Structure, electrical and nonlinear optical properties of $M@C_{20}$ ($M = \text{Li, Na, K, Be, Mg and Ca}$) nanoclusters

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Abstract. The decoration of Li, Na, K, Be, Mg and Ca metal atoms on C_{20} fullerene was studied using the density functional theory (DFT) method. It was shown that the structure of the fullerene was intensely affected by the metal atom present. All metal atoms have exothermic adsorption on C_{20} fullerene, while Be has the highest value of adsorption energy, enthalpy and free energy. The presence of the metal atom also has a slight effect on E_g while the lowest value of E_g was obtained for $Ca@C_{20}$. The calculations of polarizability and the first hyperpolarizability show that the metal atoms highly influence fullerenes. Among metal atoms, Ca atom had the highest effect and the other metal atoms led to an increase of the first hyperpolarizability to a value of approximately 42000 a.u. The time-dependent (TD)-DFT studies showed that $Ca@C_{20}$ has the lowest excitation energies which is in agreement with the calculated first hyperpolarizability.

Keywords. NLO; C_{20} fullerene; first hyperpolarizability; alkali metal atom; Ca atom.

1. Introduction

Materials with large nonlinear optical (NLO) responses play a useful role in optical interconnections, optical switching and signal processing [1,2]. In recent years, extensive studies have been performed to develop novel materials with a high NLO response and technological requirements for various applications [3–19].

Fullerene molecules and their derivatives [20,21] show a strong NLO effect at high-intensity laser beams and thus could be useful for practical optical limiters. The optical limiting properties of fullerenes and their derivatives have been studied by doping into solid materials [22–24] or solutions [25,26]. This property of fullerene is due to the expectedly large nonlinearities originating in three-dimensional π -electron-conjugated systems [27]. The endohedral or encapsulate metallofullerenes and substitute doping (SD) on fullerenes, i.e., substituting one or more carbon atoms of fullerenes by other atoms, was proposed to enhance its properties. Experimental and theoretical studies have been performed on fullerenes doped with alkali, alkaline earth and lanthanide metal atoms [28].

The smallest irregular fullerene is the C_{20} cage, with pentagon faces. This fullerene has larger vibronic coupling than C_{60} . Thus, the solid form of this fullerene could be a good choice for a superconductor [29].

Lemi Türker [30] showed that C_{20} has a trend for performance as an electron acceptor than as a donor and the states C_{20}^{-1} and C_{20}^{-2} are more stable than C_{20} . Yi-Peng *et al* [31] have investigated the transport properties of the fullerene C_{20} and the endohedral $Li@C_{20}$ metallofullerene based on

the density functional theory (DFT) method and showed that the conductivity balance of $Li@C_{20}$ metallofullerene is larger than the empty C_{20} fullerene molecule. Recently, the M_3O ($M = \text{Li, Na and K}$) has been used to increase the NLO response [32].

In this paper, the NLO properties of the C_{20} and $M@C_{20}$ nanoclusters have been studied using DFT, where $M = \text{Li, Na, K, Be, Mg and Ca}$ denote the metal atoms. We investigated metallofullerenes because the metal decoration on it can increase the NLO properties and create new types of NLO substances.

2. Computational details

All the calculations were performed using the Gaussian 09 package [33]. The optimized geometries of all structures are gathered at the unrestricted B3LYP and 6-31+G(d) computational levels of theory [34,35]. With the GaussSum program [36], the electronic density of states (DOS) for all structures was obtained. The spin-unrestricted approach is used to explain the geometry optimization, electronic structure and NLO properties of all structures. The linear and NLO properties were calculated with the coulomb-attenuated hybrid exchange–correlation functional (CAM-B3LYP) [37] which is suitable to predict the large molecular system. Thus from this functional, we can draw good quality conclusions for electronic excitation energies [38,39].

