Optical Absorption in Higher Fullerenes: Effects of Symmetry Reduction

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Abstract
Optical absorption spectra of higher fullerenes (C_{70} and C_{76}) as well as of C_{60} are calculated by a tight binding model with a long range Coulomb interaction. A reasonable parameter set gives calculated spectra which are in overall agreement with the experiments of of C_{60} and C_{70} in solutions. The variations of the spectral shape are discussed relating with the symmetry reduction going from C_{60} and C_{70} to C_{76}: the optical gap decreases and the spectra have more small structures in the dependences on the excitation energy.

Keywords: optical absorption, fullerene, C_{60}, C_{70}, C_{76}, CI calculation, theory

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Recently, the fullerene family \( C_N \) with hollow cage structures have been intensively investigated. Various optical experiments have been performed, and interesting properties due to \( \pi \) electrons delocalized on molecule surfaces have been revealed. They include the optical absorption spectra of \( C_{60} \) and \( C_{70} \),\(^{1,2}\) and the large optical nonlinearity of \( C_{60} \).\(^{3,4}\) The absorption spectra of higher fullerenes (\( C_{76}, C_{78}, \text{etc.} \)) have been obtained also.\(^{5,6}\) In order to analyze the optical properties, we have studied the linear absorption and the third harmonic generation of \( C_{60} \) by using a tight binding model\(^7\) and a model with a long range Coulomb interaction.\(^8\)

The purpose of this paper is to extend the calculation of \( C_{60} \)\(^8\) up to one of higher fullerenes, \( C_{76} \). The main purpose is to look at how the optical absorption changes as the symmetry of the molecule reduces going from \( C_{60} \) and \( C_{70} \) to \( C_{76} \). There have been two possible isomers for \( C_{76} \) which satisfy the isolated pentagon rule.\(^9\) They have \( D_2 \) [Fig. 1(a)] and \( T_d \) symmetries [Fig. 1(b)]. Owing to the NMR experiment,\(^5\) the molecular structure has been identified. There is only the molecule with the \( D_2 \) symmetry. We, however, calculate the optical absorption for both of them in order to look at symmetry reduction effects extensively.

We use the following hamiltonian:

\[
H = H_0 + H_{\text{bond}} + H_{\text{int}}. \tag{1}
\]

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

\[
H_0 = -t \sum_{(i,j),\sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}), \tag{2}
\]
where $t$ is the hopping integral and $c_{i,\sigma}$ is an annihilation operator of a $\pi$-electron with spin $\sigma$. If $t$ depends on the bond length, the results do not change so strongly, because main contributions come from the strong Coulomb potential. Effects of zero point vibrations and thermal fluctuation of the lattice are described by the bond disorder model which is the second term of eq. (1):

$$H_{\text{bond}} = \sum_{\langle i,j \rangle, \sigma} \delta t_{i,j}(c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}).$$

Here, $\delta t_{i,j}$ is the Gaussian disorder potential at the bond $\langle i, j \rangle$. We can estimate the strength of the disorder (standard deviation) $t_s$ from the results by the extended Su-Schrieffer-Heeger model.\textsuperscript{10} The value would be $t_s \sim 0.05 - 0.1t$. This is of the similar magnitude as in the fullerene tubules and conjugated polymers. We shall treat interactions among $\pi$-electrons by the following model:

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

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

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

is the Ohno potential. The quantity $U$ is the strength of the onsite 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 we used in the previous
papers.\textsuperscript{8,11} In ref. 11, we have varied the parameters of the Coulomb interaction and the disorder potential, and have searched for the data which reproduce overall features of experiments of C\textsubscript{60} and C\textsubscript{70} in solutions. We have found that the common parameters, $U = 4t$, $V = 2t$, $t_s = 0.09t$, and $t = 1.8\text{eV}$, are reasonable. We use the same parameter set for higher fullerenes, too. For C\textsubscript{70}, the anisotropic spectra with respect to the orientation of the molecule against the electric field of light, as reported in the free electron model (Hückel theory),\textsuperscript{12} have been averaged by rotating the molecule. The averaged data can be compared with experiments of molecules in solutions.\textsuperscript{1,12} We use the same procedure for C\textsubscript{76}. Samples of the orientation of the molecule and the disorder potential are changed 100 times. This is enough to obtain smooth numerical data.

