Endohedral Complexes
Chapter 6

Confinement effect of $C_{60}$ cage on Polynitrogen clusters

6.1 Introduction

The $C_{60}$ cage has already been explored for endohedral doping with alkali metals [14], transitional metals [19], non-metals [20] and noble gases [4]. Interestingly, the confinement provided by the fullerene molecules can stabilize such clusters which would not exist in free space [5]. Recently, N has been predicted to exist in polymeric form ($N_8$) in confinement of nanostructures i.e. Carbon Nanotubes. It was proposed that $N_8$ stabilizes as a chain which is stable up to room temperature [12]. Therefore, apart from extreme condition of high temperature and pressure, confinement offers an alternate environment for stabilization of polynitrogen compounds. Since the environment of $C_{60}$ has been extensively studied by our group [8,13] as well as others [9,10], it offers a new possibility for polynitrogen encapsulation. Among all endohedral complexes, N-doped $C_{60}$ are quite interesting and needs further investigation. As per our knowledge, $N@C_{60}$ is the only endohedral complex which has been explored extensively theoretically [9–12] as well as experimentally [21, 22]. However, $N_2@C_{60}$ was successfully synthesized using pressure heating [15] and one isolated study of its stabilization energy has been recently reported [16]. Till date, the higher members of N family ($n>2$) have not been explored at endohedral position in $C_{60}$. Keeping
this in view, further efforts are needed to be invested in both experimental and theoretical sides to help in designing new ways for generating $N_n@C_{60}$ compounds and understand their stability in different environments.

**Why Polynitrogen?**

In recent years, interest in polynitrogen or polymeric nitrogen (N) has drawn considerable attention because of its theoretical interest and its possible application as high energy density material (HEDM) [1, 2]. Polynitrogen molecules are formed by a combination of lower order bonds and while decaying into dinitrogen ($N_2$) molecules, they release enormous amount of energy and are environmentally safe.

Over the last few decades, there have been consistent efforts to predict new exotic forms of all-N molecules using various experimental and theoretical techniques [3, 5–7]. The higher members of N cluster family ($N_n$ for $n>3$) are unstable in the free space and therefore, present a challenge to their synthesis. In 1999, Christe et al. [9] synthesized successfully a $N_5^+$ salt $N^+AsF^-$ which is third readily accessible homonuclear polynitrogen species. Subsequently, the same group reported the stability of $N_6^+SbF_6^-$ up to 70°C and its relative insensitivity to impact [24]. This discovery opened a new dimension to explore neutral polynitrogen compounds and basis for the first synthesis of stable N allotropes.

N-rich compounds such as N-hydrides ($N_mH_n$) ($m > n$) could also be used as starting materials to produce $N_n$ species, since deprotonation of $N_4H^+$ [25] and dehydrogenation of $N_4H_6$ and $N_4H_4$ [26, 27] may lead to the formation of neutral $N_4$. Nitrosyl oxide $N_4O$ has been experimentally observed [28] which dissociates to form $N_2 + N_2O$ with small activation energy of 28 kJ mol$^{-1}$. Further, it has been suggested that higher $N_n$ could be synthesized via direct or indirect excitation of electronic states in liquid and solid N followed by collision addition of a ground state N and excited $N_{n-1}$ or $N_{n-2}$ thereby forming higher $N_n$ compounds. For example, by combining different $N_n$ moieties such as $N_5$ and $N_3$ might lead to formation of $N_8$ species [29]. In 2002, Cacace et al. [30] demonstrated
the existence of the tetranitrogen molecule ($N_4$) as a metastable species whose life time exceeds 1 $\mu$s at 298K. The identification of $N_4$ represents the first addition in nearly half a century to the family of the polynitrogen molecules. Hammerl and Klapotke [10] explored the possibility to find experimental evidence for a pentazole compound with the highest possible N content and their theoretical calculations were used to predict the stability of several tetrazolepentazole species. At the most fundamental level, a molecule will exist only if it has high enough energy barrier that keeps it away from dissociation.

