

Electron-phonon coupling in the quarter-filled TCNQ salt $\text{NPrQ}(\text{TCNQ})_2$

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The optical conductivity in the high- and low-temperature phases of the semiconducting charge-transfer salt $\text{NPrQ}(\text{TCNQ})_2$ has been analyzed using a one-dimensional twofold-degenerate commensurate charge-density-wave model. The agreement with the model is good in the high-temperature state; it is somewhat poorer at temperatures below the structural phase transition, an indication of the increased complexity of the electronic structure. Above T_c , the semiconducting energy gap is found to have an almost equal contribution from the external cation potential and the intrinsic chain distortion whereas below T_c it is primarily due to the intrinsic chain distortion.

The infrared and optical properties of the “quarter-filled” semiconducting organic charge-transfer salt $\text{N-propylquinolinium}(\text{TCNQ})_2$ were recently reported at temperatures both above and below the 220 K structural phase transition.¹ One of the most prominent features in the optical conductivity of $\text{NPrQ}(\text{TCNQ})_2$, as in most TCNQ charge-transfer salts, is the appearance of the normally infrared-inactive totally symmetric A_g vibrational modes of the TCNQ molecule,²⁻⁴ which become infrared active due to coupling with the charge-transfer process.^{5,6} In the previous study,¹ these infrared features were analyzed within the framework of two isolated-cluster models: the dimer model, with one electron on two sites,⁶ and the tetramer model, with two electrons on four sites.⁷ While the tetramer model was more successful than the dimer model, neither accurately reproduced several important aspects of the infrared spectra, including the overall intensity of the electronic and vibrational features, as well as the line shape of the midinfrared electronic band. The aforementioned fundamental problems are thought to have their origin in (a) the noninteracting “ n -mer” approximation, which is of questionable validity for infinite chains of dimers or tetramers, and (b) the shape of the electronic conductivity spectrum, which for finite width energy bands is not well represented by a Lorentzian line shape.

An alternative description of these systems is to consider the electron wave functions to be extended (rather than localized on noninteracting clusters) along the chains.⁵ The fact that the chains are distorted produces a charge-density wave (CDW), and may introduce gaps in the conductivity spectrum. In cluster models, the A_g modes became optically active by coupling to a charge-transfer band; in the CDW case they become optically active by coupling to the phase oscillations of the CDW (a “phase-phonon” model). A comprehensive theory for the optical properties of one-dimensional molecular systems with twofold-commensurate CDW’s was presented by Bozio *et al.*⁸

The fact that the phase-phonon model has been suc-

cessful in describing the optical properties of quasi-one-dimensional semiconductors, where cluster models fail,⁹ suggests a reexamination of the optical conductivity and the nature of the electron-phonon coupling in $\text{NPrQ}(\text{TCNQ})_2$. Such a study also allows a more detailed examination of the nature and various contributions to the semiconducting energy gap, which have important implications for charge transport. Based upon the spectral similarity between $\text{NPrQ}(\text{TCNQ})_2$ and other quinoid-based TCNQ charge-transfer salts, it is possible to gain insight as to the nature of the transport gap in these materials as well.¹⁰⁻¹⁴ In addition, $\text{NPrQ}(\text{TCNQ})_2$ is a particularly difficult and interesting case for this model; although it is a quasi-one-dimensional, large- U material, $\text{NPrQ}(\text{TCNQ})_2$ has strong TCNQ lattice tetramerization in both the high- and low-temperature phases.^{15,16}

