

Optical absorption spectra and geometric effects in higher fullerenes

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Abstract

The optical excitations in C_{70} and higher fullerenes, including isomers of C_{76} , C_{78} , and C_{84} , are theoretically investigated. We use a tight binding model with long-range Coulomb interactions, treated by the Hartree-Fock and configuration-interaction methods. We find that the optical excitations in the energy region smaller than about 4 eV have most of their amplitudes at the pentagons. The oscillator strengths of projected absorption almost accord with those of the total absorption. When the projection is performed on each pentagon and pentagon dimers, the resultant spectrum in the low energy region is quite different from that of the total absorption. The spectral shapes of the

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total absorption are turned out to be determined mainly by the geometrical distributions of the pentagons in the fullerene structures.

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1. Introduction

Recently, the fullerene family C_N with hollow cage structures has been intensively investigated. A lot of optical experiments have been performed, and excitation properties due to π -electrons delocalized on molecular surfaces have been measured. For example, the optical absorption spectra of C_{60} and C_{70} [1,2] have been reported, and the large optical nonlinearity of C_{60} [3,4] has been found. The absorption spectra of higher fullerenes (C_{76} , C_{78} , C_{84} , etc.) have also been obtained [5,6]. For theoretical studies, we have applied a tight binding model [7] to C_{60} , and have analyzed the nonlinear optical properties. Coulomb interaction effects on the absorption spectra and the optical nonlinearity have been also studied [8]. We have found that the linear absorption spectra of C_{60} and C_{70} are well explained by the Frenkel exciton picture [9] except for the charge transfer exciton feature around the excitation energy 2.8 eV of the C_{60} solids [2]. Coulomb interaction effects reduce the magnitude of the optical nonlinearity from that of the free electron calculation [8], and thus the intermolecular interaction effects have turned out to be important.

In the previous paper [10], we have extended the calculation of C_{60} [9] to one of the higher fullerenes C_{76} . We have discussed variations of the optical spectral shape in relation to the symmetry reduction from C_{60} and C_{70} to C_{76} : the optical gap decreases and the spectra exhibit a larger number of small structures in the dependences on the excitation energy. These properties seem to be natural when we take into account of the complex surface patterns composed of pentagons and hexagons. In order to understand the patterns clearly, the idea of the “phason line” has been introduced [11] using the projection method on the honeycomb lattice plane [12]. There are twelve

pentagons in C_{76} . Six of them cluster on the honeycomb lattice, with one hexagon between the neighboring two pentagons. There are two groups of the clustered pentagons. The “phason line” runs as if it divides the two groups.

The purpose of this paper is to investigate relations between the optical properties and geometric structures in higher fullerenes. The phason lines can characterize the geometries of fullerenes. We define the “pentagonal” carbons as the atoms located at the points of pentagons. Then, the carbon atoms along the phason lines can be regarded as the remaining atoms after the pentagonal carbons are taken out. We will calculate the optical absorption spectra at a certain combination of the pentagonal carbons. We project wavefunctions to selected pentagons, and calculate dipole moments using the projected wavefunctions. Thus, the contributions from a part of the fullerene to the optical spectra can be extracted.

The main results are as follows:

- (1) The optical excitations in the energy region smaller than about 4 eV have most of their amplitudes at the pentagonal carbons. The oscillator strengths of absorption projected onto these carbons almost accord with those of the total absorption.
- (2) When the projection is performed on a smaller set of the pentagonal carbons, the resultant spectrum in the low energy region is quite different from that of the total absorption. The structures in the absorption cannot be decomposed into contributions from subsets of pentagonal carbons.
- (3) The contributions from pentagon dimers in several kinds of higher fullerenes (e.g., two isomers of C_{78} and C_{84}) are compared. We find that small peak structures are mutually different. The spectral shapes of the total absorption are

mainly determined by the geometrical distributions of the pentagons in the fullerene structures.

In the next section, our tight-binding model is introduced and the calculation method is explained. Sections 3 and 4 are devoted to numerical results and discussion about the properties of the absorption spectra. The paper is closed with a summary in section 5.

