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著者	Sorimachi Jun-ya , Okada Susumu
journal or publication title	Japanese journal of applied physics
volume	55
number	4S
page range	04EP02
year	2016-04
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URL	http://hdl.handle.net/2241/00142728

doi: 10.7567/JJAP.55.04EP02

Energetics of H₂O Encapsulated in Fullerenes under an Electric Field

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Based on first-principles total energy calculations, we analyze the dipole energy $U = -\mathbf{d} \cdot \mathbf{E}$ of a water molecule encapsulated in fullerene isomers from C₆₀ to C₈₀, all of which satisfy the isolated pentagon rule. Our calculations show that the dipole energy exhibits unusual features not expected for an isolated water molecule in vacuum. The dipole energy depends sensitively on the electronic structure of fullerenes and their cage network topology when situated in an external electric field. We also demonstrate that the electrostatic potential inside the fullerene exhibits an anisotropic feature with respect to the applied field.

1. Introduction

Over the past three decades, carbon molecules with hollow-cage structures,¹⁾ namely fullerenes, have maintained a premier position in the field of nanosciences and nanotechnology as representatives of nanometer-scale materials exhibiting unusual chemical and physical properties not seen in conventional carbon allotropes.²⁾ The detailed electronic structures of fullerenes strongly depend on the cage size and symmetry.^{3–5)} Various electronic structures enable a variety of electronic and energy devices to be constructed. In contrast, the nearly spherical hollow-cage structures of fullerenes yield common electronic features for their π electron states. The electronic energy levels associated with π electrons tend to bunch up, as the spherical harmonics Y_{lm} corresponding to the electrons are confined to a spherical shell or a sphere.³⁾ For instance, C₆₀ possesses five-fold and three-fold degenerated states for the highest occupied and the lowest unoccupied states, respectively, arising from its nearly spherical cage structure with I_h symmetry.⁶⁾ These highly degenerated states cause a large Fermi-level instability that leads to magnetic⁷⁾ and superconducting^{8–11)} behaviors by injecting an appropriate number of electrons or holes: Alkaline-atom-doped C₆₀ fullerenes, A₃C₆₀, exhibit superconductivity at a few tens of kelvins that is ascribed to the half-filled lowest unoccupied states

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(t_{1u} states). The transition temperature of the compounds depends on alkaline atom species.

From a geometrical view, fullerenes have hollow-cage structures of nanometer diameter,¹²⁾ so that they can accommodate atoms or molecules¹³⁾ to form endohedral fullerenes. Several metal atoms^{14–16)} and metal complexes^{17–19)} have been encapsulated into large fullerenes, such as C_{80} , C_{82} , and C_{84} . In addition to these metal atoms and metal complexes, H_2 ^{20–22)} and H_2O ^{23,24)} molecules have been encapsulated into C_{60} using molecular surgery techniques. Within the fullerene cages, encapsulated atoms and molecules exhibit unusual geometric and electronic properties caused by confinement effect and hybridization with the C atoms of the cage. Indeed, at very low temperatures, a pair of water molecules encapsulated in the C_{60} dimer possess an unusual mutual arrangement which is the least stable arrangement because of the influence of the small electron density around the atoms associated with [2+2] cycloaddition.²⁵⁾ This fact indicates that the energetics of the dipole moment of the encapsulated water molecule strongly depends on the fullerene size, cage symmetry, and mutual cage arrangement. However, the detailed energetics of water molecules inside various fullerenes is still uncertain, as is their screening capability of the static electric field. In particular, whether the dipole energy for the water molecules, $U = -\mathbf{d} \cdot \mathbf{E}$, inside the fullerene cages is equal to that in the vacuum described by classical electrodynamics.

In the present paper, we aim to theoretically investigate the dipole energy of a water molecule encapsulated in all fullerene isomers from C_{60} to C_{80} , which satisfy the isolated pentagon rule (IPR),^{26,27)} in terms of the external static electric field to provide theoretical insight into the electrodynamics for nanoscale-confined spaces. Using the density functional theory combined 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, anisotropic properties of the dipole energy in terms of the field direction have been observed for several fullerenes. These findings imply that the details of the cage network topology with respect to the electric field decisively determine the electrostatic potential inside the cage. Furthermore, we also demonstrate that screening of the fullerene cages for an external field is weakly correlated with the energy gap of the fullerenes.

