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Nonlinear Optical (NLO) Response of $Si_{12}C_{12}$ Nanocage Decorated with Alkali Metals (M = Li, Na and K): A Theoretical Study

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Abstract Electronic structure and nonlinear optical (NLO) response of $Si_{12}C_{12}$ nanocage decorated with alkali metals (M = Li, Na and K) are investigated by means of density functional theory (DFT) and second order Møller–Plesset (MP2) calculations with $6-31+G(d)$ basis set. The results of present study indicate that interaction of alkali metals with $Si_{12}C_{12}$ nanocage narrow the HOMO–LUMO gap of nanocage remarkably. It is shown that, decoration of $Si_{12}C_{12}$ with alkali metals play significant role in enhancement of first hyperpolarizability (β_0) and consequence NLO response of $Si_{12}C_{12}$ nanocage.

Keywords $Si_{12}C_{12}$ nanocage · Alkali metals · Hyperpolarizability

1 Introduction

Design and fabrication of the nonlinear optical (NLO) materials is an important task in current researches due to their wide applications in optical communication, optical computing, photonic and electro-optical devices and laser [1, 2]. Many guidelines have been introduced for the design of new NLO materials [2–8]. Interaction of alkali metals with nanomaterials, through excess electrons redound to enhancement in first hyperpolarizability and large NLO response in electronic devices [9–11]. In addition, doping of alkali metal atoms is an effective strategy for significant change in the electronic and nonlinear optical properties of nanomaterials [1, 5, 8, 12].

Excellent physicochemical properties of silicon carbide nanomaterials such as high-power, high frequency, high temperature semiconductors, wide band gap and high thermal conductivity [13–15], lead to abundant study of these materials in contemporary investigations.

Theoretical results have shown that $Si_{12}C_{12}$ nanocage appears to be more stable than the other silicon carbide derivatives [13]. This nanocage has many applications in laser devices, optical communication, optical computing, and optical data storage [16, 17].

The motivation of the present study is investigation influence of interaction between alkali metals (M = Li, Na and K) with $Si_{12}C_{12}$ nanocage in enhancement of first hyperpolarizability (β_0) and NLO response of $Si_{12}C_{12}$ nanocage for the first time. The prospect of this research is providing more useful information for the development of new devices based on nanoscale silicon carbon materials with large NLO response.

2 Computational Details

The geometries of all considered systems are fully optimized at WB97XD/$6-31+G(d)$ level of theory [18]. The geometry optimization, electronic structure, and NLO properties of interacted nanocage with Li, Na and K atoms described by the spin-unrestricted approach whereas the restricted approach is used for the pristine nanocage. The nature of the stationary points have been checked through frequency analysis at the same computational level.

The natural bond orbital (NBO) charges [19], interaction energies (E_{int}), the vertical ionization energies (VIE)

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and the basis set superposition error (BSSE) [20] analysis have been performed using the WB97XD/6 − 31 + G(d) method in the present study. The stabilization energy (ΔE) due to the interaction of the alkali atom with the considered nanocage is obtained as follow:

$$\Delta E = E_{Si_{12}C_{12}-M} - E_{Si_{12}C_{12}} - E_M - E_{BSSE} \quad M = Li, Na \text{ and } K \tag{1}$$

where $E_{Si_{12}C_{12}-M}$ represents the total electronic energy of the $Si_{12}C_{12}$−M. $E_{Si_{12}C_{12}}$ and E_M are the total electronic energy of isolated $Si_{12}C_{12}$ nanocage and the M atom, respectively. The full counterpoise (CP) method [21] was used to correct the stabilization energy from the inherent basis set superposition error (BSSE).

The VIE values are determined using the following Eq. (2):

$$VIE = E(Y^+) - E(Y) \tag{2}$$

where E(Y) is the energy of the $Si_{12}C_{12}$−M and $E(Y^+)$ is the energy of the $(Si_{12}C_{12}-M)^+$ cation at optimized neutral geometry of $Si_{12}C_{12}$−M. The HOMO–LUMO gap (HLG) of the intended systems defined as:

$$HLG = (\varepsilon_L - \varepsilon_H) \tag{3}$$

where ε_H is the highest occupied molecular orbital (HOMO) energy and ε_L is the lowest unoccupied molecular orbital (LUMO) energy, respectively. The total density of states (TDOS) spectra, for intended systems were visualized using the GaussSum program [22], based on the data from WB97XD/6 − 31 + G(d) calculations.

The polarizability (α) and first hyperpolarizability (β_0) have been evaluated by the finite-field (FF) approach under an electric field magnitude of 0.001 a.u. at MP2/6 − 31 + G(d) computational level for $Si_{12}C_{12}$−M complexes. MP2 method is suitable for calculation and prediction of (hyper) polarizability and NLO properties [23–25], therefore is satisfactory choice for the present systems.

