

Structural and optical properties of the endohedral complex $\text{Li}@C_{60}$

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Abstract

The lithium atom effect on the optical and structural properties of the $\text{Li}@C_{60}$ molecule are investigated using PPP (Pariser-Parr-Pople) and SSH (Su-Schrieffer-Heeger) models. In addition the movement of lithium atom effect on mentioned properties of $\text{Li}@C_{60}$ is calculated using the HF-CI-SOS (Sum-Over-State) and SSH methods. Our calculations indicated that the Na atom effect on the (first) polarizability and the bonds length of C_{60} is dramatic. This study proposes such a novel way to synthesize and design new NLO materials by using the alkali atom

PACs: 71.10.Fd; 71.10.Li; 71.15.Dx; 71.20.Tx; 78.20.Bh

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1. Introduction

Fullerenes are a new class of carbon molecules that consist of hollow cages composed of sp^2 -bonded networks of carbon atoms. The cage-like structure of fullerenes can be used to encapsulate metal atoms on a molecular scale creating an endohedral (an atom within a closed-cage fullerene). Encapsulation of one or more atoms inside hollow fullerene cages (endohedral) has long attracted special attention because it could lead to new spherical molecules with novel properties unexpected for empty fullerenes.

Scanning tunneling microscopy (STM) images of metallofullerenes $\text{Sc}@C_{74}$ and $\text{Sc}_2@C_{74}$ on a silicon surface [1] show the molecules to be spherical with cage diameters of $\sim 9.5 \text{ \AA}$. High-resolution TEM images of a $\text{Sc}_2@C_{84}$ crystal [2] lead to the conclusion that the scandium atoms are inside the carbon cage, which has a diameter of $\sim 8.4 \text{ \AA}$. Intermolecular spacing measurements in $\text{Sc}_2@C_{84}$ and C_{84} indicate that the charge transfer to the cage in $\text{Sc}_2@C_{84}$ does not significantly increase the size of the carbon cage [1-2].

Jingnan Lin et al. [3] used the SSH model to calculate structural properties of the endohedral complex $\text{Na}^+@C_{60}$. Also Jinxing Dong et al [4] used the same method to study nonlinear optical properties of the substituted fullerenes. Harneit [5], Suter and Lim [6] and Twamley [7] presented the concepts for quantum computation using endohedral fullerenes as spin-qubits, and a microwave pulse controlled magnetic dipolar interaction between qubits. Also in most endohedral fullerenes, introduction of metal atoms into carbon cage leads to an increase in the electron affinity compared with the corresponding empty -cages [8-

9]. By varying the encapsulated metal cluster the optical and electronic properties can be altered, without changing the structural features of the outer carbon shell [10]. Furthermore a new mechanism for increasing the third-order nonlinear optical susceptibility is described for endohedral metallofullerenes [11]. The electronic responses of various atoms at the center of C_{60} have been computed by a number of workers [12-14]. Calculations of the electronic structure for the endohedral metallofullerenes $\text{K}@C_{60}$ and $\text{Cs}@C_{60}$ show charge transfer of one electron, from the endohedral metal atom to the C_{60} shell [15-17]. The charge-transfer from dopant atoms to the fullerene cage can be considered similar to the effect of optical excitation of the corresponding empty cage fullerene. That is, electrons are placed into the lowest unoccupied molecular orbital (LUMO), although there are no holes produced in the highest occupied molecular orbital (HOMO) as there are in the case of optical excitation. Analogy is particularly important because optical excitation has been shown both theoretically and experimentally to produce orders of magnitude enhancement in the hyperpolarizability of simple conjugated molecules [18-20]. M. Aichinger et al. using density functional theory, a jellium model for the C_{60} molecule and a pseudopotential for the magnesium ion, determined the energetic of the magnesium endohedral complex as a function of the magnesium ion's displacement from the fullerene's centre [21]. More detailed calculations for a variety of metallofullerenes show that the ions tend to lie off center and the negative charge on the fullerene cage is delocalized [22, 23]. Also the amount of off-center displacement has been shown to depend on the charge transfer and the size of the ion. The dependence on the ion size is estimated by comparing the equilibrium position of Na, Li, K, La and Y in C_{60} [23]. A 4-31G

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Table 1. The bond variable for $\text{Li}@C_{60}$. values are in Å.(short bond, r_{\min} , long bond, r_{\max} , and the length difference between the short and long bonds, Δr)

