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Effect of triplet encapsulated atoms in [60] fullerenes: a theoretical analysis

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Abstract: The present investigation reports on the interaction of the C/O triplet atoms inside of the [60] fullerene (C_{60}) species with small polar molecules (H_2O, CH_3OH, HF, NH_3) using Density Functional Theory (DFT) calculations. The calculations show that in all the computed cases the encapuslated complexes with the molecules are more stable than without internal atoms.

Keywords: Fullerene; Polar molecule interactions; Density functional theory (DFT); Absorption.

Introduction

There have many several efforts in the use and evaluation of the physical properties of nano-materials. These investigations include the elucidation of the reactivity and structural capacities of the [60] fullerene (C_{60}) species [1-10]. Such experiments are of use in surface chemistry as they permit the solvation properties to be modified [11]. An example of this phenomena is on the La@C_{60} system which has been shown to have metal-like conductive properties above 29 K [12].

This work is significant from the viewpoint of the theoretical design of new fullerene species that can be implemented as transport vesicles [13]. Our primary motivation is the amelioration of the chemical nature of these structures to improve polar molecule interactions [14-16]. Such intermolecular forces reduce the hydrophobic and toxic nature of the nanostructure. The dispersion of charge in guest materials can cause the guest material to be insensitive to the applied electrical field.

Other recent efforts in our group have demonstrated that the encapsulation of metals inside of fullerenes improves external interactions with small polar molecules [17-18]. In these efforts first

and second group metals were used to improve the interactions of the fullerenes to external polar species. Oxygen was employed in the study reported herein to analyze the affect that it has on the charge structure of the fullerene. From previous references [19] it has been shown that oxygen in the triplet state interacts well with the fullerenes leading to modifications of their external molecule solvation properties. To this end we have considered carbon and oxygen insertion (that both exist as triplets) in C_{60}. It is our assertion that this charge transfer property can permit the fullerenes to form increased interactions with external polar molecules.

Computational methods

Density functional theory (DFT) calculations have been done with the DMol3 [20] numerical-based computer software implemented in the Materials Studio Modeling 3.1 package from Accelrys, Inc. Optimizations of the structural parameters and frequency calculations were performed with the BLYP general-gradient potential approximation in conjunction with the double-numerical plus diffusion basis set (all-electron

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core treatment) was employed (denoted as DND). The adsorption energies (ΔE) for the complexes are defined as:

$$\Delta E = E_{C/O@C60\text{-}polar\ species} - (E_{C/O@C60} + E_{polar\ species}).$$

The small polar molecules that were used are H_2O, CH_3OH, NH_3 and HF that have adequate affinities to the fullerene surface upon charge transfer. The adsorption energies are a measure of the strength of the interaction with the external polar molecules. Additionally, the vibrational frequencies have been studied to verify if the structures were local minimum structures.

Results and discussion

From previous discussions the encapsulated atoms inside of the fullerene species are carbon and oxygen that both tend to exist in the triplet state naturally. The purpose of this study is to investigate the three body interactions with the fullerene and the external polar species. Several positions of the polar molecule and the endohedral atoms were performed in order to ensure that the minimum was indeed the lowest energy structure along the potential energy surface.

We will start the discussion by a description of the geometrical properties of the complexes studied. Scheme 1 shows the general interaction sites of the fullerene surface with values depicted in Table 1. The optimized BLYP/DND CC bond lengths for the fullerene are 1.40/1.46 Å that are in close experimental agreement. Also, the off-center displacements of the C/O atoms in the C_{60} species is 0.0 Å, meaning that the atoms prefer to maintain a position at the center of the system.
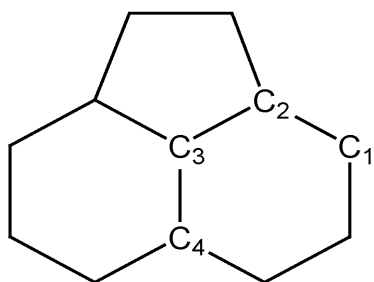
Scheme 1. Representation of the geometrical parameters used in Table 1.