The polarizability (α) and first hyperpolarizability (β_0) are assessed according to the following equations:

$$\alpha = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{4}$$

$$\beta_0 = (\beta_x{}^2 + \beta_y{}^2 + \beta_z{}^2)^{1/2} \tag{5}$$

where

$$\beta_i = 3/5(\beta_{iii} + \beta_{ijj} + \beta_{ikk}) \quad i, j, k = x, y, z \tag{6}$$

Time-dependent density functional theory (TD-DFT) [26, 27] calculations were performed at the WB97XD/6 − 31 + G(d) method to obtain the crucial excited states, and the differences of dipole moments between the ground state and crucial excited state. All calculations were performed using Gaussian 09 program package [28].

3 Results and Discussions

The optimized geometry of the $Si_{12}C_{12}$ nanocage at WB97XD/6 − 31 + G(d) computational level is depicted in Fig. 1. This nanocage is consisted with six tetragonal and eight hexagonal rings. Two individual Si–C bonds are distinguishable in the $Si_{12}C_{12}$ nanocage, one is shared between two hexagons (b66) with length about 1.767 Å and the other is shared between a tetragon and a hexagon (b64) with length of 1.823 Å (see Fig. 1). It seems that the participation of p orbital is increased for (b64) bonds in comparison to (b66). Therefore, the bond lengths of (b64) are larger than (b66). The pictorial representation of the HOMO–LUMO distribution of the considered nanocage is exhibited in Fig. 2. The obtained energies of HOMO, LUMO and HOMO–LUMO gap of $Si_{12}C_{12}$ nanocage are −8.10, −1.09 and 7.01 (eV) respectively. The semiconductor characteristic of $Si_{12}C_{12}$ nanocage is validated with this value of HLG. In the pristine $Si_{12}C_{12}$ nanocage, the HOMO is concentrated over the C atoms of the cage but the LUMO is located over the Si atoms. In order to more accurate display HLG, the total density of states (TDOS) of the pristine nanocage, is depicted in Fig. 2.

The nonlinear optical response of the $Si_{12}C_{12}$ nanocage is investigated in the next step. The calculated values of polarizability (α) and hyperpolarizability (β_0) are listed in Table 2. The results show that first static hyperpolarizability of $Si_{12}C_{12}$ is null ($\beta_0 = 0.00$ a.u.), so this considered nanocage has no NLO response.

In the present study interaction between $Si_{12}C_{12}$ nanocage and alkali metals (M = Li, Na and K) and consequence effect of it on the electronic and nonlinear optical properties of nanocage is investigated. For this purpose, different initial positions for alkali atom over the nanocage including: the on top of a C or Si atom, over hexagonal and square rings, and on the top of a b66 or a b64 bond, are considered. After full optimization of considered systems, two stable structures with no imaginary vibrational frequencies were identified for each $Si_{12}C_{12}$−M (M = Li, Na and K) complexes. These stable structures are obtained from interaction of alkali atoms on the C atom (S1) and over hexagonal ring (S2) of $Si_{12}C_{12}$ nanocage (Fig. 1). The vertical distances between the alkali atom and the C (S1 configurations) adherence to the following trend: 2.003 (S1–Li) < 2.353 (S1–Na) < 2.793 (S1–K). Hence, it is obvious that interaction of Li atom with C atom of $Si_{12}C_{12}$ nanocage is more prominent that other alkali metals.