In this paper we present fits of the 300 and 100 K optical conductivities of $\text{NPrQ}(\text{TCNQ})_2$ to a phase-phonon model for one-dimensional systems with twofold-commensurate CDW’s by Bozio *et al.*⁸ The optical conductivity is calculated from the complex dielectric function

$$\tilde{\epsilon}(\omega) = \epsilon_\infty - \frac{4\pi}{NV_m} \left[\chi(\omega) + \sum_\alpha \frac{I_\alpha(\omega) \langle Q_\alpha(\omega) \rangle}{E(\omega)} \right], \quad (1)$$

where $E(\omega)$ is the electric field, V_m is the volume per TCNQ molecule, and N is the number of molecules in the chain. The important terms in Eq. (1) are $\chi(\omega)$, $I_\alpha(\omega)$, and $\langle Q_\alpha(\omega) \rangle$. These are defined in the following way:

$$\chi(\omega) = \sum_k \sum_{n,m} \frac{\hbar^2}{(E_{kn} - E_{km})^2} \frac{f(E_{kn}) - f(E_{km})}{E_{kn} - E_{km} - \hbar\omega - i\hbar\Gamma} \times |j_{nm}(k, 0)|^2 \quad (2)$$

is the dielectric susceptibility for a single-particle excitation across the gap. The energy bands are defined as $E_{kn} = \pm\sqrt{\epsilon_k^2 + |\Delta_k|^2}$, with $\epsilon_k = -2t \cos(kd)$ and

$\Delta_k = \Delta_s + i\Delta_b \sin(kd)$ the gap, with the subscript indicating the nature of the distortion (s for site-centered or b for bond-centered CDW's). The condition $\Delta_s \neq 0$ is associated with an alternating-molecular distortion, which is not observed in $\text{NPrQ}(\text{TCNQ})_2$. The function $f(E_{kn})$ is the Fermi-Dirac distribution for spinless fermions,¹⁷ and $j_{nm}(k, 0)$ are the matrix elements of the current operator for a distorted linear chain.^{8,18} The quantity $\langle Q_\alpha(\omega) \rangle$ is a Fourier transformed generalized coordinate and is defined by the relation

$$\langle Q_\alpha(\omega) \rangle = D_\alpha(\omega) \left[\sum_\beta T_{\alpha\beta}(\omega) \langle Q_\beta(\omega) \rangle + E(\omega) I_\alpha(\omega) \right], \quad (3)$$

where

$$D_\alpha(\omega) = \begin{cases} (1/M)[(\omega + i\gamma_\alpha)^2 - \omega_\alpha^2(q_0)]^{-1} & \text{(external),} \\ (2\omega_\alpha/\hbar)[(\omega + i\gamma_\alpha)^2 - \omega_\alpha^2]^{-1} & \text{(internal),} \end{cases} \quad (4)$$

is the phonon propagator for either an external acoustic mode, where M is the mass of the TCNQ molecule, or one of a number of internal A_g modes, each of which is characterized by an unperturbed frequency ω_α , a linewidth γ_α , and an electron-molecular vibrational (EMV) linear coupling constant g_α . Finally, $T_{\alpha\beta}(\omega)$ and $I_\alpha(\omega)$ may be described in phenomenological terms as a phonon-phonon (self-) interaction and a phonon-amplitude function where α and β index the phonon modes.⁸ The contribution of the cation chains to the total distortion gap is

$$\Delta_b = B_x + \left(\frac{\partial t}{\partial u} \right)_0 u_0, \quad (5)$$

where B_x is the counterion contribution and $(\partial t/\partial u)_0$ is the linear coupling of the electrons to the acoustic mode.⁸ The Peierls (or intrinsic stack distortion) contribution to

the total gap is calculated as $\Delta_b - B_x$. The frequency shifts of the internal modes have been calculated in the usual way.⁸

Using this model, what we calculate are the optical properties due to interband transitions and phase-phonon modes in the $U \rightarrow \infty$ limit for a *half-filled* system of spinless electrons (or holes). This is the appropriate case for $\text{NPrQ}(\text{TCNQ})_2$, a *quarter-filled* system, which, in the limit of large U , has a half-filled lower Hubbard band.