Molecule	x(Å)	r_{\max}	r_{\min}	Δr
$\text{Li}@C_{60}$.00	1.449387	1.404817	4.456992E-02
	.50	1.452525	1.402965	4.955960E-02
	1.0	1.453289	1.401356	5.193243E-02
	1.5	1.460453	1.399768	6.068555E-02
	2.0	1.499518	1.398046	1.014719E-01
	2.5	1.543500	1.394984	1.485143E-01

basis-set Hartree-Fock calculation on $\text{Na}^+@C_{60}$ has given the minimum energy when the sodium ion was displaced 0.66 Å away from the center. This asymmetrical result has been confirmed in linear combination of Gaussian type orbital (LCGTO) local density functional (LDF) calculations for $\text{Na}^+@C_{60}$ [14].

In this paper using HF-CI model, we study optical properties of $\text{Li}@C_{60}$ molecule. Since the ionic radii of the alkali metal ions Li^+ is much smaller than Na^+ , K^+ , Rb^+ and Cs^+ ions, a number of unusual structural phenomena might be expected and are indeed observed [24]. Calculations show that enclosed Li^+ ion moves off-center that is bigger than the off-center distance of the Na^+ [25, 26]. Jantoljak et al. [27] carried out a vibrational study on lithium-implanted fullerene films (LiC_{60}). F.Zerbetto et al. calculated the static first and second hyperpolarizabilities of $\text{Li}@C_{60}$ [10, 28].

2. The SSH Model

We extend the SSH Hamiltonian for $\text{Li}@C_{60}$ molecule as:

$$H_{SSH} = \sum_i (\epsilon_i + V_{0i}) c_i^* c_i + \sum_{(i,j)} [-t_0 + c\alpha(y_{ij})] (c_i^* c_j + HC) + \frac{1}{2} K \sum_i (y_{ij})^2. \quad (1)$$

Also, describe the conduction electrons interaction with the Li by a local pseudo-potential of the form $(\epsilon_i + V_{0i})$ [21].

Here y_{ij} is the change of the bond length between sites i and j , t_0 is the hopping integral and α is the electron-phonon coupling constant, c_i^+ (c_i) is the creation (annihilation) operator of the π electron at the site i , K is the spring constant, the sum is taken over nearest-neighbor pairs $\langle i, j \rangle$, ϵ_i is the orbital energy of π electrons that describes the additional Coulomb interactions between the inner metal ion and the cage.

$$\epsilon_i = -\frac{e}{r_{0i}}, \quad (2)$$

r_{0i} is the distance between the Li ion and the carbon atom at site i on the cage.

Also, V_{0i} describes the Coulomb interaction between the Li ion and the carbon atoms of the cage.

$$V_{0i} = A \frac{e^{-\beta r_{0i}}}{r_{0i}^2} \quad (3)$$

where A is a strength factor and $\frac{1}{\beta}$ is the Screening length.

We list all the parameters used in our calculations as [3]:

$$t_0 = 2.5 \text{ eV}, \alpha = 3.37 \frac{\text{eV}}{\text{\AA}}, k = 28.4 \text{ eV/\AA}^2$$

We also used parameters in SSH model of C_{60} from Harigaya paper [29].

3. The Hartree – Fock Configuration – Interaction Method

In the work, the PPP Hamiltonian is used with addition of a local pseudo-potential of the form $(\epsilon_i + V_{0i})$ [21]:

$$H = \sum_i (\epsilon_i + V_{0i}) c_i^+ c_i + \sum_{(i,j)} [-t_0 + \alpha(y_{ij})] (c_i^+ c_j + HC) + H_{int} \quad (4)$$

The first term of equation 1 was discussed in the previous section.

The H_{int} term is the long-rang Coulomb interaction in the form of Ohno potential that presents the electron-electron interaction between π electrons [30,31]:

$$H_{int} = U \sum_i \left(c_{i,\uparrow}^+ c_{i,\uparrow} - \frac{1}{2} \right) \left(c_{i,\downarrow}^+ c_{i,\downarrow} - \frac{1}{2} \right) + \sum_{ij,i \neq j} W(r_{i,j}) \left[\sum_{\sigma} (c_{i,\sigma}^+ c_{i,\sigma} - 1) \sum_{\tau} (c_{j,\tau}^+ c_{j,\tau} - 1) \right], \quad (5)$$

where the operator c_i^+ (c_i) creates (annihilates) a $2P_z$ electron of spin σ at site i (the i^{th} carbon atom), and

Table 2. The different components of the static linear polarizability (in a.u, 1a.u = 1.483×10⁻²³esu) and ΔE=|E_{LUMO}-E_{HOMO}| (in eV, 1eV ≈ 0.036 a.u) at model of PPP for the displacement(x) of the Lithium ion from the center along the z axis of C₆₀.

