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Optical absorption spectra and geometric effects in higher fullerenes

Kikuo Harigaya† and Shuji Abe

Physical Science Division, Electrotechnical Laboratory, Umezono 1-1-4, Tsukuba, Ibaraki 305, Japan

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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 region where the energy is 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 onto 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 total absorption turn out to be determined mainly by the geometrical distributions of the pentagons in the fullerene structures.

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 analysed the nonlinear optical properties. Coulomb interaction effects on the absorption spectra and the optical nonlinearity have also been 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 the complex surface patterns composed of pentagons and hexagons. In order to allow us 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

† E-mail address: harigaya@etl.go.jp.

them cluster on the honeycomb lattice, with one hexagon between the neighbouring 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 relationships 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 for a certain combination of the pentagonal carbons. We project wavefunctions onto 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 region where the energy is lower 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 onto 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 fullerene (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 the summary and discussion in section 5.

2. Model

We use the following Hamiltonian:

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

The first term of equation (1) is the tight-binding model:

$$H_0 = -t \sum_{(i,j),\sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{HC}) \quad (2)$$

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 the main contributions come from excitonic effects due to the strong Coulomb potential. The results do not change so substantially if we consider changes of hopping integrals by bond distortions. We assume the following form of Coulomb interactions among π -electrons:

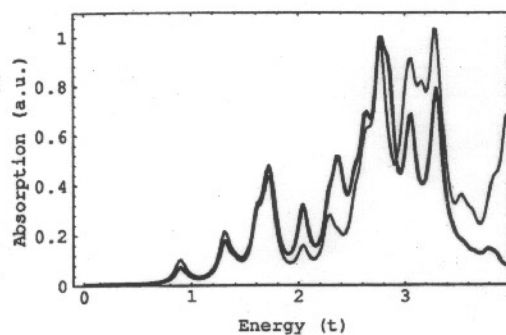
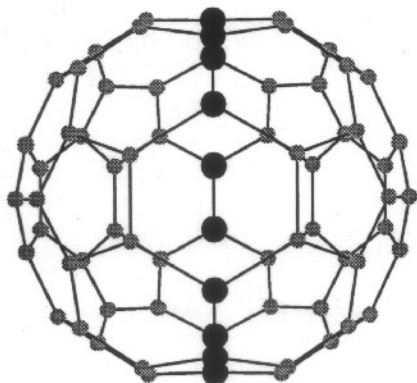
$$H_{\text{int}} = U \sum_i \left(c_{i,\uparrow}^\dagger c_{i,\uparrow} - \frac{1}{2} \right) \left(c_{i,\downarrow}^\dagger c_{i,\downarrow} - \frac{1}{2} \right) + \sum_{i \neq j} W(r_{i,j}) \left(\sum_{\sigma} c_{i,\sigma}^\dagger c_{i,\sigma} - 1 \right) \left(\sum_{\tau} c_{j,\tau}^\dagger c_{j,\tau}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

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

$$W(r) = \frac{1}{\sqrt{(1/U)^2 + (r/r_0V)^2}} \quad (4)$$

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.

(a) C₇₀ D_{5h}



(b) C₇₆ D₂

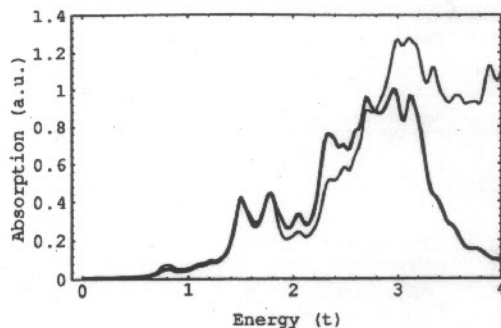
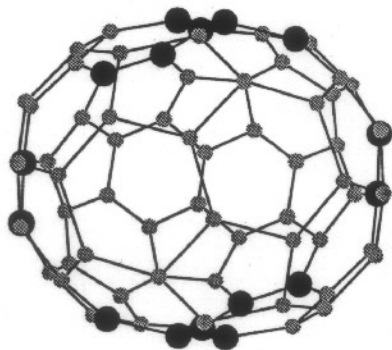


Figure 1. Molecular structures and theoretical optical spectra of (a) D_{5d}-C₇₀ and (b) D₂-C₇₆. In the molecules, the black atoms are along the phason lines, and the hatched atoms are the pentagonal carbons. In the absorption spectra, the bold line is the total absorption, and the thin line is the absorption by the wavefunctions projected onto 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 $\gamma = 0.06t$.

