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Continuum theory for defect vibrations in conjugated polymers

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A microscopic continuum theory for phonons in conjugated polymers is developed and applied to study defect vibrational spectra for solitons and polarons in polyacetylene. The study reveals a new class of bound vibrations localized at these centers which are sensitive to the topology of the defects and can be used to spectroscopically identify photogenerated and doping-induced centers in conjugated polymers.

A striking phenomenon which has been observed in experiments on a number of conjugated polymers is that the production of charged defects either by doping[1,2] or photoexcitation[3,4] induces new, very intense features in the absorption spectra at infrared frequencies. These features are understood to result from vibrations of the polymer which are localized at the defect site and which derive their large oscillator strengths from a very efficient coupling to the excess charge trapped at the center.[5] Theoretical analyses of this phenomenon have focused mainly on $(CH)_x$ as a simple prototypical system; the most successful of these efforts has been the amplitude-mode (AM) formalism[6] which describes these vibrations as elementary excitations of the static distortion of the bond-alternation amplitude induced by the presence of the excess charge. In this model the optically active vibrations are described as linear combinations of the "sliding" modes associated with each of a number of possible structural degrees of freedom which are locally distorted by the excess charge. With only a few parameters the model is able to account successfully for the ir activity in $(CH)_x$ and $(CD)_x$ and even account for subtle differences between the photoinduced and doping-induced spectra. However, this model has also provided a crucial counterintuitive insight about the origin of the defect vibrational spectra, namely, that the ir spectra depend only on the presence of a mobile charged defect which spontaneously breaks the translational symmetry of the chain. The subsequent translations of the various components of the bond-alternation defect and not the specific structure of the defect are responsible for the strong ir response. Thus, for example, solitonlike and polaronlike centers, which are topologically very different objects, are expected to possess an identical infrared response.

In this Rapid Communication we show that there exist observable features in the spectrum of bound vibrations which will allow one to experimentally discriminate between these various bond-alternation defects. We have applied a continuum theory of the coupled electron-phonon system to explore the defect vibrational properties in this system. Our model is not as compact as the AM formulation, though it has the important advantage of introducing a microscopic Hamiltonian for the electronic structure into the lattice dynamics in an accurate and manageable manner. Two very significant results emerge. First, the theory provides a microscopic derivation of the AM formalism, and explains the remarkable appearance of a class of defect vibrations which canot depend on the internal structure of a mobile defect. Second, the model reveals, in addition, a set of heretofore overlooked bound vibrational excitations which depend explicity on the shape of the defects and can thus be used to distinguish between them. These occur outside the space to which the AM formalism has been applied; nevertheless, they are experimentally accessible as we show below, and emerge in a natural manner from the full microscopic theory. In this Rapid Communication we outline our microscopic formulation of this problem, motivate the appearance of a spectrum of bound vibrations with some simple physical arguments, and finally demonstrate their appearance in the defect spectra for solitons and polarons in polyacetylene.

To study the polymer vibrational spectrum, we adopt a Hamiltonian which couples a set of weighted displacement fields $[\Delta_\alpha(x,t)]$ to the density fluctuations of the filled π-electron sea whose eigenfunctions are described by the two-component field $\Psi(x)$:

$$H=\sum_s\int dx\,\Psi_s^\dagger(x,t)\left[-iv_F\frac{\partial}{\partial x}\sigma_3+\Delta(x,t)\sigma_1\right]\Psi_s(x,t)+\sum_\alpha\frac{1}{\pi v_F\lambda_\alpha}\int dx\left[\Delta_\alpha^2(x,t)+\frac{1}{(\omega_\alpha^0)^2}\dot{\Delta}_\alpha^2(x,t)\right]\ , \quad (1)$$

where v_F is the Fermi velocity of the π electrons, λ_α is the coupling strength to the αth displacement field with bare frequency ω_α^0, and the σ's are the Pauli matrices. As in the AM formalism $\sum_\alpha\Delta_\alpha(x,t)=\Delta(x,t)$ and we define $\sum_\alpha\lambda_\alpha=\lambda$. The theory then consists of integrating out the electronic degrees of freedom in (1) for a given set of occupation numbers for the electronic states to obtain a potential from which the equilibrium static displacement field, $\overline{\Delta}_\alpha$ and an equation of motion for small oscillations, $\Delta_\alpha(x,t)-\overline{\Delta}_\alpha(x)=\delta_\alpha(x,t)$, can be obtained. We consider three special cases for the electronic part of (1) which can be easily diagonalized and for which the equilibrium configurations are known. These are (1) a neutral chain with $\overline{\Delta}(x)=\Delta$, with Δ being constant, (2) a charged soliton[7] with $\overline{\Delta}(x)=\Delta\tanh(x/\xi)$, with $\xi=v_F/\Delta$, and (3) a singly charged polaron[8] with

