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Coulomb interaction and optical absorption in polydiacetylene chains

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The ground- and excited-state properties of polydiacetylene chains are discussed using a model which includes Coulomb interactions. The effects of Coulomb interactions on the optical absorption are analyzed in detail. It has been demonstrated that Coulomb interactions stabilize collective localized excitations in conjugated polymers. Relevant experimental observations in polydiacetylene are compared with theoretical results.

I. INTRODUCTION

Polydiacetylenes (PDA's) are unique in that they are available in the forms of single crystals, solutions, and multilayer films.[1] Using highly ordered single crystals of PDA, one can make detailed studies on the electronic and optical properties of the conjugated π-electron system on the backbone chains. The results of such studies, in turn, serve as a fundamental knowledge for exploring new technological applications of these polymers.[2]

PDA's are conjugated polymers obtained from solid-state polymerization of various diacetylene or butatriene monomers; their conjugated backbone exhibits one of the two mesomeric structures represented by the acetylenic $(=RC\text{—}C\equiv C\text{—}CR=)_n$ and the butatriene $(\text{—}RC=C=C=CR\text{—})_n$ bonding sequences which we shall refer to as the A and B phases, respectively. After obtaining a fairly good understanding of the ground-state properties, researchers have gradually shifted their interest to excited states. Abundant data have been accumulated about the optical properties of diacetylenes. Orenstein *et al.* reported a single sharp peak at 1.4 eV in the photoinduced absorption spectrum.[3] Kanetake *et al.* published the absorption spectra obtained using light irradiation with thermal annealing on vacuum-deposited polydiacetylene (12-8 PDA) film.[4] However, they did not give a detailed theoretical explanation of the relevant experimental results.[5]

In this paper the ground- and excited-state properties of polydiacetylene chains are discussed using a model which includes Coulomb interactions. The optical-absorption spectra of the chains are then calculated numerically using the two-particle Green function; the effects of Coulomb interactions on the optical absorption are analyzed in detail and the comparison with experimental results are made.

II. THE MODEL HAMILTONIAN

The Su-Schrieffer-Heeger (SSH) model has been employed by Cade and Movaghar to investigate polaron states in polydiacetylene,[6] but the interaction between electrons was not included. We use a model which includes a Coulomb interaction on the above Hamiltonian. The total Hamiltonian H is given by

$$
\begin{aligned}
H = {} & \sum_{n,s} \varepsilon a_{n,s}^{\dagger} a_{n,s} - \sum_{n,s} t_{n+1,n}\left(a_{n+1,s}^{\dagger} a_{n,s} + a_{n,s}^{\dagger} a_{n+1,s}\right) + \tfrac{1}{2}\sum_{n} K_{n+1,n}(u_n - u_{n+1})^2 \\
& + \tfrac{1}{2}\sum_{n} M \dot{u}_n^2 + (U/2)\sum_{n,s} a_{n,s}^{\dagger} a_{n,\bar{s}}^{\dagger} a_{n,\bar{s}} a_{n,s} + (V/2)\sum_{n,s,s'} a_{n+1,s}^{\dagger} a_{n+1,s} a_{n,s'}^{\dagger} a_{n,s'} \\
& + (V_1/2)\sum_{n,s,s'} a_{n+2,s}^{\dagger} a_{n+2,s} a_{n,s'}^{\dagger} a_{n,s'} \;, \qquad (1)
\end{aligned}
$$

where the $a_{n,s}^{\dagger}$ are creation operators for electrons of site n with spin s, $K_{n+1,n}$ are the σ-bond spring constant, the u_n are the lattice displacements relative to some σ-bond equilibrium positions, M is the ionic mass, ε is the on-site kinetic energy, U is the Hubbard on-site, opposite-spin interaction, V is the nearest-neighbor Coulomb interaction, and V_1 is the next-nearest-neighbor Coulomb interaction. The nearest-neighbor overlap integrals t_{ij} for C—C bonds are taken to be

$$t_{ij} = \beta \exp(-\alpha l_{ij}) \;, \qquad (2)$$

where l_{ij} is the appropriate C—C bond length. $\alpha = 2.683$ Å^{-1} and $\beta = 111.8$ eV are empirical parameters. The σ-bond lengths and the elastic constants in the absence of the π electrons are $l_0 = 1.275$ Å, $l_1 = 1.363$ Å, $l_2 = 1.402$ Å, and $K_0 = 142.6$ eV Å^{-2}, $K_1 = 94.6$ eV Å^{-2}, and $K_2 = 68.9$ eV Å^{-2}, respectively. In contrast with polycetylene there are two order parameters u and v. In the uniform ground state $u = u_0 = 0.039$ Å and $v = v_0 = 0.024$ Å give a band gap $E_g = 2.4$ eV.

