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C₆₀ with O defects: localized states in the gap and oxygen clustering

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Abstract. We propose a Su–Schrieffer–Heeger-type electron–phonon model for C₆₀ with O defects and solve it by using the adiabatic approximation. Two new properties are obtained: (i) the dimerization becomes weaker around the oxygen, two localized states appear deep in the gap, and optical transition between them is allowed—this accords with the recent optical absorption data; (ii) oxygens are predicted to cluster on the surface of C₆₀.

1. Introduction

The fullerene carbon clusters have been intensively studied. They have hollow structures and their surface is composed of a closed network of carbons. The C₆₀ molecule has a shape like a football. There are twelve pentagons and twenty hexagons on the surface. The molecule has the icosahedral symmetry.

There is a very sharp peak due to C₆₀ with a large amount in the mass spectra data of the laser-ablated graphite [1]. However, the mass spectra of the sample in solvents indicate the presence of oxidized molecules: C₆₀O_n (1 ≤ n ≤ 5) [2]. The amounts of C₆₀O_n in solvents (with and without ultraviolet light) become larger with increasing exposure time, becoming as large as 1–10% or more under the ultraviolet irradiation. The molecular structures of the oxidized C₆₀ have been reported in recent experiments [3]. It has been found that an oxygen atom makes two bonds with carbon; this double bond is a short bond. A recent calculation using tight-binding molecular dynamics [4] has suggested the stability of this structure. In other words, it is energetically more favourable to attach an oxygen along the short (double) bond than along the long (single) bond.

What changes take place in lattice and electronic structures when oxygen atoms make bonds with C₆₀? This problem is important because it has been shown [2,3] that significant amounts of C₆₀ oxides may be present under some experimental conditions. It is necessary to know what will be observed due to the presence of the oxygen defects. This knowledge is lacking at present. We should distinguish effects due to the oxygen defects in the experimental data.

In this paper, we study a variant of the Su–Schrieffer–Heeger (SSH) model [5] which has been used in studies of conjugated polymers. The application of the model

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for C_{60} with no defect has been successful [6, 7]. First, we consider a geometry shown schematically in figure 1. An oxygen atom is attached to two sites where otherwise there would be a short bond. We show a large intrusion of two localized states into the gap. This change will give rise to new observations. Symmetries of wavefunctions indicate that optical transition between them is allowed. Next, the geometric configuration of up to three oxygen atoms on the surface is investigated. A quite new property, i.e., oxygen clustering, is certainly predicted for all the parameters we take. Consequences for experiments are discussed.

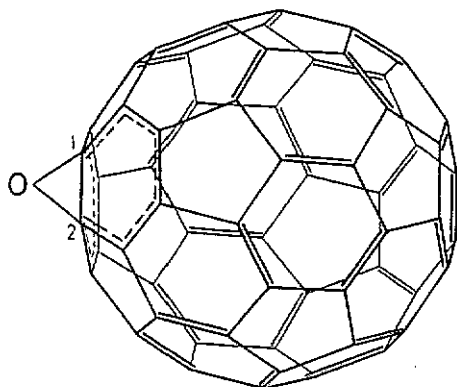


Figure 1. C_{60} with an O defect. The numbers 1 and 2 indicate two carbons making bonds with the oxygen.

2. Model and formalism

The SSH model [5] is extended to C_{60} with an O defect,

$$H = H_{C_{60}} + H_O \quad (1)$$

$$H_{C_{60}} = \sum'_{\langle i,j \rangle, s} [-t + \alpha(u_i^{(j)} + u_j^{(i)})](c_{i,s}^\dagger c_{j,s} + \text{HC}) + \frac{K}{2} \sum'_{\langle i,j \rangle} (u_i^{(j)} + u_j^{(i)} - C)^2 \quad (2)$$

$$H_O = E_O \sum_s d_s^\dagger d_s - t_O \sum_s [d_s^\dagger (c_{1,s} + c_{2,s}) + \text{HC}]. \quad (3)$$

