

# Evolution of Bond Distortion in $C_{60}$ by an Electron Uptake

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When an electron is transferred to  $C_{60}$ , the bond structure is distorted due to the electron-lattice interaction and a polaron-like state is formed. The evolution process of the bond distortion is studied by the dynamical equation of atomic lattice, and time-dependent changes of the bond lengths are determined. Then it can be estimated that the relaxation time to form the polaron-like state is a fraction of a picosecond.

## Introduction

One of the most remarkable properties of  $C_{60}$  is the superconductivity.<sup>1</sup> When  $C_{60}$  is doped with alkali metal,  $M_3C_{60}$  becomes superconductor with fairly high transition temperature ( $T_c \sim 30$  K). During the doping, the electrons are transferred from the alkali metal to  $C_{60}$ . Obviously the charge transfer plays an important role in the superconductive mechanism which has not been revealed yet. Many groups<sup>2-6</sup> have studied the process of charge transfer in  $C_{60}$ . They commonly find that the bond structure of the neutral  $C_{60}$  is unstable against the charge transfer. When an electron enters the lowest unoccupied molecular orbitals (LUMO), the original truncated icosahedral structure with symmetry  $I_h$  is distorted by the interaction with the extra electron. The distortion depends on the electron-lattice coupling. Usually the symmetry of the charged  $C_{60}$  is reduced from  $I_h$  to  $D_{3d}$ ,<sup>5,6</sup> but if the electron-lattice coupling is strong enough<sup>6</sup>, the symmetry can be further reduced to  $C_{2v}$  or  $C_s$ .

In order to demonstrate the lattice distortion distinctly, the truncated icosahedron of  $C_{60}$  is oriented in such a way that the top and bottom faces are the pentagons, which are shown in Figure 1, then all 90 bonds in  $C_{60}$  are divided into 13 layers indicated by the numbers in Figure 1. Before the charge transfer, there are only two kinds of bond in the neutral  $C_{60}$ : the single bonds in the border between the pentagon and hexagon, and the double bonds in the border between two hexagons. The former is a long bond with length  $d_1 = 1.43$  Å and the latter is a short bond with length  $d_2 = 1.39$  Å. The layers with numbers 1, 3, 5, 6, 8, 9, 11, 13 are single bonds, and the rest are double bonds.

After the charge transfer the lattice structure is distorted and the bond lengths change. The bonds in the same layer get same changes in their bond lengths, but the change  $\Delta d$  of the bond length depends on the layer. In the case of  $D_{3d}$  the layer-dependence of the changes  $\Delta d$  is shown in Figure 2. It can be seen from Figure 2 that the distortion mainly takes place in the equator area (6, 7, 8-th layers).

Other layers have only little distortion. Such localized distortion is called as "string polaron".

However, all these existing results about the bond distortion of charged  $C_{60}$  are static studies, which only tell the final distortion of the bond structure of charged  $C_{60}$ . They do not give the evolution process how the bond structure

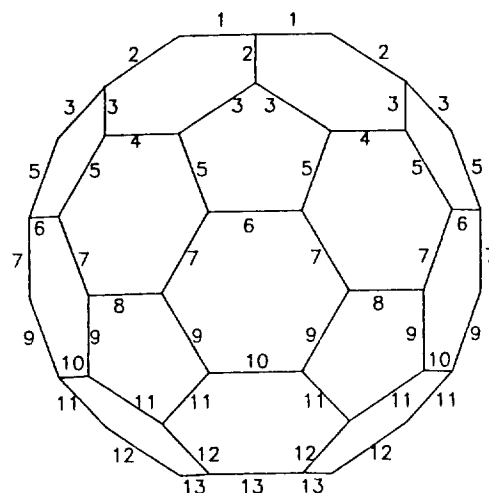


Figure 1. The layer structure of bonds in  $C_{60}$ .

