



Theoretical Study on the Enhancement of Nonlinear Optical and Electronic Responses of Sumanene through Interaction with Alkali Metals (Li, Na, and K)

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ABSTRACT

Sumanene molecule with highly symmetric (C_{3v}) is polycyclic aromatic hydrocarbons. In this work, we report a quantum chemical calculation on the considered complexes, which were obtained by sumanene decorated with alkali metals (Li, Na, and K). Interestingly, the adsorption alkali metals by sumanene molecule lead to reduction E_g gap because of high energy levels which are formed under influence of interactions with alkali metals. The results indicate that the effect of alkali metals adsorption by sumanene is to greatly increase the β_0 value. Among the obtained complexes, the largest first hyperpolarizability (β_0) of the sumanene@Na and sumanene@K complexes were 2336323 au and 2904321 au, respectively.

1. Introduction

Design and fabrication of new materials with nonlinear optical responses for application in optical devices has gained attention in contemporary investigations [1-5]. Various types of materials possess nonlinear optical properties [6-9]. Nowadays scientists are interested in nanoscale materials because of their unique properties and extreme different functionalities [10-20]. Many investigations have demonstrated that the families of carbon nanostructures have superior nonlinear optical properties due to their individual structures [21-32]. It is shown that excess electron plays a significant role in increasing the first hyperpolarizability (β_0) [30, 33-41], so molecular moieties involving the excess electron can display the significant nonlinear optical (NLO) response. Recently, NLO properties of conjugated π -electron systems have been a focus of attention due to large ultrafast non-resonant NLO responses [42, 43]. The development of

empirical databases that correlate NLO response and molecular structures is an important component of research in the field. Such databases are important to verify theoretical and computational approaches to the prediction of NLO properties and evaluation of molecular engineering strategies seeking to potential candidates for high-performance NLO materials.

Sumanene ($C_{21}H_{12}$) exhibits bowl-shaped molecular structure with C_{3v} symmetry. It is composed of alternating benzene and cyclopentadiene rings arranged around the central benzene ring, forming a π -conjugated molecule. The arrangement aligns with the most minimal C_{3v} -symmetric component for the structural patterns of fullerenes or the end-caps of carbon nanotubes [44, 45]. Sakurai et al. accomplished the synthesis of sumanene in solution-phase in 2003. This synthetic approach facilitated the study of sumanene's unique physical properties, including its bowl-shaped structure, bowl inversion, columnar crystal packing, electron conductivity, metal complexes, and bowl chirality [46]. Purushotham and Sastry [47] recently

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undertook an extensive study of acene-fused buckybowls, revealing their electronic properties' potential for practical applications. Furthermore, experimental results from Amaya et al. [48] underscore the significant potential of sumanene as an electronic material. Two non-equivalent π -surfaces, concave (endo) and convex (exo), are readily accessible in sumanene molecule as a clear-cut model molecule for examining the differences and similarities of metal binding sites on both types of curved faces [49, 50]. "Hub" carbon (Ch) specified by six internal carbon atoms, and "rim" carbons (Cr) determined by nine outermost [51]. Bridge carbons (Cb) have been distinguished by the six carbon atoms between the rim and hub of sumanene (See Fig. 1a). Sumanene may have potential applications for the adsorption of various species, particularly on either the concave or convex side, as indicated by the literature [52-55].

Sumanene was introduced as potential materials of hydrogen storage and ion battery [56-59]. Also, the interaction between sumanene and alkali cations has been studied theoretical and experimental in recent years [60, 61]. In the previous study, Asif and co-worker [61] have shown that superalkali-doped sumanene systems as ideal NLO prospects for future NLO applications. The main contribution of the present study is to investigate the influence of the interaction of the alkali atoms with the sumanen molecule on its electro-optical features. Our results reveal that first hyperpolarizability of sumanene molecule decorated with Na and K atoms are increased remarkably in comparison with previous studies [21]. Since the sumanene molecule has unique physiochemical properties, the result of the present study may lead to design and fabrication of a nanosheet with tunable electro-optical properties.

