

Energetics of H₂O encapsulated in fullerenes under an electric field

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Abstract

Based on density functional theory with effective screening medium method, we studied the dipole energy of a water molecule encapsulated in fullerene isomers up to C₈₀ under the external electric field. Our calculations show that the dipole energy strongly depends on the electronic structure and mutual arrangement of C₆₀ with respect to the external field.

1. Introduction

Fullerenes are capable of accommodating atoms or molecules inside their C-C networks because of their hollow-cage structures with nanometer diameters. Following the macroscopic production of C₆₀, fullerenes encapsulating metal atoms (metallofullerenes) were synthesized by laser evaporation experiments using carbon rods containing metal atoms. 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. More interestingly, recently, a water molecule has been encapsulated into inner space of C₆₀ by using the molecular surgery technique [1]. In the nanospacing in fullerenes, a water molecule exhibit unusual physical properties, which is different from that observed in vacuum condition. For instance, we have demonstrated that water molecules encapsulated into C₆₀ dimer with dumbbell form possess unusual mutual intermolecular arrangements: In the C₆₀ dimer, water molecules possess a tail-to-tail arrangement as the ground state [2]. The fact indicates that fullerene cages decisively affect the energetics of the encapsulated molecules. Thus, in the present work, we aim to theoretically investigate the dipole energy of a water molecule encapsulated in all fullerene isomers up to C₈₀ which satisfy the isolated pentagon rule, in terms of the external static electric field for providing theoretical insight into the electrodynamics for nanoscale confined spaces.

2. Calculation Method

All calculations were performed using density functional theory as implemented in the Simulation Tool for Atom TEchnology (STATE) package. We use the local spin density approximation to treat the exchange-correlation energy of interacting electrons. Ultrasoft pseudopotentials generated using the Vanderbilt scheme were used to describe the interaction between electrons and ions. The valence wave functions and charge density were expanded by the plane-wave basis set with cutoff energies of 25 and 225 Ry, respectively. We also use effective screening medium

method (ESM) to simulate the fullerenes encapsulating H₂O under the static electric field of 5×10⁻³ HR/au within the formalism of the density functional theory.

3. Results

Figure. 1 shows the dipole energy of water molecule encapsulated into C₆₀ and C₇₄ fullerenes with three mutual orientations of the water molecule with respect to the electric field. The dipole energies, $U = -\mathbf{d} \cdot \mathbf{E}$, are evaluated by the energy difference between the total energies with and without electric field. The dipole energies are measured from that of the water molecule with perpendicular arrangement inside the fullerene cages. In the C₆₀, the dipole energy of water exhibits symmetric nature with respect to the direction of the dipole moment. The absolute value of the calculated dipole energy is 25 meV. In sharp contrast, in the C₇₄, the dipole energy exhibits asymmetric nature with respect to that of the perpendicular arrangement. Furthermore, the dipole energies are smaller by one-fifth or half than that in C₆₀. The small dipole energy inside C₇₄ is ascribed to their large screening capability against the electric field. As shown in Fig. 2, the potential gradient inside C₇₄ is smaller than that in C₆₀. The fact indicates that the energetics of dipole moment inside fullerene strongly depend on the fullerene species. Furthermore, by changing the fullerene arrangement with respect to the electric field, we

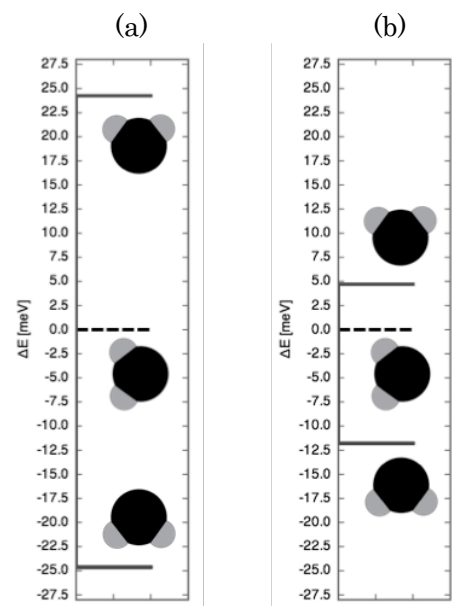


Fig. 1; Dipole energy of H₂O inside (a) C₆₀ and (b) C₇₄ three dipole directions.

also find that the dipole energies are modulated, indicating that the cage topology is also an important factor to determine the energetics of a water molecule inside fullerene.

