Pak. J. Engg. Appl. Sci. Vol. 31 July, 2022 (p.1-11)

Doping of multi alkali and transition metals: Strengthening of electronic & NLO properties of $Al_{12}N_{12}$ nanocages

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Abstract

Current studies were performed to overview the literature on strengthening of the electronic and non-linear optical properties by doping of multi alkali and transition metals on $Al_{12}N_{12}$ nanocages. Nonlinear optical (NLO), geometric and electronic properties of alkali and Cu doped $Al_{12}N_{12}$ nanocages were studied by density function theory (DFT) calculations. The study shows a significant decrease in HOMO-LUMO gap of the nanocages. Adsorption of Cl_2 on $Al_{12}CN_{12}$ was higher as compared to its adsorption on pure $Al_{12}N_{12}$. Upon adsorption of Cl_2, a significant change in energy gap of $Al_{12}N_{12}$ ($\Delta Eg = 79\%$) was observed as compared to the change in energy gap of $Al_{12}CN_{12}$ ($\Delta Eg = 43\%$). UV-Vis spectral analysis demonstrates that the λ_{max} for the adsorption of Cl_2 on nanocages lies in the red region. Industrially important gases such as C_2H_2 and C_2H_4 exhibit a change in their properties after adsorption on aluminium nitride (AlN) and nickel doped nanocluster; the adsorption energy of C_2H_2 after doping on $Al_{12}N_{12}$ nanocages increases from 294 to 410 kJ/mol. A relatively higher orbital hybridization and a lower interaction distance was observed upon the adsorption of gases on AlN nanocage surfaces. In addition, a study also demonstrates an increase in optical, electronic and sensor abilities of nanocages after doping with different alkali and transition metals.

Keywords: doping, alkali, transition-metals, $Al_{12}N_{12}$, optimization, electronic, optical

1. Introduction

Computational studies have gained importance to elucidate the important structural features [1-3] and properties [4-6] of molecules. DFT calculations can be carried out to examine the non-linear optical (NLO) properties of metal-doped $Al_{12}N_{12}$ nanocages [7-10]. A nanocage is a stable material like a fullerene (C60) with a spherical shape and magic arrangement. After doping of alkali metals on $Al_{12}N_{12}$, nonlinear optical (NLO) properties (such as polarization, hyper polarizability and dipole moment) could be enhanced by adjusting the bond length, extended conjugation and by leading the intra-molecular charge transfer [11-14]. For example, Faizan Ullah and coworkers investigated the influence of first row transition metals on structural, electronic and NLO properties of aluminium phosphide inorganic fullerene through DFT method and fairly reduced the HOMO-LUMO energy gap of aluminium phosphide nanoclusters. Authors attributed the decrease in energy gap to formation of new high HOMO energy levels [15].

Materials having extensive nonlinear properties act as excellent applicants for optoelectronic devices [16, 17]. Since almost last 50 years, this work experienced a rapid growth because of an ongoing extensive research on the exploration of some better and new materials [18, 19]. Different methodologies are being designed and employed to strengthen the NLO properties of many organic and inorganic materials [20-23]. The donor-acceptor π-bridge technique has been used to improve the NLO response of organic materials [24, 25]. The metal-ligand framework (where charge transfer phenomenon would take place between metal and ligand) can be designed to enhance the NLO properties [26, 27]. For example, alkali metal doped $Al_{12}N_{12}$ shows a significant increase in NLO properties up to a value of 8.89×10^5 au [28].

Keeping in view fantastic applications of density functional theory (DFT) to understand the structures and properties of molecules/materials, the present work reviews the literature on doping of multi alkali and transition metals on $Al_{12}N_{12}$ nanocages for the purpose of strengthening their electronic and non-linear optical properties.