2. Computational details

The M06-2X functional [62] which is acceptable to be employed in many nanoscales molecular systems [63, 64] in combination with new DFT-D3 method that was recently reported by Grimme et al. [65, 66] has been used in this study. Therefore, the geometries of the sumanene molecule by the restricted approach and their complexes with alkali metals (M= Li, Na and K) by the spin-unrestricted approach were fully optimized at the M06-2X-D3 with the standard 6-31+G(d) basis set. The correlated $\langle S^2 \rangle$ values are about 0.764–0.769 for multiplicity 2, in the sumanene-M (M= Li, Na and K). These results are very similar to the value of 0.750, for the pure doublet states. Therefore, the spin

contamination is insignificant and the computational results are reliable. The harmonic vibrational frequencies were also calculated at the same level of optimization to prove that an optimized geometry has only real frequencies. The charge transfer between the sumanene and the alkali metals is calculated by using natural bond orbitals (NBO) analysis [67] in B3LYP-D3 method to prevent of overestimates LUMO and energy gap. All calculations were performed using Gaussian 09 quantum chemistry code [68] with default convergence criteria.

The energy gap (E_g) of the intended structures explains as:

$$E_g = (\varepsilon_L - \varepsilon_H) \quad (1)$$

where ε_H is the highest occupied molecular orbital (HOMO) energy and ε_L is the lowest unoccupied molecular orbital (LUMO) energy, respectively. Indeed, total density of states (TDOS) and partial density of state (PDOS) analysis was performed employing the GaussSum program [69].

The system energy in the weak and homogeneous electric field can be shown as [70, 71].

$$E = E^0 - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \dots \quad (2)$$

where E^0 and F_i are the molecular total energy without the electric field and the electric field component along i direction, respectively. The μ_i , α_{ij} and β_{ijk} denote dipole, polarizability, and the first hyperpolarizability, respectively. The magnitude of the polarizability (α) and total first static hyperpolarizability (β_0), a scalar quantity distinguished as nonlinear optical response (NLO) coefficient, is assessed using these components according to the following equations.

$$\alpha = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3)$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (4)$$

in which

$$\beta_i = \frac{3}{5} (\beta_{iii} + \beta_{ijj} + \beta_{ikk}) \quad i, j, k = X, Y, Z \quad (5)$$

The first static hyperpolarizability has been evaluated by the finite-field (FF) approach under an electric field magnitude of 0.001 a.u., utilizing M06-2X-D3 functional with 6-31+G(d), basis set.

The interaction energy (E_{int}) due to the interaction of sumanene molecule with alkali atoms (M=Li, Na and K) is obtained as:

$$E_{int} = E_{sumanene-M} - E_{sumanene} - E_M + E_{BSSE}$$

M= Li, Na and K (6)

where $E_{\text{sumanene-M}}$ represents the total electronic energy of the sumanene-M structure. The term E_{sumanene} and E_M terms are the total electronic energy of isolated sumanene molecule and the alkali atoms (M=Li, Na and K), respectively. The basis set superposition error (BSSE) is also involved in the computation of the interaction energy using counterpoise method [72].

3. Results and Discussions

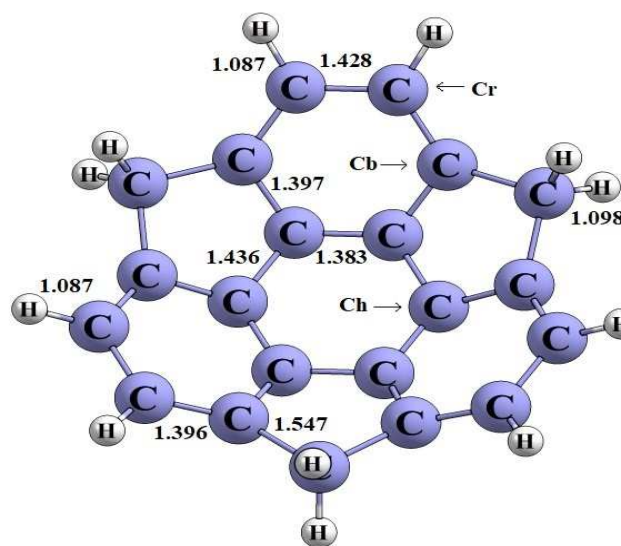
3.1. Optimized structure and NLO response of sumanene molecule

The optimized structure of sumanene is presented in Fig 1. The important geometrical parameters have been shown in Fig. 1a. These results are in good agreement with the previous reports [56, 57]. The electronic and optical properties of this molecule are also investigated. The obtained frontier molecular orbital energies (ϵ_H and ϵ_L), and the calculated E_g value for the considered nanostructure are listed in Table 1. The obtained E_g for this molecule is 4.69 eV. Total density of state (TDOS) spectra of the sumanene molecule is depicted in Fig. 1b. The calculated values of polarizability (α) and hyperpolarizability (β_0) are also listed in Table 1. The obtained results indicate that this considered molecule has not strong NLO response due to the insignificant amount of first hyperpolarizability.

