An anomalous dipole-dipole arrangement of water molecules encapsulated into C_{60} dimer

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Abstract

Based on first-principles total energy calculations, we demonstrate that two water molecules encapsulated in the C_{60} dimer form a peculiar tail-to-tail dipole arrangement that is energetically unfavorable in classical electrodynamics. This arrangement is ascribed to charge depression at the wall of C_{60} associated with [2+2] cycloaddition in the dimer structure resulting in a decrease of the energy cost of Coulomb repulsive interaction in the arrangement. First-principles molecular dynamics simulations also show that the water molecules retain the peculiar arrangement up to the temperature of about 10 K.

Keywords: C_{60} dimer, Water molecules, Encapsulation, Dipole–dipole arrangement

1. Introduction

Following the discovery of hollow-cage carbon clusters, i.e., fullerenes, by the mass spectroscopy of carbon soot [1], it has been suggested that the nanometer-scale space inside the fullerene molecule is capable of accommodating foreign atoms and molecules, leading to various complexes with interesting physical and chemical properties [2]. Indeed, soon after the macroscopic production of fullerenes [3], fullerenes encapsulating metal atoms (metallofullerenes) were synthesized by laser evaporation experiments

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using carbon rods containing metal atoms [4, 5]. In addition to the metal atoms, recent experiments have demonstrated that N and C atoms can also be encapsulated in the fullerene cage together with the metal elements by forming interesting complexes [6, 7]. In low-dimensional nanometer-scale spaces, the encapsulated guest atoms and molecules form unusual condensed structures that are totally different from their bulk phases. For example, in the inner space of carbon nanotubes, fullerenes form one-dimensional chains whose electronic structures are slightly different from those expected from the simple sum of the fullerenes and nanotubes [8, 9, 10]. Furthermore, water molecules are known to form one-dimensional tubular structures with various conformations inside carbon nanotubes depending on the tube diameter [11]. Inside fullerenes, encapsulated atoms also have various morphologies, e.g., monatomic forms [4], diatomic forms [5], and molecular forms with N and C atoms [6, 7], depending on the size of the fullerene cages and the encapsulated atom species.
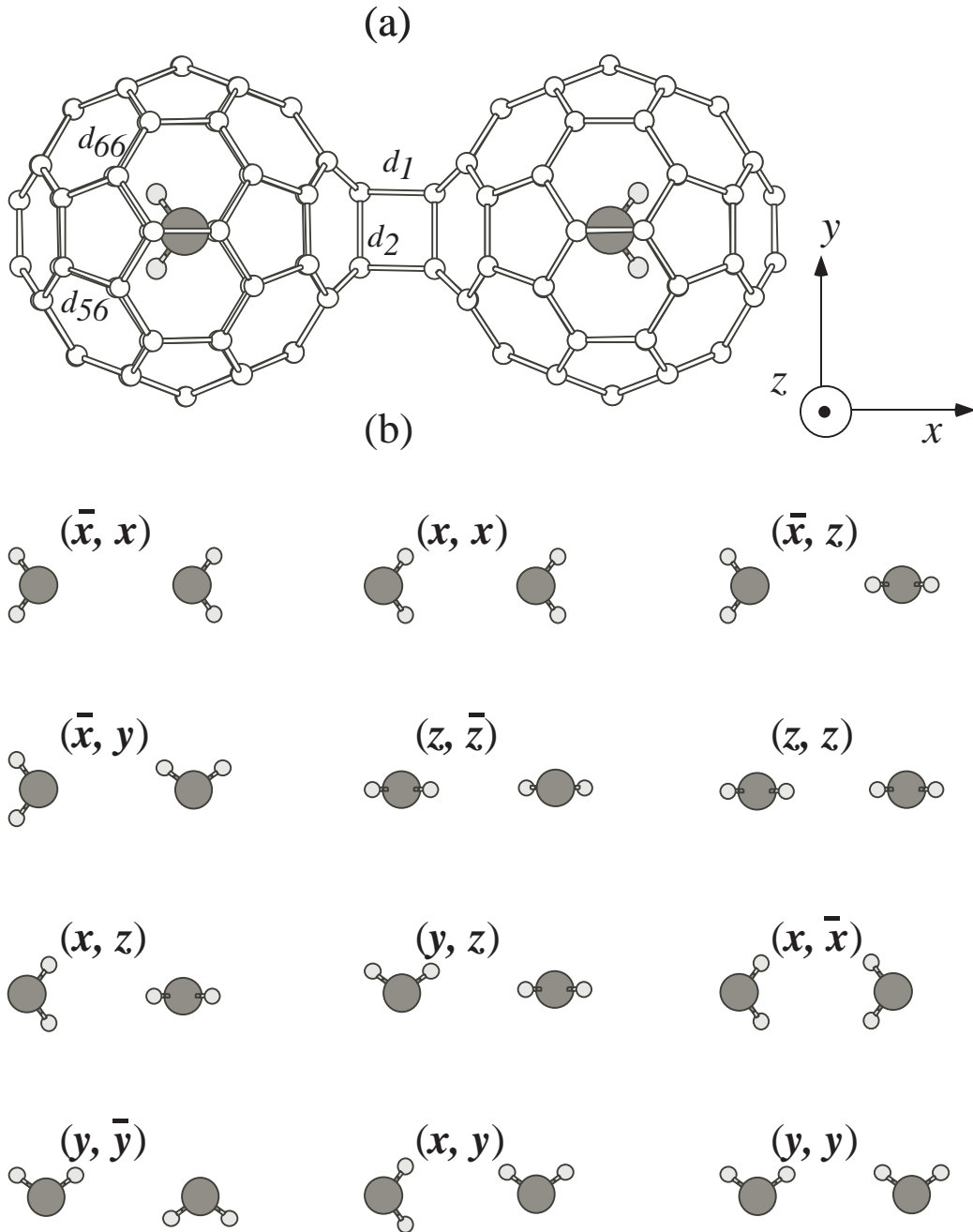
