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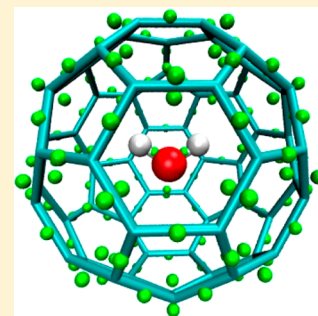
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On the Polarity of Buckminsterfullerene with a Water Molecule Inside

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ABSTRACT: Since the recent achievement of Kurotobi and Murata to capture a water molecule in a C₆₀ fullerene (Science 2011, 333, 613), there has been a debate about the properties of this H₂O@C₆₀ complex. In particular, the polarity of the complex, which is thought to be underlying the easy separation of H₂O@C₆₀ from the empty fullerene by HPLC, was calculated and found to be almost equal to that of an isolated water molecule. Here we present our detailed analysis of the charge distribution of the water-encapsulated C₆₀ complex, which shows that the polarity of the complex is, with 0.5 ± 0.1 D, indeed substantial, but significantly smaller than that of H₂O. This may have important implications for the aim to design water-soluble and biocompatible fullerenes.



■ INTRODUCTION

Endohedral fullerenes are fascinating molecular complexes that consist of a nanoscale carbon cage and an encapsulated guest atom, ion, or molecule. They have opened a new way to study small molecular species in confined isolation but also provide an interesting means to alter the properties of the otherwise rather inert fullerenes. Recently, Kurotobi and Murata found a synthetic route to surgically insert a single water molecule into the most common fullerene, the C₆₀ "buckyball".¹ This is a remarkable feat considering that water under normal conditions prefers to exist in a hydrogen-bond-forming hydrophilic environment. As the strong dipole moment of the water molecule is expected to polarize the symmetric nonpolar C₆₀ cage, the H₂O@C₆₀ complex may be an important step forward toward the aim to make fullerenes that are water-soluble and biocompatible.^{2,3}

Among the extensive analysis that Kurotobi and Murata performed to characterize the H₂O@C₆₀ moiety, they showed that the complex can be relatively easily separated from the empty fullerene by liquid chromatography, which is a first indication that indeed the outside properties of the carbon cage have changed after encapsulating a water molecule. They also performed density functional theory (DFT) calculations and computed that the dipole moment of the H₂O@C₆₀ complex is 2.03 D—a surprisingly high value considering that it is equal to that of an isolated water molecule (2.02 D) at the same M06-2X/6-311G(2d,p) level of theory.¹ While this result was very recently confirmed by Bucher⁴ using the DFT-BLYP-D functional (2.0 D), it is in sharp contrast to the result of earlier work by Ramachandran and Sathyamurthy, who found 0.54 D using Hartree–Fock and MP2,⁵ and by Yagi and Watanabe, who found 0.61 D using DFT-B3LYP.⁶ Balch attributes this discrepancy to the lower level of sophistication of the earlier calculations.² See Table 1 for a compilation of the

published values for the dipole moment at the different levels of theory.

Table 1. Literature Values for the Dipole Moment (D)

method	basis set	H ₂ O@C ₆₀	H ₂ O	ref
M06-2X	6-311G(2d,p)	2.03	2.02	1
BLYP-D	80 Ry	2.0	1.86	4
HF	6-31G	0.54	2.5	5
B3LYP	cc-pVDZ/STO-3G	0.61	1.94	6

Here we present our careful analysis of the dipole moment of the H₂O@C₆₀ complex in order to resolve the inconsistency among the different literature results of the dipole moment. For this aim, we reproduced the previous ab initio estimates and performed additional benchmark DFT calculations. We also analyze the effect of the water encapsulation on the electronic density distribution of the C₆₀ cage. Using ab initio molecular dynamics simulations, we measure the dipole distribution and the relaxation of the orientational time correlation at finite temperatures.

■ METHOD

We performed all-electron Hartree–Fock (HF) and second-order Møller–Plesset perturbation theory (MP2) calculations as well as density functional theory (DFT) calculations with, among others, the B3LYP⁷ and M06-2X⁸ hybrid-functionals using the Gaussian program.⁹ The CPMD program¹⁰ was used to perform DFT calculations and DFT molecular dynamics (MD) simulations using pure GGA functionals augmented with Grimme's¹³ dispersion interactions. We used norm-conserving Troullier–Martins pseudopotentials with a plane waves cutoff

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of 70 Ry. The MD simulations were performed in the NVT ensemble, using a Nose–Hoover chain thermostat and a simulation length of about 10 ps for the $T = 50$ and 300 K runs and 25 ps for the $T = 100$ K runs. The time step was 4 au (≈ 0.1 fs) and the fictitious electron mass was 500 au.

