Studies on Electronic Structure and Bonding in Some Weakly Bound Systems

Abstract

The present thesis analyses the structure, stability, reactivity, and pertinent bonding situation in chemical systems involving weak interactions such as different non reactive species consisting of noble gases (Ng), coinage metals (so-called noble metals: Cu, Ag and Au) and molecular hydrogen. *Ab initio* and density functional theory (DFT) based calculations are carried out to study Ng non-insertion compounds like $[NgM\text{-}(bipy)]^+$ (bipy = bipyridyl, M= Cu, Ag and Au) and insertion compounds such as MNgCCH, MCCNgH, MNgCN and NCNgNSi involving novel bonding motifs especially M-Ng-C, C-Ng-H and C-Ng-N. The $[M\text{-}(bipy)]^+$ complexes can form bonds with the Ng atoms (Ar-Rn) and $[NgM\text{-}(bipy)]^+$ complexes are viable at room temperature which signifies that noble gas-noble metal interaction is partially covalent. The counter-ion stability of $[NgM\text{-}(bipy)]^+$ complexes is checked considering SbF_6^- anion. Ng-insertion compounds like MNgCCH, MCCNgH, MNgCN and NCNgNSi are found to be metastable when investigated through the thermodynamically feasible but kinetically protected dissociation channels at 298K and 1 atm pressure. The effect of halogen substitution in the dodecahedrane ($C_{20}H_{20}$) cage on bonding in the confined He dimer is analyzed. The possibility of cucurbit[7]urils acting as an effective host for seperating SO_2 gas from flue or other gas mixtures is explored. Binding of small gas molecules by $[M\text{-}(bipy)]^+$ and possible bond activation are investigated through DFT based computations. The nature of bonding is thoroughly investigated via natural population analysis, electron density analysis, non-covalent interaction indices, energy decomposition analyses and adaptive natural density partitioning methods. Hydrogen trapping ability of unprecedented inorganic double-helical Li_nP_n (n=7-9) clusters and Ni-decorated polycyanogen $C_{12}N_{12}$ nanoclusters are investigated for their possible use as hydrogen storage materials. Also, we have analyzed the influence of Ni on the aromatic behavior of $C_{12}N_{12}$ nanocluster as well as the microsolvation behavior of the rare Li_7P_7 clusters.

Keywords: Non-reactive Species; Metastable Compounds; Inclusion Compounds; Bond Activation; Hydrogen Storage; Microsolvation.