Classification of Disorder and Extrinsic Order in Polymers By Resonant Raman Scattering

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Resonant Raman scattering is used to quantify the effect of disorder and extrinsic order on Peierls systems such as $(\mathrm{CH})_x$. We introduce "$\tilde{\lambda}$ plots" in which the phonon and gap distribution are related and characterize the system by the functional dependence of the gap 2Δ on the coupling $\tilde{\lambda}$. For *cis*-rich *trans*-$(\mathrm{CH})_x$ the disorder is extrinsic with energy Δ^p and $p=1$. For all *trans*-$(\mathrm{CH})_x$ the $\tilde{\lambda}$ plot yields intrinsic disorder, i.e., variation in the *e-p* coupling. *cis*-$(\mathrm{CH})_x$ is ordered with a 5% extrinsic gap of the full energy gap of 1.95 eV.

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It is now well established that fully conjugated polymers, of which *trans*-polyacetylene is the simplest example, undergo a spontaneous symmetry-breaking dimerization due to the Peierls instability.[1] The strong electron-phonon (*e-p*) interaction renormalizes the phonons and thus uniquely allows analysis of the electronic system by investigation of the phonon spectrum. The technique most suitable for this is resonant Raman scattering (RRS), since the RRS cross section is strongly peaked at the electronic energy gap, 2Δ.[2,3]

In this work we introduce a method based on RRS which permits analysis of various modifications of the Peierls-type interaction using a "$\tilde{\lambda}$-plot," a plot of an experimentally determined parameter $\tilde{\lambda}$ [see Eq. (3) below], or $1/\tilde{\lambda}$, vs $\ln(2\Delta)$. The method is especially powerful in quantifying the effect of disorder on inhomogeneous Peierls systems, where the phonon and gap distributions are correlated.

When our method is applied to polyacetylene (PA) it is found that while the disorder in all *trans*-PA is intrinsic and originates from variations in the *e-p* coupling λ, that of *cis*-rich *trans*-PA is extrinsic and reflects a breaking of the twofold ground-state degeneracy. In ordered systems having an extrinsic gap Δ_e in addition to the dimerization gap Δ_d, $\Delta=\Delta_d+\Delta_e$,[4] each contribution can be determined separately. For *cis*-PA we find $2\Delta_e=0.11$ eV and $2\Delta=1.95$ eV.

We describe the resonantly enhanced Raman vibrations in terms of amplitude modes (AM) associated with oscillations of the dimerization.[2,3] In this theory the gap and the phonon spectrum are respectively determined by the first and second derivatives of the electronic condensation energy $\langle H_{\mathrm{el}}\rangle=-N(0)E_i$, defined as the electronic energy in the dimerized state. $N(0)$ is the density of states at the Fermi energy in the undimerized chain, $N(0)=(\pi t)^{-1}$, where t is the nearest-neighbor transfer integral. In the dimerized chain, the ground-state gap 2Δ is determined by the equilibrium condition

$$\partial E_i(\Delta)/\partial\Delta_d=\Delta_d/2\lambda. \tag{1}$$

The renormalized phonon frequencies ω_n^R are given by the solutions of

$$D_0(\omega)=\sum_n\frac{\lambda_n}{\lambda}\frac{(\omega_n^0)^2}{\omega^2-(\omega_n^0)^2}=-\frac{1}{1-2\tilde{\lambda}}, \tag{2}$$

where ω_n^0 and λ_n are the bare phonon frequency and the corresponding dimensionless *e-p* coupling, respectively, for each mode, and $\lambda=\sum\lambda_n$. In Eq. (2) $\tilde{\lambda}$ is the renormalization parameter given by

$$2\tilde{\lambda}=1-2\lambda\,\partial^2E_i(\Delta)/\partial\Delta_d^2. \tag{3}$$

$2\tilde{\lambda}$ can be evaluated from the RRS experimental frequencies, by use of the product rule for AM[2,3]: $\prod(\omega_n^R/\omega_n^0)^2=2\tilde{\lambda}$.

The AM RRS cross section σ_R is strongly peaked[2,3] at the laser energy $\hbar\omega_L=2\Delta$. Therefore it is obvious from Eqs. (1)–(3), how one can analyze the electronic system using RRS: σ_R is peaked at 2Δ determined by E_i', while the ω_n^R are determined by E_i''. Therefore, the form of $E_i(\Delta)$ can be inferred from the experimentally determined relation $\Delta(\tilde{\lambda})$. Since $E_i(\Delta)$ contains all the interactions (e.g., *e-p*, *e-e*, impurities, and disorder) the experimental determination of its form is essential.