Table 1. The intermolecular distances (in Å) between the polar molecules and carbon atoms complexes.

Molecule	Intermolecular Distances (in Å)[d]		
	Non-metal	C	O
H_2O[a]	3.25-4.33	3.27-4.23 [0.13]	3.28-4.22 [0.12]
CH_3OH[b]	3.84 4.34-4.81	3.92 4.38-4.76 [0.08]	3.86 4.21-4.88 [0.05]
NH_3[c]	2.68-2.83	2.82-3.03 [0.06]	3.04-3.24 [0.03]
HF[a]	3.47-2.88	3.25-3.13 [0.07]	3.71-3.56 [0.08]

[a] The coordination of the hydrogen atom with the C1/C2 atoms without atoms, and coordination between the oxygen atom (or fluorine) and C2/C3 atoms with C/O.
[b] Two interactions which are established as: 1) between the H atom and C4 atom, and 2) for the O distance with the C3/C4 atoms.
[c] Coordination of a hydrogen atom with the C2/C3 atoms.
[d] Relative distortions from the center of the fullerene (in the C/O@C_{60} we cases we computed a distortion of 0.0 Å).

From the first table we can see that for the H_2O and HF cases it is clear that the hydrogen atom coordinates with C1/C2 without C/O present and the oxygen atom (or fluorine) with C2/C3 in the encapsulated complexes. In the case of CH_3OH one can observe two primary interactions which are with the hydrogen atoms and C4 and for oxygen we obtain one interaction with C3/C4. Finally, in the case of ammonia (NH_3) there is an interaction between the C2/C3 atoms and hydrogen.

In the absence of the endohedral species, the interaction of water happens at a an intermolecular separation of 3.25 and 4.33 Å for the distance of the hydrogen to C1 and C2, respectively. This atom will coordinate to the junction of the six-membered and five-membered rings. In the case of C this distance is now 3.27-4.23 Å and of oxygen it is 3.28-4.22 Å. The off-center displacement in the C and O cases with water is 0.13 Å and 0.12 Å, respectively.

For the next case (CH_3OH) the hydrogen atom interactions with C4 at a distance of 4.34 Å, and increases to 4.38 Å in the C@C_{60} system and 4.21 in the O@C_{60} case. The off-center displacements are smaller than for water yielding values of 0.08 and 0.05 Å, for the C and O encap-

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sulated cases, respectively. The interactions appear to be slightly shorter in the case of O in the fullerene cage as a result of favorable three body chalcogenide interactions.

For NH_3 we can observe that for the non-metal case, the closest interaction occurs with one of the hydrogen atoms and C2/C3. The intermolecular interaction in the case of the isolated C_{60}-NH_3 complex is 2.68 and 2.83 Å, respectively. Further encapsulation by C causes this distance to rise to 2.82 and 3.03 Å, and for O it is 3.04 and 3.24 Å. The off-center displacements of the C and O atoms is 0.06 and 0.03 Å, respectively. HF solvation provides a C1/C2 coordination of about 3.47/2.88 Å in the isolated case. Placement of the internal C atom causes this value to rise to 3.25/3.13 Å and with oxygen it is 3.71/3.56 Å. The off-center displacements are similar to those in methanol and are in the order of 0.07 and 0.08 Å, for C and O, respectively. The theoretical computations show interesting chemical properties due to the coordination of the polar molecules to the six-five membered ring junction. This also arises from the fact that the five membered rings do not delocalize excess charge well and can be used to enhance this property with the small polar species.

In Table 2 we present vibrational modes for the species studied. In the table we can observe that in the H_2O case the frequencies for both are quite similar with the coupling to the oxygen atom being equivalent to the rocking modes of the fullerene-polar molecule system. In the next case (CH_3OH) the coupling to the oxygen atom is attributed to the fullerene species with the breathing modes being increases. If we change the interaction to the NH_3 case, the C species exhibits a larger tendency to interact with the nitrogen atom as is apparent from the frequencies. Finally, for HF we can see that when oxygen is inserted inside of the fullerene cage the rocking modes with the fullerene tend to increase. These low-frequency vibrational modes can be used to characterize differences in the vibrational spectra of the systems under consideration.

