

## Electronic dipole moment of alkali-C<sub>60</sub> molecules

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First-principle electronic structure calculations are carried out for  $M_xC_{60}^q$ , where  $M=Li,Na,K$  using the local density functional. The calculated Mulliken charge indicates that the bonding of the alkali atom with  $C_{60}$  is mostly ionic except for lithium. The difference in the most stable geometry between lithiums and the other alkali atoms on  $C_{60}$  comes from the covalent character of the lithium-carbon bond. Our results of LDA calculations do not support the skating of the sodium droplet on  $C_{60}$  [4]. The electric dipole moments of  $Na_xC_{60}$  in the droplet and the atom-like geometry are calculated using the LDA functional. The electric polarizability estimated by the calculated dipole moment and the droplet skating picture does not agree with the experimental polarizability. The calculated bonding energy of the sodium droplet on  $C_{60}$  is at least 1 eV smaller than that of the other stable structures. Instead of the droplet, we introduce the atoms skating independently on  $C_{60}$  with screened Coulomb type repulsive interaction. The interaction between sodium atoms on  $C_{60}$  is extracted from the result of Stern-Gerlach experiment. The extracted interaction is smaller as the number of sodium atoms increased, which is consistent with the calculated result of the Mulliken charge.

Key words: Alkali Fullerene, Geometry, Dipole moment

### 1. INTRODUCTION

After the discovery of superconductivity in  $K_3C_{60}$  films, alkali-doped fullerenes have much more interest in its variety of physical properties. Works on the gas-phase exohedral alkali-doped fullerenes have been devoted to predictions of the physical and chemical properties of the solid state fullerides [1, 2, 3]. An extensive experiment of the mass spectrum of  $M_xC_{60}^+$  ( $M=Li,Na,K$ ) clusters was performed by Martin et. al. [1]. The even-odd alternation onset of  $(Na_6C_{60})_nNa^+$  is regarded as the beginning of the metal-metal bonding on the  $C_{60}$  surface. They speculated that the first seven Na atoms transferring electrons to  $C_{60}$  are placed themselves as far from one another as possible.

A systematic PES study of B. Palpant et. al. gives the vertical detachment energy (VDE) and the adiabatic electron affinity (AEA) for  $Na_xC_{60}^-$  ( $x=0-33$ ) [2]. Based on the peak positions of VDE and AEA at  $x=3,6,9,12$ , they proposed special stability of the trimers on  $C_{60}$ . A single sodium trimer on  $C_{60}$ , however, disagrees with the growth sequence proposed by Martin et. al.

The Stern-Gerlach experiment for  $Na_xC_{60}$  cluster around 300K is performed by Dugourd et. al. [4]. They suggested that the droplet of sodium atoms is formed on  $C_{60}$  to explain the result of experiment. This geometry is completely different from the most stable geometry of  $M_xC_{60}$  speculated by Martin et. al. or Palpant et. al.

The above experiments can not directly identify the geometry of these clusters. Then, the theoretical electronic structure calculation is necessary to determine the most stable geometry of these molecules.

Many articles have been devoted to the theoretical calculations of alkali fullerides [5, 6, 7, 8, 9, 10].

However, some of these calculations are the semi-empirical method MNDO which sacrifices some of accuracy compared with the first-principle calculations. Moreover, all of these calculations are performed with the assumption of symmetry restriction on the geometry of molecule. The assumption of symmetry restriction is inadequate to investigate the geometry speculated by the experiments such as the trimers of the alkali atoms on fullerene. To provide these geometries using the theoretical calculation, we should remove the symmetry restriction for the geometry of the clusters.

The number of the alkali atoms on  $C_{60}$  in the above calculations is restricted from one to three for  $Na_xC_{60}$  and  $K_xC_{60}$ . However, the interesting bonding features of the alkali atoms on  $C_{60}$  are speculated for more than the two alkali atoms on  $C_{60}$ . Therefore, the calculation for more than the three alkali atoms on  $C_{60}$  is necessary to compare the character of bonding between lithiums, sodiums, and potassiums on  $C_{60}$ .

The purpose of the present study is to investigate the bonding nature of  $M_xC_{60}$  using the geometry optimization calculation in the density functional theory without any symmetry restrictions. We especially investigate whether the droplet on  $C_{60}$  is consistent with the result of the calculated dipole moment and bonding energy. We will refer to the alkali atoms Li, Na, and K as the symbol  $M$  throughout the paper.

