# ALKALI METAL DOPED FULLERENE AS HYDROGEN STORAGE: A DFT STUDY

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Abstract - Fossil fuels are limited and unsafe for environment due to carbon emission. To minimize the dependence on fossil fuel hydrogen has been accepted as a supreme energy carrier. But the challenge of new hydrogen economy is to find appropriate materials that can store hydrogen with intermediate adsorption energy. Hence fullerene (C<sub>60</sub>) has been investigated intensively around the world for its ability to adsorb hydrogen. In this paper we present results of density functional theory (DFT) calculations of the adsorption ofhydrogen molecules on alkali metal (Li, Na, K) doped fullerene ( $C_{60}$ ). Adsorption energy, charge distribution, photon absorption, global indices, optical band gap energy etc. have been investigated for the better understanding of doped and undoped fullerene. All the parameters have been calculated by Gaussian 09 simulation package using density functional theory (DFT) with 6-31G/UB3LYP level of theory.The adsorption energies of molecular hydrogen on alkali metal doped fullerene is negative, i.e., exothermic. The attractive interaction between thesurface dipole and the dipole of polarized H<sub>2</sub>may contribute this adsorption energy. From this result it can be expected that alkali metal-decorated fullerene could be considered as a potential high-capacity hydrogen storage medium.

Keywords: fullerene, alkali metal, doping, hydrogen storage, DFT.

# **1. INTRODUCTION**

Energy, environment and economy are the most fundamental global issues for our sustainable future<sup>1-5</sup>, while energy is the most vital requirement for the progress of our civilization. It is adequately clear that the way of today's energy production and consumption is not sustainable, and we need a new direction. Our current global energyneed is about 15 Tera Watt whose about 85% comes from fossil fuels<sup>6, 7</sup>. Apart from the fact that these high-density energy sources are not renewable, they emit carbon and greenhouse gases that have an irreversible effect on environment. These greenhouse gases are responsible for global warming by trapping the sun's heat at atmosphere. It is expected that the world's energyneedwill increase with the increasing of technological and industrial development and it will be about 33% during the next 10 years<sup>8</sup>. The only way to tackle this situation is to use renewable energy sources which continually replenishes in nature, for e.g. (a) solar energy (b) wind energy (c) bio energy (d) geothermal energy (e) ocean energy (f) hydroenergy and (g) hydrogen energy<sup>7-9</sup>.

Hydrogen is the universe's most abundant element (every water molecule has two hydrogen atom) and it exhibits the highest heating value to mass ratio for any fuels. Hydrogen is a pollution-free fuel as during its combustionwater is the only by-product. Hence non-CO<sub>2</sub>emitting energy carrierhydrogen can be the most potential candidateas the 'fuel of the future'<sup>10-12</sup>! But, there are numerous hurdles associated withits production, storage and transportation.Without considering the political issues associated with energy, hydrogen can compete with otherconventional sources of energy if the hurdles being overcome. Amongthese hurdles, hydrogen storage is considered to be the biggestchallenge for the growth of new hydrogen economy as available hydrogen storage modalities are compressed gaseous hydrogen, metal hydrides, and cryogenic liquid hydrogen which are costly and hazardous.

Hydrogen molecules can interact with other materials by physisorption or chemisorption process. Physisorption (weak interaction) is one kind of molecular interaction without transferring any charge between hydrogen and material's surface whereas chemisorption (strong bonding) is an atomic interaction by transferring electrons from the surface of adsorbents to hydrogen molecules (these electrons break the molecular bond of hydrogen to split into hydrogen atoms). Thus, some materials can store large amount of hydrogen with strong binding energy, but it is not easy to desorb hydrogen (e.g.,  $CH_4$ )<sup>13</sup>. There are some other materials from where hydrogen can be desorbed easily, but cannotstore much hydrogen (e.g., carbon nanotubes)<sup>14</sup>. An ideal storage systembinds hydrogen molecularly with an intermediate binding energy between the physisorbed and chemisorbed state<sup>15</sup> Hence the main challenge for hydrogen storage is to find materials that can adsorp hydrogen with the intermediate binding energy. We have shown that alkali metal doped  $C_{60}$  fullerenes may lead to the synthesis of novelhydrogen storage materials.