We now discuss the modifications of $E_i(\Delta)$, 2Δ, and $2\tilde{\lambda}$ caused by intrinsic or extrinsic disorder. Intrinsic disorder is defined as a distribution in the coupling constant (*e-p* and/or *e-e*). Other contributions to E_i such as impurities or defects are defined as extrinsic disorder. Since the effect of extrinsic disorder on E_i is small, we expand $E_i(\Delta)$ leaving the following leading term:

$$E_i(\Delta)=E_0(\Delta)+b\Delta^p, \tag{4}$$

where $E_0(\Delta)$ is the condensation energy of the pure system. The disorder is represented by a distribution in the values of b. When $E_0(\Delta)$ has the inversion symmetry $\Delta \rightarrow -\Delta$, $p=1$ breaks this symmetry, and the ground state becomes nondegenerate. But when the disordered system itself has the symmetry $\Delta \rightarrow -\Delta$, the leading term in Eq. (4) has $p=2$.

An example of $\Delta \rightarrow -\Delta$ symmetry breaking is soliton defects in *trans*-PA.[1] Another possibility for $p=1$ is finite open chains—the ends prefer double bonds which thus determine the sign of Δ; the effect is stronger (larger b) for odd chains which contain neutral solitons. An additive extrinsic gap component Δ_e[4] fixes the sign of Δ and thus corresponds also to $p=1$. For weak impurities which collectively form one-dimensional (1D) or 2D domains with opposite dimerization signs[5] we find $p=2$.

For a 1D Peierls system $\Delta = \Delta_d$ and $E_0(\Delta)$ is given by[3,6]

$$E_0(\Delta) = \tfrac{1}{2}\Delta^2[\ln(2E_c/\Delta) + \tfrac{1}{2}], \tag{5}$$

where E_c is a cutoff energy[6]; for a tight-binding approximation $E_c = 4t$. With use of Eqs. (1) and (3) we find in this case a gap $2\Delta_0 = 4E_c \exp(-1/2\lambda)$ and a renormalization parameter $\tilde{\lambda}_0 = \lambda$.

With insertion of Eq. (5) into Eq. (4) and use of Eq. (1) the ground-state gap equation becomes

$$\ln(\Delta/\Delta_0) = bp\Delta^{p-2}. \tag{6}$$

In terms of Δ_0 and $\tilde{\lambda}_0$ of the pure system, our basic $\tilde{\lambda}$-Δ relation is

$$\tilde{\lambda}/\tilde{\lambda}_0 = (2-p)\ln(\Delta/\Delta_0) + 1. \tag{7}$$

On the other hand the $\tilde{\lambda}$-Δ relation for intrinsic disorder in the Peierls system with variation in λ is

$$1/2\tilde{\lambda} = \ln(2E_c/\Delta). \tag{8}$$

We recently[2,3] discussed the RRS from AM in *trans*-PA [Fig. 1(a)] where a distribution in $\tilde{\lambda}$ $[P(\tilde{\lambda})]$ causes the dispersion of ω_n^R with ω_L. The structure of each line is composed of a primary line ω_n^p and a satellite ω_n^s. Both components are determined by Eq. (2): the primary by the peak of $P(\tilde{\lambda})$ and the satellite by the resonance condition $\hbar\omega_L = 2\Delta(\tilde{\lambda})$. To obtain a pure experimental relationship we normalized the AM product-rule relation at $\hbar\omega_L = 2.7$ eV:

$$\prod_{n=1}^{3} [\omega_n^s(2.7)/\omega_n^s(\omega_L)]^2 = \tilde{\lambda}(2.7)/\tilde{\lambda}(\omega_L).$$

We plot this relation vs $\ln(\hbar\omega_L)$ in Fig. 2(a). The Peierls relation [Eq. (8)] is clearly consistent with the data with $E_c = 6.3$ eV. This shows that the disorder in *trans*-PA is *intrinsic* and can be described by variation in λ. From $E_c = 6.3$ eV we get $t = 1.6$ eV which is within the acceptable range of the nearest-neighbor transfer integral.[1]

