A Conceptual Density Functional Theory Perspective of Bonding and Reactivity in Some Noble Gas Compounds and in a Hydrogen Storage Material

ABSTRACT

The theoretical study of chemical systems involves examining their geometry, stability, bonding, and reactivity. Reactivity, in particular, necessitates the observation of various conceptual density functional theory (CDFT) derived reactivity descriptors and electronic structure principles such as the maximum hardness (MHP) and the minimum electrophilicity (MEP) principles. The thesis examines the periodic nature of CDFT descriptors for elements within the periodic table up to atomic number 56. Bonds that are commonly known as purely covalent or ionic are not accurately categorized due to the ubiquitous presence of both ionic and covalent characteristics in almost all chemical bonds. The level of covalency and ionicity in these bonds can be ascertained using commonly used bonding techniques such as electron localization function (ELF), energy decomposition analysis (EDA), and quantum theory of atoms-in-molecules (QTAIM).

The thesis explores the use of DFT-based electronic structure calculations in investigating various molecular systems, mostly including noble gas (Ng) elements, either to form insertion complexes or be encapsulated within caged systems. The kinetic stability of the otherwise transient coinage metal isocyanide (MNC) isomers can be improved by binding them with small interacting ligands. Their influence on the isomerization process is compared with that obtained on binding with Ng elements. The isomerization between the two isomers (HCCNSi and HCCSiN) of the astronomically important silaisocyanoacetylene is facilitated by Ng-insertion. The Ng-inserted mono-halogen substituted phosphoric acid, $XNgOPO(OH)_2$ are thermochemically and kinetically stable with partial covalent characters in the bonds on either side of the Ng atom. The interaction of a neon dimer confined within various caged systems is studied to understand the effect of confinement and fluxionality of the host cage. Further, the hydrogen storage and carbon monoxide adsorption ability of lithium and OLi_2 decorated B, N modified (2,2) γ-graphyne nanotube (GNT) is examined. It can adsorb up to three and eight H_2 molecules, respectively. The former can also adsorb up to three CO molecules. The use of CDFT and reactivity descriptors is also highlighted as a powerful tool for the study of molecular reactivity.

KEYWORDS

Conceptual DFT, Noble gas, Insertion complex, Confinement, Hydrogen storage