Nitrogen clusters inside $C_{60}$ cage and new nanoscale energetic materials

Hitesh Sharma$^{1,2}$, Isha Garg $^1$, Keya Dharamvir$^1$, and V. K. Jindal$^1$

$^1$Department of Physics, Center of Advanced Studies in Physics, Panjab University, Chandigarh, India-160014
$^2$Department of Applied Sciences, RBIEBT, Sahauran, Mohali, Punjab-140104

(Dated: August 24, 2009)

Abstract

We explore the possibility to trap polynitrogen clusters inside $C_{60}$ fullerene cage, opening a new direction of developing nitrogen-rich high energy materials. We found that a maximum of 13 nitrogen atoms can be encapsulated in a $C_{60}$ cage. The nitrogen clusters in confinement exhibit unique stable structures in polymeric form which possess a large component of ($\sim 70\text{-}80\%$) single bond character. The $N_n@C_{60}$ molecules retain their structure at 300K for $n \leq 12$. The Mulliken charge analysis shows very small charge transfer in $N@C_{60}$, consistent with the quartet spin state of N. However, for $2 < n < 10$, charge transfer take place from cage surface to $N_n$ compounds and inverse polarization thereafter. These nitrogen clusters when allowed to relax to $N_2$ molecules which are triply bonded are capable of releasing a large amount of energy.

PACS numbers: 72.80.Rj, 31.15.ae, 33.15.-e, 85.65.+h

*Corresponding author: Fax: +91 1722783336. E-mail address: jindal@pu.ac.in (V. K. Jindal)
1. INTRODUCTION

In recent years, interest in polynitrogen or polymeric nitrogen has drawn considerable attention not only because of its theoretical significance but also 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 last few decades, there have been consistent efforts to predict new exotic forms of all-nitrogen molecules using various experimental and theoretical techniques [3, 4, 5, 6]. The higher members of nitrogen 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. [7] 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 $70^\circ C$ and its relative insensitivity to impact [8]. This discovery opened a new dimension to explore neutral polynitrogen compounds and basis for the first synthesis of stable nitrogen allotropes.

Nitrogen rich compounds such as nitrogen hydrides ($N_nH_m$) ($n>m$) could also be used as starting materials to produce $N_n$ species, since $N_4H^+$, $N_4H_6$ and $N_4H_4$ [9, 10, 11] species are stable and their subsequent deprotonation may lead to the formation of neutral $N_4$. Similarly, the oxidation of nitrogen oxide $N_4O$ which is stable and has been observed experimentally [12], would also lead to the formation of $N_4$. Further, it has been suggested that higher $N_n$ could be synthesized via direct or indirect excitation of electronic states in liquid and solid nitrogen 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 [13] and $N_5^+N_5^-$ may form $N_{10}$ [14, 15]. In 2002, Cacace et al. [16] 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 [17] also reported a combined theoretical and experimental NMR study on nitrogen rich compounds. 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. Various novel polynitrogen species have
been studied in variety of forms such as cyclic, acyclic or caged conformations. The species investigated include ionic clusters [18, 19, 20], cylinders [21], cages [22, 23, 24, 25], nanoneedles [20] and helices [27]. Isomers of smaller systems $N_7$ [28], $N_{10}$ [29] and $N_{12}$ [30] 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. [31] has described the possible synthesis route for all-nitrogen systems. Dixon et al. [32] 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 success of polynitrogen molecules as a possible HEDM.

Further, the new polymeric forms of nitrogen have also been explored in extreme conditions of high pressure and temperature. The application of high pressure to nitrogen system leads to destruction of covalent bonds and may lead to formation of intermediate polymeric network of single and double bonded atoms which has been verified experimentally [33, 34, 35, 36]. Using ab initio calculations, other forms of polymeric nitrogen such as Black Phosphorous (BP) [37], A7 [38] , metallic [39], simple tetragonal phase [39] and Cubic Gauche (CG) form [36] have been proposed at extreme conditions. The CG form has also been observed experimentally [40]. Therefore, the success of ab initio studies [41] in predicting new polymeric phases of nitrogen in extreme conditions motivates us to study polynitrogen in other physical environment such as in confinement.

More recently in 2008, nitrogen has been predicted to exist in polymeric form ($N_8$) in confinement of nanostructures i.e. Carbon Nanotubes. They proposed $N_8$ stabilizes as a chain which is stable up to room temperature [42]. 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 [43, 44, 45, 46] as well as others [47, 48] it offers a new possibility for polynitrogen encapsulation. The $C_{60}$ cage has already been explored for endohedral doping with alkali metals [49], transitional metals [50], non-metals [51] and noble gases [52]. Among all endohedral complexes, nitrogen-doped $C_{60}$ are quite interesting and needs further investigation. As per our knowledge, $N@C_{60}$ is the only endohedral complex which have been explored extensively theoretically [47, 48, 53, 55] as well as experimentally [56]. However,
$N_2@C_{60}$ was successfully synthesized using pressure heating \cite{57} and one isolated study of its stabilization energy has been recently reported \cite{58}. Till date, the higher members of nitrogen family ($n>2$) have not been explored at endohedral position in $C_{60}$. New techniques have been developed to deal with nitrogen (as impurity) in nanostructures such as chemical vaporization deposition (CVD) method \cite{60} which is capable of synthesizing nitrogen doped carbon nanotubes. And recently in 2008, $C_{57}N_3$ was reported using surface-catalyzed cyclodehydrogenation from aromatic precursors \cite{61} and further expressing a strong possibility of synthesizing other nitrogen-based hetero and endohedral fullerenes. 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 $N_n$ compounds and understand their stability in different environments.