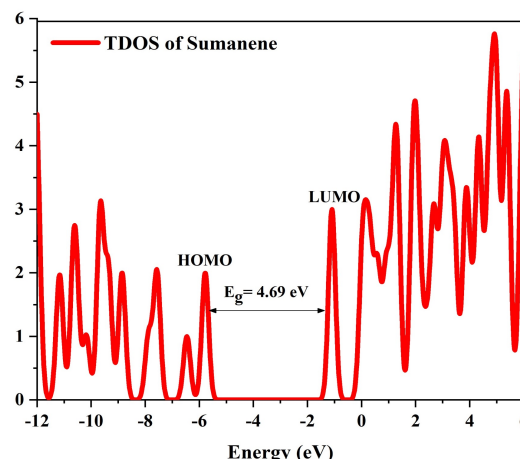
3.2. Geometrical characteristic and Natural Bond Orbital (NBO) of sumanene@M (M= Li, Na and K)

Alkali atoms have been considered to be adsorbed on the surface of the sumanene molecule. Some various initial adsorption sites are selected including a top of different carbon atoms and C-C bonds, in concave and convex positions of the sumanene molecule. This section involves the determination of the minimum energy conformation among all sumanene@M (M= Li, Na and K) systems shown in Fig. 2. After full optimization of the considered systems using M06-2X-D3/6-31+G(d) theory, two stable structures with real vibrational frequencies were identified for sumanene@Li complexes in which the lithium atom interacted with sumanene molecule in concave and convex situation as panels A and B in Fig. 2, respectively. However, four stable structures with real vibrational frequencies was identified for sumanene@M

complexes (M= Na and K) in which the alkali atom interacted with sumanene molecule in the concave and convex situations (C-J configurations).



(a)



(b)

Fig. 1. (a) The optimized geometry, and (b) Total density of states (TDOS), of pristine Sumanene (The dashed line in TDOS plots indicates Fermi energy).

Some important geometrical parameters are shown in Fig. 2. In these complexes, the interaction distances are about 2.179-3.265 Å.

