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Structure and properties of $Li@C_{60}$–PF_6 endofullerene complex

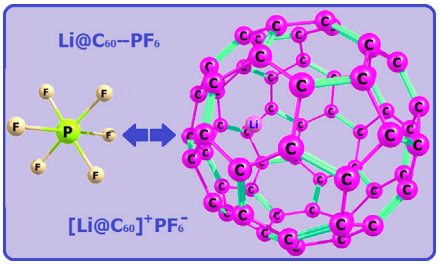
Ambrish Kumar Srivastava, Abhishek Kumar, Neeraj Misra *

Department of Physics, University of Lucknow, Lucknow 226007, India

HIGHLIGHTS

- Li@C60-PF6 endofullerene complex has been studied.
- The complex is stabilized by charge transfer from Li@C60 to PF6 superhalogen.
- The spectral properties of Li@C60-PF6 agree with the experiments.
- Li@C60-PF6 possesses significant nonlinear optical response.

GRAPHICAL ABSTRACT



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ABSTRACT

$Li@C_{60}$ is a prototype endofullerene, which has been widely studied. Employing density functional theory we study the interaction of $Li@C_{60}$ with PF_6 superhalogen, which leads to the formation of $Li@C_{60}$–PF_6 endofullerene complex. The spectral properties such as infrared and UV-visible spectra have been calculated, which agree well with corresponding experimental data. The vibrational assignments and electronic transitions in the complex have been explored. We have noticed that this complex is stabilized by charge transfer from $Li@C_{60}$ to PF_6, which results in its large dipole moment (20 Debye), high mean polarizability (494 a.u.) and significant mean hyperpolarizability (1500 a.u.). We, therefore, believe that $Li@C_{60}$–PF_6 endofullerene complex might attract further attention for their possible electrooptical applications due to its enhanced nonlinear optical properties.

1. Introduction

Endohedral fullerenes or endofullerenes (EFs) [1] have been widely known for their unique structures, novel electronic properties, and potential applications in a variety of fields, such as nanoelectronics, nanotechnology, and biomedical applications [2]. $La@C_{60}$ was first endofullerene discovered by Heath et al. [3]. It has been recognized that the dynamic behavior of encapsulated (positively charged) metal atoms makes a major contribution to the electronic and chemical properties of the EFs. $Li@C_{60}$, being a prototype alkali metal doped C_{60} fullerene, has been extensively studied [4–9]. The reactivity of $Li@C_{60}$ endofullerene leads to the formation of dimer [10] and complexes [11,12]. Wang et al. [13] have theoretically studied the structures and nonlinear optical (NLO) properties of $Li@C_{60}$–BX_4 (X = F, Cl, Br) complexes. In this complex, the charge transfer takes place from $Li@C_{60}$ due to high electronegativity of BX_4 moiety. The large NLO response of the complex is expected due to electron transfer from donor $Li@C_{60}$ and acceptor BX_4. In fact, the electron affinity of BX_4 exceeds that of halogen atom, so that it behaves as superhalogen [14–18]. Superhalogens are hypervalent species, which need an extra electron to complete their octet. Aoyagi et al. [11] have experimentally synthesized $Li@C_{60}$–$SbCl_6$ complex and subsequently the synthesis of $Li@C_{60}$–PF_6 complex is reported by Okada et al. [12]. Like BX_4, $SbCl_6$ and PF_6 also possess superhalogen properties. Superhalogens are known for their high oxidizing capacity. For instance, superhalogens are capable to oxidize Xe atom and O_2 molecule [19]. Due to this virtue of superhalogens, the extraction of pure $Li@C_{60}$ has

* Corresponding author.
E-mail addresses: neerajmisra11@gmail.com, mishra_neeraj@lkouniv.ac.in (N. Misra).

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been suggested by their complexes [11,12]. It has been recently shown that superhalogen anions show electronic integrity, irrespective of the nature of species. For instance, BF_4^- anion possesses similar electronic properties as those of PF_6^- [20]. This motivated us to perform a theoretical study on the Li@C_{60}–PF_6 complex. We focus on the structural, spectral and electronic properties of the complex. The large NLO response of this complex is particularly highlighted.

2. Computational details

We have used density functional theory based B3LYP method with 6–31 G(d) basis set as implemented in GAUSSIAN 09 program [21]. B3LYP is a hybrid form of exchange-correlation functional which combines parameterized Becke's exchange term [22] and correlation term devised by Lee, Yang and Parr [23]. Recently, B3LYP method has been used to provide accurate results at affordable cost in various C_{60} derivatives and related systems [13,24–27]. Furthermore B3LYP has also been employed to study anionic clusters of fluorine, which behave as superhalogens [28]. The geometry optimization has been carried out without any symmetry constraint in the potential energy surface. The vibrational frequencies of optimized structures have been computed at the same level of theory.