2. Materials and Methods

Calculations and geometry optimizations of all the structures were performed by using Gaussian 09 suit of programs, whereas all the structures were optimized by B3LYP/6-31G (d, p) basis set i.e. a method of DFT [29]. The stability of doped nanocages was determined by calculating the binding energy [30]. The binding energy formula is given below in equation 1.

$$E_b = E_{M@Al12N12} - (E_{Al12N12} + E_M) \qquad \text{(Eq 1)}$$

Hyperpolarizability, polarizability and natural bond orbital (NBO) charges of doped $Al_{12}N_{12}$ nanocages were evaluated by B3LYP/6-311+g (d) [31] and B3LYP/6-31G (d, p) level of theory. This method is considered as the most appropriate one to evaluate the NLO properties of nanocages. Different orientations of C_2H_2 and C_2H_4 on $Al_{12}N_{12}$ and Ni-doped $Al_{12}N_{12}$ nanoclusters have been observed by applying the basis sets as described in the Gaussian 09 suit of programs. Geometry and optimization of Cl_2, $Al_{12}N_{12}$ and $Al_{12}CN_{12}$ was evaluated by DFT method B3LYP and binding energies were determined by using DFT basis sets B97-D/6-311++ G** and B3LYP-D/6-311++ G** methods which explain the interaction details and adsorption behavior of the gas molecules on the inorganic nanocages [10, 32]. By applying the time dependent density functional theory (TD-DFT) calculations, UV/Vis spectrum of adsorbed Cl_2 over AlN and AlCN fullerenes was used. Before and after adsorption of Cl_2, the binding energies were calculated by the formulae given in equations 2 and 3.

$$E_{ad} = E_{Al12N12\text{-}Cl2} - (E_{Al12N12} + E_{Cl2}) + E_{BSSE} \qquad \text{(Eq 2)}$$

$$E_{ad} = E_{Al12CN12\text{-}Cl2} - (E_{Al12CN12} + E_{Cl2}) + E_{BSSE} \qquad \text{(Eq 3)}$$

The method of DFT calculations B3LYP/6-311G (d, p) is suitable to perform nanocages calculations and is excellent to obtain results at low cost, whereas global charges of system during the optimization remain neutral.

3. Doping of alkali/transition metals on $Al_{12}N_{12}$ nanocages

The DFT was employed to determine the effect of alkali metal doping in $Al_{12}N_{12}$ nanocages. The authors reported a significant decrease in the band gap [33, 34]. Munsif and Ayub employed DFT calculations to study the diffusion behavior of alkali metals on the surface of $Al_{12}N_{12}$ and $B_{12}N_{12}$ nanocages. The authors examined barriers for the diffusion of alkali metal atoms (Li, Na, K) on the nanocages [19]. It has also been shown that after encapsulation of alkali metals on group III nitrides (such as $B_{12}N_{12}$), the hyper polarizability among nanocages increases up to a value of 1.23×10^5 au [35]. DFT was further applied to investigate a series of nanocages for catalysis of CO_2 to hydrogenated products. Endothermal doping of alkali metals led to an increased band gap, increased charge separation and thus an increased adsorption energy [36].

The stability of new inorganic electride compounds $M@x\text{-}Al_{12}N_{12}$ (M = Li, Na, and K; $x = b_{66}$, b_{64}, and r_6) were studied by *ab initio* computations. The stability was achieved by doping M (alkali metals) on the fullerene-like $Al_{12}N_{12}$ nanocages; where M was located over the six-membered ring (r_6 site) or Al–N bond (b_{66}/b_{64} site). It was found that band gap between the HOMO and the LUMO ($E_{H\text{-}L}$ = 6.12 eV) of the pure $Al_{12}N_{12}$ nanocage lowered by 0.49–0.71 eV due to doping of M, irrespective of the atomic number and doping position. Fascinating n-type properties were demonstrated by doped AlN nanocages; it is due to the introduction of a new HOMO high energy orbital (having excess electrons) in the original gap of pure $Al_{12}N_{12}$. Significant first hyperpolarizabilities (β_0) were observed for the doped AlN nanostructures due to diffuse excess electrons. The observed β_0 values were 5.48×10^4 au for $K@r_6\text{-}Al_{12}N_{12}$, 1.36×10^5 au for $Na@r_6\text{-}Al_{12}N_{12}$, 8.89×10^5 au for $Li@r_6\text{-}Al_{12}N_{12}$, 7.58×10^4 au for $K@b_{64}\text{-}Al_{12}N_{12}$, 1.62×10^4 for $Na@b_{64}\text{-}Al_{12}N_{12}$, 1.10×10^4 for $Li@b_{64}\text{-}Al_{12}N_{12}$ and 1.09×10^4 au for $Li@b_{66}\text{-}Al_{12}N_{12}$. It was concluded that the larger β_0 value is obtained by doping heavier Na/K atom over the Al–N bond. However in case of doping, the alkali atom over the six-membered ring, a larger β_0 value was obtained by doping the lighter Li atom [37].