2. Methods and Models

All theoretical calculations are performed based on the density functional theory (DFT)^{28,29)} as implemented in the program package for the Simulation Tools for Atom TEchnology (STATE).³⁰⁾ We use the local density approximation (LDA)^{31,32)} to treat the exchange correlation potential for interacting electrons. Ultrasoft pseudopotentials generated by the Vanderbilt scheme are adopted to describe the interaction between electrons and ions.³³⁾ Valence wave functions and charge density are expanded in terms of the plane wave basis set with the cutoff energies of 25 and 225 Ry, respectively. Γ -point sampling is used for Brillouin zone integration. To simulate isolated fullerene molecules encapsulating a water molecule, we considered a large cuboid cell with cell parameters 30, 30, and 26 Å for the x , y , and z directions. Along the z direction, we impose an open boundary condition in which planar parallel electrodes are situated at the cell boundaries. By applying an external electric field between these electrodes, we investigate the a dipole energy of a water molecule inside the fullerenes. We also use the effect screening medium (ESM) method, in which Poisson's equation for electrons in the self-consistent DFT calculations is treated by the appropriate boundary condition (Fig. 1).³⁴⁾

In the present study, we have investigated the energetics and electronic structures of all IPR isomers up to C₈₀ encapsulating a water molecule to determine the dipole energy under the external electric field (Fig. 2). To investigate the dipole energy of the water molecule inside fullerenes, we sandwich these endohedral fullerenes between the parallel planar electrodes simulated by ESM with infinite permittivity (Fig. 1).^{35,36)} As most of the large fullerenes possess structural anisotropy, we consider two representative fullerene orientations to the field, as (A) and (B) orientations for each fullerene in Fig. 2, to investigate the effect of cage network topology on the dipole energy. The geometric structures of fullerenes are fully optimized until the remaining force acting on each atom is less than 1.33×10^{-3} HR/a.u. A water molecule is situated at the center of fullerenes with three mutual molecular arrangements, in which their dipole moment is parallel, perpendicular, and antiparallel with respect to the electric field. During calculations under electric field of 5.0×10^{-3} HR/a.u., all atoms are fixed in their initial configuration.

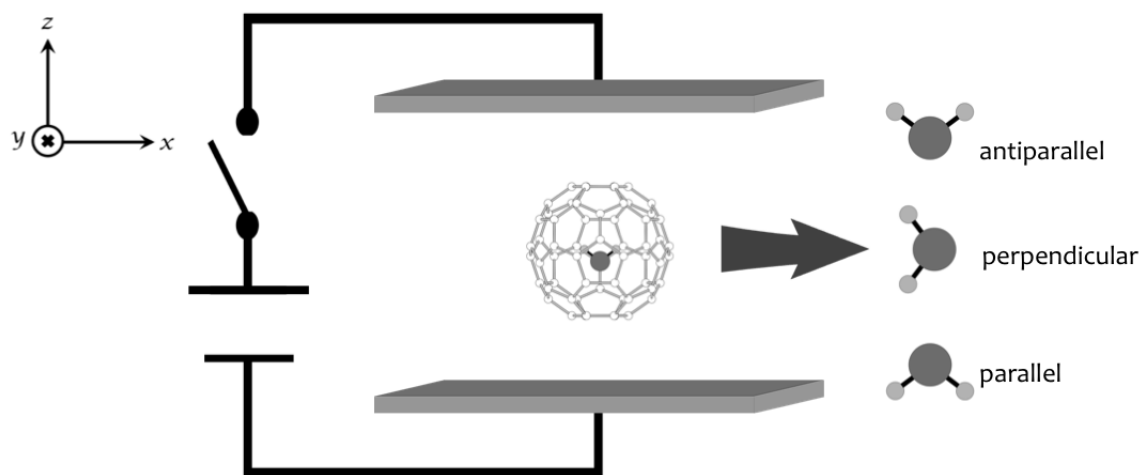


Fig. 1. Structural model to investigate the energetics of H₂O encapsulated in fullerenes under a parallel electric field. Gray slabs represent the parallel electrodes simulated by an effective screening medium with infinite relative permittivity.

3. Results and Discussion

Figure 3 shows the dipole energy of a water molecule encapsulated into fullerene cages with various mutual orientations of both fullerene cages and water molecules with respect to the electric field: $U = -\mathbf{d} \cdot \mathbf{E}$, where \mathbf{d} and \mathbf{E} denote the dipole moment of a water molecule and the external electric field, respectively. The dipole energies are calculated from the difference between the total energies with and without the electric field: $U = E(\mathbf{E} \neq 0) - E(\mathbf{E} = 0)$ where $E(\mathbf{E} \neq 0)$ and $E(\mathbf{E} = 0)$ denote the total energy of H₂O@fullerene under finite and zero electric fields, respectively. The dipole energies are measured from that of the water molecule with a perpendicular arrangement inside the fullerene cages. For fullerenes C₇₀ and larger, we consider two representative molecular orientations of the fullerenes with respect to the electric field because of their lower symmetries, as these are expected to reflect their screening capability in the external field.