2. Model

We use the following Hamiltonian:

$$H = H_0 + H_{\text{int}}. \quad (1)$$

The first term of eq. (1) is the tight binding model:

$$H_0 = -t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}), \quad (2)$$

where t is the hopping integral and $c_{i,\sigma}$ is an annihilation operator of a π -electron with spin σ at the i th carbon atom of the fullerene. It is assumed that t does not depend on the bond length, because main contributions come from excitonic effects due to the strong Coulomb potential. The results do not change so largely if we consider changes of hopping integrals by bond distortions. We assume the following form of Coulomb interactions among π -electrons:

$$\begin{aligned} H_{\text{int}} = & U \sum_i (c_{i,\uparrow}^\dagger c_{i,\uparrow} - \frac{1}{2})(c_{i,\downarrow}^\dagger c_{i,\downarrow} - \frac{1}{2}) \\ & + \sum_{i \neq j} W(r_{i,j}) (\sum_\sigma c_{i,\sigma}^\dagger c_{i,\sigma} - 1) (\sum_\tau c_{j,\tau}^\dagger c_{j,\tau} - 1), \end{aligned} \quad (3)$$

where $r_{i,j}$ is the distance between the i th and j th atoms and

$$W(r) = \frac{1}{\sqrt{(1/U)^2 + (r/r_0 V)^2}} \quad (4)$$

is the Ohno potential. The quantity U is the strength of the on-site interaction, V means the strength of the long-range Coulomb interaction, and r_0 is the average bond length.

The model is treated by the Hartree-Fock approximation and the single excitation configuration interaction method, as was used in the previous papers [9,10]. In ref. 9, we have varied the parameters of the Coulomb interactions, and have searched for the data which reproduce overall features of experiments of C_{60} and C_{70} in solutions. We have found that the common parameters, $U = 4t$ and $V = 2t$, are reasonable. Thus, we use the same parameter set for higher fullerenes. The quantity t is about 2 eV as shown in ref. 9. The Coulomb interaction strengths depend on the carbon positions. We use the lattice coordinates which are obtained by the public program “FULLER” [13,14]. The optical spectra become anisotropic with respect to the orientation of the molecule against the electric field of light, as reported in the free electron model (Hückel theory) [15]. We obtain numerical optical absorption spectra by summing the data of three cases, where the electric field of light is along the x -, y -, and z -axes.

We use a projection operator in order to extract contributions to the optical spectra from a certain part of fullerenes. If we write the a projection operator to a part of lattice site set as P , the oscillator strength between the ground state $|g\rangle$ and the excited state $|\kappa\rangle$ is written:

$$\begin{aligned}
 f_{\kappa,x} &= E_{\kappa}[|\langle\kappa|PxP|g\rangle|^2 \\
 &+ |\langle\kappa|(1-P)x(1-P)|g\rangle|^2 \\
 &+ \langle g|PxP|\kappa\rangle\langle\kappa|(1-P)x(1-P)|g\rangle]
 \end{aligned}$$

$$+ \langle g|(1-P)x(1-P)|\kappa\rangle\langle\kappa|PxP|g\rangle, \quad (5)$$

where E_κ is the excitation energy, and the electric field is parallel with the x -axis. In eq. (5), the first term is the contribution from the projected part, and the three other terms are the remaining part. The total optical absorption is calculated by the formula:

$$\sum_{\kappa} \rho(\omega - E_\kappa)(f_{\kappa,x} + f_{\kappa,y} + f_{\kappa,z}), \quad (6)$$

where $\rho(\omega) = \gamma/[\pi(\omega^2 + \gamma^2)]$ is the Lorentzian distribution of the width γ . The projected absorption is calculated by eqs. (5) and (6). The projected part does not satisfy a sum rule. So, this results in a singularity where excitation energy is large. We will discuss the optical spectra in the energy region far from the singularity.

3. Optical absorption in C_{70} and C_{76}

Figure 1 shows the molecular structures and optical spectra of the C_{70} molecule and C_{76} with the D_2 symmetry, which have been found in experiments. The black atoms are the carbons along the phason lines. The hatched circles are the pentagonal carbons. In C_{70} , the phason line runs along the ten carbons which are arrayed like a belt around the molecule. In C_{76} , the phason line is located almost along the outer edge of the molecule of Fig. 1(b). The total optical absorption is shown by the bold line, and the absorption from all the pentagonal carbons is shown by the thin line. We find that the optical excitations in the energy region lower than $2t$ are almost composed of the excitations at the pentagonal sites. This property is common to C_{70} and D_2 - C_{76} , and also to the T_d - C_{76} for which the calculated data are not shown. In higher energy

regions, the thin lines give relatively larger oscillator strengths, but this is an artifact of the projected wavefunctions. The absorption spectra calculated from the projected wavefunctions do not satisfy the sum rule, i.e., the area between the abscissa and the curve does not become constant regardless of the excitation wavefunctions. The similar artifact will be found in the figures shown afterwards. We believe that the projected optical absorption spectra are reliable in low energy regions only. Therefore, we limit our comparison of the spectra to the energy region lower than about $2t \sim 4$ eV.