DFT method was used to study the effect of doping of alkali metals (K, Na, and Li) in $(AlN)_{12}$ nanocage. Theoretically six new and stable compounds of $M@Al_{12}N_{12}$ and $M@Al_{11}N_{12}$ were fabricated where an atom (Al/N) was replaced by an alkali metal. Binding energy calculations were employed to determine the stability of doped nanocages. It was found that the band gap decreases significantly due to doping of alkali metals in nanocage. NLO properties of the doped system were evaluated by calculating polarizability and first hyperpolarizability on long-range separating methods. $M@Al_{12}N_{11}$ nanocages show higher hyperpolarizability than that of the $M@Al_{11}N_{12}$ nanocages. This hyperpolarizability trend is due to extra diffuse electrons [33].

In another work, the ab initio quantum chemistry method was used to investigate the structures and NLO properties of electrides doped with alkali metal ($B_{12}N_{12}$–M where M = K, Na, Li). The energy bang gap of $B_{12}N_{12}$ decreased up to 3.96-6.70 eV by doping alkali metals. The doping also resulted in significantly large first hyperpolarizabilities (β_0) due to diffuse excess electrons [38].

The literature survey does not only demonstrate a huge change in properties of inorganic nanocages after doping with transition metals, but, the substitution doped Mg12O12 nanocages with 3d transition metal also show the highest first hyper polarizability value of 4.7×104 au [39]. Transition metals can be incorporated in AlN nanocages and can be doped in different ways e.g., by encapsulation or replacement of the atom of nanocages with transition metal. In some studies, anexohedral doping of transition metal has been performed to examine the strong effect of placement of alkali metal and super-alkalis on the surface of nanocages [28, 40]. Therefore, DFT calculations can be performed to increase the NLO and electronic properties by doping the alkali and transition metals. The exohedral doping of the first series of transition metals (such as Cu, Fe, V, Zn, Ni, Ti, Co, and Sc) on the surface of AlN nanocages in different orientations has been studied. Doping of C20 fullerene with transition metals [41, 42] is observed, but this phenomenon is not observed for the entire row of transition metals. Four spin state is being explored to reveal some lower energy states. Some research works explore new possible means to design the AlN based nanostructures by transition and alkali metals, that can have more effective applications.

Adsorption of different gases on the surface of different nanocages was studied to enhance the electronic properties of materials by reducing their energy gap. For example, the adsorption of Cl2 over Al12N12 and Al12CN12 altered the optoelectronic properties by subtracting their energy gap and Fermi level. This theoretical work also delivers a valuable information on the ejection of toxic gases by improving the NLO properties of Al12N12 [43]. In another work, adsorption of multi gases on the groups III-IV nanocages like semiconductors such as Al12N12, Al12P12, B12N12 has been studied [44]. The Al12N12 nanoclusters demonstrated an exceptional behavior amongst all the studied semiconductors due to their low electron attraction and extensive thermo-physical properties [45]. Al12N12 nanoclusters are more stable as compared to other different AlN nanoclusters [46]. Sensing properties of AlN nanocages can be improved by adsorption of ethylene and acetylene. With the help of DFT, C2H4 and C2H2 were adsorbed onto AlN nanoclusters. As a result of such adsorptions some very favourable results in terms of values of binding energies, HOMO-LUMO distributions, and charge transfer of all pure and complexes of AlN nanocages were obtained [47].

4. Structure optimization and geometry

Theoretical studies show a drastic change in geometric and electronic properties of nanocages after a metal doping [28, 48-50]. All possible doping positions of Cu have been examined on an AlN nanocage. The studied doping positions include surfaces above the aluminium and nitrogen atoms, over the bond fused between four-member ring (b64), over the bond fused between 6-membered ring (b66), and over the bond fused between 4-membered ring (b66) and the center of 6-membered (R6) and 4-membered (R4) ring and finally at the interior core of nanocage. Their stabilities were determined by binding energies. The negative values favored the feasibility of the process. The values of -63.9 and -63.0 kcal/mol are the binding energies for Cu@b64 and Cu@b66 respectively, and are larger than the values of Cu@R6 and Cu@endo (-45.0 and 44.1 kcal/mol respectively) [51]. After this evaluation, it was noted that the value of distance ranges between Cu-Al and dCu-Al are from 2.24 to 2.39Å and thus no significant change was noted. Nevertheless, greater distance ranges of Cu-N and dCu-N have been observed. Cu@endo showed the lowest binding energy of -44 kcal/mol due to an increased interaction distance (dCu-N) of 2.40Å [52]. An increased binding energy of Cu@R6 is because of reduction in distance to 2.23 Å. Due to larger binding energy values for Cu (-63.0 and -63.9 kcal/mol), dCu-N in the structure decreased to 1.84 Å. Out of the two structures studied, the second structure showed more stabilization by an amount of 0.9 kcal/mol. Therefore, it can be concluded that there is an inverse relation between binding energy and interaction distance [52].