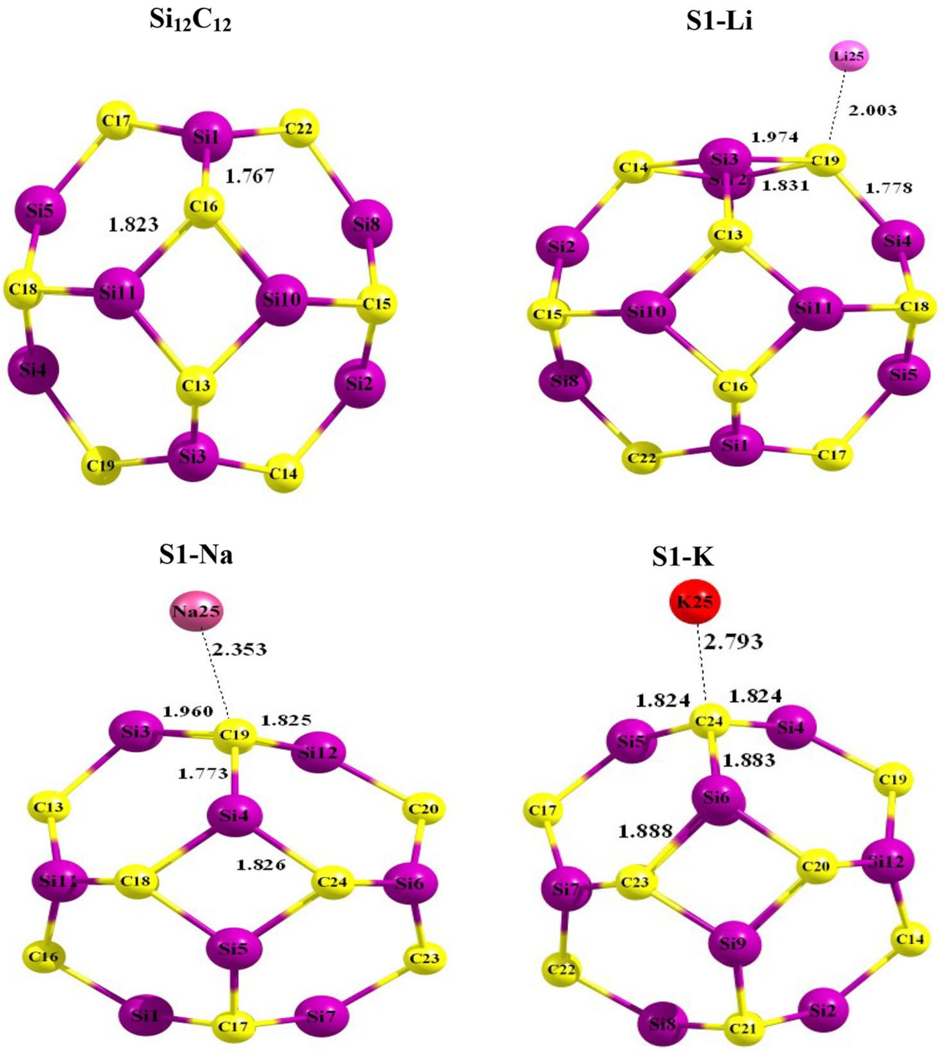


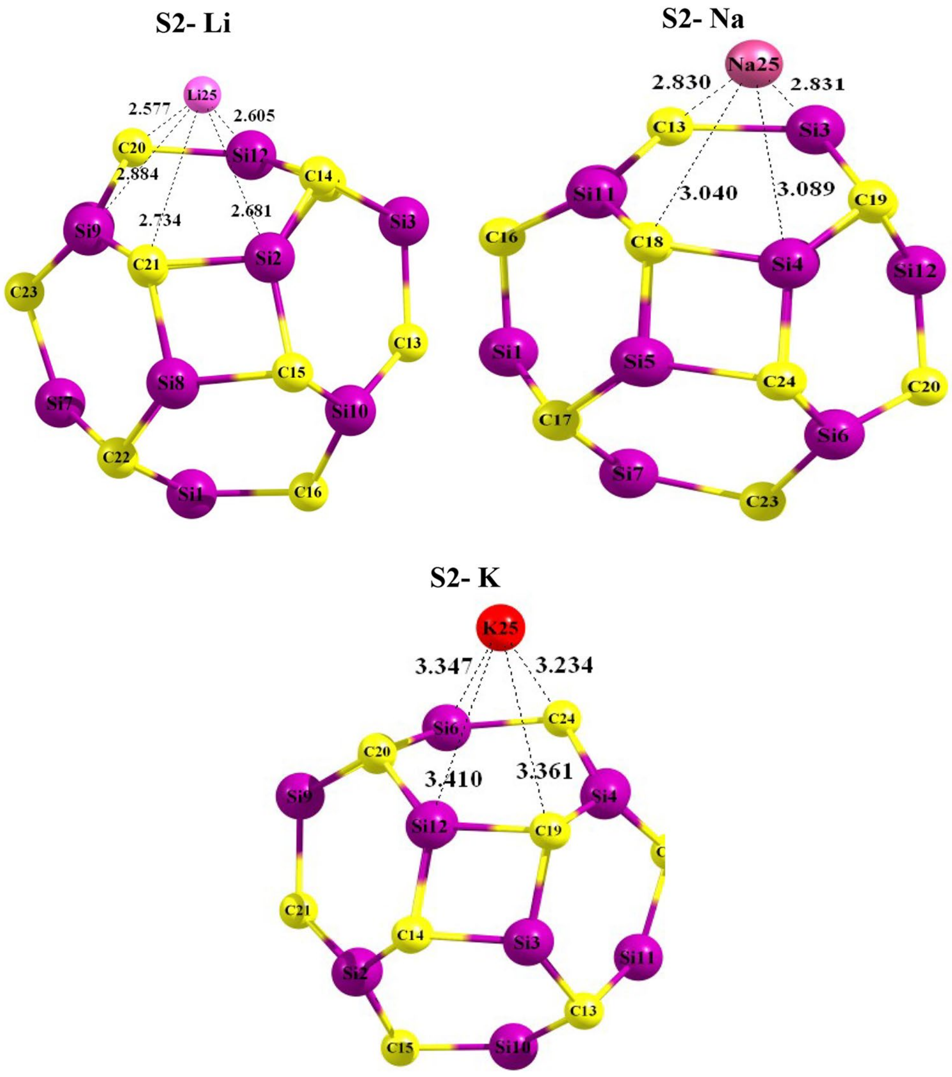
Fig. 1 The optimized structures of pristine $Si_{12}C_{12}$ and $Si_{12}C_{12}$–M (M = Li, Na, K) complexes