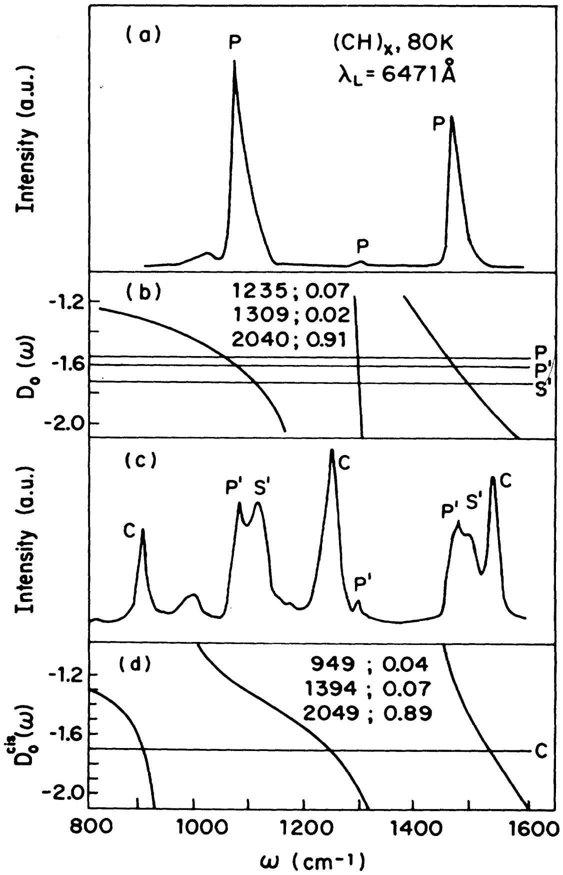

FIG. 1. (a),(c) RRS spectrum of all *trans*-$(CH)_x$ and a 95%-*cis*–5%-*trans* sample [data of Lefrant *et al.* (Ref. 8)]. (b),(d) The function $D_0(\omega)$ for the *trans* and *cis* isomers and the respective ω_n^0, λ_n/λ values. The horizontal lines P, P', S', and C give respectively the frequencies of the primary peaks in all *trans*-$(CH)_x$ [P in Fig. 1(a)], the primary and satellite peaks of the 5% $t(c)$ sample [P' and S' in Fig. 1(c)], and the peaks of the *cis* isomer [C in Fig. 1(c)].

The experimental straight line of Fig. 2(a) can be used to test any theory that attempts to include direct Coulomb interaction or short-chain distribution to explain the RRS data in *trans*-PA. Consideration of a distribution in the *e-e* interactions in either Hartree-Fock theory[6] or in strictly 1D system[7] leads to $\tilde{\lambda}$-Δ relations which are incompatible with the data. This justifies our formalism, retaining only *e-p* interactions. The Hückel-type short-chain model[8-11] is also not compatible with the experimental $\tilde{\lambda}$-Δ relation of Fig. 2(a), unless one postulates an *ad hoc* variation in both t and λ with the length of the chain.

The dispersion $\omega_n^R(\omega_L)$ in *trans* chains in partially isomerized PA samples [denoted $t(c)$] is very different from that of *trans*-PA. This is shown in Fig. 1(c) for a 5% $t(c)$ sample[8] [similar behavior is observed also for a 20% $t(c)$ sample[9,12]]: (i) The primary frequencies of $t(c)$, $\omega_n^{p\prime}$, are higher than those of