RESULTS

The molecular structure of the $\text{H}_2\text{O}@C_{60}$ complex, the empty C_{60} cage, and the isolated H_2O molecule were each setup with a molecule builder program and optimized with the Gaussian program at the DFT level of theory using the M06-2X density functional and the 6-311G(2p,d) Gaussian basis set. We then used the obtained structures for single-point calculations to obtain the total energy and the dipole moment at a variety of levels of theory. The different levels of theory, listed in Table 2,

Table 2. Computed Dipole Moment and Interaction Energy

method	dipole moment (D)		ΔE (kcal/mol)
	$\text{H}_2\text{O}@C_{60}$	H_2O	
HF	0.62	2.09	−0.90
MP2	0.62	2.09	−21.8
MP2 ^a	0.53	2.23	−15.4
BLYP	0.40	1.93	−0.79
PBE	0.40	1.94	−6.70
PBE-D	0.40	1.94	−20.1
B3LYP	0.45	1.98	−3.34
M06-2X	0.52	2.02	−21.5
M06-2X ^b	0.54	2.03	−21.4
M06-2X ^c	0.54	2.06	−15.3

^aUsing the 6-31G* instead of 6-311G(2d,p). ^bUsing the geometry of ref 1. ^cAs for footnote b with counterpoise BSSE correction.

are HF, MP2, and DFT using the BLYP¹¹ and PBE¹² pure GGA functionals, the PBE functional augmented with the D3 van der Waals correction parametrization by Grimme,¹³ and the hybrid B3LYP and meta-hybrid M06-2X functionals. All data reported in the table were obtained with the 6-311G(2p,d) basis set, except for the MP2 calculation (third row), for which we also list the result obtained with the smaller 6-31G* basis set. The table shows our results for the dipole moment and for the interaction energy between the water molecule and the fullerene cage.

The following three observations are apparent from Table 2: (1) the different methods show good agreement about the dipole moment of the $\text{H}_2\text{O}@C_{60}$ complex and of the isolated water molecule; (2) the dipole moment of the complex, in the range 0.4–0.6 D, is significantly smaller than that of H_2O , which is found to be 1.9–2.1 D; and (3) the interaction energies show instead a significant spread among the different methods, ranging from −0.8 to −21.5 kcal/mol.

The consistency among the results for the dipole moment computed with the different methods can be understood from the fact that typically the total electron density of the molecule is mainly determined by the kinetic and Coulombic energy terms of the Hamiltonian. Instead, the interaction energy is the difference of total energies in which the kinetic and Coulombic terms largely cancel each other and the result is much more sensitive to the (chemically relevant) description of the exchange energy and the correlation energy, including the dispersion interaction. The argument that the large spread in the literature values for the computed dipole moment of $\text{H}_2\text{O}@C_{60}$ (see Table 2) is caused by the lower level of sophistication

of the older calculations compared to the newer results is therefore not a very strong one. Rather, we suspect that the M06-2X result of ref 1 and the BLYP-D result of ref 4 are related to the dipole moment of only the water molecule that is either computed in the basis set of the total complex or feeling the field of the C_{60} , but not, as the authors claim, the dipole moment of the entire $\text{H}_2\text{O}@C_{60}$ complex.

The large spread in the results for the interaction energy between the water molecule and the C_{60} cage is remarkable. The weakest interaction, of less than 1 kcal/mol, is found with HF and BLYP. Intermediate values are found with B3LYP (−3.3 kcal/mol) and PBE (−6.7 kcal/mol), whereas a strong attraction of 20–22 kcal/mol is found with PBE-D, M06-2X, and MP2. The last three methods are the most sophisticated methods employed here, which leads us to believe that the water– C_{60} interaction is remarkably attractive. The important difference between this group of methods and the other two groups is that PBE-D, M06-2X, and MP2 all account for dispersion interaction, while the other methods do not. Indeed the water– C_{60} interaction is expected to have a large dispersion contribution. For example, the water–acene (benzene, graphene) dispersion contribution was found to be of the same magnitude (about −3 kcal/mol) as the total interaction using DFT-based symmetry-adapted perturbation theory.¹⁶ Also from classical force field molecular dynamics simulations it is known that there is a strong dispersion attraction between water and C_{60} , which would turn the hydrophilic C_{60} water-soluble if it were not for the even stronger C_{60} – C_{60} attraction.¹⁷ As the strong dispersion attraction is a rather isotropic interaction inside the C_{60} cage, unlike for example the directional hydrogen bond interaction in bulk water, the water molecule is not expected to feel a significant barrier for rotation, in agreement with recent NMR data¹⁸ and molecular dynamics simulations.⁴

