

## Relaxation process of the self-trapping exciton in C<sub>60</sub>

X. Sun, G. P. Zhang,\* Y. S. Ma, R. L. Fu, and X. C. Shen

*T. D. Lee Laboratory, Department of Physics, Fudan University, Shanghai 200433, China  
and National Laboratory of Infrared Physics, Academia Sinica, Shanghai 200083, China*

K. H. Lee and T. Y. Park

*Department of Chemistry and Department of Physics Education, Won Kwang University, Iksan City 570-749, Korea*

Thomas F. George and Lakshmi N. Pandey

*Department of Chemistry and Department of Physics, Washington State University, Pullman, Washington 99164-1046*

(Received 10 March 1995; revised manuscript received 26 September 1995)

When C<sub>60</sub> is photoexcited, a self-trapping exciton (STE) is formed: The bond structure is distorted from symmetry  $I_h$  to  $D_{5d}$  while the states  $A_{1u}$  and  $A_{2u}$  are pulled into the energy gap from highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively. A dynamical scheme is employed to simulate the relaxation process of STE. The evolution of both bond structure and electronic states shows that the relaxation time to form STE is about 100 fs. It should be noted that this relaxation time is much shorter than that of charge transfer in C<sub>60</sub>. The origin for this large difference is discussed. [S0163-1829(96)03920-3]

Recently, photoinduced charge transfer (PCT) in the C<sub>60</sub> complex has attracted considerable attention. Ultrafast PCT in C<sub>60</sub>/N,N-dimethylaniline was conducted by Sension *et al.*,<sup>1</sup> although the fraction of charge transfer ( $\delta$ ) in their experiments was not clear, the ultrafast linear absorption spectrum definitely showed that the time scale of charge transfer (CT) state formation was picoseconds. Sariciffic *et al.*<sup>2</sup> extensively studied PCT in many C<sub>60</sub> complexes, such as C<sub>60</sub> poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-*p*-phenylen], and found the relaxation time of PCT to be shorter than 1 ps.

Although experimental research on PCT has been performed extensively, theoretical studies about PCT are limited. The existing theoretical work about the excited states in fullerene mainly concerns its static properties. Fagerström and Stafaström<sup>3</sup> and Suzuki *et al.*<sup>4</sup> discussed the Jahn-Teller effect in the excited states of C<sub>60</sub> with different schemes, i.e., the former through electron correlation under configuration-interaction and the latter through the  $h_g$  modes. By the Bogoliubov-de Gennes formalism, Wang *et al.*<sup>5</sup> examined the lattice relaxation of a self-trapped exciton (STE) and biexciton. However, none of these studies were concerned with the dynamics of the excited states, which is crucial to understand PCT.

As has been shown in the static studies,<sup>6</sup> the original bond structure of the excited C<sub>60</sub> with symmetry  $I_h$  is not stable, and the bond structure is distorted to form a polaronlike exciton, which actually is a self-trapping exciton. Consequently, both the electronic states and the lattice configuration are changed. Originally, highest occupied molecular orbital (HOMO) is fivefold degenerate, and lowest unoccupied molecular orbital (LUMO) is three-fold [see Fig. 1(a)]. After C<sub>60</sub> is photoexcited, HOMO is split into  $A_{1u}$ ,  $E_{1u}$ , and  $E_{2u}$ , where  $E_{1u}$  and  $E_{2u}$  do not distinctly shift from the original HOMO level, but  $A_{1u}$  is lifted up into the gap. Meanwhile, LUMO is split into  $A_{2u}$  and  $E_{1u}$ , and only  $A_{2u}$  is pulled down into the gap. These gap states  $A_{1u}$  and

$A_{2u}$  are bound states localized in the equatorial area of the fullerene. In the bond structure, its symmetry is reduced from  $I_h$  to  $D_{5d}$ . The bond distortion is also mainly in the equatorial area, with the largest change of bond length in the seventh layer [see Fig. 1(b)]. So the dynamical relaxation process from the electron-hole pair to STE can be described by two evolutions: one is the evolution of levels  $A_{1u}$  and  $A_{2u}$  split from HOMO and LUMO, respectively; the other is that of