The calculated stabilization energies (ΔE) and the VIE of $Si_{12}C_{12}$–M complexes, at the WB97XD/6–31 + G(d) level are summarized in Table 2. The ΔE values ranges from −29.46 to −42.42 (kcal/mol). The conspectus consideration of results show that, S1–Li configuration is the most stable complex among studied complexes with ΔE = −42.42 (kcal/mol). Moreover, the $Si_{12}C_{12}$–M complexes exhibited large VIE values in ranges from 5.93 to 6.44 eV. High VIE values of $Si_{12}C_{12}$–M complexes indicated that these complexes are very stable.

NBO analysis performed on the $Si_{12}C_{12}$–M complexes at the WB97XD/6 − 31 + G(d) levels. The results have been collected in Table 1. The alkali metal atoms in the studied complexes exhibited the positive charge ranges from 0.87 to 0.97 e, indicating that charge transfer is occurred from alkali metal atom to the $Si_{12}C_{12}$ nanocage. The NBO charges of the C and Si atoms in the pristine $Si_{12}C_{12}$ are −1.822 and 1.822 e respectively which will be more negative (−2.068 and 1.338 e, respectively) in the S1–Li configuration. This results show that Li atom is polarized due to interaction with nanocage and excess electron of it will increase NLO response of nanocage. This situation is occurred for all studied complexes, so $Si_{12}C_{12}$–M (M = Li, Na, K) should have large value of β_0 and NLO response.

The electronic properties of the interacted nanocage are also investigated; the obtained frontier molecular orbital energies ε_H, ε_L and HOMO–LUMO gap (HLG) values for this mentioned nanocage are listed in Table 1. The obtained results indicate that interaction of alkali metals with $Si_{12}C_{12}$ nanocage significantly narrows the HOMO–LUMO gaps, and leads to decrease of HLG from 7.01 eV for pristine $Si_{12}C_{12}$ to range of 5.31–5.53 eV for six studied complexes. The TDOS for S1 and S2 configurations are shown in Fig. 2. According to this figure, it is

Fig. 1 (continued)



obvious that the interaction of the alkali atoms with these nanocage leads to the formation of a high energy level as the new HOMO level locating between the original HOMO and LUMO of pristine nanocage, resulting in the small HLG value for these interacted compounds. On the other hand the low HLG value might lead to large β_0 values of the studied nanocage.

The calculated polarizability (α) and the first hyperpolarizability (β_0) of $Si_{12}C_{12}$–M (M = Li, Na, K) complexes at MP2/6 − 31 + G(d) level are summarized in Table 2. The value of α for pristine $Si_{12}C_{12}$ is 370.87 a.u. After interaction of alkali metals with $Si_{12}C_{12}$, the $Si_{12}C_{12}$–M (M = Li, Na, and K) complexes exhibit large α values ranging from 393.49 to 414.97 a.u. According to Table 2, our results reveal that first hyperpolarizability (β_0) is observed in $Si_{12}C_{12}$–M due to the interaction of alkali atoms with nanocage. The obtained β_0 values are 4277.06 (Li), 5771.99 (Na) and 4015.57 (K) a.u. for S1 configurations and 851.37 (Li), 1889.38 (Na), and 1252.11 (K) a.u. for S2 configurations, respectively. The first hyperpolarizability (β_0) values for S2 configuration are less than corresponding values in S1 configuration.

To understand how interaction of different alkali metals affects the β_0 value in studied complexes, the famous two-level model is used as follows [29, 30].

$$\beta_0 = \frac{3\Delta\mu f_0}{2\Delta E^3} \tag{7}$$

where ΔE, f_0, and Δμ are the transition energy, the oscillator strength, and the difference in dipole moment between the ground state and the crucial excited state (the excited state with the largest oscillator strength), respectively.

