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Organic Linear Conductors as Systems for the Study of Electron-Phonon Interactions in the Organic Solid State

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A model calculation shows that each phonon band which couples to the electron density in an organic linear-chain semiconductor effectively develops an infrared activity along the chain axis. The origin of the effect lies in *phase* oscillations of additional charge-density-wave distortions which inevitably arise in the presence of electron-phonon interactions. This suggests that organic linear conductors may constitute unique systems for the study of electron-phonon interactions in the organic solid state.

I have calculated the frequency-dependent conductivity, $\sigma(\omega)$, of an organic linear-chain semiconductor on the basis of a model which attempts to allow for all the possible (i.e., symmetry allowed) conduction-electron-phonon couplings that can be expected to be present in such a semiconductor.[1] The result is remarkable in that it suggests that organic linear conductors, for example, triethyl ammonium tetracyanoquinodimethane [TEA(TCNQ)$_2$], tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ), and related charge-transfer salts,[2] may constitute rather unique systems for the experimental and theoretical study of electron-phonon (e-p) interactions in the organic solid state.

The model is a linear-chain system defined by the Hamiltonian ($\hbar = 1$)

$$H = \sum_k \epsilon_k \theta(\epsilon_B - |\epsilon_k|) a_k{}^\dagger a_k + V(\rho_{q_0} + \rho_{-q_0}) + \sum_n \sum_q [b_n{}^\dagger(q) b_n(q) + \tfrac{1}{2}]\,\omega_n(q) + N^{-1/2} \sum_n \sum_q g_n Q_n(q) \rho_{-q}. \tag{1}$$

The first two terms describe a system of n conduction electrons per unit length with energies $\epsilon_k = (|k| - k_F)v_F$ lying within the range $|\epsilon_k| < \epsilon_B$ (relative to their Fermi energy) moving in a periodic potential V ($|V|/\epsilon_B$ assumed small) of wave vector $q_0 = 2k_F$. They represent a simple model of the semiconductor in the absence of e-p coupling. k_F, v_F, and $a_k{}^\dagger$ denote, respectively, the conduction-electron Fermi wave vector, velocity, and creation operator. The operator $\rho_q = \sum_k a_k{}^\dagger a_{k+q}$ creates an electronic density fluctuation of wave vector q. The fourth term describes a coupling of the conduction electrons to a set of G distinct phonon bands labeled by the index n ($n = 1, 2, \ldots, G$). I do not specify the precise nature of these bands; in general they will be determined by the group symmetry of the underlying molecular and electronic structure. Note, however, that in organic systems many of them will be associated with those *intra*molecular vibrations which induce modulation of the local conduction-electron, molecular-orbital (MO) energy, i.e., with the totally symmetric (a_g) molecular vibrational modes which, in the isolated molecule, are infrared-*non*active.[1] $Q_n(q) = b_n(q) + b_n{}^\dagger(-q)$ denotes the dimensionless normal-mode displacement operator associated with the nth phonon band and g_n denote the symmetry-allowed e-p coupling constants. The third term is the Hamiltonian for the set of G noninteracting phonon bands, the phonon frequencies of the nth band being $\omega_n(q)$. The model (1) purports to describe a linear conducting chain of N chemically similar organic molecules. The potential V may be considered to simulate the effect of a static periodic modulation of the conduction-electron MO energy caused by the external presence of a donor chain structure[2] [e.g., the Cs^+ chain in $Cs_2(TCNQ)_3$ or the TEA chain in $TEA(TCNQ)_2$].

In the absence of e-p coupling the semiconducting state arises from the action of the periodic potential V of inducing the conduction electrons to condense into a charge-density wave (CDW) of wave vector q_0.[3] The expectation value of ρ_q, $\delta\rho_q = \langle \rho_q \rangle$, is nonvanishing for $q = \pm q_0$. The phase of the CDW is fixed by the (fixed) phase of V and the single-electron energy states are $E_k^0 = \mathrm{sgn}(\epsilon_k)(\epsilon_k^2 + V^2)^{1/2}$ The frequency-dependent conductivity, $\sigma_0(\omega)$, is due simply to single-electron transitions between the two sub-bands contained in E_k^0, and may be calculated to be[4] $\sigma_0(\omega) = (ne^2/i\omega m)[f(\omega/2V) - f(0)]$, where $m = k_F/v_F$ is the conduction-electron mass and

$$f(\bar{\omega}) = \{\pi i + \ln[(1-S)/(1+S)]\}/(2S\bar{\omega}^2) \qquad (2)$$

in which $S = (1 - \bar{\omega}^{-2})^{1/2}$, and $f(0) = 1$.

