sup>38–40</sup> and B3PW91<sup>40,41</sup>), and MP2 methods<sup>42</sup> in combination with the 3-21G, 6-31G, 6-31G\*, and correlation-consistent cc-pVDZ basis sets.<sup>43</sup> The largest basis set corresponds to the 6-31G\*basis set, which contains 915 contracted basis functions, and is slightly larger than the cc-

pVDZ set (854 contracted functions) for C<sub>60</sub>O. Although even the basis set of this size cannot be considered a converged basis set, it could help to understand the tendency for structural and energetic change with basis set for this molecule. For optimized geometries of the epoxide and open form, the energy difference ( $\Delta E_{iso}$ ) between the two isomers was computed at each level of theory. To investigate the vibrational and thermal effect on the stability and simulate the IR absorption spectrum of each isomer, frequency calculations at the B3PW91/cc-pVDZ level was performed. Finally, to locate the transition state(s) and examine the reaction pathway between the [6,6] and [5,6] form, transition state optimization along with IRC (intrinsic reaction coordinate) calculations were performed at the same B3PW91/cc-pVDZ level. For the saddle points obtained from transition state optimizations, frequency calculations were performed to confirm the character of the optimized saddle point geometries. For MP2 calculations, frozen core approximation was adopted.<sup>44</sup> All calculations were performed with the Gaussian program package.<sup>45</sup>

## III. Results and Discussion

In Table 1, we present the change in the bond distances and bond angle involved in oxygen binding of fullerene for the [6,6] and [5,6] isomers of C<sub>60</sub>O according to electron correlation and basis set. In Table 1,  $R_{C-C}$  and  $R_{C-O}$  represent the carbon–carbon and carbon–oxygen distance, respectively, and  $\alpha_{C-O-C}$  is the between angle adjoining C–O–C. Previous optimization results at low levels of theory such as B3LYP/3-21G level are in close agreement with the corresponding results reported in Table 1.<sup>25</sup> From the results in Table 1, it is evident that use of proper electron correlation method and basis set is important in obtaining reliable geometries for both isomers of C<sub>60</sub>O. This is well manifested if one compares the results for the HF/3-21G and MP2/6-31G\* level, although the latter results do not represent the fully converged results in terms of electron correlation and basis set. It is worthwhile to note the difference of more than 3° in angle  $\alpha$  for both isomers between the HF/3-21G and MP2/6-31G\* level results. Similar large difference in  $\alpha$  is also observed for the HF/3-21G and B3PW91/6-31G\* (or B3LYP/6-31G\*) results. The large differences in geometries between these two results are, of course, due to differences in both electron correlation and basis set. It is interesting to note, however, that while, for the [6,6] isomer, electron correlation

**TABLE 2: Electronic Energy Differences ( $\Delta E_{\text{iso}}$ )<sup>a</sup> between [6,6] and [5,6] Isomer of C<sub>60</sub>O Isomers**

method	basis set			
	3-21G	6-31G	cc-pVDZ	6-31G*
HF	-9.3	-4.9	-1.0	-2.2
B3LYP	-8.1	-4.4	-2.9	-2.1
B3PW91	-5.4	-2.0	0.1	0.7
MP2	-5.8	-1.3	-0.8	0.1
MNDO (AM1) <sup>b</sup>	-5.8 (-12.5)			

<sup>a</sup>  $\Delta E_{\text{iso}} = E_{\text{opt}}([5,6]) - E_{\text{opt}}([6,6])$  (in units of kcal/mol where  $E_{\text{opt}}$  represents the energy of the isomer at the optimized geometry of C<sub>60</sub>O at respective theoretical level). <sup>b</sup> Value in parentheses correspond to the AM1 results from ref 33.