### 2. METHOD

We performed self-consistent field calculations for  $M_xC_{60}$  using the density functional theory (DFT). The calculations were carried out using Amsterdam Density Functional program system (ADF) [11] which is a DFT code using the linear combination of atomic orbitals (LCAO) approach together with Slater type

atomic orbitals. The bases set used in the calculations is the double-zeta bases set. In this work, we applied the local density approximation (LDA) using the exchange-correlation potential of Vosko, Wilk, and Nusair [12].

We performed the geometry optimization of  $M_xC_{60}$  which is divided into two steps. First, geometry of  $C_{60}$  is optimized without any symmetry constraint. In the next step, we performed the geometry optimization of  $M_xC_{60}$  without any symmetry constraint. In order to save computer work, we assumed the position of  $C_{60}$  to be fixed to the geometry obtained in the first step.

### 3. BONDING NATURE OF $M_xC_{60}$

In this section, we will review the result of the geometry optimization calculation of  $M_xC_{60}$  of our previous work [14]. Throughout the following sections, we use the adsorption energy  $\Delta E$  which is defined as

$$\Delta E \equiv E(C_{60}^q) + xE(M) - E(M_xC_{60}^q), \quad (1)$$

where  $E(X)$  is the total energy of molecule  $X$  and  $q$  is the ionicity ( $0, \pm 1$ ).

Figure 1 shows the Mulliken charges per alkali atom of  $M_xC_{60}$  ( $x = 1, 2, 6, 12$ ) for various geometries. If many alkali atoms are lying on  $C_{60}$ , we take their average over each alkali atom. The lines in the figure are obtained by the linear least square fit to the data for each kind of alkali atom.

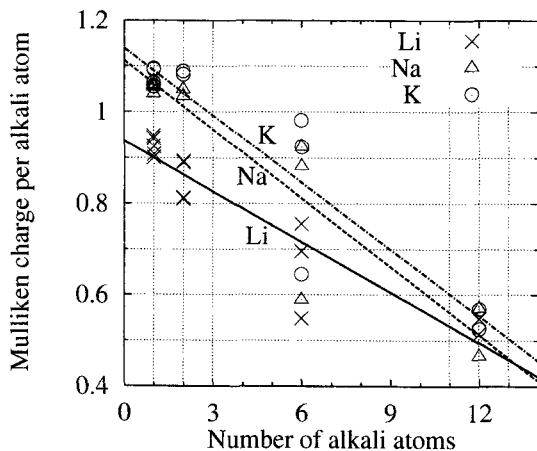


Fig. 1: The Mulliken charges per alkali atom (in electrons) in  $M_xC_{60}$  as a function of  $x$ .

We find from figure 1 that the Mulliken charges are decreased for all kinds of the alkali atoms according as the number of the alkali atoms is increased. The lines in the figure indicate that the Mulliken charges of sodium and potassium behave similar as a function of the number of the alkali atoms. The charges of lithium are smaller than those of sodium and potassium for all number of the alkali atoms which we investigated. The decrease of the Mulliken charges for larger number of the alkali atoms result from the more covalent character of bonding between the lithium atom and the carbon atom, which is also true for the alkali-graphite intercalation[16] and

organolithium compounds[17]. The enhanced covalency in lithium-carbon interaction comes from the contribution of the 2p electrons of the lithium atom.

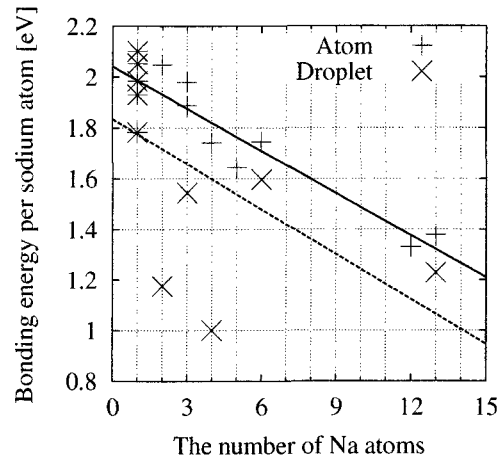


Fig. 2: The bonding energy of  $Na_xC_{60}$  for droplet-like geometry and atom-like geometry as a function of  $x$ .

We discuss the bonding nature of  $M_6C_{60}$  and  $M_6C_{60}^-$  which have six and seven valence electrons, respectively. We obtain the result for two types of geometries named as P6 and PH5. In the P6 geometry, the alkali atoms are located above the pentagonal rings of which the positions are as close to one another as possible. In the PH5 geometry, one of the alkali atoms is located above the pentagonal ring. The others are located above the hexagonal rings surrounding this pentagonal ring.