For C₆₀, the dipole energies of the parallel and antiparallel water molecular arrangements are symmetric with respect to those of the perpendicular arrangement, because of their I_h cage symmetry which yields a highly isotropic electrostatic potential inside the cage. For the large fullerenes possessing higher symmetry or pseudospherical shapes, we also find a symmetric dipole energy for the parallel and antiparallel molecular arrangements with respect to the perpendicular molecular arrangement. In contrast, for fullerenes with lower symmetry or anisotropic cage shapes, the dipole energy exhibits

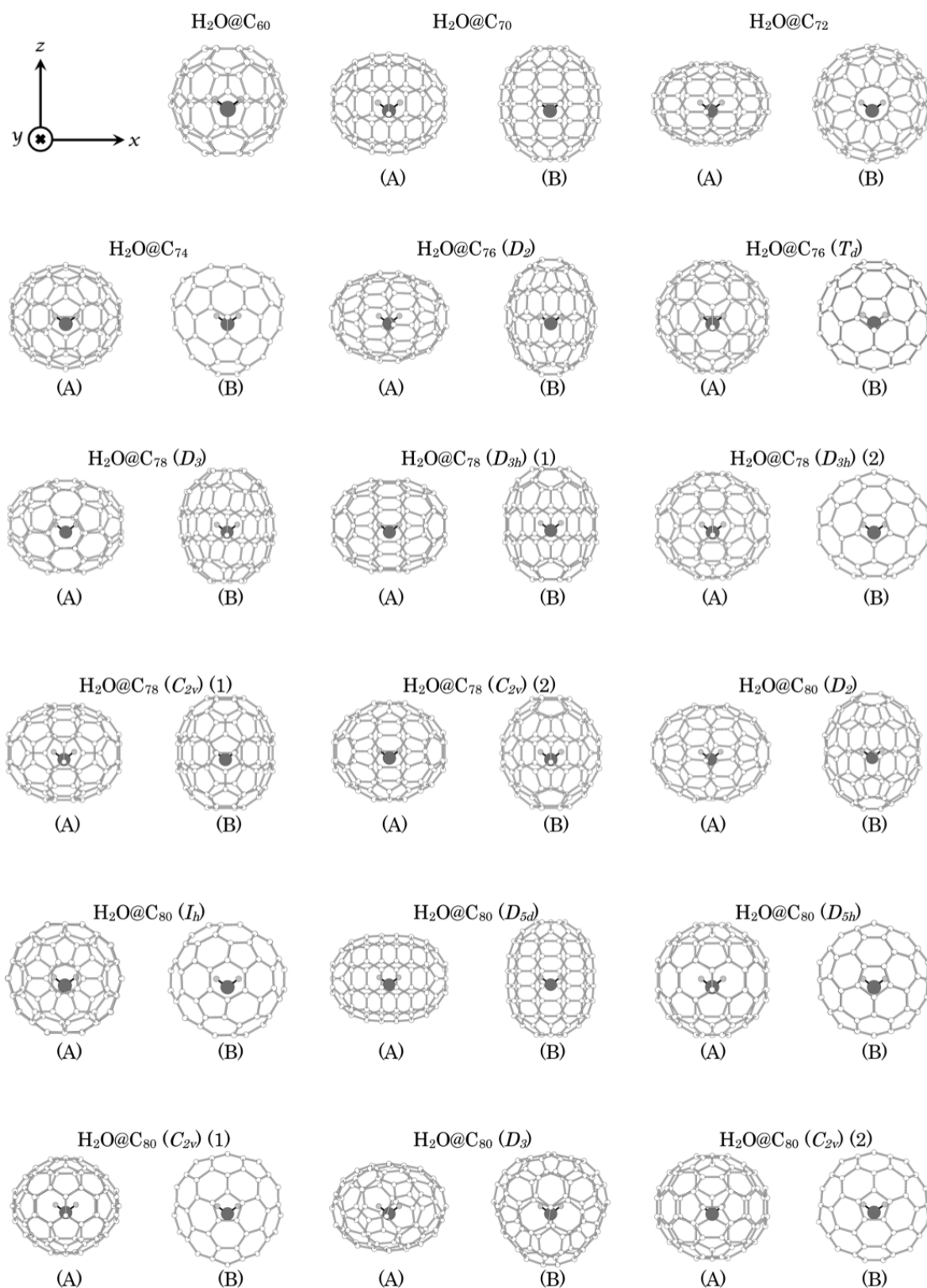


Fig. 2. All IPR isomers of fullerenes up to C_{80} encapsulating H_2O molecule.