This possibility has been explored theoretically as various novel polynitrogen species have been studied in variety of forms such as cyclic, acyclic or caged conformations. The species investigated include ionic clusters [32], cylinders [?], cages [33], nanoneedles [34] and helices[35]. Isomers of smaller systems $N_7$ [36], $N_{10}$ [37] and $N_{12}$ [38] have also been reported theoretically in free space. Majority of these studies have focused on the evaluation of these novel forms of molecular nitrogen. However, Wang et al. [39] has described the possible synthesis route for all-nitrogen systems. Dixon et al. [40] has successfully demonstrated the ability of the theory to predict the stability of such compounds. In spite of these efforts, so far no higher members ($n>4$) of polynitrogen family in free space have been synthesized experimentally. The present difficulties in synthesizing the polynitrogen molecules motivates us to look for new avenues to realize the stability of polynitrogen molecules.

Further, the new polymeric forms of N have also been explored in extreme conditions of high pressure and temperature. The application of high pressure to N system leads to destruction of covalent bonds and may lead to the formation of intermediate polymeric network of single and double bonded atoms which has been verified experimentally [41–44]. Using \textit{ab initio} calculations, other forms of polymeric N such as Black Phosphorous (BP) [45], A7 [46] , metallic [47], simple tetragonal phase [47] and Cubic Gauche (CG) form [44] have been proposed at extreme conditions. The CG form has also been observed experimentally [11]. Therefore, the success of \textit{ab initio} studies [49] in predicting
new polymeric phases of N in extreme conditions motivates us to study polynitrogen in other physical environment such as in confinement.

In this chapter, we have extended our earlier work on azafullerenes [50] to N at endohedral position of C_{80} cage. We have presented here the results of our ab initio calculations on N_{n}@C_{80} for n ≤ 16, which describes the novel possibility of stabilizing the higher members of all-N molecules in confined environment of C_{80}. We intend to show that C_{80} can act as an ideal candidate to trap N in polymeric form. The present study would provide some valuable information for synthesizing more stable all-N clusters to develop the novel materials for future.

6.2 Computational details and validation

We have used the Spanish Initiative for Electronic Simulation with thousands of atoms (SIESTA) computational code which is based on numerical atomic orbital density functional theory method [24, 26]. We have used 1s^2, 2s^2, 2p_x, 2p_y, 2p_z (4S_{3/2}) configuration of atomic N corresponding to spin quartet state which is consistent with the experimental observation [22]. The calculations are carried out using generalized gradient approximation (GGA) that implements Becke gradient exchange correlation functional (BLYP) [27]. Core electrons are replaced by non-local, norm-conserving pseudopotentials factorized in the Kleinman-Bylander form [28], whereas valence electrons are described using linear combination of numerical pseudo atomic orbitals of the Sankey-Niklewski type [29] but generalized for multiple-ζ and polarization functions. In this work, we have used a split valence double-ζ (DZP) basis set with energy shift equal to 100 meV. The real space cutoff grid energy is taken as 200 Ry. Periodic boundary conditions have been considered using simple cubic shell of 20 Å that is large enough to avoid any significant spurious interactions with periodically repeated images.

Our investigation begins with the encapsulation of N clusters inside C_{80}. We started with different initial atomic configurations of N_{n} for n = 1-16. The following
considerations were taken into account while starting and determining the final structure for particular configuration. (a) N atoms were placed sufficiently away from the walls of C$_{60}$ so that there is no likelihood to form any C-N bond. (b) N atoms were allowed to form bonds among themselves and make polynitrogen compounds. (c) Each structure was allowed to relax till forces on each atom converges up to 0.001 eV/Å. (d) The structure with minimum energy is considered as the final stable polymeric form of N. (e) All the optimized N clusters inside C$_{60}$ were also relaxed in free space at 0K. (f) The structures of N$_n$@C$_{60}$ were also relaxed at room temperature (300K) to confirm their stability (g) The spin polarized calculations were performed on final stable polymeric N$_n$@C$_{60}$ to determine the spin states (h) Also harmonic vibrational frequency analysis on all optimized structures was performed to further ensure their ground state geometries.

Test calculations

Test calculations on the C$_{60}$ and N$_2$ molecules were performed. For a C$_{60}$ cage, the C=O and C-C bond distances are 1.40 Å and 1.46 Å in agreement with experimental values [30]. In N$_2$ molecule, the N-N bond distance and ionization potential are found to be 1.12 Å and 15.43 eV which are in good agreement with experimental values of 1.15 Å and 15.60 eV respectively [33]. In previous chapters, we have described the structural, electronic and vibrational properties of N-doped heterofullerenes [50] which validates the applicability of our calculations on carbon and N-based systems.

