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The subtle effect of vdW interactions upon the C_{60} fullerene structure

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ABSTRACT

The experimental data seem to suggest that the C_{60} fullerene shrinks slightly in the nearby presence of nonbonding molecules. This paper reports on extensive calculations aiming at confirming this effect. The first tests were done on the C_{60}-benzene complex, where we found that indeed C_{60} shrinks slightly for certain conformations of the approaching benzene. The presence of more that one benzene molecule strengthens the effect upon the fullerene making it clear that the effect is cumulative. The fact that even single benzene molecule at a distance much larger than equilibrium causes the fullerene to shrink indicates that the shrinking effect is long-ranged. Our investigations exclude the possibility of numerical errors in calculations as the source of the observed shrinking. The main goal of this paper is to understand the role of van der Waals interactions in the variations of the C_{60} radius.

1. Introduction

The van der Waals (vdW) complexes are an important part of the fullerenes chemistry [1]. The properties of such complexes are the subject of active current research [2–9]. The geometries and the energetics of those complexes are hard to evaluate from a theoretical viewpoint, as the presence of dispersion is difficult to model and, due to large size of the studied systems, only methods that are not computationally demanding are feasible.

We will focus here on the C_{60} fullerene, also called Buckyball or Buckminsterfullerene. When isolated, it has a truncated icosahedron shape and the I_h point group symmetry [10,11]. In that symmetry only two types of bonds determine the C_{60} structure: the longer, p bond, in the pentagons and the shorter, h bond, connecting separated pentagons (see Fig. 1). The p bond has a mostly single bond character, while h can be considered as closer to a double bond [12].

To describe the fullerene size we will use the $R_{C_{60}}$, the distance between any of the carbon atoms and the center of mass (CM) of the molecule. If the I_h symmetry is broken, we will use for $R_{C_{60}}$ the average value of the distance between the CM and the carbon atoms.

Table 1 collects the C_{60} structural parameters from several experiments. These experimental results suggest that the fullerene is slightly smaller in solid phase. When another molecule is present in the crystal lattice the effect is stronger. It appears that the C_{60} fullerene shrinks slightly upon complexation.

The effect is rather small and, in some cases, it falls within the error bars of these measurements. One may dispute its reality and

origin, as the experiments were performed in different conditions and using various methods. We will show that this shrinking effect is real, as the theoretical calculations find the same effect of complexation.

One of the experimental variables is the temperature of the measurements. It is well known that the crystal lattice expands with temperature, with a jump at phase transition [18]. The larger gas phase result in Table 1 corresponds to some thermal averaging, the smaller value is one consistent with scattering equations. Usually the bonds are longer when averaged over thermal vibrations, indeed the thermal averaged values yield a larger Buckyball. For that reason one may expect that use of this $R_{C_{60}}$ will artificially amplify the shrinking. Consequently, $R_{C_{60}} = 3.555$ Å, the value consistent with the scattering equation, should be used for the gas phase.

The thermal effect may explain the shrinking of the Buckyball as it goes from gas to solid but it cannot explain the further shrinking as it goes from solid to c-solid. This paper seeks the understanding of the observed variations in the fullerene radius.

After a careful *ab initio* study of various C_{60} complexes, we will argue that the shrinking effect is neither an error of the measurement nor a simple effect of the temperature, but a clear consequence of the vdW interaction present in Buckyball complexes.

2. Methods

The modified NWChem 6.1.1 [19] program was used for all the MP2, DFT and CCSD(T) calculation of isolated molecules. The modifications we introduced provide more control over the dispersion correction within DFT-D method. The periodic boundary condition calculations were performed using Crystal 09 program [20,21]. The double- and triple-ζ basis set of Pople [22,23] were used. It was determined that including polarization and diffusion functions

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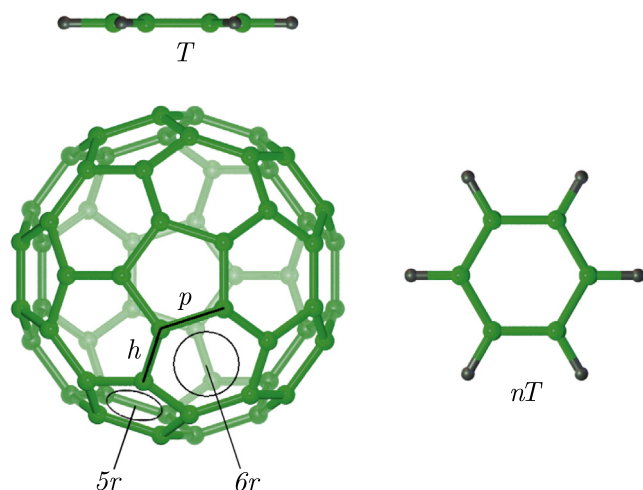
Fig. 1. The general structure of the C_{60} fullerene and its complexes: p and h are distinct fullerene bonds, the $5r$ and $6r$ are respectively the five and the six members rings; in the T conformation, benzene is parallel to local fullerene curvature and in nT it is perpendicular.

Table 1
The experimental structural parameters of C_{60} molecule. Units are K for temperature and Å for length. The c-solid is the complex of C_{60} with another molecule present in the crystal lattice.

