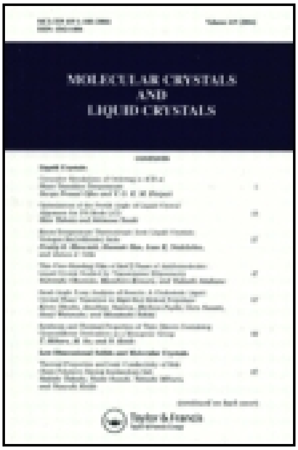

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Conjugation Lengths and Resonant Raman Spectrum of Trans-Polyacetylene

L. Piseri [a], R. Tubino [a], P. Piaggio [b] & G. Dellepiane [b]

[a] Istituto Chimica Macromolecole, C.N.R., Via E. Bassini, 15/A, Milano, Italy

[b] Istituto Chimica Industriale, Università, Corso Europa, 30, Genova, Italy

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CONJUGATION LENGTHS AND RESONANT RAMAN SPECTRUM OF TRANS-POLYACETYLENE [+]

L. Piseri and R. Tubino
Istituto Chimica Macromolecole, C.N.R.
Via E. Bassini, 15/A - Milano, Italy

P. Piaggio and G. Dellepiane
Istituto Chimica Industriale, Università,
Corso Europa, 30 - Genova, Italy

The interpretation of the Resonant Raman bandshapes of trans polyacetylene is reviewed in relation to a lattice dynamical calculation which considers both short and long range forces. The contribution to the Raman scattering of the phonon singularity at the zone center is discussed. It is also suggested that the selective activation of phonons with intermediate $\underline{q}$ vectors is responsible for the observed bandshapes.

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INTRODUCTION

In this paper we will discuss and review the implications of the lattice dynamics of trans polyacetylene in determining the Resonant Raman bandshapes and their variation with the exciting laser frequency. The most relevant spectral features[1-4] can be summarized as follows. Of the four in-plane Raman active modes two are resonantly enhanced in the $(CH)_x$ ($\nu_{C=C}$ at ∿ 1453 cm^{-1} and ν_{C-C} at ∿ 1080 cm^{-1}) and three in the $(CD)_x$ ($\nu_{C=C}$ at ∿ 1340 cm^{-1}, ν_{C-C-H} at ∿ 1200 and ν_{C-C} at 850 cm^{-1}). These modes are mostly polarized along the chain axis and are therefore coupled to the $\pi \rightarrow \pi^*$ electronic transition. In the case of the hydrogenated polymer both the observed bandshapes are strongly affected by the excitation frequency (Ω_L), namely, when the laser frequency is tuned in the red region only one sharp peak is observed, whose asymmetric shape is reminiscent of an inverse square root type singularity typical of a 1-d phonon density of states rounded off by finite phonon lifetimes and/or by 3-d interchain interactions. As the laser frequency is tuned towards higher energies in addition to this exciting frequency independent peak, a broad feature appears in the high frequency side of the Raman band, whose position moves towards higher frequencies as Ω_L is increased. In the case of the deuterated polymer this behaviour is observed only for $\nu_{C=C}$ stretching, the shapes of the other two bands being quite insensitive on Ω_L.

The spectral features described above have been interpreted as arising from the presence of segments of conjugated double bonds of various lengths. As the absorption frequency depends upon the conjugation length, segments containing a different number of conjugated double bonds are selectively brought into resonance conditions by changing the laser exciting line.

Most of the proposed models[5-6] do not seem to properly account for the scattering coming from very long conjugation lengths, as they assume a linear dependence of both electronic and vibrational frequencies on the inverse conjugation length (1/n). However it is well known that for infinite chains a quadratic dependence of the vibrational frequencies on the wavevector (for nondegenerate modes) is required at the center of the Brillouin zone. Reliable dispersion curves are therefore necessary to describe the contribution coming from such singularity in the density of the vibrational states.

For this purpose we shall first review the lattice dynamics of an idealized infinite chain of conjugated double bonds in the trans configuration.

LATTICE DYNAMICS

The total electronic energy of an infinite polyene chain can be expressed as

$$E_T = E_\sigma + E_\pi \qquad (1)$$

where E_σ and E_π are energies due to σ and π electrons respectively.
E_σ can be written as

$$E_\sigma = \frac{1}{2} \sum_{ij} F_{ij}\, \delta R_i\, \delta R_j \qquad (2)$$

where δR_i and δR_j are the internal coordinates (bond stretchings, bendings etc.) which are usually taken as a basis for the description of the lattice dynamics of organic systems and F_{ij} are the force constants describing the mutual interactions among these coordinates.
Within the framework of Hückel approximation, the energy E_π is given by