In this paper, we report the results of our \textit{ab initio} calculations on $N_n@C_{60}$ for $n \leq 16$, which describes the novel possibility of stabilizing the higher members of all-nitrogen molecules in confined environment of $C_{60}$. We intend to show that $C_{60}$ can act as an ideal candidate to trap nitrogen in polymeric form and can be used as a possible high energy density material. The present study would provide some valuable information for synthesizing more stable all-nitrogen clusters to develop the novel materials for future.

2. COMPUTATIONAL DETAILS AND VALIDATION

We have used the Spanish Initiative for Electronic Simulation with thousands of atoms (SIESTA) computational code\cite{62} which is based on numerical atomic orbital density functional theory method \cite{63,64,65}. We have used $1s^2, 2s^2, 2p^1_x, 2p^1_y, 2p^1_z$ ($4S_{3/2}$) configuration of atomic nitrogen corresponding to spin quartet state which is consistent with the experimental observation \cite{56}. The calculations are carried out using generalized gradient approximation (GGA) that implements Becke gradient exchange correlation functional (BLYP)\cite{66}. Core electrons are replaced by non-local, norm-conserving pseudopotentials factorized in the Kleinman-Bylander form \cite{67}, whereas valence electrons are described using linear combination of numerical pseudo atomic orbitals of the Sankey-Niklewski type \cite{68} 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 2 nm that is large enough to avoid any significant spurious interactions with periodically repeated images.

We first performed test calculations on the C$_{60}$ and N$_2$ molecules. In C$_{60}$, we found the C=C and C-C bond distances as 0.140 nm and 0.146 nm in agreement with experimental values $^{[69]}$. The ionization potential and electron affinity were found to be 6.9 eV and 2.70 eV, in good agreement with experimental values of $7.5 \pm 0.01$ $^{[70]}$ and $2.689 \pm 0.008$ $^{[71]}$ respectively. In N$_2$ molecule, the N-N bond distance and ionization potential are found to be 0.112 nm and 15.43 eV which are in good agreement with experimental values of 0.115 nm and 15.60 eV respectively $^{[72]}$.

We now proceed with the investigation of nitrogen clusters inside C$_{60}$. 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) Nitrogen atoms were placed sufficiently away from the walls of C$_{60}$ so that there is no likelihood to form any C-N bond. (b) Nitrogen 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 nitrogen. (e) All the optimized nitrogen 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.

3. RESULTS AND DISCUSSION

The optimized ground state structures of polynitrogen compounds inside C$_{60}$ are shown in Figure 1-3. We started our calculation with single nitrogen, the nitrogen was placed at different positions inside C$_{60}$ and the SCF total energy isosurface is explored throughout region inside C$_{60}$. We found the atomic nitrogen at center as stable structure with small zero point vibrations. Since the atomic nitrogen is highly reactive so if we place nitrogen at a distance of more than 0.150 nm from center of cage, it has tendency to form a weak covalent bond of the order of 0.154 nm with two adjacent carbon atoms of hexagon-hexagon...
interface of $C_{60}$ inner surface [73]. When two nitrogen atoms are placed inside $C_{60}$ at different positions, they form $N_2$ molecule which is found to stabilize at the center of the $C_{60}$. The resultant structure is $N_2$ molecule with N≡N bond distance of 0.112 nm which is same as in free space.

In $N_3@C_{60}$, $N_3$ in linear form with $D_{\infty h}$ symmetry is found to be stable at the center with N-N bond length of 0.119 nm. However, the triangular structure $D_{3h}$ is found to be another stable isomer inside $C_{60}$. Interestingly, most of initial $N_3$ configurations including the combination of $N_2$ and single N at distance results in an isosceles triangular structure with bondlengths of 0.133 nm and 0.158 nm and bond angles 53.5° and 73.1° respectively. The energy difference between both the structures is of the order of 0.9 eV. $N_4$ is found to exist as two dimers of $N_2$ with bond length of 0.111 nm and placed at a distance of 0.226 nm symmetrically across the center of cage. The arrangement of two $N_2$ molecules on either side of center of $C_{60}$ may be explained on the basis of extra stability of $N_2$ and its reluctance to form lower order bond. The structure with $T_d$ and $D_{2h}$ symmetry are found to be the other stable isomers. However, in free state $N_4$ has been predicted to be stable in $C_{2h} - T$, $T_d$ and $D_{2h}$ symmetries respectively [74]. $N_5$ is found to be stable at center in perfect pentagon shape having $D_{5h}$ symmetry with each bond length of 0.132 nm 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 $C_{60}$.

