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EXCITON AND LATTICE-FLUCTUATION EFFECTS IN OPTICAL SPECTRA OF C_{60}

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Abstract A theory of optical excitations by using a tight binding model with long-range Coulomb interactions is developed. The model is applied to a C_{60} molecule and a cluster, and is treated by the Hartree-Fock approximation followed by a configuration interaction method. Lattice fluctuations are taken into account by a bond disorder model. We first examine what strength of Coulomb interaction is appropriate to describe the electronic structures observed by photo-electron and optical absorption spectroscopy. Then, we demonstrate that the photo-excited states are mainly intramolecular (i.e. Frenkel) excitons with small charge-transfer components. We examine to what extent the dipole forbidden transitions of a single C_{60} molecule become dipole-allowed by lattice fluctuations or intermolecular interactions.

INTRODUCTION

Optical experiments on fullerenes C_N have revealed many interesting properties associated with π electrons delocalized on molecule surfaces. The optical absorption spectrum of C_{60},[1] provides basic information about its electronic structure. A large third-order nonlinear susceptibility $\chi^{(3)}$ of the order 10^{-11}esu has been observed in the third-harmonic generation (THG) from C_{60}.[2,3]

In order to analyze the optical properties and to clarify mechanisms of the large nonlinearity, we have studied the linear absorption and the THG of C_{60} by using a tight binding model[4] and a model with a long-range Coulomb interaction.[5] A free electron model yields THG magnitudes which roughly coincide with the experimental values of C_{60},[1] while the calculated linear absorption spectrum is not in satisfactory agreement with experiments.[4] If Coulomb interactions are taken into account, the absorption spectra are in overall agreement with the experiment, although the magnitude of $\chi^{(3)}$ becomes smaller by one order of magnitude.[5] We suggested that the observed values of $\chi^{(3)}$ may be explained by taking local field corrections into account.

In this paper we first address the fundamental question of what strength of Coulomb interaction is appropriate in order to describe the electronic structures observed by photo-electron and optical absorption spectroscopy. The parameter of the bond disorder simulating the lattice fluctuations is also specified. Then, we study the character of the photo-excited states: whether excitons are confined in a single molecule or they are distributed among several molecules. We also examine how dipole forbidden transitions of the C_{60} molecule become dipole-allowed by lattice fluctuations and by intermolecular interactions.

MODEL AND METHOD

In the calculation of an isolated C_{60} molecule, the hopping integrals, $t + (2/3)t'$ and $t - (1/3)t'$ are assigned for the double and single bonds for π electrons, respectively. The bond alternation $t' = 0.1t$ of a typical value is used in this paper. The average hopping integral t is treated as an adjustable parameter in the present study, being around 2eV. In order to simulate lattice fluctuation effects in the molecule, Gaussian bond disorder is introduced in the hopping integral. The disorder strength is similar to that of the zero point fluctuations.[6] The Pariser-Parr-Pople model with long range Coulomb interactions is adopted to describe exciton effects. We use the Ohno potential $W(r) = 1/\sqrt{(1/U)^2 + (r/r_0V)^2}$ for the electron-electron interactions, where 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.

To discuss solid state effects, we consider a cluster of four molecules, which corresponds to a unit cell of the simple cubic lattice in the low temperature phase of the C_{60} solid. The periodic boundary condition is imposed. In the system, one of pentagons on one C_{60} molecule faces to one of double bonds on a neighboring C_{60} molecule. We assume weak intermolecular hopping integrals t_w between each of the two double-bonded sites and its three closest sites on the facing pentagon. The distances of these intermolecular connections are fairly large, about 3Å, and t_w is estimated to be around 0.1 - 0.2eV. We use $t_w = 0.1t$ in the present paper. In addition to the intermolecular hopping, we take into account intermolecular electron-electron interactions by assuming the Ohno potential also between sites on different molecules. A proper long-distance cutoff is introduced for the potential to harmonize with the cyclic boundary condition.