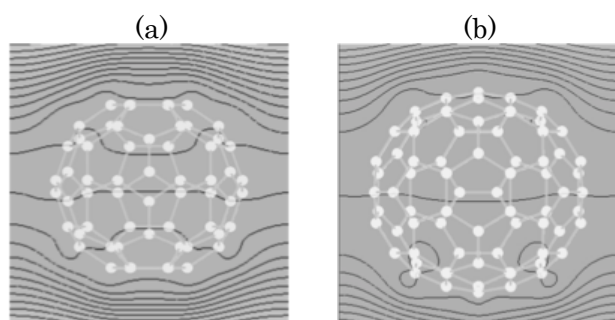


Fig.2: Contour plots of electrostatic potential of empty (a) C_{60} and (b) C_{74} fullerenes.

To give further insight into the energetics, we study the correlation between the HOMO-LUMO gap of fullerene and screening ability against an electric field. Figure. 3 shows a scatter plot of the HOMO-LUMO gap and the screening ability for all IPR fullerenes up to C_{80} . We find that the fullerene with large HOMO-LUMO gap tend to possess less screening ability compared with those with small HOMO-LUMO gap. Thus, the electronic structure of fullerene cage is also important for the dipole energy of a water molecule encapsulated into the nanoscale spacing.

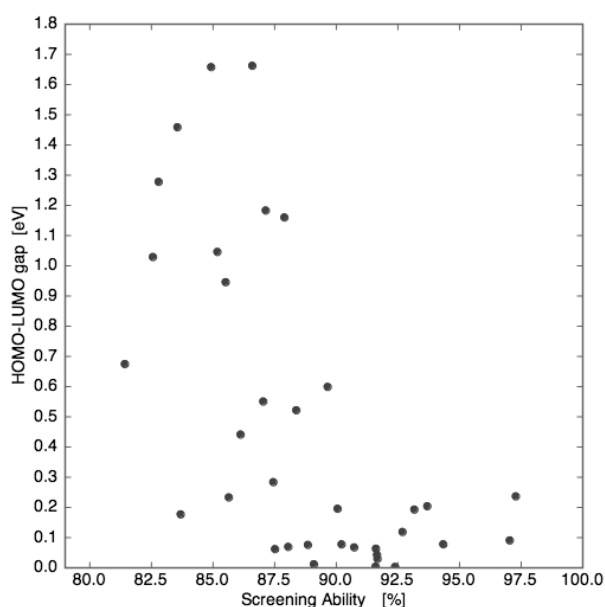


Fig. 3: A correlation between the screening ability and HOMO-LUMO gap of all IPR fullerenes up to C_{80} .

Summary

Using the density functional theory combining with the effective screening medium method, we find that the dipole

energy of a water molecule inside the fullerenes strongly depends on the fullerene species and orientation with respect to the external electric field. In particular, asymmetric properties of dipole energy in terms of the field direction have observed inside several fullerenes. These facts imply that the detailed cage network topology with respect to the electric field decisively affects the electrostatic potential inside the cage. Furthermore, we also demonstrate that the screening ability of the fullerene cages against an external field weakly correlated with the energy gap of fullerenes.

References

- [1] K.Kurotobi et.al., *Science* **333**, 613 (2011)
- [2] K.Nomura et.al., *Chem. Phys. Lett.* **608**, 351 (2014)