Infrared and Raman activities of organic linear conductors*

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Phonon spectra of organic linear conductors in the Peierls (semiconducting) phase are considered. It is shown that infrared absorption and Raman scattering can give information on the electron-phonon couplings of the various phonons. A rather sharp structure is predicted also above the electronic gap which is due to interference effects.

Rice[1] has recently provided an analysis of the frequency-dependent conductivity of a one-dimensional electron system below the Peierls transition, simultaneously coupled to several phonon branches. This general formulation leads to a set of amplitude and phase modes,[2] involving coupling between the various vibration modes via their coupling to the electron system.

The consequent effects on the electrical conductivity $\sigma(\omega)$, and the Raman scattering are of considerable experimental interest, as Rice showed for $\sigma(\omega)$ in the regime $\omega < 2\Delta, 2\Delta$ being the electronic gap in the Peierls state. We have also studied this problem, using Rice's model, and find that additional interesting results can be obtained from the conductivity in the region $\omega > 2\Delta$ and from Raman scattering. Specifically, (i) the indentations in the optical absorption which were suggested by Rice are prominent and sharp enough to merit experimental attention. Because of the highly coupled phonon system this effect cannot be analyzed as a set of independent Fano interferences. (ii) We present an analysis of the Raman frequencies, as they follow from the model. Thus, we call to consideration that the differences of the amplitude and phase mode frequencies, $\omega_R^n - \omega_\phi^n$, allow a determination of the electron-phonon coupling constants λ_n without knowing the bare phonon frequencies ω_0^n. ($n = 1, 2, \ldots, G$, is the number of modes.) The frequencies ω_0^n are not known in general, except for propagating intramolecular modes which have a very small dispersion, and ω_0^n may then be approximated by the known single-molecular vibration frequency.

The frequencies of the amplitude modes, ω_R^n, can be determined by Raman scattering,[3] while ω_ϕ^n are determined by absorption intensities.[1,2] As shown by Rice, for $\omega < 2\Delta$ the absorption peaks are expected to be very sharp since the phonon modes are not damped by electron-hole excitations. As we demonstrate now, the structure for $\omega > 2\Delta$ is also rather sharp due to the interference effects.

We assume a pure electron-phonon system, the instability being caused solely by the electron-phonon interaction. The propagator of the nth mode is

$$D_0^n(\omega) = \frac{2\omega_0^n}{\omega^2 - (\omega_0^n)^2 + i\delta}, \quad (\delta = +0), \tag{1}$$

where we assume that the bare phonons have zero width, namely, that any broadening of these phonons will be due to their interaction with the conduction electrons and, indirectly, with the other phonons. The self-energies of the phase and amplitude modes are

$$\Pi_\phi(\omega) = 1/2\lambda + (\omega^2/8\Delta^2) f(\omega), \tag{2}$$

$$\Pi_R(\omega) = 1/2\lambda + (\omega^2/8\Delta^2 - \tfrac{1}{2}) f(\omega), \tag{3}$$

where $\lambda = \sum \lambda_n$, and

$$f(\omega) = \int \frac{2\Delta^2 \tanh(E/2T)}{E[4E^2 - (\omega + i\delta)^2]}, \tag{4}$$

where $E = (\epsilon^2 + \Delta^2)^{1/2}$. The propagator of the nth mode, renormalized by all the phonons via the electron-hole bubble diagram is given by

$$D_{\phi,R}^n(\omega) = D_0^n(\omega)\left(1 - \lambda_n \omega_0^n D_0^n(\omega) \frac{\Pi_{\phi,R}(\omega)}{1 + 2\lambda D_0(\omega)\Pi_{\phi,R}(\omega)}\right), \tag{5}$$

where

$$D_0(\omega) = \sum_{n=1}^{G} \frac{(\lambda_n/\lambda)(\omega_0^n)^2}{\omega^2 - (\omega_0^n)^2 + i\delta}. \tag{6}$$