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 nitrogen atoms in polynitrogen compounds, which are very stable and are placed symmetrically across the center. The other observed isomeric structures, though stable, are found distinctly less stable by an energy difference of $\sim 0.5$-$2.0$ eV. The minimum energy configuration structure of $N_6$ comes out to be a boat-shaped cyclic ring with bond lengths of the order of 0.128-0.135 nm and bond angles 108.8° and 122.5°. In free state $N_6$ is found to be stable in hexaazadewarbenzene structure with $C_{2v}$ symmetry which is also one of the stable isomers in confinement [75].

$N_7$ is found to exist as an assembly of a pentagon with bond lengths 0.128-0.132 nm and a dimer having bond length 0.111 nm as two separate units. 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 $N_2$ do exist as a close energy isomer as shown in Figure 1. $N_8$ is found to exist in two planar rings having distinct bond lengths of 0.127, 0.138, 0.145 and 0.138 nm which are connected together with a weak N-N bond of 0.157 nm. $N_9$ exhibits a stable structure with $N_5$ and $N_4$ planar rings connected together with a bond of 0.148 nm. The bond lengths for both the rings are in the range 0.127-0.150 nm. $N_{10}$ 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 0.150 nm. $N_{11}$ polynitrogen compound is also stable in ring structure with one planar pentagon and one non-planar hexagon connected by a bond distances 0.142 and 0.145 nm respectively. $N_{12}$ stabilizes itself symmetrically into two non-planar boat shaped hexagons connected by N-N bond of 0.139 nm.

For $n > 12$, the polynitrogen compounds do not show any symmetry in distribution of nitrogen 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. $N_{14}$ and $N_{15}$ compounds make distorted endohedral complex with nitrogen undergoing chemisorption at the surface breaking the surface C-C and C=C bonds and making C-N bond of 0.136 nm. 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 0.760 nm and 0.730 nm respectively. At $n=16$, the chemisorption of three nitrogen atoms results in the opening of the $C_{60}$ cage.

The encapsulation energy is defined as

$$\Delta E = E[N_n @ C_{60}] - E[C_{60}] - E[N_n],$$

where $E[N_n @ C_{60}]$ is the energy of the complex, $E[C_{60}]$ is the energy of an isolated $C_{60}$ and $E[N_n]$ is the energy of an isolated $N_n$ cluster. These energies have been calculated for all the structures and are tabulated in Table I. We would like to add here that the energy of $N_n$ cluster in isolation is different from the $N_n$ in confinement as their structures are very different. These constrained polynitrogen molecules disintegrate into smaller clusters when relaxed in isolation. The encapsulation energy of $N_2 @ C_{60}$ is found to be 13.8 kcal/mol, which is in agreement with the value of 9.11 kcal/mol reported using B3LYP [58]. However we would like to mention here that B3LYP does not describe the non bonding systems accurately [59].
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 HOMO-LUMO gap variation as a function of number of nitrogen atoms 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 using DZP basis in Figure 4. Also electronic density of states (DOS) for the structures are shown in Figure 5-6. 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 (\( Q_{up down} \)) and are tabulated in Table II.

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 \( N@C_{60} \) \[47, 53, 54\]. 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 \[73\]. All the structures with even number of nitrogen atoms show spin doublet states \((s=1/2)\) whereas when odd number of nitrogen atoms are present they show spin singlet \((s=0)\) state except for \( n=13 \) which shows a spin quartet state \((s=3/2)\).

The net charge on the polynitrogen compounds and the fullerene cage atoms are investigated by Mulliken charge analysis. 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 \( N@C_{60} \). It was observed that using SZ basis N shows a small charge loss of 0.04 electrons to \( C_{60} \) 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 \( C_{60-n}N_n \) \[76\] and it reproduced the experimental parameters of \( C_{60} \) and \( N_2 \) very accurately.

For \( N@C_{60} \), 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 \( N@C_{60} \) using various \textit{ab initio} calculations. Kobayashi et al. \[77\] using 6-31G(d) basis set and B3LYP functional has
reported slightly large spin density at N in N@C$_{60}$ than in N@C$_{70}$ consistent with observed hyperfine coupling constants. Lu et al.\cite{78} 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 C$_{60}$ cage to N atom at the center. Further, Mauser et al.\cite{73} using semi empirical and DFT(B3LYP) and Greer\cite{79} using TZVP spin-unrestricted DFT optimized geometry within DZP basis sets have predicted no charge transfers between N and C$_{60}$. For n=2-10, we found charge transfer from cage to 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 0.31 from carbon atoms to the polynitrogen compounds inside up to n=10 except for N$_2$ which shows inverse nature. For n>10, charge transfer of 0.05-0.47 electrons takes place from nitrogen 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 C$_{60}$ till date.