The HOMO–LUMO gap (E_g) values are used to examine electronic properties of the considered fullerenes. This

Figure 1. Structure of C_{20} fullerene (A), $Li@C_{20}$ (B), $Na@C_{20}$ (C), $K@C_{20}$ (D), $Be@C_{20}$ (E), $Mg@C_{20}$ (F) and $Ca@C_{20}$ (G) nanoclusters.

quantity is defined as follows:

$$E_g = \varepsilon_L - \varepsilon_H$$

where ε_H is the highest occupied molecular orbital (HOMO) and ε_L is the lowest unoccupied molecular orbital (LUMO) energies. The energy of a system in the weak and homogeneous electric field can be defined as [40,41]

$$E = E^\circ - \mu_\alpha F_\alpha - 1/2\alpha_{\alpha\beta} F_\alpha F_\beta - 1/6\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \dots$$

where E° is the molecular total energy without the electric field and F_α is the electric field component along the α direction. The μ_α , $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ denote dipole, polarizability and the first hyperpolarizability, respectively. The polarizability (α) and the first hyperpolarizability (β) are defined as

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

$$\beta^\circ = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

in which

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

β° is the first hyperpolarizability, which is a third-rank tensor and known as NLO response coefficient.

3. Results and discussion

3.1 Structural and energetic properties

The smallest fullerene, C_{20} with symmetry I_h has 12 pentagonal faces. Each pentagon shape joins with three bond types, one in the base of pentagon and four bonds create two types of bonds. The structure can be modified by adding substituents to different parts of the structure. The structure of pristine C_{20} is a closed-shell electronic but $M@C_{20}$ has one more electron and is an open-shell electronic structure. In figure 1, the structures of C_{20} fullerene, and $M@C_{20}$ nanoclusters ($M=Li, Na, K, Be, Mg$ and Ca) are illustrated.

In figure 1A three bond lengths are depicted which are in agreement with the values shown by Baei *et al* [42,43]. As shown in figure 1, the structure of C_{20} fullerene was affected by the presence of M atom and the C–C bond length increases. The Be atom has the shortest interaction distance among other atoms; however, it has an increased C–C bond length than the other atoms.

The value of adsorption energy (E_{ads}), for all considered metal atoms is calculated as follows:

$$E_{ads} = E[M@C_{20}] - E[C_{20}] - E[M]$$

where $E[M@C_{20}]$ is the energy of the decorated cluster with the M atom and $E[C_{20}]$ is the energy of the pristine fullerene,

Table 1. Adsorption energy (kcal mol^{−1}), Gibbs free energy and enthalpy of adsorption (kcal mol^{−1}) of $M@C_{20}$ ($M=Li, Na, K, Be, Mg$ and Ca).

System	E_{ads} (kcal mol ^{−1})	ΔG (kcal mol ^{−1})	ΔH (kcal mol ^{−1})
Li@C ₂₀	−48.88	−40.56	−49.16
Na@C ₂₀	−33.72	−26.61	−34.43
K@C ₂₀	−35.48	−29.93	−36.85
Be@C ₂₀	−62.01	−50.85	−60.73
Mg@C ₂₀	−16.01	−6.02	−15.78
Ca@C ₂₀	−25.45	−16.29	−25.62

while $E[M]$ is the energy of the isolated metal atom. The values of adsorption energy and thermodynamic data for the C_{20} fullerene and $M@C_{20}$ ($M=Li, Na, K, Be, Mg$ and Ca) are reported in table 1.

As shown in table 1, the adsorption of all metal atoms on the C_{20} fullerene is highly exothermic. The Be atom had the highest negative value of doping energy which is in accordance with the shortest bond length of Be with the C_{20} cluster. The trend of enthalpy and free energy of metal atom adsorption on the fullerene surface is similar to adsorption energy.

3.2 Electronic properties

The effect of transition metal doping on electronic properties of fullerene was studied. DOS plots for all mentioned structures are depicted in figure 2.

Using the DOS spectrum, the energies of the HOMO and LUMO orbitals were calculated. The E_{HOMO} , E_{LUMO} and energy gap (E_g) values for all considered configurations are compiled in table 2. Additionally, the charge transfer values were estimated by NBO calculation and are reported in table 2.

Data in table 2 show that the E_g of C_{20} fullerene was decreased by way of decorating its surface with Li, Na, K, Mg and Ca metal atoms. However, the E_g of the Be atom decorated was increased which may be the result of its higher stability. The minimum value of E_g was obtained for the adsorption of calcium atom on the fullerene surface. Potassium decorated fullerene had maximum value for the dipole moment. The values of charge transfer may demonstrate the flow of electrons from the M atoms to the C_{20} nanoclusters which show that the charge transfer from the Ca atom to the fullerene is larger than the others.

