

Lattice relaxation in the lowest excited state of C_{60}

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Lattice relaxation due to the Jahn-Teller instability in the lowest excited singlet state of C_{60} is investigated. It is found that the symmetry of the molecular structure in the relaxed excited state is approximately the C_{2h} symmetry. We also elucidate strongly interacting normal modes with the low-lying excited states. Consequently, it is found that the h_g mode of the lowest frequency and of the fourth lowest frequency are the most strongly and the next strongly interacting modes, respectively. Furthermore, we find that the frequencies of these two h_g modes show significant splittings in the relaxed excited state.

1. INTRODUCTION

One of the most remarkable features of the fullerene C_{60} is its extraordinary high symmetry, i.e., the I_h symmetry [1]. As a result, the molecular orbitals of C_{60} show substantial degeneracy. For example, the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) are fivefold degenerate h_u and threefold degenerate t_{1u} , respectively [2].

Furthermore, such high degeneracy of the molecular orbitals also causes the excited states of C_{60} to be degenerate extensively, e.g., the low-lying excited singlet states induced by the excitation of an electron from HOMO to LUMO are composed of fifteen states of even parity, i.e., $t_{1u} \times h_u = T_{1g} + T_{2g} + G_g + H_g$ [3, 4]. Although these levels are slightly split due to the electron correlation, one expects that the Jahn-Teller effect plays an important role in the excited states of C_{60} .

In fact, the optical absorption and the fluorescence bands relating to the low-lying excited states show complicated vibrational structures [5, 6]. Accordingly, it seems indispensable to investigate the interaction between the excited states and the intramolecular vibrations in order to explain some important phenomena such as optical properties.

The purpose of the present paper is to study several properties of the lowest excited singlet state of C_{60} with respect to the Jahn-Teller effect. First, we examine the symmetry of the molecular structure in the relaxed excited state. Next, we elucidate the normal modes which significantly

contribute to the lattice relaxation in the relaxed excited state. Finally, we present the results of the calculations on the frequencies of the normal modes in the relaxed excited state.

2. METHOD OF CALCULATION

We first elaborate on the low-lying excited states of C_{60} . By removing an electron from HOMO a and adding to LUMO m , one obtains the excited state, $|ma\rangle$, where $m = 1, 2, 3$ and $a = 1, 2, 3, 4, 5$. In the present study, we use the states, ${}^1T_{1g}$, ${}^1T_{2g}$, 1G_g , and 1H_g , to describe the low-lying excited states by transforming the basis from $|ma\rangle$ into $|\Gamma I\rangle$; we denote the I th state of the Γ level by $|\Gamma I\rangle$ where Γ is a label for T_{1g} , T_{2g} , G_g , or H_g . $|\Gamma I\rangle$ are obtained by using the projection operators of the I_h group. Consequently, we find

$$|\Gamma I\rangle = \sum_{ma} C_{ma}^{\Gamma I} |ma\rangle, \quad (1)$$

where

$$C_{ma}^{\Gamma I} \propto \sum_G D_{II'}^{(\Gamma)}(G)^* D_{mm'}^{(T_{1u})}(G) D_{aa'}^{(H_u)}(G)^*. \quad (2)$$

Here $D_{II'}^{(\Gamma)}(G)$ is the I, I' th element of the Γ representation of the group element G . Also, we choose $C_{ma}^{\Gamma I}$ so as to normalize $|\Gamma I\rangle$.

Next we proceed to formulate the electron-phonon interaction. Individual electrons are subjected to the screened attractive potential due to the sixty carbon nuclei. By expanding this with respect to the displacement u_k of the k th carbon atom from its equilibrium position \mathbf{R}_k^0 , one

finds the electron-phonon interaction, $V^{\text{ep}}(\mathbf{r}, \mathbf{u})$, where we denote the whole of the displacements $\{\mathbf{u}_k | k = 1, \dots, 60\}$ by \mathbf{u} :

$$V^{\text{ep}}(\mathbf{r}, \mathbf{u}) = -\frac{Ze^2}{\epsilon} \sum_{k=1}^{60} \frac{\mathbf{u}_k \cdot (\mathbf{r} - \mathbf{R}_k^0)}{|\mathbf{r} - \mathbf{R}_k^0|^3}. \quad (3)$$

Here $Z (= 6)$ is the atomic number of carbon and ϵ is the dielectric constant. We assume $\epsilon = 6$ in the present study, referring to the dielectric constant of diamond ($\epsilon = 5.93$). Therefore, the one-electron matrix elements between the molecular orbitals are given by

$$V_{ij}^{\text{ep}}(\mathbf{u}) = \int d\mathbf{r} \phi_i(\mathbf{r})^* V^{\text{ep}}(\mathbf{r}, \mathbf{u}) \phi_j(\mathbf{r}), \quad (4)$$

