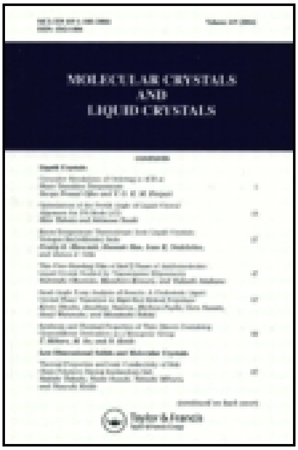

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Resonance raman results in polyacetylene

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RESONANCE RAMAN RESULTS IN POLYACETYLENE*

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Inelastic light scattering experiments with tunable lasers give unique information on the morphology and excitations in undoped polyacetylene. The characteristics of these spectra and the current state of their interpretation are reviewed here. In the case of trans $(CH)_x$, the model relating the Raman and absorption profiles to an inhomogeneous distribution of conjugation lengths is described and quantitative implications presented. New results reported include the following: measurements and analysis of Raman profiles indicating the large contribution from short conjugation lengths in trans $(CH)_x$; the lack of direct evidence for photogenerated solitons in recent two-beam Raman spectra (there may be evidence for soliton formation in the excited state linewidth, however); and the markedly different resonance Raman behavior and photoluminescence in cis $(CH)_x$ and short segments of trans $(CH)_x$.

INTRODUCTION

In this paper I review the current status of resonance Raman results in undoped polyacetylene. The interest in these results focuses primarily on two questions: 1) what can they tell us about real, as opposed to ideal, polyacetylene and 2) in what ways, if any, do these spectra reflect the presence of solitons?

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* Work supported in part by the NSF.

The experiments have been carried out now for a number of years in several laboratories, at Cornell, Orsay, Vienna, Tokyo, and lately Pennsylvania. There is general agreement about most of the experimental observations, at least in the best samples. The disagreement comes in interpretation. The results I am reporting are those from Cornell obtained by Kuzmany, Imhoff, Sarhangi, and especially by Lichtmann in his comprehensive thesis investigation of Raman scattering in polyacetylene.[1]

The experiment is simple in concept. Undoped polyacetylene, with the optical absorption spectrum shown in Figure 1, is exposed to an incident cw laser beam at various photon energies close to or above the band edge. The laser frequencies used span most of the visible and near ultraviolet range as indicated at the top of the figure.

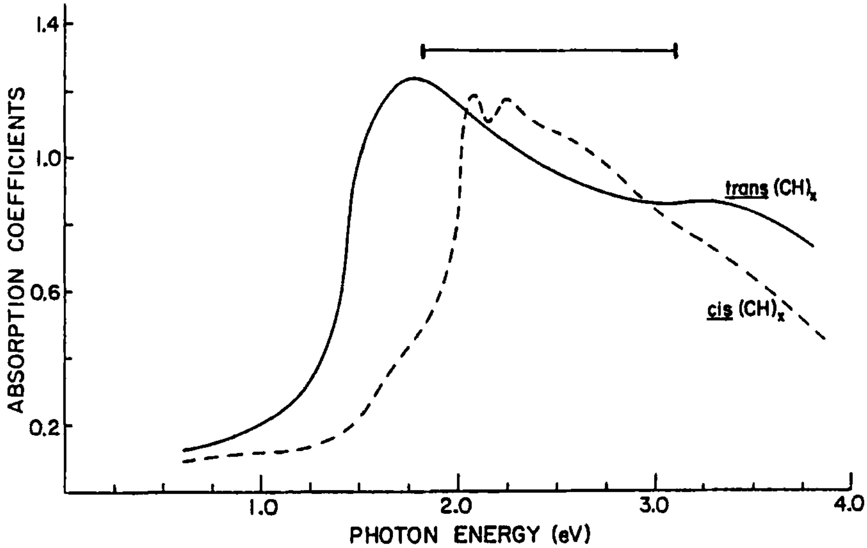

FIGURE 1 Optical absorption spectra for thin films of cis and trans $(CH)_x$ at 78K. Range of laser frequencies used is indicated at the top.

The spectrum of the outgoing light from the sample is analyzed. Under these excitation conditions, this outgoing light includes luminescence and resonance Raman scattering as well as the ordinary non-resonant Raman scattered light.

TRANS $(CH)_x$

A typical spectrum of the outgoing light for a sample of trans $(CH)_x$ at 78K is shown in Figure 2. Most prominent are the two bands with frequency shifts in the range 1050-1150 and 1450-1550 cm^{-1}. These correspond to Raman scattering from backbone vibrations; a few weak overtones and combinationsalso appear. No luminescence is seen.

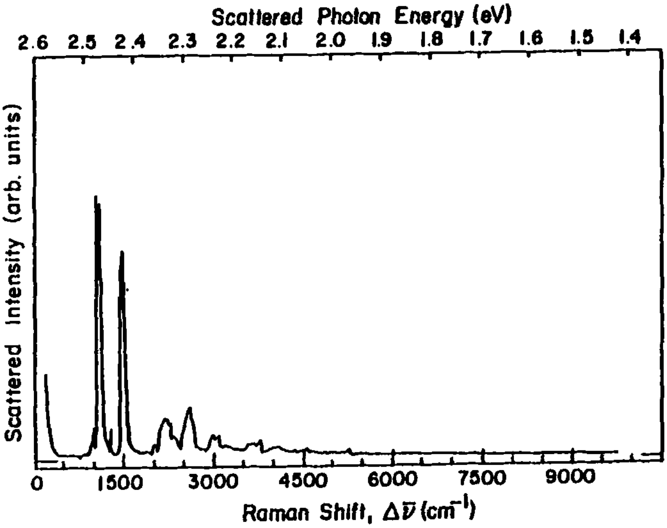

FIGURE 2 Spectrum of the outgoing light for a sample of trans $(CH)_x$ excited at 476.5 nm at 78K. (From Ref. 1)