The NLO properties of Li@C_{60}–PF_6 complex have been explored by calculating, static dipole moment (μ), mean polarizability (α_o) and first order static mean hyperpolarizability (β_o). The α_o and β_o are given as:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

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

$$\beta_o = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2}$$

$$\beta_i = \frac{3}{5}\left(\beta_{iii} + \beta_{ijj} + \beta_{ikk}\right)$$

where μ_i, α_{ij} and β_{ijk} are the components of dipole moment vector, polarizability and hyperpolarizability tensors along directions specified by subscripts, i, j and $k = x, y$ and z. The components of polarizability and hyperpolarizability are evaluated by numerical differentiation using uniform electric field of magnitude 0.001 a.u.

3. Results and discussion

3.1. Structural properties

The equilibrium structure of Li@C_{60}–PF_6 calculated at B3LYP/6–31G(d) level has been shown in Fig. 1. For Li@C_{60}, Li atom goes away from centre of C_{60}, whose distance from centre (d_{centre}) is 1.52 Å, as already reported by Li and Tománek [29,30]. The d_{centre} reduces to 1.26 Å, by interaction of Li@C_{60} with PF_6. Due to large electronegativity difference between P and F in PF_6, the electrons are delocalized over F atoms such that P becomes positively charged (2.73e). This causes to repel electropositive Li and decrease d_{centre} value. PF_6 is hypervalent species, which needs an extra electron for stability. Net NBO charges on Li and PF_6 are obtained to be 0.65e and −0.87e, respectively, which suggest that Li@C_{60}–PF_6 complex is stabilized by the electron transfer from Li atom to PF_6 superhalogen moiety. In order to get insights into interaction of PF_6 with Li@C_{60}, we have performed quantum theory of atoms in molecule (QTAIM) analysis [31]. QTAIM describes interaction between two atomic basins using topological parameters such as Laplacian of electron density ($\nabla^2\rho$), ratio of Hessian eigen-values ($|\lambda_1|/\lambda_3$) at bond critical points (BCPs). The nature of interaction is characterized by $\nabla^2\rho < 0$ and $|\lambda_1|/\lambda_3 > 1$, for covalent bonding, whereas ionic bonding is described by $\nabla^2\rho > 0$ and $|\lambda_1|/\lambda_3 < 1$. The molecular graph of Li@C_{60}–PF_6 complex obtained by QTAIM analysis is displayed in Fig. 2. One can note that the PF_6 interacts to Li@C_{60} via three F atoms, whose bond lengths are depicted in Fig. 1. It is clear (see Fig. 1) that F1, F2 and F3 of PF_6 interacts with C1, C2 and C3 of Li@C_{60} with bond distances of 2.99 Å, 2.56 Å and 2.55 Å, respectively. In addition, F1 also interacts with C2 interacts with the bond distance of 2.97 Å. The $\nabla^2\rho$ values for all these interactions range from 0.0379 to 0.0645 a.u., whereas $|\lambda_1|/\lambda_3$ values lie between 0.1134 and 0.1819 a.u. These values suggest that the interaction between PF_6 and Li@C_{60} is essentially ionic. The binding energy (ΔE) of Li@C_{60}–PF_6 complex can be estimated as follows:

$$\Delta E = E\left[PF_6\right] + E\left[Li@C_{60}\right] - E[Li@C_{60} - PF_6]$$

where E[.] represents the electronic energy of the respective species including zero point correction. The ΔE value calculated at B3LYP/6–31G(d) level is found to be 4.45 eV Although, the basis set superposition error [32] is not included in this binding energy, the calculated value is large enough to establish the stability of the complex. In order to analyze the stability of Li@C_{60}–PF_6 complex

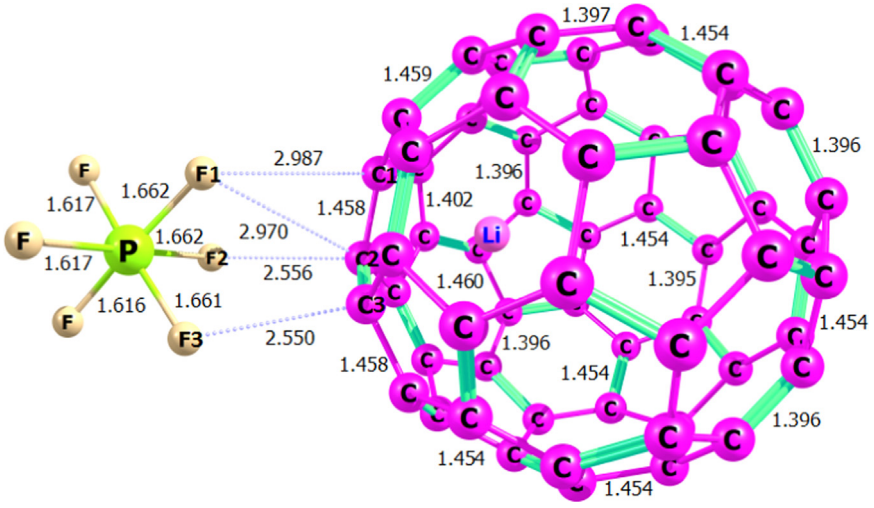

Fig. 1. Equilibrium structure of Li@C_{60}–PF_6 obtained at B3LYP/6-31 G(d) level. Selected bond lengths (in Å) are displayed.