In order to find out the electron-phonon interaction from the above Hamiltonian, we expand ε and $t_{n+1,n}$ to first order in ionic displacement u_n, for instance

$$t_{n+1,n}a^{\dagger}_{n+1,s}a_{n,s} \rightarrow [t^{0}_{n+1,n}+t'_{n+1,n}(u_{n+1,n}-u_{n})]a^{\dagger}_{n+1,s}a_{n,s} , \tag{3}$$

and then quantize the phonon field:[7]

$$u_n=\sum_{q} A \exp(iqj)\epsilon_{\lambda}(q)(b_{-q}+b^{\dagger}_{q}) \tag{4}$$

with $\epsilon_{\lambda}(q)$ the polarization of the phonon field. The terms which correspond to the electron-phonon interaction could be written in the form

$$(N)^{-1/2}(b+b^{\dagger})g_{n,n'}a^{\dagger}_{n,s}a_{n',s'} . \tag{5}$$

It is found that in the mean-field approximation

$$\langle b \rangle = -N^{-1/2}(\hbar\omega)^{-1}g_{n,n'}\rho^{s,s'}_{n,n'} , \tag{6}$$

where

$$\rho^{s,s'}_{n,n'}=\langle a^{\dagger}_{n',s'}a_{n,s} \rangle \delta_{ss'} . \tag{7}$$

In diagonalizing the operator part of the linearized Hamiltonian, the translational invariance can be exploited by introducing Bloch operators

$$a_{ks}=N^{-1/2}\exp(-ikj)a_{js} . \tag{8}$$

The ground state of the system at zero temperature corresponds to filling the lower band and leaving the upper band empty. Defining the static susceptibilities

$$\chi^{s}_{n}=N^{-1}\sum_{k}\cos^{n}(k)(2\chi^{s}_{k})^{-1}\tanh(\beta\chi^{s}_{k}/2) , \tag{9}$$

where $2\chi^{s}_{k}$ is the energy band gap, a self-consistent equation is obtained,

$$\begin{aligned}\varepsilon^{s}_{k}=\varepsilon+(U/2)\sum_{k}\tanh(\beta\chi^{s}_{k}/2)\\ +(V+V_1)\sum_{k}\tanh(\beta\chi^{s}_{k}/2) .\end{aligned} \tag{10}$$

Its values of the electronic densities and expectation value of the Hamiltonian could be calculated using above parameters.

The magnetization M is defined to be the difference in charge densities between up and down spins on each site,

$$M=\rho^{\uparrow\uparrow}_{ijij}-\rho^{\downarrow\downarrow}_{ijij}=(\chi^{\uparrow}-\chi^{\downarrow})/u . \tag{11}$$

The charge polarization Q is the net charge on each site,

$$Q=\rho^{\uparrow\uparrow}_{ijij}-\rho^{\downarrow\downarrow}_{ijij}-1=(\chi^{\uparrow}+\chi^{\downarrow})(-U+4V-4V_1+P^{2}_{3})^{-1} , \tag{12}$$

where $P_3=4\varepsilon'/(M^{1/2}_{c}\Omega)$ corresponds the Fröhlich interaction.