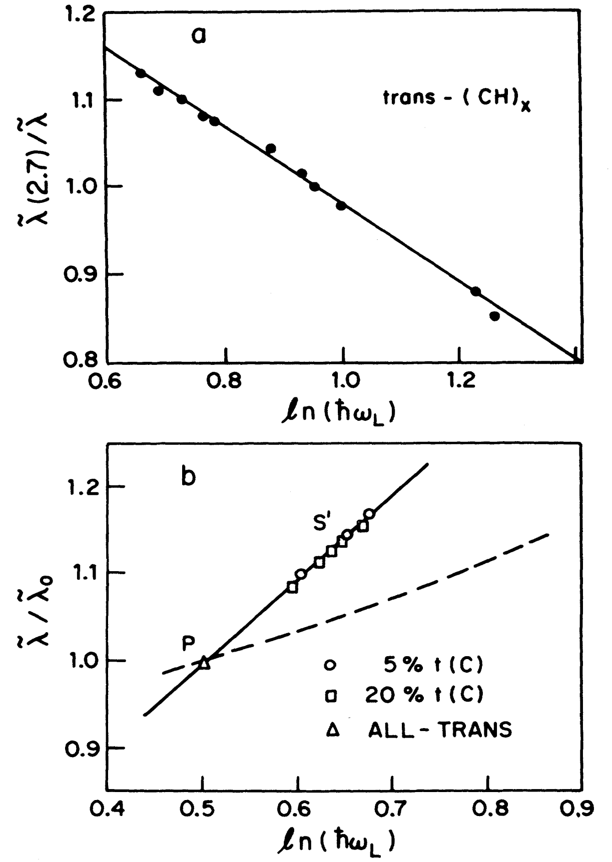

FIG. 2. (a) The product $\prod[\omega_n^s(2.7)/\omega_n^s]^2=\tilde\lambda(2.7)/\tilde\lambda$ ($n=1$–3) vs $\ln(\hbar\omega_L)$ for all *trans*-(CH)$_x$ at 300 K (Ref. 3). (b) The product $\prod(\omega_n^{s\prime}/\omega_n^p)^2=\tilde\lambda/\tilde\lambda_0$ ($n=1$–3) vs $\ln(\hbar\omega_L)$ for $t(c)$ samples at 80 K (Refs. 8 and 12). P corresponds to the primary frequencies of all *trans*-(CH)$_x$. The full line through the data points is a linear fit with slope of 1. The dashed curve describes the expected variation for an intrinsic disorder mechanism [Eq. (8)].

all *trans*, ω_n^p. (ii) The satellite frequencies $\omega_n^{s\prime}$ shift to substantially higher frequencies compared with ω_n^s in all *trans* [Figs. 1(a) and 1(c), $\lambda_L=647$ nm]. (iii) $\omega_n^{s\prime}$ are extremely sensitive to small changes in ω_L. This is demonstrated in Fig. 1(b) where the horizontal lines intersect the $D_0(\omega)$ of *trans*-PA and yield ω_n^p, $\omega_n^{p\prime}$, and $\omega_n^{s\prime}$ at $\lambda_L=647$ nm. We conclude that $\tilde\lambda$ which determines the peak of $P(\tilde\lambda)$ is higher in $t(c)$ samples compared with that of all *trans*-PA and that the $\tilde\lambda(\omega_L)$ relationship in the $t(c)$ samples of *cis*-rich PA is extremely different from that of all *trans* samples. This means that the inhomogeneity in $t(c)$ is quite different from that of all *trans*.

To obtain a pure experimental relationship we normalize the AM product-rule relation for $\omega_n^{s\prime}$ in $t(c)$ by ω_n^p of *trans*-PA:

$$\prod_{n=1}^{3}(\omega_n^{s\prime}/\omega_n^p)^2=\tilde\lambda/\tilde\lambda_0.$$

We plot this relation in Fig. 2(b) vs $\ln(\hbar\omega_L)$ for 5% $t(c)$ [8] and 20% $t(c)$.[12] The straight line has a slope of 1 and from Eq. (7) we conclude that $p=1$ and $b>0$. To emphasize the difference between the RRS dispersion in $t(c)$ and that in *trans*-PA, we plot in Fig. 2(b) (dashed line) the $\tilde\lambda$-Δ relation for intrinsic disorder [Eq. (8) with $E_c=6.3$ eV] as $\tilde\lambda$ vs $\ln(\hbar\omega_L)$. The dashed curve clearly does not fit the $t(c)$ data. We therefore conclude that the disorder in $t(c)$ is *extrinsic* with $p=1$. In general $p=1$ corresponds to a structural asymmetry, i.e., a breaking of ground-state degeneracy induced in the *trans* chains during the isomerization process. In *cis*-rich $t(c)$ samples where short-chain effects are probably more relevant, the $\tilde\lambda$ plot of Fig. 2(b) is very different from that of Fig. 2(a) for *trans*-PA This indicates that short chains are unlikely to account for the RRS data in *trans*-PA.

