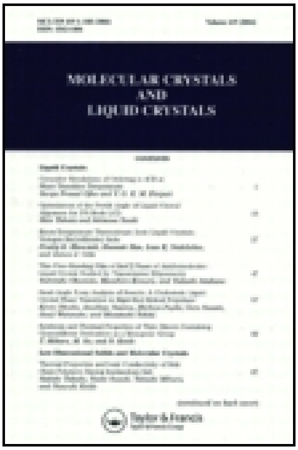

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Amplitude Modes in Mixed Polymers Trans $[C_2H_2)_y(C_2D_2)_{1-y}]_x$

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AMPLITUDE MODES IN MIXED POLYMERS
TRANS $[(C_2H_2)_y(C_2D_2)_{1-y}]_x$

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Abstract- Resonant Raman Scattering and doping induced IR absorption are explained in terms of amplitude modes of the 1-d gap. The RRS frequencies and relative intensities of the renormalized phonon lines at the various concentrations are readily obtained.

In Resonant Raman scattering of pure trans-polyacetylene(PA) three lines are observed, and as excitation energy increases, satellite lines develop and shift to higher frequencies. This behavior was earlier explained in terms of amplitude modes(AM)$^{(1)}$. In mixed PA spectra there are seven primary RRS as shown in fig.1. Fig. 2. shows the aproximate frequency variation of these lines with isotope concentration. The higher frequency line shows a one mode behavior,while the others show a two mode behavior. If regarded as regular phonons some of the features are hard to explain: in the case of the 1100cm^{-1} line the frequency increases with the change in D concentration(1). Also the dispersion acts definitely different from that of the pure compounds(fig. 3),though there is no grand to assume a change in chain length distribution. These phenomena are readily understood in terms of the A.M.: The data describe the behavior of the renormalized phonons of the dimerized chain$^{(2)}$. To

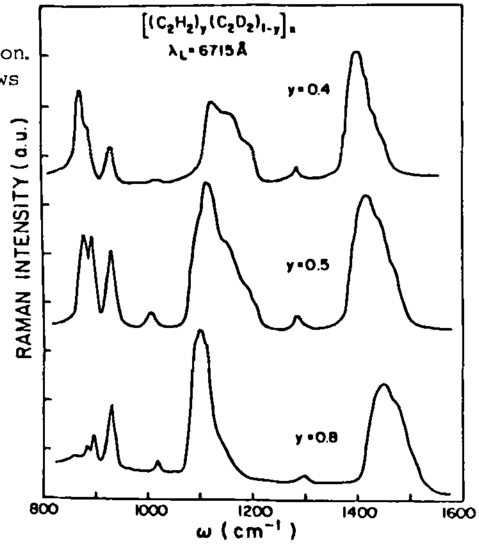

Fig. 1: RRS spectra at different concentrations.

understand the behavior of the Raman lines and IR spectra (from Takeuchi et. al (3)), we study the bare phonon frequenceis of the undimerized chain, $^{o}_{n}$, and their corresponding electron-phonon(e-p) coupling parameter, $_{n}$. Based on the RRS data we assume seven oscillators for the mixed polymers, then the amplitude modes are described by:

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

where the e-p coupling constant is $\lambda = \sum \lambda_n$, and $\tilde{\lambda}$ is defined by $1-2\tilde{\lambda} = 2\lambda E_i''(\Delta)$ (2) . $E_i''(\Delta)$ is the second derivative of $E_i(\Delta)$, the electronic condensation energy, where 2Δ is the dimerization gap. A narrow distribution in $\tilde{\lambda}$ is assumed, meaning also a distribution in Δ, as in the pure compounds. Thus $\tilde{\lambda}$ is defined by the resonance condition $\hbar\omega_L = 2\Delta(\tilde{\lambda})$, determining the renormalized phonons and their properties: frequencies (ω_R^n) and intensities (I(ω_R^n)). RRS spectra at $\hbar\omega_L$ =1.87eV and

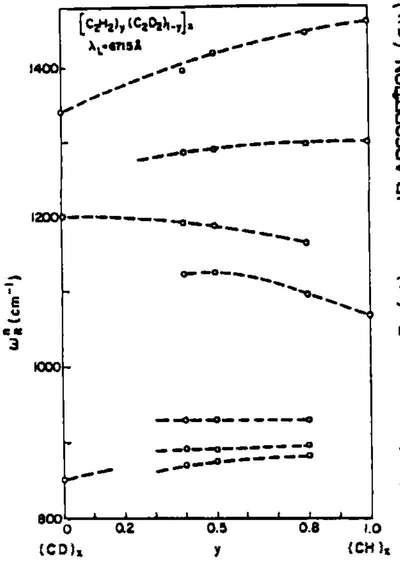

Fig. 2: Frequencies of the observed Raman Lines at different concentrations.