6.3 Results

6.3.1 Structural Analysis

We started our calculation with single N atom placed at different positions inside C$_{60}$ and the SCF total energy isosurface is explored throughout the region inside C$_{60}$. We found the atomic N at center as stable structure with small zero point vibrations. Since the atomic N is highly reactive so if we place N at a distance of more than 1.50 Å from center
of cage, it has tendency to form a weak covalent bond of the order of 1.54 Å with two adjacent carbon atoms (see Figure 6.1) of hexagon-hexagon interface of C₆₀ inner surface [34].

![Figure 6.1: Optimized geometry of N@C₆₀ showing the formation of weak covalent bond between N atom and C atoms.](image)

When two N atoms are placed inside C₆₀ at different positions, they form N₂ molecule which is found to stabilize at the center of the C₆₀. The resultant structure is N₂ molecule with N≡N bond distance of 1.12 Å which is same as in free space (see Figure 6.2(a)).

In N₃@C₆₀, N₃ in linear form with D₅₇h symmetry is found to be stable at the center with N-N bond length of 1.19 Å (Figure 6.2(b)). However, the triangular structure D₃h is found to be another stable isomer inside C₆₀. Interestingly, most of initial N₃ configurations including the combination of N₂ and single N at distance results in an isosceles triangular structure with bond lengths of 1.33 Å and 1.58 Å and bond angles 53.5° and 73.1° respectively. The energy difference between both the structures is of the order of 0.9 eV (see Figure 6.2(c)). N₄ is found to exist as two dimers of N₂ with bond length of 1.11 Å and placed at a distance of 2.26 Å symmetrically across the center of cage. The arrangement of two N₂ molecules on either side of center of C₆₀ may be explained.
on the basis of extra stability of $N_2$ and its reluctance to form lower order bond (Figure 6.2(d)). The structure with $T_d$ and $D_{2h}$ symmetry are found to be the other stable isomers (Figure 6.2(e) & (f)). However, in free state $N_4$ has been predicted to be stable in $C_{2h}$, $T_d$ and $D_{2h}$ symmetries respectively [35].

$N_5$ is found to be stable at center in perfect pentagon shape having $D_{5h}$ symmetry with each bond length of 1.32 Å and bond angle of 108.0 °. We tried various initial
configurations of $N_5$ (including dimers and single atom). It was observed that all the configurations lead to the formation of pentagon structure which may be due to confined environment of $C_{60}$ (Figure 6.3(a)). For $n \geq 6$, different combinations of $N$, $N_2$, $N_3$ and higher polynitrogens were considered as separate substitutional identities in $C_{60}$. We found interesting pattern in the arrangement of $N$ atoms in polynitrogen compounds, which are very stable and are placed symmetrically across the center. The minimum energy configuration structure of $N_6$ comes out to be a boat-shaped cyclic ring with bond lengths of the order of 1.28-1.35 Å and bond angles 108.8° and 122.5° (Figure 6.3(b)). The other observed isomeric structures, though stable, one with $C_{2v}$ symmetry and the other having two triangles connected by a single bond of 1.43 Å, are found distinctly less stable by an energy difference of ~ 0.5-2.0 eV (see Figure 6.3(c) & (d)). In free state $N_6$ is found to be stable in hexaazadewarbenzene structure with $C_{2v}$ symmetry which is also

![Figure 6.3: (a) & (b) $N_5$ and $N_6$ exist as a pentagon ring and a non-planar distorted hexagon with 100 % single bond character (c) $N_6$ with $C_{2v}$ symmetry as first isomer (d) $N_6$ with two triangles connected by a single bond of 1.43 Å forms the second isomer.](image-url)
one of the stable isomers in confinement [36].

$N_7$ is found to exist as an assembly of a pentagon with bond lengths 1.28-1.32 Å and a dimer having bond length 1.11 Å as two separate units (Figure 6.4(a)). The presence of $N_5$ as an independent identity is responsible for lowering the energy of $N_7@C_{60}$ indicating its extra stability. However, one closed structure involving $N_5$ and $N_2$ exist as an isomer with an energy difference of 1.98 eV (Figure 6.4(b)). Another isomer as an interconnected structure of one triangle and rectangle with a single bond of 1.42 Å with a relative energy difference of 3.69 eV is shown (Figure 6.4(c)).