In C_{60} , the edges of the pentagons are the long bonds, and the bonds between the neighboring hexagons are short bonds. The wavefunctions of the fivefold degenerate highest-occupied-molecular-orbital (HOMO) have the bonding property, and that the threefold degenerate lowest-unoccupied-molecular-orbital (LUMO) has the antibonding property. As the carbon number increases, hexagons are inserted among pentagons. The wavefunctions near the LUMO of the higher fullerenes still have the antibonding properties, thus they tend to have large amplitudes along the edges of pentagons which have the characters like long bonds of C_{60} . Recently, the bunching of the six energy levels higher than the LUMO has been discussed in the extracted higher fullerenes [16]. The wavefunctions near the LUMO distribute on the pentagons. This fact can be understood as the properties characteristic to antibonding orbitals. As the excited electron mainly distributes at the pentagonal carbons, the electron-hole excitation has large amplitudes at these pentagons. Thus, the oscillator strengths of the low energy excitations are mainly determined by wavefunctions at the pentagonal carbons. This is the reason why the projected absorptions nearly accord with the total absorptions in the energy regions smaller than

about $2t$.

If the projections are performed onto each pentagon, we can know contributions to optical spectra from the projected carbon sites. We would like to look at this feature, for example, in D_2 - C_{76} . There are three carbon atoms, which are not equivalent with respect to symmetries, in this isomer. These pentagons are indicated by the symbols, A-C, in Fig. 2(a). The projected absorption spectra are shown by thin curves, superposed with the total absorption in Figs. 2 (b-d). The projected absorption is multiplied by the factor 12, in order to compare with the total absorption. We find that the projected absorption exhibits small structures in the energy region smaller than $2t$. The structures depend on the kind of carbons. The spectral shapes and oscillator strengths are much far from those of the total absorption. It would be difficult to assign experimental features of the total absorption with a set of the limited number of carbon atoms. The excitation wavefunctions at the twelve pentagons give rise to the shape of the absorption spectra totally.

4. Optical absorption in C_{78} and C_{84}

Figures 3 and 4 show the molecular structures and the calculated optical absorption spectra of the extracted isomers of C_{78} and C_{84} , respectively. The notations in Figs. 3 and 4 are the same as in Fig. 1. The property, that the low energy excitations have most of their amplitudes at the twelve pentagons, is seen in these five isomers. The bold line and the thin line almost agree in the energy region lower than about $2t \sim 4$ eV. It is of course that the agreement becomes a little bit worse from that in C_{70} and C_{76} of Fig. 1,

because the number of atoms along the phason lines increases as the fullerenes become higher. But, the similar wavefunction properties seem to persist in the calculated fullerenes, C_{78} and C_{84} .

The pentagon dimers exist in the regions surrounded by the phason lines in the two C_{2v} isomers of C_{78} [Figs. 3 (a) and (b)] and also in the D_{2d} isomer of C_{84} [Fig. 4 (a)]. These three molecules have pentagon dimer structures commonly. The dimers are shown by the black pentagons in molecular structures of Fig. 5. It is of some interests to look at whether these pentagon give rise to similar contributions to the optical spectra or not. The data of the thin lines are multiplied by the factor 6, in order to compare with the total absorption. We find that small peak structures are mutually different: for a typical example, the large feature around the energy $1.5t$ represented by the thin line in Fig. 5(c) is not present in Figs. 5(a) and (b). We thus conclude that the spectral shapes of the total absorption are mainly determined by the geometrical distributions of the pentagons in the fullerene structures.

5. Summary

We have studied optical excitations in C_{70} and higher fullerenes, including isomers of C_{76} , C_{78} , and C_{84} . We have used a tight binding model with long-range Coulomb interactions, and have treated by the Hartree-Fock and CI methods. We have found that the optical excitations in the energy region smaller than about 4 eV have most of their amplitudes at the pentagonal carbons. Thus, the oscillator strengths of absorption projected onto these carbons almost accord with those of the total absorption. When the projection

is performed on a smaller set of the pentagonal carbons, for example, on each pentagon, the resultant spectrum in the low energy region is quite different from that of the total absorption. Therefore, the structures in the absorption cannot be decomposed into contributions from subsets of pentagonal carbons.