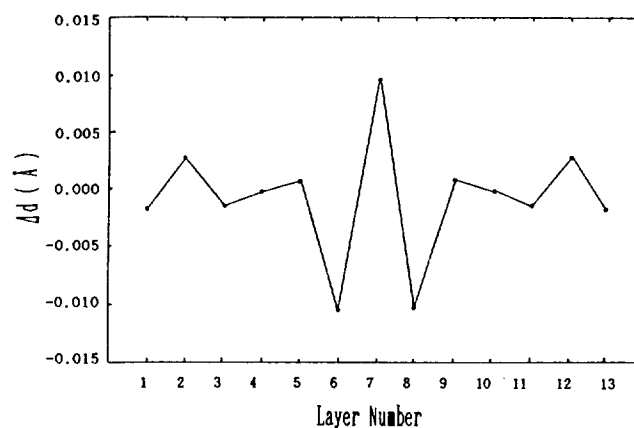


Figure 2. The layer-dependence of bond-length changes  $\Delta d$  in  $C_{60}$  by an Electron Uptake.

changes from the original configuration with symmetry  $I_h$  to the distorted configuration with lower symmetry  $D_{3d}$ . This paper studies the evolution of the bond distortion caused by the charge transfer in  $C_{60}$  by means of dynamical equation, which can give the time-dependence of the bond distortion and estimate the relaxation time to form the polaron.

## Theoretical Method

Following the previous papers,<sup>2-6</sup> a tight binding method is used to describe the  $\pi$  electrons in C<sub>60</sub> which hop between the nearest neighbor carbon atoms. Each carbon atom has three nearest neighbors and the hopping constant  $t(\vec{r}_i, \vec{r}_j)$  depends on the distance  $|\vec{r}_i - \vec{r}_j|$  between two nearest neighbor atoms sitting at  $\vec{r}_i$  and  $\vec{r}_j$ ,

$$t(\vec{r}_i, \vec{r}_j) = t_0 - \alpha(|\vec{r}_i - \vec{r}_j| - d_0) \quad \text{for nearest neighbors,} \\ = 0 \quad \text{otherwise,} \quad (1)$$

where  $t_0$  is the average electron hopping constant,  $\alpha$  the electron-lattice coupling constant,  $d_0$  the bond length for diamond. Then the tight-binding Hamiltonian is written as<sup>2-6</sup>

$$H = \sum_{ij} t(\vec{r}_i, \vec{r}_j) (a_{i\sigma}^\dagger a_{j\sigma} + h.c.) + K \sum_{ij} (|\vec{r}_i - \vec{r}_j| - d_0)^2. \quad (2)$$

Here,  $a_{i\sigma}^\dagger$  and  $a_{i\sigma}$  are the creation and annihilation operators of electron in atom  $i$  with spin  $\sigma$ ;  $K$  is the elastic constant; and the summation in the second term is given over only nearest-neighbor sites  $i$  and  $j$ . All the parameters in Hamiltonian (2) can be determined by fitting the lengths of single- and double-bonds and the energy difference between the LUMO and the highest occupied molecular orbitals (HOMO) of neutral C<sub>60</sub>. These values<sup>5</sup> are  $t_0 = 1.8$  eV,  $\alpha = 3.5$  eV/Å, and  $K = 15.0$  eV/Å<sup>2</sup>.

By diagonalizing the first term of Hamiltonian (2), we can obtain the energy spectrum  $E_\alpha(\{\vec{r}_i\})$  of  $\pi$  electrons, which is a functional of atom configuration  $\vec{r}_i (i = 1, 2, 3, \dots, 60)$ . The total energy is

$$E(\{\vec{r}_i\}) = \sum_{\alpha}^{\text{occ}} E_\alpha(\{\vec{r}_i\}) + K \sum_{ij} (|\vec{r}_i - \vec{r}_j| - d_0)^2, \quad (3)$$

where the summation in the first term is over the occupied states. For the neutral C<sub>60</sub>, there are 60 electrons filled in the low-lying energy orbitals. After the charge transfer, one more electron enters into C<sub>60</sub>, and the first term in Eq. (3) includes 61 electrons. According to the variational principle, the equilibrium positions of sixty carbon atoms  $\vec{r}_i (i = 1, 2, \dots, 60)$  can be determined by minimizing the total energy with respect to  $\vec{r}_i$ ,

$$\delta E(\{\vec{r}_i\}) / \delta \vec{r}_i = 0. \quad (4)$$

In the case of neutral C<sub>60</sub>, the variational equation (4) gives the equilibrium configuration with symmetry  $I_h$ . There are two kinds of bonds: the single bond with bond length 1.43 Å and the double bond with length 1.39 Å. The energy difference between the LUMO and the HOMO is 1.8 eV. All these values agree with the experimental data<sup>7</sup>.