The model is treated by the Hartree-Fock approximation for the ground state and the single-excitation configuration interaction (single CI) method for excited states. All the quantities with the energy dimension are shown in the units of t. We varied the parameters of Coulomb interaction within $0 \leq V \leq U \leq 5t$, and we report here the representative cases: $U = 4t$ and $V = 2t$, results of which turn out to be in overall agreement with experiments. In the calculation of the single molecule with bond disorder, the average over 100 samples is taken. This is sufficient for obtaining smooth optical spectra.

OPTICAL ABSORPTION IN C_{60} MOLECULES

Fig. 1(a) shows the calculated absorption spectrum, and Fig. 1(b) shows the experimental data obtained by Ren et al. for C_{60} in a solution and a C_{60} thin film[1] for comparison assuming $t = 1.8$eV. There are three main features at about $2.0t$, $2.6t$, and $3.1t$ in the calculated spectrum. Their relative positions in energy agree well with the experimental data. The relative oscillator strengths also agree well. Furthermore, the widths of the observed absorption peaks are well simulated by the broadening in the bond disorder model. In reality, the broad absorption bands

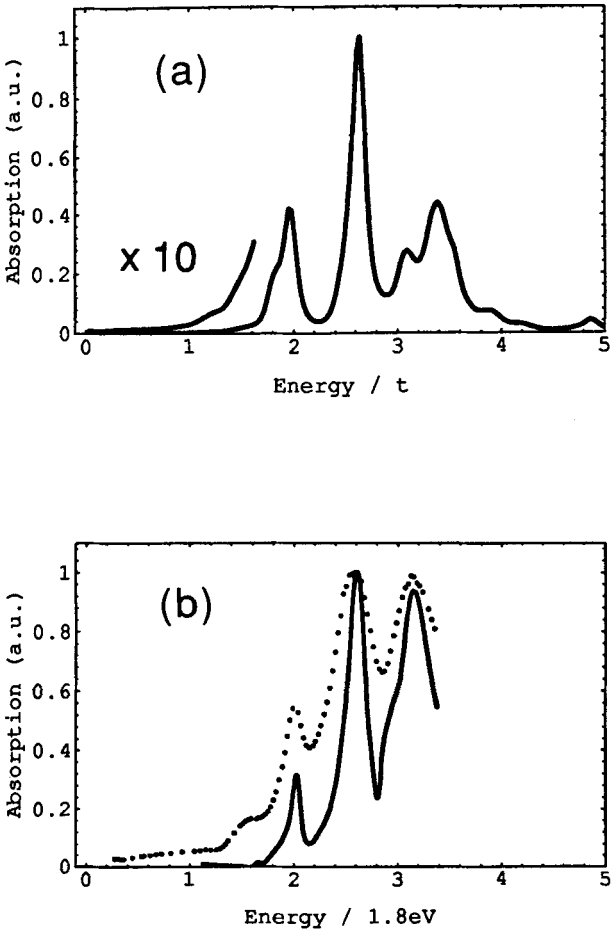

FIGURE 1 Optical absorption spectra for a C_{60} molecule shown in arbitrary units. In (a), the spectrum is calculated with the parameters $U = 4t$, $V = 2t$, and the bond disorder of the strength $t_s = 0.09t$. The abscissa is scaled by t. (b) The experimental spectra (Ref. 1) of molecules in a solution (solid line) and of a C_{60} film (dotted line). We use $t = 1.8$eV.

might contain fine structures due to many phonon modes including intermolecular librations and intramolecular vibrations. However, they are not resolved in the experiments presumably because they are smeared out by some other weak broadening mechanisms (such as life-time broadening). The disorder strength adopted here simulates well the overall width due to the gross contributions from the many phonon modes.