Recently, the development of the molecular surgery technique has allowed molecules, such as H_2 [12, 13, 14] and H_2O [15], to be inserted into fullerene cages. Inside the cages, these molecules are expected to exhibit unusual physical properties that are absent in their isolated form because of the interaction between the encapsulated molecules and the fullerene cages [16, 17], as in the case of encapsulated molecules inside carbon nanotubes. In addition to water encapsulation in fullerenes, water molecules have also been encapsulated in the C_{60} dimer [18], which is two C_{60} molecules connected via [2+2] cycloaddition [19], as in the case of C_{60} polymers [20, 21, 22, 23, 24]. There are two possible complexes of the C_{60} dimer encapsulating water molecules: a single water molecule occupying one of the two C_{60} cages and water molecules occupying both of the C_{60} cages. Although previous studies have demonstrated that encapsulation does not affect the detailed geometric structure and chemical reactivity of the C_{60} dimer, the mutual arrangement and dipole–dipole interaction of the water molecules inside the C_{60} dimer is scientifically interesting and important for the molecular sciences of confined nano-spaces. Furthermore, such complexes can be applicable molecular mechanical engineering of C_{60} due to the dipole moment inside the cage that allow us to control the motion of $H_2O@C_{60}$ molecules and dimers by an external electric field [25]. Therefore, it is important to elucidate the detailed structural and dynamical properties of water molecules encapsulated in the C_{60} dimer.

In this letter, we investigate the energetics of C_{60} dimers encapsulating water molecules by first-principles total energy calculations within density

functional theory (DFT) to elucidate the mutual arrangements of encapsulated water molecules. Our DFT calculations show that the encapsulated water molecules possess a peculiar mutual arrangement that is the energetically least favorable dipole–dipole configuration outside the cages by classical electrodynamics. We clarify the physical origin of this anomalous dipole arrangement, which is ascribed to the lower valence charge density at the wall of the C_{60} dimer associated with [2+2] cycloaddition. We further investigate the dynamical properties of the water molecules inside the C_{60} dimer by first-principles molecular dynamics (MD) simulations. The MD simulations show that the water molecules retain the anomalous arrangement up to 10 K for 100 fs simulation time.