After the charge transfer, the original lattice configuration is no longer at the equilibrium positions. There emerge force exerting on the carbon atoms,

$$\vec{f}_i = -\delta E(\{\vec{r}_i\}) / \delta \vec{r}_i. \quad (5)$$

Such force makes the atoms move. Since the carbon atom is much heavier than electron, the quantum effect of lattice motion can be neglected. Then the classical dynamic equation can be used to study the movement of carbon atoms. Because all the 60 carbon atoms sit on the surface of a sphere with radius  $r_0$ , the radial modulus of elasticity is much larger than the tangential ones. It means that the car-

bon atoms are movable mainly on the surface. Then each carbon atom has two polar coordinates  $\theta_i$  and  $\phi_i$  and the dynamical equations are:

$$\ddot{\theta}_i - \dot{\phi}_i^2 \sin\theta_i \cos\theta_i = -\frac{1}{m} \frac{1}{r_0^2} \frac{\delta E(\{\theta_i, \phi_i\})}{\delta \theta_i}, \\ \ddot{\phi}_i + 2\dot{\theta}_i \dot{\phi}_i \cot\theta_i = -\frac{1}{m} \frac{1}{r_0^2 \sin^2\theta_i} \frac{\delta E(\{\theta_i, \phi_i\})}{\delta \phi_i}, \quad (6)$$

where the dot denotes the derivative with respect to time, and  $m$  is the mass of carbon atom.

The initial conditions are that the 60 atoms sit at the original positions  $\theta_i$  and  $\phi_i$  with the symmetry  $I_h$ , and their initial velocities are zero. The 61 electrons occupy the states with the lower energies associated with the initial lattice configuration, *i.e.*

$$\theta_i|_{t=0} = \theta_i(0), \quad \phi_i|_{t=0} = \phi_i(0), \\ \dot{\theta}_i|_{t=0} = 0, \quad \text{and} \quad \dot{\phi}_i|_{t=0} = 0. \quad (7)$$

