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LATTICE RELAXATION STUDY ON SELF-TRAPPED EXCITON AND BIEXCITON IN NEUTRAL AND CHARGED FULLERENES

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Abstract The formation and dynamical properties of D_{5d}-symmetry self-trapped exciton (STE) derived from the electronic $h_u \rightarrow t_{1u}$ parity-forbidden transition of neutral buckyball are studied in the presence of Coulomb interactions using the Bogoliubov-de Gennes formalism. Within the lattice relaxation theory, the multi-mode vibronic structures in the luminescence and absorption spectra related to STEs are elucidated in good agreement with experiments. The STEs arising from the allowed $t_{1u} \rightarrow t_{1g}$ transition of C_{60}^{1-} and C_{60}^{2-} as well as the possibility of forming a self-trapped biexciton (STBE) in C_{60}^{1-} are also considered.

INTRODUCTION

Since its discovery as the third stable form of carbon and a novel prototype for high-temperature superconductivity[1], fullerene family has quickly emerged as one of the most attractive topics in physics and chemistry. Extensive optical and magnetic resonance studies on C_{60} in solutions, matrices and solid films[2–8] have provided very strong evidence for self-trapped excitons (STE) with the following properties: (i) For neutral C_{60} the singlet STE is derived from the dipole forbidden transition[2–5] and is mainly responsible for the photo-absorption (PA) and photo-luminescence (PL). (ii) The vibronic structures have been resolved in solutions[3,4] and in solid films[2,5] which show clearly the importance of the e-ph interactions and lattice relaxation. (iii) As evidenced by the energy transfer[2] as well as photo-luminescence detected ESR (PLDSR) and light induced ESR (LESR) studies[2,6], the lowest excited state is a

triplet with a singlet-triplet splitting $\sim 0.2eV$ which shows the presence of e-e correlations, although not very strong. (iv) The optical and ESR measurements on anions in solutions manifest dynamical Jahn-Teller (JT) distortions in the allowed $t_{1u} - t_{1g}$ transition[7,8]. It is, therefore, interesting to explore whether one can interpret this rich variety of experimental data within a simple formalism, grasping the essential physical features, without resulting to heavy computations. Due to the weakness of the Van der Waals force between molecules the electronic and vibrational properties of solid C_{60} are rather close to those of a single molecule, at least above the spinning transition temperature. In this study we consider the buckyball itself and ignore all possible solid state effects.

MODEL AND ITS GROUND STATE PROPERTY

The SSH Hamiltonian[9], which has grasped the main physics of dynamical symmetry breaking due to 1D Peierls instability and the nonlinearity of excitations in conducting polymers[10], is adopted to describe the Jahn-Teller active 2D buckyball[11]. In order to consider the optical transitions between symmetry broken states and the effect of e-e correlations of C_{60}, a SSH-like Hamiltonian with the Hubbard and nearest-neighbour e-e interactions included can be expressed as[12] $H = H_e + H_{ph} + H_{int}$ with

$$\begin{aligned} H_e = & -\sum_{<i,j>,s} t_0(c^\dagger_{i\,s}c_{j\,s} + h.c.) + U\sum_i n_{i\uparrow}n_{i\downarrow} + V\sum_{<i,j>,s,s'} n_{i\,s}n_{j\,s'} \\ & + \sum_\nu \alpha(< b^\dagger_\nu > + < b_\nu >)F^\nu + \sum_\nu \hbar\omega_\nu < b^\dagger_\nu >< b_\nu > \ , \\ H_{ph} = & \sum_\nu \hbar\omega_\nu[(b^\dagger_\nu - < b^\dagger_\nu >)(b_\nu - < b_\nu >) + \frac{1}{2}] \ , \\ H_{int} = & \sum_\nu (\alpha F^\nu + \hbar\omega_\nu < b_\nu >)(b^\dagger_\nu - < b^\dagger_\nu >) + h.c. \ , \end{aligned} \tag{1}$$

where

$$F^\nu = \frac{\hbar}{\sqrt{2\hbar\omega_\nu M}} \sum_{<i,j>,s} (\vec{\xi}^\nu_i - \vec{\xi}^\nu_j)\cdot \frac{\vec{l}_1(ij)}{l_1(ij)}(c^\dagger_{i\,s}c_{j\,s} + h.c.) \ . \tag{2}$$

