Optical absorption spectra of $A_6C_{60}$:
Reduction of effective Coulomb interactions

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Abstract
Optical absorption spectra of $C_{60}^{6^-}$ are theoretically investigated in order to analyze the optical properties of alkali metal doped fullerenes $A_6C_{60}$. We use a tight binding model with long ranged Coulomb interactions and bond disorder. Optical spectra are obtained by the Hartree-Fock approximation and the CI method. The Coulomb interaction parameters which are relevant to the optical spectra of $A_6C_{60}$ are almost the half of those of the neutral $C_{60}$. The reduction of the effective Coulomb interactions is concluded for the heavily doped case of $C_{60}$.

Keywords: optical absorption, fullerene, $A_6C_{60}$, $C_{60}^{6^-}$, CI calculation, theory

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§1. Introduction

Since the C$_{60}$ solid and A$_3$C$_{60}$$^{1}$ with the novel high temperature superconductivity were discovered, fullerenes have been intensively investigated. As the $\pi$ electrons are delocalized on their surfaces, the fullerenes show optical responses that are similar to those in $\pi$ conjugated polymers.$^2$ For example, the absorption spectra of C$_{60}$ (refs. 3 and 4) and C$_{70}$ (ref. 3) reflect the existence of excitons (mainly Frenkel excitons) which are important when the excitation energy is larger than the order of 1eV. The nonlinearity of C$_{60}$ in the third harmonic generation (THG) is of the order $10^{-11}$ esu,$^5,6$ and the similar magnitudes have been observed in polydiacetylenes.

Recently, we have studied the linear absorption and the THG of C$_{60}$ by using a tight binding model$^7$ and a model with a long ranged Coulomb interaction.$^8,9$ A free electron model yields the THG magnitudes which are in agreement with the experiment of C$_{60}$$^5,6$. However, when the Coulomb interactions are taken into account, the THG magnitudes decrease.$^8$ We have discussed that the local field correction would be necessary in order to recover the agreement. The model with Coulomb interactions has been turned out to describe well the linear absorption spectra of C$_{60}$ and C$_{70}$ in solutions.$^9$

In this paper, we consider the optical spectra of A$_6$C$_{60}$ ($A = K, Rb, Cs,$ etc). The system is a fullerite maximumly doped with alkali metals, and is an insulator like the neutral C$_{60}$. The optical spectra have been measured in several papers.$^{10,11}$ The peak structures in the energy dependence are quite different from those of the neutral C$_{60}$, even though each peak could be ex-
plained as an optical transition between molecular orbitals. The absorption spectra of the neutral C$_{60}$ and A$_3$C$_{60}$ are rather similar, but the data of A$_6$C$_{60}$ are largely different. It seems that main peaks of the neutral C$_{60}$ spectra move to lower energies. This fact could be explained by reduction of the effective Coulomb interaction strengths. The principal purpose of the present calculations is to confirm this conjecture. The calculation method is the same as that used in the previous paper.\textsuperscript{9)} We start from the Hartree-Fock approximation and perform configuration interaction calculations which are limited to single electron-hole excitations (single CI). In the experiments of A$_6$C$_{60}$,\textsuperscript{10,11)} intermolecular interactions seem to be relatively weak, because there is not a peak structure owing to the intermolecular interactions (like the 2.8eV structure in the C$_{60}$ films\textsuperscript{4)}). Therefore, we shall limit our considerations to the system C$_{60}^{-}$.

In the next section, we explain our model briefly. In §3, we show results and give discussion relating with molecular orbital structures. The final section is devoted to the summary.

\section{Model}

In order to consider optical spectra of C$_{60}^{-}$, we use the following hamiltonian:

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

The first term $H_0$ of eq. (1) is the free electron part:

$$H_0 = -t \sum_{\langle i,j \rangle,\sigma} (c^\dagger_{i,\sigma} c_{j,\sigma} + \text{h.c.}), \quad (2)$$
where \( c_{i,\sigma} \) is an anihilation operator of the \( \pi \)-electron at site \( i \) with spin \( \sigma \); the sum is taken over all the pairs \( \langle i, j \rangle \) of neighboring atoms; and \( t \) is the hopping integral. In the \( C_{60}^{6-} \) which is geometrically optimized by the SSH model\(^\text{12)}\) the dimerization is negligible. So, we assume the constant hopping integral. The second term of eq. (1) is the bond disorder model simulating lattice fluctuations:

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

This model was sometimes used in the literatures\(^9,13^\text{)}\). The third term is the long ranged Coulomb interaction in the form of the Ohno potential:

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

where \( r_{i,j} \) is the distance between the \( i \)th and \( j \)th sites and

\[
W(r) = \frac{1}{\sqrt{(1/U)^2 + (r/r_0V)^2}}
\]

is the Ohno potential. The quantity \( W(0) = U \) is the strength of the onsite interaction, and \( V \) means the strength of the long range part.