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 reference [9], we varied the parameters of the Coulomb interactions, and searched for the data which reproduce overall features on experiments on C₆₀ and C₇₀ in solutions. We 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 reference [9]. The Coulomb interaction strengths depend on the carbon positions. We use the lattice coordinates which are obtained using the public-domain 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 for 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 the fullerenes. If we write the projection operator describing projection onto 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 as

$$f_{\kappa,x} = E_{\kappa} [|\langle \kappa | PxP | g \rangle|^2 + |\langle \kappa | (1-P)x(1-P) | g \rangle|^2 + \langle g | PxP | \kappa \rangle \langle \kappa | (1-P)x(1-P) | g \rangle + \langle g | (1-P)x(1-P) | \kappa \rangle \langle \kappa | PxP | g \rangle] \quad (5)$$

where E_{κ} is the excitation energy, and the electric field is parallel to the x -axis. In equation (5), the first term is the contribution from the projected part, and the other three terms are the remaining part. The total optical absorption is calculated using 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 using equations (5) and (6). The projected part does not satisfy a sum rule. So, this leads to 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 figure 1(b). The total optical absorption is shown by the bold line, and the absorption from all of the pentagonal carbons is shown by the thin line. We find that the optical excitations in the region where the energy is 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. A similar artifact will be found in the figures shown later. 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 region where the energy is lower than about $2t \sim 4$ eV.

In C_{60} , the edges of the pentagons are the long bonds, and the bonds between the neighbouring hexagons are short bonds. The wavefunctions of the fivefold-degenerate highest occupied molecular orbital (HOMO) have bonding properties, and that of the threefold-degenerate lowest unoccupied molecular orbital (LUMO) has antibonding properties. As the carbon number increases, hexagons are inserted among pentagons. The wavefunctions near the LUMO of the higher fullerenes still have antibonding properties, and thus they tend to have large amplitudes along the edges of pentagons which have characteristics like long bonds of C_{60} . Recently, the bunching of the six energy levels

