

Optical absorption from polarons and bipolarons in a tetrahedrally bonded homopolymer

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The optical absorption associated with polarons and bipolarons in a tetrahedrally bonded homopolymer is studied within the Rice-Phillpot continuum model. Analytical expressions for the absorption coefficients are obtained and compared with those of polyenes. Both the intragap transitions involving the localized and extended states exhibit square-root singularities at their respective absorption edges.

I. INTRODUCTION

The one-electron model of polyenes¹ has been recently extended and successfully applied to describe tetrahedrally bonded homopolymers.² An interesting feature of the latter system is that these polymers can support polaronlike excitations with localized gap states and infrared vibrational characteristics similar to those found in models of conjugated polymers with nondegenerate ground states provided the electron-lattice interaction is not so strong that scission of the polymer occurs. In particular, there is a paramagnetic polaron, a diamagnetic bipolaron, and a charge-neutral polaron excitation, the latter being the relaxed photoexcitation of the polymer.

In recent years, on the other hand, the optical-absorption properties of polaronlike excitations in half-filled-band conducting polymers have been extensively studied both experimentally and theoretically. Particularly, the optical-absorption coefficients for polarons have been obtained³ for degenerate conducting polymers [e.g., *trans*-(CH)_x] within the continuum model⁴ of Takayama, Lin-Liu, and Maki (TLM) and for polarons and bipolarons in nondegenerate polymers [e.g., *cis*-(CH)_x, polythiophene, etc.] within the Brazovskii-Kirova model.⁵ This work was extended to the case of degenerate diatomic polymers⁶ (e.g., polycarbonitrile-tetrathiafulvalene-chloranil, etc.) for the continuum model of Rice and Mele.^{7,8} The role of symmetry and singularities at the absorption edges became clear in the latter work. In this paper we obtain the expressions for the optical-absorption coefficients of polarons and bipolarons in tetrahedrally bonded homopolymers within the continuum model of Rice and Phillpot.² Optical-absorption experiments provide one of the most effective ways to ascertain the existence of polaronlike excitations in a polymer system. Thus, our results furnish important information for such experiments.

Some examples of saturated homopolymers include polysilylenes,⁹ polygermylenes,¹⁰ and a wide class of carbon-based polymers. Moreover, derivatives of the above such as aliphatically substituted silicon,¹¹ e.g., poly(dimethylsilylene) (PDMS), can also be described by the Rice-Phillpot model. These polymers have band gaps in the ultraviolet (uv) region. For instance, for an infinitely long chain of poly(organosilylene) (PS) (Refs. 11

and 12) the observed energy of maximum uv absorption is about 4 eV. Polarons and bipolarons involve localized regions of reduced bond order. The width of the neutral polaron in the uv-sensitive PS is only a few bond lengths¹² and thus provides a mechanism for energy localization in these polymers.

Corresponding to a polaron (or a bipolaron) there are two localized levels symmetrically located about the midgap at $\pm\epsilon_p$. Therefore, in view of the description of the number and location of localized states in the band gap for polarons (bipolarons), we expect six (five) classes of transitions. Charge-conjugation symmetry, however, reduces the number of independent transitions to four (three) for a polaron (bipolaron). These are denoted in Fig. 1 along with the notation. The intragap transition between the two localized levels for a bipolaron is precluded due to the occupancy of these levels (fully occupied for electron bipolarons and empty for hole bipolarons).

