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Theoretical Study on the Motion of a La Atom Inside a C_{82} Cage

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The motion of a single lanthanum atom inside a C_{82} (C_{2v}) fullerene cage has been investigated by means of the hybrid density functional method (B3LYP). The obtained potential energy surface (PES) suggests that the encapsulated La atom can oscillate only around the minimum energy potential well, which is apparently different from the scenario of a giant bowl-shaped movement at room temperature described by Nishibori et al. (Nishibori, E.; Takata, M.; Sakata, M.; Tanaka, H.; Hasegawa, M.; Shinohara, H. *Chem. Phys. Lett.* **2000**, *330*, 497−502.) Interestingly, our calculations show that the La atom may probably undergo a boat-shaped movement when the temperature is high enough. In addition, the computed ^{13}C NMR spectrum of the C_{2v} $[La@C_{82}]^-$ is in an excellent agreement with the experimental nuclear magnetic resonance (NMR) spectrum (Tsuchiya, T.; Wakahara, T.; Maeda, Y.; Akasaka, T.; Waelchli, M.; Kato, T.; Okubo, H.; Mizorogi, N.; Kobayashi, K.; Nagase, S. *Anew. Chem.* **2005**, *117*, 3346−3349), which confirms that the isomer of $La@C_{82}$ with the C_{2v} symmetry is the most stable.

1. Introduction

As new spherical molecules, endohedral metallofullerenes have attracted special interest both from experimental and theoretical researches for many years. The geometry structures and electronic properties of many these particular molecules have been determined especially in recent years. Among them, intensive effort has been made to $La@C_{82}$ since 1991, when it was first macroscopically produced and solvent extracted.[3] The scenario of La atom in motion inside C_{82} spherical cavity (with C_2 symmetry) was predicted first by Andreoni and Curioni using ab initio molecular dynamics (MD) method in 1996.[4] Kobayashi and Nagase described further that the encapsulated La atom can move about in the flat bottom of electrostatic potential valley of C_{82}^{3-} (C_{2v}) at room temperature.[5] On the other hand, the first experimental evidence of lanthanum atom movement inside the cage was disclosed by the maximum entropy method (MEM)/Rietveld analysis using synchrotron powder diffraction data in 2000 by Nishibori et al., who also verified that $La@C_{82}$ is of the C_{2v} symmetry and the La atom locates at an off-centered position in the same paper.[1] The similar results were reviewed by Shinohara, who summarized that the La atom is close to one of the six-membered rings passing through the C_2 axis of the cage, and the distance between the metal atom and the center of the cage is about 1.9 Å.[6] Interestingly, Nishibori et al. showed us that the movement trajectory of La atom inside C_{82} cage is like a bowl or a hemisphere at room temperature on the basis of an anomalous charge density distribution of La atom. However, some other works have been reported that the MEM/Rietveld method[7,8] cannot reliably determine metallofullerene structures of $Gd@C_{82}$,[9,10] $Eu@C_{82}$,[10] $Sc_3@C_{82}$,[11,12] $Sc_2@C_{66}$,[13] and $Sc_2@C_{84}$.[14] So, it is necessary to verify further the conclusions drawn by this kind of experiment.

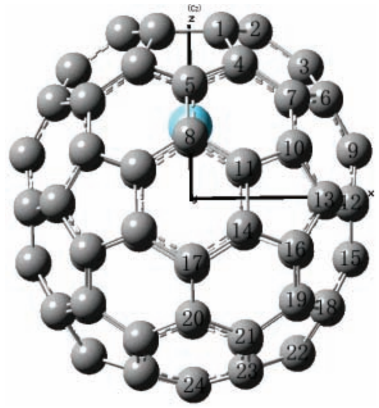

Figure 1. Optimized C_{2v} structure of $La@C_{82}$.

To the best of our knowledge, so far, few theoretical studies have been reported with the exact purpose of exploring the definite motion trajectory of La in C_{82},[4,5] which is probably because of the heavy computational load. This gives us a chance to carry out the present theoretical work. In this paper, by using the hybrid density functional method (B3LYP), we investigated the potential energy surface (PES) of La inside the C_{2v} symmetry of C_{82} fullerene to make clear the scenario of the lanthanum atom in motion. The remainder of the paper is structured as follows. Section 2 describes the details of the computational methods, while the PES of La atom movement inside C_{82} as well as the calculated nculear magnetic resonance (NMR) spectra are reported in section 3. Finally, a brief summary is concluded in section 4.