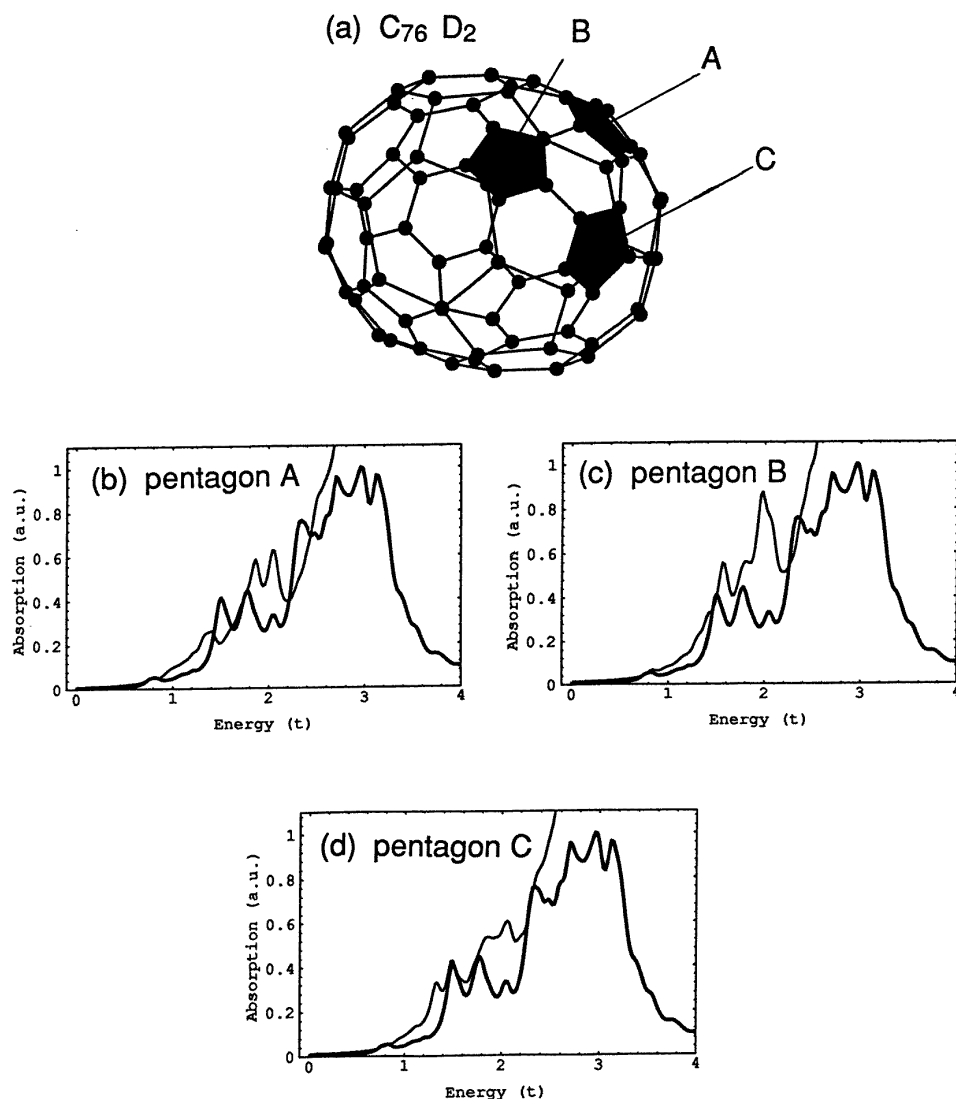


Figure 2. (a) The molecular structure of D₂-C₇₆. The symbols A–C indicate the symmetry-nonequivalent pentagons. (b), (c) and (d) compare the absorption projected onto one of the three pentagons with the total absorption. The bold line is the total absorption, and the thin line is the projected absorption. The units of the abscissa are taken as arbitrary, and the energy is scaled by t . The thin-line data are multiplied by the factor 12. The parameters are $U = 4t$, $V = 2t$, and $\gamma = 0.06t$.

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 a property characteristics of antibonding orbitals. As the excited electron mainly distributes on 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 why the projected absorptions nearly

accord with the total absorptions in the regions where the energy is smaller than about $2t$.

If projections onto each pentagon are performed, we can find the contributions to the 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 figure 2(a). The projected absorption spectra are shown by thin curves, superposed on the total absorption, in figures 2(b)–2(d). The projected absorption is multiplied by the factor 12, in order to allow comparison with the total absorption. We find that the projected absorption exhibits small structures in the region where the energy is smaller than $2t$. The structures depend on the kind of carbon. The spectral shapes and oscillator strengths are very different 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 notation in figures 3 and 4 is the same as in figure 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 region where the energy is lower than about $2t \sim 4$ eV. Of course, the agreement becomes a little bit worse from that in C_{70} and C_{76} shown in figure 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 fullerenes for which calculations were performed, 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} (figures 3(a) and 3(b)) and also in the D_{2d} isomer of C_{84} (figure 4(a)). These three molecules commonly have pentagon dimer structures. The dimers are shown by the black pentagons in the molecular structures of figure 5. It is of some interest to look at whether these pentagons give rise to similar contributions to the optical spectra or not. The data shown by the thin lines are multiplied by the factor 6, in order to allow comparison with the total absorption. We find that small peak structures are mutually different: for a typical example, the large feature at around the energy $1.5t$ represented by the thin line in figure 5(c) is not present in figures 5(a) and 5(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 and discussion

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 it using the Hartree–Fock and CI methods. We have found that the optical excitations in the region where the energy is smaller than about 4 eV have most of their amplitudes at the pentagonal carbons. Thus, the oscillator strengths of the absorption projected onto these carbons almost accord with those of the total absorption. When the projection is performed onto a smaller set of the pentagonal carbons—for example, onto each pentagon—the resultant spectrum in the low-energy region is quite different from that