Equations (2)–(6) may be obtained from Refs. 1 and 4. The eigenfrequencies of the system are the poles of Eq. (5). The lowest phase mode is the Fröhlich mode with frequency $\omega_\phi = 0$, with all the phonon branches contributing to its strength.[5] Assuming that $\sum[\lambda_n/(\omega_0^n)^2] \simeq \lambda_1/(\omega_0^1)^2$, one gets the frequency of the lowest amplitude mode

$$\omega_R^1 \simeq \omega_0^1 \lambda / [\lambda_1 + \lambda(\lambda - \lambda_1)]^{1/2}, \tag{7}$$

Each of higher eigenfrequencies of Eq. (5) is dominated by one of the bare modes. For $\omega < 2\Delta$, $f(\omega)$ is real and the eigenmodes are sharp. As-

suming weak coupling constants and hence small shifts of ω_ϕ^n and ω_R^n with respect to ω_0^n, one finds

$$\omega_R^n - \omega_\phi^n \simeq \tfrac{1}{2}\lambda_n f(\omega_R^n)$$

$$= \tfrac{1}{2}\lambda_n \omega_R^n \left[1 + \frac{(\omega_R^n)^2}{6\Delta^2} + O\left(\frac{\omega_R^n}{2\Delta}\right)^4\right]. \qquad (8)$$

Numerical calculations of the poles of Eq. (5) would yield a more accurate relation between the $\lambda_n - s$ and the shifts $\omega_R^n - \omega_\phi^n$. At frequencies $\omega > 2\Delta$, the eigenmodes are damped by electron-hole excitations and each of them acquires a width of $\Delta\omega \simeq \frac{1}{2}\pi\lambda_n\omega_0^n$. At the same time we obtain, for $\omega \gg 2\Delta$,

$$\omega_R^n - \omega_\phi^n \simeq -2\lambda_n(\Delta^2/\omega_R^n)\ln(\omega_R^n/\Delta), \qquad (9)$$

which is smaller than the width of each of the phonon lines. In Figs. 1 and 2 we show the spectral density of the phase and amplitude modes in systems with two and three phonons, respectively. The lowest mode in each case corresponds to a phonon with $\omega_0^n < 2\Delta$, while the higher modes have $\omega_0^n > 2\Delta$. Note that $\omega_R - \omega_\phi$ has opposite signs below and above 2Δ.

In view of the significant widths of the phonons with $\omega_0^n > 2\Delta$, one would expect the overlapping of phonon lines in this region with the result of smearing out any structure in the reflectivity or conductivity curves. It turns out, however, that the interference between the phonons and the electron-hole excitations produces sharp minima between any two neighboring phonons. This effect is seen in the total conductivity, which is given

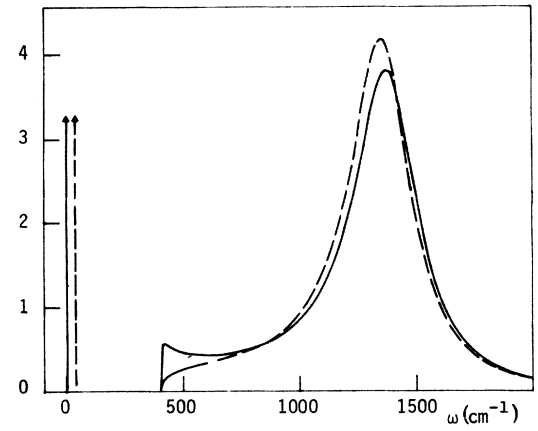

FIG. 1. Spectral representation, $-\omega_0^n \operatorname{Im} D_{\phi,R}^n(\omega)/\pi$ of the phase modes (full line) and the amplitude modes (dashed lines). The system has two phonons: $\omega_0^1 = 60\ \mathrm{cm}^{-1}$, $\lambda_1 = 0.1$; and $\omega_0^2 = 1600\ \mathrm{cm}^{-1}$, $\lambda_2 = 0.1$. The gap is $2\Delta = 400\ \mathrm{cm}^{-1}$ $(T=0)$. The contribution of the phonon ω_0^1 at $\omega > 2\Delta$ is negligible.