In this work, we study the electronic, energetic and geometric properties of the fullerene  $C_{60}$  and different H<sub>2</sub>-

 $C_{59}X$  complexes, where X = Li, Na, K. The investigation will also help to understand the doping effect on physical and chemical properties fullerene  $C_{60}$  to adsorp hydrogen.

### 2. COMPUTATIONAL DETAILS

The geometry of alkali metal doped and undoped  $C_{60}$ (fullerene) structures were optimized by DFT calculations employing unrestricted B3LYP functional (suitable for metal doped nanocluster) with 6-31G basis set<sup>16, 17</sup>. Gaussian 09 packages were used to perform all quantum mechanical calculations.

The adsorption energies were calculated by the following equation<sup>18, 19</sup>

$$E_{ad} = E(Fullerene + X + H_2) - E(Fullerene + X) - E(H_2)$$
(1)

Where  $E(Fullerene + X + H_2)$  is the total energy of metal (X=Li, Na, K) doped fullerene absorbed with hydrogenmolecules, E(Fullerene + X) is the total energy of the metal (X=Li, Na, K) doped fullerene, and  $E(H_2)$  is the total energy of thehydrogen molecule.

The work function  $\phi$  is the minimum energy needed (Fig. 1) to extract one electron from the Fermi level of a material to an infinitedistance<sup>20</sup>.

$$\Phi = V_{el\,(+\infty)} - E_F \tag{2}$$

Where  $V_{el(+\infty)}$  is considered to be zero which is the electrostatic potential energy of the electron at infinite distance from the surface, and  $E_F$  is Fermi level energy.

The Fermi level energy is calculated as<sup>21</sup>

$$E_F = E_{HOMO} + \frac{(E_{LUMO} - E_{HOMO})}{2}$$
(3)

where  $E_{HOMO}$  is the energy of the highest occupied molecular orbital and  $E_{LUMO}$  is the energy of the lowest unoccupied molecular orbital.

The band gap energy of the material is calculated as<sup>22</sup>



Fig.1. A schematic view of Femi level energy, work function, and HOMO and LUMO levels ofa semiconductor. The energy in vacuum is assumed to be zero.

The hardness  $(\eta)$  and softness (S) of the adsorbent was calculated using the Koopmans' theorem <sup>23</sup> through the following equations

$$\eta = \frac{(E_{LUMO} - E_{HOMO})}{2} \tag{5}$$

$$S = \frac{1}{2\eta} \tag{6}$$

Chemical potential ( $\mu$ ) <sup>24</sup>and electrophilicity ( $\omega$ )<sup>25, 26</sup> of the system is defined by the equation given below:

$$\mu = -(E_{LUMO} + E_{HOMO}) \tag{7}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{8}$$

#### **3. RESULTS AND DISCUSSION**

#### 3.1 Optimized Structure Study

The optimized structure of fullerene and Li, Na and K doped fullerene was investigated by density functional theory along with B3LYP hybrid correlational and 6-31G basis set using Gaussian 09 simulation packages. Figure 2(a) represents the optimized geometry of the pristine fullerene structure consisting sixty carbon atoms. The frontier molecular orbitals were also observed for the pristine and doped structures, as quantum chemically it is important to understand the interaction between two reactants<sup>27</sup>. For the optimized pristine fullerene structure, the HOMO and LUMO orbitals and charge distribution are shown in the figure 2 (b) and 2 (c).



Fig.2. Optimized (a) structure, (b) HOMO iso-charge distribution, and (c) LUMO charge distribution of fullerene (C<sub>60</sub>)

Doping of the metallic atoms to the pristine fullerene changes the bond length between the metallic atom and

carbon significantly. For the single bonded Li with C the bond length was observed as 2.167 angstrom while for the double bonded Li with C the bond length was observed as 2.108 angstrom. The bond length of metal-carbon was further increased with the increase in the electron density. For Na doped fullerene the single bonded metal-carbon bond was 2.534 angstrom while double bonded metalcarbon bond length was 2.372 angstrom. This bond length was maximum for the potassium doped fullerene structures. For K doped fullerene the single bonded metalcarbon bond length was 2.982 angstrom and the double bonded metal-carbon bond length was 2.811 angstrom. So, from the analysis it is clear that the doping with less electronegative atoms than carbon increases the bond length and every metal-carbon bond is greater in length than carbon-carbon bonds. It further increases with the doping with the atoms of higher electron density and hence the highest metal-carbon bond length was observed for the potassium-carbon bond as K has the highest electron density among our doping atoms.