effect appears most noticeable in predicting  $R_{\text{C-C}}$ , as exemplified in the results of HF/cc-pVDZ ( $R_{\text{C-C}} = 1.501 \text{ \AA}$ ) and MP2/cc-pVDZ ( $R_{\text{C-C}} = 1.594 \text{ \AA}$ ) level, in the case of the [5,6] isomeric form, between angle  $\alpha$  appears to be more significantly affected than bond distances by the electron correlation effect as manifested in the results of HF/6-31G\* ( $\alpha = 103.0^\circ$ ) and MP2/6-31G\* ( $\alpha = 99.5^\circ$ ) level. By contrast, compared to the [5,6] form which exhibits little sensitivity of between angle  $\alpha$  on the basis set, use of appropriate basis set appears critical in predicting the correct angle  $\alpha$  in case of the [6,6] isomer. These distinct effects of correlation and basis set on respective isomer indicates the importance of employing both proper correlation level and converged (or near-converged) basis set in predicting the correct geometries of different isomers of C<sub>60</sub>O and evaluating their relative stability. Compared to the previous semiempirical geometries,<sup>17,23</sup> it is noticed that there is a very large difference in the values of  $\alpha$  in the [6,6] form between the semiempirical and MP2 (or DFT) results with 6-31G\* or cc-pVDZ basis sets. For example, in the case of the [6,6] form, MNDO gives  $\alpha = 57^\circ$  compared to  $\alpha = 67^\circ$  for MP2/6-31G\* optimization. This kind of large geometrical difference in one type of isomer between the semiempirical (or low level ab initio treatment such as HF/3-21G) and MP2 (or DFT) results could lead to a different conclusion about the relative stability of the [6,6] and [5,6] isomers from the previous studies as shall be shown in Table 2.

In Table 2, we present the energy difference ( $\Delta E_{\text{iso}}$ ) between the [6,6] and [5,6] forms according to electron correlation and basis set. The most noticeable feature in Table 2 is the strong dependence of energy difference  $\Delta E_{\text{iso}}$  on basis set, regardless of electron correlation treatment. For smaller basis set such as 3-21G or 6-31G, the [5,6] open form is found to be much more stable than the [6,6] form in all theoretical levels, which is in agreement with the previous study results by Raghavachari.<sup>30,31</sup> However, as the basis set becomes larger,  $\Delta E_{\text{iso}}$  tends to decrease, and the two isomers appear to be almost iso-energetic if proper electron correlation effect is taken into account, which is well manifested in the MP2/6-31G\* or B3PW91/cc-pVDZ optimization results. Therefore, from this tendency, there appears to be a possibility of reversal of stability between the [6,6] and [5,6] form at the basis set limit, insofar as proper electron correlation level is employed. Further investigation using larger basis sets than employed in this study would be necessary to confirm this point.

Besides the electronic contribution to the stability of the [6,6] over [5,6] isomer, the stability of the [6,6] form over the [5,6] form of C<sub>60</sub>O also appears to derive from the difference in vibrational motions. To explore this point, we computed the zero point energies of the two isomers at the B3PW91/cc-pVDZ level as well as the difference in total energies, enthalpies, and