Initial fits agreed well with the data at low frequencies, but gave too large values for the conductivity at high frequencies. This larger oscillator strength can be attributed to the neglect of the upper Hubbard band in the model. To solve this problem, a phenomenological approach was taken where the energy bands were rescaled by introducing an effective bandwidth $t' = \xi t$. Two other parameters in the calculation must also be rescaled: $g'_\alpha = \sqrt{\xi} g_\alpha$ and $\epsilon(\omega) = \xi^{-1} \epsilon'(\omega)$, where ξ is the scaling parameter. A simple model calculation for $\xi = 1$ and $\xi = 2$ is shown in Fig. 1. When applied to $\text{NPrQ}(\text{TCNQ})_2$, the results using $\xi = 2$ are much better than those for $\xi = 1$, suggesting that rescaled energy bands are a better approximation of the band structure for quarter-filled systems.

A comparison of the experimental and the calculated frequency-dependent conductivity for $\text{NPrQ}(\text{TCNQ})_2$ at 300 K is shown in Fig. 2. Model parameters, unperturbed phonon frequencies, and electron-phonon coupling constants are presented in Table I. The description of the EMV coupling as a phase-phonon process improves on the more localized tetramer model approach used earlier¹ for $\text{NPrQ}(\text{TCNQ})_2$. With the exception of the overall level in the far infrared the phonon intensities and asymmetric line shapes are in very good agreement with the experimental spectrum. This is especially noticeable near the band edge, where the difference between the joint density of states for one-dimensional energy bands is quite different from the Lorentzian line shape used in cluster models. Model parameters characterize the high-temperature phase of $\text{NPrQ}(\text{TCNQ})_2$ as a semiconduc-

TABLE I. One-dimensional twofold-commensurate CDW model parameters for a bond-centered CDW fit to the chain axis optical conductivity of $\text{NPrQ}(\text{TCNQ})_2$ at 300 K and 100 K. The structural parameters used in the calculations were $d = 3.26 \text{ \AA}$, $u_0 = 0.08 \text{ \AA}$ and $V_m = 750 \text{ \AA}^3$ at 300 K, and $d = 3.15 \text{ \AA}$, $u_0 = 0.14 \text{ \AA}$ and $V_m = 720 \text{ \AA}^3$ at 100 K; $N = 200$.

	300 K					100 K			
T									
t	2240 cm^{-1}					2340 cm^{-1}			
2Δ	1545 cm^{-1}					2090 cm^{-1}			
Γ	1120 cm^{-1}					285 cm^{-1}			
B_x/Δ	0.56					≈ 0			
A_g mode (TCNQ)	ω_α (cm^{-1})	(δ_α) (cm^{-1})	γ_α (cm^{-1})	g_α (cm^{-1})	ω_α (cm^{-1})	(δ_α) (cm^{-1})	γ_α (cm^{-1})	g_α (cm^{-1})	
ν_2^a	2193	(24)	32	464	2186	(16)	5.6	384	
ν_3^a	1595	(41)	67	603	1599	(13)	1.8	345	
ν_4^a	1345	(29)	33	505	1354	(45)	10	642	
ν_5^a	1160	(43)	52	613	1167	(33)	16	544	
ν_6	957	(1.3)	11	105	961	(3.8)	2.6	186	
ν_7	702	(8.5)	17	266	715	(17)	1.7	391	
ν_8	605	(2.0)	6.7	127	610	(4.1)	2.5	193	
ν_9	305	(14)	24	346	330	(17)	3.6	393	

^aThese modes appear as doublets below T_c .

