Optical absorption spectra of $A_6C_{60}$ and $A_6C_{70}$:

Reduction of effective Coulomb interactions
in Frenkel excitons

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ABSTRACT
We theoretically investigate optical absorption spectra of $C_{60}^-$ and $C_{70}^-$, and discuss relations with the optical properties of alkali metal doped fullerides $A_6C_{60}$ and $A_6C_{70}$. This is a valid approach for systems where Frenkel exciton effects are dominant. 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 configuration interaction method. We find that the Coulomb interaction parameters, which are relevant to the optical spectra of $A_6C_{60}$ ($A_6C_{70}$) in order to explain the excitation energies and relative oscillator strengths of absorption peaks, are almost the half of those of the neutral $C_{60}$ ($C_{70}$). The reduction of the effective Coulomb interactions is concluded for
the heavily doped case of $C_{60}$ and $C_{70}$. This finding is closely related with the experimental fact that dielectric constants of fullerides which are maximumly doped with alkali metals become about twice as large as those of the neutral systems.

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I. 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 π electrons are delocalized on their surfaces, the fullerenes show optical responses that are similar to those in π 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 experiments 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 turned out to describe well the linear absorption spectra of C$_{60}$ and C$_{70}$ in solutions.\(^9\)

In the first half part of this paper, we perform calculations for C$_{60}$ and consider the optical spectra of A$_6$C$_{60}$ ($A = K, Rb, Cs,$ etc). This compound is a fulleride 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 explained 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 viewpoint. The calculation method is the same as that used in the previous paper. 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$_{60}$, 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$^4$). Therefore, we shall limit our considerations to the system C$_{6-}$$_{60}$. This is a reasonable approximation for systems where single molecular contributions (Frenkel exciton effects) are dominant.

The reduction of the Coulomb interactions means that dielectric constants of the doped systems increase. Actually, the electron-energy-loss spectroscopy (EELS) studies of Rb$_x$C$_{60}$ and Rb$_x$C$_{70}$ ($x = 0, 3, 6$)$^{12}$ have revealed that the real part of the dielectric function at zero frequency increases from $x = 0$ to 6, and the magnitude becomes about twice. In our calculations by single molecule models, this enhancement of the dielectric functions is represented by the decrease of the phenomenological parameters in Coulomb interactions.

In the last part of the paper, we consider C$_{70}^{6-}$ in order to discuss optical properties of the insulating phase A$_6$C$_{70}$. Frenkel excitons would be dominant
in this system again. We demonstrate that the picture of the reduction of Coulomb strengths is relevant to C$_{70}$ also. Therefore, the reduction of Coulomb interaction strengths is a common property seen in two kinds of fullerenes. In fact, the EELS studies$^{12}$ have concluded that $\pi$ electronic systems in Rb$_x$C$_{60}$ and Rb$_x$C$_{70}$ show a non-rigid-band behavior and excitation energies become smaller upon doping.

In the next section, we explain our model briefly. In Sec. III, we show results of C$_{60}^-$ and give discussion relating with molecular orbital structures. In Sec. IV, we consider C$_{70}^-$.$^9$. The final section is devoted to the summary.

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