$$E_\pi = \sum_n \alpha_n + 2 \sum_{nm} p_{nm}\, \beta_{nm} \qquad (3)$$

where p_{nm}, α_n, β_{nm} are bond order, Coulomb integral and resonance integral; n,m (m=n±1) label the carbon atom in the chain. By assuming β to be a linear function of bond length, the second derivative of E_T yields the following expression for a "generalized force constant" [7]

$$K_{ij,kl} = F_{ij} + \Pi_{ij,kl} \left(\frac{\partial\beta}{\partial R}\right)_o^2 \qquad (4)$$

where ij,kl refer to the atoms of the interacting bonds. The first term in eq. 4 represents localized force constants, arising from the ground state electronic energy, which have directional character and short range properties and can be therefore described in terms of a valence force field. The second term which is expressed in terms of bond--bond polarizability and electron phonon coupling ($\partial\beta/\partial R$), comes from the modulation of Peierls electronic gap through skeletal vibrations and is responsible for long range interactions. It has been shown [8] that

$$\Pi_{ij,kl} = \frac{1}{(2\pi)^2} \iint_{-\pi}^{\pi} \frac{d\theta d\theta'}{\varepsilon_v(\theta)-\varepsilon_c(\theta')} \times$$

$$\times\{(C^*_{vk}(\theta)C_{cl}(\theta')+C^*_{vl}(\theta)C_{ck}(\theta'))(C_{vi}(\theta)C^*_{cj}(\theta') + \tag{5}$$

$$+ C_{vj}(\theta)C^*_{ci}(\theta'))+C.C.\}$$

where θ represents the electronic wavevector of the valence band (v) and θ' the wavevector of the conduction band (c). In eq. 5 the C's are the expansion coefficients of the π electrons wavefunction in terms of the atomic orbital for the conduction and the valence state whose energies are ε_c and ε_v respectively. In Table I of ref. 8 the values of $\Pi_{ij,kl}$ are reported for all the possible bond-bond interactions. These interactions give a non negligible contribution for a bond separation up to seven chemical units.

These generalized force constants allow inclusion of effects of the electron-phonon (e-p) coupling in the calculation of the phonon dispersion. To do this the dynamical matrix $\underline{\underline{D}}(\underline{q})$, expressed in the internal coordinate basis, must be diagonalized for values of the phonon wavevector ($\underline{q}$) within the first Brillouin zone.
The expression for $\underline{\underline{D}}(\underline{q})$ is [9]

$$\underline{\underline{D}}(\underline{q}) = \underline{\underline{M}}^{-\frac{1}{2}}\ \underline{\underline{B}}^{+}(\underline{q})\ \underline{\underline{K}}(\underline{q})\ \underline{\underline{B}}(\underline{q})\ \underline{\underline{M}}^{-\frac{1}{2}} \tag{6}$$

where $\underline{\underline{M}}$ is a diagonal matrix containing the atomic masses, $\underline{\underline{B}}(\underline{q})$ is the linear transformation matrix between internal and cartesian phonon coordinates, $\underline{\underline{K}}(\underline{q})$ is an hermitian matrix describing the force field in internal coordinates, whose elements are given in eq. 4.
It has been shown elsewhere that, within the framework of the tight binding-next-neighbours approximation, only the carbon-carbon stretching force constants and their interactions are affected by the e-p coupling and therefore the dispersion of the skeletal vibrations are strongly dependent on this parameter. By using for ∂β/∂R the value deri-

ved from the experimental energy gap E_g[10] ($E_g = 2u|\partial\beta/\partial R|$; u = bond alternation), we have obtained the dispersion curves for $(CH)_x$ reported in fig. 1.

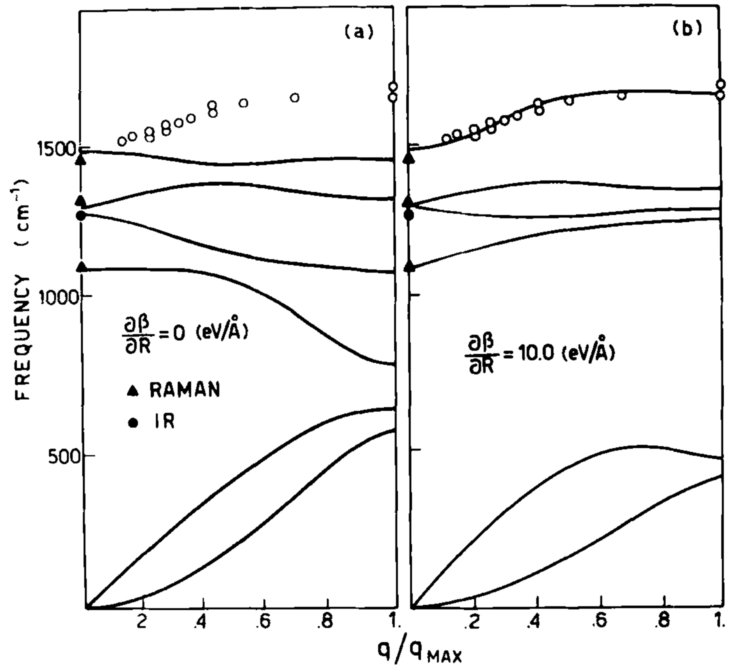

Fig. 1 Calculated dispersion curves for trans $(CH)_x$ for $\partial\beta/\partial R = 0$ (a) and for $\partial\beta/\partial R = 10$ ev/Å (b). Open circles are the c=c stretching frequencies for short polyenes according to ref.11. See text.

