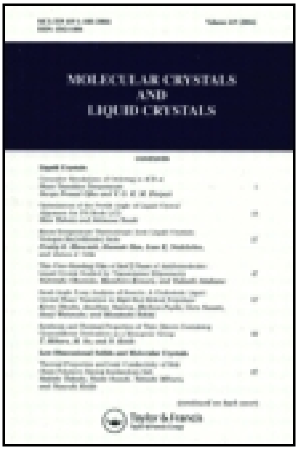

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RESONANT RAMAN SCATTERING IN THE POLYACETYLENE SYSTEM

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Abstract The amplitude mode approach for describing the resonant raman scattering in dimerized chains is reviewed and applied to the polyacetylene system. trans-$(CH)_x$ is disordered with a variable electron-phonon coupling constant. cis-$(CH)_x$ is ordered with an extrinsic gap of ~ 5% of the full gap. A distribution of extrinsic gaps is shown to exist in trans-$(CH)_x$ chains in partially isomerized polyacetylene.

Recently we have shown[1,2] that the resonant Raman scattering (RRS) from trans-polyacetylene (PA) can be described as scattering from amplitude modes (AM) associated with oscillations of the dimerization gap. The dimerization gap in PA, as in other conjugated long molecules, is the result of the strong electron-phonon (e-p) interaction of the π-electrons with the underlying backbone chain consist of σ-bonds. The vibrational modes of the chain are then renormalized and the observed Raman frequencies thus reflect electronic gap oscillations. In this communication we apply the AM approach to the cis isomer of PA and to partially isomerized cis-trans PA system.

A fundamental energy variable of the dimerized system is the electronic condensation energy, $-N_0E_1(\Delta)$, defined as the expectation value of the total electronic energy including kinetic, electron-electron and e-p terms ($N_0 = 1/\pi t$ is the electron density of states for a chain with an average transfer integral t). Both the ground state energy gap 2Δ and the renormalized phonon frequencies are determined by $E_1(\Delta)$ and are given as the solution of the following equations:[2]

$$E_1'(\Delta) = \Delta/2\lambda \quad ; \qquad D_o(\omega) \equiv \sum_n \frac{\lambda_n}{\lambda}\,\frac{(\omega_n^0)^2}{\omega^2 - (\omega_n^0)^2} = \frac{-1}{1-2\tilde{\lambda}} \tag{1}$$

where ω_n^0 are the bare phonon frequencies of the underlying chain, λ_n are the corresponding dimensionless e-p coupling constants and $\lambda = \sum_n \lambda_n$. $\tilde{\lambda}$ is defined by $1-2\tilde{\lambda} = 2\lambda E_1''(\Delta)$ and it can experimentally be determined using the product rule relation

$$\Pi(\omega_n^R/\omega_n^0) = 2\tilde{\lambda} \tag{2}$$

where ω_n^R are the observed RRS frequencies. For a Peierls chain (i.e., no e-e interaction and no extrinsic gaps) the equilibrium gap is given by the Peierls relation $2\Delta_0 = 4E_c \exp(-1/2\lambda)$ where E_c is a cutoff energy ($E_c = 4t$ for the infinite Huckel chain).

A unique feature of the RRS in trans-PA is the dispersion (i.e., broadening and shifting) of the spectrum with increasing laser excitation energies $\hbar\omega_L$.[1,3] This effect of dispersion shows that the system is inhomogeneous with a spatial distribution in $\tilde{\lambda}$. By fitting RRS frequencies from a large number of excitation energies we were able to show that the Peierls relation, with $\tilde{\lambda} = \lambda$ and $E_g = 2\Delta_0 = \hbar\omega_L$, holds for trans-PA with fixed $E_c = 6.3$ eV. Furthermore, the disorder (or inhomogeneity) is the result of a distribution in the e-ph coupling constant λ.

Unlike the symmetric trans isomer, the asymmetry in the cis backbone structure causes the third nearest neighbor distance to alternate in phase with the dimerization pattern.[4] Therefore, an extrinsic gap component $2\Delta_e$ originating from the third nearest neighbor transfer integral t_3 ($2\Delta_e = 4t_3$) adds linearly to the dimerization gap $2\Delta_d$, such that the total gap is $2\Delta = 2\Delta_d + 2\Delta_e$. The equilibrium condition then yields the following Δ-λ relations

$$\Delta = \Delta_0 \exp(\gamma) \quad ; \qquad 2\tilde{\lambda} = 2\lambda + \Delta_e/\Delta \tag{3}$$

where Δ_0 is defined above and $\gamma = \Delta_e/(2\lambda\Delta)$ is the confinement parameter.[5]

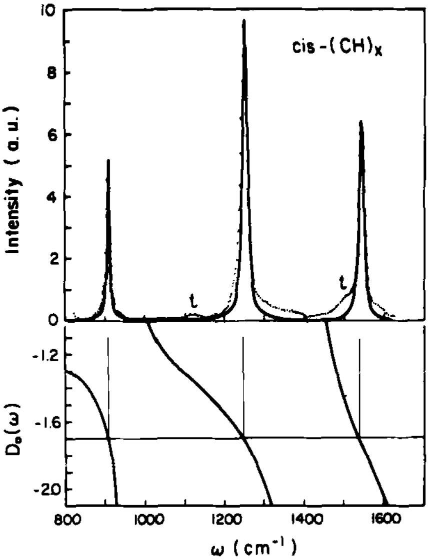

FIGURE 1

Raman spectrum of cis-$(CH)_x$ at 300K. Dots are experimental and full lines are theoretical fits. $D_0(\omega)$ is also shown.