In this paper, most of the quantities with the energy dimension are shown in the units of \( t \). The same convention has been used in the previous paper\(^9^\text{)}\). We vary the Coulomb interaction strengths within \( 0 \leq V \leq U \leq 5t \) in order to fix appropriate parameters. When disorder effects are included, data are averaged over 100 samples. This is enough to obtain smooth numerical data.
§3. Results and Discussion

Figure 1(a) shows the optical spectrum of the free electron model. Four low energy peaks are named with Roman symbols. The meaning of each transition is interpreted in the energy level structures shown as Fig. 2. The $t_{1u}$ orbital near the energy 0 is filled up with six electrons, and the orbitals above it are not occupied. The $C_{60}^{-}$ has the closed shell structure. The absorption spectrum of the neutral $C_{60}$ has been calculated in ref. 7. The peaks, b and d, are present in that calculation. The oscillator strengths are the same as in the present calculation. The peaks, a and c, are characteristic to $C_{60}^{-}$. The experiments\textsuperscript{10,11) have interpreted the lowest feature around 1.2eV as originated from the peak a. It seems that this assignment is a natural understanding.

In the previous study,\textsuperscript{9) we have shown that the peak positions and the distribution of oscillator strengths in the optical absorption of the neutral $C_{60}$ are reasonably explained by the theory with $U = 4t$, $V = 2t$, and $t = 1.8$eV. This is the intramolecular excitonic effect. We shall apply the same formalism to $C_{60}^{-}$. If the same parameters, $U = 4t$, $V = 2t$, and $t = 1.8$eV, are relevant to $C_{60}^{-}$, we theoretically expect that the peak at 2.0$t$ does not move so much, as the doping proceeds. However, in experiments,\textsuperscript{9) the corresponding 3.6eV peak of the neutral $C_{60}$ moves to 2.8eV in $C_{60}^{-}$. This large shift cannot be explained by the theory with the same parameters, because the half of characters of optical transitions are the same: the transition b shown in Fig. 2 is common to $C_{60}$ and $C_{60}^{-}$.

We have searched for Coulomb parameters which reproduce overall features
of the optical spectrum of K$_6$C$_{60}$ (ref. 10). We find that the parameters, $U = 2t$, $V = 1t$, and $t = 2.0$eV, would be reasonable. Figure 1(b) shows the calculated spectrum. The several peaks in Fig. 1(a) move to higher energies, and oscillator strengths become relatively larger in higher energies. These are the Coulomb interaction effects.

Experimental spectra$^{10,11}$ are broad mainly due to lattice fluctuations. The effects are simulated by the bond disorder model with Gaussian distribution of the standard deviation $t_s = 0.20t$. The result is shown in Fig. 1(c). The experimental data are taken from ref. 10, and are shown as Fig. 1(d) for comparison. We could say that two features around 1.2eV and 2.8eV are reasonably explained by the present calculation. The broadening is simulated well by the bond disorder. The disorder strength $t_s = 2.0t$ is about the twice as large as that of the neutral C$_{60}$. This indicates that A$_6$C$_{60}$ is more disordered than the neutral C$_{60}$. The broad feature in the energies higher than 3.6eV in the experiment might correspond to the two broad peaks around 2.2$^t$ and 3.0$^t$ of the calculation. In these energies, the agreement is not so good. The same fact has been seen in the neutral C$_{60}$ case.$^9$ Excitations which include $\sigma$ orbitals would be mixed in this energy region. This effect could be taken into account by using models with $\pi$ and $\sigma$ electrons. However, this is beyond our interests.

Our main conclusion, the reduction of the effective Coulomb interactions, seems to be the remarkable difference between the neutral and heavily doped C$_{60}$. The electron density of C$_{60}^{6-}$ is 10% larger than that of the neutral C$_{60}$. The relevant Coulomb interaction strengths could be different in heavily doped
molecules and solids. One of the origins of the reduction would be the fact that the environments around C$_{60}$ molecules are different between the neutral C$_{60}$ and A$_6$C$_{60}$. Actually, the C$_{60}$ solid is the simple cubic lattice, and A$_6$C$_{60}$ is the body centered cubic lattice. The distance between the neighboring C$_{60}$ is larger in A$_6$C$_{60}$ due to the intercalated alkali metal ions. The research of the intermolecular interaction effects in the neutral C$_{60}$ crystal is in progress, and will be reported elsewhere.\(^{14}\) We should consider interactions among molecules in A$_6$C$_{60}$, and calculate the optical spectra in future.

§4. Summary

We have considered optical excitations of C$_{60}^{6-}$ by treating the long ranged Coulomb interaction with the Hartree-Fock approximation and the single CI method. We have searched for the parameter set in order to reproduce overall features of the optical spectrum of A$_6$C$_{60}$. The parameters, $U \sim 2t$, $V \sim 1t$, and $t \sim 2.0$eV, have been turned out to be relevant. The magnitudes of $U$ and $V$ are almost the half of those which were used for the neutral C$_{60}$. This might be due to the different environments around molecules in crystals. Calculations which include intermolecular interactions would be desirable for further understandings of electronic structures.

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Figure Captions

Fig. 1. Optical absorption spectra for C₆₀ shown in arbitrary units. The abscissa is scaled by $t$. The spectra are calculated with the parameters (a) $U = V = 0$, (b,c) $U = 2t$ and $V = 1t$. The Lorentzian broadening $\gamma = 0.01t$ is used. In (c), lattice fluctuations are taken into account by the bond disorder of the strength $t_s = 0.20t$. (d) The experimental spectrum (ref. 10) of K₆C₆₀ is shown with using $t = 2.0$eV.

Fig. 2. Energy level structures of the free electron (Hückel) model. Each energy level is shown against its degeneracy. Several dipole allowed transitions are indicated by the Roman symbols. The corresponding peak positions in Fig. 1(a) are shown by the same symbols.