5. Electronic properties

Because of the higher energy gap between HOMO and LUMO, $Al_{12}N_{12}$ nanocages behave as insulators [53-55]. An energy gap of 3.39 eV was calculated between HOMO and LUMO. However, after doping with Cu, the energy gap decreased from 3.39 to 1.88 eV. In case of Cu@R6, 52% reduction was observed and the energy gap lowered to 2.16 eV because of Cu@endo. In Cu@b66 and Cu@b64, energy gaps reduced to 44% and 41% respectively. In addition, the energies of Fermi level increased to a higher level after doping with Cu. Thus, the results of this study indicate that the energies of HOMO greatly increase as compared to the energies of a LUMO orbital due to the interaction of Cu atoms among all structures and cause the reduction in eg as shown in Figure 1. Due to reduction of e.g., nanocages behave as conductors which makes them potential candidates for electronic devices [56-58].

6. Optical properties of metal doped $Al_{12}N_{12}$

Polarizability and hyper polarizability values were modified by changing the phase and frequency when a beam of light interacts with the medium. The polarizability values of undoped and doped $Al_{12}N_{12}$ are 287 au and 418 au, respectively. On the other hand, the dielectric polarization responds linearly to electric field as a linear optical. In a similar fashion, the hyper polarizability values increased. Largest polarizability ($\beta 0$) for Cu@R6 is 1.8×10^4 au and hyper polarizability of Cu@endo is 4.3×10^3 au. A structure with higher values of binding energies and a high NLO response is considered as a better applicant [59].

7. Cl_2 adsorbed on $Al_{12}N_{12}$ and $Al_{12}CN_{12}$ fullerenes

NBO analysis calculated the point charge values for Al and N before and after doping the nanocages by B3LYP-D and B97-D functional methods, respectively. After doping point charge, the values for Al, C, and N are +0.343, -0.433, -0.169 eV respectively calculated by B3LYP-D and are +0.918, -0.857, -0.947 eV respectively calculated by B97-D functions simultaneously. The positive and negative charge values upon Al and N atoms of $Al_{12}N_{12}$ are +1.823 and -1.823 eV respectively [60]. The charge density surface of HOMO-LUMO orbital over $Al_{12}N_{12}$ shows that HOMO is localized on N and LUMO is uniformly occupied through Al and N atoms [61]. The complete summary of the effect of the adsorption of Cl_2 on $Al_{12}N_{12}$ and $Al_{12}CN_{12}$, computed energy levels, and symmetries of the HOMO-LUMO differences are shown in Figure 2. The decomposition of Cl_2 on to the nitrogen and aluminium shows an adsorbate-adsorbent interaction as well as the chemisorption nature of processes [62].

8. Adsorption of acetylene

The strong interaction of acetylene on AlN and Ni-AlN fullerene indicates an increase in bond distance between Ni-Al and Ni-N to 2.23 and 1.90 Å from 2.19 and 1.73 Å, respectively [47].

9. Adsorption of ethylene

The bond distance of the carbon-to-carbon atom in C_2H_4 showed a strong coordination between C_2H_4 and Ni-AlN nanocages. The bond lengths in ethylene P2 and P1 geometries are 1.44Å. By comparing both geometries summarized (before and after) doping on the surface of nanocages), the strong interaction of ethylene with Ni-AlN is obvious. The effect is more pronounced for P2 structural geometry where Ni-N and Ni-Al bond lengths are increased to 1.90 and 2.23 Å from1.73 and 2.19 Å respectively (please see Figure 3) [47].