2. Calculation Methods and Structural Model

In the present work, all of the calculations were performed within the framework of density functional theory [26, 27] using the STATE package [28]. For calculation of the exchange–correlation energy between electrons, we used the local density approximation with a functional form fitted to the Monte Carlo results for a homogeneous electron gas [29, 30]. With the choice of the exchange–correlation potential, we can give qualitative discussion on the stable geometries and relative total energy of the water molecules encapsulated in C_{60} dimer [31]. Ultrasoft pseudopotentials generated by the Vanderbilt scheme were used to describe the electron–ion interactions [32]. The valence wave functions and charge density were expanded in terms of plane-wave basis sets with cutoff energies of 25 and 225 Ry, respectively. Structural optimization was performed until the residual forces acting on each atom were less than 5 mRy/Å. Γ point sampling was used for the Brillouin zone integration. To simulate an isolated C_{60} dimer encapsulating water molecules, we considered a large cuboid cell with cell parameters 30, 16, and 16 Å for the x, y, and z directions. We used an open boundary condition along the z direction to avoid dipole–dipole interactions between the periodic images. In contrast, we apply the periodic boundary condition along x and y directions. With the choice of the boundary condition, the system intrinsically contains the numerical error in their total energy at least 3 meV per unit cell due to the boundary condition difference between z and $x(y)$ directions. The molecular dynamics simulations were performed using the velocity scaling method to maintain the temperature constant during the simulations. Each MD step sets to 1.92 fsec for all MD calculations. In this study, we focus on a C_{60}

Figure 1: (a) Optimized structure of the C_{60} dimer encapsulating water molecules. (b) The 12 mutual arrangements of water molecules inside the C_{60} dimer. White, dark gray, and light gray circles denote C, O, and H atoms, respectively.

dimer in which the C_{60} molecules are connected via a four-member ring generated by [2+2] cycloaddition [Fig. 1(a)]. To elucidate the energetics of the mutual arrangements of encapsulated water molecules inside C_{60} dimer, we consider 12 arrangements of H_2O molecules inside the C_{60} dimer, as shown in Fig. 1(b).

3. Results and Discussion

Figure 1(a) shows the fully optimized geometry of the C_{60} dimer encapsulating two water molecules. As reported by an X-ray analysis experiment [18], the encapsulation of water molecules does not affect the detailed geometric structures of the C_{60} dimer. The optimized bond lengths associated with the [2+2] cycloaddition are $d_1 = 1.57$ and $d_2 = 1.57$ Å after water encapsulation. These bond lengths are the same as those of the empty C_{60} dimer within numerical error. Furthermore, these lengths agree well with those observed in the experiment [18, 33]. This confirms that encapsulation of the water molecules does not affect the detailed geometric structure of the C_{60} dimer.

Although encapsulation of water does not affect the geometric structure of the C_{60} dimer, the encapsulation of water substantially stabilizes the C_{60} dimer. We evaluated the encapsulation energy ΔE for the reaction

$$2 \times H_2O + C_{60} \text{ dimer} \rightarrow (H_2O)_2@C_{60} \text{ dimer} + \Delta E.$$
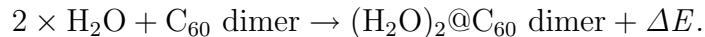
The calculated encapsulation energy is 1.1 eV per dimer which indicates that the encapsulation reaction is exothermic. The calculated energy gain is almost twice that obtained in an isolated C_{60} encapsulating water molecule (0.547 eV per C_{60}). This indicates that the interaction between C_{60} cage and the water molecules is dominant for determining the energetics of the hybrid system. Furthermore, the dipole-dipole interaction is not expected to affect the mutual arrangement of them in the C_{60} dimer. The large encapsulation energy is composed of the electrostatic interaction between the dipole moments of the water molecules and the inhomogeneous charge density induced by the dipole and the bond alternation on C_{60}. Note that, charge transfer between the water molecules and the C_{60} dimer does not occur upon encapsulation.