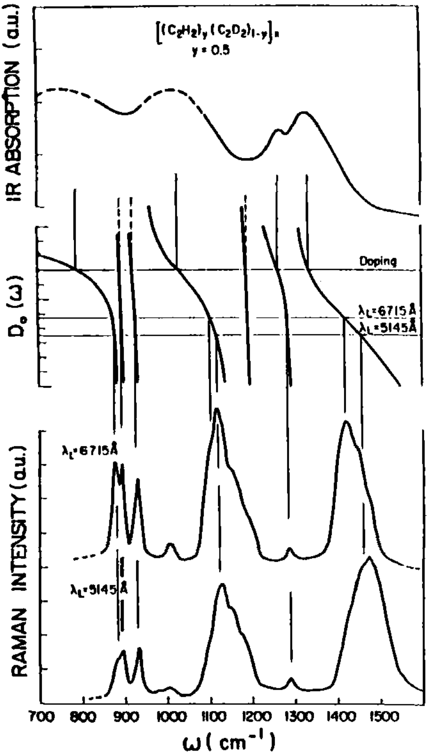

Fig. 3: RRS spectra (bottom) and IR absorption (top). $\tilde{\lambda}$ and α_p define horizontal lines which intersect $D_o(\omega)$ at the renormalized phonon frequencies.

$\hbar\omega_L$=2.41 eV are shown in fig. 3(bottom). The horizontal lines for a given excitation energy are calculated using the Peierls relation:

$$\hbar\omega_L = 2E_c \exp(-1/2\tilde{\lambda}) \qquad (2)$$

with E_c=6.3 eV. This 2 can be evaluated using the product rule relation:

$$\prod_{n=1}(\omega_n^R/\omega_n^0)^2 = 2\tilde{\lambda} \qquad (3)$$

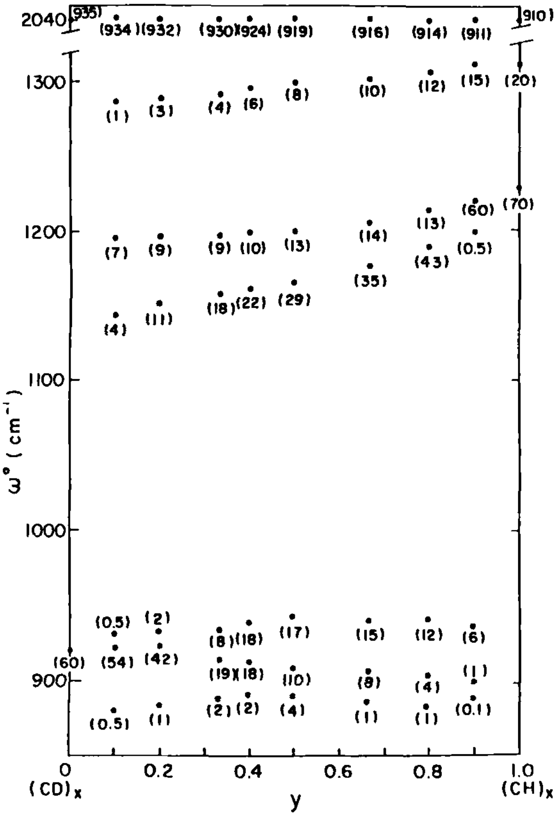

Fig. 4. The bare phonon frequencies ω_n^0 vs. concentration, λ_n are given in parentheses.

Once having $\tilde{\lambda}$ we solve the equation for the A.M.(4).The intersection of the horizontal lines with $D_0(\omega)$ yield the renormalized phonons and their intensities, given by:

$$I(\omega_n^R) = \left[\frac{\partial D_0(\omega)}{\partial\omega}\right]^{-1}_{\omega_n^R} \qquad (4)$$

Hence the fit uses 13 parameters with a sufficient number of RRS data frequencies at $\hbar\omega_L$=1.87,2.41 and 2.60 eV, as well as doped induced IR absorption$^{(3)}$. With the same $D_0(\omega)$ and a single pinning parameter, α_p, we obtain the whole IR spectra, with $D_0(\omega) = -1/(1-\alpha_p)$, as shown in fig. 3(top). The relative IR intensities are also given by (4), when instead of using ω_n^R we use ω_n^0. From the upper part of fig (3) and eq. (4)it is obvious that only the first of the three lower frequency lines can be expected to be seen in IR, as is really the case$^{(3)}$. The results are summarized in fig. 4 where ω_n^0 and (λ_n) are given for the various concentrations. In this representation a normal concentration dependence is shown, which involves interaction with a mode having the same symmetry: the 1200 cm^{-1} ($(CD)_x$) and the 1218 cm^{-1} $(CH)_x$) bare phonons they define the behavior of the 1100 cm^{-1} line (fig. 3, middle of the renormalized phonon.

The lower part of the spectra is composed of three low frequency lines. The lowest frequency seems to be caused by disorder of the crystals, and is the highest for the largest disorder (λ_1 =0.004 for Y=0.5). The other two bare phonons show also an interaction which might be between the 918 cm^{-1} trans$(CD)_x$ bare phonon and another phonon, which might belong to remmants of Cis$(CH)_x$, which has a bare phonon at 950cm^{-1}.

In conclusion: The AM model is very useful to understand the RRS spectra of polyacetylene, pure or mixed, giving an easy aproach to the understanding of their behaviour. It gives a mean to predict which frequencies and intensities we are going to receive for any given excitation energy, since they are linked together by $D_0(\omega)$.

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