10. Conclusions

DFT studies of all possible structures revealed that the energy gap is reduced significantly between HOMO and LUMO orbitals and improvement/modification in properties of $Al_{12}CN_{12}$ nanocages is observed when doping of sodium, potassium, lithium, copper, nickel, iron, vanadium, zinc, titanium, cobalt, scandium etc is performed on the surface of $Al_{12}N_{12}$. The doping results in significant improvement in geometric, optical, and electronic properties of nanocages used in optoelectronic devices. Adsorption of Cl_2 (in different orientations) on pure AlN and $Al_{12}CN_{12}$ also modifies the electronic properties by reducing their energy gap and Fermi level. Acetylene and ethylene adsorption on pure and complex structures of AlN nanocages brings about an alteration in dipole moments. These studies make nanocage structures more useful, potential applicants to many electronic devices, and environment friendly because of a reduced energy gap between EH-EL molecular orbitals.

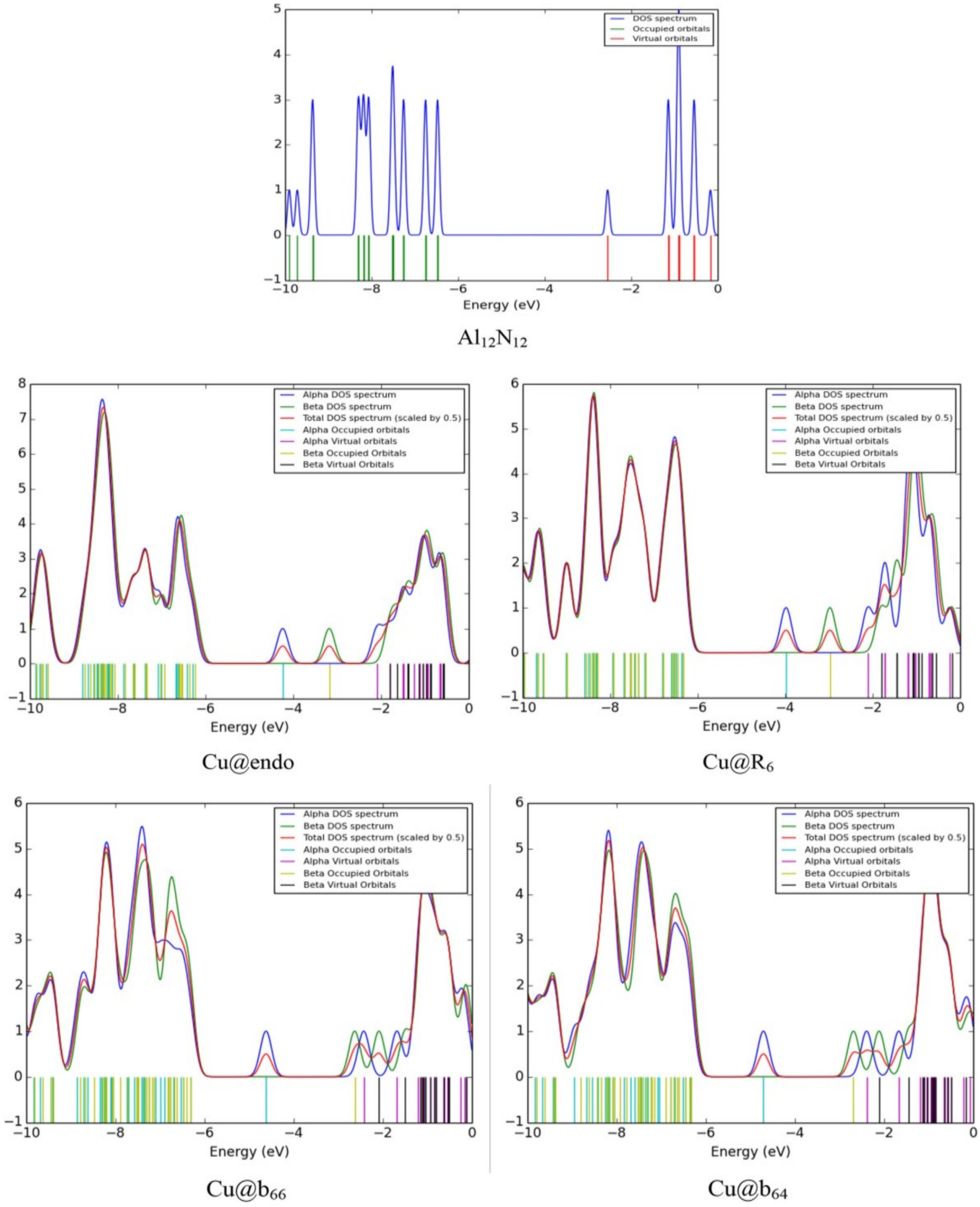
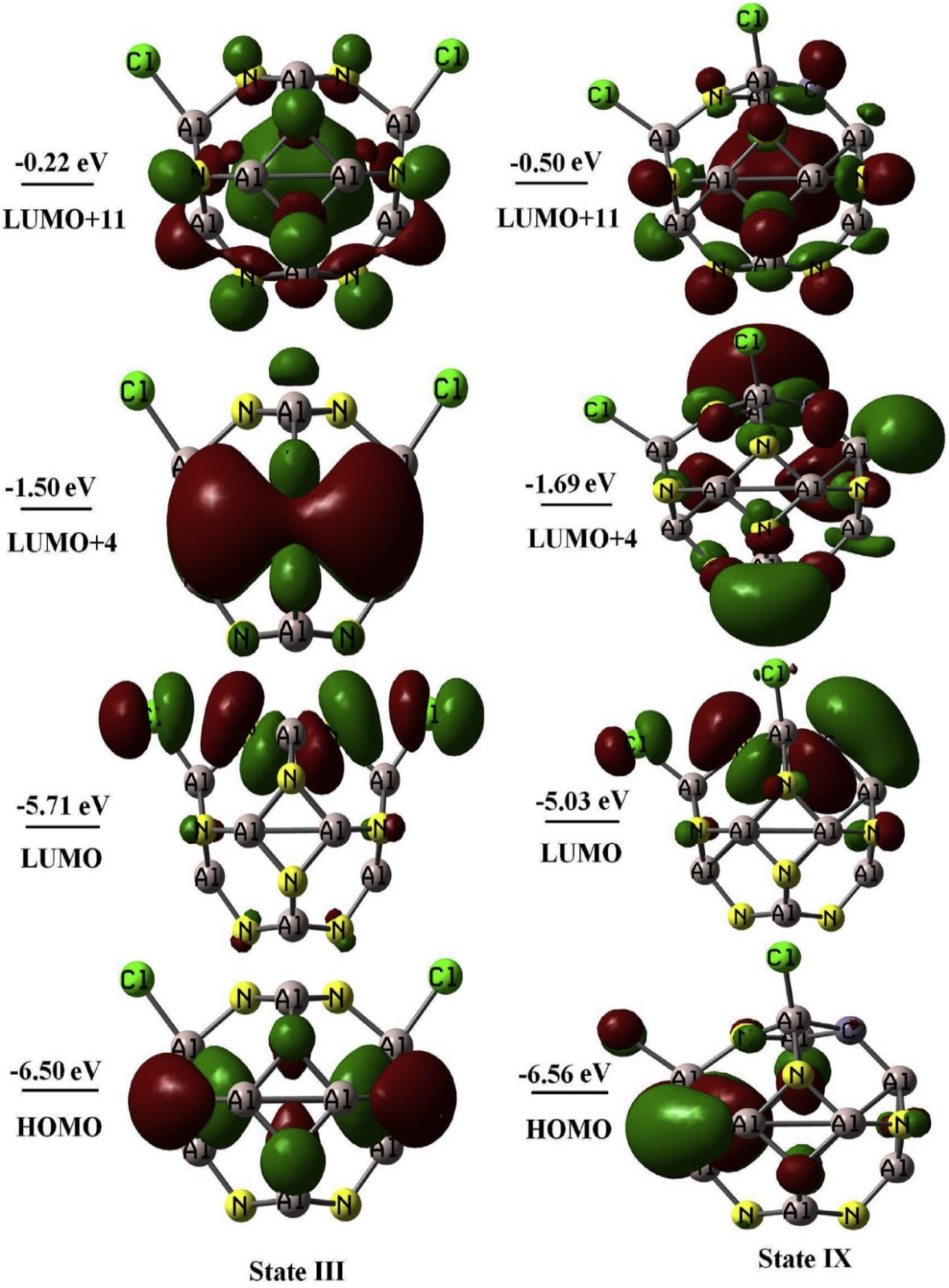