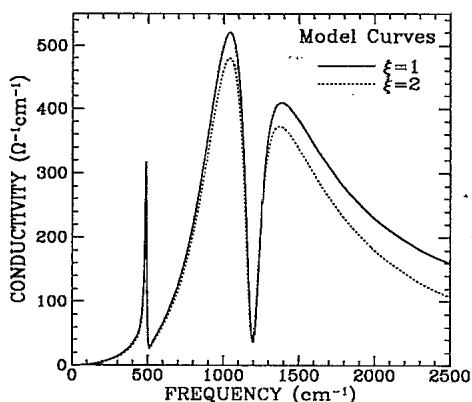


FIG. 1. Model calculations showing the effect of scaling the energy bands; the solid line is for $\xi = 1$, and the dotted line is for $\xi = 2$. The energy band parameters are $t = 1000 \text{ cm}^{-1}$, $2\Delta = 1000 \text{ cm}^{-1}$, and $\Gamma = 300 \text{ cm}^{-1}$. There are two phonons at 500 and 1200 cm^{-1} with widths of 4 cm^{-1} and EMV coupling constants of 200 and 400 cm^{-1} , respectively. Note that the main effect of rescaling is to reduce the midinfrared spectral weight.

tor. The CDW is centered on the "bonds," and commensurate with the TCNQ lattice. If a low-frequency external acoustic mode is included in the calculations at $\omega_e(q_0) = 50 \text{ cm}^{-1}$, it is found that the gap consists of a $\approx 60\%$ Peierls contribution and a $\approx 40\%$ external cation potential contribution.

The calculated unperturbed frequencies and EMV coupling constants agree well with previous estimates for $\text{NPrQ}(\text{TCNQ})_2$,¹ as well as with calculated and phase-phonon model estimates for other TCNQ charge-transfer salts of this type.¹⁹⁻²¹ However, the phonon linewidths above T_c are unusually large, indicative of charge delocalization on the TCNQ stack. The A_g modes appear as singlets, with the exception of the $\nu_4(A_g)$ mode which appears as a very weak doublet at room temperature. The absence of splitting on a larger scale is another indication that despite the tetramerized nature of the system, the charge is not localized in the high-temperature phase.

The result of phase-phonon model fit to the 100 K (well below T_c) frequency-dependent conductivity is shown in

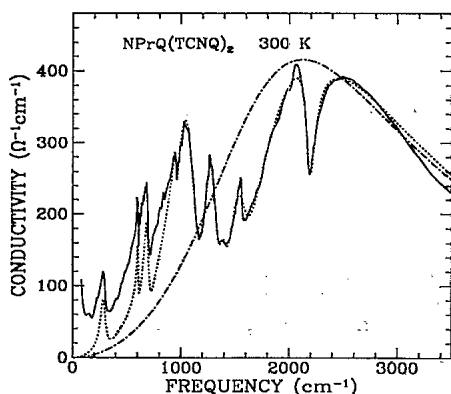


FIG. 2. A fit of the twofold-degenerate CDW model for $\xi = 2$ (double-dashed line) to the optical conductivity of $\text{NPrQ}(\text{TCNQ})_2$ at 300 K (solid line). The dashed line is the bare electronic continuum in the absence of electron-phonon interactions. Parameters are listed in Table I.

Fig. 3. As given in Table I, t and 2Δ have both increased, while the interband damping has decreased significantly. The contribution of the counterion potential to the gap has vanished completely.

Below T_c , the overall quality of fit is somewhat poorer than for the high-temperature phase. This behavior is most notable in three areas: (1) below 1000 cm^{-1} where there is a lot of residual conductivity below the gap, (2) near the extremely broad charge-transfer-like feature at $\approx 1000 \text{ cm}^{-1}$, and (3) above 2200 cm^{-1} where the overall phonon line shapes are not well reproduced in the neighborhood of 2Δ . These features indicate the increased complexity of the electronic structure in the low-temperature phase, and show that there is some charge localization in this phase, which is more nearly tetramerized than the room-temperature phase.

In terms of the vibrational structure,⁹ the unperturbed phonon frequencies are similar (within experimental error) for the two phases. The phonon linewidths, unusually broad at 300 K , are significantly reduced below T_c , indicative of increased order. Several of the EMV coupling constants change appreciably between the high- and low-temperature phases. These large differences are unexpected in light of numerous reports of the relative insensitivity of these parameters to structural phase transitions.^{6,22} The largest changes are related to the appearance of doublet structures in the low-temperature phase, which suggests that the transition to a more tetramerized state may also be accompanied by a subtle realignment of the TCNQ molecules within the chain.