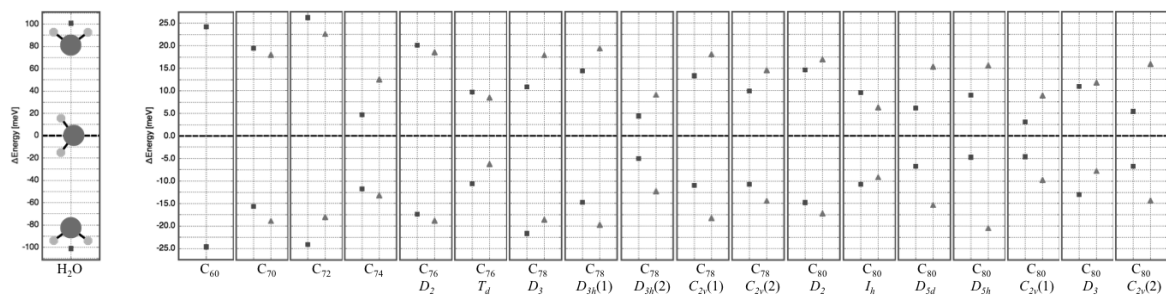


Fig. 3. Dipole energies of an isolated water molecule and of a water molecule encapsulated in a fullerene with various orientations with respect to the electric field. Energies are measured relative to the dipole energies under the perpendicular water arrangement. Squares and triangles denote the dipole energy of a water molecule inside fullerenes with their orientations (A) and (B), respectively, in Fig. 2.

an asymmetric nature with respect to the perpendicular arrangement. In particular, the dipole energies of a water molecule inside C_{74} exhibit a large asymmetry. An absolute value of the dipole energy for the parallel molecular arrangement is three-times as large as that for the antiparallel molecular arrangement.

It should be noted that an encapsulated water molecule is dislodged from the center of fullerene cage. At this equilibrium position in the fullerenes, furthermore, the water molecule prefer the particular orientation with respect to sp^2 networks.³⁷⁾ However, since the dipole energies are calculated from the difference between the total energies of $H_2O@fullerene$ with and without the electric field, the dipole energy, in principles, does not contain the interaction between the water molecule and fullerene cages. Indeed, dipole energies of the water molecule at the equilibrium position in C_{60} and C_{70} are the qualitatively the same results presented above.

In addition to the cage symmetry and network topology, the mutual orientation of fullerene cages to the field also affects the energetics of the dipole moment within the fullerenes. The change in the dipole energy increases with those in molecular orientation for C_{74} , $C_{78}(D_{3h})(2)$, $C_{78}(D_{3h})(1)$, $C_{78}(C_{2v})(2)$, $C_{78}(D_{3h})(2)$, $C_{80}(D_2)$, $C_{80}(D_{5d})$, $C_{80}(D_{3h})$, $C_{80}(C_{2v})(1)$, and $C_{80}(C_{2v})(2)$. In contrast, the energies decrease for C_{72} , $C_{76}(T_d)$, and $C_{80}(I_h)$. This finding indicates that the electron distribution over the covalent network of a fullerene significantly affects the energetics of the dipole moment of the water molecule inside fullerenes under an applied electric field.

To clarify the physical origin of the asymmetry associated with the dipole energy inside $C_{74}(A)$, we investigate the electrostatic potential of empty C_{60} , $C_{74}(A)$, and