Here α is the e-ph coupling constant, $\vec{\xi}^\nu_i$ is the amplitude of normal mode ν in the homogeneous ground state [11], and $\vec{l}_1(ij)/l_1(ij)$ is the unit vector along the unrenormalized bond $< i,j >$. $b^\dagger_\nu$ (b_ν) is the phonon creation (annihilation) operator for mode ν, while $< b^\dagger_\nu >$, $< b_\nu >$ are the order parameters of dynamic symmetry breaking. They represent the phonon equilibrium positions with respect to the unrenormalized origin,

and can be determined self-consistently within the BdeG formalism[10] through the gap equations $\hbar\omega_\nu < b_\nu > = -\alpha < e|F^\nu|e >$, where $|e>$ is the many-electron state found from the corresponding BdeG equations. Here the unrestricted Hartree-Fork approximation has been applied to deal with the e-e interactions in H_e, which will affect the electronic and lattice structures of the ground state and the exciton formation. The set of parameters is chosen as $t_0 = 1.75eV$, $\alpha = 4.75eV/\AA$, $U = 4.0eV$, $V = 0.15eV$. For the homogeneous ground state, the electronic HOMO-LUMO gap is 2.00eV, while the difference of the two kinds of bond lengths is $0.04\AA$, which are compatible with the previous results[11]. It is noted that only the totally symmetric A_g modes can contribute to $< b_\nu >$, *i.e.* only these modes can condense to induce the bond length alternation in the I_h-symmetric ground state of the buckyball.

STE OF NEUTRAL C_{60}

After one electron is photo-excited from HOMO to LUMO via a phonon-assisted process, the JT lattice instability will finally cause the whole system to relax to a stable excited state. According to our calculations using the dynamic evolution method, this final stable excited state is a STE with symmetry breaking from I_h to D_{5d}. The same symmetry breaking of I_h is also found for the electron-doped C_{60}^{-1} [11] since the perturbed electronic states are similar in these two cases. Other symmetry-breaking STEs have also been checked, but only D_{5d} STE is found to be stable. This result is consistent with the PLDMR and LERS evidences[2,6]. Since the e-e interactions have already been included in our consideration, the splitting of the spin-singlet and triplet STE can be calculated within the lowest order configuration interaction approximation[13]. The self-consistently determined wave function of the singlet (triplet) STE is given as $|\Psi_\pm >= \frac{1}{\sqrt{2}}(|\Psi_{\alpha\beta} > \pm|\Psi_{\beta\alpha} >)$, where $|\Psi_{\alpha\beta} >= C^\dagger_{\alpha\uparrow}C^\dagger_{\beta\downarrow}|\mathcal{V} >$, α, β denote the two relaxed singly-occupied states of STE, $|\mathcal{V}>$ represents the rest of the spin-doublet states. This splitting $\Delta\mathcal{E}_{s-t}$ resulting from the correlation of $|\Psi_{\alpha\beta}>$ and $|\Psi_{\beta\alpha}>$ turns out to be 0.20eV. Hence, the energy of the singlet STE is determined to be 1.93eV, while that of the triplet STE is 1.73eV, which is compatible with the experimental observations [3,4]. The order parameters $< b_\nu >$ are calculated for all modes, but non-vanishing values are obtained only for some Raman-active A_g modes and H_g modes. The appearance of H_g modes is due to the symmetry breaking from I_h to D_{5d}. Meanwhile, the Huang-Rhys factors[12], which characterize the difference of lattice relaxations for the ground state and STE, can be determined

through the definition $S_\nu = (< b_\nu >_{\rm STE} - < b_\nu >_g)^2$. It is essential to notice that out of all calculated S_ν, only five S_ν corresponding to the pentagon pinch A_g mode and $H_g(1)$, $H_g(4)$, $H_g(7)$ and $H_g(8)$modes (experimentally 273, 774, 1428 and 1575cm^{-1}) do not vanish, with values 0.24, 1.53, 0.24, 0.13 and 0.55, respectively.