First, we discuss the calculated optical absorption of C\textsubscript{60} and C\textsubscript{70}. The C\textsubscript{60} has the high $I_h$ symmetry, and C\textsubscript{70} has the lower $D_{5h}$ symmetry. Figure 2(a) shows the spectrum of C\textsubscript{60}, and Fig. 2(b) displays that of C\textsubscript{70}. Experimental data are taken from refs. 1 and 2, and are shown by thin lines. Here, we concentrate upon effects of the symmetry reduction from $I_h$ to $D_{5h}$. There are three main features in the C\textsubscript{60} absorption. They are around the energies, 3.5\text{eV}, 4.7\text{eV}, and 5.6\text{eV}. When we turn to C\textsubscript{70}, we could say that several small peaks in the energy interval from 1.7\text{eV} to 3.6\text{eV} come from the 3.5\text{eV} feature of C\textsubscript{60} after splitting. Both the 4.7\text{eV} and 5.6\text{eV} features of C\textsubscript{60} join into the large feature which is present in the energy region larger than 3.6\text{eV}. The optical gap decreases from 3.1\text{eV} (C\textsubscript{60}) to 1.7\text{eV} (C\textsubscript{70}). These changes would be due to the symmetry reduction from the C\textsubscript{60} soccerball to the C\textsubscript{70}.
rugbyball.

Next, we show optical spectra of C_{76}. Figures 3 (a) and (b) show the calculated results for the D_2 and T_d symmetries, respectively. The average by the rotation has been performed. The optical gap is about 1.2eV in Fig. 3(a) and about 0.7eV in Fig. 3(b). These values are smaller than the optical gaps of C_{60} and C_{70}. In Fig. 3(a), there are two broad large features around 2.7eV and 4.5eV with fine structures. We could say that several small peaks around 2.7eV and 4.7eV in the C_{70} data become fragmented to form the two wide features in the C_{76} data. There is still a dip near 3.2eV as in C_{70}. The position of the dip does not change so much. In Fig. 3(b), the spectral shape becomes broad totally and many small structures develop as well. These variations could be regarded as owing to the further reduction of the symmetry of the higher fullerene C_{76}.

The experiments^{5,6} show that the optical gap decreases in higher fullerenes (C_{76}, C_{78}, C_{82}, and so on), and thus this property is consistent with the present calculation. However, many small structures in the absorption of C_{76}^{5} which is shown in Fig. 3(a) are not so apparent. Therefore it seems difficult to compare with calculations in detail. The agreement with experiments is worse for higher fullerenes. This fact indicates that the model with only \pi electrons is so simple for larger fullerenes. The mixing between \pi and \sigma orbitals is different for each carbon atom due to the low symmetries of C_{70} and C_{76}. Inclusion of the \sigma orbitals would be desirable for more detailed comparison with experiments.

There is a common trend in C_{60}, C_{70}, and D_2-C_{76}: the deviation of the
theory from experiments is larger in the excitation energy region 5.0-6.0eV. Excitations among $\sigma$ orbitals would be mixed in this energy region. This effects could be taken into account by using models with $\pi$ and $\sigma$ electrons.

We could note the following point, even though the present model turned out to be so simple for higher fullerenes. As is evident for the two possible isomers of C$_{76}$, the calculated spectral shapes are different each other. Therefore, optical measurements are good methods for identification of various isomers of more higher fullerenes (C$_{78}$, C$_{82}$, etc.), for which the number of isomers rapidly increases.

To summarize, we have considered optical spectra of the higher fullerenes, C$_{70}$ and C$_{76}$, as well as the buckyball C$_{60}$. A reasonable parameter set gives calculated spectra which are in overall agreement with the experiments of of C$_{60}$ and C$_{70}$ in solutions. We have mainly looked at how the optical absorption changes as the symmetry of the molecule reduces from C$_{60}$ and C$_{70}$ to C$_{76}$. We have pointed out that the optical gap decreases and the spectra have more small structures in the energy dependences as the number of carbons increases.

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Figure captions

Fig. 1. Molecular structures for C\textsubscript{76} with (a) \textit{D}\textsubscript{2} and (b) \textit{T}\textsubscript{d} symmetries.

Fig. 2. Optical absorption spectra for (a) C\textsubscript{60} and (b) C\textsubscript{70}, shown in the arbitrary units. The abscissa is scaled by \textit{t}. The parameters in the Ohno potential are $U = 4t$ and $V = 2t$ ($t = 1.8\text{eV}$). Experimental data are shown by thin lines. They are taken from ref. 2 for (a), and from ref. 1 for (b).

Fig. 3. Optical absorption spectra for C\textsubscript{76} with (a) \textit{D}\textsubscript{2} and (b) \textit{T}\textsubscript{d} symmetries, shown in the arbitrary units. The abscissa is scaled by \textit{t}. Parameters in the Ohno potential are $U = 4t$ and $V = 2t$ ($t = 1.8\text{eV}$). Experimental data of \textit{D}\textsubscript{2}-C\textsubscript{76} are shown by the thin line. They are taken from ref. 5.