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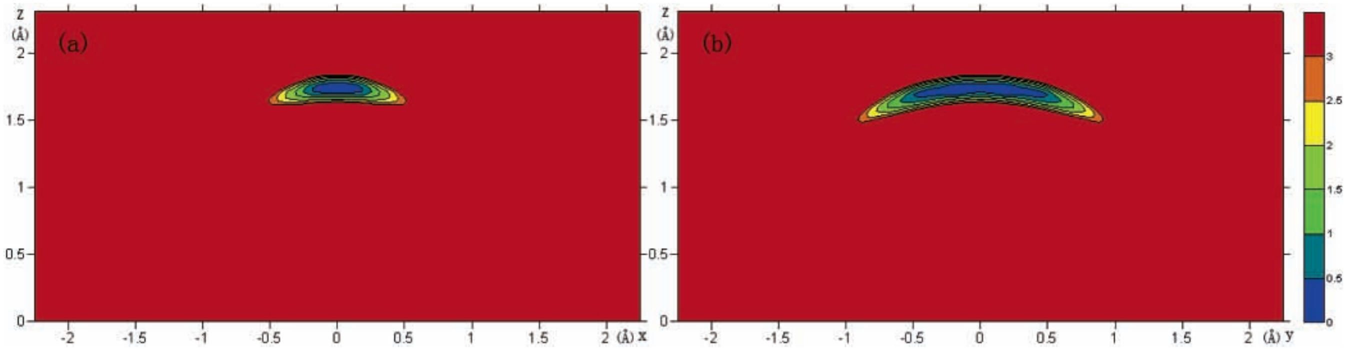

Figure 2. The energy contours of two σ_v planes of La@C_{82} (C_{2v}) (energy in kcal mol^{-1}), only the region of which the energy is less than 3 kcal mol^{-1} is shown. (a) The *xz* plane; (b) the *yz* plane.

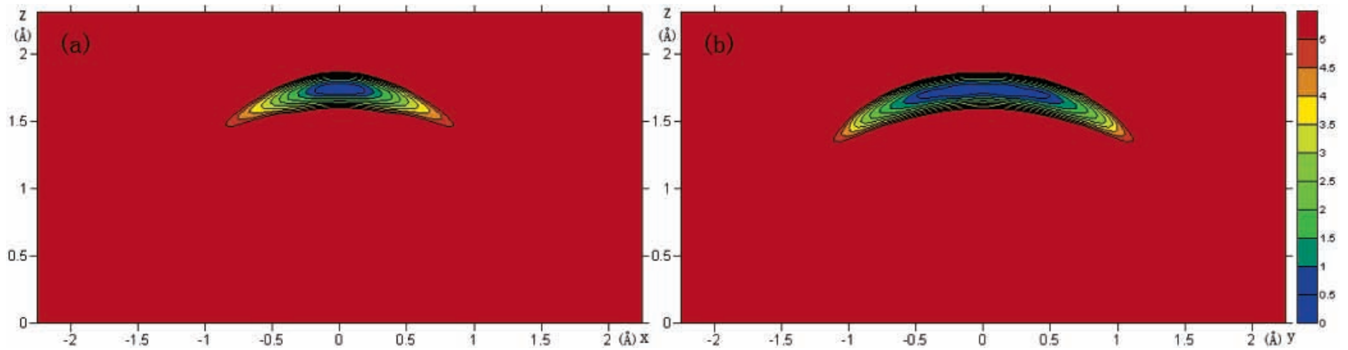

Figure 3. Same as in Figure 2 except the energy cutoff value is set to 5 kcal mol^{-1}.

2. Computational Methods

The density functional theory (DFT) computations were carried out with the Gaussian 03 program package[15] at Becker's[16] three-parameter functional with the nonlocal Lee–Yang–Parr correlation functional (B3LYP) level.[17] According to ref 18, the effective core potentials for lanthanum were used with the corresponding contraction basis set (5s5p3d)/[4s4p3d], while the standard split-valence 3-21G basis set[19] was used for carbon atoms. The theoretical NMR spectrum of $[La@C_{82}]^-$ anion was calculated using gauge-independent atomic orbital (GIAO) method[20] with a large 6-31G* basis set[21] for C instead of the 3-21G basis set at the optimized geometry.

3. Results and Discussion

3.1. PES. The fully optimized C_{2v} structure of La@C_{82}, which has been confirmed to be the major isomer of this metallofullerene by several works,[1,5,18,22–24] is shown in Figure 1 (the coordinates of the center of the cage are set to be [0,0,0]). In the minimum energy structure, the La atom is 2.624 Å away from the nearest hexagonal carbon atom. Because the same theory level was used, this optimized endohedral structure was in line with previous research results presented by Kobayashi and Nagase.[18]

To disclose the possible motion region of La atom, we scanned the potential energy surfaces of La in C_{82} cage on two σ_v reflection planes (the *xz* and *yz* reflection planes) at B3LYP level, respectively. The energy contours are shown in Figure 2 and Figure 3.