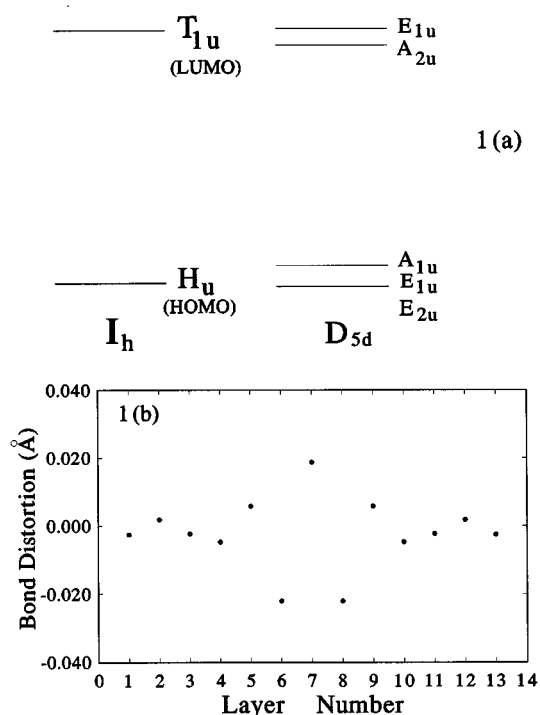


FIG. 1. (a) When C<sub>60</sub> is photoexcited, HOMO and LUMO are split into  $A_{1u}$ ,  $E_{1u}$ ,  $E_{2u}$ , and  $E_{1u}$ ,  $A_{2u}$ , respectively, with symmetry  $D_{5d}$ . (b) The changes of the bond length in different layers.