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References

- [1] J. P. Hare, H. W. Kroto and R. Taylor, *Chem. Phys. Lett.* 177 (1991) 394.
- [2] S. L. Ren, Y. Wang, A. M. Rao, E. McRae, J. M. Holden, T. Hager, K. A. Wang, W. T. Lee, H. F. Ni, J. Selegue and P. C. Eklund, *Appl. Phys. Lett.* 59 (1991) 2678.
- [3] J. S. Meth, H. Vanherzeele and Y. Wang, *Chem. Phys. Lett.* 197 (1992) 26.
- [4] Z. H. Kafafi, J. R. Lindle, R. G. S. Pong, F. J. Bartoli, L. J. Lingg and J. Milliken, *Chem. Phys. Lett.* 188 (1992) 492.
- [5] R. Ettl, I. Chao, F. Diederich and R. L. Whetten, *Nature* 353 (1991) 149.
- [6] K. Kikuchi, N. Nakahara, T. Wakabayashi, M. Honda, H. Matsumiya, T. Moriwaki, S. Suzuki, H. Shiromaru, K. Saito, K. Yamauchi, I. Ikemoto and Y. Achiba, *Chem. Phys. Lett.* 188 (1992) 177.
- [7] K. Harigaya and S. Abe, *Jpn. J. Appl. Phys.* 31 (1992) L887.
- [8] K. Harigaya and S. Abe, *J. Lumin.* 60&61 (1994) 380.
- [9] K. Harigaya and S. Abe, *Phys. Rev. B* 49 (1994) 16746.
- [10] K. Harigaya, *Jpn. J. Appl. Phys.* 33 (1994) L786.
- [11] M. Fujita, *Fullerene Science and Technology*, 1 (1993) 365.
- [12] M. Fujita, R. Saito, G. Dresselhaus and M. S. Dresselhaus, *Phys. Rev. B* 45 (1992) 13834.
- [13] M. Yoshida and E. Ōsawa, *Proc. 3rd IUMRS Int. Conf. Advanced Materials*, 1993.
- [14] M. Yoshida and E. Ōsawa, *The Japan Chemistry Program Exchange, Program No. 74*.
- [15] J. Shumway and S. Satpathy, *Chem. Phys. Lett.* 211 (1993) 595.

[16] S. Saito, S. Okada, S. Sawada and N. Hamada, Phys. Rev. Lett. 75 (1995) 685.

Figure Captions

Fig. 1. Molecular structures and theoretical optical spectra of (a) D_{5d} - C_{70} and (b) D_2 - C_{76} . In the molecules, the black atoms are along the phason lines, and the hatched atoms are the pentagonal carbons. In the absorption spectra, the bold line is the total absorption, and the thin line is the absorption by the wavefunctions projected on the twelve pentagons. The units of the abscissa are taken as arbitrary, and the energy is scaled by t . The parameters are $U = 4t$, $V = 2t$, and $\gamma = 0.06t$.

Fig. 2. (a) The molecular structure of D_2 - C_{76} . The symbols, A-C, indicate the symmetry nonequivalent pentagons. The figures, (a), (b), and (c), compare the absorption projected on one of the three pentagons with the total absorption. The bold line is the total absorption, and the thin line is the projected absorption. The units of the abscissa are taken as arbitrary, and the energy is scaled by t . The data of the thin line are multiplied by the factor 12. The parameters are $U = 4t$, $V = 2t$, and $\gamma = 0.06t$.

Fig. 3. Molecular structures and theoretical optical spectra of (a) C_{2v} - C_{78} , (b) the other C_{2v} - C_{78} , and (c) D_3 - C_{78} . In the molecules, the black atoms are along the phason lines, and the hatched atoms are the pentagonal carbons. In the absorption spectra, the bold line is the total absorption, and the thin line is the absorption by the wavefunctions projected on the twelve pentagons. The units of the abscissa are taken as arbitrary, and the energy is scaled by t . The parameters are $U = 4t$, $V = 2t$, and $\gamma = 0.06t$.

Fig. 4. Molecular structures and theoretical optical spectra of (a) D_{2d} - C_{84} and (b) D_2 - C_{84} . In the molecules, the black atoms are along the phason lines, and the hatched atoms are the pentagonal carbons. In the absorption spectra, the bold line is the total absorption, and the thin line is the absorption by the wavefunctions projected on the twelve pentagons. The units of the abscissa are taken as arbitrary, and the energy is scaled by t . The parameters are $U = 4t$, $V = 2t$, and $\gamma = 0.06t$.

Fig. 5. Molecular structures and theoretical optical spectra of (a) C_{2v} - C_{78} , (b) the other C_{2v} - C_{78} , and (c) D_{2d} - C_{84} . In the molecules, the pentagon dimers are shown by the black pentagons. The each figure compares the absorption projected on the pentagon dimer with the total absorption. The bold line is the total absorption, and the thin line is the projected absorption. The units of the abscissa are taken as arbitrary, and the energy is scaled by t . The data of the thin line are multiplied by the factor 6. The parameters are $U = 4t$, $V = 2t$, and $\gamma = 0.06t$.