(b) (c) Fig.3. (a) Optimized structure, (b) HOMO iso-charge distribution, and (c) LUMO iso-charge distribution of fullerene (C<sub>59</sub>Li)

To analyze the charge transfer characteristics of the complexes, the HOMO-LUMO charge distribution was observed for the both pristine and metal doped fullerene (MDF). The result is shown in the figure 2 (b, c), 3 (b, c), and 3 (b, c). Here, some atoms worked as a donors and some as acceptors and the energy difference between

those bonding and anti-bonding orbitals cause the molecules to interact <sup>28</sup>. This charge transfer changes the bang gap of the structures which is clearly observed and tabulated in the Table 1. So, the adsorption process of  $H_2$  molecule on MDFs can be understood by HOMO-LUMO charge distribution. Furthermore,  $H_2$  adsorbed MDF was optimized to observe the effect of adsorption of  $H_2$  to the MDFs which was shown in the Fig 6.



Fig.4. (a) Optimized structure, (b) HOMO iso-charge distribution, and (c) LUMO iso-charge distribution of fullerene (C<sub>59</sub>Na)

Depending on the electron density, the distance between the metal and H<sub>2</sub> molecule also varied. The least distance between the metal and H<sub>2</sub> molecule was observed for H<sub>2</sub>-C<sub>59</sub>Li system as 2.2558 and 2.2557 angstrom and the maximum distance was observed for H<sub>2</sub>-C<sub>59</sub>K, as expected, as 3.3735 and 3.3729 angstrom while it is 2.77 and 2.74 angstrom for the H<sub>2</sub>-C<sub>59</sub>Na system. As clearly C<sub>59</sub>Li has less distance from the absorbent structure than the other structure, it can be concluded that  $C_{59}$ Li has the higher adsorption ability than the other doped fullerene. The adsorption of the H<sub>2</sub> molecule on the MDFs also changed the bond length between the metal and carbons. In H<sub>2</sub>-C<sub>59</sub>Li system, the bond length of the single bonded metal-carbon was 2.17 angstrom while it was 2.01 angstrom for the double bonded metal-carbon bond. Similarly, it was 2.54 and 2.37 angstrom for H<sub>2</sub>-C<sub>59</sub>Na system while 2.98 and 2.81 angstrom for H<sub>2</sub>-C<sub>59</sub>K system for the single and double bonded metal-carbon bonds respectively.



Fig.5. (a) Optimized structure, (b) HOMO iso-charge distribution, and (c) LUMO iso-charge distribution of fullerene (C<sub>59</sub>K)

# 3.2 Energy Study

The structural strength of the adsorbed nanocluster can be realized by the investigation of the adsorption energy  $(E_{ad})$  of that system. Negative values of the systems indicate a stable one and more negative the value of adsorption energy is, more stable the system is. In our investigated structures all of the H<sub>2</sub> molecule adsorbed structures can be concluded as stable structures as they possess negative values for the adsorption energies. The most negative value for the adsorption energy was found for the  $H_2$ - $C_{59}$ Li structure as -0.7 eV where the least value was found as -0.03 eV for H<sub>2</sub>-C<sub>59</sub>K system. For H<sub>2</sub>-C<sub>59</sub>Na system the value was found as -0.05 eV. So, depending on adsorption energies of the H<sub>2</sub> molecule adsorbed MDFs the most stable system can be concluded as the  $H_2$ -C<sub>59</sub>Li system as it possesses the most negative value of the adsorption energy compared to other two MDFs, H2- $C_{59}$ Na and  $H_2$ - $C_{59}$ K.