The polaron binding energy $\epsilon_B(\nu)$ is seen to vary² as ν^3 , where $\nu=2+\nu_+-\nu_-$ denotes the effective occupation number and ν_+ and ν_- are the occupations of the upper and lower localized levels in the gap, respectively. Therefore, there is a strong tendency for two polarons ($\nu=1$) on the same chain to form a bipolaron ($\nu=2$). Thus, at

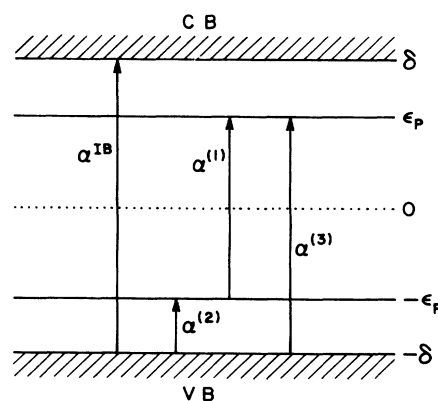


FIG. 1. Nomenclature for possible optical transitions associated with a polaron (bipolaron) in a tetrahedrally bonded homopolymer. Note that $\alpha^{(1)}(\omega)$ is suppressed for a bipolaron.

low doping single polarons are expected to be dominant with two localized electronic levels (at $\pm\varepsilon_p$, $\varepsilon_p < \delta$)¹³ which lead to three distinct intragap ($\omega < 2\delta$) contributions to $\alpha(\omega)$, the optical-absorption coefficient: (1) $\alpha^1(\omega)$, a δ -function transition between the two localized levels occurring at $\omega = 2\varepsilon_p$; (2) $\alpha^2(\omega)$, an absorption which begins at $\omega = \delta - \varepsilon_p$ and involves transitions between the valence band and the $-\varepsilon_p$ level (for hole polarons) or between the $+\varepsilon_p$ level and the conduction band (for electron polarons); and (3) $\alpha^3(\omega)$, an absorption which begins at $\omega = \delta + \varepsilon_p$ and involves transitions between the valence band and the $+\varepsilon_p$ level (or between the $-\varepsilon_p$ level and the conduction band). On the basis of the energy arguments given above, bipolarons are expected to be the dominant excitations at moderate doping. Bipolaron localized levels, ε_B , are closer to midgap compared to the polaron localized levels ($\varepsilon_B < \varepsilon_p$ for the same system parameters). In addition, an interband transition, $\alpha^{IB}(\omega)$, occurs at $\omega = 2\delta$ between the valence and conduction bands.

In Sec. II we briefly review the electron-phonon continuum model of the saturated homopolymers.² Analytic solutions for the polaron as well as the extended states are given. In Sec. III we derive optical-absorption coefficients in the presence of polarons (and bipolarons). The nature of singularities at the absorption edges is discussed and the results are compared with that of both $(A)_x$ - and $(AB)_x$ -type polyenes. Section IV contains a comparison of the continuum model of homopolymers with that of polyenes and establishes a one-to-one relationship between certain parameters of the two systems. This enables us to shed some light on the optical-absorption properties. Finally, in Sec. V we summarize and discuss the polymer systems in which one could experimentally observe the optical absorption and verify our results.

II. SYSTEM DEFINITION

The adiabatic Hamiltonian in the continuum limit for a tetrahedrally bonded homopolymer is given by²

$$H = \int \frac{dx}{a} \Psi^\dagger(x) \left[\left[-\delta + \gamma u(x) - \frac{Va^2}{2} \frac{\partial^2}{\partial x^2} \right] \sigma_1 - iVa\sigma_2 \frac{\partial}{\partial x} \right] \Psi. \quad (1)$$

$\Psi^\dagger = [A^*(x), B^*(x)]$ is a two-component spinor describing the electron. σ_i denote Pauli matrices and a is the lattice constant. $2\delta = 2(V - \Delta)$ is the covalent energy gap where Δ denotes the matrix element between a and b orbitals on the same atomic site and $V = V(r_0)$ is the hopping integral between a and b orbitals on neighboring sites, r_0 being the equilibrium bond length. γ is the first derivative of $V(r)$ with respect to r , evaluated at r_0 . $u(x)$ describes the lattice field such that $\gamma u(x)$ is the potential felt by the electrons as a result of $u(x)$. Variation of (1) with respect to the spinor components yields the one-electron equations

$$\varepsilon_n A_n(x) = \left[-\delta - \frac{Va^2}{2} \frac{\partial^2}{\partial x^2} + \gamma u(x) - Va \frac{\partial}{\partial x} \right] B_n(x), \quad (2a)$$

$$\varepsilon_n B_n(x) = \left[-\delta - \frac{Va^2}{2} \frac{\partial^2}{\partial x^2} + \gamma u(x) + Va \frac{\partial}{\partial x} \right] A_n(x). \quad (2b)$$