Molecule	X(Å)	α _{xx}	α _{yy}	α _{zz}	α	ΔE
C ₆₀						3.62
Li@C ₆₀	.00	1498.09	3594.23	3790.89	2961.07	2.42
	.50	1211.85	2869.78	3052.35	2377.99	2.37
	1.00	1019.02	2192.69	1916.73	1709.48	2.28
	1.50	709.47	1740.96	1530.54	1326.99	2.13
	2.00	1503.66	70.28	1424.80	999.58	2.05
	2.50	1594.57	2405.04	1372.47	1790.69	1.83

$$W(r) = \frac{1}{\sqrt{(1/U)^2 + (r/r_0V)^2}}, \quad (6)$$

is the Ohno potential [33]. Here U , is the interaction strength at $r=0$, V is strength of the long-rang part. The Coulomb interaction is treated by the HF approximation and the single CI for the Coulomb potential. The adiabatic approximation is forced on the bond variables are determined self- consistently using the SSH method.

If we write the HF ground state, $|g\rangle = \prod_{\lambda=occ} c_{\mu,\uparrow}^+ c_{\lambda,\downarrow} |0\rangle$ and the single electron-hole excitation states, $|\mu\lambda\rangle = c_{\mu,\sigma}^+ c_{\lambda,\tau} |0\rangle$ where λ and μ are occupied and unoccupied states and $|0\rangle$ is vacuum state, then we can divide the total Hamiltonian (1) into $H = H_{HF} + H'$ where H' is given by:

$$H' = U \sum_i (c_{i,\uparrow}^+ c_{i,\uparrow} - \rho_{i,\uparrow}) (c_{i,\downarrow}^+ c_{i,\downarrow} - \rho_{i,\downarrow}) + \sum_{ij,i \neq j} W(r_{i,j}) \left[\sum_{\sigma} (c_{i,\sigma}^+ c_{i,\sigma}) \sum_{\tau} (c_{j,\tau}^+ c_{j,\tau} - \rho_{j,\tau}) + \sum_{\sigma} (\tau_{i,j,\sigma} c_{j,\sigma}^+ c_{i,\sigma} + \tau_{j,i,\sigma} c_{i,\sigma}^+ c_{j,\sigma} - \tau_{i,j,\sigma} \tau_{j,i,\sigma}) \right], \quad (7)$$

with $\rho_{i,\sigma} = \langle c_{i,\sigma}^+ c_{i,\sigma} \rangle$ and $\rho \tau_{i,j,\sigma} = \langle c_{i,\sigma}^+ c_{i,\sigma} \rangle$. The matrix elements of H_{HF} and H' with respect to the electron-hole states are equal to

$$\langle \mu' \lambda' | (H_{HF} - \langle H_{HF} \rangle) | \mu \lambda \rangle = \delta_{\mu',\mu} \delta_{\lambda',\lambda} (E_{\mu} - E_{\lambda}), \quad (8)$$

and

$$\langle \mu' \lambda' | (H' - \langle H' \rangle) | \mu \lambda \rangle = 2J\delta_s - K, \quad (9)$$

where E_{μ} is the HF state energy and $\delta_s = 1$ is used for the spin singlet and $\delta_s = 0$ is used for the triplet states. The J and K terms in equation have the following forms [32,33]:

$$J(\mu', \lambda; \mu, \lambda) = \sum_{i,j} V_{i,j} \langle \mu' | i \rangle \langle \lambda' | j \rangle \langle j | \mu \rangle \langle i | \lambda \rangle,$$

$$K(\mu', \lambda'; \mu, \lambda) = \sum_{i,j} V_{i,j} \langle \mu' | i \rangle \langle \lambda' | j \rangle \langle j | \mu \rangle \langle i | \lambda \rangle, \quad (10)$$

$$K(\mu', \lambda'; \mu, \lambda) = \sum_{i,j} V_{i,j} \langle \mu' | i \rangle \langle \lambda' | j \rangle \langle j | \mu \rangle \langle i | \lambda \rangle, \quad (11)$$

where $V_{i,i} = U$ and $V_{i,j} = W(r_{i,j})$ or $i \neq j$ and $U=2V=4t$. Diagonalization of the total Hamiltonian H , gives the singlet and triplet excitonic states of $Li@C_{60}$. In the actual calculation, we limit the spin configuration to the singlet excitations.