Fig.6.Optimized structure of (a)  $H_2\text{-}C_{59}Li,$  (b)  $H_2\text{-}C_{59}Na,$  and (c)  $H_2\text{-}C_{59}K$ 

The HOMO-LUMO energy and energy gap of the structures was observed and analyzed as several significant changes was observed due to the doping of the metallic atoms into the pristine fullerene and H<sub>2</sub> molecule adsorption into those MDFs. The HOMO energy of the pristine fullerene was observed as -6.2486 eV while it was decreased due to the doping of the metallic atoms into it. Among the metal doped structures, the maximum value for the HOMO energy was observed for theC<sub>59</sub>Li system as -5.5402 eV along with the minimum value as -4.7462 eV for C<sub>59</sub>K system while it was -5.1079 eV for the C<sub>59</sub>Na system. The adsorption of H<sub>2</sub> molecule further reduced the value of the HOMO energies of the MDFs. As the MDFs, the highest value for H<sub>2</sub> molecule adsorbed MDF was observed for  $H_2$ -C<sub>59</sub>Lias -5.5204 eV while the least value was observed for H2-C59K as -5.5204 eV. For H2-C<sub>59</sub>Na it was observed as -5.0893 eV. The LUMO energies of the structures showed some interesting variation. For the pristine fullerene it was observed as -3.3753 eV and it increases, for the doping of Li atom, to -3.9685 eV for the  $C_{59}$ Li system. Then it reduced to -3.6118 and -3.2289 eV for C59Na and C59K system respectively. The adsorption of H<sub>2</sub> molecule slightly reduced the values of the LUMO energies of the MDFs. The maximum value for the LUMO energy was observed for the H<sub>2</sub>-C<sub>59</sub>Li system as -3.9421 eV and the least was observed for H<sub>2</sub>-C<sub>59</sub>K system as -3.2226 eV while it was -3.5900 eV for H<sub>2</sub>-C<sub>59</sub>Na system. After these variation in the HOMO and LUMO energies, the overall HOMO-LUMO energy gap of the MDFs was decreased compare to the pristine fullerene. For the pristine fullerene the HOMO-LUMO energy gap was 2.8733 eV while it reduced to 1.5717 eV for C<sub>59</sub>Li system. It further reduced to 1.4961 and 1.5173 eV for C<sub>59</sub>Na and C<sub>59</sub>K systems respectively.

Structure	E <sub>ad</sub> (eV)	$E_{\rm HOMO} (eV)$	$\mathbf{E}_{\mathbf{F}}\left(\mathbf{eV}\right)$	E <sub>LUMO</sub> (eV)	$E_{g}(eV)$	φ (eV)	μ (eV)
C <sub>60</sub>		-6.2486	-4.81195	-3.3753	2.8733	4.81195	9.6239
C <sub>59</sub> Li		-5.5402	-4.75435	-3.9685	1.5717	4.75435	9.5087
C <sub>59</sub> Na		-5.1079	-4.35985	-3.6118	1.4961	4.35985	8.7197
C <sub>59</sub> K		-4.7462	-3.98755	-3.2289	1.5173	3.98755	7.9751
H <sub>2</sub> -C <sub>59</sub> Li	-0.0686	-5.5204	-4.73125	-3.9421	1.5783	4.73125	9.4625
H <sub>2</sub> -C <sub>59</sub> Na	-0.0452	-5.0893	-4.33965	-3.5900	1.4993	4.33965	8.6793
H <sub>2</sub> -C <sub>59</sub> K	-0.0267	-4.7429	-3.98275	-3.2226	1.5203	3.98275	7.9655

Table 1.The adsorption energy (Ead, eV) of H<sub>2</sub> from C<sub>60</sub> and Li, Na, K-doped fullerene. Energy of HOMO, LUMO, Fermi level ( $E_F$ ), Energy gap ( $E_g$ ), work function ( $\phi$ ) and chemical potential ( $\mu$ ) are in eV.

Furthermore, the adsorption of the  $H_2$  molecule to the MDFs slightly increased the values of HOMO-LUMO energy gap. Here, the maximum was found as 1.5783 for  $H_2$ -C<sub>59</sub>Li system and the least was found as 1.4993 eV for  $H_2$ -C<sub>59</sub>Na system while it was 1.5203 eV for  $H_2$ -C<sub>59</sub>K system.