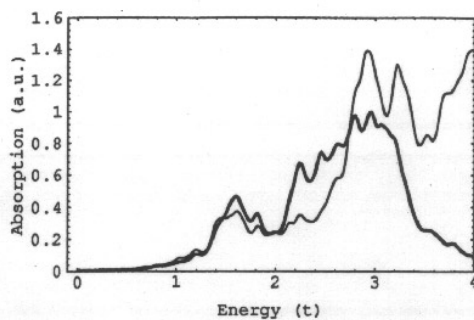
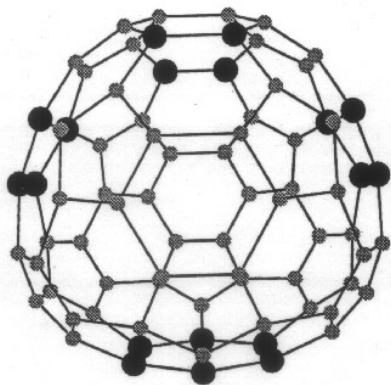
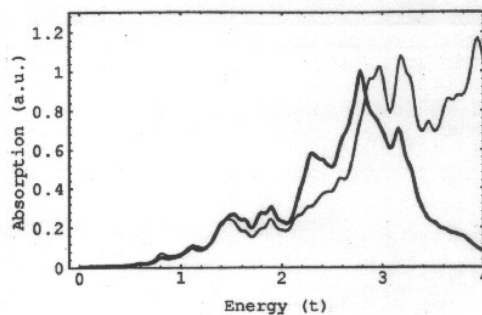
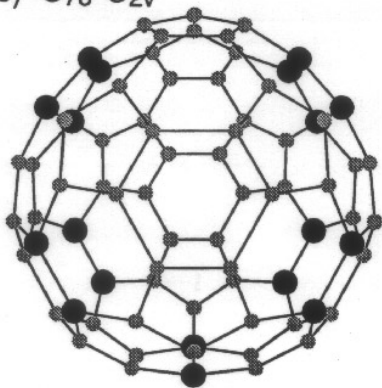
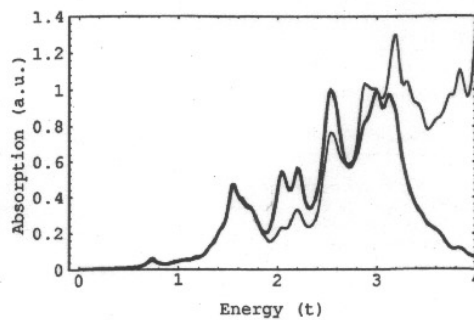
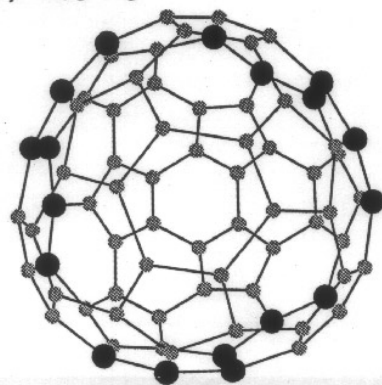
(a) $C_{78} C_{2v}$ (b) $C_{78} C_{2v}$ (c) $C_{78} D_3$ 

Figure 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 onto 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 $\gamma = 0.06t$.

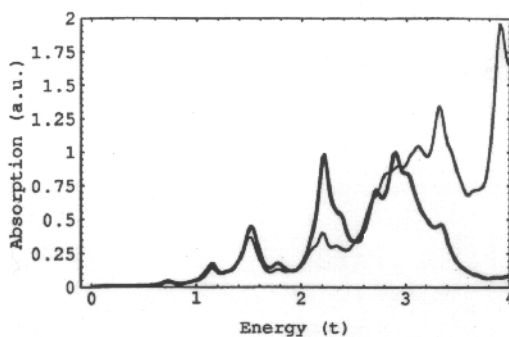
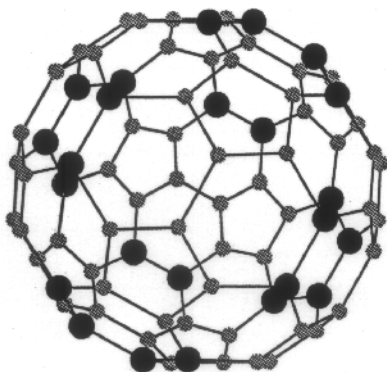
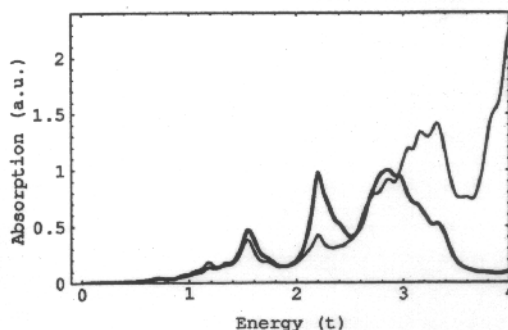
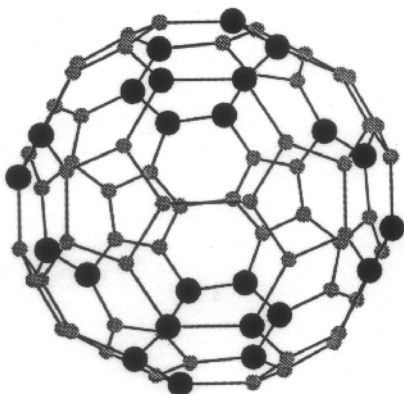
(a) C₈₄ D_{2d}(b) C₈₄ D₂