3.3 Optical properties

Polarizability (α) and the first hyperpolarizability (β°) that represents linear and NLO properties are calculated and are listed in table 3.

In table 3, it was illustrated that decoration of all metal atoms on the C_{20} surface increases its polarizability and the

Figure 2. Electronic DOS spectra of the C_{20} and $M@C_{20}$ ($M=Li, Na, K, Be, Mg$ and Ca) nanoclusters.

first hyperpolarizability. However, the calcium adsorption on the fullerene surface leads to the highest increase in the values of polarizability and the first hyperpolarizability. In this case, the first hyperpolarizability increases to about 42000 a.u.

3.4 Time dependent (TD)-DFT study

A two-level model [44,45] was used to relate the increase in the first hyperpolarizability of C_{20} nanoclusters. In this model, the first hyperpolarizability was considered

Table 2. Frontier molecular orbital energies E_{HOMO} and E_{LUMO} (eV), energy gap E_g (eV), dipole moment μ (Debye) and value of charge transfer (Q_T).

System	HOMO	LUMO	ε_g	μ	$Q_T e $
C ₂₀	−6.79	−2.63	4.16	0.00	–
Li@C ₂₀	−6.12	−2.18	3.94	7.26	0.86
Na@C ₂₀	−5.78	−1.88	3.90	11.22	0.88
K@C ₂₀	−5.57	−1.57	4.00	13.48	0.95
Be@C ₂₀	−6.53	−2.23	4.30	3.27	1.09
Mg@C ₂₀	−6.01	−2.80	3.21	5.60	1.03
Ca@C ₂₀	−5.32	−2.72	2.60	9.82	1.21

Table 3. Values of polarizability α (a.u.) and the first hyperpolarizability β° (a.u.) of the M@C₂₀ (M=Li, Na, K, Be, Mg and Ca).

System	α	β°
C ₂₀	188.00	0.19
Li@C ₂₀	211.81	1565.87
Na@C ₂₀	225.05	8579.44
K@C ₂₀	216.38	1335.71
Be@C ₂₀	226.94	4115.75
Mg@C ₂₀	308.95	16217.78
Ca@C ₂₀	403.79	42363.37

Figure 3. Calculated UV–visible adsorption spectra for Li, Na and K@C₂₀ (A) and Be, Mg and Ca@C₂₀ (B) nanoclusters.

as follows:

$$\beta_0 \text{ (two-level)} \propto \frac{\Delta\mu \cdot f_0}{\Delta E^3}$$

where ΔE , f_0 and $\Delta\mu$ are the transition energy, oscillator strength and difference in the dipole moments between the ground state and the crucial excited state with the largest oscillator strength. In the above equation, the β_0 value is reversely related to the third power of the transition energy, so small variation in it, radically influences the first hyperpolarizability. TD-DFT calculations were performed to estimate the transition excited state properties. The values of excitation state energies can be obtained by the UV–visible spectra predicted by TD-DFT calculation. In figure 3, the calculated UV–visible adsorption spectra for M@C₂₀ nanoclusters are shown.

It is evident from figure 3, between the mentioned nanoclusters, the transition energy of Ca@C₂₀ is lower which can explain its larger first hyperpolarizability.

4. Conclusion

The effect of decorating Li, Na, K, Be, Mg and Ca metal atoms on the structural, electronic, linear and NLO properties of C₂₀ fullerene has been investigated by the DFT method. It was shown that the all metal atoms had an evident effect on the structure of C₂₀ fullerene. All metal atoms have exothermic adsorption of the C₂₀ fullerene while the value of adsorption energy for Be adsorption is higher than the others. The metal atoms had a distinct effect on E_g of the C₂₀ nanoclusters. However, the Ca had the largest effect on E_g and the Ca@C₂₀ has minimum value of E_g . It was shown that the polarizability of the C₂₀ fullerene was increased in the presence of all metal atoms. The presence of the metal atom increases the first hyperpolarizability of C₂₀ and thus its NLO properties were drastically improved. The charge transfer shows electron flow from the metal atoms towards the fullerene nanoclusters. The calcium atom leads to the highest increase in the values of polarizability and the first hyperpolarizability of C₂₀. The charge transfer order for Ca is larger than the others. The TD-DFT studies showed that Ca@C₂₀ has lower excitation energies which showed higher value of the calculated first hyperpolarizability.

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