MULTI-PHONON VIBRONIC TRANSITION

The pure electronic transition from HOMO to LUMO is parity forbidden, so the observed sub-gap vibronic structures are attributed to the phonon-assisted STE, and this vibronic transition is assigned to the singlet sector of the lowest STE[2,4]. However, according to our calculation within the Condon approximation, the electronic dipole moment related to the transition from the ground state ^1A_g to the lowest singlet STE $^1T_{2g}$ is unfortunately very small compared with the first parity-allowed transition $^1T_{1u}$, because the lattice relaxation leading to D_{5d} STE is still not enough to break the parity of the electronic states effectively, as illustrated by the small values of the Huang-Rhys factors for the relaxed modes. Thus the optical intensities from higher electronic states should be lent to trigger the actual transition with the assistance of the corresponding phonon process[14]. As the intermediate states are introduced through the first order perturbation of e-ph interactions H_{int} representing the effect of quantum lattice fluctuations on electrons at the equilibrium lattice configuration, the actual optical intensity is effectively provided by the transition from the first-order perturbed mixed state $|e_i n_i>$ to the final state $|e_f n_f>$ in the multi-phonon processes. Thus the optical spectral function of this phonon-assisted transition in the low temperature limit is derived as

$$
\begin{aligned}
I(\hbar\omega) = \sum_{\{n_f^{0\mu}\}} \Big| \sum_\mu [& \boldsymbol{M}_{fi}^{\mu} < n_f^{0\mu}|1> + \boldsymbol{M}_{fi}^{\mu+} \sqrt{n_f^{0\mu}} < (n_f^{0\mu}-1)|0> \\
& + \boldsymbol{M}_{fi}^{\mu-} \sqrt{n_f^{0\mu}+1} < (n_f^{0\mu}+1)|0>] \prod_{\mu'(\neq\mu)} < n_f^{0\mu'}|0> \Big|^2 \delta(\hbar\omega - \mathcal{E}_{STE} \mp \sum_\mu n_f^{0\mu}\hbar\omega_\mu) \\
& + \sum_{\{n_f^{0\mu}\}} \sum_\nu \left| \boldsymbol{M}_{fi}^{\nu} + \boldsymbol{M}_{fi}^{\nu+} \right|^2 \prod_\mu \left| < n_f^{0\mu}|0> \right|^2 \delta(\hbar\omega - \mathcal{E}_{STE} \mp \sum_\mu n_f^{0\mu}\hbar\omega_\mu \mp \hbar\omega_\nu) \quad (3)
\end{aligned}
$$

where

$$
\begin{aligned}
\boldsymbol{M}_{fi}^{l} &= \sum_{s(\neq i)} \frac{< e_s^0|\alpha F^l|e_i^0 >}{\epsilon_i^0 - \epsilon_s^0 + \hbar\omega_l} < e_f^0|\hat{\boldsymbol{r}}|e_s^0 > \ , \\
\boldsymbol{M}_{fi}^{l\pm} &= \sum_{t(\neq f)} \frac{< e_f^0|\alpha F^l|e_t^0 >}{\epsilon_f^0 - \epsilon_t^0 \pm \hbar\omega_l} < e_t^0|\hat{\boldsymbol{r}}|e_i^0 > . \qquad (4)
\end{aligned}
$$