The model parameters of Table I characterize both the high- and low-temperature phases of $\text{NPrQ}(\text{TCNQ})_2$ as a semiconductor. Above T_c , $2\Delta = 1545 \text{ cm}^{-1}$, a value higher than the previous estimate.¹ Below T_c , 2Δ increases to 2090 cm^{-1} , in reasonable agreement with previous spectral and transport estimates of the gap.^{1,23} As expected, the magnitude of the semiconducting gap is significantly larger in the low-temperature phase.

These calculations provide information about the various contributions to the semiconducting gap. Above T_c , we find that the gap contains a 40% contribution from

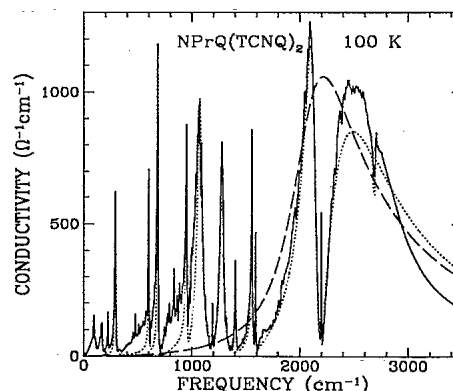


FIG. 3. A fit of the twofold-commensurate CDW model for $\xi = 2$ (double-dashed line) to the optical conductivity of $\text{NPrQ}(\text{TCNQ})_2$ at 100 K (solid line). The dashed line is the bare electronic continuum in the absence of electron-phonon interactions. Parameters are listed in Table I.

the NPrQ cation potential and a 60% contribution from the intrinsic chain (or Peierls) distortion. Below T_c , the gap is dominated by the Peierls contribution. Thus, we find that between the high- and low-temperature phases, the contribution of the counterion potential to the semiconducting gap is significantly reduced.

The question naturally arises as to the changing constituency of the gap through the structural phase transition. Based upon the evidence for a gradual, second-order phase transition in $\text{NPrQ}(\text{TCNQ})_2$,^{1,23,24} it is reasonable to postulate that the Peierls contribution to the transport gap increases gradually (and thus, the counterion potential contribution decreases gradually) with decreasing temperature (between the two limits of 300 K and 100 K that are discussed in this paper). Support for this supposition can be found in the temperature dependence of intensity of the A_g modes as a measure of the size of the Peierls gap.¹¹ Our spectra¹ provide clear evidence for a gradually increasing Peierls contribution to the gap through the phase transition.

Our results also have implications for the understanding of the charge-transport process in the high-temperature phase of $\text{NPrQ}(\text{TCNQ})_2$, which has been described as "weakly metallic."^{23,24} As first suggested by Jánossy *et al.*,²³ a strong counterion potential could influence the interaction between the NPrQ cations and the two lowest orbitals of the TCNQ tetramer causing a significant reduction of their energy splitting or even lead to overlap of these states, resulting in metallic behavior. The effect of the counterion potential,²³ taken together with the strong electronic damping and extremely broad phonon linewidths, provides evidence for such a delocalized electronic state.

Based upon our results for a dominant Peierls gap at 100 K, combined with spectral evidence¹ for a gradually increasing Peierls contribution to below the structural transition, we suggest this unusual phase transition is the result of two simultaneous processes. First, the

counterion contribution to the gap is gradually reduced, and is completely absent at 100 K. Second, the Peierls distortion grows to dominate 2Δ . As discussed above, the reduced cationic interaction is expected to play a significant role in the loss of metallic character and the evolution of a transport gap below T_c .²³ The formation of a gap that is increasingly due to the intrinsic chain distortion results in the increased intensity of the A_g modes in the infrared, a localization of charge (as compared to the high-temperature phase), and a reduction of σ_{dc} . Finally, the increasing Peierls contribution to the gap combined with the simultaneously decreasing counterion contribution may even explain the unusually sharp drop in σ_{dc} through the phase transition.

