

Computing Fullerene Encapsulation of Non-Metallic Molecules: $N_2@C_{60}$

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ABSTRACT

As $N_2@C_{60}$ has been observed, there is also a clear interest in computational description. Owing to a relationship to $N@C_{60}$, they should have some potential for nanoscience studies. The computations deal with a search for stationary points by geometry optimizations using density-functional theory (DFT) methods. In the optimized stationary points, the analytical harmonic vibrational analysis was carried out in order to check their physical nature. The lowest-energy structure has the N_2 unit oriented towards a pair of parallel pentagons so that the complex exhibits D_{5d} symmetry. The highest computational level estimates the stabilization upon encapsulation by an energy term of -9.3 kcal/mol. Moreover, the entropy term for the encapsulation is also evaluated which leads to the standard Gibbs-energy change upon encapsulation at room temperature of -3.3 kcal/mol. The computed structural and vibrational characteristics are reported, too, and possibilities for encapsulation of other small molecules are discussed.

Keywords: Carbon-based nanotechnology; molecular electronics; non-metal fullerene encapsulations; optimized syntheses; Gibbs-energy evaluations.

1 INTRODUCTION

$N_2@C_{60}$ and $N_2@C_{70}$ were first prepared by Peres *et al.* [1] using heating under high pressure. Out of two thousand C_{60} molecules about one was observed to incorporate N_2 . The nitrogen molecule containing endohedrals were present even after several-hours heating at 500 K. $N_2@C_{60}$ was also reported [2,3] in the chromatographic separation after the nitrogen-ion implantation into C_{60} . This ion bombardment is primarily used for the $N@C_{60}$ production [4,5] though with very low yields ($Li@C_{60}$ was also prepared by the ion bombardment method [6]). Still, $N@C_{60}$ and its derivatives have been studied vigorously [7-11]. Other non-metallic endohedrals are represented by complexes of fullerenes with rare gas atoms, in particular with He [12-16]. Very recently, molecular hydrogen [17] and even a water molecule [18] were placed inside open-cage fullerenes. This paper presents computations on $N_2@C_{60}$ in order to judge its stability and compare with other available endohedral data [19-23], especially for $N@C_{60}$.

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2 COMPUTATIONS

The computations started with a search for stationary points by geometry optimizations using density-functional theory (DFT) methods. The standard 3-21G basis set was used at this stage and applied in two different DFT approaches. One of them employs Becke's [24] three parameter exchange functional with the non-local Lee-Yang-Parr [25] correlation functional (B3LYP) with the above basis set, i.e., the B3LYP/3-21G treatment. The other approach uses Perdew and Wang's [26] exchange and correlation functionals known as PW91. The geometry optimizations were carried out using the analytical energy gradient. In the optimized stationary points, the analytical harmonic vibrational analysis was carried out in order to check their physical nature by the number of imaginary vibrational frequencies. The ultra-fine grid in numerical integrations of the DFT functional and the tight SCF convergence criterion were used. The reported computations have been carried out with the Gaussian program package [27].

In the optimized B3LYP/3-21G and PW91/3-21G geometries, additional single point energy calculations B3LYP/6-31G* and PW91/6-31G*, respectively, were carried out using the standard 6-31G* basis set. Moreover, the second order Møller-Plesset (MP2) perturbation treatment [28,29] with frozen core (FC) option, in which inner-shells are excluded from the correlation calculation, was also performed with the same basis set (MP2=FC/6-31G*). The basis set superposition error (BSSE) was estimated by the Boys-Bernardi counterpoise method [30].

In addition to the interaction (dimerization) energy, the standard entropy change upon the encapsulation was also evaluated (the 1 atm standard-state choice). The conventional rigid-rotator and harmonic-oscillator partition functions [31] were used and no frequency scaling was applied.

3 RESULTS AND DISCUSSION

The B3LYP treatment is considered as the most reliable choice for the thermochemical computations [32] and the B3LYP functional has been the most common DFT option in the computations [33,34] of fullerenes and endohedrals. However, it was pointed out recently [35,36] that the Becke exchange functional due to its erroneous asymptotic behavior does not produce physically acceptable description of the attraction between weakly bonded systems. It was shown [37] that the

BLYP or B3LYP treatments do not show weak energy minima in the long-range region otherwise well established by the MP2 or coupled cluster calculations. It was suggested [35-37] to use Perdew and Wang's [26] exchange and correlation functionals PW91 instead. The PW91 functional at least partly recovers the attraction [37]. Its error in the computed binding energies [37] for the hydrogen-bonded complexes was 20% in the worst case though somewhat bigger in some still weaker complexes. With this picture, the DFT computations here are carried out side by side with the B3LYP and PW91 functionals.