In this next step we will discuss the physical properties of the molecules studied in this work. The dissociation energies (ΔE) isolated case has a ΔE value of -0.14 kcal/mol with the H_2O molecule. Upon insertion with C and O this value is more favorable yielding quantities of -1.59 and -1.21 kcal/mol, respectively. The C, O atoms are known to be excellent quenchers of excited states [21] that can lead to the results obtained. The triplet states

Table 2. Vibrational modes and their corresponding frequencies (in cm^{-1}).

Polar Species	C	O	Description
H_2O	230.8	230.2	C_{60} - $O(H_2O)$ stretching
	231.5	231.7	rocking
	299.5	299.9	rocking
	335.4	335.0	breathing
CH_3OH	231.2	231.3	$M^{a,b}$ - $O(CH_3OH)$ stretching
	298.1	299.2	asymmetrical stretching
	300.6	300.5	stretching
	334.8	335.9	stretching
	370.0	377.9	breathing
NH_3	167.5	89.0	C_{60} - $N(NH_3)$ stretching
	230.8	231.4	breathing
	231.6	232.2	stretching
	300.5	300.0	asymmetrical stretching
	335.7	336.1	stretching
HF	100.5	148.4	C_{60} - $F(HF)$ stretching
	174.2	230.0	HF rocking
	231.9	234.4	stretching
	300.2	300.5	breathing
	316.8	308.1	breathing
	336.9	336.3	asymmetrical stretching

[a] M corresponds to the endohedral atoms.
[b] This mode can be used to quantify the strength of the interactions with CH_3OH.

**Table 3.** Adsorption energies (ΔE) in kcal mol^{-1}.

System	C_{60}	$C@C_{60}$	$O@C_{60}$
H_2O	-0.140	-1.594	-1.211
CH_3OH	-0.576	-0.585	-1.091
NH_3	-1.040	-1.214	-1.521
HF	-0.603	-4.396	-2.200

tend to interact with the external polar molecule slightly improving their capacity to solvate.

For the CH_3OH case the absorption energies in both case is reduced however the O case is slightly larger. This molecular species is less polar and perhaps causes steric hindrance by the extra methyl group on this molecular species. For NH_3 complexes again we see larger absorption energies after insertion of the C and O species with the O stabilization being larger. Finally, for HF the stabilization energies increase dramatically which can be caused by a favorable coupling between the C and O atoms as is apparent by the vibrational modes in Table 2.

Figure 1 graphically represents the HOMO molecular orbital density of the species studied. We

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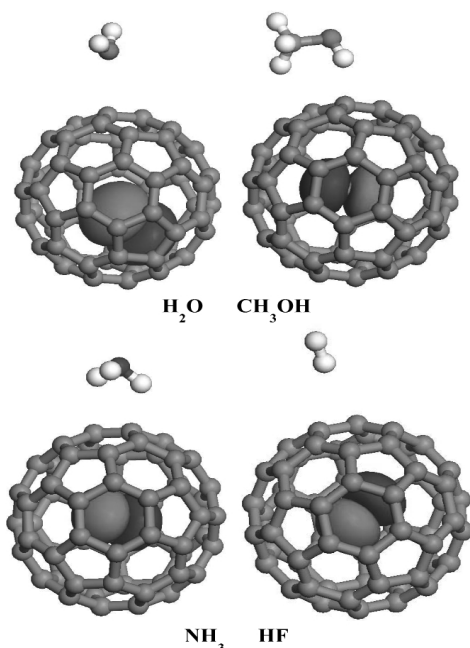
Figure 1. HOMO isosurfaces (at a 0.04 a.u. contour level) for interactions of the endohedral systems with the small polar molecules.

observe that in all cases the endohedral atom localizes the majority of the electronic density therefore only yielding slight stabilization of the external polar species. In other cases [17] we have shown that Li, K and Na are excellent donors of electronic density and appear to show orbital mixing between the fullerene and the external polar species. In this case this localization leads to minimal charge transfer however, there is some degree of interaction between the C, O atoms and the external interacting polar molecule.