The order parameter Δ describing the bond alternation is the difference in space charge between neighboring sites. The maximum value that any of these order parameters can be taken is 1. In the case of the magnetization and charge polarization this is because there is only one π-electron per site and in the case of the bond alternation it is because of the normalization of the electronic wave function. From now on this will be assumed the spin labels will be dropped from these quantities; that is, mixed ionic and spin-density-wave (SDW) states will not be discussed. In this case,

$$\begin{aligned}\Delta(u)=[(V+P^{2}_{1}-P_0P_1)(t^{0}_{0}-t_0-P_0P_3Q/2)\\ -(V+P^{2}_{0}-P_0P_1)(t^{0}_{1}-t_1+P_1P_3Q/2)]\\ \times[V(V+P^{2}_{0}+P^{2}_{1})]^{-1} ,\end{aligned} \tag{13a}$$

$$\begin{aligned}\Delta(v)=[(V+P^{2}_{2}-P_1P_2)(t^{0}_{1}-t_1-P_1P_3Q/2)\\ -(V+P^{2}_{1}-P_1P_2)(t^{0}_{2}-t_2+P_2P_3Q/2)]\\ \times[V(V+P^{2}_{1}+P^{2}_{2})]^{-1} ,\end{aligned} \tag{13b}$$

where $P_0=4t'_0/(M^{1/2}_{c}\Omega)$, $P_1=4t'_1/(M^{1/2}_{c}\Omega)$, and $P_2=4t'_2/(M^{1/2}_{c}\Omega)$.

Note that the magnetization separates from the bond alternation but the charge polarization couples through the Fröhlich interaction P_3. The displacements of the ions are given by

$$\begin{aligned}u=M^{-1/2}_{c}\Omega^{-1}[P_0(t^{0}_{0}\chi_0+t^{0}_{1}\chi_1)\\ -P_1(t^{0}_{0}\chi_1+t^{0}_{1}\chi_0)-P_3Q] ,\end{aligned} \tag{14a}$$

$$\begin{aligned}v=M^{-1/2}_{c}\Omega^{-1}[P_1(t^{0}_{1}\chi_1+t^{0}_{2}\chi_2)\\ -P_2(t^{0}_{1}\chi_2+t^{0}_{2}\chi_1)-P_3Q] .\end{aligned} \tag{14b}$$

For an initially distorted state, the bond alternation (BA) order parameters $\Delta(u)$ and $\Delta(v)$ are always nonzero and so the lattice always further distorts for a finite electron-phonon interaction.

III. GROUND- AND EXCITED-STATE PROPERTIES

The ground- and excited-state properties of the Hamiltonian described by Eq. (1) depend very much not on the magnitudes but also on the symmetry of the parameters in the Hamiltonian. For polydiacetylene it is distorted because different side groups made neighboring carbon atoms inequivalent. In this case, all of the possible states have a periodic lattice distortion (PLD) associated and there is no spontaneous symmetry breaking because the system is already symmetry broken. The transitions between SDW and BA and between ionic and BA states become second order instead of first. There exists a BA solution for all values of the parameters. The electron-phonon interaction competes with the Hubbard interaction, decreasing the magnetization in the SDW state. The dependence of the magnetization on Hubbard U and on electron-phonon interaction shows that M goes continuously to zero in both cases. The presence of the magnetization stiffens the lattice causing the bond alternation Δ's to decrease. Increasing V and P_0 (or P_1) lowers the energies of the SDW (or BA) state.

In order to determine whether or not these states are stable, the two-particle Green's function $\mathbb{L}$ is calculated. The energies of the collective modes [poles of $\mathbb{L}(\omega)$] are functions of U and P_0.

A phase diagram in the U-V_1 plane is given in Fig. 1. The BA-SDW and BA-ionic transitions are second order but the SDW-ionic transition is still first order. Increas-