From the structural analysis of all the N$_n$@C$_{60}$ structures and their isomers it may be concluded that N atoms have preferential sites for its stabilization inside fullerenes. Moreover, due to confinement the nitrogen atoms are forced to form lower order bonds. We found that the threshold size of polynitrogen compounds to exist inside as stable molecule is N$_{13}$. Any further addition of nitrogen inside leads to the formation of C-N bond and heptagon involving nitrogen atom on the surface. All the nitrogen clusters in N$_n$@C$_{60}$ for n>4 has 70-80 % single bond character which confirms the polymeric nature of nitrogen compounds as shown in Figure 7. The structural distortion expressed in terms of elongation defined as $\epsilon = (\frac{R}{R_0} - 1)$ where R and R$_0$ are the average radii of expanded and pure C$_{60}$ is shown in Figure 8. The percentage elongation shows a linear increase with the number of nitrogen 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 nitrogen atoms exert this extra pressure from within when their number is increased beyond 2, till the stability limit of C$_{60}$ is reached.

Further, the stability of each structure is verified by displacing the nitrogen atoms up to 0.5 nm and observing the result. We find 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 ground state geometries for polynitrogen $N_n$ compounds, when relaxed in free space, leads to fragmentation with large number of $N_2$ molecule units. This suggests that the polynitrogen compounds are forced to remain stable inside due to confinement and any mechanism triggering the breaking of $C_{60}$ cage may lead to the release of enormous amount of energy. The energy released can be approximately estimated based on the energy of $N_nC_{60}$ and $C_{60}$ and equivalent ($\frac{1}{2}n$ of $N_2$ molecules). Assuming all $n$ atoms of N in $N_nC_{60}$ clusters are singly bonded (with energy 158.9 kJ/mole), the energy released on formation of $N_2$ molecules comes out to be around 3-6 kcal/gm of nitrogen atoms. This is several times larger than the energy release in the case of TNT.

We performed 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. It was observed that 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 nitrogen 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 preliminary calculations on addition of few water molecules in $N_n@C_{60}$ for $n=8-10$, indicates that the polynitrogen dissociates resulting in breaking of $C_{60}$ cage.

The experimental synthesis of these novel hybrid systems would be a challenging task. Owing to the instability of $N_n$ clusters in free space, the most feasible and promising way is to trap them in some nanostructures such as fullerenes, nanotubes and transition metal complexes. It appears to us that $N_n@C_{60}$ could be synthesized by nitrogen enrichment using prolonged ion implantation of N ions or pressure heating $^{57}$. It is well known that laser ablation of graphite can produce copious amounts of $C_{60}$. When graphite, intercalated with desired specie of atom/ molecule is laser ablated, endohedral $C_{60}$ results. Therefore, even if short-lived $N_n$ clusters could be intercalated before laser ablation, there is good possibility of their getting trapped inside $C_{60}$ cage.

4. 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 nitrogen encapsulation inside fullerene. The maximum number of nitrogen 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. This suggests the strong possibility of synthesizing polynitrogen compounds in confinement which could be triggered with suitable combinations of oxygen and hydrogen for extracting tremendous amount of energy. The amount of energy density from conversion of lower order bonds to triple bonds comes out to be about three times in contrast to the conventional chemical energetic materials.

ACKNOWLEDGEMENTS
Authors are thankful to SIESTA group for providing their computational code and greatly acknowledge the computational support provided by Prof. D. G. Kanhere, University of Pune, Pune. Isha Garg is thankful to University Grants Commission, New Delhi for providing financial support.

[1] Klapotke TM. Structure and Bonding-High Energy Density Materials. Springer Vol. 125, 2007.
[2] Haskins PJ, Fellows J, Cook MD, Wood A. Molecular Level Studies of Polynitrogen Explosives. Proc. 12th Int. Detonation Symp., California, 2002.
[3] Boates B, Bonev SA. First-Order Liquid-Liquid Phase Transition in Compressed Nitrogen. Phys Rev Lett 2009;102:015701-4.
[4] Mukherjee GD, Boehler R. High-Pressure Melting Curve of Nitrogen and the Liquid-Liquid Phase Transition. Phys Rev Lett 2007;99:225701-4.
[5] Trojan IA, Eremets MI, Medvedev SA, Gavriliuk AG, Prakapenka VB. Transformation from molecular to polymeric nitrogen at high pressures and temperatures: In situ x-ray diffraction study Appl Phys Lett 2008;93:0919071-3.
[6] Zahariev F, Dudiy SV, Hooper J, Zhang F, Woo TK. Systematic Method to New Phases of
Polymeric Nitrogen under High Pressure. Phys Rev Lett 2006;97: 1555031-4.

[7] Christe KO, Wilson WW, Sheehy JA, Boatz JA. \( N_5^+ \): A Novel Homoleptic Polynitrogen Ion as a High Energy Density Material. Angew Chem Int Ed 1999;38:2004-9.

[8] Vij A, Wilson WW, Vij V, Tham FS, Sheehy JA, Christe KO. Polynitrogen Chemistry. Synthesis, Characterization, and Crystal Structure of Surprisingly Stable Fluoroantimonate Salts of \( N_5^+ \). J Am Chem Soc 2001;123:6308-13.

[9] Shi LW, Chen B, Zhou J-H, Zhang T, Kang Q, Chen M-B. Structure and Relative Stability of Drum-like \( C_{4n}N_{2n} \) (n = 3-8) Cages and Their Hydrogenated Products \( C_{4n}H_{4n}N_{2n} \) (n = 3-8) Cages. J Phys Chem A 2008;112(46):11724-30.