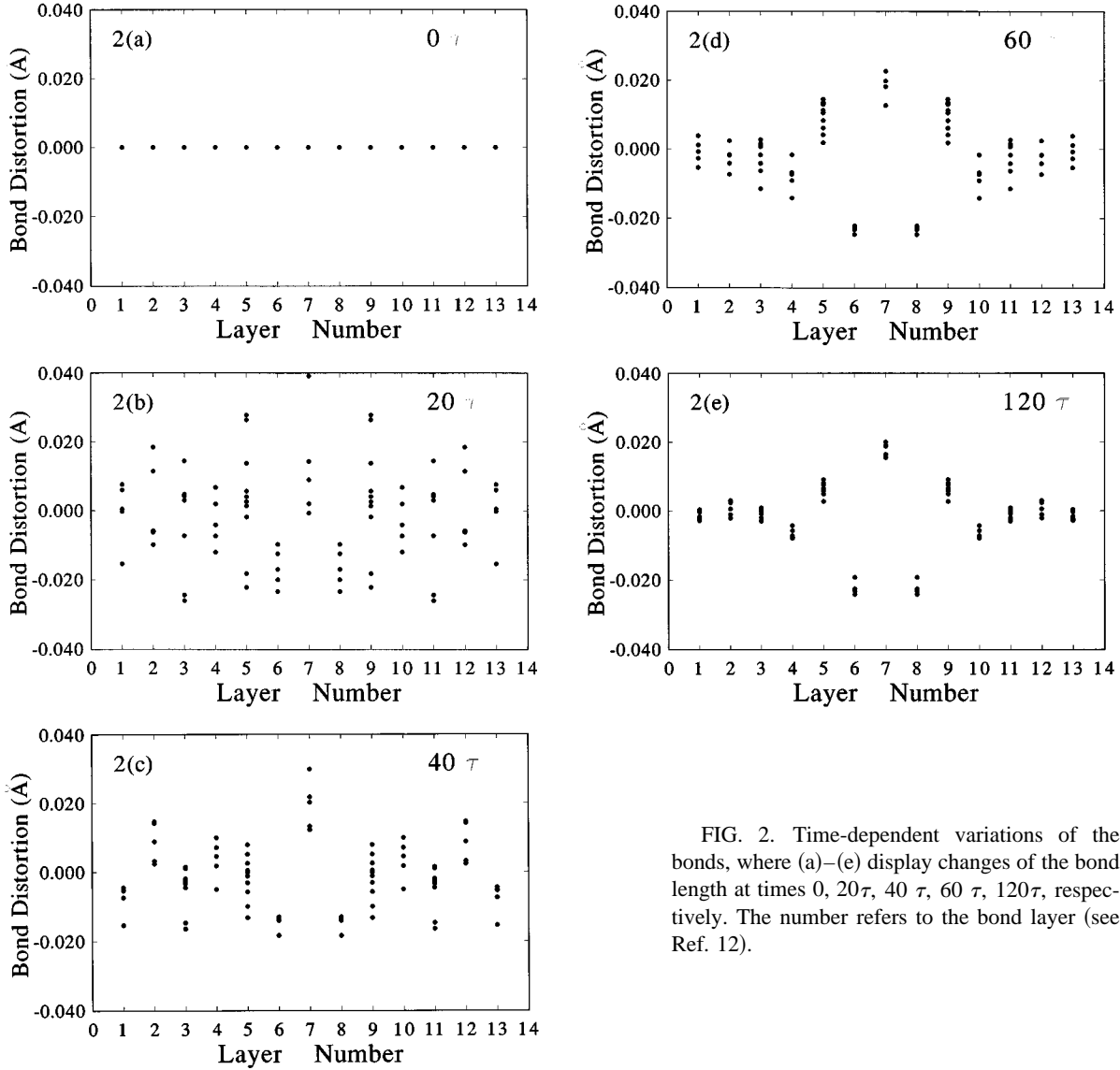


FIG. 2. Time-dependent variations of the bonds, where (a)–(e) display changes of the bond length at times  $0$ ,  $20\tau$ ,  $40\tau$ ,  $60\tau$ ,  $120\tau$ , respectively. The number refers to the bond layer (see Ref. 12).

changes of the bond lengths. Then the relaxation time can be estimated from these two evolutions.

In this paper, a dynamical scheme is employed to study the evolution of excited state in  $C_{60}$ . A similar method has been used to study the dynamics in polyacetylene<sup>7</sup> and the  $MX$  chain.<sup>8</sup> From our calculation, it is found that the relaxation time for the self-trapping exciton is about 100 fs and the largest change of the bond length is  $0.02 \text{ \AA}$ . In comparison with the relaxation of CT, one discovers that the relaxation of the exciton is about three times quicker than that of CT, and the bond distortion of STE is twice as large as that of CT.

$C_{60}$  is a quasi-two-dimensional system with  $\pi$  electrons on the spherical surface. A band theory calculation<sup>9</sup> clearly shows that the interball electron hopping is very small, so that the bandwidth is very narrow. Fitting the *ab initio* results, Chen *et al.*<sup>10</sup> found that the interball hopping is typically at  $0.01 \text{ eV}$ , which is much smaller than the intraball hopping  $1.8 \text{ eV}$  (see below). Therefore, the bulk properties of  $C_{60}$  are well characterized by the on-ball characters. Since the electron hopping between nearest-neighbor (NN) sites on the ball is much more important than the other hoppings, the

tight binding approximation is commonly accepted in  $C_{60}$  studies and gives reasonable results for the characteristics of  $C_{60}$ , such as the energy gap and the bond length.<sup>11</sup> Under the above assumption, we can write down the Hamiltonian as

$$\hat{H} = - \sum_{i,j,\sigma} t_{ij} (\hat{C}_{i,\sigma}^\dagger \hat{C}_{j,\sigma} + \text{H.c.}) + \frac{K}{2} \sum_{i,j} (|\vec{r}_i - \vec{r}_j| - d_0)^2, \quad (1)$$