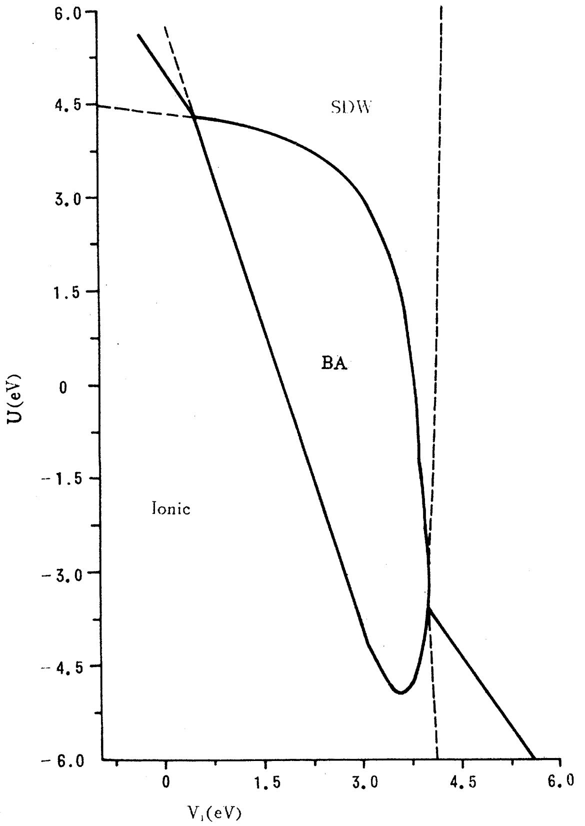

FIG. 1. Phase diagram in the U-V_1 plane. Solid line indicates lines of equal energy, dashed line indicates lines of boundaries of metastable states.

ing the electron-phonon interaction only has the effect of enlarging the BA area.

The SDW and ionic states are still degenerate but the BA is not, there being different solutions for which t_0 is greater than t_1, and vice versa, for a given t_0 and t_1. This opens the way for discussion of the effects of having two nondegenerate minima, as done, for example, by Bishop,[8] who considered solitons in polydiacetylenes. Although there are regions where these two states are minima, the parameters which were used in Fig. 1 make the higher-energy state unstable for all U and V_1. Note that the BA state is never metastable, but that it is unstable when the next nearest-neighbor interaction V_1 is zero for reasonable values of the electron-phonon interaction.

The coupling of the electrons to the phonons renormalizes the phonon energy. Increasing P_0 from 0 to 2 $\mathrm{eV}^{1/2}$ causes the energy of the phonon mode to drop by $\sim 8\%$ in the BA state and less in the SDW state, the presence of a magnetization stiffening the lattice. Note that it would require an extremely large electron-phonon interaction to make this mode go completely soft as Chan and Heine[9] suggest it might. In any case, this treatment would be expected to break down because the ionic displacement becomes so large that the expansion of the electronic kinetic energy to only first order in the displacement is clearly unsatisfactory.[10] This is illustrated in Fig. 2, which shows the ionic displacements u and v as functions of P_0 and P_1 with the mass of the unit cell.

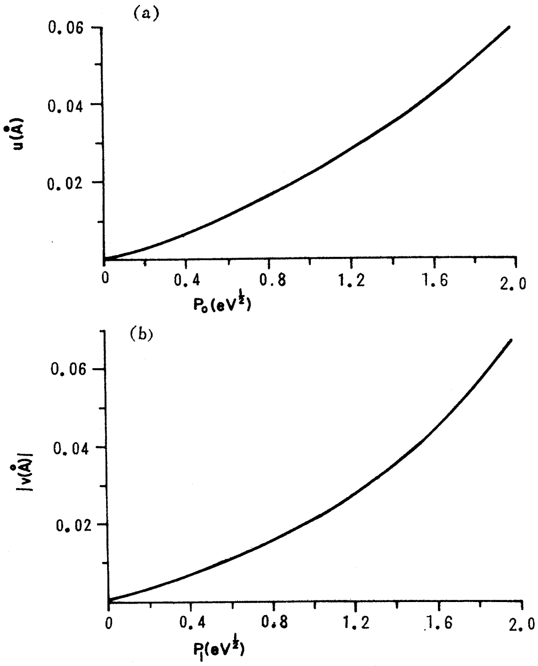

FIG. 2. Dependence of distortion u,v on electron-phonon interactions P_0,P_1 for the bond-alternated state.

IV. THE TWO-ELECTRON GREEN'S FUNCTION AND THE OPTICAL ABSORPTION

Many different solutions of the self-consistent Eq. (10) can be found and, of course, the energies of the corresponding states can be compared with each other to find the lowest energy, but this does not say anything about their stability. In fact, the self-consistent Hartree-Fock approximation only gives solution extrema; they can be maxima, minima, or saddle points. To determine what kind of extremum a solution is, it is necessary to calculate the linear response of the system to an external perturbation. This is equivalent to calculating the two-particle electron Green's function. The derivation of a relationship between the absorption cross section of light by a system and its linear response is a standard one.