Table 1 shows the total energy of the C_{60} dimer encapsulating water molecules with various mutual arrangements. As shown in Table 1, the tail-to-tail arrangement, i.e., the $(\bar{\boldsymbol{x}}, \boldsymbol{x})$ arrangement, is the most stable mutual

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Table 1: Total energy of the C_{60} dimer encapsulating the 12 possible mutual arrangements of two water molecules. The energies are measured from that of the ground state configuration in which the two dipoles are arranged in the tail-to-tail manner.

H_2O-H_2O arrangement	Relative total energy (eV)
$(\bar{\boldsymbol{x}}, \boldsymbol{x})$	0.000
$(\boldsymbol{x}, \boldsymbol{x})$	0.012
$(\bar{\boldsymbol{x}}, \boldsymbol{z})$	0.013
$(\bar{\boldsymbol{x}}, \boldsymbol{y})$	0.015
$(\boldsymbol{z}, \bar{\boldsymbol{z}})$	0.019
$(\boldsymbol{z}, \boldsymbol{z})$	0.020
$(\boldsymbol{x}, \boldsymbol{z})$	0.024
$(\boldsymbol{y}, \boldsymbol{z})$	0.025
$(\boldsymbol{x}, \bar{\boldsymbol{x}})$	0.026
$(\boldsymbol{y}, \bar{\boldsymbol{y}})$	0.028
$(\boldsymbol{x}, \boldsymbol{y})$	0.029
$(\boldsymbol{y}, \boldsymbol{y})$	0.030

arrangement studied here. The total energy is lower than the other arrangements by 10 to 30 meV per molecule. This dipole–dipole configuration is inconsistent with the stable configuration from the viewpoint of classical electrodynamics. In classical electrodynamics, the two interacting dipoles favor the $(\boldsymbol{x}, \boldsymbol{x})$ or $(\bar{\boldsymbol{x}}, \bar{\boldsymbol{x}})$ configurations, in which the two dipole moments are aligned in a head-to-tail manner or a tail-to-head manner. Indeed, our DFT calculations of the two water molecules separated by 0.89 nm gives physically reasonable results: the $(\boldsymbol{x}, \boldsymbol{x})$ configuration is the energetically most stable while the $(\bar{\boldsymbol{x}}, \boldsymbol{x})$ configuration is the least stable, with a total energy 13 meV higher than the most stable configuration (Table 2). The energy difference is quantitatively the same as that obtained using the analytic formula of the total energy of the two dipole moments.

By analyzing Tables 1 and 2, we can discuss the contribution of the water-C_{60} dimer interaction for the 12 possible mutual arrangements. The water-cage interaction in the $(\bar{\boldsymbol{x}}, \boldsymbol{x})$ arrangement exceptionally larger than those for the other mutual arrangements studied here. The calculated interaction is larger than the other arrangement 30 meV. In sharp contrast, the interaction in the remaining arrangements are almost the same each other within the variance of a few meV. Therefore, the remarkable stability of the $(\bar{\boldsymbol{x}}, \boldsymbol{x})$ is ascribed to the interaction between water molecule and C_{60} cage network.
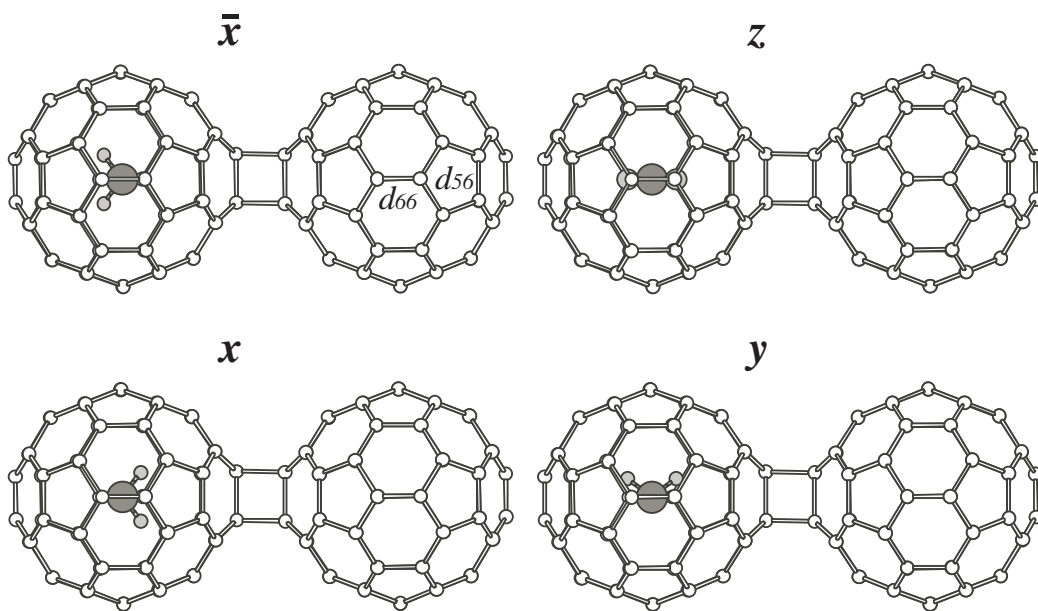
Figure 2: Optimized structures of the C_{60} dimer encapsulating a single water molecule in the left cage with four different dipole directions. White, dark gray, and light gray circles denote C, O, and H atoms, respectively.