Furthermore, the wave functions $A_n(x)$ and $B_n(x)$ must satisfy the self-consistency condition

$$v(x) = \gamma u(x) = -(2\gamma^2/K_0) \sum_n [P_n(x) - P_n^0] v_n, \quad (3a)$$

where $P_n(x)$ is the local bond order

$$P_n(x) = (a/2) [A_n^*(x)B_n(x) + A_n(x)B_n^*(x)] \quad (3b)$$

and v_n is the occupancy of the n th electronic level. K_0 denotes the unscreened force constant. P_n^0 is the bond order in the homogeneous ground state; $v(x)$ is defined so that $u(x) = 0$ for the homogeneous ground-state semiconductor. The wave functions (electron orbital amplitudes) are normalized according to

$$\int dx [|A_n(x)|^2 + |B_n(x)|^2] = 1, \quad (4)$$

where the integral extends over $L = Na$.

The polaron (and bipolaron) solution to Eqs. (2) and (3) is described by the profile²

$$u_p(x \pm x_0) = u_0 \operatorname{sech}^2[(x \pm x_0)/\xi_p], \quad (5a)$$

where

$$u_0 = \gamma a v / 2K_0 \xi_p, \quad v = (2 + v_+ - v_-), \quad (5b)$$

$$\xi_p = 4\Delta K_0 x_0 / \gamma^2 v, \quad x_0 = Va / 2\delta.$$

The corresponding electronic wave functions are found by solving (2) and (3) with $u(x)$ given by (5). Solving these equations one finds² that the spectrum consists of two localized levels at $\pm\varepsilon_p$, where

$$\varepsilon_p^2 = \delta^2(1 - V\Delta a^2/\xi_p^2\delta^2) = \delta^2(1 - \gamma^4 v^2/4V\Delta K_0^2) \quad (6)$$

and continua with $\varepsilon(k) = +\omega(k) = (\delta^2 + \Delta V\delta^2 k^2)^{1/2}$ (conduction band) and $\varepsilon(k) = -\omega(k)$ (valence band) where k denotes the wave vector. The wave function (A_0, B_0) for the electronic levels at $\pm\varepsilon_p$ is

$$A_0^\pm = [1/2(\xi_p)^{1/2}] \operatorname{sech}[(x - x_0)/\xi_p], \quad (7a)$$

$$B_0^\pm = \pm [1/2(\xi_p)^{1/2}] \operatorname{sech}[(x + x_0)/\xi_p]. \quad (7b)$$

For the continua, one has the wave functions

$$A_n^\pm = N_k e^{ikx} \{ (1/\xi_p) \tanh[(x - x_0)/\xi_p] - ik \}, \quad (8a)$$

$$B_n^\pm = \pm N_k e^{ikx} \{ (1/\xi_p) \tanh[(x + x_0)/\xi_p] - ik \} e^{i\chi_n}, \quad (8b)$$

where the phase χ_n ensures that $A_n(x)$ and $B_n(x)$ obey the self-consistency relation (3). The normalization factor is given by

$$N_k = [2L(k^2 + 1/\xi_p^2) - 4/\xi_p]^{-1/2} \quad (9a)$$

and

$$\chi_n = \tan^{-1} \left[\frac{\sqrt{\Delta V} a}{\delta} k \right]. \quad (9b)$$

The wave vectors are obtained from $kL = 2\pi p + \theta_k$, $p = 0, \pm 1, \pm 2, \dots$ and $\theta_k = 2 \tan^{-1}(1/k\xi_p)$ is the phase shift experienced by the extended states near the region of a polaron.