The absorption cross section is

$$\sigma_{\mathrm{abs}}(\omega)=4\pi^2e^2/(\omega C)\sum_n |\langle n|j^{\lambda}_{-k}|0\rangle|^2\delta(E_n-E_0-\hbar\omega)\ . \tag{15}$$

In the dipole approximation j_k is replaced by $-i\omega P^{\lambda}$ (Ref. 11), where P^{λ} is the dipole operator:

$$P^{\lambda}_{kk'}=\int \psi^{\dagger}_{k}(\mathbf{r})\left[\mathbf{r}-N^{-1}\sum_j \mathbf{R}_j\right]\psi_{k'}(\mathbf{r})d^3\mathbf{r}\cdot\epsilon_{\lambda}\ , \tag{16}$$

where ϵ_{λ} is the polarization. This approximation is valid for long photon wavelengths and for solids in which the motion of the electrons may be described by a tight-binding approximation. Hence,

$$\sigma_{\text{abs}}(\omega) = -4\pi e^2\omega/C\{\text{Im}[P^{\lambda_1^+}_{k_1k_1'}\mathbb{L}_{k_1k_1'k_2k_2'}(\omega)P^{\lambda_1}_{k_2k_2'}]\}\ , \tag{17}$$

where $\mathbb{L}$ is the two-particle Green's function for the matter system defined by

$$\begin{aligned}\mathbb{L}_{k_ak_a'k_bk_b'}(\omega) &= -(i\hbar)^{-1}\int_{-\infty}^{\infty} dt\,\exp(i\omega t) \\ &\quad\times\langle T[\psi_{k_a}(t)\psi^{\dagger}_{k_a'}(t)\psi^{\dagger}_{k_b}\psi_{k_b'}]\rangle\ .\end{aligned} \tag{18}$$

The matrix $\mathbb{L}$ is given by the Bethe-Salpeter equation

$$\mathbb{L} = L + L\Gamma\mathbb{L}\ , \tag{19}$$

where L is the two-particle Green function for a noninteracting system and the four-point vertex Γ is defined as

$$\Gamma(x,x;y,y) = \pm(i\hbar)^{-1}\delta\Xi(\chi,\chi')[\delta G(y,y')]^{-1}\ , \tag{20}$$

The $+$ and $-$ signs being for bosons and fermions, respectively, and Ξ is the self-energy of the one-particle Green function G.

When $\varphi = \phi + \phi^{\dagger}$ describes a boson field, a boson Green function D could be defined similarly by

$$D(x,x') = (i\hbar)^{-1}\langle T[\tilde{\varphi}(x)\tilde{\varphi}(x')]\rangle\ , \tag{21}$$

where the tilde indicates the Heisenberg representation. It is found that

$$D(x,x') = D_0(x,x') + D_0(x,x_1)g(x_1)\Theta(x_1^-,x_1^+;x')\ , \tag{22}$$

where D_0 is the Boson Green function for the noninteracting system, and Θ is an anomalous Green function coupling the two fields,

$$\Theta(x,y;z) = -(i\hbar)^{-1}\langle T[\tilde{\psi}(x)\tilde{\psi}^{\dagger}(y)\tilde{\varphi}(z)]\rangle\ . \tag{23}$$

By defining the self-energy

$$\Pi(x,y) = g(x)\Theta(x^-,x^+;x_1)D^{-1}(x_1,y) \tag{24}$$

it is seen that

$$D = D_0 + D_0\Pi D \tag{25}$$

and

$$\begin{aligned}D(x,x') &= D_0(x,x') + D_0(x,x_1)g(x_1)\mathbb{L}(x_1^-,x_1^+;x_2^+,x_2^-) \\ &\quad\times g(x_2)D_0(x_2,x')\ .\end{aligned} \tag{26}$$

It is shown that D and $\mathbb{L}$ have similar pole structure.[12] The two-particle fermion Green function contains all the poles of the boson Green function. The boson Green function only contains the poles of $\mathbb{L}$ that are allowed by the symmetry of the interacting g.