There are three important sources of error to consider. In the first place, our computational resources limit the ab initio level of theory to MP2/6-311G(2d,p). However MP2 calculations can overestimate two-body dispersion energies¹⁹ and higher levels, such as CCSD(T), might further improve the interaction energy. Second, the 6-311G(2d,p) basis set may still be far from the basis set limit, as indicated by comparing the MP2/6-31G* results of −15.4 with the MP2/6-311G(2d,p) number of −21.8 kcal/mol. And third, the interaction energy is overestimated due to basis-set superposition error (BSSE). We estimated the BSSE for the M06-2X calculation by computing the energies of the isolated H_2O and C_{60} fragments using the total basis set of the complex, known as the counterpoise correction.²⁰ After correction, the attraction is reduced to −15.3 kcal/mol.

To test the hypothesis that the dipole moment of the water molecule is very little affected by encapsulation in the hydrophobic environment of the fullerene, we performed the maximally localized Wannier function analysis^{14,15} using the CPMD program, similarly to what was done in ref 4. Each Wannier function represents a two-electron function in a closed-shell calculation. The dipole moment is obtained by

$$\mu = \sum_i^n \mathbf{r}_i q_i + \sum_\alpha^N \mathbf{R}_\alpha q_\alpha$$

in which the first term sums over the center positions \mathbf{r} of the Wannier functions with a charge $q = -2|e|$ and the second term accounts for the ions. Summing over selected ions and Wannier centers allows for the calculation of the dipole moment of only

part of the molecule, such as here only the water molecule or only the cage of the complex.

An advantage of using a plane wave basis set instead of localized Gaussian basis functions is that the interaction energy is not affected by BSSE. However, a disadvantage is that the periodicity of the plane waves leads to a spurious interaction with neighboring cells that has to be compensated for. Here we have used the method of Tuckerman²¹ and the method of Hockney²² to neutralize the electrostatic repulsion between periodic images. However, despite these methods, the convergence of the dipole moment with the box size is very slow, as seen in Figure 1. This slow convergence can be

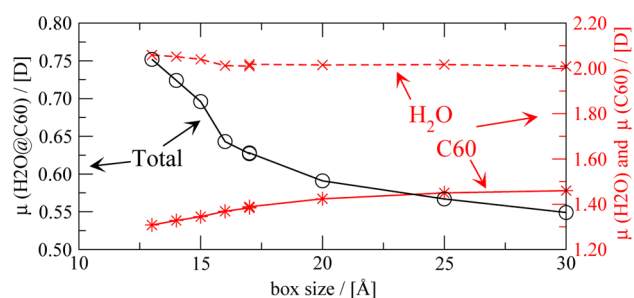


Figure 1. Convergence of the dipole moment with the box size computed for the total $\text{H}_2\text{O}@C_{60}$ complex (black, left axis) and the partial dipole moments of H_2O and C_{60} parts in the complex (red, right axis).

attributed to the significant charge density that is delocalized over the C_{60} cage, leading to electrostatic interactions between the periodic images that are not perfectly compensated by the Tuckerman method or the Hockney method, which both use an atom-centered fitting of the charge density.

Figure 2 illustrates the polarization of the $\text{H}_2\text{O}@C_{60}$ complex using the difference of the electron density of the complex with respect to the isolated H_2O and C_{60} parts. Here, the $\text{H}_2\text{O}@C_{60}$ complex is oriented with the water dipole moment vector pointing upward. The main shift of density occurs in between the carbons, which points to the involvement of the π -electrons,