[10] Leininger M, Van Huis TJ, Schaefer FH. Protonated High Energy Density Materials: \( N_4 \) Tetrahedron and \( N_8 \) Octahedron. J Phys Chem Sect A 1997;101:4460-4.

[11] Ball WD. Tetrazane: Hartree-Fock, Gaussian-2 and -3, and Complete Basis Set Predictions of Some Thermochemical Properties of \( N_4H_6 \). J Phys Chem Sect A 2001;105(2):465-70.

[12] Schulz A, Tornieporth-Oetting IC, Klapotke MT. Nitrosylazid \( N_4O \), ein intrinsisch instabiles Stickstoffoxid. Angew Chem Int Ed Engl 1993;32:1610-12.

[13] Nguyen MT, Ha TK. Azidopentazole is Probably the Lowest-Energy \( N_8 \) Species. A Theoretical Study. Chem Ber 1996;129:1157-9.

[14] Fau S, Wilson KJ, Bartlett RJ. On the Stability of \( N_5^+N_5^- \). J Phys Chem Sect A 2002;106:4639-44.

[15] Evangelisti S, Leininger T. Ionic nitrogen clusters. J Mol Struct Theochem 2003;621:43-50.

[16] Cacace F, Petris Gde, Troiani A. Experimental Detection of Tetranitrogen. Science 2002;295:480-1.

[17] Hammerl A, Klapotke TM. Tetrazolylpentazoles: Nitrogen-Rich Compounds. Inorg Chem 2002;41:906-12.

[18] Li PC, Guan J, Li S, Quian SL, Wen GX. A theoretical study on the stability of \( N_{15}^+ \) cluster. Phys Chem Chem Phys 2003;5:111622.

[19] Cheng L, Li Q Xu W, Zhan S. A computer-aided quantum chemical study of the \( N_{15}^- \) cluster. J Molec Model 2003;9:99-107.

[20] Liu YD, Yiu PG, Guan J, Li QS. Structures and stability of \( N^{-11} (+) \) and \( N^{-11} (-) \) clusters. J Mol Struct (THEOCHEM) 2002;588:37-43.

[21] Zhou H, Wong N-B, Zhou G, Tian A. What Makes the Cylinder-Shaped \( N_72 \) Cage Stable? J
Phys Chem A 2006;110:7441-6.

[22] Zhou H, Wong N-B, Zhou G, Tian A. Theoretical Study on Multilayer Nitrogen Cages. J Phys Chem A 2006;110:3845-52.

[23] Zhou G, Pu X-M, Wong N-B, Tian A, Zhou H. Theoretical Investigation on the Replacement of CH Groups by N Atoms in Caged Structure (CH). J Phys Chem A 2006;110:4107-14.

[24] Wang LJ, Zgierski MZ. Super-high energy-rich nitrogen cluster $N_{60}$. Chem Phys Lett 2003;376:698-03.

[25] Strout DL. Why Isn’t the $N_{20}$ Dodecahedron Ideal for Three-Coordinate Nitrogen? J Phys Chem A 2005;109:1478-80.

[26] Wang JL, Lushington GH, Mezey PG. Stability and Electronic Properties of Nitrogen Nanoneedles and Nanotubes. J Chem Inf Model 2006;46:1965-71.

[27] Wang L, Mezey PG. Predicted High-Energy Molecules: Helical All-Nitrogen and Helical Nitrogen-Rich Ring Clusters. J Phys Chem A 2005;109:3241-3.

[28] Zhao JF, Li QS. Structures and kinetic stability of $N_7$ cluster. Chem Phys Lett 2003;368:12-19.

[29] Wang LJ, Mezey PG, Zgierski MZ. Stability and the structures of Nitrogen clusters $N_{10}$. Chem Phys Lett 2004;391:338-43.

[30] Li QS, Zhao JF. Theoretical Study of Potential Energy Surfaces for $N_{12}$ Clusters. J Phys Chem A 2002;106:5367-72.

[31] Wang LJ, Warburton P, Mezey PG. Theoretical Prediction on the Synthesis Reaction Pathway of $N_6$ ($C_{2h}$). J Phys Chem A 2002;106:2748-52.

[32] Dixon DA, Feller D, Christe KO, Wilson WW, Vij A, Vij V et al. Enthalpies of Formation of Gas-Phase $N_3$, $N_3^-$, $N_5^+$, and $N_5^-$ from Ab Initio Molecular Orbital Theory, Stability Predictions for $N_5^+N_3^-$ and $N_5^+N_5^-$, and Experimental Evidence for the Instability of $N_5^+N_3^-$. J Am Chem Soc 2004;126:834-43.

[33] Reichlin R, Schiferl D, Martin S, Vanderborgh C, Mills RL. Optical Studies of Nitrogen to 130 GPa. Phys Rev Lett 1985;55:1464-7.