According to statistical mechanics, the kinetic energy of a free atom at room temperature is about 1 kcal mol^{-1}; even if we consider the contribution of the surrounding, to our knowledge, the La atom within the cage can only overcome an energy barrier of about 2–3 kcal mol^{-1}. Therefore, to explore clearly the region of the La atom's movement, we set a cutoff energy of 3 kcal mol^{-1}, which is a theoretical energy barrier the La atom cannot overcome at room temperature. Shielding the energy block zone and setting the lowest energy (the structure shown in Figure 1) to zero, we obtained the free movement region for La atom at room temperature as shown in Figure 2. Similar to the electrostatic potential valley near the hexagonal ring on C_2 axis reported in previous work,[5] the bottoms of our potential wells are fairly flat. It can be seen that the scope with energy less than 3 kcal mol^{-1} is limited to a relatively small region in the figure. That means, unlike the MEM/Rietveld experiment had suggested, a giant motion of La atom cannot be realized at room temperature according to this potential energy profile. When the energy cutoff, which determines how large scope the metal atom can move about in, is set as 5 kcal mol^{-1} (it means that the temperature is high), the metal atom inside the cage reveals a motion of larger amplitude (Figure 3). Following this, a comparison between a and b of this figure indicates that the calculated energies along the *y*-axis are lower than those along the *x*-axis. In the *yz* plane, the La atom can move to the position about 1.25 Å above the central plane (i.e., the *xy* plane) of the cage, while it is only about 1.5 Å in the other plane (the *xz* plane). Figure 3 also shows that the La atom can move along the *y*-axis from the *xz* plane to about 1.2 Å away, while the distance from the *yz* plane is less than 0.8 Å along the *x*-axis. This kind of energy distribution means that La atom prefers moving along the *y*-axis to the *x*-axis. The amplitude of motion along the *y*-axis is remarkably larger than that along *x*-axis. Therefore, it can be anticipated from Figure 3 that the La atom would not perform a bowl-shaped motion but a shape like a boat at high temperature. The bow and the stern are along the *y*-axis direction and the shipboard is along the *x*-axis direction in the metallofullerene coordinates. The center of the bottom of the boat corresponds to the position where the La atom stays at in the optimized structure as shown in Figure 1. Notice that the boat-shaped region where La atom in motion keeps the C_{2v} symmetry of

TABLE 1: Comparison between the Calculated ^{13}C NMR Chemical Shifts of $[La@C_{82}]^-$ and Experimental Results

carbon no.	δ [ppm][a]	δ [ppm][b]
1	136.5	133.4607
2	140.0	138.0329
3	134.7	132.837
4	140.6	137.8661
5	148.9	149.6368
6	138.4	137.8568
7	137.5	138.3392
8	133.9	132.1463
9	143.5	145.3802
10	146.8	146.2656
11	156.1	156.942
12	135.1	136.6609
13	148.1	148.6175
14	149.1	148.2505
15	140.1	142.0017
16	152.4	152.2891
17	149.1	150.3655
18	147.8	148.8284
19	148.2	148.1589
20	139.5	139.3343
21	144.3	143.4367
22	144.4	144.4347
23	137.8	136.0005
24	140.1	141.0152

[a] ^{13}C NMR lines of $[La@C_{82}]^-$ provided in ref 2. [b] This work, internal standard: CS_2 ($\delta = 194.7618$).

La@C_{82}, which is in agreement with recent work by Slanina et al.[23] who predicted the isomer with C_{2v} symmetry, is the major isomer even in a high-temperature region from 1000 K to 1300 K. Furthermore, boat-shaped motion shape had also been concluded using the electrostatic potential valley presented by Kobayashi and Nagase. They pointed out that electrostatic interactions should play a dominant role in determining the endohedral structures. This dissymmetrical distribution is due to the difference of electrostatic interactions between the cage and the encapsulated atom on the two distinct σ_v planes of La@C_{82}. In fact, the boat-shaped motion can be easily deduced from the C_{2v} symmetry of the carbon cage.

3.2. NMR Analysis. To our knowledge, a theoretical NMR spectrum of La@C_{82} (C_{2v}) has not yet been reported before. Experimentally, the first ^{13}C NMR measurement of $[La@C_{82}]^-$ was performed by Akasaka et al. in 2000.[24] Recently, a precise 2D NMR spectrum of the anion was reported by Tsuchiya et al.[2] A successful assignment of the ^{13}C NMR spectrum provided in the work enables us to compare our calculated chemical shifts with the experimental results. Table 1 lists the computed ^{13}C NMR chemical shifts of $[La@C_{82}]^-$, together with the experimental data given by Tsuchiya et al. (carbon atoms are numbered in order of distance from La atom as they are in ref 2; please refer to Figure 1).

Obviously, our computational results ranging from 132.1 to 156.9 ppm agree very well with the experimental data ranging from 133.9 to 156.1 ppm. Also, the positions of the calculated ^{13}C NMR peaks are all in perfect line with the experiment. Thus, the distribution of the peaks shows good agreement between theory and experiment. The comparisons of NMR lines confirm strongly that this La@C_{82} isomer observed in previous experiments does have C_{2v} symmetry.[2,24]

4. Conclusions

In conclusion, a small motion and a boat-shaped motion were suggested for La atom inside C_{82} (C_{2v}) fullerene cage at room temperature and at high temperature, respectively, by means of DFT calculations. The motion mode is different from the bowl or hemisphere model obtained from the maximum entropy method (MEM)/Rietveld-based X-ray synchrotron powder diffraction experiment reported by Nishibori et al. at room temperature. Also, the major C_{2v} symmetry of La@C_{82} was justified undoubtedly by our ^{13}C NMR calculation.

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