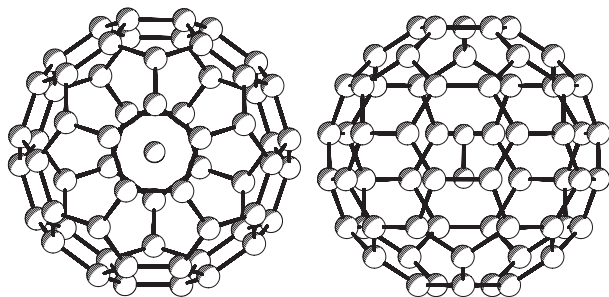


Fig. 1. Two views of the PW91/3-21G optimized structure of $N_2@C_{60}$.

In both the B3LYP/3-21G and PW91/3-21G treatments, the lowest-energy structure $N_2@C_{60}$ found has the N_2 unit oriented towards a pair of parallel pentagons so that the complex exhibits D_{5d} symmetry (5:5 structure, see Fig. 1). The stationary point was reached without symmetry constraints so that some numerical inaccuracy could influence the point-group determination. In fact, the G98 symmetry finder extracts only C_i symmetry. However, application of a procedure [38] allowing for variable precision of the optimized coordinates concludes the D_{5d} symmetry. Moreover, N_2 is to exercise motions around the equilibrium position with an averaging effect. It has been known [39] that more symmetric structures for endohedrals can in fact be saddle points. Then, it is sometimes actually more effective to optimize their structures without symmetry constraints. In any case, the vibrational analysis is an important check for the optimized endohedral structures. The harmonic vibrational analysis confirms that the 5:5 structure is indeed a local energy minimum though the interaction hypersurface is very shallow.

Another optimized $N_2@C_{60}$ stationary point has the N_2 unit oriented towards a pair of parallel hexagons - a 6:6 structure. The 6:6 structure is however not a local energy minimum but a saddle point. Still, it is very close in energy to the 5:5 structure. In both the B3LYP/3-21G and PW91/3-21G approaches the 6:6 species is located less than 0.1 kcal/mol above the 5:5 structure. This feature documents that the interaction hypersurface is very shallow and at elevated temperatures the N_2 unit should exhibit large-amplitude motions. In the 5:5 equilibrium position the closest computed N-C distance is 3.046 and 3.049 Å in the B3LYP/3-21G and PW91/3-21G method, respectively. The Mulliken partial charge on the N atoms is positive but very small, about 0.01, so that the charge transfer to the cage is negligible.

The computed interaction or stabilization energies have thermochemically the meaning of the potential-

energy change along the formal encapsulation process:



In the B3LYP/3-21G geometry, the interaction energies are positive before and after the BSSE correction, this being true for both the B3LYP/3-21G and B3LYP/6-31G* approaches. Hence, this computational level would not speak for a $N_2@C_{60}$ formation. In the PW91/3-21G geometry, there is a stabilization effect at the PW91/3-21G level before the BSSE correction, but vanishes after the Boys-Bernardi counterpoise method is applied. The PW91/6-31G* approach does not show a stabilization even before the BSSE correction. There is however a substantial change at the MP2=FC/6-31G* level with a stabilization of -17.5 kcal/mol before the BSSE correction. This value corresponds to the -7.3 kcal/mol computed [22] at the same level for $N@C_{60}$. After addition of the BSSE correction, the MP2=FC/6-31G* stabilization for $N_2@C_{60}$ is reduced to still significant -9.3 kcal/mol. It is however likely [21] that the value will still be modified when larger basis-set computations will be possible.