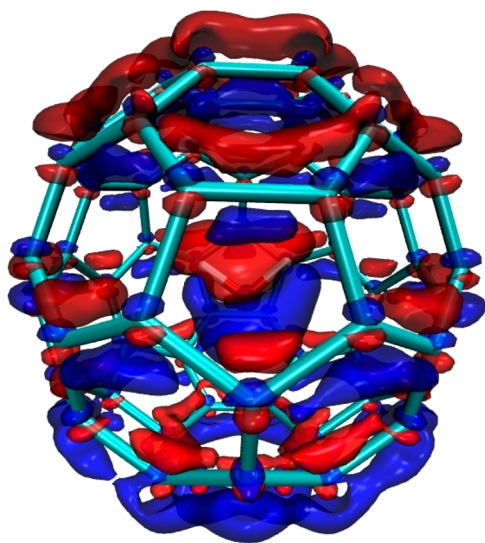


Figure 2. Polarization of $\text{H}_2\text{O}@C_{60}$ illustrated by the increase (red) and decrease (blue) of electron density relative to the empty C_{60} and isolated H_2O . Isosurfaces shown at ± 0.002 electron/ b^3 .

in the upward direction. A much smaller shift in the downward direction is localized at the carbon atoms. Clearly the overall response of the C_{60} cage to the water molecule dipole moment is a charge density shift in the opposite direction. This is confirmed by the Wannier center-based calculation of the dipole moment, which shows a dipole moment of 2.01 D at the water molecule, an induced dipole moment of 1.46 D on the C_{60} cage, and a total dipole moment of 0.55 D, at the largest box size of $L = 30$ Å used here (see also Figure 1). Indeed, the dipole moment of the water molecule is hardly affected by the C_{60} cage (although some density shift can be observed in Figure 2) and practically unchanged from its value in a vacuum. Subtracting the significant induced dipole moment of the cage results in the total dipole moment of $\text{H}_2\text{O}@C_{60}$ in agreement with our Gaussian results.

We also performed ab initio (DFT) molecular dynamics simulations of the complex to investigate the effect of temperature on the dynamics of the complex and on the dipole moment. Simulations were performed at three temperatures, $T = 50$, 100, and 300 K. At lower temperatures quantum rotation of the water molecule becomes significant,¹⁸ which is not captured by our method. To assess the contribution of the dispersion interaction on the dynamics, we performed the simulations using the PBE functional with the van der Waals correction by Grimme for all temperatures and for $T = 100$ K once more using PBE without correction. The main results are summarized in Figure 3. The dipole moment distributions are shown in the top panel for the $\text{H}_2\text{O}@C_{60}$ moiety and the C_{60} and H_2O components within the complex. The simulations were performed using a cubic box with an edge of 12.0 Å, which causes a shift of the absolute values of the dipole moments as

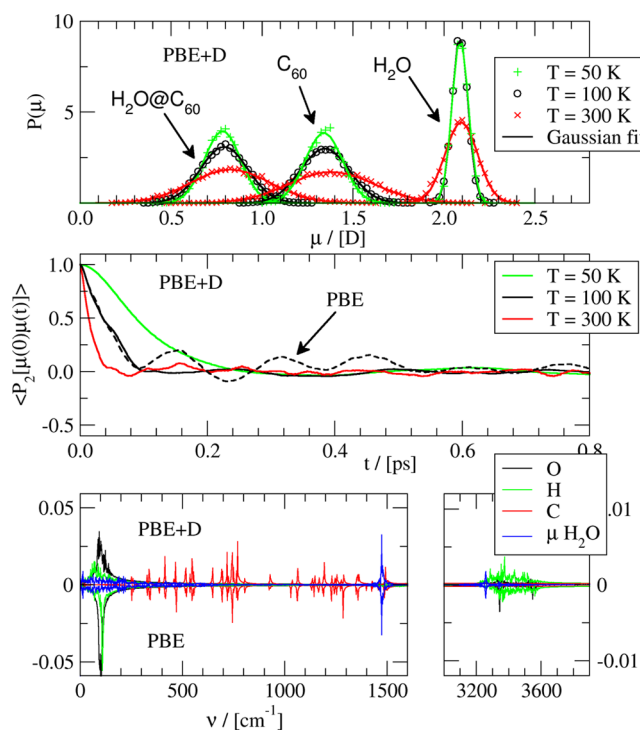


Figure 3. Top panel: dipole moment distributions of the $\text{H}_2\text{O}@C_{60}$ complex and its C_{60} and H_2O components. Middle panel: velocity autocorrelation of the total dipole moment of $\text{H}_2\text{O}@C_{60}$. Bottom panels: Infrared spectra computed with PBE (lower, upside-down graphs) and PBE+D (top graph).

discussed before (see Figure 1). For example, at $T = 100$ K the dipole moments of the water molecule, the C_{60} cage, and the total complex are $2.09(\pm 0.043)$, $1.34(\pm 0.13)$, and $0.79(\pm 0.13)$ D, respectively, with the parenthesized numbers being the standard deviation σ read from a Gaussian fit. At $T = 300$ K, the distributions broaden significantly and for the C_{60} cage and the total complex also shift a little upward to $1.38(\pm 0.24)$ and $0.82(\pm 0.22)$ D. The H_2O distribution shows with $2.09(\pm 0.22)$ D only a broadening.