$$\overline{\Delta}(x)=\Delta(1-(1/\sqrt{2})\{\tanh[(x+x_0)/\sqrt{2}\xi]-\tanh[(x-x_0)/\sqrt{2}\xi]\})$$

and $\sinh\sqrt{2}x_0\xi=1$. Perturbation theory yields an integral equation for the components of a multidimensional state vector, $\Phi_{ik}=\{\phi_{\alpha,ik}\}$, describing small amplitude oscillations of the bare displacement fields ($\phi_\alpha=\lambda_\alpha^{-1}\delta_\alpha$):

$$\omega_{ik}^2\phi_{\alpha,ik}(x)=(\omega_\alpha^0)^2\phi_{\alpha,ik}(x)+2\sum_\beta\int dy\, C_{\alpha\beta}(x,y)\phi_{\beta,ik}(y) \quad . \tag{2}$$

Here, i is a band index, k labels the eigenstates within the band, and $C_{\alpha\beta}$ is a nonlocal coupling which arises from the polarization of the electron gas. In the AM formalism explicit evaluation of the nonlocal terms is avoided by clever use of a self-consistency requirement which relates the displacement fields $\delta_\alpha(x,t)$ in a particular mode. This yields "universal" features of the vibrational spectra which are independent of $\Delta_\alpha(x)$. However, Eq. (2) also suggests that $C_{\alpha\beta}$ contains important physics specific to each defect configuration and we have chosen to evaluate it.

To illustrate the important features of the vibrational spectra obtained from (2) for the various defect configurations listed above, it is useful to study the model with a single displacement field.[9] In the absence of electron-phonon coupling we obtain an Einstein spectrum which is shown as the dashed lines in Fig. 1. For the defect free chain (case 1) the nonlocal term distorts the Einstein spectrum, yielding a minimum at $q=0$ with positive quadratic dispersion. For the soliton configuration (case 2) the spectrum of scattered states is identical to case 1 though the eigenfunctions are phase shifted passing through the defect. For the kink, two bound modes are obtained; the lowest of these two at $\omega=0$ is the Goldstone mode, the second describes a width oscillation of the domain wall. The scattered states for the polaron configuration (case 3) again exhibit the same dispersion as those for the ideal chain. For the polaron there are three bound modes in addition to the $\omega=0$ Goldstone mode. The most interesting of these is the mode (A^-), which has the same spatial symmetry as the translational mode and can thus also couple to an external radiation field. Figure 1 demonstrates that a universal feature of these spectra (independent of the defect identity) is the Goldstone mode at $\omega=0$. However, the nonlocal term in Eq. (2) clearly governs the structure of the higher-lying bound modes, yielding a vibrational spectrum which depends explicitly on the topology and shape of the defect. It is striking that the polaron which may be regarded as a bound kink-antikink pair, binds twice as many modes as the soliton; these may be approximately regarded as a linear combination of the bound kink vibrations.[10]

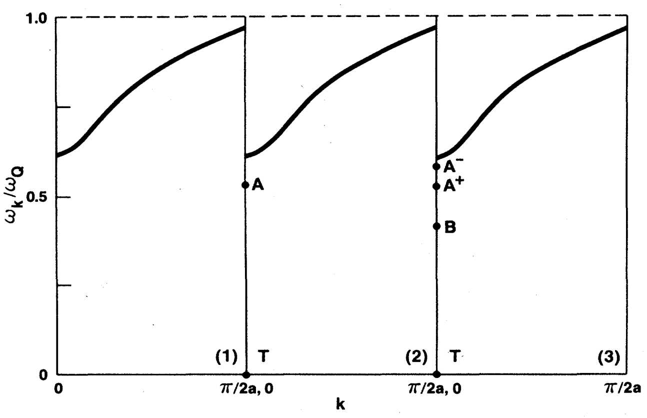

FIG. 1. Vibrational excitations in the one-component theory; case 1: ideal dimerized chain; case 2: charged soliton; case 3: singly charged polaron.