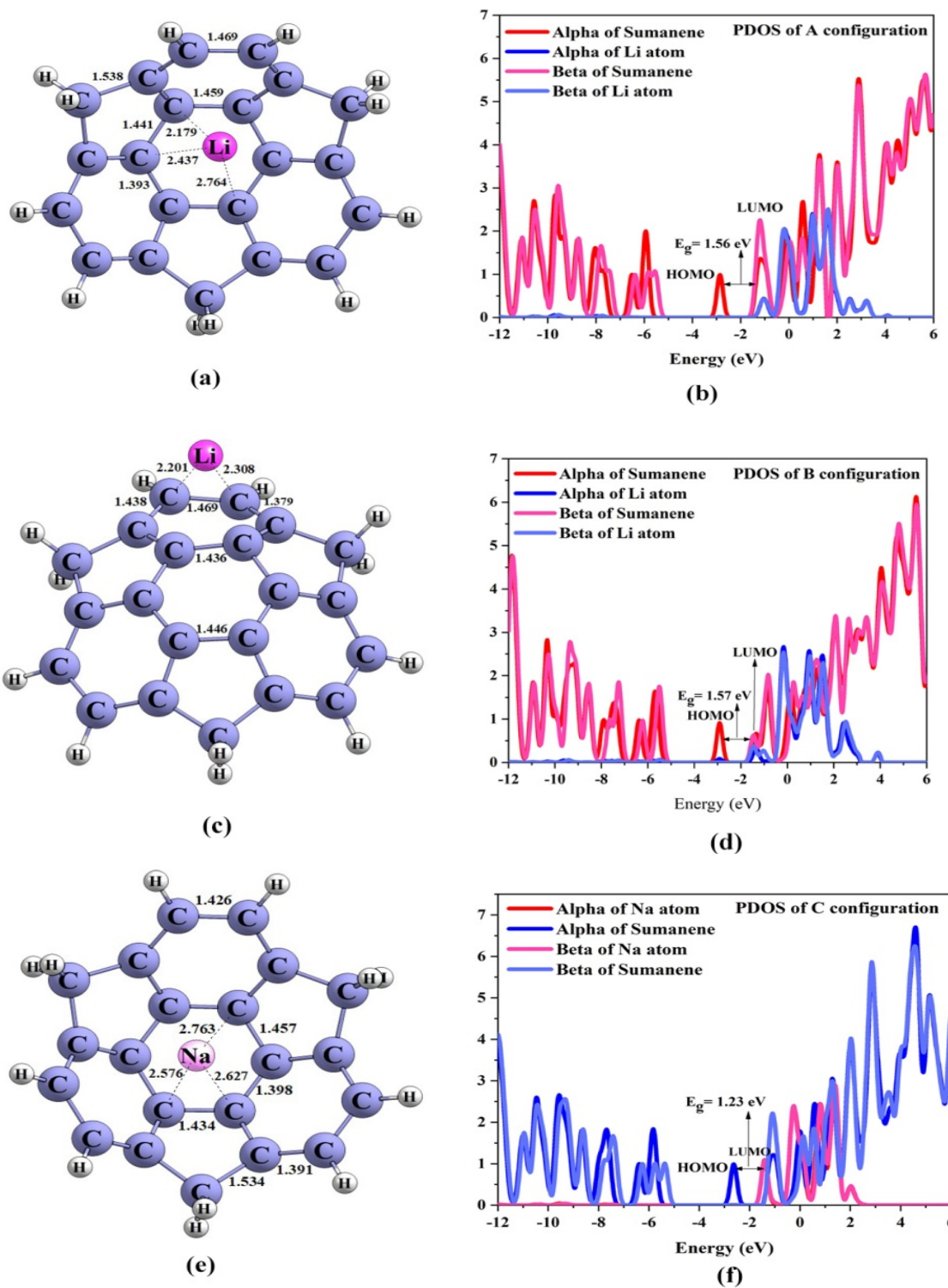


Fig. 2. The optimized geometry obtained structures a) A, c) B, e) C, g) D, i) E, k) F, m) G, o) H, q) I, and s) J configuration and Total density of states (TDOS) (b, d, f, h, j, l, n, p, r, and t) for Sumanen@M (M=Li, Na and K) configuration.