Figure 4. Molecular structures and theoretical optical spectra of (a) D_{2d}-C₈₄ and (b) D₂-C₈₄. 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 onto 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 $\gamma = 0.06t$.

of the total absorption. Therefore, the structures in the absorption cannot be decomposed into contributions from subsets of pentagonal carbons.

There are many experimental studies which have reported the optical gaps of C₆₀, C₇₀, and higher fullerenes. The reported values are: 1.8 eV for C₆₀ [17], 1.3 eV for C₇₀ [18], 1.3 eV for C₇₆ [19], 1.4 eV for C_{2v}-C₇₈ and 1.5 eV for D₃-C₇₈ [20], and 1.2 eV for C₈₄ [21]. The molecular energy gap with the assumption of $t = 1.8$ eV in the present calculations is: 2.9 eV for C₆₀, 1.7 eV for C₇₀, 1.2 eV for D₂-C₇₆, 1.1 eV for C_{2v}-C₇₈ (figure 3(a)), 0.9 eV for C_{2v}-C₇₈ (figure 3(b)), 1.2 eV for D₃-C₇₈, 1.3 eV for D_{2d}-C₈₄, and 1.2 eV for D₂-C₈₄. Even though we have not obtained quantitative agreement, the property that the energy gap of higher fullerenes is smaller than that of C₆₀ and C₇₀ is present both in the experiments and the theory. In the absorption spectrum of C₇₆ [6], a low-energy feature exists at around

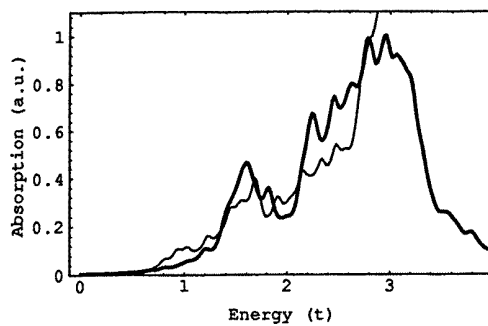
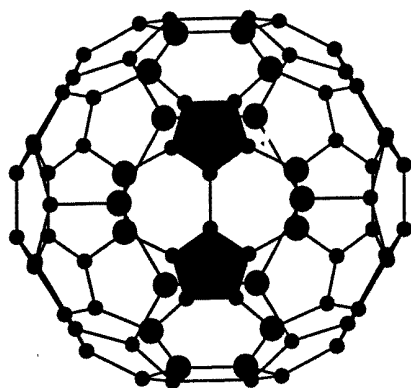
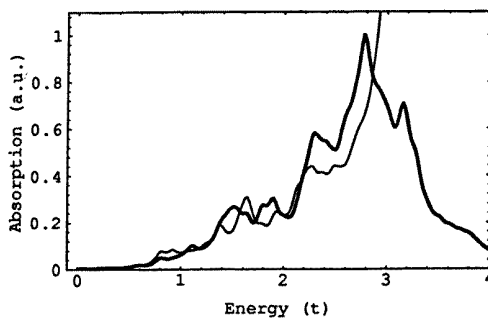
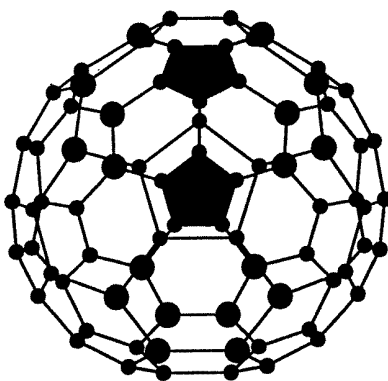
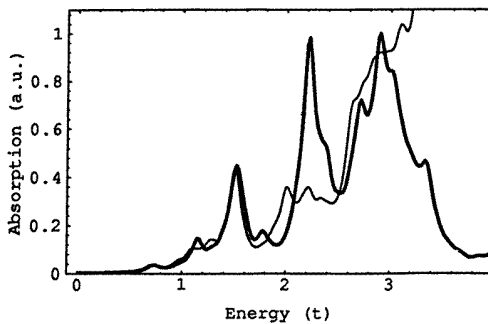
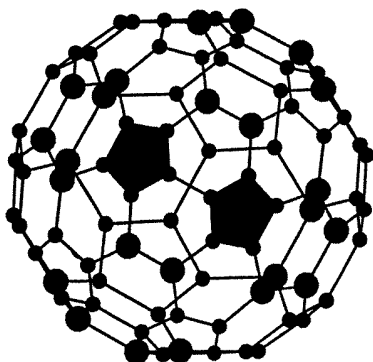
(a) $C_{78} C_{2v}$ (b) $C_{78} C_{2v}$ (c) $C_{84} D_{2d}$ 

