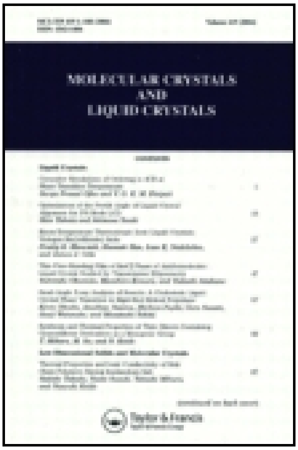

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Resonance raman scattering from partially isomerized polyacetylene

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RESONANCE RAMAN SCATTERING FROM PARTIALLY ISOMERIZED POLYACETYLENE

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A study of Raman scattering from partially isomerized polyacetylene films with varying cis-trans content is presented. Major differences are discovered in the dispersion of trans-$(CH)_x$ Raman bands between pure trans- and cis-rich samples. It is shown that the unusual dispersion of the trans-$(CH)_x$ Raman bands in partially isomerized samples cannot arise from a distribution of short chains. These results are discussed in terms of the complex response of the lattice to the presence of photoinjected electron-hole pairs.

INTRODUCTION

Light scattering experiments in cis- and trans-$(CH)_x$ show remarkable differences in the luminescence and Raman spectra of the two isomers.[1,2] The scattered light spectrum from cis-$(CH)_x$ contains a broad luminescence peak centered near

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the bandedge together with a series of multiple order Raman lines. Both effects are absent in trans-$(CH)_x$. Instead, the two strongly resonance enhanced Raman lines of trans-$(CH)_x$ show a most unusual dispersion which changes dramatically with the excitation energy of the incident light. Whereas an understanding of the difference in the luminescence results of the two isomers has been achieved in terms of the soliton model,[2] a coherent interpretation of the Raman spectra of the two isomers has not been developed.

In this work we present a study of Raman scattering from partially isomerized films of polyacetylene of varying cis-trans content. The motivation for this work has been two-fold; to shed more light on the unusual behavior of the Raman bands of trans-$(CH)_x$, and to stimulate an in-depth study of the cis-trans isomerization process by providing some experimental results which in principle are susceptible to the microscopic details of the distortions involved. Our results indicate that major differences in the profiles of the trans-bands exist between pure trans-$(CH)_x$ and partially isomerized cis-$(CH)_x$. We have also observed new features in the Raman spectra from trans-$(CH)_x$ segments in mostly cis-samples. We have shown that these results are incompatible with the "short chain" model[3-4] proposed to explain the unusual behavior of the trans-$(CH)_x$ Raman bands. The implications of these results on the dynamics of soliton formation are discussed.

Experimental results

The Raman spectra have been obtained at 77K from the shiny side of free standing films immersed in liquid nitrogen. The experiments carried out at Université Paris - Sud and at the University of Pennsylvania showed good agreement in the Raman spectra of similar samples. The cis-trans content of the samples was evaluated using the relative intensity of the characteristic infrared absorption bands of cis- and trans-$(CH)_x$.[5] As prepared cis-rich film was nominally 80% cis-$(CH)_x$. By using special handling, we were able to obtain one film having a cis-content greater than 90%. Subsequent isomerization of the cis-rich films at 140°C under vacuum for periods of 1 to 10 minutes resulted in films having 30-60% trans-content.

In Fig. (1) we compare the Raman spectra of pure trans-$(CH)_x$ and cis-rich ($\simeq$ 80%) $(CH)_x$ using various excitation frequencies. In 100% trans-$(CH)_x$, the Raman bands broaden and develop a double peak structure as the laser excitation is changed from 1.9 eV (red) to 2.7 eV (blue). The opposite behavior, however, is observed for the trans-bands in the mostly cis-sample.