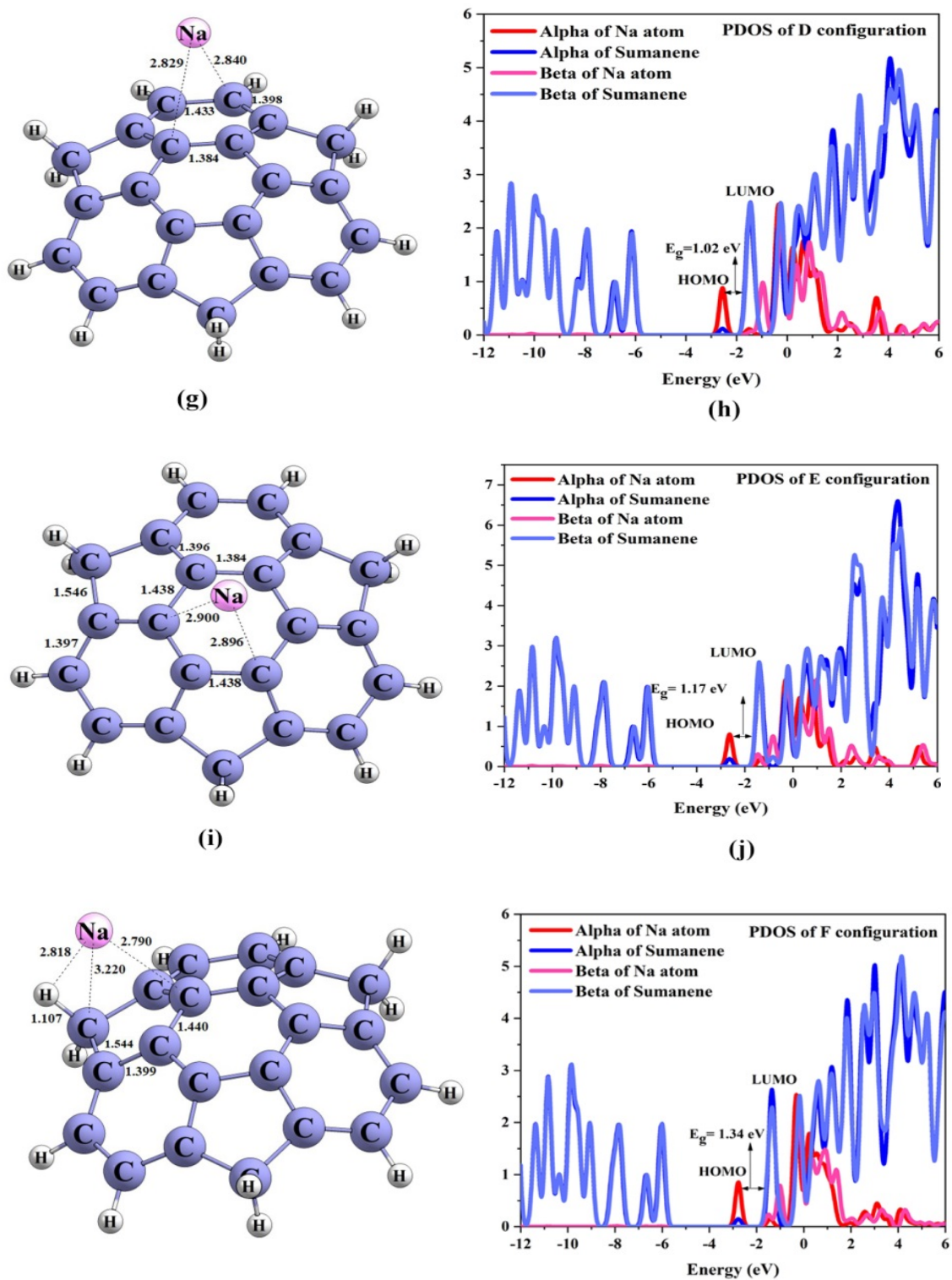
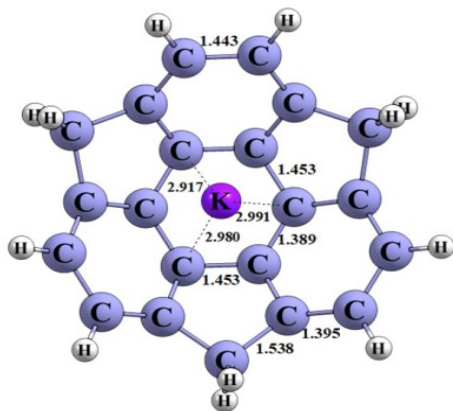
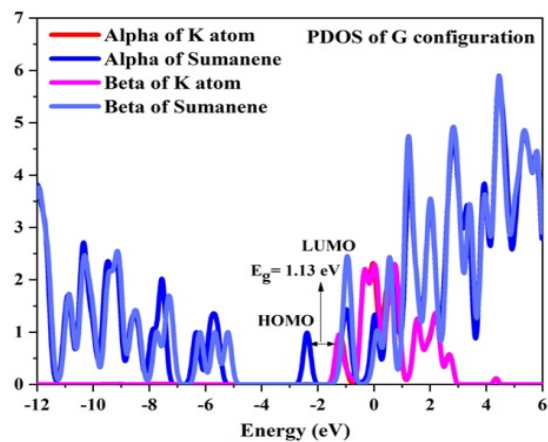


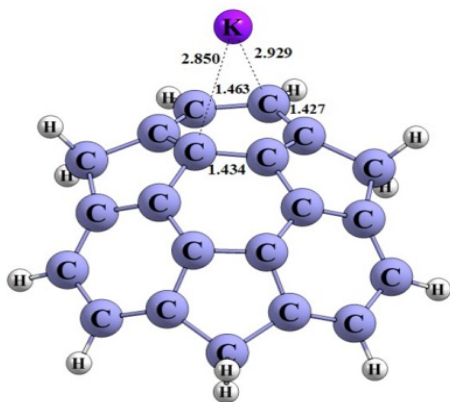
Fig. 2. In continued.