To apply the observations to the practical case of a conjugated polymer like $(\mathrm{CH})_x$, two important questions remain: at what frequencies are the new optically active vibrations analogous to A^- to be found in a realistic model, and how strongly do these couple to the radiation field? To answer these questions we apply the formalism outlined above to the multicomponent model described in Eq. (1). Following previous work[11] we treat three structural degrees of freedom which include intracell longitudinal stretching, transverse stretching, and out of phase H bending. The bare frequencies and coupling constants are listed in Table I. The extension of the one-component results of Fig. 1 to the three-component problem turns out to be unexpectedly straightforward. Since the nonlocal kernel is expressed as $C_{\alpha\beta}(x,y)=g_\alpha\Pi(x,y)g_\beta$, where $\Pi(x,y)$ is the polarization kernel in the one-component problem ($2g_\alpha^2=\pi v_F\lambda_\alpha\omega_\alpha^2$), and $\Pi(x,y)$ can be reconstructed from the one-component solutions as

$$\Pi(x,y)=\sum_k[(\omega_k^2-\omega_Q^2)/2g^2]\Phi_k(x)\Phi_k^*(y) \quad ,$$

where ω_k and ω_Q are the dispersion relation and unscreened Einstein frequency, respectively, for the problem with a single displacement field, it follows that Φ_{ik} can be decomposed as $\Phi_{ik}(x)=(A_{1,ik},A_{2,ik},A_{3,ik})\Phi_k(x)$. With some algebra we then find that the eigenvalues of the three-component problem can be determined from ω_k and ω_Q by solving the following secular equation:

$$D_0(\omega)=\sum_\alpha\frac{\lambda_\alpha}{\lambda}\frac{(\omega_\alpha^0)^2}{\omega_{ik}^2-(\omega_\alpha^0)^2}=-\frac{\omega_Q^2}{\omega_Q^2-\omega_k^2} \quad . \tag{3}$$

Physically, the calculations leading to (3) demonstrate that each solution of the one-component problem generates a trio of solutions of the multicomponent problem with no mixing of the spatial dependence of these states. It follows that for the polaron we expect three bound modes seeded by A^- of Fig. 1. It is worth noting that for the Goldstone mode $\omega_k=0$ for either the polaron or solitons, and that the multicomponent solutions for this class of modes are then identical, which is the central result of the AM formalism. Solutions of Eq. (3) for the full spectrum of bound modes of the one-component problem are listed in Table II.

To emphasize the experimental importance of these results we have also calculated the real part of the infrared conductivity due to the vibrational spectra. We calculate

$$\mathrm{Re}\,\sigma(\omega)=\frac{1}{\omega}\sum_{i,k}|P_{ik}|^2\frac{\pi\delta(\omega-\omega_{ik})}{2\omega_{ik}} \quad , \tag{4}$$

TABLE I. Bare frequencies and coupling constants for the continuum electron-phonon model.

α	ω_α^0 (cm)$^{-1}$	λ_α
1	1234	0.07
2	1309	0.02
3	2040	0.91

TABLE II. Frequencies of bound vibrations of bond-alteration defects in polyacetylene.

	$\alpha=1$	$\alpha=2$	$\alpha=3$
		Soliton	
T_α	0	1279	1354
A_α	965	1289	1412
		Polaron	
T_α	0	1279	1354
B_α	776	1285	1379
A_α^+	965	1289	1412
A_α^-	1040	1291	1440

where the matrix elements P_{lk} are obtained from the projection

$$P_{lk} = \sum_{\alpha} A_{\alpha,lk} \int dx\, \phi_k(x) J_\alpha(x) \quad . \tag{5}$$

