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Dimerized Organic Linear-Chain Conductors and the Unambiguous Experimental Determination of Electron-Molecular-Vibration Coupling Constants

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We demonstrate that dimerized organic linear-chain conductors afford an unambiguous experimental determination of symmetry-allowed electron-molecular-vibration coupling constant.

The relevance of organic linear-chain conductors to the study of electron-molecular-vibration (E-MV) interactions in the organic solid state has been stressed by a number of authors.¹⁻⁴ The purpose of this Letter is to demonstrate that polarized-infrared (IR) reflectance measurements on the subclass of organic linear-chain conductors which exhibit *dimerization* afford, for the first time in the organic solid state, an *unambiguous* experimental determination of symmetry-allowed E-MV coupling constants. The physical mechanism involved is different from the charge-density-wave phase-oscillation effect previously considered^{3,4} and, unlike the latter mechanism, enables the E-MV coupling constants to be experimentally determined *independently of the details of the actual nature of the electronic states in the crystal*. Moreover, we believe that the accuracy with which the E-MV coupling constants can be determined will be limited only by the accuracy of the experimental reflectance data. These considerations are explicitly verified for the dimerized anion radical salt potassium-tetracyanoquinodimethane⁵ (K-TCNQ) for which the required polarized-IR reflectance data has been recently obtained by Tanner *et al.*⁶

The physical effect we consider is reminiscent of the Ferguson-Matson "charge-oscillation" ef-

fect⁷ known for molecular charge-transfer (C-T) complexes. In the present case the mixing of the unpaired electrons of pairs of molecular ion radicals plays the role of a potential C-T complex. Consequently, the molecular vibrations which couple to the unpaired electrons drive long-wavelength *plasmalike electron oscillations in the range of molecular frequencies*, polarized in the direction of the linear chains. That an effect of this kind would be necessary to account for breakdown of vibrational selection rules in ion-radical salts has been stressed by Anderson and Devlin.⁸

We consider a molecular crystal whose salient structure is that of a system of parallel linear stacks of planar ion-radical dimers and whose electronic and vibrational excitations are described by the Hamiltonian ($\hbar = 1$)

$$H = \sum_{j,\lambda} E_0 n_{j,\lambda} + V + \sum_{j,\lambda,\alpha} \omega_\alpha (b_{j,\lambda,\alpha} \dagger b_{j,\lambda,\alpha} + \frac{1}{2}) + \sum_{j,\lambda,\alpha} n_{j,\lambda} g_\alpha Q_{j,\lambda,\alpha}. \quad (1)$$

The subscript j denotes the crystallographic position, \vec{R}_j , of the j th dimer and $\lambda = 1, 2$ the subpositions of the two member molecular ions comprising the j th dimer. In the absence of vibronic coupling the exact crystalline electronic states of the unpaired electrons originating from the

molecular ions are described by the first two terms, H_e , of H , in the representation of the unpaired-electron molecular-orbital (MO) states of the isolated ions. The latter are assumed nondegenerate. $n_{j,\lambda}$ denotes the occupation operator for the MO state of energy E_0 at the (j, λ) ion site. The exact interaction operator V , peculiar to the crystalline state, is arbitrary: Among other things, it will lead to states describing intradimer and interdimer C-T excitations in the chain direction z . The complex frequency-dependent conductivity associated with such excitations will be given by $\sigma_{zz}(\omega) = (\omega/i)(N_d e^2 a^2/4)\chi(\omega)$ where, from (zero-temperature) linear response theory,

$$\chi(\omega) = \sum_{\beta} |\langle \beta | \delta n | 0 \rangle|^2 2\omega_{\beta 0} / [\omega_{\beta 0}^2 - (\omega + i\delta)^2] \quad (2)$$

is the reduced C-T electronic polarizability in which $\delta n = N^{-1} \sum_j (n_{j,1} - n_{j,2})$, $\omega_{\beta 0} = E_{\beta} - E_0$, and $|\beta\rangle$ and E_{β} are the exact eigenstates and eigenvalues of H_e . $\beta=0$ labels the ground state. N denotes the total number of dimers and N_d the number of dimers per unit volume. In view of the Coulomb repulsion which the unpaired electrons will be obliged to overcome, the characteristic C-T excitation frequencies $\omega_{\beta 0}$ may be anticipated to be of the order of an electron volt.⁹