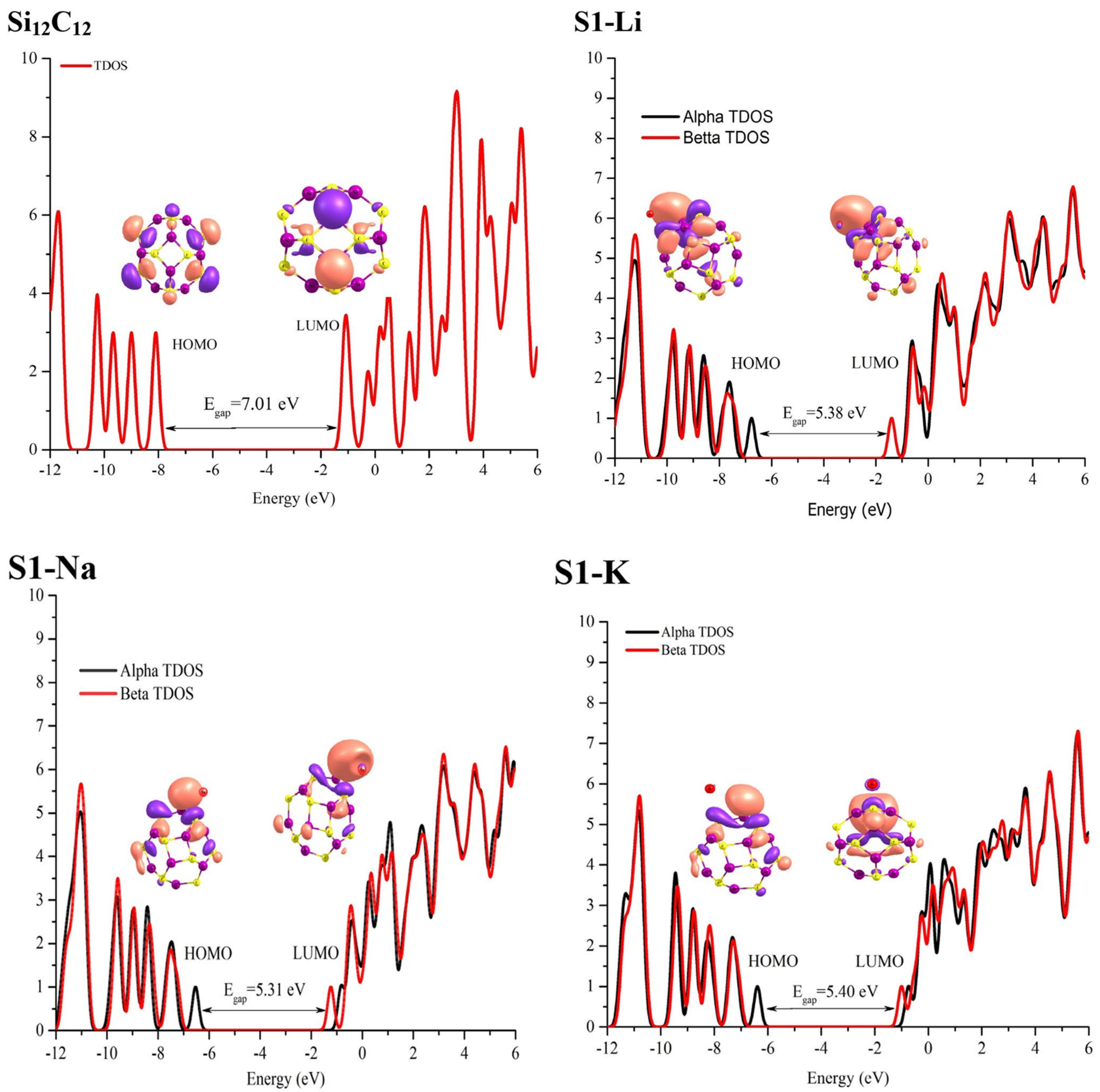


Fig. 2 TDOS of pristine $Si_{12}C_{12}$ and $Si_{12}C_{12}$−M (M = Li, Na, K) complexes

In the two-level expression, the third power of the transition energy is inversely proportional to the β_0 value, so the transition energy is the decisive factor in the first hyperpolarizability. In this study, the ΔE, Δμ and the largest oscillator strengths (f_0) values of the $Si_{12}C_{12}$−M (M = Li, Na, K) complexes were calculated using the TD-WB97XD method with 6 − 31 + G(d) basis set and the results are listed in Table 3. According to the results, there is no peak for pristine $Si_{12}C_{12}$. As can be seen from Table 3, the ΔE values for each $Si_{12}C_{12}$−M with (M = Li, Na and K) which the alkali atom (M) interacted on the C atom (S1 configurations) increase in the following order: S1–Na < S1–Li < S1–K. For each $Si_{12}C_{12}$−M with (M = Li, Na and K) which the alkali atom (M) interacted over hexagonal ring of $Si_{12}C_{12}$ nanocage systems (S2 configurations), ΔE values are in the order of S2–Na < S2–K < S2–Li. The