Here $\hat{r}$ is the electronic dipole moment operator treated in the Condon approximation. ϵ_s^0, ϵ_i^0 are the unperturbed electronic energies of the states $|e_s^0>$ and $|e_i^0>$. The unperturbed intermediate states $|e_s^0 n_s^0>$ and $|e_t^0 n_t^0>$ are defined w.r.t. the corresponding phonon vacua of $|e_i^0 n_i^0>$ and $|e_f^0 n_f^0>$, so only single-phonon process can take place. $\mp$ corresponds to absorption or emission, respectively; μ, μ' denote modes with nonvanishing Huang-Rhys factors, while ν denotes other unrelaxed modes. $< n_f^\mu|1 >$ and $< n_f^\mu|0 >$ are the Franck-Condon overlap integrals related to the Huang-Rhys factors S_μ [12].

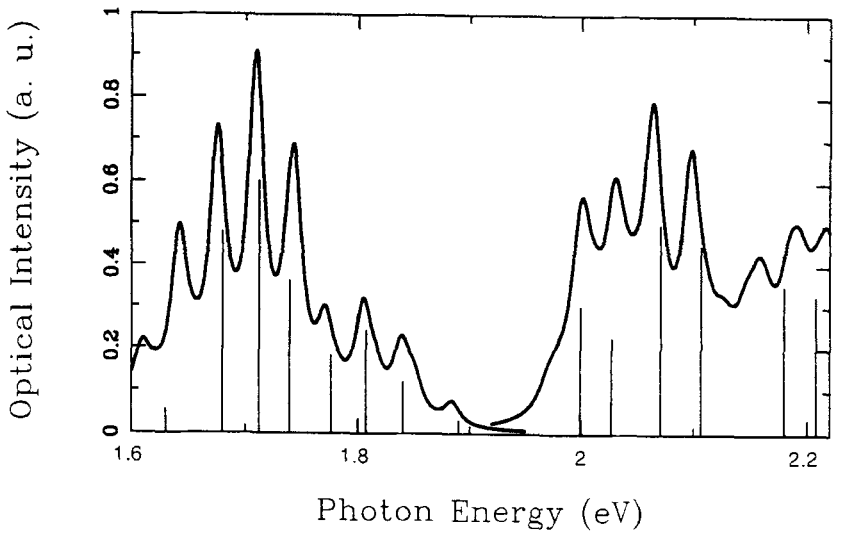

FIGURE 1. The calculated luminescence and absorption spectra due to STE at $T \sim 0K$. The vertical bars indicate the experimental results of Refs. 3 & 4, while the Lorentzian broadening is 0.01eV.

The calculated luminescence and absorption spectra driven by the singlet STE are shown in Fig. 1, where the experimental observed lines of Refs. 3 and 4 are also marked. It is noted that the contribution from the first-term of Eq.(3) to the optical intensity represents the exciton effect by itself, which is found to be about two orders of magnitude smaller than the second term representing the effect of linear vibronic coupling. For luminescence, the one-phonon Stokes shifts mainly originate from IR-active $T_{1u}(4)$, (experimentally $1429cm^{-1}$) and $H_u(1)$, $H_u(4)$ and $H_u(7)$ modes, while

for absorption, the peaks arising from the one-phonon shifts are mainly due to $T_{1u}(3)$, $T_{1u}(4)$ and $H_u(1)$, $H_u(4)$, $H_u(7)$ modes. The calculated vibronic structures consisting of replicas belonging to buckyball pinch mode, and the four JT active H_g mode depicted in Fig. 1 agree very well with the observations by Wang for luminescence[4] and by Whetten *et al.* for absorption[3]. The obtained intensities for luminescence and absorption are lower by about two orders of magnitude than that of parity-allowed ${}^1T_{1u}$ transition which is also consistent with observations. On the other hand, the present result, which is applicable to the gas or solution spectrum (since only a single buckyball is considered), cannot be directly applied to explain the difference between the experiments in solutions and solids. The symmetry properties of the single buckyball would be modified by the solid-state effects, which will suppress some phonon overtones and bring about other types of excitons with different sizes and symmetries as evidenced by PLDMR[6].