In Figure 1 we show the RRS spectrum of cis-$(CH)_x$ excited by $\hbar\omega_L = 2.1$ eV. There are, as in trans-$(CH)_x$, three resonantly enhanced lines, but unlike the trans isomer they are narrow and do not shift with ω_L, indicating that cis-$(CH)_x$ is a homogeneous system without a spatial distribution of energy gaps. Similar data is observed for the deuterated isomer cis-$(CD)_x$. In order to find the parameters for the cis system, we combined the data (frequencies and relative intensities) of the two cis-PA isotopes and assumed that both have the same bare-frequency for the c-c stretching mode (as in trans-PA)[1,6] and the same $\tilde{\lambda}$ value. Fitting the data under these assumptions we show in Figure 1 that we were able to find a function $D_0(\omega)$ that fits the RRS spectrum (data for cis-$(CD)_x$ are not shown here). The parameters ω_n^0 and λ_n are listed in Table I, and the value found for $2\tilde{\lambda}$(cis) is 0.42 (corresponds to the horizontal line at $D_0(\omega) = -1.72$ in Figure 1). Comparing the parameters for the cis and trans isomers shown in Table I we note that the c-c stretching vibrations ω_3^0 are nearly equal, as may be expected from structural considerations. Assuming the same e-p coupling λ for the two isomers ($2\lambda = 0.37$) we find using

TABLE I ω_n^0 (cm^{-1}) and λ_n/λ for trans and cis(CH)$_x$

Isomer	ω_1^0	λ_1/λ	ω_2^0	λ_2/λ	ω_3^0	λ_3/λ
trans	1235	0.07	1309	0.02	2040	0.91
cis	949	0.04	1394	0.07	2049	0.89

Eq. (3): $2\Delta_e = 0.11$ eV, 2Δ(cis) = 1.95 eV and $\gamma = 0.14$. Our value of 2Δ(cis) coincides with the photoluminescence emission observed[7] at 1.95 eV. We note also that the value of γ found here is much smaller than that anticipated earlier.[5]

The RRS from trans-(CH)$_x$ chains in partially isomerized cis-rich PA shows also a dispersion behavior (Figure 2). It differs however from the all-trans spectrum as can be seen by comparing Figures 2a and 2c. At λ_L = 6471Å RRS from 5% trans in cis-rich PA shows already a large splitting into a primary (P′) and satellite (S′) lines, whereas in all-trans this splitting is considerably smaller and almost unnoticeable (Figure 2a). The frequency of the

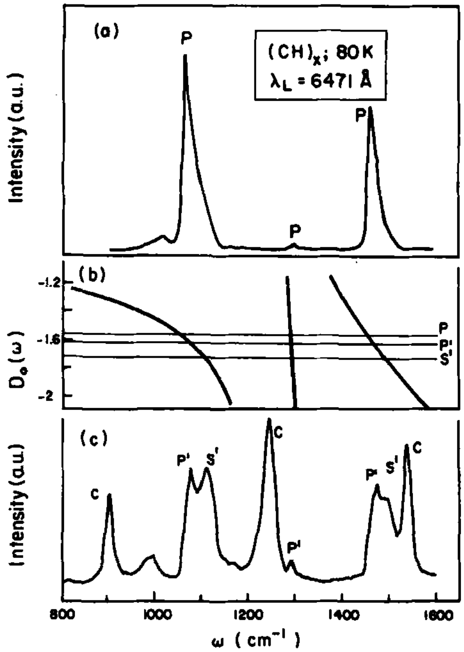

FIGURE 2

(a) and (c): RRS spectra of all-trans-CH)$_x$ and a 95% cis-5% trans sample (data of Lefrant et al. Ref. 3 p. 247).
(b): The function $D_o(\omega)$ for the trans-(CH)$_x$. The horizontal lines P, P′ and S′ give the respective frequencies P, P′ and S′. C markes the cis isomer lines.

satellites S′ is very sensitive to small variations in λ_L. Thus, the inhomogeneity in the trans chains in cis-rich PA is different from that of all-trans. A possible inhomogeneity mechanism is a varying additive extrinsic gap component Δ_c, which may arise, for instance, from structural asymmetries. In such a case we can analyze the data using Eqs. (3) above. The product rule for the primary peaks (P′) yields for the 5% trans in cis-rich $(CH)_x$ an average gap of $\bar{E}_g = 1.74$ eV compared with $E_g = 1.64$ eV in all-trans at 80K. By analyzing the satellite (S′) frequencies and intensities in Figure 2c we obtained a mean extrinsic gap $2\Delta_c = 0.04$ eV with a distribution width of 0.01 eV.

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