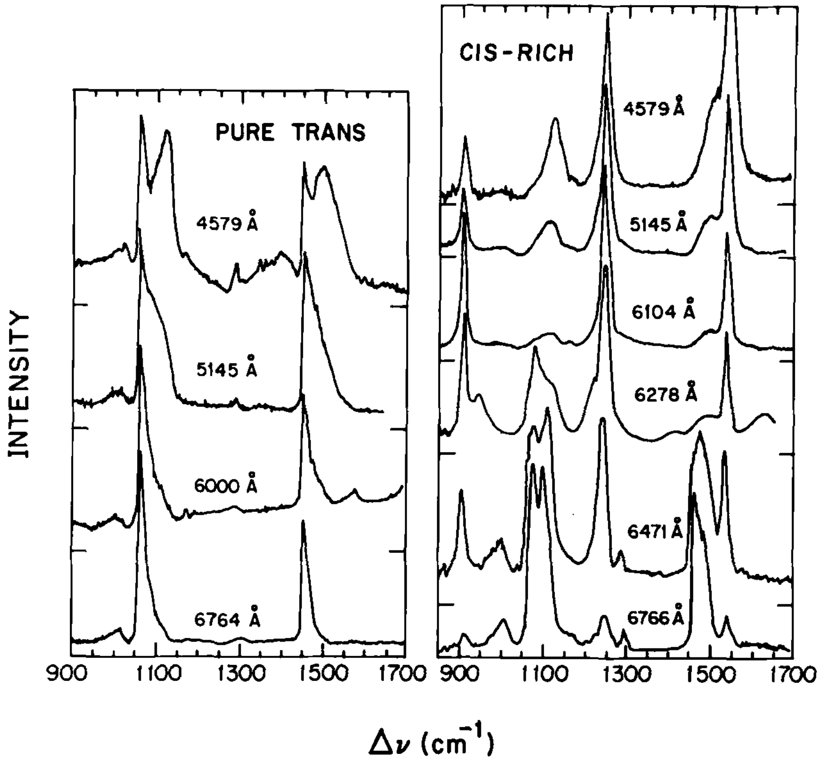

FIGURE 1 Raman spectra from pure trans-$(CH)_x$ and cis-rich $(CH)_x$ using different laser excitations.

In Fig. 2 we show the variation in the profile of the trans-Raman bands with changing trans-content for deep red excitations (6471 Å and 6764 Å). These spectra reveal triplet structures not previously reported for trans-Raman bands. For ~ 20% trans-$(CH)_x$ sample, the two trans bands show very different lineshapes using 6471 Å laser excitation, whereas, 6764 Å excitation produces similar band profiles. It can be seen in Fig. 2 that this behavior is exactly reversed in the sample having greatest cis-content (> 90%). Moreover, the Raman bands from the 10% trans film show a shift toward lower frequency as compared to the 20% trans sample. Since the 10% and 20% trans-$(CH)_x$ films were obtained from different sample preparations, it is not clear to what extent the observed shift is intrinsic.

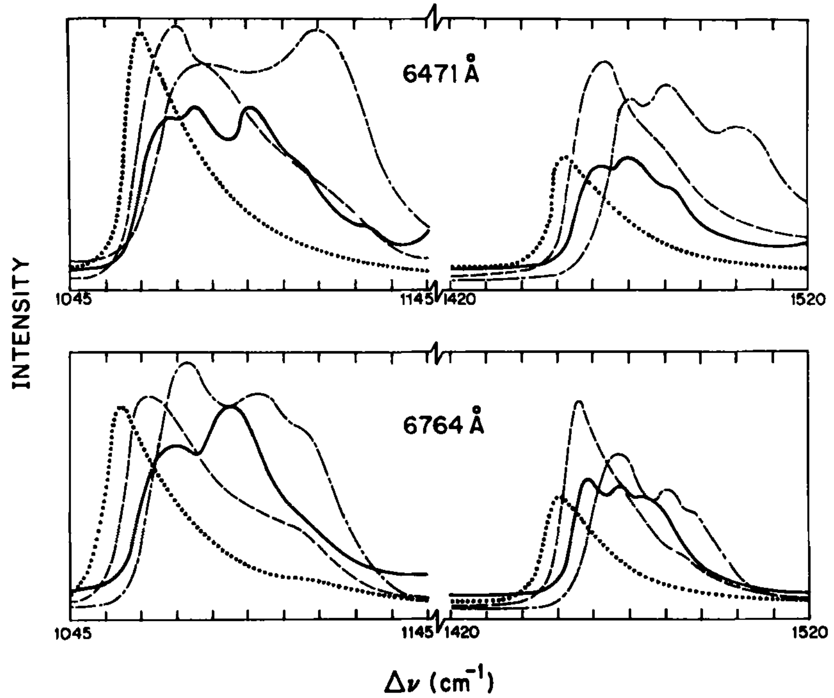

FIGURE 2 Raman spectra of *trans*-$(CH)_x$ bands in • • • 100% *trans*, --- 50% *trans*, – • – 20% *trans*, and ——— 10% trans.