The distance in the optimized geometry of PH5 are 3.39, 3.67, and 4.11 Å for  $Li_6C_{60}$ ,  $Na_6C_{60}$ , and  $K_6C_{60}$ , respectively. The results of the distance between the alkali atoms for the PH5 geometry are approximately equal to the twice of the atomic radius which are 3.12, 3.82, and 4.70 Å for the Li, the Na, and the K atom, respectively. We expect, therefore, that the bonding between the alkali atoms is weak for the P6 geometry and strong for the PH5 geometry.

The adsorption energies of  $Li_6C_{60}$ ,  $Na_6C_{60}$ , and  $K_6C_{60}$  for the P6 geometry are 2.47, 0.89, and 0.54 eV higher than those of the PH5 geometry, respectively. The most stable geometry is the PH5 geometry for  $Na_6C_{60}^-$  and  $K_6C_{60}^-$ , while P6 is the most stable geometry for  $Li_6C_{60}^-$ . Similar values are obtained for the adsorption energies of  $Na_6C_{60}$  for the different geometries, which is also true for  $Na_6C_{60}$ . The most stable geometry is, however, changed to the PH5 geometry. For  $K_6C_{60}^-$ , we find a large difference of the adsorption energy between the PH5 geometry and the other geometries ( 1 eV ).

### 4. STERN-GERLACH EXPERIMENT

From the result of the Stern-Gerlach experiment at 300 K for  $Na_xC_{60}$ , Dugourd et. al. proposed "classical droplet model" in which the droplet of sodium atoms skates on the  $C_{60}$  surface [4]. They assumed that one electron is transferred from the sodium

droplet to the  $C_{60}$ . A permanent dipole  $\mu_{\text{drop}}$  induced by this electron transfer is estimated using the classical formula [15]. To investigate whether the droplet can be formed at the experimental temperature, we have calculated the bonding energies for the “droplet-like” and “atom-like” geometries of  $Na_xC_{60}$ , respectively. In the atom-like geometry, sodium atoms are located above the pentagonal or hexagonal ring of which the positions are not neighboring each other. As shown in figure 2, the bonding energies of the droplet-like geometries are at least 1 eV smaller than the atom-like geometries. Therefore, it is difficult to populate  $Na_xC_{60}$  with the droplet-like geometry even at the experimental temperature (300 K). This result contradicts the classical droplet model.

We consider two kind of models to compare the experimental polarizabilities with the dipole moment estimated by the LDA calculation. One is the “droplet-like model” in which the droplet on  $C_{60}$  can freely skates on the  $C_{60}$  surface. The weak interaction between electric dipole moment and  $C_{60}$  may cause thermal equilibrium of a single electric dipole moment. Under the thermal equilibrium assumption, we can calculate the polarizability of  $Na_xC_{60}$  using the Langevin function which is well known in the statistical theory of paramagnetism. Then, the polarizability for  $Na_xC_{60}$  is  $\frac{1}{3} \frac{\mu_{\text{drop}}^2}{k_B T}$ , where  $\mu_{\text{drop}}$  is the magnitude of the dipole moment of  $Na_xC_{60}$  with the droplet-like geometry. The dipole moment  $\mu_{\text{drop}}$  is calculated using the LDA functional.

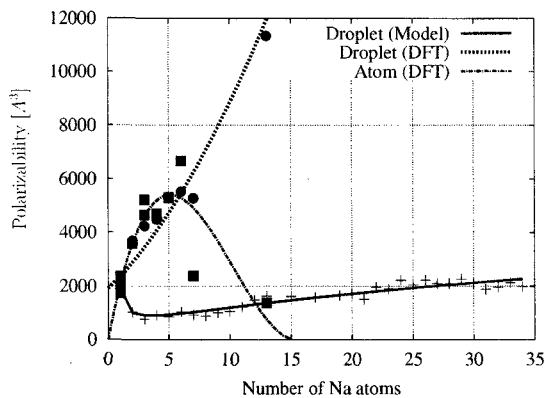


Fig. 3: The polarizability of  $Na_xC_{60}$  evaluated by three kinds of methods. The “Droplet (Model)” is a classical model to fit the experiment [4]. In the “Droplet (DFT)” and “Atom (DFT)”, the dipole moment is evaluated by the DFT calculation for droplet-like and atom-like model, respectively.