Table 2: Total energy of the 12 possible mutual arrangements of two water molecules in vacuum separated by 0.89 nm, which corresponds to the water–water distance inside the C_{60} dimer. The energies are measured with respect to the $(\boldsymbol{y}, \boldsymbol{z})$ configuration, which corresponds to the zero energy in an analytic formula of the total energy of the two dipole moments.

H_2O-H_2O arrangement	Relative total energy (eV)
$(\bar{\boldsymbol{x}}, \boldsymbol{x})$	0.005
$(\boldsymbol{x}, \boldsymbol{x})$	-0.008
$(\bar{\boldsymbol{x}}, \boldsymbol{z})$	-0.002
$(\bar{\boldsymbol{x}}, \boldsymbol{y})$	-0.003
$(\boldsymbol{z}, \bar{\boldsymbol{z}})$	-0.004
$(\boldsymbol{z}, \boldsymbol{z})$	0.005
$(\boldsymbol{x}, \boldsymbol{z})$	0.001
$(\boldsymbol{y}, \boldsymbol{z})$	0.000
$(\boldsymbol{x}, \bar{\boldsymbol{x}})$	0.006
$(\boldsymbol{y}, \bar{\boldsymbol{y}})$	-0.004
$(\boldsymbol{x}, \boldsymbol{y})$	0.000
$(\boldsymbol{y}, \boldsymbol{y})$	0.003

The C_{60} dimer causes differences in the energetics of the encaged and isolated water molecules. To qualitatively discuss this issue, we investigated the energetics of the C_{60} dimer encapsulating a single water molecule in the left C_{60} cage with various molecular directions (Fig. 2). Among the four directions studied here, the total energies of three directions, i.e., the $\boldsymbol{x}$, $\boldsymbol{y}$, and $\boldsymbol{z}$ directions, are almost the same (Table 3). In contrast, the $\bar{\boldsymbol{x}}$ direction has remarkably lower total energy (Table 3). This indicates that O atom favors the C atoms associated with the cycloaddition. As shown in Fig. 2, the optimized bond lengths associated with the [2+2] cycloaddition

Table 3: Total energy of the C_{60} dimer encapsulating a water molecule in the left cage with four different dipole directions. The energies are measured with respect to the ground state configuration.