In the first term of $H_{C_{60}}$, the quantity t is the hopping integral of the system with the uniform bond length; α is the electron-phonon coupling; the operator $c_{i,s}$ annihilates a π -electron at the i th carbon atom with the spin s ; particularly the labels $i = 1, 2$ are used for two carbons adjacent to the oxygen atom, as shown in figure 1; $u_i^{(j)}$ is the displacement of the i th atom in the direction opposite to the j th atom; the sum is taken over nearest-neighbour pairs of $\langle i, j \rangle$. The quantity $u_i^{(j)} + u_j^{(i)}$ is the change of length of the bond between the i th and j th atoms. When it is positive, the bond becomes longer and the hopping integral decreases from t ; accordingly we take the sign before α to be positive. The prime symbol on the summation indicates that the pair of nearest-neighbour atoms adjacent to O, $\langle 1, 2 \rangle$, is not included in the sum. The second term is the elastic energy of the phonon system; the quantity K is the spring constant. We include the constant C in order to remove the contraction of the lattice;

it is determined to reproduce the previous calculation [6] of the undoped C₆₀. The term H_O represents the interaction between the C₆₀ molecule and the oxygen. As the details of the character of bonds between oxygen and carbon are not well known, we assume one effective orbital which forms two bonds with π -electrons of carbons. This is a valid assumption because the atomic levels of the oxygen would be present deep in the occupied states of C₆₀, and the electronic structures around the energy gap of C₆₀ would not be sensitive to details of the electronic structures of the oxygen. The electronic states at the oxygen are denoted by the operator d_s with the atomic energy E_O . The quantity t_O is the hopping integral between the carbon and oxygen atoms. We assume the electronic states with the nearly closed shell. This is parametrized by the energy E_O which is much deeper than the Fermi energy. The d-states would be filled with nearly two electrons. We do not include an intra-site Coulomb interaction because we limit our discussion to static electronic structures. This assumption would be more or less valid when there are even numbers of electrons. The interaction should be taken into account when we investigate dynamical properties in detail.

The model (1) is solved by using the adiabatic approximation for the lattice. The eigenvalue equation for electrons is

$$\varepsilon_\kappa \phi_{\kappa,s}(i) = \sum_{(i,j)} (-t + \alpha y_{i,j}) \phi_{\kappa,s}(j) \quad \text{for } i \neq 1, 2 \quad (4)$$

$$\varepsilon_\kappa \phi_{\kappa,s}(i) = \sum_{(i,j)} (-t + \alpha y_{i,j}) \phi_{\kappa,s}(j) - t_O \chi_{\kappa,s} \quad \text{for } i = 1, 2 \quad (5)$$

$$\varepsilon_\kappa \chi_{\kappa,s} = E_O \chi_{\kappa,s} - t_O [\phi_{\kappa,s}(1) + \phi_{\kappa,s}(2)] \quad (6)$$

where ε_κ is the eigenvalue of the κ th eigenstate, $\chi_{\kappa,s}$ is the amplitude at the O site, and $y_{i,j} = u_i^{(j)} + u_j^{(i)}$ is the bond variable. The self-consistency equation for the lattice is

$$y_{i,j} = -\frac{2\alpha}{K} \sum_{\kappa,s}^{\text{occ}} \phi_{\kappa,s}(i) \phi_{\kappa,s}(j) + C \quad (7)$$

where the notation, 'occ', means the sum over the occupied states. Equations (4)–(7) are solved by the numerical iteration method used in previous publications [6].

3. Results

All the quantities involving energy units will be given in units of t . We take $\alpha/t = 2.52 \text{ \AA}^{-1}$ and $K/t = 19.9 \text{ \AA}^{-2}$; these give the dimensionless electron-phonon coupling: $\lambda \equiv 2\alpha^2/\pi Kt = 0.20$ [6]. For the parameter C , we use $C = 0.0131164 \text{ \AA}$. The number of electrons is $N_{el} = 62$; the sixty electrons are from C₆₀ and the other two are from the oxygen. The realistic value of t is about 2.5 eV [6].

Figure 1 shows the lattice geometry. The π -conjugation is broken along the bond between the sites 1 and 2 in the present model. The length difference between the short and long bonds of two hexagons adjacent to these sites becomes smaller. We cannot distinguish between the short and long bonds clearly; therefore, the bonds of two hexagons are shown by dashed lines in figure 1. In other words, the dimerization

becomes weaker around the O defect. When the site is further away from the defect, the dimerization strength becomes nearer to that in perfect C_{60} . We do not show each bond length explicitly because it is very complex to depict twenty-five different lengths. However, it is very likely that the dimerization is most perfect around sites which are located at the side opposite to the oxygen in the football.