[34] Bini R, Ulivi L, Kreutz J, Jodl HL. High-pressure phases of solid nitrogen by Raman and infrared spectroscopy. J Chem Phys 2000;112:8522-9.

[35] Olijnyk H, Jephcoat AP. Vibrational Dynamics of Isotopically Dilute Nitrogen to 104 GPa. Phys Rev Lett. 1999;83:332-5.

[36] Mitas L, Martin RM. Quantum Monte Carlo of nitrogen: Atom, dimer, atomic, and molecular
solids. Phys Rev Lett 1994;72:2438-41.

[37] Mailhiot C, Yang LH, McMahan AK. Polymeric nitrogen. Phys Rev B 1992;46:14419-35.

[38] Lewis SP, Cohen ML. High-pressure atomic phases of solid nitrogen. Phys Rev B 1992;46:11117-20.

[39] Martin RM, Needs RJ. Theoretical study of the molecular-to-nonmolecular transformation of nitrogen at high pressures. Phys Rev B 1986;34:5082-92.

[40] Eremets MI, Gavriliuk AG, Trojan IA, Dzivenko DA Boehler R. Single-bonded cubic form of nitrogen. Nature Mater 2004;3:558-63.

[41] Mattsson WD, Sanchez-Portal D, Chiesa S, Martin RM Prediction of New Phases of Nitrogen at High Pressure from First-Principles Simulations. Phys Rev Lett 2004;93:125501-4.

[42] Abou-Rachid H, Hu A, Timoshevskii V, Song Y, Lussier LS. Nanoscale High Energetic Materials: A Polymeric Nitrogen Chain $N_8$ Confined inside a Carbon Nanotube. Phys Rev Lett 2008;100:196401-4.

[43] Bajwa N, Ingale A, Avasthi DK, Ravi Kumar, Tripathi A, Dharamvir K, Jindal VK. Role of Electron Energy Loss in Modification of $C_{60}$ Thin Films by Swift Heavy Ions. J Appl Phys 2008;104:054306-13.

[44] Kaur N, Gupta S, Dharamvir K, Jindal VK. Formation of dimerized molecule of $C_{60}$ and their solids. Carbon 2008;46:349-58.

[45] Kaur N, Dharamvir K, Jindal VK. Dimerisation and fusion of two $C_{60}$ bucky balls. Chem Phys 2008;344:176-84.

[46] Kaur N, Gupta S, Dharamvir K, Jindal VK. Behaviour of Bucky ball under extreme internal and external pressure Proceedings of the 26th International Symposium on Shock Waves ISSW26,Germany, Springer-Verlag 2007.

[47] Waiblinger M, Lips K, Heineit W, Weidinger A. Thermal stability of the endohedral fullerenes $NaC_{60}$, $NaC_{70}$, and $PaC_{60}$. Phys Rev B 2001;63:045421-5.

[48] Weiden N, Goedde B, KaB H, Dinse K-P. Squeezing of Nitrogen Atomic Orbitals in a Chemical Trap. Phys Rev Lett 2000;85:1544-7.

[49] Hebard AF, Rosseinsky MJ, Haddon RC, Murphy DW, Glarum SH, Palstra TTM et al. Superconductivity at 18 K in potassium-doped $C_{60}$. Nature 1991;350:600-1.

[50] Bethune DS, Johnson RD, Salem JR, de Vries MS, Yannoni CS. Atoms in carbon cages: the structure and properties of endohedral fullerenes. Nature 1993;366:123-8.
[51] Sanville E, BelBruno JJ. Computational Studies of Possible Transition Structures in the Insertion and Windowing Mechanisms for the Formation of Endohedral Fullerenes. J Phys Chem B 2003;107:8884-9.

[52] Closiowski J, Nanayakkara A. Endohedral fullerites: A new class of ferroelectric materials. Phys Rev Lett 1992;69:2871-3.

[53] Dietel E, Hirsch A, Pietzak B, Waiblinger M, Lips K, Weidinger A et al. Atomic Nitrogen Encapsulated in Fullerenes: Effects of Cage Variations. J Am Chem Soc 1999;121:2432-7.

[54] Dinse K-P. EPR investigation of atoms in chemical traps. Phys Chem Chem Phys 2002;4:5442-7.

[55] Murphy TA, Pawlik T, Weidinger A, Hohne M, Alcala R, Spaeth J-M. Observation of Atomlike Nitrogen in Nitrogen-Implanted Solid C\textsubscript{60}. Phys Rev Lett 1996;77:1075-8.

[56] Knapp C, Dinse K-P, Pietzak B, Waiblinger M, Weidinger A. Fourier transform EPR study of N@C\textsubscript{60} in solution. Chem Phys Lett 1997;272:433-7.

[57] Peres T, Cao B, Cui W, Khong A, Jr.Cross JR, Saunders M et al. Some new diatomic molecule containing endohedral fullerenes. Int J Mass Spectrometry 2001;210/211:241-7.

[58] Slanina Z, Pulay P, Nagase S. H\textsubscript{2}, Ne, and N\textsubscript{2} Energies of Encapsulation into C\textsubscript{60} Evaluated with the MPWB1K Functional. J Chem Theory Comput 2006;2:782-5.