The Fermi energy level ( $E_F$ ), work function ( $\phi$ ) and chemical potential  $(\mu)$  was also calculated and analyzed. The Fermi energy level also gradually decreased with the doping with metallic atoms. For pristine fullerene it was found at -4.81195 eV and decreased to -4.75435 eV for C<sub>59</sub>Li system. The least value was observed as -3.98755 eV for C<sub>59</sub>K system and it was -4.35985 for C<sub>59</sub>Na system. Adsorption of the H<sub>2</sub> molecule to the MDFs further reduced the value of Fermi energy level. Here, the maximum value was found as -4.73125 eV for H<sub>2</sub>-C<sub>59</sub>Li system along with a least value for H<sub>2</sub>-C<sub>59</sub>K system as -3.98275 eV. For H<sub>2</sub>-C<sub>59</sub>Na system it was -4.33965 eV. The work function of the system was also analyzed as it is important to know about the emission behavior of the structures. Work functions of the structures also follows exactly same trend as the Fermi energy level and it was tabulated in the Table 1. Following the same trend as the Fermi energy and the work function, the chemical potential of the fullerene also decreased with the doping with metallic atoms and it was further decreased with the adsorption of the H<sub>2</sub> molecule. The highest value for the chemical potential was found for pristine fullerene as 9.6239 eV when it was reduced to 9.5087 eV for C<sub>59</sub>Li system. It further reduced to 8.7197 and 7.9751 eV for C<sub>59</sub>Na and C<sub>59</sub>K systems respectively. For H<sub>2</sub> adsorbed MDFs the highest value of the chemical potential was found as 9.4625 eV for H<sub>2</sub>-C<sub>59</sub>Li system with a least value as 7.9655 eV for  $H_2$ -C<sub>59</sub>Na system while it was 8.6793 eV for H<sub>2</sub>-C<sub>59</sub>Na system.

#### 3.3 Optical Properties Study

The optical properties were studied by investigating the computed UV-Vis spectra, IR spectra and circular dichroism (CD) data. Among these methods UV-Vis spectra of the structures was used to understand its absorbance behavior to lights from different wavelengths, IR spectra was used to observe different modes of vibrations hence its stability and possibility of synthesis, and CD spectrum shows the difference in absorbance of right and left circular polarized light when electromagnetic radiation is absorbed by a substance.

Figure 7 shows the comparison of the absorption of light photon by Li, Na and K decorated fullerene nanostructures. We have theoretically calculated the excited state of our structures by considering thirty number of states by using Gaussian 09 program package.Two of the MDFs, C<sub>59</sub>Li and C<sub>59</sub>Na, showed a very wide optical band compared to the other MDF C<sub>59</sub>K as shown in the Fig. 7. The Li doped fullerene adsorbed lights mostly from the infra-red regions with a range of 460 nm to 3400 nm while it most efficiently absorbs red lights as a maximum peak was found at 632 nm in the UV-Vis spectra of C<sub>59</sub>Li system. On the other side, C<sub>59</sub>Na system showed almost similar optical behavior as C<sub>59</sub>Li system when it comes to the UV-Vis spectra. This Na doped fullerene system also absorbs light from 500 nm to 3000 nm with a peak absorption at 710 nm. But unlike these two systems, K doped fullerene shows a narrow optical band gap and absorbs the lights from 520 nm to 1750 nm with a peak absorption at 864 nm. So, as C<sub>59</sub>Li and C<sub>59</sub>Na have excellent wide band gap, apart from its application as hydrogen storage device, it can be used in the high temperature device fabrication industry with some medical applications<sup>29-31</sup>.



Fig. 7. UV Visible Spectra for doped fullerene

The IR spectra of the structures were investigated and the result is shown in the Figure 8.



Fig. 8. IR Spectra for doped and undoped fullerene

None of the structures showed any imaginary frequency which indicate its possibility of synthesis and finding in the nature in a stable form. This spectroscopy is usually done by the absorptions of mid-range IR radiation to the structures and then observe its transitions between the molecular vibrational levels. The IR spectroscopy then measures those particular transitions. In our case, we investigated the simulated data of IR spectra up to 1750 cm<sup>-1</sup>. The pristine fullerene shoes four peaks in the IR spectra at 554, 586, 1208, and 1480 cm<sup>-1</sup> with the maximum peak at 554 cm<sup>-1</sup>. On the other side the Li doped fullerene showed several peaks starting from 161 cm<sup>-1</sup> and goes up to 1623 cm<sup>-1</sup> with a maximum peak at 384 cm<sup>-1</sup>. The Na doped fullerene also have many peaks starting from 110 cm<sup>-1</sup> with a maximum peak at 1477 cm<sup>-1</sup> and goes up to 1566 cm<sup>-1</sup>. Finally, like other two MDFs the K doped fullerene also have several peaks from 61

cm<sup>-1</sup> to 1566 cm<sup>-1</sup> with a maximum peak at 153 cm<sup>-1</sup>. Another importance of the vibrational spectrum of a system is it can be used as the fingerprint of that system to identify in the future. So, our investigated vibrational modes of these MDFs will help scientists to characterize these structures in the future.