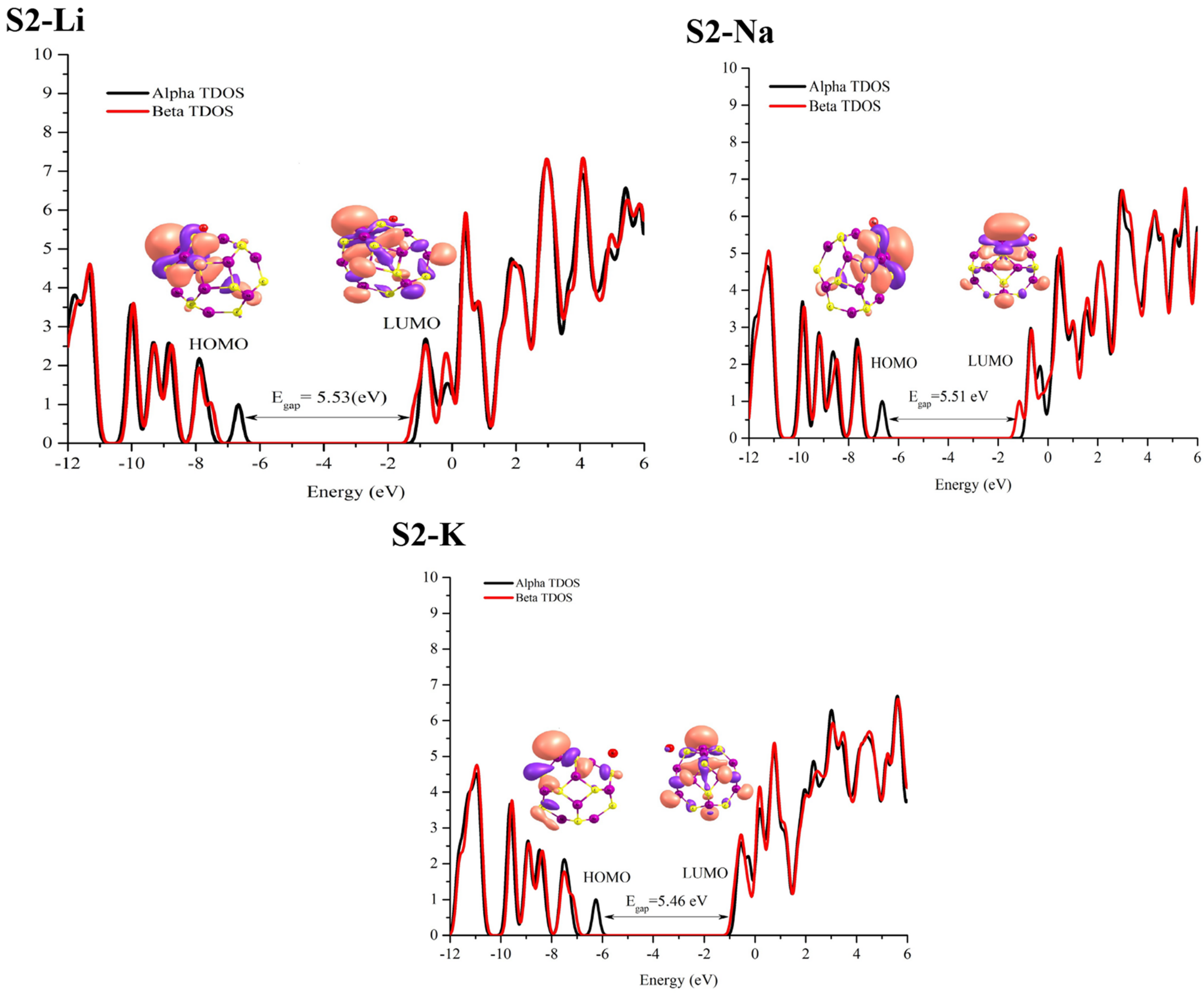


Fig. 2 (continued)

Table 1 Point group, NBO charges on alkali atoms, C and Si atoms, vertical ionization energies (VIE), highest occupied molecular orbital energy (HOMO), lowest unoccupied molecular orbital energy (LUMO), HOMO–LUMO Gaps (HLG) and %ΔE gap of $Si_{12}C_{12}$–M (M = Li, Na and K)