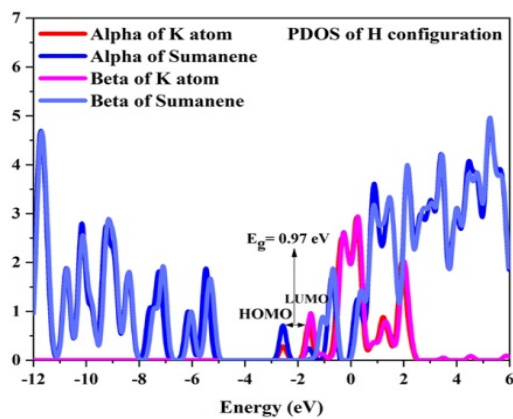
(m)



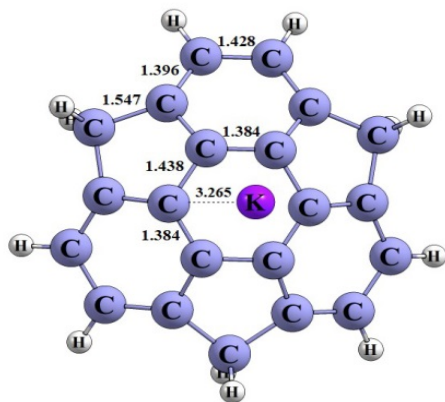
(n)



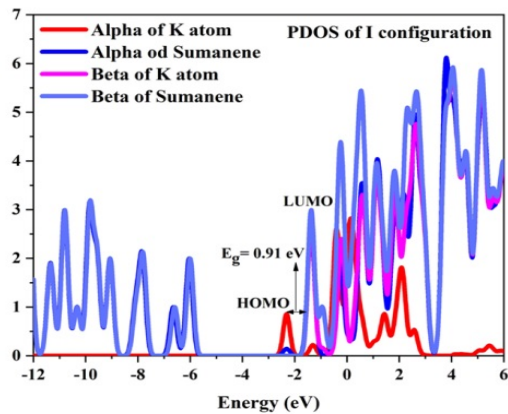
(o)



(p)



(q)



(r)

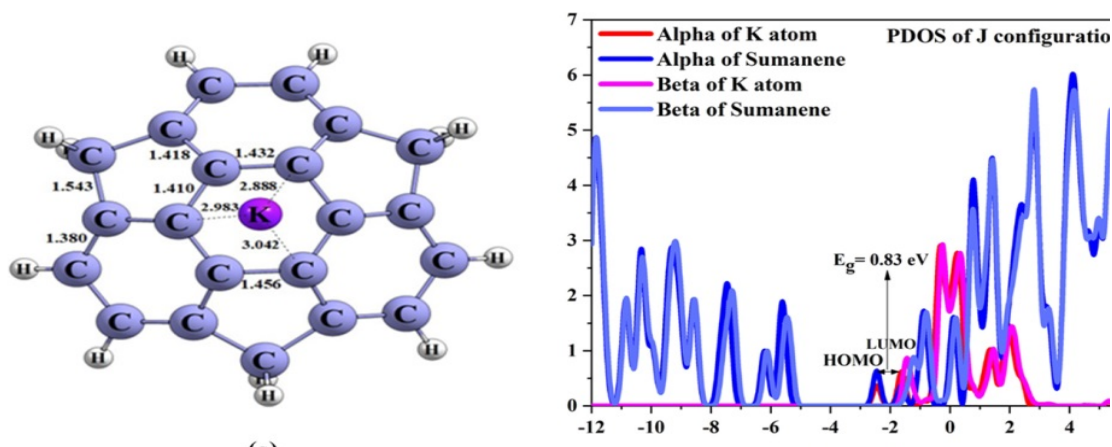


Fig. 2. In continued.