Also the phonon dispersion curves for $\partial\beta/\partial R = 0$ are shown for comparison. In the same figure are also reported the experimental $\nu_{c=c}$ stretching frequencies for short polyenes[11]. Even though the force constants for conjugated molecules are not additive and therefore their frequencies do not necessarily fall on the dispersion curve of the infinite chain, we can nevertheless expect that the dependence of $\nu_{c=c}$ on the phonon momentum q in trans polyacetylene should be similar, at least qualitatively, to the dependence of $\nu_{c=c}$ on the inverse conjugation length in short polyenes. The e-p coupling derived from the experimental energy gap seems therefore to provide a good description of the c=c phonon dispersion throughout the Brillouin zone. An analogous dependence on the wavevector is predicted by our calculations for the c-c stretching vibration. Even though no experimental data are available for the c-c stretching in short polyenes, the Raman bandshapes are well accounted for by the calculated phonon dispersion as we will discuss in the next section.

RESONANT RAMAN BANDSHAPES

The theory of the Raman scattering from a perfect crystal implies that only $\underline{q}=0$ motions are coupled with the radiation thus giving rise to a sharp symmetric peak whose half-width is related to the lifetime of the created phonon. As already discussed, the observed Raman bands of trans polyacetylene exhibit an asymmetric broad structure. When the translational symmetry is destroyed, as in the case of a crystal containing a small concentration of non interacting defects, also phonons corresponding to intermediate $\underline{q}$ vectors can contribute to the Raman scattering. Within the approximation that the vibrational frequencies of short polyenes fall onto the dispersion curve of the infinite chain, the breakdown of the translational symmetry corresponds to the activation of modes originating from segments of finite conjugation lengths. The Raman cross section for a defect--containing crystal is given by

$$\sigma(\nu)\propto g(\nu)\,|\alpha(\nu)|^2 \qquad (7)$$

where $g(\nu)$ is the density of the vibrational states of the perfect crystal and $\alpha(\nu)$ is the polarizability matrix element. As far as the density of the states is concerned the two stretching modes exhibit peaks at the zone center, corresponding to the frequency of the infinite chain (figure 2). It is apparent that the shape of the calculated density of states is very similar to the low-frequency side peak of the Raman bands. In the case of the experimental spectra, the inverse square root singularity is smoothed by 3-d interchain coupling and by finite lifetime of the phonons. Moreover in the presently available experimental data, chains with infinite conjugation lengths are never under strict resonance conditions, that is at a laser frequency corresponding to the absorption edge. Figure 2 also illustrates the behaviour of the square of the polarizability for short

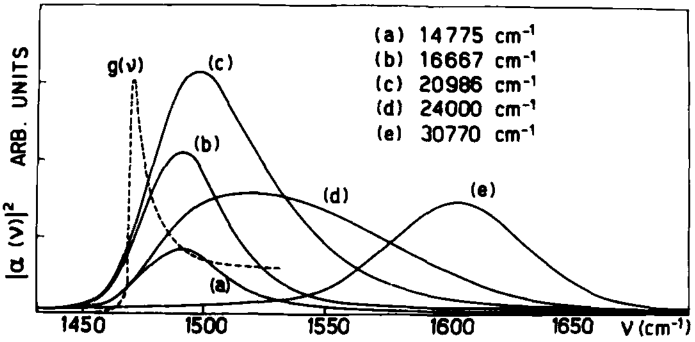

Fig. 2 Calculated density of states g(ν) for the c=c stretching of trans $(CH)_x$ (---). Calculated $|\alpha(\nu)|^2$ as a function of the vibrational frequency for different excitation lines for short conjugated segments (——). See text.