$N_8$ is found to exist in two planar rings having distinct bond lengths of 1.27, 1.38, 1.45 and 1.38 Å which are connected together with a weak N-N bond of 1.57 Å (see Figure 6.4(d)). Another interesting structure with a closed 8 atom ring (Figure 6.4(e)) exists inside $C_{60}$, though it differs by an energy difference of 3.1 eV w.r.t ground state structure. $N_9$ exhibits a stable structure with $N_5$ and $N_4$ planar rings connected together with a bond of 1.48 Å (see Figure 6.4(f)). The bond lengths for both the rings are in the range 1.27-1.50 Å.

$N_{10}$ forms a structure with two planar symmetrical pentagon rings on either side of center of $C_{60}$ ($D_{5h}$ symmetry) connected to each other with a single bond of 1.50 Å (Figure 6.5(a)). $N_{11}$ polynitrogen compound is also stable in ring structure with one planar pentagon and one non-planar hexagon connected by a bond distances 1.42 and 1.45 Å respectively (Figure 6.5(b)). $N_{12}$ stabilizes itself symmetrically into two non-planar boat shaped hexagons connected by N-N bond of 1.39 Å (Figure 6.5(c)).

For $n>12$, the polynitrogen compounds do not show any symmetry in distribution of N atoms due to the availability of less space. They make complex yet stable structures. $N_{13}$ is found to exhibit a geometry with one planar pentagon connected to a non-planar closed $N_8$ ring with significant distortion on $C_{60}$ cage (Figure 6.6(a)). Another isomer with N atoms not forming any symmetric structure differs by a small energy difference of 0.57 eV is shown in (Figure 6.6(b)). The ground state structures of polynitrogen clusters
Figure 6.4: (a) $N_7$ exists as $N_5$ and $N_2$ as separate units and forms the most stable structure (b) $N_7$ as an interconnected structure of $N_5$ and $N_2$ units forms the first isomer (c) Second isomer of $N_7$ exists as an interconnected structure of one triangle and rectangle with a single bond of 1.42 Å (d) $N_8$ exist as two planar rings of $N_4$ placed symmetrically and connected by weak N-N bond (1.57 Å) (e) $N_9$ also forms a non-planar closed ring structure as its isomer (f) $N_9$ exist as two planar rings of $N_4$ and $N_5$ connected by weak N-N bond (1.48 Å)
Figure 6.5: (a) $N_{10}$ exists as two planar and slightly inclined pentagon rings connected by weak N-N bond (1.50 Å) (b) $N_{11}$ exist as interconnected structure of planar $N_5$ and non-planar $N_6$ placed across center (c) $N_{12}$ exist as symmetrically placed two boat shaped hexagons connected by N-N bond distance of 1.39 Å

Figure 6.6: (a) $N_{13}$ exists as interconnected structure of planar $N_5$ and a heavily distorted $N_8$ however, the less interstitial space inside $C_{60}$ forces the N atoms to make bonds with surface carbon atoms (b) A close energy isomer of $N_{13}$
inside \( C_{60} \) along with their bond lengths and bond angles are shown in Figure 6.7.

\( N_{14} \) and \( N_{15} \) compounds make distorted endohedral complex with N undergoing chemisorption at the surface breaking the surface C-C and C=C bonds and making C-N bond of 1.36 Å (Figure 6.8(a) & (b)). This leads to the formation of heptagon in the cage which results in very large distortion and the maximum and minimum diameter is observed to be 7.60 Å and 7.30 Å respectively. At \( n=16 \), the chemisorption of three N atoms results in the opening of the \( C_{60} \) cage (Figure 6.8(c)).

Further, to have an idea of the stabilization of polynitrogen clusters formed inside \( C_{60} \) cage, we have calculated the total energy \( E_{N_n@C_{60}} \) of polynitrogen complex (tabulated in Table 6.1). We have also listed the energy of N complex \( (E_{N_n}) \) alone by defining it as

\[
E_{N_n} = E_{N_n@C_{60}} - E_{C_{60}}
\]

in Table 6.1. This energy per N atom as a function of size of polynitrogen cluster is plotted in Figure 6.9.

It seems there is a systematic increase in N energy inside \( N_n@C_{60} \) complexes and there is a variation of \( \approx 5 \) eV per N atom from the smallest cluster to the largest cluster inside \( C_{60} \). Thus bigger clusters tend to release energy on lowering the cluster size by each successive N-atom by an amount \( \approx 5 \) eV.