where  $\hat{C}_{i\sigma}^\dagger$  creates a  $\pi$  electron at site  $i$  with spin  $\sigma$ , and  $t_{ij} = t_0 - \alpha(|\vec{r}_i - \vec{r}_j| - d_0)$  is the hopping integral between the nearest-neighbor atoms sitting at  $\vec{r}_i$  and  $\vec{r}_j$ . The first summation in (1) is for the electrons, while the second one is for the elastic energy. These two summations run over NN sites only. Through fitting two bond lengths,  $1.43$  and  $1.39 \text{ \AA}$ , and the optical gap, the above parameters are found to be  $t_0 = 1.8 \text{ eV}$ ,  $\alpha = 3.5 \text{ eV/\AA}$ , and  $K = 15.0 \text{ eV/\AA}^2$ . Also,  $d_0 = 1.54 \text{ \AA}$ . The total energy can be calculated from

$$E(\vec{r}_i) = \sum_{\alpha}^{\text{occ}} \mathcal{E}_{\alpha}(\{\vec{r}_i\}) + \frac{K}{2} \sum_{i,j} (|\vec{r}_i - \vec{r}_j| - d_0)^2, \quad (2)$$

where  $\mathcal{E}_a(\{\vec{r}_i\})$  is the electronic energy spectrum. The first summation is taken over the occupied orbitals only.

After  $C_{60}$  is photoexcited, there appears an electron-hole pair, namely, an electron in LUMO, while leaving a hole in HOMO; the original equilibrium configuration with symmetry  $I_h$  is not stable. Due to the electron-lattice interaction, atom  $i$  experiences a force calculated by

$$\vec{f}_i = - \frac{\delta E(\vec{r}_i)}{\delta \vec{r}_i}. \quad (3)$$

For the photoexcited  $C_{60}$ , the initial condition is that one electron is in LUMO and one hole in HOMO, while all the atoms are at their original positions. With this initial condition, one can solve the combined dynamical equations step by step. Each step should last a very short interval  $\tau$  so that, within this interval, the change of forces can be ignored. (The details of the calculation is described in Ref. 12.) As before, we chose the step interval  $\tau = 2.11$  fs, which is much shorter than the period  $\tau_0$  of atom vibration  $10^{-14}$  s, and the damping  $\lambda = 10^{13}$ /sec, should be much smaller than  $1/\tau_0$ .

A prominent feature of the movement of the atoms should be mentioned. The atoms move in three-dimensional space, but the numerical result shows that the relaxation, in the radial direction, is much smaller than in the tangential direction, which means that the atoms mainly move on the sphere. The reason for this feature is that the coupling between the electron and pure radial phonon mode is very weak. Thus, the radial displacements can be neglected. Consequently, the positions of all atoms on the sphere at any time can be calculated, and the corresponding electron spectra are obtained.

In Fig. 2(a)–(e), we plot the relaxation process of bond distortion at different times  $t = 0\tau, 20\tau, 40\tau, 60\tau, 120\tau$ , where the small dots represent the bond-length modification from

its original length and the numbers denote the layers in  $C_{60}$  (see Ref. 12). At  $t = 0$ , an electron is in LUMO and a hole in HOMO, and the atoms begin to move while the bond lengths begin to change. At earlier stages [e.g.,  $t = 20\tau$ , Fig. 2(b)], the changes of the bonds are rather diverse, even the bonds in the same layer experience very different modifications, which is similar to the relaxation process of CT. After about  $50\tau$ , the typical laminar structure appears roughly, and the changes of different bonds in the same layer get close to each other [see Fig. 2(d)]. From this evolution, one can estimate that the relaxation time  $T_{ex}$  is about 100 fs, and at  $t = 120\tau$ , the bond distortion [see Fig. 2(e)] is very close to the equilibrium configuration of excited  $C_{60}$  [see Fig. 1(b)]. In a comparison with the relaxation time  $T_{CT}$  of charge transfer, which is estimated as 0.4 ps in our previous work,<sup>12</sup>  $T_{ex}$  is much shorter.