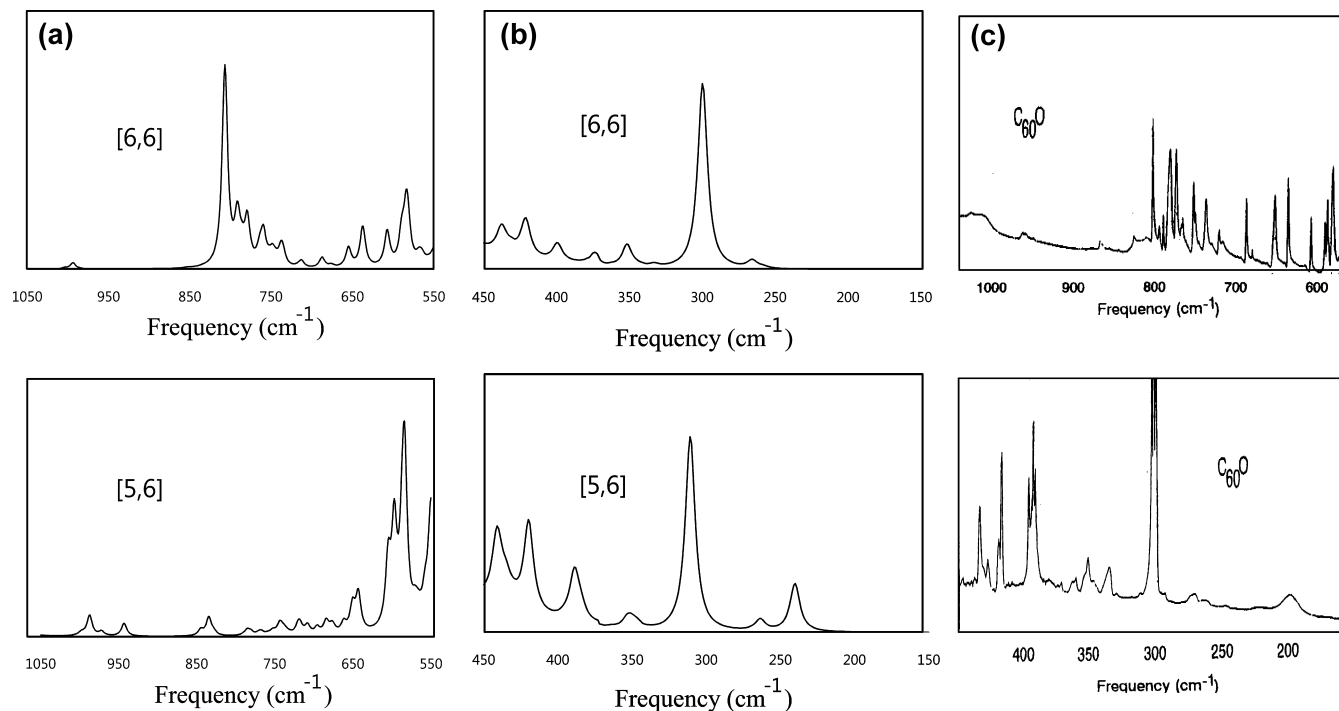
**TABLE 3: Zero-Point Energies (ZPE)<sup>a</sup> and Differences<sup>b</sup> in Energy ( $\Delta E$ ), Enthalpy ( $\Delta H$ ), and Gibbs Free Energy ( $\Delta G$ ) between [6,6] and [5,6] Isomers of C<sub>60</sub>O at 298 K<sup>c</sup>**