In conclusion, we have presented an analysis of the optical conductivity of $\text{NPrQ}(\text{TCNQ})_2$ using a one-dimensional twofold-degenerate commensurate charge-density-wave model. Above T_c , the semiconducting energy gap is shown to have two important contributions; below T_c , the Peierls contribution to the gap increases with decreasing temperature and, at 100 K, it is wholly due to the Peierls distortion. Based upon changes in the gap composition with temperature and the proposals of Jánossy *et al.*,²³ it is concluded that the "weakly metallic" nature of the high-temperature phase is the result of the strong cationic interaction with the TCNQ chain. The large electronic damping and broad phonon linewidths confirm the earlier conclusion of charge delocalization above T_c . Below T_c , it can be argued that the simultaneous reduction of the counterion gap contribution and the increase in the Peierls contribution results in the formation of a semiconducting state and the observation of a gap in transport measurements.

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¹ J.L. Musfeldt *et al.*, Phys. Rev. B **45**, 10197 (1992).

² A. Girlando and C. Pecile, Spectrochim. Acta A **29**, 1859 (1975).

³ R. Bozio *et al.*, J. Chem. Soc. Faraday Trans. II **74**, 235 (1978).

⁴ R. Bozio and C. Pecile, in *Spectroscopy of Advanced Materials*, edited by R.J.H. Clark and R.E. Hester (John Wiley, Chichester, 1990).

⁵ M.J. Rice, Phys. Rev. Lett. **37**, 36 (1976).

⁶ M.J. Rice *et al.*, Phys. Rev. B **21**, 3437 (1980).

⁷ V.M. Yartsev, Phys. Status Solidi B **126**, 501 (1984).

⁸ R. Bozio *et al.*, Phys. Rev. B **36**, 7795 (1987).

⁹ C.C. Homes and J.E. Eldridge, Phys. Rev. B **42**, 9522 (1990).

¹⁰ R.P. McCall *et al.*, Mol. Cryst. Liq. Cryst. **120**, 59 (1985); Synth. Met. **11**, 231 (1985).

¹¹ R.P. McCall *et al.*, Phys. Rev. B **39**, 7760 (1989).

¹² E.M. Conwell and I.A. Howard, J. Phys. (Paris) Colloq. **44**, C3-1487 (1983).

¹³ E.M. Conwell and I.A. Howard, Phys. Rev. B **31**, 7835 (1985); Synth. Met. **13**, 71 (1986).

¹⁴ A.J. Epstein and E.M. Conwell, Solid State Commun. **24**, 627 (1977); A.J. Epstein *et al.*, Mol. Cryst. Liq. Cryst. **120**, 43 (1985).

¹⁵ T. Sundaresan and S.C. Wallwork, Acta Crystallogr. B **28**, 1163 (1972).

¹⁶ G. Rindorf *et al.*, Synth. Met. **25**, 189 (1988).

¹⁷ J.F. Kwak and G. Beni, Phys. Rev. B **13**, 652 (1976).

¹⁸ P.F. Maldague, Phys. Rev. B **16**, 2437 (1977).

¹⁹ N.O. Lipari *et al.*, Int. J. Quant. Chem. **11**, 583 (1977).

²⁰ M.J. Rice *et al.*, Solid State Commun. **21**, 757 (1977).

²¹ A. Painelli *et al.*, Solid State Commun. **52**, 801 (1984).

²² V.M. Yartsev and C.S. Jacobsen, Phys. Rev. B **24**, 6167 (1981).

²³ A. Jánossy *et al.*, Mol. Cryst. Liq. Cryst. **85**, 1623 (1982).

²⁴ M. Erő-Gečs *et al.*, Solid State Commun. **32**, 845 (1979).