The third and fourth terms of H describe, respectively, the symmetric (a_g) internal vibrations of the molecular ions and their linear, symmetry-allowed,^{10,11} coupling to the unpaired MO states. $Q_{j,\lambda,\alpha} = b_{j,\lambda,\alpha} + b_{j,\lambda,\alpha}^{\dagger}$ denotes the dimensionless normal-mode displacement operator of the symmetric vibrational mode α ($\alpha=1, 2, \dots, G$) of the (j, λ) ion, where $b_{j,\lambda,\alpha}^{\dagger}$ is the usual vibrational creation operator. The quantities g_{α} denote the G symmetry-allowed E-MV coupling constants. The vibrational frequencies are denoted by ω_{α} . It will be convenient to introduce the normal-mode operators for the j th dimer: $(q_{j,\alpha}, s_{j,\alpha}) = 2^{-1/2}(Q_{j,1,\alpha} \mp Q_{j,2,\alpha})$. According to (1) their equations of motion are

$$\ddot{q}_{j,\alpha} + \omega_{\alpha}^2 q_{j,\alpha} = -\sqrt{2} g_{\alpha} \omega_{\alpha} \delta n_j, \quad (3)$$

$$\ddot{s}_{j,\alpha} + \omega_{\alpha}^2 s_{j,\alpha} = -\sqrt{2} g_{\alpha} \omega_{\alpha} N_j, \quad (4)$$

where $\delta n_j = n_{j,1} - n_{j,2}$ and $N_j = n_{j,1} + n_{j,2}$.

Equation (3) shows that a nonvanishing value of the antisymmetric mode $q_{j,\alpha}$ induces an electronic C-T polarization in the z direction at the j th dimer site. Long-wavelength ($\vec{k} \rightarrow 0$) oscillations $q_{j,\alpha} = q_{\alpha}(\omega) \exp(i\vec{k} \cdot \vec{R}_j + i\omega t)$ will therefore drive plasmlike bulk electron oscillations in the range of molecular frequencies, polarized in the z direction. On the other hand, the mean dimer elec-

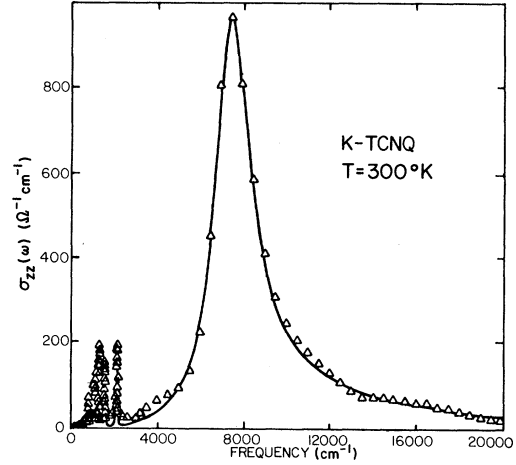


FIG. 1. Fit of Eq. (5) (—) to the experimental data (Δ) of Tanner *et al.* The primary electronic C-T band, accurately described by the sum of two Lorentzian line shapes, determines the reduced C-T polarizability $\chi(\omega)$.

tron occupation $\nu = N^{-1} \sum_j N_j$ is invariant with respect to long-wavelength oscillations in the symmetric mode $s_{j,\alpha}$ and, consequently, the only effect of the vibronic coupling in (4) is, at long wavelengths, to lead to the usual polaron shift in the MO energy E_0 . The $\vec{k}=0$ oscillations in $s_{j,\alpha}$, which will be Raman active, occur at the unshifted molecular frequencies ω_{α} .