III. OPTICAL ABSORPTION

In this section we evaluate the optical-absorption coefficients. Analytic expressions for the static polaron and bipolaron wave functions given above allow closed-form expressions for these quantities. Within the framework of a linear-response dipole approximation, the optical-absorption coefficient, $\alpha(\omega)$, for the Hamiltonian given in Eq. (1) is

$$\alpha(\omega) = (1/\omega) \sum_{1,2} |\langle \varepsilon_2 | \sigma_2 | \varepsilon_1 \rangle|^2 \delta(\omega - \varepsilon_1 + \varepsilon_2), \quad (10)$$

where the summation extends over all allowed transitions

from eigenstate $|\varepsilon_1\rangle$ to eigenstate $|\varepsilon_2\rangle$ with energies ε_1 and ε_2 , respectively.

With the use of wave functions of Sec. II we perform the relevant spatial integrals (similar to the ones described in Ref. 3) and obtain the following expressions for the matrix elements and the optical-absorption coefficients.

(i) Transition between localized levels. Using (7) in (10) we find the matrix element

$$\langle \varepsilon_1 | \sigma_2 | \varepsilon_2 \rangle = i2x_0/\xi_p \sinh(2x_0/\xi_p), \quad (11)$$

so that in our normalization the absorption coefficient is

$$\alpha^1(\omega) = [4x_0^2/\omega\xi_p^2 \sinh^2(2x_0/\xi_p)] \delta(\omega - 2\varepsilon_p), \quad (12)$$

where the δ -function enforces energy conservation. The integrated intensity is given by

$$\int \alpha^1(\omega) d\omega = 2x_0^2/[\varepsilon_p \xi_p^2 \sinh^2(2x_0/\xi_p)]. \quad (13)$$

(ii) Transitions between the valence band and the lower (upper) localized level. These are equivalent to transitions between the upper (lower) localized level and the conduction band. Using (8) and (9) we have for the matrix element

$$\begin{aligned} \langle \mp \varepsilon_p | \sigma_2 | v \rangle = & \frac{i\pi N_k \operatorname{sech}(\xi_p \pi k / 2)}{2(\xi_p)^{1/2} \tanh(2x_0/\xi_p)} [e^{i(kx_0 + \chi_k)} \pm e^{-ikx_0} \mp \operatorname{sech}(2x_0/\xi_p) (e^{ikx_0} \pm e^{-i(kx_0 - \chi_k)})] \\ & + (i\pi/2) N_k k (\xi_p)^{1/2} \operatorname{sech}(k\xi_p \pi / 2) (e^{i(kx_0 + \chi_k)} \mp e^{-ikx_0}) \end{aligned} \quad (14)$$

and the corresponding absorption coefficient is

$$\begin{aligned} \alpha^i(\omega) = & \frac{\pi \operatorname{sech}^2(\xi_p \pi K_i / 2)}{8\omega \Delta V a^2 K_i [K_i^2 + (1/\xi_p)^2]} \left\{ \frac{1}{\xi_p \tanh^2(2x_0/\xi_p)} \{ \delta [1 + 2 \operatorname{sech}^2(2x_0/\xi_p)] \cos(2K_i x_0) \right. \\ & \left. - a \sqrt{\Delta V} K_i \sin(2K_i x_0) - 4 \operatorname{sech}(2x_0/\xi_p) [\omega(K_i) \cos(2K_i x_0) + \delta] \right\} \\ & + 2K_i^2 \xi_p [\omega(K_i) - \delta \cos(2K_i x_0) + a \sqrt{\Delta V} K_i \sin(2K_i x_0)] \\ & \left. + [4K_i / \tanh(2x_0/\xi_p)] [\delta \sin(2K_i x_0) + a \sqrt{\Delta V} K_i \cos(2K_i x_0)] \right\}, \end{aligned} \quad (15)$$

where

$$\begin{aligned} K_i = & (1/a \sqrt{\Delta V}) [(\omega \pm \varepsilon_p)^2 - \delta^2]^{1/2}, \\ \omega(K_i) = & \omega \pm \varepsilon_p \quad (i=2,3). \end{aligned} \quad (16)$$

Note that Eq. (15) does not diverge at $\omega=0$ since the minimum allowed value of ω is $\delta \pm \varepsilon_p$ for $\alpha^i(\omega)$, $i=2,3$.