conjugated segments as a function of the vibrational frequency for different excitation lines. It is apparent that this function shows a maximum for vibrational frequencies corresponding to electronic transitions in resonance with Ω_L. An interpretation of the observed bandshapes and their variation with the exciting frequency can now be proposed. When the laser frequency is tuned towards the absorption edge, the square of the polarizability peaks at the same frequency as the density of states and therefore only one sharp asymmetric peak is observed. As the laser frequency is tuned towards higher energies in addition to the frequency independent peak coming from the phonon singularity, a broad feature originating from $|\alpha(\nu)|^2$ appears which moves to higher vibrational frequencies as shorter conjugation lengths are brought into resonance. As a matter of fact for excitations in the U.V. region, $|\alpha(\nu)|^2$ is peaked at $\sim$ 1600 cm^{-1} in agreement with the experimental observations by Harada *et al.* [11]

The assumption that phonons with intermediate $\underline{q}$ are activated in the Raman scattering is further supported by the comparison of the Raman bandwith with the calculated phonon dispersion for both hydrogenated and deuterated polyacetylene [12]. For the hydrogenated polymer a large dispersion is predicted for both the stretching modes, in very good agreement with the broad experimental bandshapes observed (fig. 3a).

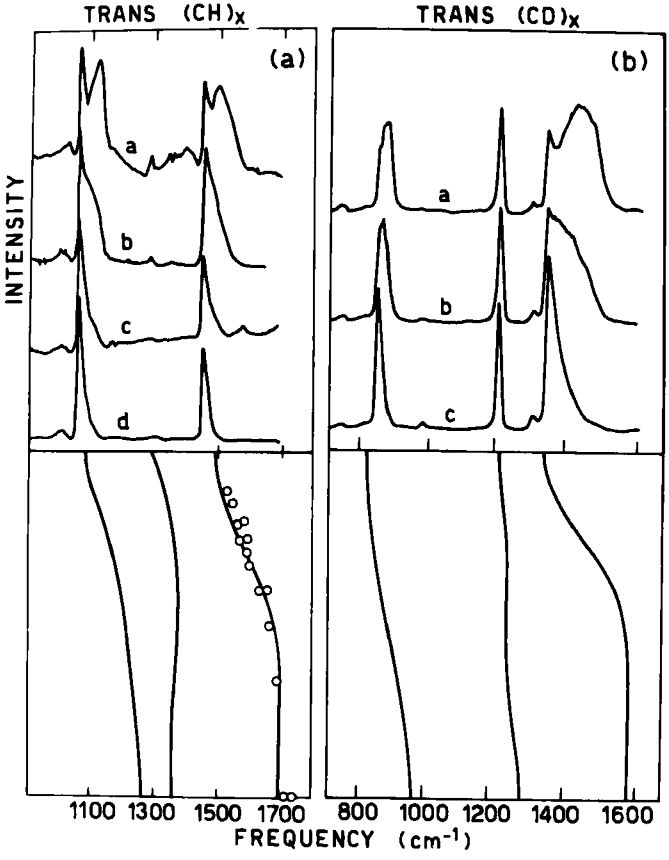

Fig. 3 Comparison between experimental Raman bandshapes [3,4] at different exciting lines (a- 457.9 nm, b- 514.5 nm, c- 600 nm, d- 676.4 nm) with the calculated dispersion curves for trans $(CH)_x$ (a) and for trans $(CD)_x$ (b).

For the deuterated polymer only the shape of the c=c stretching mode changes dramatically with the excitation frequency, while the other two resonant Raman bands are fairly narrow and independent on the laser frequency. This behaviour is well accounted for by the calculated dispersion curves corresponding to the Raman active frequencies (see fig. 3b).

CONCLUSIONS

In our opinion the analysis of the resonant Raman bandshapes suggests that the contribution to the scattering intensity coming from the presence of very long chains is essential to reproduce the most relevant experimental features. The Raman spectra provides also evidence for the presence of short conjugated segments, whose intensity is strongly enhanced by resonance conditions. Further experiments with laser excitation lines in the region between 450 and 325 nm could confirm our interpretation, since the feature originated by the peak in the polarizability matrix element should progressively move towards the 1600 cm^{-1} limit.
A quantitative estimate of the conjugation length distribution requires further work. However preliminary calculations show that roughly 20% of the polymer consists of short segments whose average conjugation length is $\sim$ 18. However it must be stressed that these figures can vary from sample to sample depending on polymerization conditions and on the history of the sample.

A few comments can be added for the cis polymer. In this case the shapes of the Raman bands are fairly sharp and symmetric and do not appreciably change in shape with the excitation frequency. By using the arguments discussed for the trans polyacetylene two different explanation are possible

i) the dispersion curves are essentially flat

ii) a very limited number of defects are present so that no breakdown of the $\underline{q}$=0 selection rule occurs. It is therefore our intention to extend the present lattice dynamical calculation to the cis polymer in order to understand the effect of the e-p coupling on its dispersion curves. This calculation should clarify if the defects, responsible for the activation of phonons with intermediate $\underline{q}$ vectors in the trans polymer, are generated during the polymerization or are formed by the process of thermal isomerization.

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