Consider an operator $\rho_M^{\dagger}$ which creates a state (or collective mode) of energy E_M and satisfies the condition

$$[H,\rho_M^{\dagger}]|0\rangle = E_M|0\rangle\ , \tag{27}$$

where $|0\rangle$ is assumed to be the ground state.[13] In this representation the two-particle electron Green function in frequency space is given by

$$\begin{aligned}\mathbb{L}_{M'M}(\omega) &= (i\hbar)^{-1}\int_{-\infty}^{\infty} dt\,\exp(i\omega t - \eta|t|\hbar^{-1}) \\ &\quad\times\langle 0|T[\rho_{M'}(t)\rho_M^{+}]0\rangle\ .\end{aligned} \tag{28}$$

Inserting a complete set of states, $\sum_n |n\rangle\langle n|$, and performing the integration on the right-hand side of Eq. (28), it is found that

$$\begin{aligned}\mathbb{L}_{M'M}(\omega) = [&-(\langle 0|\rho_M\rho_M^{\dagger}|0\rangle)(E_M - \hbar\omega - i\eta)^{-1} \\ &-(\langle 0|\rho_{M'}^{\dagger}\rho_{M'}|0\rangle)(E_{M'} - \hbar\omega - i\eta)^{-1}]\delta_{M'M}\ .\end{aligned} \tag{29}$$

$\mathbb{L}$ is diagonal in the representation in which ρ is diagonal and the poles of $\mathbb{L}(\omega)$ give the energies of the collective modes of the system. In the static limit ($\omega \to 0$), Eq. (29) becomes

$$\begin{aligned}\mathbb{L}_{M'M}(0) = -(&\langle 0|\rho_M\rho_M^{\dagger}|0\rangle E_M^{-1} \\ &+\langle 0|\rho_{M'}^{\dagger}\rho_{M'}|0\rangle E_{M'}^{-1})\delta_{M'M}\ .\end{aligned} \tag{30}$$

Hence the eigenvalues of $\mathbb{L}(0)$ must be negative since the quantity in parentheses and the energy of the collective mode E_M must be positive. If it is found that any eigenvalue of $\mathbb{L}$ is positive then there must exist an E_M which is less than zero. This contradicts the assumption that $|0\rangle$ is the ground state since the creation of a collective mode could lower the energy of the system. Hence a positive eigenvalue of $\mathbb{L}$ means that the system is unstable. At the point at which this occurs a collective mode becomes soft (i.e., has zero energy).

In fact, the above argument holds if $|0\rangle$ is not the lowest-energy state but one in which the creation of a single excitation does not lower its energy. That is, $|0\rangle$ need only be a minimum and might be metastable. In principle, then, the stability of a particular state may be investigated by calculating the static two-particle Green function and looking at the signs of its eigenvalues.

In order to calculate $\mathbb{L}$, it is necessary to find L and Γ in some representation such that the integral equation can be converted into a finite-dimensional matrix equation. This can be done, as pointed out by Cade and Young,[14] by choosing a localized site and cell representation in which Γ can be reduced to a 10×10 matrix because of the short-range nature of the interaction in total Hamiltonian. The resulting expressions will be published elsewhere.[15]

The absorption spectra of Langmuir-Blodgett 12-8 PDA films and of a TCDU [R is —$(CH_2)_4OCONHC_6H_5$, see Fig. 3] single crystal are shown in Fig. 4.[16] They consist of the main peak A and the peak A'. The main peak A is located at about 1.95 eV, and associated with the lowest π-π^* exciton. The second peak A' is its vibronic sideband. It is suggested that the form showing the lower-energy absorption band (A) has the acetylene-type ($=RC$—C$\equiv$C—$CR=$) backbone structure (phase A) and the other showing the higher-energy band (B) has the butatriene-type