If we treat the perturbation of the electronic C-T polarization by the antisymmetric modes within the framework of linear response theory, $\sigma_{zz}(\omega)$ in the presence of vibronic coupling may be calculated in a straightforward fashion.¹² The result is

$$\sigma_{zz}(\omega) = (\omega/i)(N_d e^2 a^2/4)\chi(\omega) / [1 - \tilde{\chi}(\omega)D(\omega)], \quad (5)$$

where $\tilde{\chi}(\omega) = \chi(\omega)/\chi(0)$ and

$$D(\omega) = \sum_{\alpha} \lambda_{\alpha} \omega_{\alpha}^2 / (\omega_{\alpha}^2 - \omega^2 - i\omega\gamma_{\alpha}) \quad (6)$$

in which the dimensionless constants $\lambda_{\alpha} = (g_{\alpha}^2 / \omega_{\alpha})\chi(0)$ characterize the strengths of the individual vibronic couplings, and γ_{α} denote the natural widths of the originally uncoupled vibrational modes. That the λ_{α} may be expected to be small ($\lambda_{\alpha} \sim 10^{-2}$ eV/1 eV) justifies the use of linear response at molecular frequencies. Equation (5) shows that the reduced C-T polarizability is renormalized to

$$\frac{\chi(\omega)}{1 - \tilde{\chi}(\omega)D(\omega)} = \chi(\omega) + \frac{\chi(\omega)\tilde{\chi}(\omega)D(\omega)}{1 - \tilde{\chi}(\omega)D(\omega)};$$

the latter term describes the additional presence

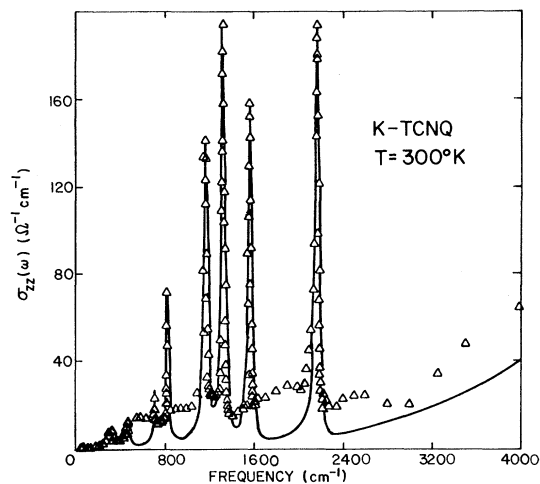


FIG. 2. Fit of Eq. (5) (—) to the experimental data (Δ) of Tanner *et al.*: the region of molecular frequencies.

of a series of G sharp absorption bands in the region of molecular frequencies. These will be well separated from the primary electronic transitions $\omega_{\beta 0}$ described by the former term, and to a good approximation their frequencies will be given by the G solutions of $\text{Re}D(\omega)=1$. The merit of Eq. (5) is that it expresses the apparent IR activity of the molecular a_g modes generally in terms of the polarizability $\chi(\omega)$ of the vibronically uncoupled electron system, a quantity which may be *experimentally* determined in the range of the primary C-T frequencies $\omega_{\beta 0}$.

The data of Tanner *et al.*⁶ for $\text{Re}\sigma_{zz}(\omega)$ for K-TCNQ are shown in Figs. 1 and 2. Eight narrow absorption bands appear in the range of the molecular vibrations of the TCNQ anion. The full curves are a fit of Eq. (5) to these data. With the known values⁵ $N_a=1.8 \times 10^{21} \text{ cm}^{-3}$ and $a=3.4 \text{ \AA}$, and the value $\chi(0)=2.53 \text{ eV}^{-1}$ obtained from fitting the primary electronic C-T band (Fig. 1), the fit in the region of molecular frequencies (Fig. 2) determines *unique* values for the sets of parameters $(\omega_\alpha, g_\alpha, \gamma_\alpha)$ for eight of the ten possible¹¹ a_g molecular modes of the TCNQ anion. The uniqueness of these values are determined solely by the quality of the experimental data. The absence of a vibrational band in the region of the TCNQ⁻ a_g C-H stretch mode ($\approx 3050 \text{ cm}^{-1}$) indicates negligible coupling of this mode to the $b_{2g}(\pi)$ MO, in accordance with previous conclusions.^{4,13} The incompleteness of the data below 200 cm^{-1} precludes the expected observation of a vibrational band in the region of the lowest-frequency

TABLE I. TCNQ⁻ electron-molecular-vibration coupling parameters.

ω_α (cm^{-1})	TCNQ ⁰ a_g modes ^a (cm^{-1})	λ_α	g_α (meV)	g_α (calculated) ^b (meV)
2225	2229	0.049	73	52
1632	1602	0.086	83	131
1395	1454	0.073	71	49
1206	1207	0.028	41	28
848	948	0.043	42	29
723	711	0.012	21	33
485	602	0.022	23	2
333	334	0.031	22	24

^aRef. 14.