Configuration		P.G.	q (M)	q (C)	q (Si)	VIE (eV)	HOMO (eV)	LUMO (eV)	HLG (eV)	%ΔEgap
$Si_{12}C_{12}$	–	T_h	–	−1.822	1.822	–	−8.10	−1.09	7.01	–
S1	Li	C1	0.88	−2.068	1.338	6.44	−6.76	−1.39	5.38	−23.25
	Na	C1	0.92	−2.026	1.340	6.20	−6.53	−1.22	5.31	−24.24
	K	C1	0.95	−1.985	1.328	6.04	−6.39	−0.99	5.40	−22.99
S2	Li	C1	0.87	–	–	6.36	−6.67	−1.13	5.53	−21.03
	Na	C1	0.91	–	–	6.32	−6.65	−1.14	5.51	−21.39
	K	C1	0.97	–	–	5.93	−6.25	−0.79	5.46	−22.09

Table 2 The calculated polarizability (α), static first hyperpolarizability (β_0) energy of the basis set superposition error (E_{BSSE}) and corrected stabilization energy (ΔE) of $Si_{12}C_{12}$–M (M = Li, Na, K) complexes

Configuration		α(au)	β_0 (au)	E_{BSSE} (kcal/mol)	ΔE (kcal/mol)
$Si_{12}C_{12}$	–	370.87	0	–	–
S1	Li	407.17	4277.06	1.10	−42.42
	Na	414.22	5771.99	1.95	−33.34
	K	414.97	4015.57	0.81	−38.08
S2	Li	393.49	851.37	1.00	−32.08
	Na	400.58	1889.38	1.73	−29.46
	K	405.46	1252.11	0.93	−34.87

obtained results for these systems indicate that Δμ values decrease in the reverse of above trend, which is consistent with the trend of the calculated β_0 values. The smallest ΔE and greatest Δμ and f_0 are belonged to S1–Na configuration with 2.48 eV, 0.566 a.u. and 0.0345, respectively. For S1–Na configuration, the crucial transition is from HOMO (α) to LUMO (α), which reveals that CT occurs between Na and nanocage (see Fig. 3). Thereupon, the interaction between the 3s electron and the core electrons of Na is extremely weakened. Hence interaction of alkali atom with the nanocage enhance the degree of CT by decreasing the excited energy, which leads to remarkable improvement of the static first hyperpolarizability.

Moreover, the computed linear absorption spectra of systems are reported in Table 3. According to this table, for S1 configurations the strongest peak with large oscillator strengths is essentially at 463.42, 498.99 and 416.69 nm in the visible region and for S2 configurations at the 319.65, 324.37 and 324.58 nm in the UV region, respectively. This is corresponds to the transition of the excess electron. To sum up, the NLO response of silicon carbide nanocage is tunable by interaction of alkali metals (M = Li, Na and K) with this nanocage.