**Bond Character**

We have calculated the bond character in the polynitrogen clusters and identified all the distances as: the bond distance \( \geq 1.35 \) Å as N-N, distance \( \geq 1.25 \) Å as \( N = N \) and between the range 1.12-1.24 Å as \( N=E=N \) bond, though it is not easy to distinguish between the N-N and N=N bond character. As we can observe from the Figure 6.10, most of the polynitrogen clusters stabilize in a mixture of N-N and N=N bond character. Only for \( n=7 \), because of the splitting of \( N_7 \) as \( N_5 \) and \( N_2 \), there is a formation of one triple bond.
Figure 6.7: Geometries of polynitrogen clusters for \( n = 2-13 \) inside \( C_{60} \) cage along with the bond lengths (in black), connecting bonds (red) and bond angles (purple).
Figure 6.8: (a) $N_{14}@C_{60}$ exits as a distorted complex with $N_{12}$ existing as interconnected structure of $N_5$ and $N_7$. Two $N$ atoms undergo chemisorption resulting in 62 atom cage with the formation of two heptagons on surface. (b) $N_{15}@C_{60}$ doesn’t show any pattern in structure of polynitrogen molecule. Hexagons and pentagons of $C_{60}$ show heavily distortion with C-C bond distances increasing up to 1.65-1.67 Å which is the breaking point for $C_{60}$ cage. (c) $N_{16}@C_{60}$ exists as a polymeric complex with three $N$ atoms getting substituted at the surface and making a heptagon and octagon which henceforth leads to the opening of the cage indicating the threshold limit for $N$ encapsulation at 0 K. In above structures, due to less available space $N$ tends to make bonds with the surface atoms as well as undergoing chemisorption. These structures are unstable at room temperature.
Figure 6.9: The variation of total energy of $N_n$ complexes inside $C_{60}$ cage per $N$ atom vs number of atoms in a polynitrogen cluster.

Table 6.1: Bond distances (in Å) for polynitrogen molecules inside $C_{60}$, the total energy ($E_{N_n@C_{60}}$) of $N_n@C_{60}$ complexes and $N$ complex energy $E^N_{N_n}=(E_{total}-E_{C_{60}})$ in eV are tabulated. Total energies of $C_{60}$ molecule and $N_2$ are taken as -9226.65 eV and -538.84 eV respectively.

<table>
<thead>
<tr>
<th>$N_n@C_{60}$</th>
<th>N-N</th>
<th>N=N</th>
<th>N≡N</th>
<th>$E_{N_n@C_{60}}$ (eV)</th>
<th>$E^N_{N_n}$ (eV)</th>
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<tbody>
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<td>$N@C_{60}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-9490.2</td>
<td>-263.55</td>
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<td>$N_2@C_{60}$</td>
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<td>-</td>
<td>1.12</td>
<td>-9766.0</td>
<td>-539.35</td>
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<td>-</td>
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<td>-10030.5</td>
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<td>-2662.75</td>
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<td>1.24-1.34</td>
<td>-</td>
<td>-12678.6</td>
<td>-3451.95</td>
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6.3.2 Electronic Properties

The encapsulated polynitrogen clusters results in distortion of icosahedral symmetry of the \(C_{60}\) thereby altering the electronic properties of \(N_n@C_{60}\) significantly. The Highest occupied molecular orbital (HOMO) and the Lowest unoccupied molecular orbital (LUMO) gap is calculated from Kohn-Sham eigen values and the HOMO level, LUMO level and HOMO-LUMO gap are tabulated in Table 6.2. The gap varies as a function of number of N atoms which shows gradual decrease with higher values for \(n= 2, 4, 6, 8, 10\). To visualize this we have plotted the Kohn Sham energy levels for \(N_n@C_{60}\) complexes in Figure 6.11.

Electronic density of states (EDOS) for the structures are shown in Figures 6.12 and 6.13 showing a substantial difference between EDOS near fermi level as a function of encapsulated cluster size. For odd \(n\), the EDOS is significant at fermi level whereas there is no EDOS at fermi level for even \(n\). The innermost states are found to vary from -23.60 eV for \(C_{60}\) to -25.23 eV for \(N@C_{60}\), -27.86 eV for \(N_2@C_{60}\), -31.44 eV for \(N_8@C_{60}\)
Table 6.2: The HOMO, LUMO, HOMO-LUMO Gap ($E_{gap}$), the Spin multiplicities ($M$) along with the net charge $Q_n$ on the $C_{60}$ cage for $N_n@C_{60}$ complexes. Charge loss/gain is denoted by positive/negative sign respectively.