^bRef. 13.

TCNQ⁻ a_g mode ($\approx 140 \text{ cm}^{-1}$). We have verified that allowance in Eq. (5) for a range of theoretically assumed couplings to this mode leads to insignificant changes in the values deduced for the eight sets of parameters $(\omega_\alpha, g_\alpha, \gamma_\alpha)$. The eight values determined for ω_α and g_α are listed in Table I, in which the values of g_α are also compared with the recent MO and valence-force-field calculations of Lipari *et al.*¹³ The natural widths were found to be $\gamma_\alpha=30 \pm 5 \text{ cm}^{-1}$ for all α . Also displayed in Table I are the deduced coupling strengths λ_α and the known¹⁴ a_g frequencies of the neutral TCNQ molecule. Further discussion of these results will appear in a full account of the work of this Letter.

Since dimerized organic linear-chain compounds exist for a variety of ion-radical species, the effect and method outlined here suggest the possibility of a comprehensive program of experimental and theoretical study.

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Primary Pyroelectric Effect in LiTaO₃

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By a careful analysis of the pyroelectric effect in LiTaO₃ between 10 and 200°K, we have demonstrated for the first time the dominance of the lowest-order (polar-mode) contributions to the primary pyroelectric effect over a wide temperature range in a strongly pyroelectric material. In doing so we confirm, as an excellent approximation for the effect, a simple analytic form the theoretical origins of which go back to a paper by Boguslawski in 1914.

The first calculation of the pyroelectric effect based on nonclassical physics was presented by Boguslawski¹ more than sixty years ago using an Einstein-oscillator formalism. The theory predicted an expression for the temperature dependence of the pyroelectric coefficient $\Pi = |dP_s/dT|$ (where P_s is the spontaneous polarization) proportional to the Einstein specific-heat function. Since the lowest-order contributions to the pyroelectric coefficient for a crystal at constant *strain* (the so-called primary pyroelectric coefficient Π_{prim}) are now recognized as coming from the polar optic lattice-vibrational modes, for which an Einstein approximation per mode is presumably quite realistic, Boguslawski's finding remains essentially valid in the slightly embellished form,

$$\Pi_{\text{prim}}^{(1)} = \sum_i C_i E(\hbar\Omega_i/2kT), \quad (1)$$

in which C_i are coefficients describing the relative amplitudes of the contributions from each pertinent Einstein mode i (of frequency Ω_i), superscript (1) denotes the lowest-order contribution, and the Einstein function is given by

$$E(x) = x^2 / \sinh^2 x. \quad (2)$$

In spite of the striking simplicity of this finding, no convincing experimental verification that Einstein terms of the form (1) do indeed dominate

the primary pyroelectric coefficient Π_{prim} for *any* pyroelectric has ever been forthcoming. Indeed, controversy continues concerning the possibility that higher-order terms may dominate the primary coefficient in real pyroelectrics²⁻⁵ and even as to what form these higher-order terms should take.⁶⁻⁸ This Letter provides a verification of Eq. (1) over a wide temperature range for LiTaO₃. Lithium tantalate is actually a high-temperature ferroelectric with Curie temperature $T_C \approx 890^\circ\text{K}$. However, below room temperature it is a conventional pyroelectric (i.e., with essentially temperature-independent phonon modes) and with a moderately strong pyroelectric coefficient at 300°K of $0.018 \pm 0.001 \mu\text{C cm}^{-2} \text{K}^{-1}$.

In general, a convincing experimental verification of the form (1) is difficult for two reasons. Firstly, conventional measurements of Π are performed either statically or at frequencies well below the fundamental crystal resonances. They therefore measure the pyroelectric response $\Pi = \Pi_{\text{prim}} + \Pi_{\text{sec}}$ at constant *stress* which includes, in addition to the constant-strain term Π_{prim} , a secondary contribution

$$\Pi_{\text{sec}} = d_{ij} c_{jk} \alpha_k, \quad (3)$$

where i , j , and k label coordinate directions (with direction i parallel to the spontaneous po-