For the evolutions of the gap states  $A_{1u}$  and  $A_{2u}$ , the difference between photoexcitation and charge transfer is more prominent. The results are shown in Fig. 3, where the ordinate is the level of the state  $A_{1u}$  and the abscissa is the level of  $A_{2u}$ . Each dot represents the values of levels  $A_{1u}$  and  $A_{2u}$  at different time; for instance, the dot in the upper left corner represents the values of levels  $A_{1u}$  and  $A_{2u}$  at  $t = 0$ . The arrow denotes the direction of time going, and the time interval between two successive dots is  $1\tau$ . The center of the dark area in Fig. 3 denotes the final positions of the gap states  $A_{1u}$  and  $A_{2u}$ . From Fig. 3(a), one can easily observe that, for photoexcitation, it takes only about three turns to reach the dark area, which again indicates the relaxation time  $T_{ex}$  is about 100 fs. Comparatively, for CT [see Fig. 3(b)], it needs to run more than ten turns to reach the dark center. Thus, the evolutions of both the bond structure and electronic states indicate that  $T_{ex}$  is three times shorter than  $T_{CT}$ . This large difference between STE and CT is not a surprising result. Actually, the same phenomenon has been observed in polymers.<sup>7</sup> In trans-polyacetylene, there are also two kinds of relaxations: (a) the relaxation of charge transfer, i.e., one electron (or hole) is transferred into the conduction band (or valence band), where it interacts with the lattice to form a negative (or positive) polaron, and its relaxation time is about 0.2 ps; and (b) the relaxation of photoexcitation, where an electron-hole pair decays into a soliton and anti-soliton pair, and the relaxation time is about 40 fs, which is 5 times faster than CT.

This large difference must have some physical reasons. Although a complete understanding is not available, one plausible reason is that, in the case of photoexcitation, an

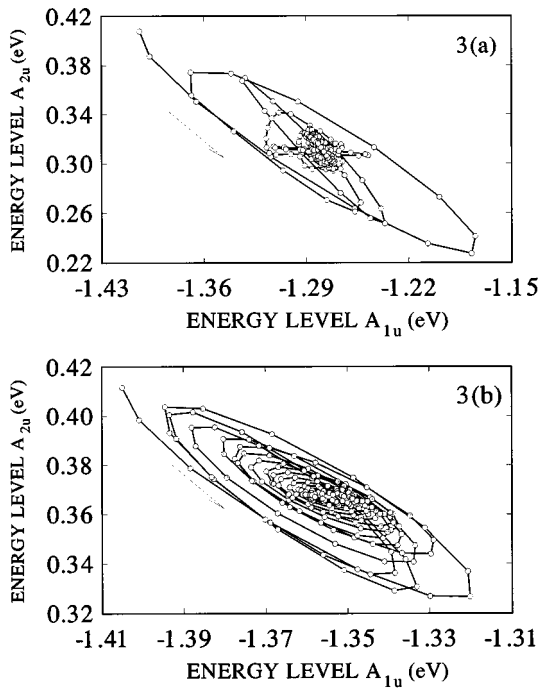


FIG. 3. Evolutions of  $A_{1u}$  and  $A_{2u}$ , where (a) is for STE and (b) for CT.

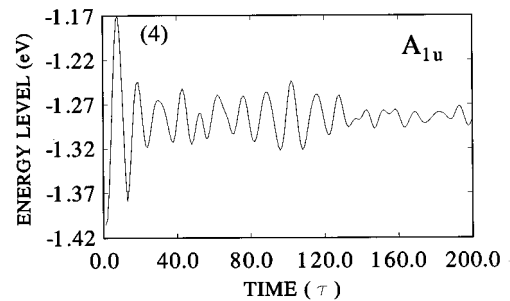


FIG. 4. Evolution of  $A_{1u}$  without damping.

electron sits in the LUMO state, while the hole is in HOMO, then both the electron and the hole exert the forces on the atoms. Under these forces, the atoms move quickly to a new equilibrium configuration. However, in the formation of a polaron, there is only one electron added in the LUMO, such that the force is relatively weaker than that of the former. Therefore, the formation of STE is faster than that of a polaron. This origin can also be used to explain why the distortion of the exciton is almost twice as large as that of charge transfer.