In the presence of e-p coupling, however, the induced CDW must lead to a *periodic distortion of the molecular lattice.* This is evident from the stability condition[1] $\omega_n(q)\,\delta Q_n(q) + (2/\sqrt{N})g_n\,\delta\rho_{-q} = 0$ which is implied by the Hamiltonian (1). Thus $\delta Q_n(q) = \langle Q_n(q) \rangle$ becomes nonvanishing for $q = \pm q_0$ for all n. Consequently, the total periodic potential now becomes $\tilde{\Delta} = V = \sum_n \Delta_n \exp(i\varphi_n)$, where Δ_n and φ_n are, respectively, the amplitude and *phase* (relative to the fixed phase of V) of the distortion-induced potential $(g_n/\sqrt{N})\,\delta Q_n(q_0)$. Clearly, the phase of each distortion component is an open parameter. The induced CDW assumes a corresponding form $\delta\rho_{q_0} = \delta\rho_V + \sum_n \delta\rho_n \exp(i\varphi_n)$ (the components $\delta\rho_i$ may be calculated in terms of the potentials V and Δ_n via linear response theory,[1] if required). The electronic energy states become $E_k = \mathrm{sgn}(\epsilon_k)(\epsilon_k^2 + |\tilde{\Delta}|^2)$ and the stationary equilibrium values of Δ_n and φ_n may be determined by minimizing the total ground-state energy of the arbitrarily distorted semiconductor,

$$N[\mathfrak{N}(0)/2]\textstyle\sum_n(\Delta_n^2/\lambda_n) + \sum_k E_k\theta(k_F - |k|), \qquad (3)$$

with respect to these variables. This yields $\varphi_n = 0$ and $\Delta_n = (\lambda_n/\lambda)(\Delta - V)$ for all n, where

$$1 - V/\Delta = \lambda \ln(2\epsilon_B/|\Delta|) \quad (2\epsilon_B \gg |\Delta|) \qquad (4)$$

determines the stationary value of the total gap parameter $\Delta = V + \sum_n \Delta_n$. In (4) $\lambda = \sum_n \lambda_n$, where $\lambda_n = \mathfrak{N}(0)g_n^2/\omega_n(q_0)$ is the dimensionless e-p coupling parameter with respect to the nth phonon band and $\mathfrak{N}(0)$ is the noninteracting conduction-electron density of states. Note that in the limit $V \to 0$, (4) still yields an energy gap: This corresponds to a Fröhlich CDW state[5,6] in which the gap is due entirely to molecular distortion.

The new single-electron contribution to $\sigma(\omega)$ is given by the previous formula for $\sigma_0(\omega)$ but with V now replaced by Δ. The key point of this paper, however, is that in addition to the latter single-electron contribution, *there will arise collective contributions associated with oscillations in the phases φ_n of the combined lattice and charge distortions about their zero equilibrium values.* Such oscillations involve a bodily displacement of an appropriate component of condensed charge and are therefore optically active along the chain direction. Collective modes associated with oscillations in the amplitudes Δ_n about their stationary values can also arise but in the present model these preserve total dipole moment and consequently do not contribute to $\sigma(\omega)$. The situation closely parallels that found by Lee, Rice, and Anderson[4] for the collective modes of an acoustic-phonon–stabilized Fröhlich CDW state.