Next, we discuss localized states due to the defect. As the phenomenological tight-binding parameters appropriate for the defect are not known well, we vary them arbitrarily. The main conclusion—the presence of the localized states—does not change for all the parameter ranges we take. We report results for the parameters: $t_O = 0.5t, 0.75t$ and $-2t \leq E_O \leq 0$. Figures 2(a) and (b) are for $t_O = 0.5t$ and $0.75t$, respectively. In figure 2, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are shown by full and open circles, respectively. The next HOMO (NHOMO) and next LUMO (NLUMO) are represented by the small squares which are connected by curves. Other energy levels, which are lower than the NHOMO or higher than the NLUMO, are not shown. The small circles will be explained in a later paragraph. When E_O is varied, the energies of NHOMO and NLUMO do not change so much as those of HOMO and LUMO. This is the consequence of the fact that the wavefunctions of NHOMO and NLUMO spread over almost all the C_{60} while those of HOMO and LUMO are localized around the defect. Thus, we can regard the HOMO and LUMO as impurity states which are well known in bulk semiconductors and superconductors. The energy difference between the NHOMO and NLUMO, about $0.8t$, is very close to the value of the perfect C_{60} . Therefore, we can say that the energy gap of C_{60} itself is less affected by the defect while two new localized states are emitted into the gap due to the defect potential. This property is the same as in impurity states of bulk materials.

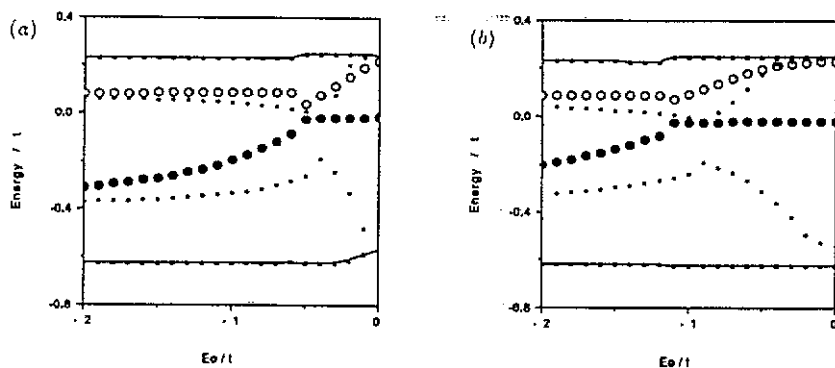


Figure 2. Energy level structures in the gap as a function of E_O . We use $t_O = 0.5t$ in (a) and $t_O = 0.75t$ in (b). The HOMO and LUMO are shown by full and open circles, respectively. The NHOMO and NLUMO are represented by small squares. The small circles are the HOMO and LUMO of C_{60} with the bond impurity of the strength, $I_b = -t_O^2/E_O$.

We look at details in the parameter dependence. When the site energy E_O is deep enough in the bonding states, the intrusion of the two localized levels in the gap is small. As E_O increases, the HOMO moves upward but the energy of the LUMO does not change so much. The level crossing between them occurs at $E_O \sim -0.5t$ and $E_O \sim -1.1t$ in figures 2(a) and (b), respectively. For larger E_O , the energy of the HOMO is almost constant but the LUMO moves upward. The wavefunction of one of the localized levels, which moves largely as E_O changes, has a large amplitude at

the oxygen site. It is totally symmetric with respect to the oxygen. On the other hand, the wavefunction of the other level has a negligible amplitude at the oxygen. It is totally antisymmetric. The difference in the variation of energies of localized states, i.e., whether the energies depend strongly on E_O , is well explained by whether the amplitude of the wavefunction is negligible at the oxygen, or not. The symmetries of the HOMO and LUMO are opposite to each other. This indicates that optical absorption is allowed between two levels. This is the consequence of the reduced symmetry from that of the pure C_{60} . In figure 1(b) of [3], the optical absorption spectrum of $C_{60}O$ has been reported. A weak peak appears at the wavelength 680 nm, while it is absent in the spectrum of C_{60} . The energy corresponding to this peak is 1.82 eV. This is close to that of the HOMO–LUMO gap of C_{60} . The forbidden transition between the HOMO and LUMO in C_{60} [6] would become allowed in $C_{60}O$. This property accords with the above result of the present theory.

In order to explain why two localized states appear in the gap, we consider a C_{60} molecule, equation (2), with a bond impurity, $I_b \sum_s (c_{1,s}^\dagger c_{2,s} + \text{HC})$, between sites where the oxygen atom exists in figure 1. The impurity potential of the strength I_b modulates the hopping integral between nearest-neighbour sites, and therefore it is called the bond impurity. The case $I_b = -t_O^2/E_O$ is investigated. We obtain two localized levels in the gap again. The results are shown by the small circles in figure 2. The tendency of the variation of energy levels is similar to that of the previous calculation. This is due to the fact that the model equation (3) is transformed into the bond impurity with $I_b = -t_O^2/E_O$ when the second-order perturbation with respect to t_O is performed. The perturbation theory becomes more accurate when the site energy E_O is much deeper. In fact, the separation between small and large circles becomes smaller for deeper E_O in figure 2. Why do two energy levels appear in the gap? The positive impurity strength I_b corresponds to a negative hopping integral between sites 1 and 2. Due to this defect potential, two localized levels are emitted in the gap; one is from the bonding states and the other from the antibonding states. Wavefunctions of these levels are localized around the bond impurity. A similar property has been discussed in the work on impurity effects in conjugated polymers [8].