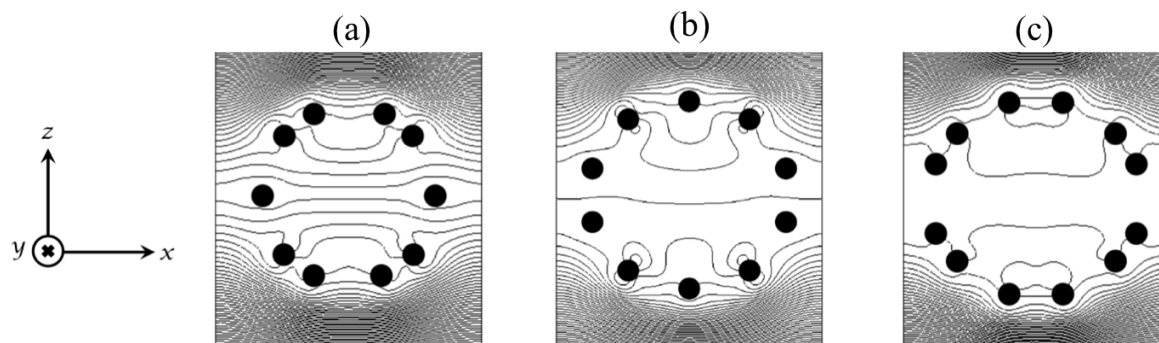


Fig. 4. Contour plot of the electrostatic potential of inside empty (a) C_{60} , (b) $C_{74}(A)$, and (c) $C_{78}(D_{3h})(2)(A)$.

$C_{78}(D_{3h})(2)(A)$ under the external electric field of 0.005 HR/a.u. (Fig. 4). As shown in Fig. 4(b), the electrostatic potential inside $C_{74}(A)$ exhibit asymmetric nature with respect to the $z = 0$ plane, in contrast to those inside C_{60} and $C_{78}(D_{3h})(2)(A)$ in which the potential exhibit symmetric properties with respect to the $z = 0$ plane. Thus, the asymmetric electrostatic potential caused by the $C_{74}(A)$ cage leads to the large asymmetry in the dipole energy of the water molecules with respect to the external field as shown in Fig. 3.

In addition to the asymmetry of dipole energy with respect to the dipole orientation to the field, we also find that the magnitude of the dipole energy depends sensitively on the detailed geometry of the fullerene cages. For instance, the dipole energy of a water molecule in C_{60} is five times as large as that for the $C_{78}(D_{3h})(2)(A)$, indicating that the cage of $C_{78}(D_{3h})(2)(A)$ screens the electric field more strongly than that of C_{60} . From Fig. 4, the gradient of the electrostatic potentials inside empty $C_{74}(A)$ and $C_{78}(D_{3h})(2)(A)$ are remarkably smaller than that inside C_{60} , indicating that the $C_{74}(A)$ and $C_{78}(D_{3h})(2)(A)$ cages strongly screen the electric field compared with the C_{60} cage.

Figure 5 shows the energy gaps between the highest occupied state (HO) and the lowest unoccupied state (LU) of the fullerene molecules as a function of their screening capability against the external electric field. The screening capability is evaluated by dividing the dipole energy of encapsulated water by that for an isolated one. We find that the screening capability correlates weakly with the HO-LU gap. Fullerenes with large HO-LU gap tend to possess lower screening capability than those with small HO-LU gap. However, as stated above, we find that the screening effects also depend on the mutual cage orientation with respect to the electric field, implying that another