The contribution, $\sigma_c(\omega)$, to $\sigma(\omega)$ arising from the phase oscillations is most conveniently calculated via diagramatic techniques.[4,7] A typical contributing diagram is shown in Fig. 1(a) and the sum of these yields $\sigma_c(\omega)$. In Fig. 1(a) the electron lines are matrix propagators with respect to electron states with wave vectors $k + \xi q_0/2$ and $k + \xi' q_0/2$, where ξ and $\xi' = \pm 1$. The phonon lines are matrix propagators with respect to phonon states with wave vectors $q + \xi q_0$ and $q + \xi' q_0$, *and* with respect to the band index n. The Dyson equations for the electron and phonon propagators are shown in Figs. 1(d) and 1(c), respectively. One obtains

$$\sigma_c(\omega) = -(ne^2/i\omega m)(\omega/2\Delta)^2 f(\omega/2\Delta)^2 \lambda D_\varphi(\omega), \qquad (5)$$

where $D_\varphi(\omega)$ is a phononlike propagator for the phase oscillations,[8] given by

$$D_\varphi^{-1}(\omega) = D_0^{-1}(\omega) + 1 - \frac{V}{\Delta} + \frac{\lambda\omega^2}{4\Delta^2} f \frac{\omega}{2\Delta}, \qquad (6)$$

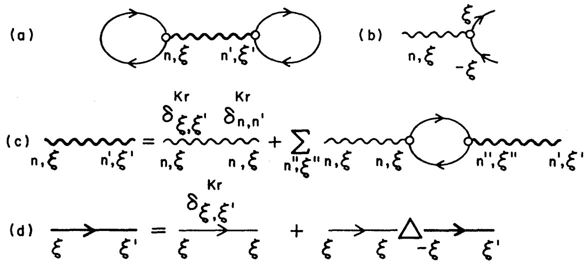

FIG. 1. Diagrams defining the calculation of $\sigma_c(\omega)$. Diagram b shows the electron-phonon vertex.

with

$$D_0(\omega) = -\sum_n \frac{(\lambda_n/\lambda)\omega_n^2(q_0)}{\omega_n^2(q_0) - \omega^2 - i\omega\Gamma_n}, \tag{7}$$

in which Γ_n denote the natural widths of the original noninteracting phonon states. The zeros of $D_\varphi^{-1}(\omega)$ determine the frequencies of the collective phase oscillations. We see from (6) and (7) that there appear a total of G collective modes, one for each e-p coupling constant, and, according to (5), each produces its own absorption band in the infrared. In particular, for $\omega < 2\Delta$, where $f(\omega/2\Delta)$ is real and decay of a collective mode via the excitation of an electron-hole pair is impossible,[7] it follows from (5) and (2) that the real part of the total conductivity $\sigma(\omega) = \sigma_0(\omega) + \sigma_c(\omega)$ is just

$$\mathrm{Re}\sigma(\omega) = (ne^2/\omega m)\lambda(\omega/2\Delta)^2 \times f(\omega/2\Delta)^2 \mathrm{Im} D_\varphi(\omega) \tag{8}$$

which describes a series of absorption bands whose sharpnesses are limited only by the natural widths Γ_n of the original phonon states. The optical oscillator strengths involved here are electronic rather than ionic in nature and significant absorption may be expected even from a collective mode whose primary association is with the presence of a weak e-p coupling constant. Any collective modes which appear above 2Δ become damped via electron-hole-pair excitation, but inspection of (5) reveals that they should give rise to indentations in the continuous single-electron absorption envelope.[9]

A useful phenomenological picture[7] of the collective modes (valid, however, only for $\omega \ll 2\Delta$) may be evolved by conceiving that a certain number, $N_s(n)$, of conduction electrons condense to form the nth component CDW with a total effective inertial mass $N_s(n)m_n^*$. For small phase displacements, $\delta\varphi_n$, the total energy (3) may be expanded as $E = E_0 = \frac{1}{2}\sum_n\sum_{n'}\gamma_{nn'}\delta\varphi_n\delta\varphi_{n'}$, leading to the effective Hamiltonian

$$H_\varphi = \tfrac{1}{2}q_0^{-2}\sum_n N_s(n)m_n^*\delta\dot{\varphi}_n^2 + \tfrac{1}{2}\sum_n\sum_{n'}\gamma_{nn'}\delta\varphi_n\delta\varphi_{n'}$$

for phase motion. The component phase oscillations are evidently coupled to each other, and solution of a $G\times G$ dynamical matrix yields a set of phase normal modes. These correspond to the G collective modes, $D_\varphi^{-1} = 0$, obtained in the microscopic theory. The dipole moment at any instant is $P_\varphi = q_0^{-1}\sum_n N_s(n)e\delta\varphi_n$ and leads to *Reststrahl* absorption at normal mode frequencies.