Finally, the CD spectrum of the structures was investigated and visualized at Fig. 9. CD spectrum indicates the optical activity of a molecule and it is seen in the absorbance band in the chiral molecule. The  $C_{60}$  structure doesn't show optical activity hence we didn't observe any CD spectrum. By observing CD spectrum from Fig.9, we see that metal doped  $C_{60}$  structures are optically active and optical activity occurs in those structures for their asymmetric charge distribution.

#### 3.4 HOMO-LUMO Orbital Analysis

The orbital analysis is done by investigating HOMO energy ( $E_{HOMO}$ ), LUMO energy ( $E_{LUMO}$ ), HOMO-LUMO energy gap ( $E_g$ ) and Fermi level energy ( $E_F$ ). The DOS plot gives the idea about HOMO-LUMO energy gap (Eg) and the unpaired electron distribution on the complex system. The values of  $E_g$  are 2.8733, 1.5717, 1.4961, 1.5173, 1.5783, 1.4993 and 1.5203eV for C<sub>60</sub>, C<sub>59</sub>Li, C<sub>59</sub>Na, C<sub>59</sub>K, H<sub>2</sub>-C<sub>59</sub>Li, H<sub>2</sub>-C<sub>59</sub>Na and H<sub>2</sub>-C<sub>59</sub>K structure respectively shown in Table 1 and we realize these values by DOS plot from Fig.10 which follow the similar trend as  $E_g$ . These  $E_g$  and DOS spectrum also reaffirm the UV-Vis spectroscopy analysis. The DOS spectrum shows the alpha and beta molecularorbital and indicates the structure has spin density and shows magnetic property.

#### 3.5 Dipole Moment and Global parameters

The dipole moment (DM) of a structure specifies that the charge distribution of a structure is symmetric or asymmetric and more dipole moment indicates more polarity. So, it is expected that, the value of the DM will increase with the increase in the charge transfer. Hence to observe and analyze the DM, the Mullikien charge transfer also observed which was tabulated in the Table 2. For, pristine fullerene no charge transfer was observed hence there wasn't any DM present. This represent a symmetric charge distribution for the pristine fullerene structure with no polarity and reactivity.





Fig. 10.Density of states (DOS) spectra for C<sub>60</sub>, C<sub>59</sub>Li, C<sub>59</sub>Na and C<sub>59</sub>K

Table 2. Mullikien charge ( $Q_{Mulliken}$ ), dipole moment ( $\mu_D$ ) in debye unit, Hardness ( $\eta$ ) electrophilicity ( $\omega$ ) in Electron Volt (eV) unit and Softness (S) in eV<sup>-1</sup> unit.

Structure	Q <sub>Mulliken</sub>	μ <sub>D</sub> (Debye)	η (eV)	S (eV <sup>-1</sup> )	ω (eV)
C <sub>60</sub>	0.002	0	1.437	0.348	32.23
C <sub>59</sub> Li	-0.328	2.29	0.786	0.636	57.53
C <sub>59</sub> Na	-0.559	6.75	0.748	0.668	50.82
C <sub>59</sub> K	-0.724	11.72	0.759	0.659	41.92
H <sub>2</sub> -C <sub>59</sub> Li	-0.24	2.66	0.789	0.634	56.73
H <sub>2</sub> -C <sub>59</sub> Na	-0.523	7.07	0.750	0.667	50.24
H <sub>2</sub> -C <sub>59</sub> K	-0.698	11.8	0.760	0.658	41.73