Finally, we report many-oxygen cases. We first carry out the calculation for two cases: one case is where two oxygens are attached along short bonds, and the other case is that one is attached along a short bond while the other along a long bond. Mutual positions of oxygens are changed, and all the positions of the entire C_{60} molecule are taken into account. In both cases, it is energetically most favourable for the two oxygens to be connected along sides of a common hexagon. In the latter case, two oxygens are connected along nearest-neighbour sides of a hexagon. The energy of this solution is lower than that of the optimum solution of the first case. Thus, the oxygens tend to cluster on the surface of the C_{60} molecule. The reason is that the mixing of energy levels, which are localized around the two oxygens, becomes larger as the distance between them is shorter. It is energetically most favourable to maximize the bonding–antibonding splitting of energy levels. The energy gain from the solution with the next lowest energy is about 0.5–1 eV. In the calculation, the oxygen clustering persists for all the values of E_O we take. Second, the calculation is extended to systems with three oxygens. We always obtain clustered configurations of oxygens in this case. However, the experimental verification of oxygen clustering depends on the synthesis and stability of $C_{60}O_n$ with $n > 1$.

4. Concluding remarks

In this paper, we have not included a hopping integral $t_{1,2}$ between sites 1 and 2. We have assumed covalent bondings between the oxygen and neighbouring carbons. Even if it can exist, the magnitude of $t_{1,2}$ will be smaller than that of t . In C_{60} without the oxygen, there is a short bond between sites 1 and 2. The larger hopping integral is assigned to this bond. The hopping $t_{1,2}$ (which is smaller than that of the short bond) in $C_{60}O$ is effective in reducing the local gap at the bond. This also gives rise to the intrusion of the two localized levels in the gap. The situation is the same as that of the effect of bond impurities in conjugated polymers [8]. Thus, our conclusion is not affected by the presence of $t_{1,2}$.

In the discussion of the impurity clustering, we have not included direct Coulomb interactions among oxygens and C_{60} . The conclusion would be valid as long as we deal with the static structures of the molecules. The similar types of covalent bond models were used for defect states (dopants [9], carbonyls ($>C=O$) [10], and sp^3 defects [11]) in conjugated polymers. The clustering was certainly concluded in polymers, too [9, 11].

In summary, the simple electron-phonon model has been proposed for C_{60} with oxygen defects. The principal conclusions are as follows. (i) The dimerization becomes weaker around the oxygen, two localized levels appear deep in the gap, and optical transition between them is allowed. This could explain the recent experimental observations in $C_{60}O$ [3]. (ii) Possible oxygen arrangements have been studied by minimizing the energy. Oxygens tend to cluster for all of the assumed parameters.

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References

- [1] Kroto H W, Heath J R, Brien S C, Curl R F and Smalley R E 1985 *Nature* **318** 162
- [2] Wood J M, Kahr B, Hoke S H II, Dejarne L, Cooks R G and Ben-Amotz D 1991 *J. Am. Chem. Soc.* **113** 5907
- [3] Creegan K M, Robbins J L, Robbins W K, Millar J M, Sherwood R D, Tindall P J and Cox D M 1992 *J. Am. Chem. Soc.* **114** 1103
- [4] Menon M and Subbaswamy K R 1991 *Phys. Rev. Lett.* **67** 3487
- [5] Su W-P, Schrieffer J R and Heeger A J 1980 *Phys. Rev. B* **22** 2099
- [6] Harigaya K 1991 *J. Phys. Soc. Japan* **60** 4001; *Phys. Rev. B* **45**
- [7] Friedman B 1992 *Phys. Rev. B* **45** 1454
- [8] Harigaya K, Terai A, Wada Y and Fesser K 1991 *Phys. Rev. B* **43** 4141
- [9] Harigaya K 1991 *J. Phys.: Condens. Matter* **3** 8855
- [10] Förner W, Seel M and Ladik J 1986 *Solid State Commun.* **57** 463
Harigaya K 1991 *J. Phys.: Condens. Matter* **3** 4841
- [11] Jeyadev S and Conwell E M 1988 *Phys. Rev. B* **37** 8262