	[6,6]	[5,6]
ZPE	239.6	239.8
$\Delta E$	0	0.3
$\Delta H$	0	0.3
$\Delta G$	0	0.3

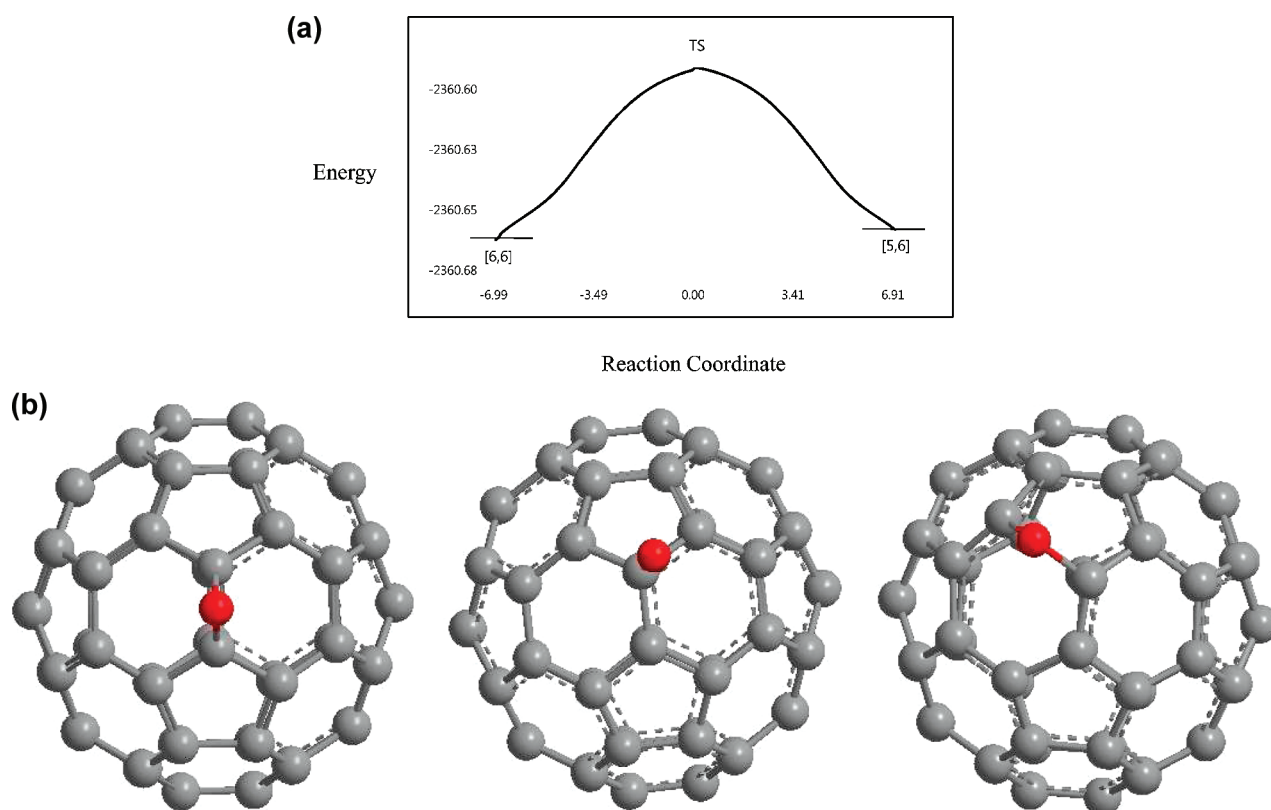
<sup>a</sup> Energies from the bottom of the potential well in units of kcal/mol. <sup>b</sup> Values with respect to the values of the [6,6] isomer in units of kcal/mol. <sup>c</sup> Results at the B3PW91/cc-pVDZ optimized geometries.

Gibbs free energies between the [6,6] and [5,6] forms of C<sub>60</sub>O at room temperature, which are presented in Table 3. The results in Table 3 show that, though small, the [6,6] isomer appears to be more stabilized than the [5,6] form by about 0.2 kcal/mol through vibrational motions at 0 K and by about 0.3 kcal/mol through thermal motions at 298 K, albeit these values are based on harmonic approximations of the vibrational motions of C<sub>60</sub>O. To confirm that the computed vibrational frequencies are close to the experimental frequencies of C<sub>60</sub>O, simulation of IR spectra using the calculated frequencies of the [6,6] and [5,6] form were carried out, which are given in Figure 1 along with the experimental IR spectrum of C<sub>60</sub>O at 10 K given previously.<sup>37</sup> From these figures, it is shown that the band shape of the simulated IR spectrum of the [6,6] isomer appears very similar to the experimental spectrum of C<sub>60</sub>O between 700–800 cm<sup>-1</sup>, suggesting a significant contribution of the [6,6] form to the spectrum. For example, the intense peak around 800 cm<sup>-1</sup> in the simulated spectrum of the [6,6] form, which corresponds to the C–O–C bending vibration mode, is clearly visible in the experimental spectrum, indicating the presence of this isomeric form in a significant amount at this temperature. By contrast, the weak and broadband near 200 cm<sup>-1</sup> in the experimental spectrum appears to be represented by a weak band between 200 and 250 cm<sup>-1</sup> in the simulated spectrum of the [5,6] form, which is hardly visible in the spectrum of the [6,6] form. Therefore, both the [6,6] and [5,6] isomers appear to contribute to the spectral features of the experimental spectrum at 10 K, suggesting near isoenergeticity of the two isomers of the C<sub>60</sub>O at this temperature. This is in accord with our calculation results in Tables 2 and 3.