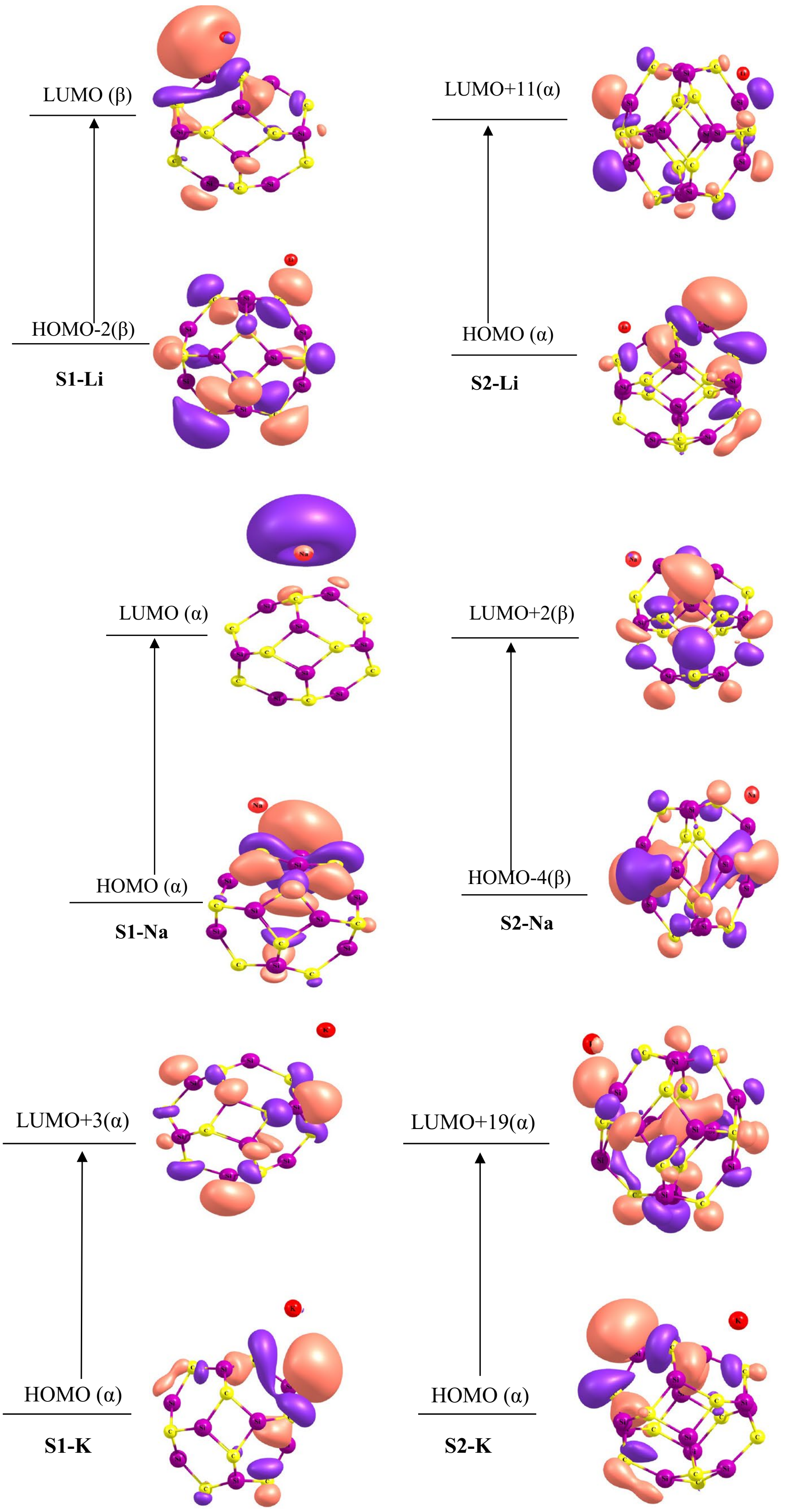
4 Conclusion

In this study, we have inspected structure, electronic properties and nonlinear optical specifications of pristine $Si_{12}C_{12}$ nanocage and $Si_{12}C_{12}$–M (M = Li, Na, K) via theoretical calculations. The density of states, and NBO analysis showed that interaction of the alkali metals with $Si_{12}C_{12}$ nanocage narrows the HOMO–LUMO gap. It is shown that electro-optical property of considered nanocage, is sensitive to the interaction with the alkali metals remarkably. Interaction of the Na atom over C atom gives largest NLO response among studied complexes. Finally,

Table 3 The transition energy (ΔE), wavelength (λ), oscillator strength (f_0), difference of dipole moment between the ground state and the crucial excited state (Δμ) and relative orbital contributions of $Si_{12}C_{12}$–M (M = Li, Na, K)

Configuration		Excited state	ΔE (eV)	λ(nm)	f_0	Δμ (au)	Assignment
S1	Li	3	2.68	463.42	0.0228	0.348	HOMO − 2 (β)→LUMO (β)
		9	3.06	404.81	0.0213	0.284	HOMO (α)→LUMO + 3 (α)
		2	2.59	478.88	0.0169	0.266	HOMO (α)→LUMO (α)
	Na	2	2.48	498.99	0.0345	0.566	HOMO (α)→LUMO (α)
		30	3.56	348.38	0.0193	0.221	HOMO − 3 (α)→LUMO + 1 (α)
		6	2.85	434.54	0.0159	0.227	HOMO (α)→LUMO + 3 (α)
	K	7	2.98	416.69	0.0243	0.334	HOMO (α)→LUMO + 3 (α)
		3	2.63	471.81	0.0202	0.313	HOMO (α)→LUMO (α)
		45	3.81	325.75	0.0172	0.184	HOMO − 6 (α)→LUMO + 1 (α)
S2	Li	45	3.88	319.65	0.0145	0.152	HOMO (α)→LUMO + 11 (α)
		7	2.95	420.97	0.0137	0.190	HOMO − 1 (β)→LUMO (β)
		36	3.70	335.43	0.0109	0.120	HOMO − 1 (α)→LUMO + 3 (α)
	Na	44	3.82	324.37	0.0276	0.294	HOMO − 4 (β)→LUMO + 2 (β)
		14	3.20	387.75	0.0100	0.127	HOMO (α)→LUMO + 4 (α)
		32	3.60	344.33	0.0082	0.093	HOMO − 2 (α)→LUMO + 4 (α)
	K	45	3.82	324.58	0.0166	0.177	HOMO (α)→LUMO + 19 (α)
		7	2.90	427.25	0.0154	0.217	HOMO (α)→LUMO + 4 (α)
		37	3.68	337.08	0.0118	0.131	HOMO − 1 (α)→LUMO + 4 (α)

Fig. 3 The crucial transitions of $Si_{12}C_{12}$–M (M = Li, Na, K) complexes



it is our expectation that interaction of the alkali metals with considered nanocage provide promising strategy for developing of high performance NLO materials.

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