Doping of the metal atom to the pristine fullerene caused some charge transfer between the metal atom and the carbon atom from the fullerene and the charge symmetry was broken. For this reason, some DM was observed for the MDFs. The highest DM was observed for the C<sub>59</sub>K as 11.72 debye with the highest amount of Mullikein charge transfer as -0.724. The least value for the DM was observed for the  $C_{59}$ Li as 2.29 debye with the least charge transfer value as -0.328. Finally, for the C<sub>59</sub>Na value for the DM was observed as 6.75 debye with a charge transfer of -0.559. Furthermore, the adsorption of H<sub>2</sub> molecule to the MDFs increased values of DM slightly with more charge transfer than MDFs. Following the same trend as MDFs, the highest value for the DM was observed for H<sub>2</sub>-C<sub>59</sub>K as 11.8 debye with the highest amount charge transfer as -0.698. And the least amount of DM was observed for  $H_2$ - $C_{59}Li$  as 2.66 debye with a charge transfer of -0.24 while for  $H_2$ - $C_{59}Na$  system the value of DM and charge transfer was 7.07 debye and -0.523 respectively. So, in terms of DM and charge transfer the most reactive system was  $H_2$ - $C_{59}K$  with the most polarity where no polarity and reactivity was observed for the  $C_{60}$ . So, doping of TM atoms increases the polarity and reactivity of the fullerene structures significantly and the adsorption of  $H_2$  further increased it.

The global parameters such as hardness  $(\eta)$ , electrophilicity (w) and softness (S) have been calculated from HOMO-LUMO energy as shown in Table-2. The doping of the metal atom to the pristine fullerene decreased the hardness of the structure along with an increase in the softness and electrophilicity. For pristine fullerene the value of the hardness was 1.437 eV and it

drops down to the 0.786 eV for  $C_{59}Li$  system. Then it further decreased for the  $C_{59}K$  and  $C_{59}Na$  and became 0.659 and 0.668 eV. The adsorption of H<sub>2</sub> molecule again slightly increased the hardness. Here, the hardness was observed for H<sub>2</sub>-C<sub>59</sub>Li as 0.789 eV while the least was found as 0.75 eV for H<sub>2</sub>-C<sub>59</sub>Na along with 0.760 eV for the H<sub>2</sub>-C<sub>59</sub>K system. As expected, the softness increases with the decrease of the hardness for the MDFs. The softness was increased to 0.636, 0.668, and 0.659 eV<sup>-1</sup> for  $C_{59}Li$ ,  $C_{59}Na$ , and  $C_{59}K$  systems respectively compared to the 0.348 eV<sup>-1</sup> for the pristine fullerene. Being opposite to the hardness, adsorption of the H<sub>2</sub> molecule further decreased the softness slightly. It became 0.634, 0.667, and 0.658 eV<sup>-1</sup> respectively for the H<sub>2</sub>-C<sub>59</sub>Li, H<sub>2</sub>-C<sub>59</sub>Na, and H<sub>2</sub>-C<sub>59</sub>K respectively.

Finally, following the same trend as the softness, the electrophilicity of MDFs also increased compared to the pristine fullerene. It was 32.23 eV for the pristine fullerene and became 57.53, 50.82, and 41.92 for the C<sub>59</sub>Li, C<sub>59</sub>Na, and C<sub>59</sub>K systems respectively. But unlike the softness, it was slightly reduced due to the adsorption of H<sub>2</sub> molecule to the MDFs. Among the H<sub>2</sub> adsorbed MDFs the highest value for the electrophilicity was observed for the H<sub>2</sub>-C<sub>59</sub>Li as 56.73 eV along with the least value for H<sub>2</sub>-C<sub>59</sub>K system as 41.73 eV while it was 50.24 eV for H<sub>2</sub>-C<sub>59</sub>Na system.

# 4. CONCLUSIONS

Various properties of C60 and alkali metal doped C60 were investigated and both the results were compared. The Mulliken charge analysis revealed that significant amount of charge transfer occurred due to the doping of metal atoms to the pristine fullerene. The adsorption energy study showed that  $C_{59}$ Li structure is more stable as it got the most negative value for the adsorption energy among our investigated systems. Our UV-Vis spectroscopystudy indicated that optical band gap decreased due to the doping ofalkali metal atom to the pristine fullerene. By CD spectrum we understood that the  $C_{60}$  become optically active material by doping. The HOMO-LUMO energy gap or optical band gap is calculated from the values of HOMO and LUMO energy and it is decreased due to the doping of metal atoms which is confirmed by DOS spectra. The global indices studies revealed the hardness, softness, and charge symmetry of the complexes. These parameters followed the same trend as observed before. So, it can be expected that alkali metal-decorated fullerene could be considered as a potential high-capacity hydrogen storage medium.

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