If we take the limit $K_i \rightarrow 0$ in Eq. (15) we have

$$\begin{aligned} \alpha^i(\omega) = & \frac{\pi \xi_p}{8\omega \Delta V a^2 K_i \tanh^2(2x_0/\xi_p)} \\ & \times \{ \delta [1 + 2 \operatorname{sech}^2(2x_0/\xi_p)] \\ & - [\delta + (\omega \pm \varepsilon_p)] 4 \operatorname{sech}(2x_0/\xi_p) \}. \end{aligned} \quad (17)$$

It is apparent from Eq. (17) that both $\alpha^2(\omega)$ and $\alpha^3(\omega)$ exhibit square-root singularities at their respective absorp-

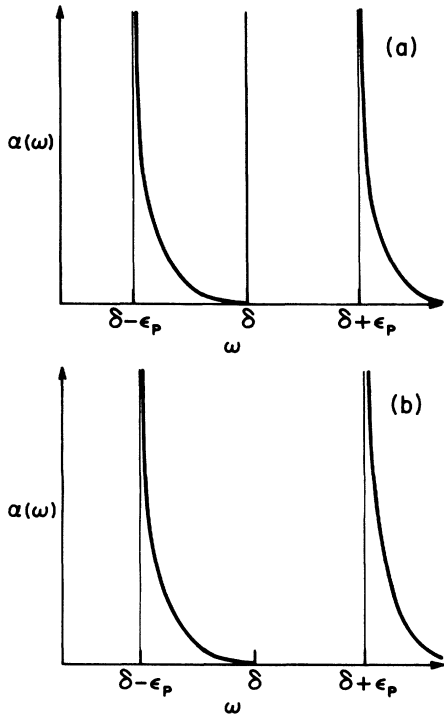


FIG. 2. Schematic diagram depicting optical-absorption spectrum below $\omega=2\delta$ for (a) a polaron and (b) a bipolaron.

tion edges. This behavior is related to the symmetries of the electronic wave functions. In this regard optical absorption from nonlinear excitations in a tetrahedrally bonded homopolymer is similar to that of a degenerate diatomic (AB) polymer⁶ such as tetrathiafulvalene chloranil.¹⁴ The latter system also exhibits square-root singularities in $\alpha^2(\omega)$ and $\alpha^3(\omega)$. However, the homopolymer system differs from both the degenerate, e.g., *trans*-(CH)_x, and nondegenerate, e.g., *cis*-(CH)_x, polyenes, since in the case of polyenes³ $\alpha^2(\omega)$ exhibits a square-root singularity while $\alpha^3(\omega)$ has a square-root vanishing point.¹⁵ This difference can partly be attributed to the linear relationship between the shape (ξ_p) and the width (x_0) of a polaron in homopolymers [see Eq. 5(b)]. For polyenes, however, shape and width of a polaron have a more complicated relationship as discussed in the next section. The optical absorption spectrum for the intragap transitions is shown schematically in Fig. 2.

Apart from the intragap transitions discussed above, an interband optical transition also exists. It is convenient to split the matrix element $\langle k' | \sigma_2 | k \rangle$ into a diagonal and an off-diagonal term where k and k' denote the wave vectors in the valence and conduction bands, respectively. Using (8) and (9) in (10) we obtain analytically the contributions to the optical-absorption coefficient from the diagonal term. To order ξ_p/L we have

$$\alpha_{\text{diag}}^{\text{IB}}(\omega) = \alpha_0^{\text{IB}}(\omega) \left\{ 1 + (\xi_p/L) \left[1 + \xi_p^2(\omega^2 - 4\delta^2)/4V\Delta a^2 \right]^{-1} \left[4 - 8x_0/\varepsilon_p \tanh(2x_0/\xi_p) + 2x_0(\omega^2 - 4\delta^2)/\delta\sqrt{V\Delta a} \right] \right\}, \quad (18)$$