Finally, to elucidate the rearrangement pathway and corresponding barrier height from the [6,6] form to the [5,6] form of C<sub>60</sub>O, we performed transition-state optimizations connecting the [6,6] and [5,6] form along with IRC<sup>46</sup> calculations to confirm the validity of the obtained transition state at the B3PW91/cc-pVDZ level. In Figure 2 a schematic view of the equilibrium and transition state structures along with the results of the IRC calculations at the B3PW91/cc-pVDZ level are plotted. As clearly seen in Figure 2a, there appear to be no intermediate states (minimum or transition state) other than the transition state displayed in Figure 2b between the [6,6] and [5,6] isomers of C<sub>60</sub>O. This is in sharp contrast to the semiempirical results, which suggested a couple of transition states along with an intermediate state corresponding to minimum in the potential energy surface (PES) connecting the [6,6] and [5,6] forms of C<sub>60</sub>O.<sup>31,33</sup> The barrier height to the [5,6] form from the [6,6] form appears to be rather high, about 54 kcal/mol at the B3PW91/cc-pVDZ level. This should make it possible to isolate the [5,6] isomer separately, which has been shown experimentally by photochemical synthesis of the [5,6] isomer of C<sub>60</sub>O by Weisman et al.<sup>28</sup> Therefore, the intermediate state found in



**Figure 1.** IR spectrum of C<sub>60</sub>O. (a) Simulated IR spectra of the [6,6] and [5,6] isomers between 550–1050 cm<sup>-1</sup>, (b) simulated IR spectrum of the [6,6] and [5,6] isomers between 150–450 cm<sup>-1</sup>, (c) experimental IR spectrum of C<sub>60</sub>O at 10 K (reproduced from ref 37).



**Figure 2.** (a) IRC plot from the [6,6] form to the [5,6] form isomer of C<sub>60</sub>O. Energy and reaction coordinate are in units of hartrees and Ångströms, respectively. (b) Schematic view of the C<sub>60</sub>O configurations corresponding to the [6,6], transition state, and [5,6] position in the IRC plot. Oxygen atoms are in red.

previous semiempirical calculations appears to be a spurious state caused by the deficiencies in the treatment of electron correlation effect in the PES of C<sub>60</sub>O.

#### IV. Summary and Conclusion

The results of this work can be summarized as follows.



(1) The structures of C<sub>60</sub>O in its [6,6] and [5,6] isomeric form are sensitive to electron correlation treatment and basis set employed for optimization. Use of proper electron correlation level and basis set appears very important for accurate structure determination. The structures from semiempirical methods such as MNDO or AM1 do not represent reliable geometries for these isomers of C<sub>60</sub>O.

(2) The energy difference between the [6,6] and [5,6] form of C<sub>60</sub>O has a strong basis set dependence as well as electron correlation dependence. The magnitude of the relative energy of the [6,6] form with respect to the [5,6] form appears to decrease with basis set and change its sign as the basis set becomes larger at correlated levels. This suggests the [6,6] isomeric form would be more stable than the [5,6] isomeric form at the basis set limit for proper electron correlation treatment, in contrast to previous results which suggested the [5,6] isomeric form is more stable than the [6,6] isomeric form based on semiempirical and low level ab initio studies.<sup>30,31,33</sup>