In the Numerical calculation we take:

$$t_0 = 1.8 \text{ eV}, \alpha = 3.54 \frac{\text{eV}}{\text{\AA}}, U = 2V = 4t, A = 40 \text{ eV}\text{\AA}^2, \frac{1}{\beta} = 0.435 \text{ \AA}.$$

It should be noted that when ion (Li^+) is in the cage center, the $Li^+@C_{60}$ properties is similar to the pristine C_{60} and we fit our parameters in this state with the C_{60} properties [31].

Parameters A and β can be determined by other results of first-principle calculation or by experiment [14].

4. Results and discussions

Using the HF, single CI and SSH models, we calculate the electronic structure of $Li@C_{60}$ molecule without spin flip. We then exploit HF-single-CI-SOS [34] approach, as developed by the other authors, to study the ion movement and the exciton effects on the optical spectra. We also used parameters in PPP model of C_{60} of other authors [35]. The property of electronic excited state was obtained by single electron excitation configuration interaction using the PPP model.

The quantities computed include total energy of this endohedral complex, the change of the bond length, the static ($\omega = 0$) linear and non linear optical (NLO) coefficients, polarizability, $\alpha_{ij}(-\omega, \omega)$ first hyperpolarizability, $\beta_{ijk}(-2\omega; \omega, \omega)$ for some positions of the Li atom inside the C_{60} cage. The tumbling average linear polarizability and first and second hyperpolarizabilities are given by:

$$\alpha = \frac{1}{3} \sum_i \alpha_{ii}(-\omega, \omega), \quad (12)$$

Table 3. The different components of the static first polarizability (in 100 a.u, 1a.u = 8.637×10⁻³² esu) for PPP model and the displacement(x) of the Lithium ion from the center along the z axis of C₆₀.

Molecule	(Å)	B _{xxx}	B _{yyy}	B _{zzz}	$\bar{\beta}_x$	$\bar{\beta}_y$	$\bar{\beta}_z$
Li@C ₆₀	.00	1.02	-8.21	11.40	-26.52	-7.04	13.17
	.50	3.98	-13.35	-96.92	10.11	-66.35	-145.64
	1.00	3.07	-1.21	-153.97	-10.43	-32.75	-203.73
	1.50	-4.97	-2.33	-152.01	7.44	-25.43	-163.99
	2.00	18.66	36.03	-155.03	-30.49	40.53	-331.72
	2.50	-18.11	17.64	-147.39	3.49	61.80	-617.88

$$\beta = \frac{1}{3} \sum_j (\beta_{ijj} + \beta_{jji} + \beta_{jij}), \quad (13)$$

where *i, j, k* and *l* represent x, y and z in Cartesian coordinates.

We study the case of an endohedral complex of Li@C₆₀ that consists of C₆₀ with a Li trapped inside. This kind of complex has one more electron and has an open-shell electronic structure. The Li atom inside the cage loses its one valence electron to the cage very easily. Therefore, in fact, it is a Li ion that is inside, but now there is N+1 π electron in the fullerene cage. The introduction of an additional electron in the fullerene cage may lead to a distortion which destroys the icosahedral symmetry and generates new minima [36, 37]. Substitution of the electron with an atom of Li similarly affects the system so that the most symmetric structure in which the endohedral atom sits at the baricentre of the pristine cage is a maximum in the potential energy surface described by the displacement of the guest atom.

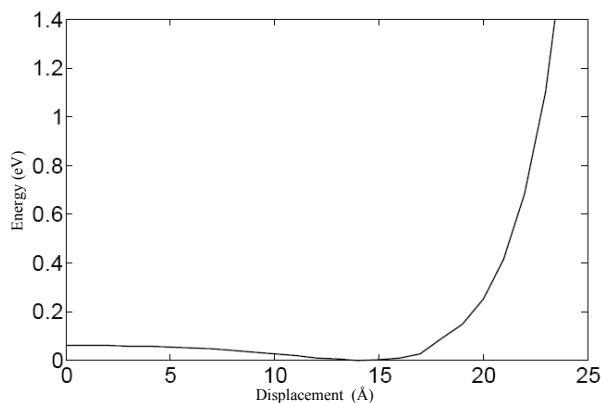


Fig. 1. The total energy versus the movement of the lithium atom along the z axis. When all the carbon atoms are stable

We keep all carbon atoms stable on the C₆₀ cage and moved the Li ion along the five fold axis and used the models that we proposed to calculate the optical spectra and structural properties of the Li@C₆₀ molecule.