There are 180 vibrational modes in $N_2@C_{60}$. One of them is the N-N bond stretching mode, five are vibrations of the N_2 unit against the cage, and the remaining 174 modes are skeletal vibrations of the C_{60} cage. The N-N bond stretching frequency is only slightly affected by the encapsulation. Interestingly enough the N-N frequency increases in the B3LYP/3-21G approach but decreases in the PW91/3-21G treatment. The shift is large enough to be significant in observation. The changes in the N-N frequency upon encapsulation are parallel with the changes in the N-N bond distance as in the B3LYP/3-21G computations the bond is slightly compressed while in the PW91/3-21G case the bond is expanded by about 0.0003 Å. The five frequencies for the N_2 -cage vibrations are low but they could be observed as it was recently possible [41,42] for $La@C_{82}$. The inter-system frequencies at the B3LYP/3-21G level are 25.4, 38.9, 83.6, 84.6, and 126.1 cm^{-1} while for the PW91/3-21G approach they read 45.9, 49.1, 55.9, 65.3, and 106.7 cm^{-1} .

The high symmetry of C_{60} considerably simplifies [43] its vibrational spectrum, for example, only four T_{1u} three-fold degenerate modes are actually active in its IR spectrum. Once the high symmetry is reduced upon introduction of N_2 , the symmetry selection rules will not be, strictly speaking, the same. However, in fact out of the 174 cage modes in $N_2@C_{60}$ just twelve show significant IR intensities. Those IR active modes are actually rooted in the original T_{1u} three-fold degenerate modes of C_{60} . For example, at the B3LYP/3-21G level we deal with the following four frequency triads: (508.4; 508.8; 509.8), (581.6; 581.6; 581.7), (1175.6; 1175.8; 1177.0), and (1451.4; 1451.5; 1451.7) cm^{-1} . The splitting could be distinguished in observed vibrational spectra.

The stabilization energy from Eq. (1) is the potential-energy change along the reaction. In order to get the related enthalpy change ΔH_T^o at a temperature T , the zero-point vibrational energy and heat-content functions are to be added though the change will be small. Once the corresponding entropy change ΔS_T^o is evaluated, one can deal with the thermodynamics controlling Gibbs-energy term ΔG_T^o . Using the partition functions from the PW91/3-21G calculations, the

$T\Delta S_T^0$ term comes as -5.9 kcal/mol for room temperature. Let us mention that the entropy evaluations require a due care paid to the symmetry numbers as quantum chemistry programs rarely produce the correct symmetry number [45,46] of 60 for C_{60} . If this entropy term is combined with the BSSE corrected MP2=FC/6-31G* stabilization energy, the ΔG_T^0 term for Eq. (1) at room temperature reads -3.3 kcal/mol which is the driving thermodynamic force for the $N_2@C_{60}$ formation according to the present computational data. The value should be further checked, especially with respect [47] to the BSSE correction and basis-set finiteness in general, when computationally feasible. There are other interesting non-metal fullerene encapsulates to be studied like $H_2O@C_{60}$ or $NH_3@C_{60}$ (Fig. 2).

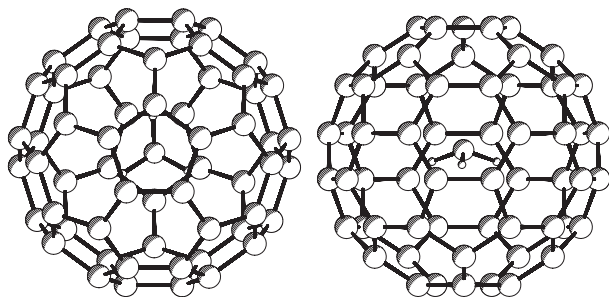


Fig. 2. Two views of the B3LYP/3-21G optimized structure of $NH_3@C_{60}$.

Interestingly enough, the entropy change for the $N_2@C_{60}$ formation is quite similar to the dimerization entropy for water in gas phase [48,49] while the stabilization energy for the water dimer is somewhat smaller. There are no entropy data available yet for formation of other fullerene endohedrals, however, it is clear that the stabilization ΔG_T^0 terms would represent a unified thermodynamic stability measure. For a complete picture, the ΔG_T^0 terms or the encapsulation equilibrium constants should be combined [50] with the typical partial pressures accessible to the fullerene cage and encapsulate under particular experimental conditions. There are however essential kinetic [51,52] and in particular catalytic [16,53-55] aspects obviously involved, too. All the steps represent important factors to be mastered before more practical applications of computational nanoscience and nanotechnology can be launched [56-60].

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