It is obvious that the vertical distances between the alkali atom and the sumanene molecule exhibit an increasing trend as the size of alkali atom increases according to the following trend: $\text{sumanene@Li} < \text{sumanene@Na} < \text{sumanene@K}$. Hence, it is expected that the Li atom in concave situation interacts more efficiently with the sumanene molecule. It should be mentioned that the structure of sumanene is changed due to the interaction with alkali metals and causes local deformation in the considered molecules. The obtained outcomes display that the C – C bonds are elongated with respect to those of the pristine molecule in all of the complexes. These changes on the structures are anticipated to remarkably affect the electro-optical properties of the studied nanostructures. The stabilities of sumanene@M complexes are investigated through the interaction energies (E_{int}) and listed in Table 1. The E_{int} values are ranging from -0.27 to -1.13 (eV). It is obvious from the results that A and G configurations is the most stable complex with $E_{int} = -1.12$ and -1.13 (eV), respectively, and Li and K atom significantly interacts with the concave situation of sumanene molecule.

Furthermore, the natural bond orbital (NBO) analysis was performed on the sumanene@M complexes at the same levels. The results have been listed in Table 1. The alkali metal atoms in the studied complexes exhibited the positive charge in the range of 0.11-0.94|e|, which implies to the charge transferred

from alkali metal atom to the sumanene molecule. These results show that alkali atom could be polarized, which demonstrates that the s valence electron of the alkali atom is ionized. Therefore, the diffuse excess electron of the alkali atom transfers to the sumanene molecule which can alter the electronic and NLO properties of the considered systems. Indeed, the natural electron configuration using the NBO analysis is applied to describe the bonding. The natural electron configurations of the considered structures are summarized in Table 2. According to the results of this table, the p-character of alkali atom in the sumanene@M interaction of the considered system are increased by adsorption of the alkali atom on the surface of the pristine sumanene.

The electronic properties of the considered complexes are also investigated; the obtained frontier molecular orbital energies (ϵ_H , ϵ_L) and energy gap (E_g) values for these mentioned complexes are listed in Table 1. The obtained results indicate that the interaction of alkali metals with sumanene molecule significantly narrows the energy gaps, and leads to a decrease of E_g from 4.69 eV for pristine sumanene to range of 0.83-1.57 eV for studied complexes. In order to provide a convenient comprehensive view of the electronic structures of the studied configurations, the PDOS for these configurations are shown in Fig. 2.

Table 1. NBO charges on alkali atoms, Highest occupied molecular orbital (HOMO), lowest unoccupied orbital (LUMO), Energy gaps (E_g), $\% \Delta E_{\text{gap}}$, polarizability (α), static first hyperpolarizability (β_0), energy of the basis set superposition error (E_{BSSE}) and corrected interaction energy (ΔE_{int}) of $\text{C}_{21}\text{H}_{12}@\text{M}$ ($\text{M}=\text{Li}, \text{Na}$ and K).

Configuration	q (e)	HOMO (eV)	LUMO (eV)	E_g (eV)	$\% \Delta E_{\text{gap}}$	α (au)	β_0 (au)	E_{BSSE} (eV)	ΔE_{int} (eV)	
Pristine	-	-5.77	-1.08	4.69	-	228.64	70.29	-	-	
Li	A	0.90	-2.85	-1.29	1.56	-66.65	253.70	1673.575	0.043	-1.12
	B	0.86	-2.90	-1.33	1.57	-66.42	269.45	24769.97	0.034	-0.98
Na	C	0.91	-2.62	-1.39	1.23	-73.86	264.69	2688.37	0.059	-0.78
	D	0.11	-2.55	-1.53	1.02	-78.27	322.37	2336323	0.055	-0.46
	E	0.17	-2.62	-1.45	1.17	-74.95	387.88	8242.76	0.060	-0.40
	F	0.12	-2.76	-1.42	1.34	-82.61	370.99	8176.77	0.055	-0.35
K	G	0.94	-2.37	-1.24	1.13	-82.98	269.17	3029.38	0.033	-1.13
	H	0.72	-2.55	-1.58	0.97	-85.41	305.03	33218.51	0.024	-0.47
	I	0.18	-2.30	-1.39	0.91	-92.20	666.14	2904321	0.20	-0.40
	J	0.64	-2.44	-1.61	0.83	-87.53	314.83	37294.24	0.025	-0.27

According to the results of this table, the p-character of alkali atom in the sumanene@M interaction of the considered system is increased by adsorption of the alkali atom on the surface of the pristine sumanene.