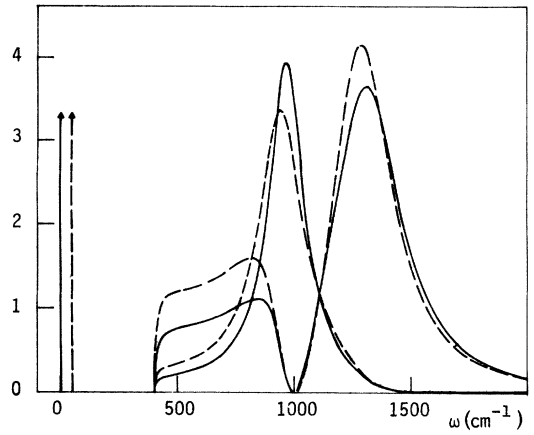

FIG. 2. Same as Fig. 1, except that the system has three phonons: $\omega_0^1 = 60\ \mathrm{cm}^{-1}$, $\lambda_1 = 0.05$; $\omega_0^2 = 1000\ \mathrm{cm}^{-1}$, $\lambda_2 = 0.025$; and $\omega_0^3 = 1600\ \mathrm{cm}^{-1}$, $\lambda_3 = 0.125$. The gap is $2\Delta = 400\ \mathrm{cm}^{-1}$, $(T=0)$. The contribution of the phonon ω_0^1 at $\omega > 2\Delta$ is negligible.

by

$$\sigma(\omega) = \frac{\omega_p^2}{4\pi i\omega}\left(f(\omega)\,\frac{1 + D_0(\omega)}{1 + 2\lambda D_0(\omega)\Pi_\phi(\omega)} - 1\right), \qquad (10)$$

where ω_p is the plasma frequency. Equation (10) is the sum of the single particle σ_0 and the phase mode σ_c contributions and it may be written in this form in view of Eq. (2) and Eqs. (5) and (6) of Ref. 1. The conductivity $\mathrm{Re}\sigma(\omega)$ will have a maximum at each value of ω for which the denominator vanishes. These maxima yield minima of the reflectivity $R(\omega)$. This itself would result in a very broad structure without the possibility to resolve close vibration modes, if not for the fact that between each pair of neighboring modes there exists a solution of the equation $\mathrm{Re}D_0(\omega) = -1$. At these points $\mathrm{Re}\sigma(\omega) = 0$. For $\omega > 2\Delta$, we find $\mathrm{Re}\epsilon(\omega) < 0$, and since $\epsilon(\omega)$ is real when $\mathrm{Re}\sigma(\omega) = 0$, it follows that at these points the reflectivity $R(\omega) = 1$. This peculiar result is due to the fact that $f(\omega)$ is complex for $\omega > 2\Delta$ and $\mathrm{Re}\sigma_c(\omega)$ involves also $\mathrm{Re}D_0(\omega)$, which is strongly oscillating. Similar effects were found in other cases where discrete modes interfere with a continuum. For example, sharp intra-atomic transitions within a continuum of ionization states,[6] or sharp transitions of impurity centers within a continuum of vibrational states.[7] However, our case is different because here the sharp structure is mainly due to the zeros of the numerator of Eq. (10) and not of its denominator. The essential point is that in this case several coupled modes interfere with the electron continuum. If, for example, we had only one such mode, the equation $\mathrm{Re}D_0(\omega) = -1$ would have a solution only at $\omega = 0$ and the picture would be different.