In the solid, the broadening is larger and a broad hump appears around the energy 2.8eV (= $1.5t$), as is shown in Fig. 1(b). There is a tiny structure at 3eV in the corresponding region of the absorption spectrum of C_{60} in a solution (Fig. 1(b)). We assume that the forbidden transitions in that energy region become partially allowed due to lattice fluctuations or intermolecular interactions. If the lattice fluctuations are effective, the effect can be simulated by the bond disorder model. In Fig. 1(a), the absorption in the low energy part multiplied by the factor 10 is also shown. The several forbidden transitions around $1.2t$ - $1.6t$ become allowed by the disorder, giving rise to an absorption tail in the lower energy region. The relative magnitude is similar to the solution data shown in Fig. 1(b). This might be also the origin of the 2.8eV hump in the solid. However, the strength of the absorption relative to the main peaks in our theory is about one order of magnitude smaller than that in the experiment.

OPTICAL ABSORPTION IN C_{60} SOLIDS

We turn to calculations for C_{60} solids. Fig. 2(a) shows the density of one-electron states calculated in the Hartree-Fock approximation. The occupied (unoccupied) states are represented by the black (white) bars, respectively. The distribution of states becomes broad due to the intermolecular hopping, and the widths of the distribution are consistent with the band calculations.[7] Thus, the hopping interaction $t_w = 0.1t$ seems reasonable. The overall density of states agrees with the photoemission and the inverse photoemission data[8] if we choose $t = 1.8$eV.

Now, we discuss the optical spectra calculated by the single CI method. Fig. 2(b) shows the density of states for dipole allowed excitations as a function of the excitation energy. The hatched region indicates the states for which the probability that the electron and the hole are located in different molecules is larger than 0.5. In other words, these states consist mainly of charge transfer components. Other states (nonhatched) correspond to primarily intramolecular excitations, namely Frenkel excitons. Fig. 2(c) shows the absorption spectrum where the Lorentzian broadening $\Gamma = 0.03t$ is used. The absorption in the low energy region $1.6t$ - $1.9t$ is slightly enhanced from those in Fig. 1(a) owing to the intermolecular interactions, although the gross features of the spectrum remain unchanged. This is consistent with the experimental data shown in Fig. 1(b). We would like to stress that the states which give rise to relatively large oscillator strengths are the states with small charge transfer components. The states with large charge transfer components give very