[59] Iwamatsu S.-I, Uozaki T, Kobayashi K, Re S, Nagase S, Murata S. A Bowl-Shaped Fullerene Encapsulates a Water into the Cage. J Am Chem Soc 2004;126:2668-9.

[60] Chai Y, Zhang FQ, Wu LJ. A simple way to C\textsubscript{N\textsubscript{x}}/carbon nanotube intramolecular junctions and branches. Carbon 2006;44:687-91.

[61] Otero G, Biddau G, Sanchez-Sanchez C, Caillard R, Lopez FM, Rogero C et al. Fullerenes from aromatic precursors by surface-catalysed cyclodehydrogenation. Nature 2008;454:865-8.

[62] www.siesta.uae.in

[63] Ordejon P, Artacho E, Soler JM. Self-consistent order-N density-functional calculations for very large systems. Phys Rev B (Rapid Comm) 1996;53:R10441-4.

[64] Soler JM, Artacho E, Gale JD, Garcia A, Junquera J, Ordejon P et al. The SIESTA method for ab initio order-N materials simulation. J Phys: Condens Matter 2002;14:2745-79.

[65] Junquera J, Paz O, Sanchez-Portal D, Artacho E. Numerical atomic orbitals for linear-scaling calculations. Phys Rev B 2001;64:235111-19.

[66] Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into
a functional of the electron density. Phys Rev B 1988;37:785-9.

[67] Kleinman L, Bylander DM. Efficacious Form for Model Pseudopotentials. Phys Rev Lett 1982;48:1425-8.

[68] Sankey OF, Niklewski DJ. Ab initio multicenter tight-binding model for molecular-dynamics simulations and other applications in covalent systems. Phys Rev B 1989;40:3979-95.

[69] Johnson RD, Meijer G, Bethune DS. C_{60} has icosahedral symmetry. J Am Chem Soc 1990;112:8983-4.

[70] Hertel IV, Steger H de Vries J, Weisser B, Menzel C, Kamke B, Kamke W. Gaint Plasmon Excitation in free C_{60} and C_{70} molecules studied by Photoionization. Phys Rev Lett 1992;68:784-7.

[71] Lichtenberger DL, Jatcko ME, Nebesny KW, Ray CD, Huffman DR, Lamb LD. Valence and core photoelectron spectroscopy of C_{60}, buckminsterfullerene. Chem Phys Lett 1991;176:203-8.

[72] Utterback NG, Miller GH. Ionization of nitrogen molecules by nitrogen molecules. Phys Rev 1996;124:1477-81.

[73] Mauser H, Nicolaas JR, Hommes van E, Clark T, Hirsch A, Pietzak B, Weidinger A, Dunsch L. Stabilization of Atomic Nitrogen Inside C_{60}. Angew Chem Int Ed 1997;36:2835-8.

[74] Minh Tho Nguyen. Polynitrogen compounds 1. Structure and stability of N_4 and N_5 systems. Coordination Chem Rev 2003;244:93-113.

[75] Tobita M, Bartlett RJ. Structure and Stability of N_6 Isomers and Their Spectroscopic Characteristics. J Phys Chem 2001;105:4107-13.

[76] Sharma H, Garg I, Dharamvir K, Jindal VK. Structural, electronic and vibrational properties of C_{60-n}N_n (n=1-12). J Phys Chem A 2009;113:9002-13.

[77] Kobayashi K, Nagase S, Dinse K-P. A theoretical study of spin density distributions ans isotropic hyperfine couplings of N and P atoms in N@C_{60}, P@C_{60}, N@C_{70}, N@C_{60}(CH_2)_6 and N@C_{60}(SiH_2)_6. Chem Phys Lett 2003;377:93-8.

[78] Lu J, Zhang X, Zhao X. Electronic structures of endohedral N@C_{60}, O@C_{60} and F@C_{60}. Chem Phys Lett 1999;312:85-90.

[79] Greer JC. The atomic nature of endohedrally encapsulated nitrogen N@C_{60} studied by density functional and Hartree-Fock methods. Chem Phys Lett 2000;326:567-72.
Table I: The encapsulation energy in eV defined as $\Delta E = E_{\text{complex}} - E_{C_{60}} - E_{N_n}$, where $E_{N_n}$ is the energy of the $N_n$ compounds in isolation in free space. Note the energy considered here are of theoretically lowest energy structures which are very different from structures in confinement and do not exit in free space for $n>3$.