The zeros of $\mathrm{Re}\sigma(\omega)$ will probably be smeared out in a calculation which goes beyond the random-phase approximation and involves phonons with momenta in the neighborhood of $\pm 2k_F$. This will also happen when the broadening of the phonon and electron energies due to sources other than the electron-phonon interaction is taken into account. If such relaxation processes are not too strong and the phonon frequencies are not too close to each other, we still expect pronounced minima of $\mathrm{Re}\sigma(\omega)$ [or maxima of $R(\omega)$] which will help to define the eigenmode frequencies and to determine the coupling constants λ_n.

The general features of $\mathrm{Re}\sigma(\omega)$ and $R(\omega)$ are shown in Fig. 3. The parameters of the full line are chosen so as to reproduce the main characteristics of tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ). At low temperatures, an absorption edge was observed[8,9] at $2\Delta = 300-400$ cm^{-1}, in agreement with the activation energy of the electrical conductivity.[10] Figure 3 shows that the conductivity peak at 1000 cm^{-1}, which was associated with 2Δ, may in principle be due to phonons. This figure only illustrates the effects described above, and it is not an attempt to explain the behavior of TTF-TCNQ. To this end, one probably has to include in the calculation more phonons. It seems that the experimental data available are insufficient to determine the various λ_n's. In particular, Raman scattering experiments in the far-infrared and low-temperature reflectivity measurements above the gap are still missing.

Another, relevant linear charge-transfer salt is triethylammonium tetracyanoquinodimethane[11] [TEA(TCNQ)$_2$]. This material is a semiconductor already at room temperature and it seems that the available data should be sufficient for a more complete analysis.[1,11] The phonon peaks are rather sharp, even for $\omega > 2\Delta$, as predicted above. The renormalized frequencies correspond to dips in the reflectivity (unlike the assignment of Ref. 11). Each peak in the reflectivity is closer to the phonon which is characterized by a weaker coupling constant. This follows from the condition $D_0(\omega) = -1$ for these peaks. From the asymmetry of the maxima in the reflectivity of TEA(TCNQ)$_2$ above the gap,[11] one can draw the qualitative conclusion that phonons with higher frequencies have lower coupling constants λ_n.

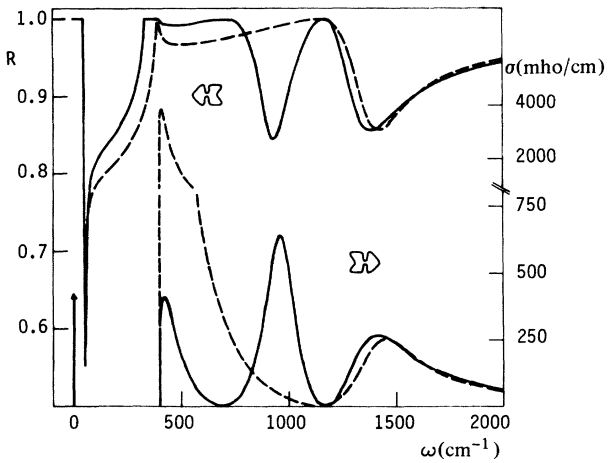

FIG. 3. Real part of the conductivity (the lower curves) and the normal reflectivity (the upper curves) with the parameters of Fig. 2 (full lines) and of Fig. 1 (dashed lines). We used $\omega_p = 7500$ cm^{-1} for the plasma frequency.

We would like to point out that the mechanism described here makes phonons of momentum $2k_F$ in a one-dimensional system observable in optical experiments involving photons of momentum $q = 0$. This was suggested by us previously.[12] One should also mention that electron-phonon interference effects in the optical conductivity of organic conductors were also discussed by Torrance *et al.*[13]

Finally we mention that the couplings λ_n of high-frequency phonons can be detected also by measuring the isotope shift of the Peierls transition temperature.[14] Such measurements although more difficult can yield even more accurate information on the couplings λ_n.

In conclusion, our results complement those presented by Rice, and demonstrate that in his model the structures in infrared activity for $\omega > 2\Delta$ and in Raman scattering can be of considerable experimental interest.

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