STE AND STBE OF CHARGED C_{60}

The dynamic evolution method is also employed to obtain the STE solutions within the BdeG formalism. The optimized stationary configurations of the ground state C_{60}^{1-} and C_{60}^{2-} molecules also possess D_{5d} symmetry[11], while those of the STE states derived from the electronically allowed transition $t_{1u} \rightarrow t_{1g}$ are determined to be of D_{2h} and C_{2h} symmetries, respectively. Taking into account the fact that there are six equivalent D_{5d} STE configurations and fifteen degenerate D_{2h} and C_{2h} STE configurations, the corresponding absorption spectra are obtained without involving additional single-phonon process, as plotted in Fig. 2. It is noted that unlike the neutral C_{60}, the phonon replica in this figure arise from the four JT active H_g modes without contribution of the A_g mode, and the mirror symmetry should be applied to obtain the corresponding emission spectra for this allowed transition. This calculated spectrum for C_{60}^{1-} is compatible with the observations by Kato *etal.*[8]. The 0.11eV blue shift of the 0-0 peak in C_{60}^{2-} with respect to that in C_{60}^{1-}, mainly results from the calculated singlet-triplet splitting 0.17eV present in C_{60}^{2-}. This shift is compatible with the observed value 0.15eV[15]. Compared with the experimental result[8], our absolute value for STE energy is shifted by 0.5eV, which we believe is due to the mean field nature of the BdeG formalism. Interestingly, the STBE of C_{60}^{1-} derived from the electronically allowed $t_{1u} \rightarrow t_{1g}$ and $h_u \rightarrow t_{1g}$ processes can be obtained with the resulting C_{2h} distortions and 0.082eV binding energy. The STBE could be

detected in the two-photon measurements as in the case of semiconductors[16], and would affect the non-linear optical properties of charged fullerene.

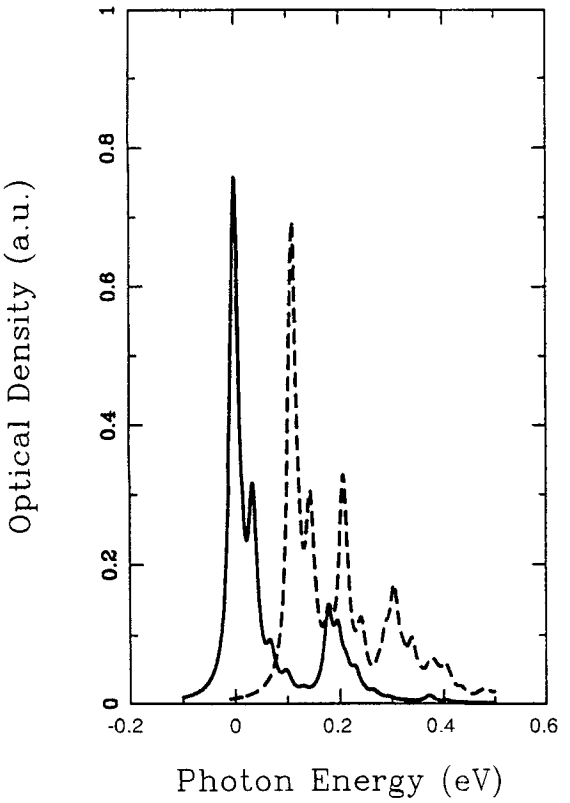

FIGURE 2. The calculated absorption spectrum for charged C_{60}. The solid line represents the result for C_{60}^{1-}, while the dot-dashed line is for C_{60}^{2-}.

SUMMARY

The lattice relaxation approach adopted here allows us to interpret the multi-phonon optical transition as a natural consequence of the dynamical symmetry breaking using the self-consistent BdeG formalism. It can also take into account the effect of quantum lattice fluctuations (*i.e.* H_{int}) on the radiative transition process. Moreover, it predicts the existence of STBE in C_{60}^{1-} to be checked by experiments.

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