(3) The stability of the [6,6] form over [5,6] form could also be enhanced by the difference in vibrational motions of the two isomers, which was evident from the difference in zero point energies of the two isomers of C<sub>60</sub>O. The IR spectra of the [6,6] and [5,6] form appear to have a very different pattern between 700 and 800 cm<sup>-1</sup> due to the difference in the C–O–C vibrational bending mode. The band shape and strong absorption observed in the experimental IR spectrum of C<sub>60</sub>O in this region suggest that the [6,6] form contribute significantly to the spectrum of the C<sub>60</sub>O. The weak absorption near 200 cm<sup>-1</sup> at 10 K, however, appears to suggest the presence of the [5,6] form also, suggesting near isoenergeticity of the two isomers of C<sub>60</sub>O at this temperature.

(4) Our DFT study results employing B3PW91 hybrid functional method suggest that there is only a single transition state connecting the [6,6] and [5,6] isomers of C<sub>60</sub>O with no intermediate states corresponding to local minima between the transition state and [6,6] (or [5,6]) isomer. The barrier height to transition state from the [6,6] form is rather high, about 54 kcal/mol at the B3PW91/cc-pVDZ level. This is in sharp contrast to previous semiempirical study results which predicted a couple of transition states and intermediate minimum between transitions states.<sup>31,33</sup>