In Fig. 1 we plot, using the SSH model, the calculated total energy of this endohedral complex versus the displacement of the Li atom from the centre of the cage along a five fold axis. The results show that at

the centre of the cage, the energy is a local maximum and the Li atom is unstable, when it moves a certain distance (here about 1.4 Å) from the cage centre. It reaches a minimum point which is lower than the energy at the centre by 0.06 eV. When the atom moves further towards the cage, the energy increases rapidly. This result is similar to the first-principles calculations [14, 25, 14].

The length of the short and long bonds and the length difference between the short and long bonds for Li@C₆₀ molecule are presented in Table 3 using SSH model. Our calculations show that effect of the movement of the ion on the length of the bond of this molecule is significant and agree well with the other works [3].

We next calculate the static polarizability using HF single CI model. In Tables 1, we present the results against position of the Li atom inside the C₆₀ cage. We compare our results with experimental data, of C₆₀ molecule and Li@calix[4] pyrool. For C₆₀ a value of 516.2 ± 54 (au) was reported for the static polarizability [38]. Wei Chen et al. [39] indicated that the static polarizability of Li@calix[4] pyrool Li@calix [4] pyrool (363 au) is bigger than calyx[4]pyrool (251 au). Our results indicate that the static polarizability of Li@C₆₀ is bigger than C₆₀. Also, the static polarizability changes by the ion (atom) movement. It appears that the order of the polarizability of Li@C₆₀ could be as high as 10⁴ (au).

Table 2 shows the static first hyperpolarizability components for some positions of the Li atom inside the C₆₀ cage using HF single CI model. They cover a wide range whose absolute value varies from 102 to 61700 (au). Both positive and negative values are found. Averaging over the motion of the Li atom should be performed to obtain a value to relate to the experimental observation since the individual values are not observables. We compare results obtained by the present model for related systems. E. B. Eleanor et al. [10] indicate that the static β of Li@C₆₀ changes by the Li atom movement and cover a wide range whose absolute value varies from 0 to 3390 (au). By means of the density functional theory method determined that the β values of alkali compound, Li⁺ (calyx [4] pyrool) M⁺ (M=Li, Na, and K), are 8.9 × 10³, 1.0 × 10⁴, and 2.4 × 10⁴ au for M = Li, Na, and K, respective-

ly[40], also the alkalide anions Li₂F⁻ and Li₆F⁻ have large first hyperpolarizabilities (the static $\beta=1.116\times 10^4$ and 17.64×10^4 au) [41] that are of the order of the static β values of Li@C₆₀. The static β value of Pristine C₆₀ (3.24au) [42] is smaller than the static β of Li@C₆₀ and roughly 10000 times smaller than the largest value of our calculation.

From Table 1, it can be seen that transition energy for Li@C₆₀ is smaller than C₆₀. As a test case, the order of ΔE for Li@C₆₀ (0.087 a.u) in the PPP model is similar to Li@C₆₀ (0.033 a.u) in reference [10]. Clearly, small transition energy is a decisive factor and leads to a considerably large (hyper) polarizability [39]. The large (hyper) polarizability of Li@C₆₀ almost comes from the excess electron of the Na atom.

5. Conclusions

We have investigated the movement of the Li atom effect on the optical spectra and the electronic structure of Li@C₆₀ using PPP-SOS and SSH models, respectively. Our results have indicated that the static (first) polarizability of Li@C₆₀ is bigger than C₆₀. Also the excess electron from the Na atom plays an important roll in the large (first) polarizability of Li@C₆₀. It had specified that the (first) polarizability value of Li@C₆₀ depend on the Li position and it must have been enhanced by choosing the proper position for the Li atom. Our calculations have indicated that the Na atom effect on the bonds length of C₆₀ is dramatic. The model that we proposed could also be applied to other endohedral complexes which consist of different kinds of atoms or ions and different fullerenes. These results may provide new means for designing high-performance nonlinear optical materials.

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