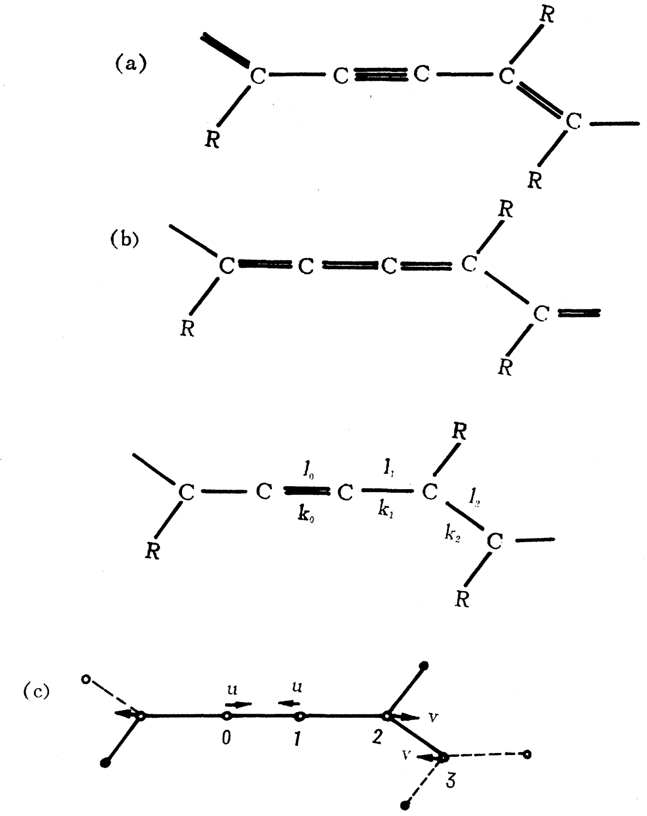

FIG. 3. (a) Schematic structure of polydiacetylene chains: phase *A* and phase *B*. (b) The bonding of the σ-bond skeleton in the absence of π bonds. (c) The two types of distortion considered in obtaining the ground state.

($—RC{=}C{=}C{=}CR—$) backbone structure (phase *B*).

If the species are in the *A* phase initially, after being irradiated by laser or heated, the peak *A* is gradually shifted to higher energy. At temperature higher than about 330 K or through irradiating for 77 min, the *B* and *B'* bands appear on the higher-energy side of the *A* and *A'* bands, being accompanied with color transformation from blue to red. From experimental results, the formation of nearly free *e-h* pairs is supposed to be the first step in this transition. Because of a strong electron-lattice interaction, these *e-h* pairs will be promptly relaxed to a locally deformed state which is in favor of a bond-structure change into the *B* form. For this initially excited species to develop into a stable *B*-form cluster, successive excitations must occur in the neighborhood of the deformed region within its finite lifetime. Otherwise, the metastable excited state returns back to the original *A*-form structure.

In order to discuss the effect of Coulomb interactions on the optical absorption in these states, it is interesting to note that these correlations not only stabilize the bipolaron excitation even in *trans*-polyacetylene, but also increase their absorption strength drastically.[17] The corresponding absorption spectra for different correlation strengths are shown in Fig. 5.

This can be understood by following argument: due to the unpaired occupation of the exciton levels with opposite spin, the correlation acts as an effective *U* term in this case. In consequence, turning on *V* enhances the effect of *U* by decreasing the spatial extent of the exciton. For the bipolaron, on the other hand, the intersite correlation *V* now acts on the full charge density and thus is opposite to the influence of the on-site term *U*; while *U*

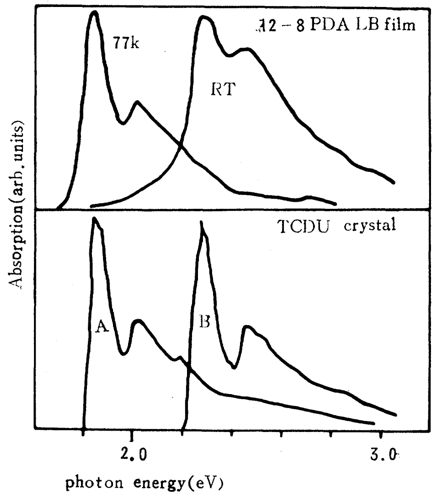

FIG. 4. Comparison between the absorption spectra of Langmuir-Blodgett (LB) 12-8 PDA with $U=0.6$, $V=0.3$, and $V_1=0.1$ (solid line), and of TCDU crystal with the same parameters.