where $\phi_i(\mathbf{r})$ and $\phi_j(\mathbf{r})$ are the one-electron wave function of the molecular orbital i and that of the molecular orbital j , respectively. In order to obtain $\phi_i(\mathbf{r})$, we carry out the first-principle calculation of the electronic ground state of C_{60} , adopting the same method employed by Disch *et al.* [7]. Furthermore, the calculation is performed by using the observed value of the single-bond length (1.46 Å) and of the double-bond length (1.40 Å) [8]. Consequently, we find the matrix element of the electron-phonon interaction between $|\Gamma I\rangle$ and $|\Gamma' I'\rangle$ [9]:

$$H_{\Gamma I, \Gamma' I'}^{\text{ep}}(\mathbf{u}) = \sum_{ma, m'a'} C_{ma}^{\Gamma I^*} C_{m'a'}^{\Gamma' I'}, H_{ma, m'a'}^{\text{ep}}(\mathbf{u}), \quad (5)$$

where

$$H_{ma, m'a'}^{\text{ep}}(\mathbf{u}) = V_{mm'}^{\text{ep}}(\mathbf{u}) \delta_{aa'} - V_{aa'}^{\text{ep}}(\mathbf{u}) \delta_{mm'}. \quad (6)$$

Furthermore, it is assumed that the vibrational properties of the molecule are described by the force-constant model. That is, the elastic energy, $E_{\text{elastic}}(\mathbf{u})$, due to the deformation of the molecule is assumed as

$$E_{\text{elastic}}(\mathbf{u}) = \frac{1}{2} \sum_{\alpha, \beta=1}^{180} u_{\alpha} k_{\alpha\beta} u_{\beta}. \quad (7)$$

Here u_{α} and u_{β} are the components of the displacements of the sixty carbon nuclei from their equilibrium positions and $k_{\alpha\beta}$ represent the elements of the force-constant matrix. Then one can obtain the eigen frequency of the γ mode, ω_{γ} , by diagonalizing the force-constant matrix $k_{\alpha\beta}$. That is,

$$E_{\text{elastic}}(\mathbf{u}) = \frac{1}{2} \sum_{\gamma, i} m \omega_{\gamma}^2 Q_{\gamma i}^2, \quad (8)$$

where m is the mass of a carbon atom and $Q_{\gamma i}$ is the i th normal coordinate of the γ mode. In the present study, we choose $k_{\alpha\beta}$ so as to reproduce the observed frequencies of the normal vibrations within the average error of $\sim 4\%$; we use the frequencies of two a_g and eight h_g modes observed in the Raman scattering spectroscopy and the frequencies of four t_{1u} modes observed in the infrared absorption spectroscopy [10, 11].

Taking account of the above preliminaries, we introduce the following model Hamiltonian:

$$H = \sum_{\Gamma I, \Gamma' I'} |\Gamma I\rangle H_{\Gamma I, \Gamma' I'}^{\text{ex}}(\mathbf{u}) \langle \Gamma' I'| + E_{\text{elastic}}(\mathbf{u}), \quad (9)$$

where

$$H_{\Gamma I, \Gamma' I'}^{\text{ex}}(\mathbf{u}) = E_{\Gamma} \delta_{\Gamma I, \Gamma' I'} + H_{\Gamma I, \Gamma' I'}^{\text{ep}}(\mathbf{u}). \quad (10)$$

In the above matrix elements, E_{Γ} is the energy of the Γ level measured from the energy of the 1A_g ground state. The outline of the calculations is as follows. Under a given atomic configuration \mathbf{u} , the Hamiltonian is diagonalized and then the lowest eigen value, $E_{\text{lowest}}(\mathbf{u})$, is determined. By minimizing $E_{\text{lowest}}(\mathbf{u})$ with respect to \mathbf{u} , one finds the relaxed configuration \mathbf{u}^* . The calculation is performed by using E_{Γ} calculated by Bendale *et al.* ($E_{T_{1g}} = 2.11$, $E_{T_{2g}} = 2.17$, $E_{G_g} = 2.23$, and $E_{H_g} = 2.52$ in eV) [3]. Also we use E_{Γ} calculated by Negri *et al.* ($E_{T_{1g}} = 2.33$, $E_{T_{2g}} = 2.29$, $E_{G_g} = 2.34$, and $E_{H_g} = 2.65$ in eV) [4], in order to examine the dependence of our results on the choice of E_{Γ} .

Before proceeding to discuss the results of the calculations, we define the interaction energy, E_{int}^{γ} , of the γ mode by its contribution to the elastic energy in the relaxed configuration, $E_{\text{elastic}}(\mathbf{u}^*)$. That is, $E_{\text{elastic}}(\mathbf{u}^*)$ is decomposed into E_{int}^{γ} from each normal mode:

$$E_{\text{elastic}}(\mathbf{u}^*) = \sum_{\gamma} E_{\text{int}}^{\gamma}, \quad (11)$$

where

$$E_{\text{int}}^{\gamma} = \frac{1}{2} \sum_i m \omega_{\gamma}^2 Q_{\gamma i}^{*2}. \quad (12)$$

Here $Q_{\gamma i}^*$ represents the displacement of the i th coordinate of the γ mode in the relaxed configuration.