Figure 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. Each figure compares the absorption projected onto 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 thin-line data are multiplied by the factor 6. The parameters are $U = 4t$, $V = 2t$, and $\gamma = 0.06t$.

1.5–1.7 eV. This feature corresponds to the small feature at around $0.8t$ of figure 1(b) in the present calculation. The low-energy tail becomes broader in experimental absorption spectra of the other higher fullerenes [6], so detailed assignment of the features seems more difficult for those fullerenes.

Acknowledgments

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References

- [1] Hare J P, Kroto H W and Taylor R 1991 *Chem. Phys. Lett.* **177** 394
- [2] Ren S L, Wang Y, Rao A M, McRae E, Holden J M, Hager T, Wang K A, Lee W T, Ni H F, Selegue J and Eklund P C 1991 *Appl. Phys. Lett.* **59** 2678
- [3] Meth J S, Vanherzeele H and Wang Y 1992 *Chem. Phys. Lett.* **197** 26
- [4] Kafafi Z H, Lindle J R, Pong R G S, Bartoli F J, Lingg L J and Milliken J 1992 *Chem. Phys. Lett.* **188** 492
- [5] Ettl R, Chao I, Diederich F and Whetten R L 1991 *Nature* **353** 149
- [6] Kikuchi K, Nakahara N, Wakabayashi T, Honda M, Matsumiya H, Moriwaki T, Suzuki S, Shiromaru H, Saito K, Yamauchi K, Ikemoto I and Achiba Y 1992 *Chem. Phys. Lett.* **188** 177
- [7] Harigaya K and Abe S 1992 *Japan. J. Appl. Phys.* **31** L887
- [8] Harigaya K and Abe S 1994 *J. Lumin.* **60&61** 380
- [9] Harigaya K and Abe S 1994 *Phys. Rev. B* **49** 16746
- [10] Harigaya K 1994 *Japan. J. Appl. Phys.* **33** L786
- [11] Fujita M 1993 *Fullerene Sci. Technol.* **1** 365
- [12] Fujita M, Saito R, Dresselhaus G and Dresselhaus M S 1992 *Phys. Rev. B* **45** 13834
- [13] Yoshida M and Ōsawa E 1993 *Proc. 3rd IUMRS Int. Conf. on Advanced Materials (Tokyo)* (Amsterdam: Elsevier)
- [14] Yoshida M and Ōsawa E *The Japan Chemistry Program Exchange, Program No 74*
- [15] Shumway J and Satpathy S 1993 *Chem. Phys. Lett.* **211** 595
- [16] Saito S, Okada S, Sawada S and Hamada N 1995 *Phys. Rev. Lett.* **75** 685
- [17] Sohmen E, Fink J, and Krätschmer W 1992 *Z. Phys. B* **86** 87
- [18] Ren Song-Lin, Wang Kai An, Zhou Ping, Wang Ying, Rao A M, Meier M S, Selegue J P and Eklund P C 1992 *Appl. Phys. Lett.* **61** 124
- [19] Armbruster J F, Romberg H A, Schweiss P, Adelman P, Knupfer M, Fink J, Michel R H, Rockenberger J, Hennrich F, Schreiber H and Kappes M M 1994 *Z. Phys. B* **95** 469
- [20] Diederich F, Whetten R L, Thilgen C, Ettl R, Chao I and Alvarez M M 1991 *Science* **254** 1768
- [21] Kuzuo R, Terauchi M, Tanaka M, Saito Y and Shinohara H 1994 *Phys. Rev. B* **49** 5054