Discussion

The unusual profile of the two resonance enhanced Raman bands of pure *trans*-$(CH)_x$ together with their change with excitation energy has attracted considerable attention. Based on the observation that the frequency of both resonance enhanced Raman lines and the energy gap of short chain polyenes decrease monotonically with increasing chain length, it has been suggested that the unusual dispersion and excitation spectrum of the Raman bands in *trans*-$(CH)_x$ primarily arise from a distribution of chain lengths[3,4]. Quantitative analysis of the chain length distribution derived from experimental results such as those shown in

Fig. 1, however, leads to a distribution with too many short chains, incompatible with other experiments.[6]

The results presented in the previous section show that the response of the trans-$(CH)_x$ lattice to the presence of a photoinjected electron-hole pair depends critically on the cis-trans composition as well as the excitation energy. The rich fine structure and the difference in the profile of the two resonance enhanced bands from cis-rich samples are indications of the complexity of the dynamics of the lattice distortion involved in the scattering process. These results are also incompatible with the "short chain" model. In this model the unusual profile of the bands arises from a convolution of an assumed chain length distribution with the known variation of the frequency of the two vibrational modes as a function of chain length. Since the two modes have a similar monotonic chain length dependence, one expects a similar profile for the two bands as seen in the results from pure trans-$(CH)_x$. Thus, the difference in the profile of the two bands in partially isomerized samples (see in Fig. 3, for example, the result from ~ 20% trans-sample using 6471 Å laser excitation) cannot be explained by the short chain model. Furthermore, in the case of pure trans-$(CH)_x$ there appear broad peaks on the high energy side of both vibrational bands with increasing excitation energy (see Fig. 1). Since the band gap of polyenes increases with decreasing chain length, these features are attributed to short chains becoming resonantly enhanced with increasing excitation frequency. However, as shown in Fig. (2), the opposite change in profile of the 1060 cm^{-1} band is observed for the 10% trans-sample, which is also inconsistent with the short chain model.

An understanding of the difference in the related luminescence results of the two isomers has been developed in terms of the soliton model. It has been noted that the quenching of luminescence upon cis-trans isomerization is concurrent with the appearance of photoconductivity which is absent in cis-$(CH)_x$[2]. This result has lead to the conclusion that solitons are the photogenerated carriers in polyacetylene. Due to the degenerate ground state in trans-$(CH)_x$, the lattice is unstable to the presence of a photoinjected electron-hole pair and distorts to form a pair of free soliton-antisolitons with associated electronic states at midgap; hence, the absence of a luminescence signal. In cis-$(CH)_x$ the ground state is nondegenerate and in the presence of a photoinjected electron-hole pair the lattice distorts to form a confined soliton-antisoliton pair with the associated electronic states near bandedge; thereby giving rise to the bandedge luminescence in the absence of photoconductivity. Since the Raman and luminescence spectra are intimately related, in the following we shall discuss the implications of our results in the context of the lattice distortion associated with the soliton formation.

In a recent treatment of the dynamical response of both cis- and trans-$(CH)_x$ lattices to photoinjected electron-hole pairs, Mele has suggested that the Raman spectra in the two isomers primarily arise from hot luminescence processes rather than a true Raman process.[7] He has been able to account for the Raman spectra of the two isomers by assuming that in the presence of a photoinjected electron-hole pair the cis-$(CH)_x$ lattice forms a shallow distortion and the trans-$(CH)_x$ lattice forms a deep, localized distortion. In trans-$(CH)_x$, for chain lengths less than 3-4 soliton widths, it is predicted that the presence of physical boundaries affects the dynamical response of the lattice resulting in an incompletely formed soliton-antisoliton pair.[8] In this context, the structures observed in the trans-Raman bands from cis-rich samples using deep red excitations may arise from the boundary effects produced by cis-segments sandwiching short trans-segments. These results indicate that the length of the trans-chains increases progressively with the extent of isomerization, consistent with the picture in which the isomerization occurs collectively with the length of all trans-chains increasing together as isomerization proceeds down a microcrystalline fibril.

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5. The reported values of cis-trans are nominal because it is assumed that the excitinction coefficients of the two

IR bands are independent of cis-trans content. In a recent thorough analysis H.W. Gibson et. al. (see this conference proceedings) have shown that the two extinction coefficients vary with cis-trans content. Using their results the 10%, 20%, and 50% trans-samples appears to contain 3%, 6%, and 45% trans-$(CH)_x$, respectively.

6. The inferred distribution for pure trans-$(CH)_x$, as analysed in Ref. 3, would indicate that most chains have less than 10 conjugations. This result is inconsistent with a variety of other experimental results; for example, the relatively unrestricted motion of the highly mobile neutral solitons. (See W.G. Clark et. al. in this proceedings.)
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