Conclusions

This work presents the results of theoretical DFT calculations of C/O@C_{60} interactions with small polar molecules (H_2O, CH_3OH, NH_3 and HF). We have adequately demonstrated that the endohedral atoms improve the affinity of the fullerenes to the external polar species. It is our assertion that the endohedral atoms can serve towards effectively improving tertiary solvent interactions. The method discussed should permit one to quantify electron-polar molecule coupling interactions on fullerene surfaces that are caused by charge-transfer mechanisms.

The carbon and oxygen atoms have the innate ability to transfer charge to a minor extent to the fullerenes that improves its affinity to external polar species. Since these are common components which are reactive it is our belief that the encapsulation process can be performed with ease. Interestingly, we found that the C and O atoms interact strongly with the HF polar species as is evident from the table. The calculations shown should be of interest and of use to workers in the field.

References

[1] H.W. Kroto, *Nature*, 318 (1985), p. 162.
[2] R. Klingeler G. Kann I. Wirth, *J. Chem. Phys.*, 115 (2001), p. 7215.
[3] Y. H. Hu, E. Ruckenstein, *J. Am. Chem. Soc.*, 32 (2005), p. 11277.
[4] A.F. Jalbout, F. Nazari, L. Turker, *J. Mol. Struct. (THEOCHEM)*, 627 (2004), p. 1.
[5] I.T. Belash, A.D. Bronnikov, O.V. Zharikov, A.V. Palnichenko *Synth. Met*. 36 (1990), p. 283.
[6] S. Guha, K. Nakamoto, *Coord Chem Rev* 249 (2005), p. 1111.
[7] L. Turker, S. Gumus, *Poly. Arom. Comp.* 26 (2006), p. 145.
[8] H. Jantoljak, N. Krawez, I. Loa, R. Tellgmann, E.E. B. Campbell, A.P. Litvinchuk, C. Thomsen C., *Z. Phys. Chem. (Munchen)* 200 (1997), p. 157.
[9] V.K. Koltover, *J. Mol. Liq.* 127 (2006), p. 139.
[10].A. Gromov, N. Krawez, A. Lassesson, D.I. Ostrovskii, E.E.B. Campbell, *Cur. App. Phys.* 2 (2002), p. 51.
[11] M. Pavanello, A.F. Jalbout, B. Trzaskowski, L. Adamowicz, *Chem. Phys. Letts.*, 442 (2007), p. 339.
[12] R. Klingeler, G. Kann and I. Wirth, *J. Chem. Phys.* 115 (2001), p. 7215.
[13] B. Trzaskowski, A.F. Jalbout and L. Adamowicz, *Chem. Phys. Lett.* 430 (2006), p. 97.
[14] A.F. Jalbout, *Chin. J. Phys.*, 45 (2007), p. 124.
[15] I.T. Belash, A.D. Bronnikov, O.V. Zharikov and A.V. Palnichenko, *Synth. Met.* 36 (1990), p. 283.
[16] B.I. Dunlap, J.L. Ballester and P.P. Schmidt, *J. Phys. Chem.* 96 (1992), p. 9781.
[17] I. Jimenez-Fabian, A.F. Jalbout, *J. Comp. Theor. Nanosci.*, 5 (2008), p. 512.
[18] a) I. Jimenez-Fabian, A. de Leon, A.F. Jalbout, *J. Mol. Struct. (THEOCHEM)*, 849 (2008), p. 17; b) F.F. Contreras-Torres, A.F. Jalbout, O. Amelinas, V.A. Basiuk, *J. Phys. Chem. C*, 112 (2008), p. 2736; c) A.F. Jalbout, I. Jimenez-Fabian, A. de Leon, Int. J. Quant. Chem. 108 (2008), p. 1076.
[19] J.M. Park, P. Tarakeshwar, K.S. Kim, T. Clark, *J. Chem. Phys.* 116 (2002), p. 10684.
[20] B. Delley. *J. Chem. Phys.*, 92 (1990), p.508.
[21] T. Nojiri, M. M. alam, H. Konami, A. Watanabe, O. Ito, *J. Phys. Chem. A* 101 (1997), p. 7943.