The distribution in the homogeneity parameter b translates into a distribution in $\tilde\lambda$ [see Eqs. (6) and (7)]. The RRS response of $t(c)$ is then double peaked [Fig. 1(c)] corresponding to ω_n^R determined by Eq. (2) with different values of $\tilde\lambda$. The primary frequencies $\omega_n^{p\prime}$ are determined by $\tilde\lambda$ of the maximum in the distribution, whereas the satellites $\omega_n^{s\prime}$ are due to $\tilde\lambda$ at resonance: $2\Delta(\tilde\lambda)=\hbar\omega_L$. We have successfully fitted the complete $t(c)$ RRS spectrum at different ω_L using $D_0(\omega)$ of *trans*-PA.[12]

For polymers with an additive extrinsic gap component Δ_e such as *cis*-PA[4] or polythiophene,[13] the full gap can be written as $2\Delta=2\Delta_e+2\Delta_d$, where Δ_e is fixed. In this case the confinement parameter[4] $\gamma=\Delta_e/2\lambda\Delta$ measures the relative strength of Δ_e; *trans*-PA corresponds to $\gamma=0$. Using Eqs. (1) and (3) in the Peierls approximation [Eq. (5)] we find for the ground-state gap $\Delta=\Delta_0\exp(\gamma)$, and for the renormalization parameter $\tilde\lambda=\lambda(1+\gamma)$. We use these relations to analyze the electronic properties of *cis*-PA.

Unlike the symmetric *trans*, the asymmetry in the *cis* backbone structure[1] causes the third-nearest-neighbor distance to alternate in phase with the dimerization pattern; $\Delta_e=2t_3$ (t_3 is the third-nearest-neighbor transfer integral). In *cis*-PA (as in *trans*-PA) the predicted[14] three A_g modes below 2000 cm^{-1} are strongly coupled to the electrons; these lines are marked by the letter C in Fig. 1(c). The RRS lines are much narrower than those of *trans*-PA and do not shift with ω_L, indicating that *cis*-PA is ordered. Using the three RRS frequencies and the two available relative intensities we show in Fig. 1(d) that we have found a function $D_0^{cis}(\omega)$ and a value of $2\tilde\lambda=0.42$ [line C in Fig. 1(d)] which fit the *cis*-PA RRS spectrum.

Using $2\tilde\lambda=0.37$ and $2\Delta_0=1.7$ eV as for *trans*-PA[2] and the relations for $\tilde\lambda(\gamma)$ and for $\Delta(\gamma)$ concluded above, we derive $\gamma=0.15$, $2\Delta=1.95$ eV, and $2\Delta_e=0.11$ eV. The value found for γ is much smaller than that anticipated before[15]; however, the calculated full gap of 1.95 eV coincides with the band-edge photoluminescence found in *cis*-PA.[16] Moreover, we found that the derived value of Δ_e is in reasonable agreement with the value of the third-nearest-neighbor transfer integral in *cis*-PA structure.

In conclusion, we have shown an efficient method of analyzing the effects of disorder in conjugated polymers and demonstrated it in *trans, trans-cis* mixtures, and *cis* polyacetylene.

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[1] Proceedings of the International Conference on the Physics and Chemistry of Conducting Polymers, Les Arc, France [J. Phys. (Paris) **44**, C3 (1983)].

[2] Z. Vardeny, E. Ehrenfreund, O. Brafman, and B. Horovitz, Phys. Rev. Lett. **51**, 2326 (1983).

[3] B. Horovitz, Z. Vardeny, E. Ehrenfreund, and O. Brafman, Synth. Metals **9**, 215 (1984).

[4] S. Brazovskii and N. Kirova, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 6 (1981) [JETP Lett. **33**, 4 (1981)].

[5] P. A. Lee and T. M. Rice, Phys. Rev. B **19**, 3970 (1979).

[6] B. Horovitz and J. A. Krumhansl, Phys. Rev. B **29**, 2109 (1984).

[7] B. Horovitz, H. Fukuyama, and G. Solym, to be published.

[8] S. Lefrant, in Ref. 1, p. 247.

[9] D. B. Fitchen, Mol. Cryst. Liq. Cryst. **83**, 1127 (1982).

[10] G. P. Brivio and E. Mulazzi, in Ref. 1, p. 261.

[11] H. Kuzmany, Phys. Status Solidi (b) **97**, 521 (1980), and in Ref. 1, p. 255.

[12] Z. Vardeny, E. Ehrenfreund, O. Brafman, and A. J. Heeger, to be published.

[13] T.-C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, Phys. Rev. B **30**, 702 (1984).

[14] G. Zannoni and G. Zerbi, Solid State Commun. **48**, 87 (1983).

[15] K. Fesser, A. R. Bishop, and D. K. Campbell, Phys. Rev. B **27**, 4804 (1983).

[16] L. Lauchlan, S. Etemad, T.-C. Chung, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B **24**, 3701 (1981).