3. RESULTS AND DISCUSSION

We now present the results of the calculations on the molecular structure of C_{60} in the relaxed excited state. It is found that the symmetry of the molecular structure is approximately C_{2h} , though the exact symmetry is C_i . The side-view and the top-view of the molecule in the relaxed excited state are given in Figs. 1(a) and (b), respectively; we show the Jahn-Teller distortion in the figure by illustrating the distortion ten times the size of the actual one. The pseudo twofold axis penetrates

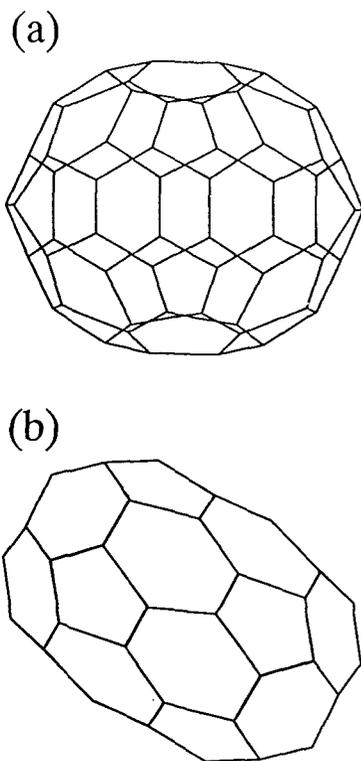


Figure 1. (a) Side-view and (b) top-view of the C_{60} molecule in the relaxed excited state. The distortion is illustrated ten times the size of the actual one. The pseudo twofold axis penetrates the molecule vertically in (a) and perpendicularly to the figure in (b).

the molecule vertically in Fig. 1(a) and also perpendicularly to the figure in Fig. 1(b). One can hardly see the deviation from the C_{2h} structure in Figs. 1(a) and (b). Consequently, we find that there are fifteen equivalent structures of the relaxed excited state because the C_{60} molecule has the fifteen twofold axes in its ground state.

Next we elucidate the normal modes which significantly contribute to the lattice relaxation in the relaxed excited state. In Table 1, we show the results of the calculations on the interaction energies, E_{int}^{γ} ; the normal modes are numbered in order of the frequency from the lowest. In the table, E_{int}^{γ} of only a_g and h_g modes are shown because E_{int}^{γ} of the other modes are two or more orders of magnitude less than those of the a_g and the h_g modes. It is found that the h_g mode of the lowest frequency, $h_g(1)$, is the most significantly interacting mode with the low-lying excited states and the h_g mode of the fourth lowest frequency, $h_g(4)$, is the next. It should be noted that their interaction energies are one or two orders of magnitude larger than those of the other modes. One should also notice that these results are almost independent of the choice of E_{Γ} .

Finally, we present the results of the calculations on the frequencies of the normal modes in the relaxed excited state. The results are listed

Table 1
Interaction energies, E_{int}^{γ} , of the a_g and the h_g modes, in eV.

Mode	E_{int}^{γ} ^a	E_{int}^{γ} ^b
$a_g(1)$	0.003	0.003
$a_g(2)$	0.003	0.003
$h_g(1)$	0.299	0.300
$h_g(2)$	0.017	0.017
$h_g(3)$	0.004	0.004
$h_g(4)$	0.113	0.113
$h_g(5)$	0.004	0.004
$h_g(6)$	0.013	0.013
$h_g(7)$	0.001	0.001
$h_g(8)$	0.001	0.001

^aObtained by using E_{Γ} due to Bendale *et al.*

^bObtained by using E_{Γ} due to Negri *et al.*

Table 2

Calculated frequencies of the normal modes in the ground state and those in the relaxed excited state, expressed in cm^{-1} .

Mode	Calculated frequencies in the ground state		Calculated frequencies ^a in the relaxed excited state			
	$h_g(1)$	282	208	243	274	274
$h_g(2)$	413	403	408	413	413	413
$h_g(3)$	598	584	589	596	596	598
$h_g(4)$	795	756	765	783	790	794
$h_g(5)$	1117	1112	1112	1114	1115	1117
$h_g(6)$	1246	1229	1236	1244	1245	1246
$h_g(7)$	1442	1431	1437	1439	1441	1442
$h_g(8)$	1627	1624	1624	1626	1626	1627

Mode	Calculated frequencies in the ground state		Calculated frequencies ^b in the relaxed excited state			
	$h_g(1)$	282	198	242	273	274
$h_g(2)$	413	402	407	413	413	413
$h_g(3)$	598	583	589	595	596	598
$h_g(4)$	795	752	764	782	790	794
$h_g(5)$	1117	1112	1112	1114	1115	1117
$h_g(6)$	1246	1228	1235	1244	1245	1246
$h_g(7)$	1442	1430	1436	1439	1441	1442
$h_g(8)$	1627	1624	1624	1626	1626	1627

^aObtained by using E_{Γ} due to Bendale *et al.*

^bObtained by using E_{Γ} due to Negri *et al.*

in Table 2; the frequencies of the other modes are unchanged from those in the ground state, so that we leave them out from the table. We find that the splittings of the frequencies of the $h_g(1)$ and the $h_g(4)$ mode attain to several tens of cm^{-1} . This also indicates that these two h_g modes strongly interact with the low-lying excited states.

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