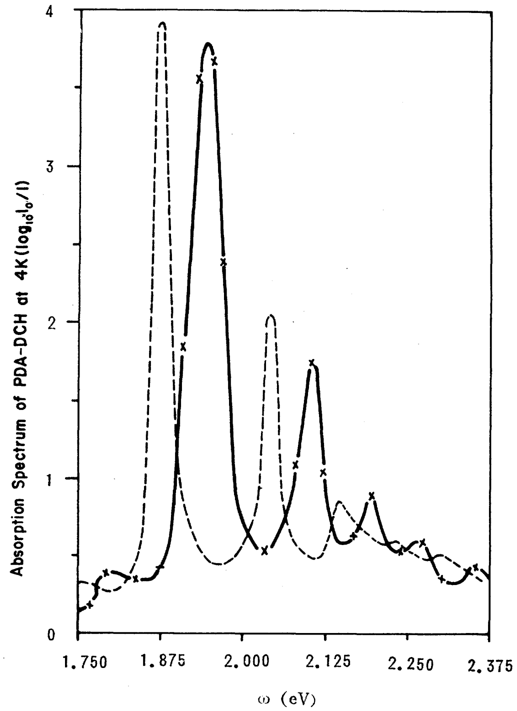

FIG. 5. Optical-absorption spectrum as a function of $\hbar\omega$ for an exciton in PDA-DCH [poly1,6-di(*N*-carbazolyl)-2,4-hexadyne], with $U=0.6$, $V=0.3$, $V_1=0.1$ (solid line), $U=0.2$, $V=0.1$, and $V_1=0$ (dashed line).

decreases this spatial extent of the bipolaron V reverses this effect. The V_1 effect will be discussed in Sec. V.

In conclusion, it has been demonstrated that Coulomb interactions stabilize collective local excitation in conjugated polymers. This manifests itself quite clearly in the characteristics of the absorption spectra as discussed.

V. DISCUSSION

The existence and stability of three types of ground-state and some excited-state properties of the model Hamiltonian (1) have been discussed. Most previous papers considered two states, usually the SDW and ionic states, and their ground state was decided by seeing which is of lower energy without verifying whether this state is a minimum or not.[14] Using values for the parameters which were used in Eq. (1), the SDW state is found to be the ground state, although sometimes the ground state is only slightly favorable to the bond alternation state, which is the usual chemists' picture of a conjugated system. It must also be said that not unreasonable parameters can be chosen which make the ionic state to be the most stable one. The effects of increasing the interaction parameters may be summarized as follows.

(1) The Hubbard on-site repulsion U favors the SDW state and works against the ionic state by making electrons of different spins occupy different sites.

(2) The nearest-neighbor Coulomb interaction V favors the ionic state by lowering the direct term in the Hamiltonian and the BA state by lowering the exchange term.

(3) Increasing the next-nearest-neighbor Coulomb interaction V_1 works against the ionic state because the system acts as decrease the interaction energy due to the repulsion between the charges on next-nearest neighbors.

(4) The effects of electron-phonon interaction P_0, P_1, and P_2 stabilize the bond-alternated state at the expense of the other state.

(5) The Fröhlich on-site electron-phonon interaction P_3 favors the ionic state.

The natures of the instabilities can be explained in terms of the above. The SDW instability is caused by the Hubbard interaction favoring the accumulation of different spins on different sites. Introducing a nearest-neighbor Coulomb repulsion can counteract the on-site term and make it favorable to have different charges on each site.

The bond-alternated state is more complicated to explain and can be produced in two ways; by an electronic instability and by an instability of the lattice, the former usually creating the bigger gap. The electronic instability occurs because it is favorable to have an asymmetry in the overlap integrals in order to minimize the nearest-neighbor exchange interaction. On the other hand, V_1 has to be large enough to counteract, via the direct interaction, the V term, which favors an ionic state. Similarly, U must not be so large (small) that it becomes favorable to form a SDW (ionic) state. The instability of the lattice comes about via the electron-phonon interaction. Expanding the hopping integrals to first order in displacement u, i.e., $J \rightarrow J^0 + uJ'$, the system can distort and make neighboring overlap integrals different, thereby gaining $-uJ'(\rho_{n+1}-\rho_n)$ in energy.

The excited states are mainly excitonic in nature and the singularity in the noninteracting density of states at the conduction-band edge is washed out by interaction. The excitons in the model discussed have an infinite lifetime (i.e., are poles of $\mathbb{L}(\omega)$ on the real ω axis) because within the approximations used, there are no allowed states into which they can decay.

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