<table>
<thead>
<tr>
<th>$N_n@C_{60}$</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_{gap}$ (eV)</th>
<th>$M=(2S+1)$</th>
<th>$Q_n$</th>
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<tr>
<td>$N@C_{60}$ [N at Center]</td>
<td>-4.55</td>
<td>-3.68</td>
<td>0.87</td>
<td>4 [4(expt)]</td>
<td>+0.03</td>
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<td>$N@C_{60}$ [N at the surface bonded]</td>
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<td>-4.54</td>
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</tr>
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<td>-3.37</td>
<td>1.00</td>
<td>4</td>
<td>-0.48</td>
</tr>
</tbody>
</table>

Figure 6.11: The Kohn-Sham energy eigen values for $N_n$ clusters (n=1, 2, 5, 6, 8, 9, 10, 12, 13)
and -32.03 eV for $N_{12}@C_{60}$.

Spin Polarized calculations

We carried out spin polarized calculations on all the optimized geometries. Multiplicities defined as $(2s+1)$, where $s$ is the spin of the system, are calculated from the difference of spin up and spin down electrons $(Q(\uparrow) - Q(\downarrow))$ and are tabulated in Table 6.2.

For $N@C_{60}$ we found a spin quartet state when the N atom is placed at the center of the $C_{60}$ cage i.e N atom retains its atomic nature, which is consistent with the experimental ESR or EPR spectra of $N@C_{60}$ [9, 11, 21]. However when the N atom moves toward the surface and makes a covalent bond with the cage, it shows a spin doublet state consistent with experimental results [34]. All the structures with even number of N atoms show spin doublet states ($s=1/2$) whereas when odd number of N atoms are present they show spin singlet ($s=0$) state except for $n=13$ which shows a spin quartet state ($s=3/2$).
Mulliken Charge Analysis

The net charge on the polynitrogen compounds and the fullerene cage atoms are investigated by Mulliken charge analysis and it is tabulated in Table 6.2. We would like to mention here that charge transfers in SIESTA are dependent on the choice of basis set. Therefore, we carried out test calculations using SZ (single zeta), DZ (double zeta) and DZP (double zeta with polarization) (with energy shift ranging from 50 meV - 250 meV) basis sets on \( \text{N} @ \text{C}_{60} \). It was observed that using SZ basis N shows a small charge loss of 0.04 electrons to \( \text{C}_{60} \) cage, whereas using DZ and DZP basis N shows a small charge gain from the cage. The magnitude of charge transfer is found to be higher when DZ is used compared to that using DZP. Within DZP basis set as we increase the energy shift the mulliken charge on N tends to increase marginally from 0.027 (energy shift 50 meV) to 0.040(250 meV). Our work on azafullerenes using DZP basis set produced reliable charge transfers in \( \text{C}_{60} - n \text{N}_n \) [50] and it reproduced the experimental parameters of \( \text{C}_{60} \) and \( \text{N}_2 \).
very accurately.

For \( \text{N@C}_{60} \), the small charge transfer of 0.04 electrons from the cage to N at center is found to be consistent with spin quartet state as obtained using spin polarized calculations. However, there are conflicting claims regarding charge transfers in \( \text{N@C}_{60} \) using various \textit{ab initio} calculations. Kobayashi et al. [38] using 6-31G(d) basis set and B3LYP functional has reported slightly large spin density at N in \( \text{N@C}_{60} \) than in \( \text{N@C}_{70} \) consistent with observed hyperfine coupling constants. Lu et al. [39] using user defined basis set (considering 2s and 2p for C and N) and carrying discrete variational local density functional calculations had reported charge transfer of 0.11 from \( \text{C}_{60} \) cage to N atom at the center. Further, Mauser et al. [34] using semi empirical method and DFT(B3LYP) and Greer [63] using spin-unrestricted DFT have predicted no charge transfer between N and \( \text{C}_{60} \).

For \( n=2-10 \), we found the charge transfer from cage to \( \text{N}_n \), which may be explained on the basis of higher values of electronegativity and ionization potential of N than C atoms. The Mulliken charge calculation suggests electron charge transfer ranging between 0.05 to 0.57 from carbon atoms to the polynitrogen compounds inside up to \( n=10 \) except for \( \text{N}_2 \) which shows inverse nature. For \( n>10 \), charge transfer of 0.05-0.48 electrons takes place from N to carbon atoms of fullerene. This reversal can be attributed to availability of less space and overlapping of orbitals which may be further responsible for destabilizing the polynitrogen compounds beyond \( n=13 \). As per our information, there are no references for comparison to any theoretical work on polynitrogen clusters in \( \text{C}_{60} \) till date.