## References and Notes

- Ganin, A. Y.; Takabayashi, Y.; Khimyak, Y. Z.; Margadonna, S.; Tamai, A.; Rosseinsky, M. J.; Prassides, K. *Nature* **2008**, *7*, 367.
- Tanigaki, K.; Ebbesen, T. W.; Saito, S.; Mizuki, J.; Tsai, J. S.; Kubo, Y.; Kuroshima, S. *Nature* **1991**, *352*, 222.
- Tycko, R.; Dabbagh, G.; Murphy, D. W.; Zhu, Q.; Fischer, J. E. *Phys. Rev. B* **1993**, *48*, 9097.
- Chauvet, O.; Oszlányi, G.; Forro, L.; Stephens, P. W.; Tegze, M.; Faigel, G.; Jánosy, A. *Phys. Rev. Lett.* **1994**, *72*, 2721.
- Oszlányi, G.; Bortel, G.; Faigel, G.; Tegze, M.; Gránágy, L.; Pekker, S.; Stephens, P. W.; Forró, L. *Phys. Rev. B* **1995**, *51*, 12228.
- Bommeli, F.; Degiorgi, L.; Wachter, P.; Legeza, A.; Jánosy, A.; Oszlányi, G.; Chauvet, O.; Forro, L. *Phys. Rev. B* **1995**, *51*, 14794.
- Kim, K. S.; Park, J. M.; Kim, J.; Suh, S. B.; Tarakeshwar, P.; Lee, K. H.; Park, S. S. *Phys. Rev. Lett.* **2000**, *84*, 2425.
- Komatsu, K.; Fujiwara, K.; Tanaka, T.; Murata, Y. *Carbon* **2000**, *38*, 1529.
- Blank, V. D.; Buga, S. G.; Serebryanaya, N. R.; Denisov, V. N.; Dubitsky, G. A.; Ivlev, A. N.; Mavrin, B. N.; Popov, M. Y. *Phys. Lett. A* **1995**, *205*, 208.
- Serebryanaya, N. R.; Blank, V. D.; Ivdenko, V. A.; Chernozatonskii, L. A. *Solid State Commun.* **2001**, *118*, 183.
- Talyzin, A. V.; Dubrovinsky, L. S.; Oden, M.; Le Bihan, T.; Jansson, U. *Phys. Rev. B* **2002**, *66*, 165409.
- Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003.
- Smith, A. B., III; Tokuyama, H.; Strongin, R. M.; Furst, G. T.; Romanow, W. J.; Chait, B. T.; Mirza, U. A.; Haller, I. J. *Am. Chem. Soc.* **1995**, *117*, 9395.
- Deng, J. P.; Mou, C. Y.; Han, C. C. *Chem. Phys. Lett.* **1996**, *256*, 96.
- Deng, J. P.; Mou, C. Y.; Han, C. C. *J. Phys. Chem.* **1995**, *99*, 14907.
- Lebedkin, S.; Ballwenweg, S.; Gross, J.; Taylor, R.; Kratschmer, W. *Tetrahedron Lett.* **1995**, *36*, 4971.
- Murray, R. W.; Iyyanar, K. *Tetrahedron Lett.* **1997**, *38*, 335.
- Beck, R. D.; Bräuchle, G.; Stoermer, C.; Kappes, M. M. *J. Chem. Phys.* **1995**, *102*, 540.
- Balch, A. L.; Costa, D. A.; Olmstead, M. M. *Inorg. Chem.* **1996**, *35*, 458.
- Fedurco, M.; Costa, D. A.; Balch, A. L.; Favcett, W. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 194.
- Tajima, Y.; Takeuchi, K. *J. Org. Chem.* **2002**, *67*, 1696.
- Balch, A. L.; Costa, D. A.; Lee, J. W.; Noll, B. C.; Olmstead, M. M. *Inorg. Chem.* **1994**, *33*, 2071.
- Matsubayashi, K.; Goto, T.; Togaya, K.; Kokubo, K.; Oshima, T. *Nanoscale Res. Lett.* **2008**, *3*, 237.
- Benedetto, A. F.; Weisman, R. B. *Chem. Phys. Lett.* **1999**, *310*, 25.
- Park, J. M.; Tarakeshwar, T.; Kim, K. S.; Clark, T. J. *Chem. Phys.* **2002**, *116*, 10684.
- Creagan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103.
- Heymann, D.; Bachilo, S. M.; Weisman, R. B.; Cataldo, F.; Fokkens, R. H.; Nibbering, N. N. M.; Vis, R. D.; Chibante, L. P. F. *J. Am. Chem. Soc.* **2000**, *122*, 11437.
- Weisman, R. B.; Heymann, D.; Bachilo, S. M. *J. Am. Chem. Soc.* **2001**, *123*, 9720.
- Tsyboulski, D.; Heymann, D.; Bachilo, S. M.; Weisman, R. B. *Abstract Volume of the 201st Meeting of the Electrochemical Society; Philadelphia*, May 12–17, 2002.
- Raghavachari, K. *Chem. Phys. Lett.* **1992**, *195*, 221.
- Raghavachari, K.; Sosa, C. *Chem. Phys. Lett.* **1993**, *209*, 223.
- Wang, B. C.; Chen, L.; Chou, Y. M. *THEOCHEM* **1998**, *422*, 153.
- Xu, X.; Shang, Z.; Wang, G.; Cai, Z.; Pan, Y.; Zhao, X. *J. Phys. Chem.* **2002**, *106*, 9284.
- Menon, M.; Subbaswamy, K. R. *Chem. Phys. Lett.* **1993**, *201*, 321.
- Wang, B. B.; Chen, L.; Lee, K. J.; Cheng, C. Y. *THEOCHEM* **1999**, *469*, 127.
- Batirev, I. G.; Lee, K. H.; Lee, W. R.; Lee, H. M.; Leiro, J. A. *Chem. Phys. Lett.* **1999**, *262*, 247.
- Cardini, G.; Bini, R.; Salvi, P. R.; Schettino, V.; Klein, M. L.; Strongin, R. M.; Brard, L.; Smith, A. B. *J. Phys. Chem.* **1994**, *98*, 9966.
- Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- Stephens, J.; Devlin, F. J.; Chabrowski, C. F.; Frisch, M. J. *Phys. Chem.* **1994**, *98*, 11623.
- Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
- Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- Pipano, A.; Gilman, R. R.; Shavitt, I. *Chem. Phys. Lett.* **1970**, *5*, 285.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.
- Gonzalez, C.; Schelegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.