State	Temp.	p	h	$R_{C_{60}}$
Gas[a]	1000	1.458(6)	1.401(10)	3.562(19)
Gas[b]	1000	1.455(6)	1.398(10)	3.555(19)
Solid[c]	295	1.455(1)	1.394(2)	3.552(3)
Solid[c]	150	1.455(1)	1.396(2)	3.553(3)
Solid[c]	4	1.460(2)	1.386(3)	3.552(5)
c-solid[d]	143	1.450(6)	1.387(6)	3.537(15)
c-solid[e]	104	1.446(5)	1.389(5)	3.532(13)
c-solid[f]	—	1.423(5)	1.388(9)	3.495(15)

[a] Electron diffraction, C_{60} Hedberg et al. [13], thermal average.
[b] Electron diffraction, C_{60} Hedberg et al. [13], scattering equation.
[c] Neutron scattering, C_{60} Damay and Leclercq [14].
[d] X-ray, $C_{60} \cdot 2(Fe(C_5H_5)_2)$ Crane et al. [15].
[e] X-ray, $C_{60} \cdot 4C_6H_6$ Balch et al. [16].
[f] X-ray, $C_{60}(OS_4)$(4-tert-butylpyridine)$_2$ Hawkins et al. [17].

did not changed the result in significant manner for these basis sets, hence only the 6-31G and the 6-311G basis sets are presented as a representatives of the double-ζ and the triple-ζ basis sets respectively.

A new set of BLYP-D2 [24] parameters designed especially for graphitic materials with various basis sets were presented recently [25]. Although different parameter values are associated with different basis sets, we will label this method as RF (only $\alpha = 6$ will be used as the DFT-D2 damping parameter in the presented study).

The Basis Set Superposition Error (BSSE) was not directly included in the optimizations of the molecular geometries, but the effects of the incompleteness of the basis set will be examined.

For obtaining and analyzing the fullerene structures the Fullerene 4.3 [26–28] program was used.

3. Results

The "gold standard" of Quantum Mechanical (QM) calculations is the CCSD(T) [29–31]: a coupled cluster method containing single, double and perturbative triple excitations.

The simplest model analog of the complexes studied here is ethylene dimer. It was studied theoretically, but without full coupled cluster geometry optimization [32]. For that reason, the coupled cluster optimization for several conformations of ethylene dimer was performed. For the CCSD(T)/aug-cc-pVDZ CCSD(T) method, when another ethylene is stacked on top of the previous one the C–C bond distances is shortened by 0.00046 Å, while in the X-shape conformation the bond is elongated by 0.00016 Å. Apparently, the change in C–C bond length depends on the conformation: in the sandwich conformation the bond is shortened, in other conformations (*i.e.* X-shaped) it could be elongated.

The less accurate, mp2/aug-cc-pVDZ method gives qualitatively the same result. Even the RF method provides analogous behavior for ethylene dimer.

A bigger model system for the C_{60} complexes is benzene dimer. Both MP2 and RF methods produce average C–C bond lengths slightly shortened for parallel conformation of benzene dimer.

The investigated model systems suggest a behavior similar to the one observed experimentally. In order to explore the presence of the shrinking effect with fullerene, we checked various systems closer to the experimental ones.

3.1. Isolated buckyball

The standard quantum mechanical calculation corresponds to an ideally isolated molecule at 0 K. Because of that we may expect that the experimental result from the gas phase [13] is the closest to our theoretical investigations.

We performed the optimization of the Buckyball with several common quantum mechanical methods and various basis set sizes. Several methods tested provide accurate C_{60} structures. Among them, only the RF and the B3LYP+D3 methods include some dispersion interactions and are useful for vdW bounded systems we are to consider later. The B3LYP+D3 has problems with the reproduction of binding energies and geometries of the benzene dimer, a model system for graphitic systems. For that reason, among the methods investigated, only the RF method with 6-31G or 6-311G basis sets are applicable to vdW bonded complexes with fullerenes.

3.2. Solid phase

There are several experimental measurements of Buckyball structural features in solid phase (see Table 1). In all cases molecular sizes seem to be slightly smaller than in the gas phase, especially when other molecules are present in the crystal lattice. The experimental data for solids are obtained assuming the I_h molecular symmetry, even if it is known that this symmetry is broken at low temperature. For that reason the bond lengths are probably the result of some averaging over all bonds of the same type.

It is known that at room-temperatures C_{60} crystallizes in space group $Fm3m$, with disordered $Fm3$ packing. Upon cooling to $\sim$250 K, the phase transition to $Pa3$ space group with simple cubic packing begins [18,33–35].

The solid phase is not our main interest. For that reason, only preliminary calculations were performed with periodic boundary conditions using RF/6-311G method. The resulting lattice constant (13.98 Å) was in good agreement with the experimental value (14.04 Å [18]). The $R_{C_{60}}$ obtained from calculations has an averages of 3.5562 Å and ranges from 3.5498 to 3.5614 Å, while the appropriate value for the isolated molecule is 3.5624 Å. This shrinking is marginally larger than that observed experimentally (theoretical shrinking of about 0.006 Å vs. experimental 0.003 Å).

In agreement with the experimental results, in our calculation the Buckyball diameter is smaller in the solid phase.

3.3. vdW complexes

The complex of C_{60} fullerene with benzene was used as a simple example of the vdW complexes of C_{60} fullerene.