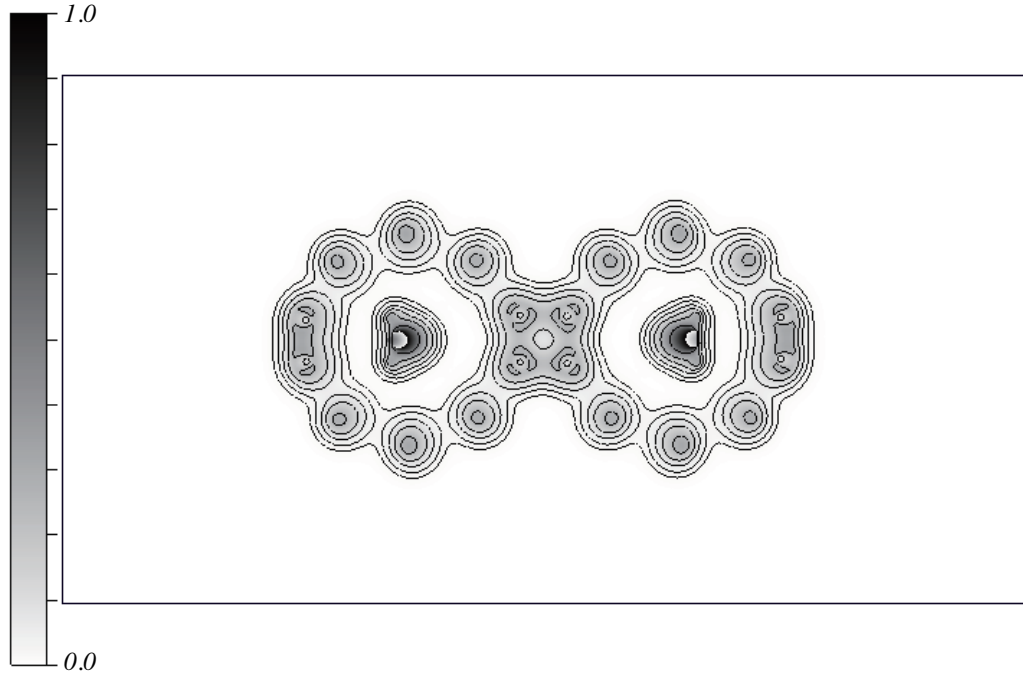| H_2O arrangement	Relative total energy (eV)
$\bar{\boldsymbol{x}}$	0.005
$\boldsymbol{x}$	0.015
$\boldsymbol{y}$	0.016
$\boldsymbol{z}$	0.014

Figure 3: Contour plot on the xy plane of the valence charge density of the C_{60} dimer encapsulating water molecules with the $(\bar{\boldsymbol{x}}, \boldsymbol{x})$ configuration. Each contour represent twice(half) of the density to that of the adjacent contours. Unit in the scale bar is $e/a.u.^3$

are $d_1 = 1.57$ Å which is slightly longer than the other C-C bond in C_{60} dimer: Typical bond lengths of C_{60} dimer with three-fold coordination are $d_{56} = 1.42$ and $d_{66} = 1.39$ Å for 56 and 66 bonds, respectively. This confirms that the detailed atomic arrangement of the C_{60} dimer substantially affects the direction of the dipole moment of water molecules inside the cage. Therefore, the arrangement is not the direct dipole-dipole interaction but the H_2O-wall interaction.