where

$$\alpha_0^{\text{IB}}(\omega) = (2L/\pi)\delta^2/[\omega^2\sqrt{V\Delta a}(\omega^2 - 4\delta^2)^{1/2}] \quad (19)$$

is the interband absorption for the ground-state polymer when there are no excitations present. The corresponding integrated intensity is given by

$$\int_{2\delta}^{\infty} \alpha_{\text{diag}}^{\text{IB}}(\omega) d\omega = \frac{L}{2\pi\sqrt{V\Delta a}} - \frac{4x_0}{\pi\xi_p\delta} + \frac{2\xi_p\sqrt{V\Delta a}\delta^2}{\pi(\delta^2\xi_p^2 - V\Delta a^2)} \left[1 - \frac{2x_0}{\xi_p} \left[\frac{1}{\tanh(2x_0/\xi_p)} - \frac{\sqrt{V\Delta a}}{\xi_p\delta} \right] \right] \\ \times \left\{ \frac{\xi_p^2}{\sqrt{V\Delta a}(\delta^2\xi_p^2 - V\Delta a^2)^{1/2}} \left[\frac{\pi}{2} - \tan^{-1} \left[\frac{\sqrt{V\Delta a}}{(\delta^2\xi_p^2 - V\Delta a^2)^{1/2}} \right] \right] - \frac{1}{\delta^2} \right\}. \quad (20)$$

The off-diagonal contribution defies analytical evaluation and must be obtained numerically. In this regard, the remarks given in Ref. 3 for $\alpha^{\text{IB}}(\omega)$ apply to the present case also.

The absorption coefficients given by (12), (15), and (18) (including the contribution from the off-diagonal interband transition) satisfy the following sum rule:

$$\int \alpha(\omega) d\omega = L/2\pi\sqrt{V\Delta a}. \quad (21)$$

The above equation¹⁶ implies that the total integrated intensity is independent of several system parameters as well as the occupation of localized levels. Furthermore, the sum rule also holds in the presence of an arbitrary

external potential, such as the Coulomb potential caused by charged dopants. In the limiting case $\varepsilon_p \rightarrow \delta$, which corresponds to the ground state, $\int \alpha^{\text{IB}}(\omega) d\omega \rightarrow 0$ and $\int \alpha_{\text{off-diag}}^{\text{IB}}(\omega) d\omega \rightarrow 0$. Thus, with appropriate level occupations at the band edges, (13) and (20) in conjunction with the integrated intensity of (15) evaluated in the above limit can be shown to satisfy the sum rule.

IV. COMPARISON WITH POLYENES

The microscopic electron-phonon model for a tetrahedrally bonded homopolymer² is an extension of the one-electron model for polyenes.¹ Although, as noted

above, both these systems possess polaronlike nonlinear excitations, there are certain intrinsic differences which arise due to the nature of the bonding in the polymer chain. For homopolymers all the bonds are sp^3 hybridized while the polyenes exhibit σ bonding (sp^2 hybrids) in addition to π bonding (p_z). This basic difference affects the nature of the solutions and eventually should be reflected in the optical absorption among other properties.

In what follows we establish a one-to-one correspondence between some of the parameters that appear in the continuum version and characterize the two systems. To this end, we decouple the one-electron equations (2) to obtain the Schrödinger equation for the homopolymer system

$$\left[\epsilon_n^2 - \delta^2 + V\Delta a^2 \frac{d^2}{dx^2} + 2\delta\gamma u(x \mp x_0) \right] \begin{pmatrix} A_n \\ B_n \end{pmatrix} = 0. \quad (22)$$