The other model is the “atom-like model” in which we consider the sodium atoms skating independently on the  $C_{60}$  sphere. The magnitude of the dipole moment of each atom  $\mu_{\text{atom}}^i$  is supposed to be the same for all atoms. The direction of  $\mu_{\text{atom}}^i$  is assumed to be parallel to the vector from the center of  $C_{60}$  to the position of each atom. Furthermore, we neglect the interaction between the sodium atoms. If

the thermal equilibrium is attained by the weak interaction of the atoms with  $C_{60}$ , the thermal average of dipole moment of each atom can be calculated using the Langevin function. Then, the polarizability for  $Na_xC_{60}$  is  $\frac{x}{3} \frac{\mu_{\text{atom}}^2}{k_B T}$ , where  $\mu_{\text{atom}}$  is the magnitude of the dipole moment of each atom. The dipole moment  $\mu_{\text{atom}}$  can be calculated using the following equation,

$$\mu_{\text{total}} = \sum_{i=1}^x \mu_{\text{atom}}^i, \quad (2)$$

where  $\mu_{\text{total}}$  is the dipole moment of  $Na_xC_{60}$  with atom-like geometry calculated using the LDA functional.

We show in figure 3 the calculated polarizability using the droplet-like and the atom-like model. We can conclude from figure 3 that both models can not explain the polarizability of Stern-Gerlach experiment. For example, the calculated polarizability for droplet-like  $Na_{13}C_{60}$  ( $11347 \text{ \AA}^3$ ) is 7 times larger than the experiment ( $1630 \text{ \AA}^3$ ). The polarizability for  $Na_6C_{60}$  evaluated using the atom-like model ( $6670 \text{ \AA}^3$ ) is 6 times larger than the experiment ( $1034 \text{ \AA}^3$ ).

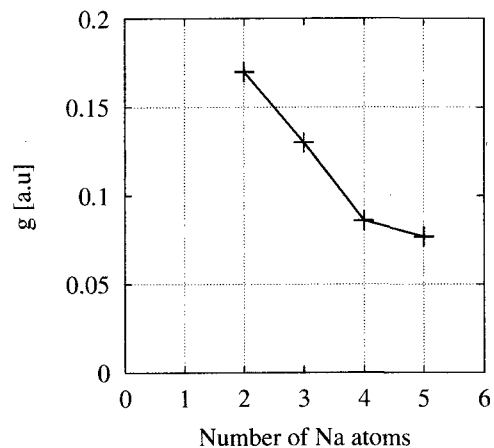


Fig. 4: The coupling parameter  $g$  of  $Na_xC_{60}$  as a function of  $x$ .

To explain these discrepancies, we introduce another model. As seen in the previous section, the Na- $C_{60}$  bond is almost ionic. Then the interaction between sodium atoms should be included. We employ the screened Coulomb type interaction between the sodium atoms. The energy of this model is

$$E = - \sum_i \mu_{\text{atom}}^i \cdot \mathbf{F} + \sum_{i < j} \frac{g}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (3)$$

where  $\mathbf{F}$  is the electric field and  $\mathbf{r}_i$  is the position of the sodium atom. If the thermal equilibrium is attained, the susceptibility  $\alpha$  can be evaluated using

$$\alpha = \lim_{F_z \rightarrow 0} \frac{\partial}{\partial F_z} \left( \frac{1}{\beta} \frac{\partial}{\partial F_z} \ln Z \right), \quad (4)$$

where  $Z$  is the partition function. We extracted the coupling factor  $g$  using the experimental data. The

extracted interaction shown in the figure 4 becomes smaller as the number of sodium atoms is increased. This is consistent with the result that the Mulliken charge per atom is decreased with the number of sodium atoms.

## 5. SUMMARY AND CONCLUSION

We have performed the LDA calculations with the LCAO approach to study the bonding nature of a single alkali atom to C<sub>60</sub> and the bonding between many alkali atoms on C<sub>60</sub>.

The Mulliken charges per alkali atom for M<sub>x</sub>C<sub>60</sub> are evaluated in the present calculation. The decrease of the Mulliken charge for larger number of the alkali atoms indicates the increase of covalency between the alkali atoms and C<sub>60</sub>. We find, in the present calculation, that the Mulliken charges of lithium are smaller than those of the other alkali atoms. The result reflects the more covalent character of the lithium-carbon interaction relative to the other alkali atoms, which is also true in the alkali-graphite intercalation compounds[16] and organolithium compounds [17].

The bonding energy of droplet-like geometry of sodium atoms on C<sub>60</sub> is the lowest within all geometries which we selected in this work. The polarizabilities obtained by the Stern-Gerlach experiment can not be explained by the droplet-like model. The interaction between sodium atoms on C<sub>60</sub> plays an important role to explain the experimental polarizability. Supposing the thermal equilibrium is attained, we extract screened Coulomb type interaction between the sodium atoms. The extracted strength of the interaction becomes smaller as the number of sodium atoms is increased. The result is consistent with the decrease of Mulliken effective charge. As pointed in ref. [18], it is not obvious to assume the thermal equilibrium. We think, however, qualitative features are not changed under the assumption. This point will be studied in the future study.

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