The middle panel shows the orientational correlation functions $C_l(t)$, given by

$$C_l(t) = \langle P_l[\vec{\mu}(0) \cdot \vec{\mu}(t)] \rangle$$

where $P_l(x)$ is the Legendre polynomial of order l and $\vec{\mu}(t)$ is the dipole moment vector at time t . These orientational correlation functions can be compared to experimental measurements. The first-order Legendre polynomials are probed by dielectric relaxation and infrared absorption spectroscopy, while the decay of the second-order polynomial is involved in measurements of the molecular dynamics with, for example, NMR, ESR, and ultrafast IR. Comparing the red, black, and green curves of $C_2(t)$, we note, as expected, a slowdown of the relaxation of the water molecule orientation inside the fullerene with decreasing temperature. We can attempt to fit the initial decay of $C_2(t)$ with a single- or a double-exponential function, as is typically done to obtain the relaxation times for water reorientation in the bulk phase, but this leads to poor fits here. Much better results are obtained by fitting with a compressed exponential:

$$y = \exp(-(t/\tau)^\beta)$$

We find for $T = 50, 100$, and 300 K values for β of 1.5, 1.4, and 1.3, and for τ_2 we obtain 0.10, 0.047, and 0.018 ps⁻¹, respectively. The interpretation of a decay by a compressed exponential with $1 < \beta < 2$ is that the rotational motion has a strong ballistic component and is not dominated by strong short-time orientational diffusion, as is the case in bulk water. Indeed, visual inspection of movies of the trajectories shows a rather ballistic, freely rotating water molecule, but with a frequently changing angle of rotation, which must be due to interactions with the C_{60} cage. This free rotation at these temperatures is in agreement with our static electronic structure calculations that show that the rather strong interaction between the water molecule and the buckyball is due to van der Waals interactions, which are isotropic, and not, for example, due to directional hydrogen-bond-like interactions with the π -electron system. The effect of omitting the dispersion interaction results in larger oscillations, shown for $T = 100$ K by the black dashed line. Here, the less strong interaction makes the system less ergodic and the rotational motion less stochastic, which results in somewhat worse statistics and larger fluctuations.

The bottom panel of Figure 3 shows the vibrational (infrared) spectrum, which was computed by taking the Fourier transform of the velocity autocorrelation function of the oxygen atoms (black line), hydrogen atoms (green), or carbon atoms (red). The spectrum can also be computed using the Fourier transform of the fluctuating dipole moment (blue line). The latter shows the OH stretch vibration at 3259 cm⁻¹ and the water bend vibration at 1474 cm⁻¹. Omission of the dispersion interaction has very little effect on the vibration

spectrum, except at very low frequencies due to the translational and rotational motions of the water molecule.

CONCLUSION

Summarizing, we have computed the dipole moment and the interaction energy of a water molecule in buckminsterfullerene at a variety of ab initio and DFT levels of theory. All methods predict a dipole moment between 0.4 and 0.6 D for the $H_2O@C_{60}$ complex, in agreement with previous Hartree–Fock and B3LYP calculations and in sharp contrast with more recent calculations that predict a dipole moment for the complex that is as high as that of an isolated water molecule. Instead, here we showed that the C_{60} cage responds to the polar water molecule inside with a strong counteracting induced dipole, resulting in the much lower total dipole. This total dipole moment of $H_2O@C_{60}$ is still significant, which could have interesting implications for future applications of fullerenes. The interaction between water and the fullerene is -15 kcal/mol, at the M06-2X level of theory after BSSE correction, which is rather strong and attributed to dispersion interaction. First principles molecular dynamics simulations at $T = 50, 100$, and 300 K show that the water molecule rotates freely in its cage, which confirms that the strong interaction is not directional.

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Notes

The authors declare no competing financial interest.

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