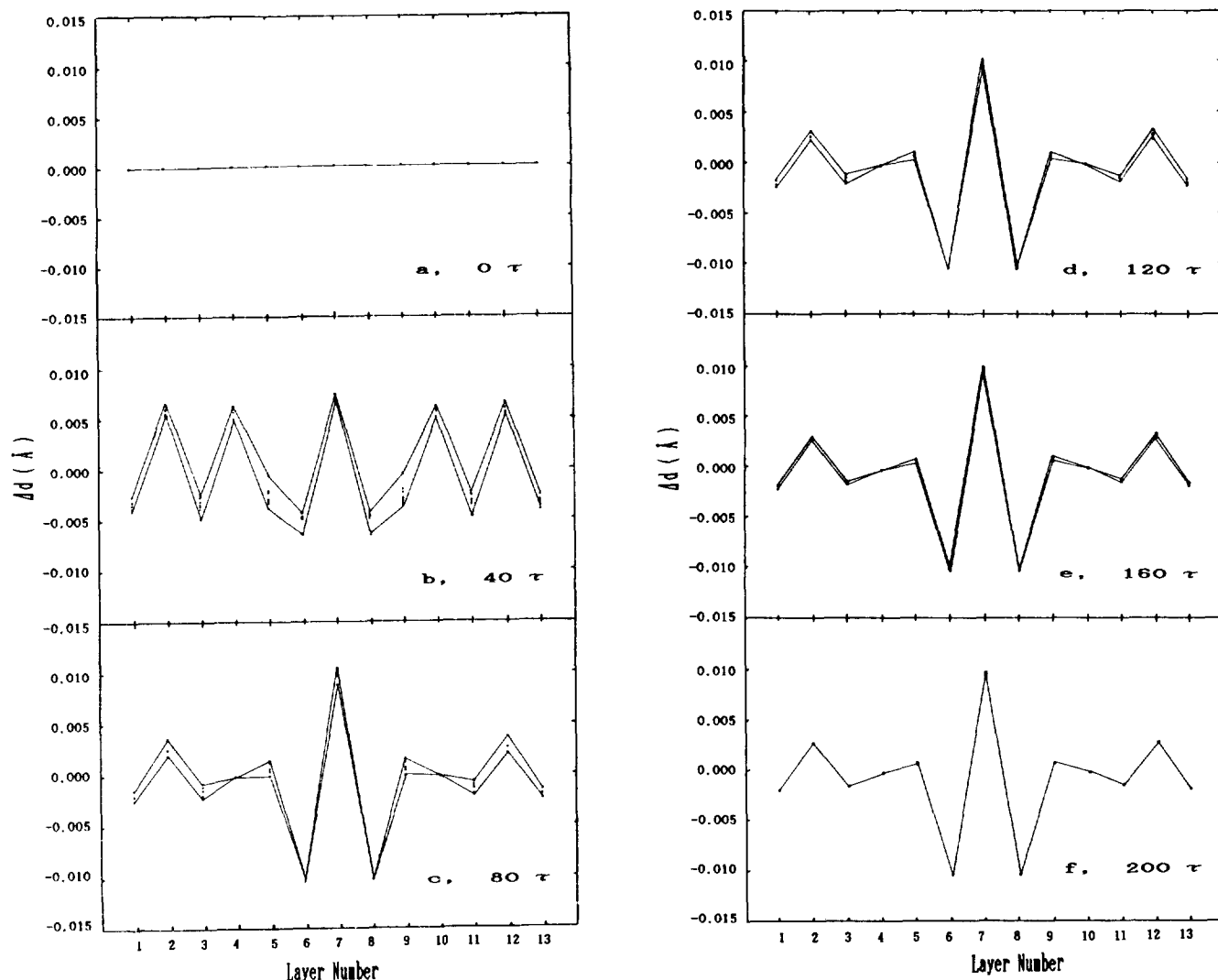
By using the Su-Shriff method,<sup>8</sup> the combined dynamic equations (6) are solved numerically step by step, and each step lasts a very short time interval  $\tau$ , in which the changes of the force are negligible. For the first step, from the initial condition, the positions  $(\theta_i(1), \phi_i(1))$  and velocities  $(\dot{\theta}_i(1), \dot{\phi}_i(1))$  at the end of the first step are obtained. These positions and velocities are taken to be the initial conditions for the second step. Following the same procedure, the positions  $(\theta_i(t), \phi_i(t))$  at any time  $t = k\tau$  are determined by completing the  $k$ -th step.

## Results and Discussion

In our numerical calculations,  $\tau = 4.22$  fs is taken to be the time interval, which is far smaller than the vibration period of the lattice. The starting time ( $t = 0$ ) is at the moment that one extra electron is put in the LUMO, then the atoms begin to move and the bond lengths are changing. In this paper, we only take a preliminary study to see the outline of the evolution. In order to make the calculation easier, the system is assumed to be quenched into zero temperature at the end of each step, the kinetic energy in the end of each step is eliminated, and the initial velocity in every step becomes zero. Then the overshooting is avoided and the computer time is reduced.

The time-dependent changes of bond-lengths are shown in Figure 3 (a-f). Figure 3a is the initial configuration, the changes of all the bond-lengths are zero. Figure 3b-3f are the changes of bond-lengths at  $t = 40\tau, 80\tau, 120\tau, 160\tau$  and  $200\tau$  respectively. These figures show the evolution of the bond distortion. In the earlier time, different bonds have different changes, and even the bonds in the same layer have different changes. However, after the time  $160\tau$ , the changes less and less depend on the time, and the changes of different bonds in the same layer converge to one point. It means that the bond distortion gradually reaches a new equilibrium structure, which is exactly the same as the static distortion as shown in Figure 2. From this evolution process, it can be estimated that the relaxation time is about  $150\tau = 0.6$  ps.

It should be mentioned that the elimination of kinetic ene-



**Figure 3.** The time-dependence of bond-length changes  $\Delta d$  in  $C_{60}$ . (a,  $t=0$ ; b,  $t=40 \tau$ ; c,  $t=80 \tau$ ; d,  $t=120 \tau$ ; e,  $t=160 \tau$ ; f,  $t=200 \tau$ ).

rgy corresponds to having a damping, which will slow the relaxation and suppress the overshooting. The further studies need to consider the kinetic energy properly. It will provide the vibrational properties in the relaxation process and tell more accurate relaxation time; such program is ongoing.

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