| $N_n@C_{60}$ | Total Energy (eV) | Encapsulation energy (eV) |
|-------------|------------------|--------------------------|
| $N@C_{60}$  | -9490.2          | -2.4                     |
| $N_2@C_{60}$ | -9766.0          | -0.6                     |
| $N_3@C_{60}$ | -10030.5         | 0.2                      |
| $N_4@C_{60}$ | -10301.0         | -3.5                     |
| $N_5@C_{60}$ | -10566.7         | 2.9                      |
| $N_6@C_{60}$ | -10831.2         | 11.8                     |
| $N_7@C_{60}$ | -11097.8         | 10.7                     |
| $N_8@C_{60}$ | -11360.1         | 9.8                      |
| $N_9@C_{60}$ | -11624.6         | 16.4                     |
| $N_{10}@C_{60}$ | -11889.4       | 25.5                     |
| $N_{11}@C_{60}$ | -12152.6        | 33.9                     |
| $N_{12}@C_{60}$ | -12414.9        | 37.7                     |
| $N_{13}@C_{60}$ | -12678.6        | 39.2                     |
Table II: The Spin multiplicites of $N_n@C_{60}$ complex and difference between spin up and spin down charge densities

| $N_n@C_{60}$                  | Q (up-down) | Multiplicity (2S+1) |
|-------------------------------|-------------|---------------------|
| $N@C_{60}$ [N at Center]      | 3           | 4 [4(expt)]         |
| $N@C_{60}$ [N at the surface bonded] | 1           | 2                   |
| $N_2@C_{60}$                  | 0           | 1                   |
| $N_3@C_{60}$                  | 1           | 2                   |
| $N_4@C_{60}$                  | 0           | 1                   |
| $N_5@C_{60}$                  | 1           | 2                   |
| $N_6@C_{60}$                  | 0           | 1                   |
| $N_7@C_{60}$                  | 1           | 2                   |
| $N_8@C_{60}$                  | 0           | 1                   |
| $N_9@C_{60}$                  | 1           | 2                   |
| $N_{10}@C_{60}$               | 0           | 1                   |
| $N_{11}@C_{60}$               | 1           | 2                   |
| $N_{12}@C_{60}$               | 0           | 1                   |
| $N_{13}@C_{60}$               | 3           | 4                   |
Figure 1. Geometries of $N_{n} @ C_{60}$. (a) $N_2$ placed at the centre of $C_{60}$ (b) $N_3$ as a linear chain placed symmetrically (c) $N_4$ exists as two independent $N_2$ molecules placed symmetrically across centre (d) & (e) $N_5$ and $N_6$ exist as a pentagon ring and a non-planar distorted hexagon with 100% single bond character (f) $N_7$ exists as $N_5$ and $N_2$ as separate units, however, its nearly isoenergetic structure is shown.
Figure 2. Geometries of N\(_x@C_{60}\) (a) N\(_8\) exist as two planar rings of N\(_4\) placed symmetrically and connected by weak N-N bond (1.57 Å) (b) N\(_9\) exist as two planar rings of N\(_4\) and N\(_5\) connected by weak N-N bond (1.48 Å) (c) N\(_{10}\) exists as two planar and slightly inclined pentagon rings connected by weak N-N bond (1.50 Å) (d) N\(_{11}\) exist as interconnected structure of planar N\(_5\) and non-planar N\(_6\) placed across centre (e) N\(_{12}\) exist as symmetrically placed two boat shaped hexagons connected by N-N bond distance of 1.39 Å (f) N\(_{13}\) exists as interconnected structure of planar N\(_5\) and a heavily distorted N\(_6\) however, the less interstitial space inside C\(_{60}\) forces the nitrogen atoms to make bonds with surface carbon atoms. The above structures of polynitrogen molecules in C\(_{60}\) show nearly 70-80% single bond character.
Figure 3 (a) \( \text{N}_{14} @ \text{C}_{60} \) exits as a distorted complex with \( \text{N}_{12} \) existing as an interconnected structure of \( \text{N}_3 \) and \( \text{N}_7 \). Two nitrogen atoms undergo chemisorption resulting in a 62-atom cage with the formation of two heptagons on the surface. (b) \( \text{N}_{15} @ \text{C}_{60} \) doesn’t show any pattern in the structure of the polynitrogen molecule. Hexagons and pentagons of \( \text{C}_{60} \) show heavily distortion with C-C bond distances increasing up to 1.65–1.67 Å which is the breaking point for the \( \text{C}_{60} \) cage. (c) \( \text{N}_{16} @ \text{C}_{60} \) exists as a polymeric complex with three nitrogen atoms getting substituted at the surface and making a heptagon and an octagon which henceforth leads to the opening of the cage indicating the threshold limit for nitrogen encapsulation at 0K.

In above structures, due to less available space nitrogen tends to make bonds with the surface atoms as well as undergoing chemisorption. These structures are unstable at room temperature.
Figure 4. Shows the Kohn-Sham energy eigen values for $N_n$ clusters ($n=1,2,5,6,8,9,10,12,13$)
Figure 5: Shows Electronic Density of States (DOS) for (a) C\textsubscript{60} (b) N@C\textsubscript{60} (c) N\textsubscript{2}@C\textsubscript{60} and (d) N\textsubscript{5}@C\textsubscript{60}.
Figure 6: Shows Electronic Density of States (DOS) for (a) $N_8@C_{60}$ (b) $N_{10}@C_{60}$ (c) $N_{12}@C_{60}$ and (d) $N_{13}@C_{60}$. 
Figure 7. Shows the percentage single bond character of polynitrogen compounds encapsulated in fullerene cage.

Figure 8. Shows the percentage relative elongation of polynitrogen compounds as a function of number of nitrogen atoms.