Note that (5) implies an interesting "optical effect" for those phonon bands which in the absence of e-p coupling are infrared *non*active, e.g., as we have remarked, the symmetric intramolecular vibrational bands. The e-p interaction, in effect, now causes such phonons—renormalized as collective modes—to become infrared active in the chain (parallel) direction. In polarized optical reflectance studies, then, these phonons would be found to be "correctly" absent in the perpendicular direction but "incorrectly" present in the parallel direction. With $V/\Delta \sim 0.1$ and $2\Delta \sim 0.2$ eV assumed to be representative values, use of the model introduced in Ref. 1 for the a_g TCNQ intramolecular e-p interactions to solve $D_\varphi^{-1} = 0$ predicts (for $\omega < 2\Delta$) shifts in the apparent a_g frequencies typically of the order of -10%.

In the limit $\omega \to 0$ the static dielectric constant ϵ_s of the semiconductor may be computed via the relation $\epsilon(\omega) = 1 + (4\pi i/\omega)\sigma(\omega)$ and is found to be

$$\epsilon_s = 1 + (\omega_p/2\Delta)^2[\tfrac{2}{3} + \lambda\Delta/V], \tag{9}$$

where ω_p is the plasma frequency, $\omega_p^2 = 4\pi ne^2/m$. Equation (9) shows that ϵ_s is enhanced over the Penn[10] dielectric constant—the second term in (9)—by a factor $3\lambda\Delta/2V$. Note that for very small V/Δ the semiconducting state corresponds to a weakly pinned but multiphonon-stabilized Fröhlich CDW state. Such a state has been recently suggested to be appropriate for TTF-TCNQ.[1]

The experimental verification of the existence in actual organic linear-chain semiconductors of the infrared-active collective modes predicted in this paper would have important ramifications for solid-state physics in this area. In the first place their observation would provide direct and rather detailed information on the underlying e-p coupling constants; to date there exists no known *definitive* experimental probe for these fundamental interactions. In the second place an opportunity would be presented to test theoretical calculations of the *e-p* coupling constants and, more generally, of the electronic band structure on which the former are in an important way dependent.[11] The present theoretical model is, of course, too simple[12] to render proper justice to this particular aspiration, but it would be possible to reperform this calculation of $\sigma(\omega)$ utilizing a realistic model for the electronic and molecular structure of a particular organic conductor.

The observation in TEA(TCNQ)$_2$ of a series of strong infrared absorption bands polarized exclusively along the chain direction was reported some years ago by Kaplunov, Panova, and Borodko,[13] and by Brau *et al.*[14] and suggested by these authors to be related to intramolecular *e-p* interaction via a mechanism whose nature had yet to be clarified. An analysis of the TEA(TCNQ)$_2$ data in the light of the present theory is currently in progress.[15] The presence of anomalous absorption bands in the far infrared has been very recently reported for TTF-TCNQ by Eldridge.[16]

Inspiration for this work grew, in part, from correspondence with P. Brüesch. Earlier conversations with H. R. Zeller and A. J. Heeger are gratefully acknowledged. I am particularly thankful to L. Pietronero and S. Strässler for a valuable scrutiny of this work. J. B. Torrance, Jr.,[17] has independently stressed the relevance of organic linear-chain conductors to the experimental study of organic intramolecular electron-phonon interactions.

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[8] In terms of the individual phonon propagators $D_{\xi\xi'}{}^{nn'}(q,\omega)$,

$$\lambda D_\varphi(\omega)=\sum_{nn'}(\lambda_n\lambda_{n'})^{1/2}\{D_{\xi\xi}{}^{nn'}(0,\omega)-D_{\xi-\xi}{}^{nn'}(0,\omega)\}.$$

Note that for the special case that q_0 and $-q_0$ are equivalent wave vectors, $D_\varphi(\omega)$ vanishes identically, and $\sigma_c(\omega)=0$ (cf. Ref. 4).

[9] I thank L. Pietronero for a discussion of this point.

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