Fig. 1: Graphical representation of energy state (X-axis) *vs* relative intensities of peaks (Y-axis) for pure and Cu-doped $Al_{12}N_{12}$ nanocages [54]



State III

State IX

Fig. 2: Molecular orbital (HOMO=LUMO) in stable states [61]

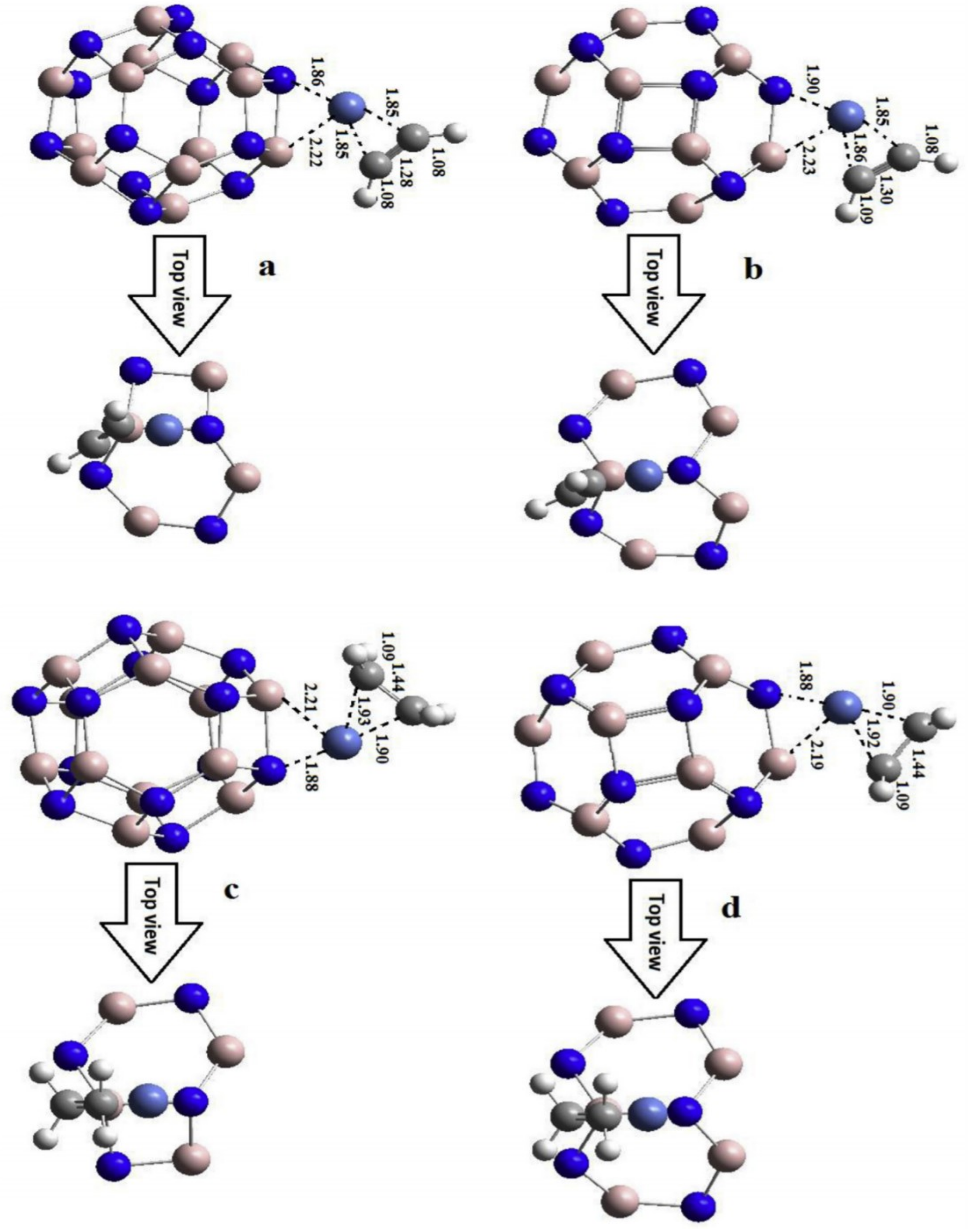


Fig. 3: Modified Ni-ALN nanocages after acetylene adsorption (a and b w.r.t position 1 and 2) and ethylene adsorption on Ni-ALN (c and d w.r.t position 1 and 2) [47]

11. References

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