Figure 3 shows a contour plot on the xy-plane of the valence charge density of the C_{60} dimer encapsulating two water molecules with configuration $(\bar{\boldsymbol{x}}, \boldsymbol{x})$. By comparing the charge densities of the inner atomic sites associ-
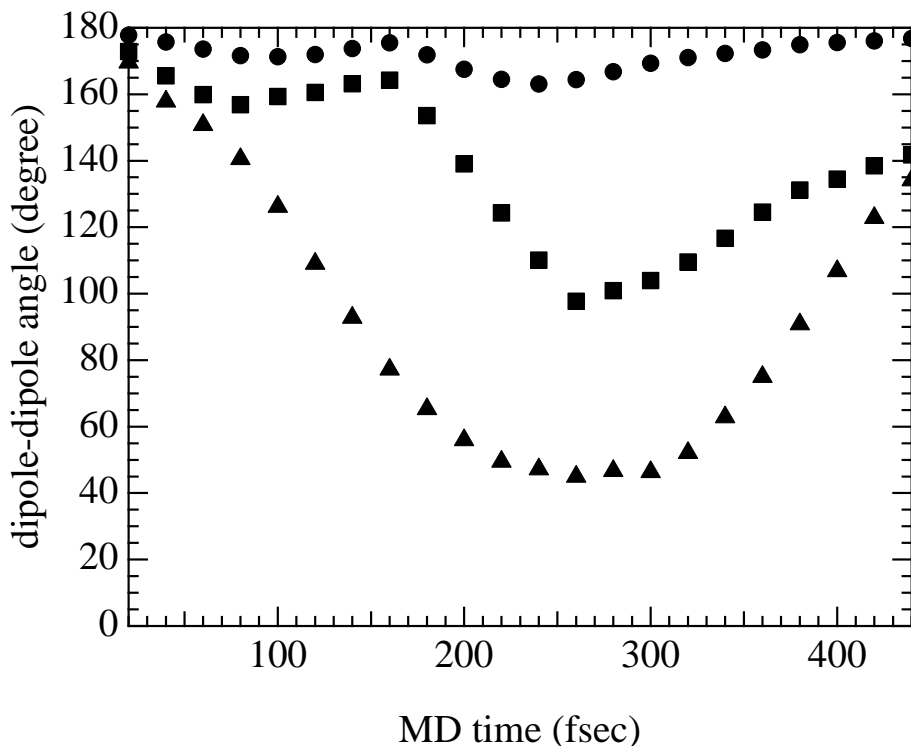
Figure 4: Dipole-dipole arrangement of H_2O molecules encapsulated into C_{60} dimer as a function of the MD simulation times. An angle of $\theta = 180$ degree corresponds with the ground state dipole-dipole arrangement ($\bar{x}$,x). Solid circles, squares, and triangles denote the mutual angles of water molecules at temperatures of 10, 50, and 100 K, respectively.

ated with the [2+2] cycloaddition and the outer atomic sites, we found that the charge density at the outer region is higher than that at the inner region because of the sp^3 nature of the inner atomic site where the π electrons are absent. Since the O atom has a high valence charge density, the tail-to-tail molecular arrangement is energetically favorable to reduce the energy cost of Coulomb repulsive interaction. Therefore, the decreased charge density at the wall of C_{60} induced by the [2+2] cycloaddition is the physical origin of the unusual tail-to-tail mutual configuration of water molecules inside the C_{60} dimer.

Finally, we investigated the dynamical properties of water molecules inside the C_{60} dimer. We performed first-principles MD simulations of the C_{60} dimer encapsulating water molecules with the ground state dipole–dipole ar-

rangement at 10, 50, 100 K for 400 fs simulation times (Fig.4). At a temperature of $T = 10$ K, the two water molecules retained their initial arrangement during the simulation. However, at temperatures of 50 and 100 K, the water molecules were free to rotate, leading to various mutual arrangements. This indicates that water molecules encapsulated in the C_{60} dimer freely rotate at room temperature. Furthermore, a very low temperature is necessary to observe the peculiar dipole–dipole arrangement inside the C_{60} dimer.

4. Conclusion

We have shown the possibility of the peculiar dipole-dipole arrangement of water molecules encapsulated in the C_{60} dimer based on first-principles total energy calculations within the framework of density functional theory. Our calculations showed that the ground state dipole–dipole arrangement of water molecules inside the C_{60} dimer is the tail-to-tail arrangement, which is the highest energy arrangement in classical electrodynamics. The decrease in charge density at the atomic sites associated with the [2+2] cycloaddition leads to the peculiar arrangement. Such a decrease in charge density decreases the energy cost associated with the Coulomb repulsive interaction between the O atom of water and walls of the C_{60} dimer. We also demonstrated that the water molecules encapsulated in the C_{60} dimer are almost freely rotatable above 50 K by first-principles molecular dynamics simulations. These results indicate the importance of the environmental conditions arising from the atomic arrangement of host materials for determining the geometric structure of encapsulated molecules with the dipole moment. Furthermore, by controlling the arrangement of [2+2] cycloaddition to C_{60} cage, it is expected to realized ferroelectricity of the water molecules encapsulated in C_{60} cages connected via [2+2] cycloaddition as in the case of C_{60} polymers.

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