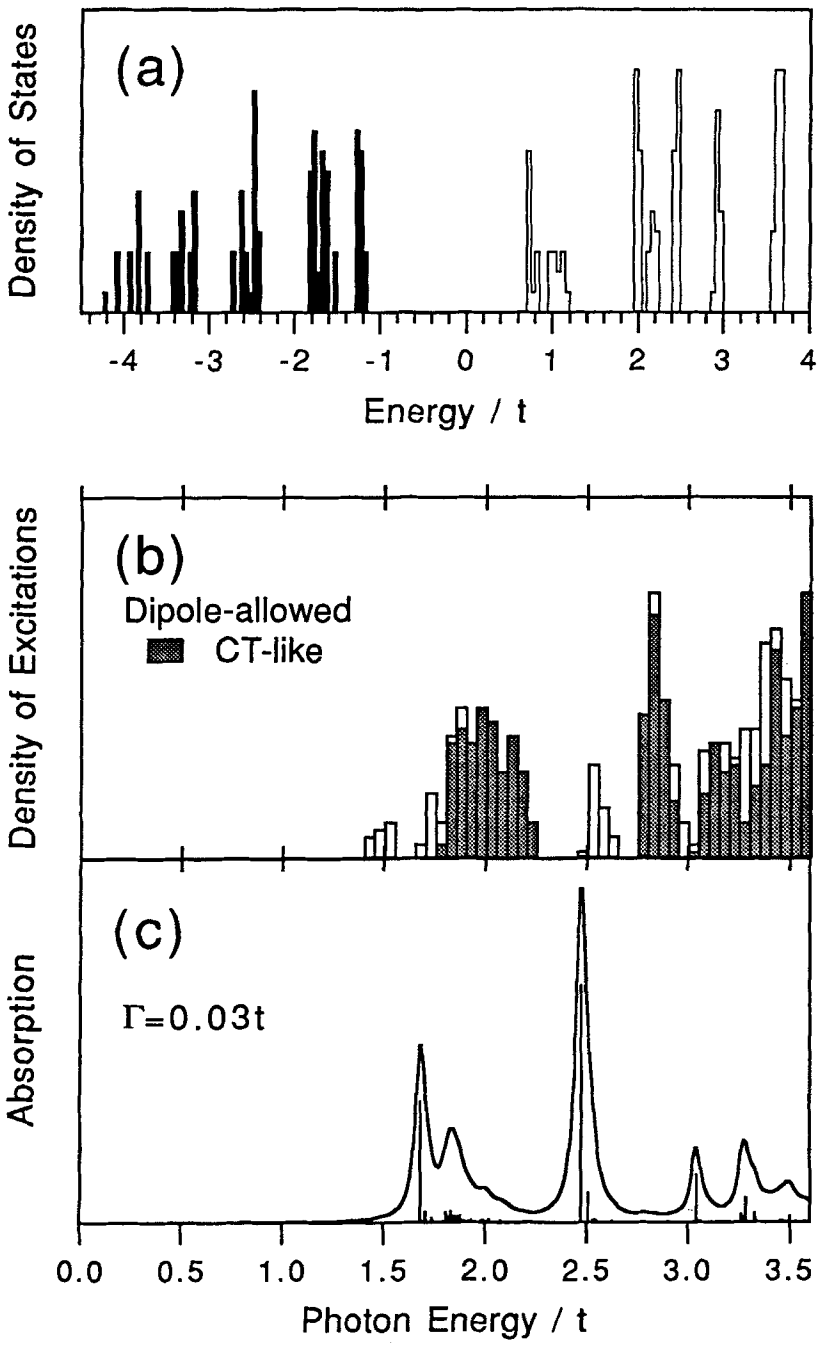

FIGURE 2 (a) Density of states of the cluster by the Hartree-Fock approximation. The occupied (unoccupied) states are shown by the black (white) bars. (b) Density of states for dipole allowed excitations as a function of the excitation energy. (c) The absorption spectrum where the Lorentzian broadening $\Gamma = 0.03t$ is used.

small oscillator strengths. Thus, we conclude that the photoexcited states are mainly Frenkel-exciton-like states. This is also in accord with the fact that the excitation energies of such states are largely shifted to low energies from the one-electron excitation energies obtained at the Hartree-Fock level. For example, the absorption peak at about $1.7t$ in Fig. 2(b) originates from the one-electron transitions between the highest occupied valence band at about $-1.2t$ and the second lowest unoccupied band at about $1.1t$, the distance between them being about $2.2t$.

The states near the energy $1.5t$ in Fig. 2(b), which are forbidden in the single molecule, become dipole allowed owing to the intermolecular interactions. However, these states give very small contributions to the spectrum. Therefore, it seems again difficult to explain the magnitude of the observed absorption below 3eV in the solid by means of the simple intermolecular interactions considered here.

SUMMARY

We have developed a theory of optical excitations of C_{60} by using a tight binding model with long-range Coulomb interactions. The parameters, $U \sim 4t$ and $V \sim 2t$, in the Ohno potential turned to be appropriate to describe the absorption spectra. The strength of the bond disorder $t_s \sim 0.1t$ seems reasonable to simulate lattice fluctuation effects. Next, we have demonstrated that the photo-excited states are mainly intramolecular (i.e. Frenkel) excitons with small charge-transfer components. We have also examined how dipole-forbidden transitions of a single C_{60} molecule at low energies become dipole-allowed by solid state effects or lattice fluctuations. Both effects give rise to a theoretical oscillator strength of about one order of magnitude smaller than in experiments for the solid. Combination of the two mechanisms or inclusion of other origins, for example, orientational disorder, may be necessary.

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