For polyenes the latter is given by⁴

$$\left[\epsilon_n^2 - \Delta_0^2 + v_F^2 \frac{d^2}{dx^2} + V(x \mp x_0) \right] \begin{pmatrix} f^+ \\ f^- \end{pmatrix} = 0, \quad (23)$$

where the symbols have their usual meaning. A comparison of above two equations directly establishes the relationship among various parameters in the two systems. This is summarized in Table I. Thus, the one-electron equations for the two systems are identical. However, the difference in these polymer systems arises from the somewhat different nature of the self-consistency relations. For polyenes the latter is given by⁴

$$\Delta(x) = -\pi v_F \lambda (i/2) \sum_n (f_n^+ * f_n^- - f_n^- * f_n^+), \quad (24)$$

where the potential $V(x)$ is related to $\Delta(x)$ as

$$V(x) = \Delta^2(x) - \frac{\partial}{\partial x} \Delta(x). \quad (25)$$

Comparison of Eqs. (24) and (25) with Eq. (3) indicates the difference which imposes different conditions on the relation between the shape and width of a polaron (bipolaron). In particular, for polyynes $2\kappa x_0 = \tanh^{-1}(\kappa \xi_p)$ while for homopolymers $2x_0/\xi_p = (\delta a/\Delta)(1/\xi_p)$. There-

TABLE I. Correspondence between the system parameters of a half-filled band polymer (polyene) and a saturated homopolymer.

Parameter	Half-filled-band polymer	Saturated homopolymer
Half-band-gap	Δ_0	$\delta = V - \Delta$
Fermi velocity	v_F	$(V\Delta)^{1/2}a$
Shape parameter	κ	$1/\xi_p$
Characteristic length	ξ	$(V\Delta)^{1/2}a/\delta$

fore, the optical-absorption coefficients are different.

V. CONCLUDING REMARKS

One of the clearest indications of the nonlinear excitations in conducting polymers are their intragap optical absorptions. Thus, one would expect strong intragap absorption features in photoinduced photoabsorption (PA) as well as in optical absorption from doped samples of polysilylenes and related saturated homopolymers. In experiments on lightly doped samples three peaks corresponding to $\alpha^{(1)}(\omega)$, $\alpha^{(2)}(\omega)$, and $\alpha^{(3)}(\omega)$ should be observed [Fig. 2(a)] since polarons are the dominant excitations in this regime. With increasing doping polarons combine to give bipolarons and $\alpha^{(1)}(\omega)$ vanishes. Therefore, in moderately doped samples and in PA only two peaks are expected [Fig. 2(b)]. The integrated intensity of these two peaks is expected to be of the same magnitude. Note that absorption in PA corresponds to the neutral bipolaron. It would be worthwhile to carry out these experiments so as to ascertain the predicted behavior of optical absorption as well as to establish the existence of polaronlike excitations in the present system.

To comment on whether the continuum equations provide an adequate description of the polaron states and the corresponding optical behavior, we note that polarons in the present model involve spatial inhomogeneities in the bond lengths and bond orders. As long as these inhomogeneities vary slowly over microscopic distances of the order of a , the results obtained from the continuum model are qualitatively very similar to those obtained from the discrete model. Indeed, a recent study¹⁷ involving optical absorption in a somewhat similar discrete electron-phonon model of polyynes indicated that the localized excitations of the system are more strongly localized in the discrete model than the continuum version. However, they are qualitatively unchanged and the same holds true for the properties associated with them.

The system Hamiltonian (1) does not take into account the effect of side groups of the polymer chain. For those side groups that do not significantly modify the local sp^3 electron spectrum, our results should qualitatively hold. Which particular side groups affect the optical-absorption requires appropriate extension of (1) as well as absorption experiments.

In summary, we have presented explicit analytic expressions for the intragap optical absorptions associated with polarons and bipolarons in a tetrahedrally bonded homopolymer. In addition, we discussed the nature of singularities in $\alpha^i(\omega)$ at the absorption edges and compared our results with those of $(A)_x$ and $(AB)_x$ polymers. Our results, in conjunction with the absorption experiments, should clarify the role of nonlinear excitations in homopolymers and possibly enhance the understanding of localized defect levels in a wider class of conducting polymers.

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