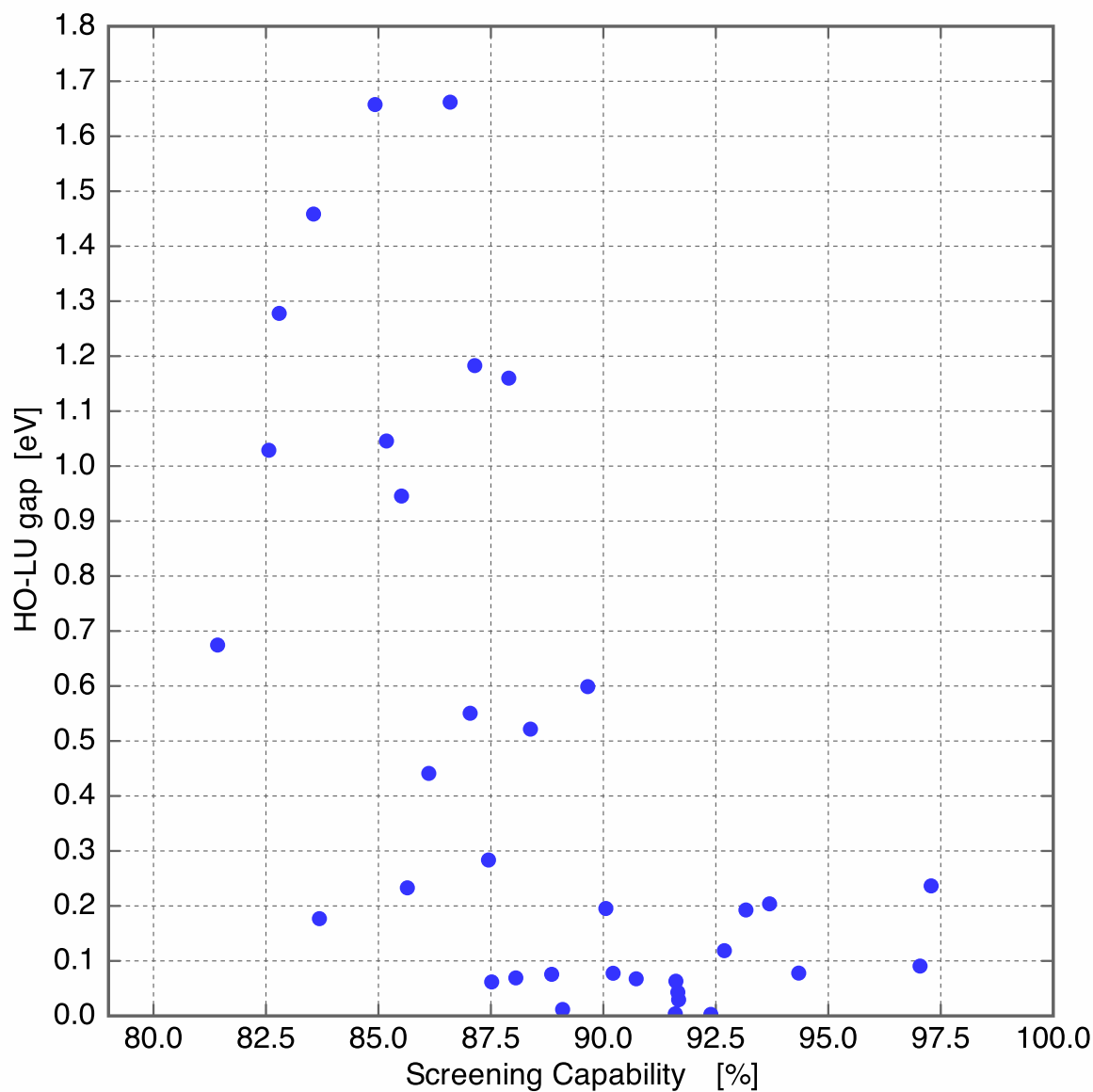


Fig. 5. (Color online) Correlation between the screening capability and HO-LU gaps for all IPR fullerenes up to C_{80} .

physical mechanism may exist for determining the screening capability of the fullerene cage.

4. Summary

Using DFT combined with the ESM method, we have investigated the dipole energy of a water molecule encapsulated in all IPR fullerene isomers up to C_{80} under an external electric field. DFT-ESM calculations have revealed that the dipole energy of a water molecule inside the fullerenes strongly depends on fullerene species and their

orientations with respect to the external electric field. For fullerenes with pseudospherical cage structures, such as C_{60} , $C_{76}(D_2)$, and $C_{80}(I_h)$, the dipole energies for parallel and antiparallel molecular arrangements are symmetric with respect to those for the perpendicular arrangement. In contrast, however, the dipole energy exhibits an asymmetry with respect to the perpendicular arrangement for fullerenes with lower symmetry or anisotropic cage shape. In particular, the dipole energies associated with a water molecule inside C_{74} exhibit a large asymmetry. In addition, we also find that the dipole energy largely depends on the mutual cage orientations in the external electric field, even though the fullerenes possess higher symmetry or spherical shape. These results indicate that details of the cage network topology in regard to the electric field strongly affect the electrostatic potential inside the cage. Furthermore, we find that the magnitude of the dipole energy also strongly depend on the fullerene species and their mutual orientations to the field. By analyzing the screening capability of the fullerene cages in terms of their energy gap between HO and LU states, fullerenes with a large HO-LU gap tend to provide less screening from the electric field. In contrast, fullerenes with small energy gaps tend to screen the field rapidly. Thus, the electronic structure of fullerene cages also plays a decisive role in determining the dipole energy of a water molecule inside fullerenes in addition to the mutual cage topology with respect to the field.

Acknowledgments

This work has been supported by CREST, from the Japan Science and Technology Agency, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan. A part of the calculations were performed on NEC SX-Ace at the Cybermedia Center at Osaka University and on NEC SX-9 at the Institute of Solid State Physics, The University of Tokyo.

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