Here $J_\alpha(x)$ is a generalized current density which is obtained (in the adiabatic approximation) from the zero-frequency Fourier transform of the correlation function coupling the true current j to the ion displacement field:

$$J_\alpha(x) = \int_{-\infty}^{\infty} i\theta(t)\langle [h_\alpha(x,t), j(0)]\rangle\, dt \quad , \tag{6}$$

with $h_\alpha(x,t) = \partial H/\partial \delta_\alpha(x)$. In Fig. 2 we compare the absorption coefficients, $\alpha = 4\pi\,\mathrm{Re}\sigma/c$, calculated for the charged soliton and polaron. The universal and nonuniversal aspects of the spectra are apparent. The trio of sliding modes (T) are common to the two types of defects and are strongly infrared active. However, in addition to these, the polaron binds a trio of new modes seeded by A^- which are also infrared active. Two of these (A_1^- at 1040 cm^{-1} and A_3^- at 1440 cm^{-1}) have oscillator strengths comparable to the 1279-cm^{-1} sliding mode and should thus be observable at experimentally realized defect densities. The additional modes are unique to the polaron configuration, and thus these features are essential for distinguishing between solitonlike and polaronlike charged defects in $(\mathrm{CH})_x$. We also note that the integrated oscillator strength in the polaron spectrum substantially exceeds that of the soliton spectrum, in agreement with previous work.[6]

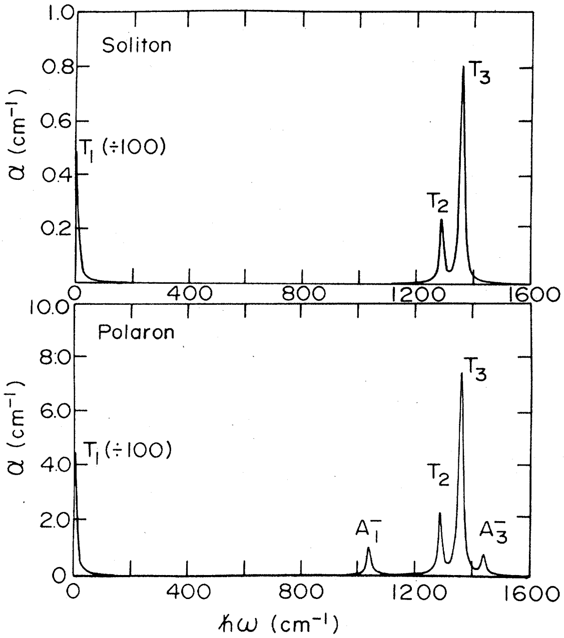

FIG. 2. Defect-induced absorption coefficient for a density $n = 10^{16}$ cm^{-3} of free solitons and polarons in polyacetylene.

To date the cleanest experimental investigations of the defect-induced ir activity in these systems have examined charged defects produced by photoexcitation. The observed photoinduced infrared spectra resemble those plotted of the soliton in Fig. 2 (except for the pinning of the lowest-frequency mode which can be easily imposed on this model) and over the frequency range examined do not possess the extra sharp structure associated with the polaron. This observation provides a clean spectroscopic confirmation that the long-lived photocarriers are trapped at solitonlike centers, a conclusion which to date has hinged on the results of photoinduced ESR studies.[12] A natural, further test of the theory is to devise an experimental situation in which polarons are the preferred charged centers, and search for the extra modes predicted here. A number of useful extensions of the theory also suggest themselves: analysis of the vibrational spectra for polarons and bipolarons in nondegenerate systems, and extension of the theory to a high-density, possibly phase-disordered, soliton lattice to address the elusive question of the presistence of these features through the observed insulator-to-metal transition in $(\mathrm{CH})_x$.

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component theory have been recently reported [for the soliton: H. Ito, A. Terai, Y. Ono, and Y. Wada, J. Phys. Soc. Jpn. **53**, 3520 (1984); J. R. Schrieffer and S. Jeyadev (unpublished); for the polaron: A. Terai, H. Ito, Y. Ono, and Y. Wada, J. Phys. Soc. Jpn. **54**, 196 (1985)]. A third weakly bound mode for the soliton and a fifth for the polaron are obtained in these references. We have noticed that this particular detail of the spectra [i.e., whether the third (fifth) solution of Eq. (2) for the soliton (polaron) is a weakly bound state or a scattering state] is sensitive to the way that the integral over the electronic spectrum in the evaluation of $C_{\alpha\beta}(x,y)$ is carried to the continuum limit. Our scheme sums over the allowed k states on a ring (periodic boundary conditions) of circumference $L=18$ (soliton) or 26 (polaron) coherence lengths (v_F/Δ). This detail of the phonon spectra has no consequences for the absorption spectra since the additional mode has negligible coupling to the current fluctuations described by Eq. (6).

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