Abstract

This thesis describes various properties of nanoclusters, fullerenes (C_{60}) and carbon nanotubes (CNTs) using the first principle methods based on density functional theory (DFT). When different foreign elements are introduced at substitutional, endohedral and exohedral sites of the nanostructures, their structural, electronic and vibrational properties are altered. In this thesis, we discuss some of the properties of doped nanostructures in detail.

In Chapter I, we introduce and present the general effects of doping on these nanostructures. The work done in this field till date is also reviewed here in detail. First principle methods based on density functional theory (DFT) have been employed for the calculations carried out in this work and are described in Chapter II. Chapter III presents an ab initio investigation of nitrogen-doped (N) fullerenes (C_{60-n}N_n for n = 1-12). N doping leads to structural deformation with the diameter showing variation from (7.14-0.24) to (7.14+0.10) Å. The binding energy per atom and HUMO-LUMO gap decrease with increasing number of N atoms. The Mulliken charge analysis shows a charge transfer from N to carbon (C) atoms showing the donor nature of N atoms. The vibrational frequencies decrease with increase in N atoms.

In Chapter IV, the ground state structures of boron-doped (B) fullerenes are obtained and it is shown that the B atoms tend to occupy two non-adjacent sites in the same hexagon. Distortion in the C_{60} cage has been measured as variation in the diameter. As a result of B substitution, The HOMO-LUMO gap of C_{60} reduces from 1.67 eV to 0.49 eV for C_{48}B_{12} indicating the increase of metallic character in B-doped fullerenes. A considerably high amount of charge redistribution in C_{60-n}B_n complexes takes place, with B gaining charge and behaving as acceptors with respect to the cage carbon atoms. In Chapter V, we present some results of investigations of N and B doped C_{60} dimer structures with gold clusters in contacts. We studied Au_n-C_{60-x}N_x-C_{60-x}B_x-Au_n complexes, where n = 1, 2, 4 and 5 and x = 1-6 where a C_{60} dimer doped with B and N is sandwiched between gold clusters of different sizes, to study the charge transfer properties. Due to the electron-rich and electron-deficient nature of N and B respectively with respect to the cage C atoms, the complexes with Au contacts behave as a molecular rectifiers. The HOMO-LUMO gaps for these complexes show a considerable decrease, from 1.39 eV for pure C_{60} dimer to 0.02 eV. These calculations will be further improved.
to present a complete picture in near future.

In Chapter VI, we explore the possibility of trapping polynitrogen clusters inside $C_{60}$ fullerene cages, using density functional theory. We find that a maximum of 13 N atoms can be encapsulated in a $C_{60}$ cage without distorting the cage significantly. The N clusters in confinement exhibit unique stable structures in polymeric form, mostly in single and double bonded formations. The $N_n@C_{60}$ molecules retain their structure even at 300 K for $n=12$. This demonstrates that the $C_{60}$ cage could provide ideal environment for stabilizing reactive species which are otherwise less stable in free space. The Mulliken charge analysis shows a very small charge transfer in $N@C_{60}$, consistent with the quartet spin state of N. However, for $2<n<10$, charge transfer takes place from cage surface to N complexes and inverse polarization thereafter.

Chapter VII describes the results of our systematic study of structural and electronic properties of $Al_n$ clusters ($n=1-23$) along with the change in their properties due to N-doping. In $Al_n$ clusters, the binding energy increases as a result of N substitution and the HOMO-LUMO gap shows variation over a wide range which can be exploited for tuning optical gap in the visible range. We have also carried out a systematic investigation of encapsulation of $Al_n$ clusters ($n=1-13$) inside armchair single-walled carbon nanotubes (CNTs) of varying diameter. Inside CNTs, $Al_n$ clusters show linear structures for $n=5$ and 3 dimensional geometries thereafter. In strong confinement, Al-C interaction becomes more dominant. However on relaxing the confinement, Al-Al interactions become relatively more important. The HOMO-LUMO gaps of the hybrid structures $Al_n@(6,6)$ for $n=1-13$ decrease to 0.1-0.2 eV. Mulliken charge analysis shows that $Al_n$ sites near to the CNT wall are significantly involved in charge transfer which takes place from C to Al atoms. These calculations done are in good agreement with the existing theoretical and experimental studies.