To make our simulation more convincing, we have studied whether the relaxation depends on the damping. Figure 4 shows the evolution of the  $A_{1u}$  state without damping. In a comparison to the case with the damping  $10^{13}/s$ , one finds that the main feature of the evolution process does not change. At the beginning, the  $A_{1u}$  level sits at  $-1.41$  eV, and after several periods, it oscillates around a new equilibrium position at  $-1.29$  eV with a small amplitude.

Finally, to check the results of the numerical simulation, we employ the multiphonon theory<sup>13</sup> to calculate analytically the relaxation time of the excited states. We find that the relaxation time for STE is about 100 fs, which is shorter than the relaxation time of the polaron formation. Since the dy-

namical simulation clearly reveals the difference between photoexcitation and charge transfer, we prefer that some relevant experiments should be performed to confirm these features. Some feasible experimental programs can be proposed. For the relaxation of the excited states, one may use time-resolved femtosecond absorption spectroscopy, where an ultrafast laser with time resolution 40–50 fs is now widely available. If the resolution is 10 fs, one may observe quantum beats, which reflects atomic vibrations. For the relaxation of charge transfer, the femtosecond time-resolved Raman gain spectroscopy can confirm the relaxation time by observing the appearance of the typical spectra line of charged  $C_{60}$ .

The authors thank Mr. Wei Chang for providing a computer and Dr. R. T. Fu and Q. F. Huang for helpful discussions. One of them (X. S.) is very grateful to the International Center for Theoretical Physics, some progress of this work was done when he visited there. This work was supported by the National Natural Science Foundation and the Foundation of National Education Committee of China, Grant No. 94-0501-11 (KOSEF).

---

\*Present address: Department of Materials Science, Fudan University, Shanghai 200433, China.

<sup>1</sup>R. J. Sension, A. Z. Szarka, G. R. Smith, and R. M. Hochstrasser, *Chem. Phys. Lett.* **185**, 179 (1991).

<sup>2</sup>N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, *Science* **258**, 1474 (1992).

<sup>3</sup>J. Fagerström and F. Stafaström, *Phys. Rev. B* **48**, 11 367 (1993).

<sup>4</sup>S. Suzuki, D. Inomata, N. Sashide, and K. Nakao, *Phys. Rev. B* **48**, 14 615 (1993).

<sup>5</sup>Wen-Zheng Wang, M. S. Miguel, N. B. Abraham, J. R. Tredicce, R. Alvarez, E. J. D'Angelo, A. Gambhir, K. S. Thornburg, and R. Roy, *Phys. Rev. Lett.* **72**, 3550 (1994).

<sup>6</sup>R. L. Fu, R. Fu, and X. Sun, *Phys. Rev. B* **48**, 17 615 (1993).

<sup>7</sup>W. P. Su and J. R. Schrieffer, *Proc. Natl. Acad. Sci. U.S.A.* **77**, 5626 (1980).

<sup>8</sup>J. T. Gammel, A. Saxena, I. Balistic', and A. R. Bishop, *Phys. Rev. B* **45**, 6408 (1992).

<sup>9</sup>S. Saito and A. Oshiyama, *Phys. Rev. Lett.* **66**, 2637 (1991).

<sup>10</sup>G. Chen, Y. Guo, N. Karasawa, and W. A. Goddard III, *Phys. Rev. B* **48**, 13 959 (1993).

<sup>11</sup>B. Friedman, *Phys. Rev. B* **45**, 1454 (1992); K. Harigaya, *ibid.* **45**, 13 676 (1992).

<sup>12</sup>G. P. Zhang, R. T. Fu, X. Sun, D. L. Lin, and T. F. George, *Phys. Rev. B* **50**, 11 976 (1994).

<sup>13</sup>C. L. Wang, W. Z. Wang, Y. L. Liu, Z. B. Su, and L. Yu, *Phys. Rev. B* **50**, 5676 (1994).