\section*{6.3.3 Summary}

From the structural analysis of all the \( \text{N}_n@\text{C}_{60} \) structures, it may be concluded that N atoms have preferential sites for its stabilization inside fullerenes. Moreover, due to confinement the N atoms are forced to form lower order bonds. The threshold size of
polynitrogen compounds to exist inside as stable molecule is $N_{13}$. Any further addition of N inside leads to the formation of C-N bond and heptagon involving N atom on the surface.

The structural distortion expressed in terms of elongation defined as $\epsilon = \left( \frac{R}{R_0} - 1 \right)$ where $R$ and $R_0$ are the average radii of expanded and pure $C_{60}$ is shown in Figure 6.14. The percentage elongation shows a linear increase with the number of N atoms up to $N_{15}$ except for $N_2$ which shows small contraction in $C_{60}$ cage. The maximum threshold elongation is found to be $\sim 6\%$ for $N_{15}$. Indeed, this elongation leads to estimation of extra pressure. Successive addition of N atoms exert this extra pressure from within when their number is increased beyond 2, till the stability limit of $C_{60}$ is reached.

![Figure 6.14: The percentage relative elongation of polynitrogen compounds as a function of number of N atoms.](image)

Further, the stability of each structure is verified by displacing the N atoms up to 0.5 Å and it was found that after relaxing the structure, it regains its optimized form. Moreover, harmonic vibrational frequency analysis is carried out on all the ground state structures and the absence of any imaginary frequency value further verifies the true energy minima.
The constant-temperature constant-volume molecular dynamics for $N_n@C_{60}$ at a temperature of 300K with time period 10 ps with interval of 1 fs was also performed. For $n \leq 12$ the polynitrogen structures remain intact and do not show any significant deviation from their structures at 0K which demonstrates the stability of polymeric N structures. But for $n \geq 13$, the $C_{60}$ cage opens up due to formation of C-N bonds as a result of thermal vibrations. Interestingly, our calculations further suggests that the presence of single water molecule or few O and H atoms inside the cage results in destabilization of $N_n@C_{60}$ for $n = 5-8$. However, more calculations are required in order to fully understand the nature of cage breaking for $n<12$.

The experimental synthesis of these novel hybrid systems would be a challenging task due to the explosive nature of N-rich compounds. However, in literature various methods have been reported trying to incorporate N inside CNTs such as magnetron sputtering [64], laser ablation [65], pyrolysis of mixtures of organometallic and N containing organic compounds [41] and chemical vapor deposition (CVD) of N-containing hydrocarbons over heterogeneous iron, cobalt or nickel catalysts [43]. From the above mentioned methods it was confirmed that it is rather difficult to obtain uniform NCNT (N-containing CNT) with a high N concentration, that is, above 20 %, with conventional techniques like CVD. For a non-CVD synthesis of CNTs, N-rich energetic compounds, such as 3,6-diazido-1,2,4,5-tetrazine and 4,4',6,6'-tetraazido-2,2'-azo-1,3,5-triazine compounds can be used [46]. Their thermal decomposition yield N-rich nanolayered, nano-clustered, and nanodendritic carbon nitrides, depending on the different heating processes [15,48].

6.4 Discussion and Conclusions

The polynitrogen compounds formed inside $C_{60}$ are found to be quite stable in confinement. The energy difference of the optimized ground state geometries to the isomeric states is found to be significant, thereby indicating clear choice of ground state structures. The spin states of $N_n@C_{60}$ are found to be quartet for $n=1$ and $n=13$, doublet
for other odd \( n \) and singlet for even \( n \). The reversal of polarization and the space available inside \( C_{60} \) may be responsible for determining the amount of N encapsulation inside fullerene. Therefore, \( C_{60} \) cage could provide ideal environment for stabilizing other reactive species which are otherwise less stable in free space. The maximum number of N atoms that can be encapsulated inside \( C_{60} \) is 13, which can form stable structure at 0K. The endohedral molecules \( N_n@C_{60} \) for \( n \leq 12 \), are found to retain their structure at room temperature. It is significant to observe that larger clusters inside the \( C_{60} \) cage raise the energy of the cluster indicating the possibility of releasing energy by going to much more stable configurations in lower clusters.
Bibliography