The electronic properties of the considered complexes are also investigated; the obtained frontier molecular orbital energies (ϵ_H , ϵ_L) and energy gap (E_g) values for these mentioned complexes are listed in Table 1. The obtained results indicate that the interaction of alkali metals with sumanene molecule significantly narrows the energy gaps, and leads to a decrease of E_g from 4.69 eV for pristine sumanene to range of 0.83-1.57 eV for studied complexes. In order to

provide a convenient comprehensive view of the electronic structures of the studied configurations, the PDOS for these configurations are shown in Fig. 2. According to this figure, it is obvious that the interaction of the alkali atoms with these complexes leads to the formation of a high energy level as the new HOMO level located between the original HOMO and LUMO of pristine sumanene, and also LUMO orbital with low energy resulting in the small E_g value for these interacted compounds. The results of PDOS display that in some configurations, new HOMO level is appeared from alkali metal part while in some of them, new LUMO level is made of alkali metal (Fig. 2). Therefore,

alkali metals can effectively reduce the energy gap of sumanene.

Table 2. The obtained natural electron configuration for the alkali atom in considered structures.

Compound	Atom	Natural electron configuration
A	Li	[He] 2S(0.04) 4p(0.01)
B	Li	[He] 2S(0.02) 4p(0.01)
C	Na	[Ne] 3S(0.04)
D	Na	[Ne]
E	Na	[Ne] 3S(0.02)
F	Na	[Ne] 3S(0.01)
G	K	[Ar] 4S(0.02) 6p(0.01)
H	K	[Ar] 4S(0.01)
I	K	[Ar]
J	K	[Ar] 4S(0.01)

The new interaction mode has been proposed to produce the excess electron, namely, through the s electron of the alkali atom interacting with the p-conjugated electron cloud (derived from p orbitals) [73] which is advantageous for introducing the excess electron in some systems. It has been shown that the existence of the diffuse excess electron can usually cause the large NLO response [30, 36, 37]. The polarizability (α) and the first static hyperpolarizability (β_0) of sumanene@M (M=Li, Na, K) complexes were calculated by M06-2X-D3/6-31+G(d) method and summarized in Table 1. The polarizability (α) value of pristine sumanene is 228.68 au. After the interaction of alkali metals with this molecule, the obtained outcomes show that the change of polarizability is insignificant. According to Table 1, our computational results exhibited that hyperpolarizability (β_0) of the pristine sumanene is enhanced due to the interaction with alkali metals. The obtained β_0 values are in range from 1673.575 au, to 2904321 au for A-J configurations. The results indicate that D and I configurations have the greatest first hyperpolarizability with the values 2336323 au and 2904321 au, respectively, which indicate that β_0 values

of sumanene@Na and sumanene@K are larger than the others. In addition, the s valence electron of the Na and K atoms are pushed out to turn into a diffuse excess electron for the whole system. The obtained results reveal that enhancement in NLO response of sumanene due to interaction with alkali metals is greater than other carbon nanostructures that have been reported in previous studies [21, 22, 32]. Decorated sumanene molecule with Na and K atoms lead to larger NLO response in comparison with functionalized bowl structure of sumanenes [21]. It seems that the interaction energy between the alkali atoms and the sumanene molecule is a key factor in enhancing the first hyperpolarizability of studied complexes. The shorter interaction energy causes the greater NLO response (see Table 1). The D and I configurations have the short interaction energy. Thus, it seems that the shorter interaction energy is responsible for greater NLO response of this structure among the studied complexes. Finally, existence of the diffuse excess electron leads to the large NLO response of sumanene@M (M=Li, Na, K) complexes with respect to pristine sumanene.

5. Conclusion

Quantum chemical calculations at DFT (M06-2X-D3 functional) level of theories were performed to study the electronic structure and NLO response of sumanene@M (M=Li, Na, K) complexes. Negative values of interaction energy values indicate that these complexes are stable. Further, the NBO in B3LYP-D3 level of theory indicate that adsorption alkali metals by sumanene molecule lead to an obvious charge transfer. As expected, the first hyperpolarizability can be greatly enhanced. The D and I configurations have the largest β_0 value ($\beta_0 = 2336323$ au and 2904321 au, respectively). Therefore, results show that alkali metal adsorption by the sumanene molecule may be potential candidates for high-performance NLO materials.

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