When such spectra are examined on an expanded scale at different laser wavelengths, then the characteristic behavior shown in Figure 3 is observed. The two strong Raman bands show dispersion with a change in Raman profile as the laser wavelength is changed. The low frequency edge of each Raman band stays fixed, but intensity develops on the high frequency side of the band as the laser wavelength decreases. (Recent measurements of these profiles with the krypton laser lines at 406.7 and 413.1 nm confirm that the high frequency shoulder continues to shift at shorter laser wavelengths, indicating that the profile cannot be simply the superposition of two bands.[2])

This shifting in the band profiles, which we call dispersion, has been characterized more quantitatively by

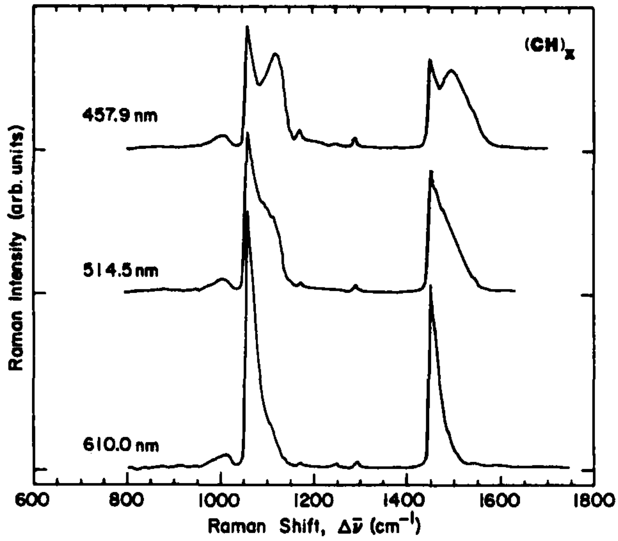

FIGURE 3 Raman spectra of trans $(CH)_x$ measured at three different laser wavelengths at 78K. (From Ref. 3.)

comparing intensities at more than twenty different laser wavelengths. The integrated intensity of each band does not vary much as the laser is tuned through the visible. However, the intensity at a particular vibrational frequency within the band does show a strong variation. Curves for intensity at different vibrational frequencies within the upper (C = C stretch) band profile are shown in Figure 4. For instance, the top curve shows the variation in intensity at the low frequency edge of the band; it is strongest for excitation in the red. The bottom curve shows the variation in intensity at the high frequency edge; it is strongest in the blue. For intermediate vibrational frequencies, the peak in the excitation curve lies in between. (Its position seems to vary monotonically.) For each vibrational frequency, the shape of the excitation curve seems to be roughly the same, indicated schematically by the solid line peaked at a different laser wavelength. The curves shown (only as a guide to the eye) are lorentzians with full width at half maximum of 7000 cm^{-1}. This is a surprisingly large width.

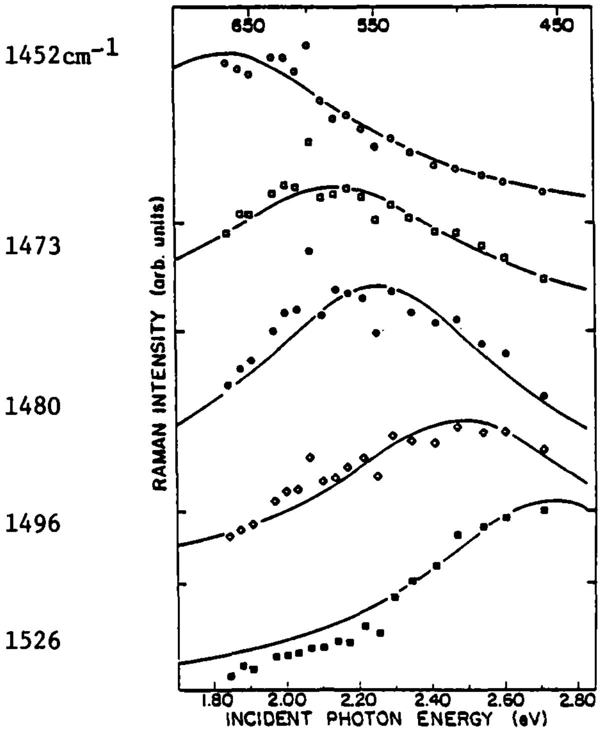

FIGURE 4 Excitation profiles for the Raman intensity at five different frequencies within the C=C band (upper band in Fig. 3). See text for explanation of curves. (From Ref.1)

If it is due to lifetime broadening it corresponds to a lifetime of about 5 10^{-15} sec for the intermediate state in the scattering process!

These Raman profiles in trans $(CH)_x$ are particularly sensitive to sample treatment. Figure 5 shows the variation in band shape measured for different samples at the <u>same</u> laser wavelength. The profiles (a) to (f) show the effect of increasing exposure to air, and less than ideal isomerization conditions. The profile in (f) is for one of our "worst" samples, while that in (a) is for one of our "best" samples. We assume that the latter profile is the limiting band shape in well-prepared samples.

Several different sorts of explanations have been suggested for this phenomenon of dispersion in the Raman profiles of trans $(CH)_x$. The most straight-forward one has puzzling implications, while some recent and intriguing

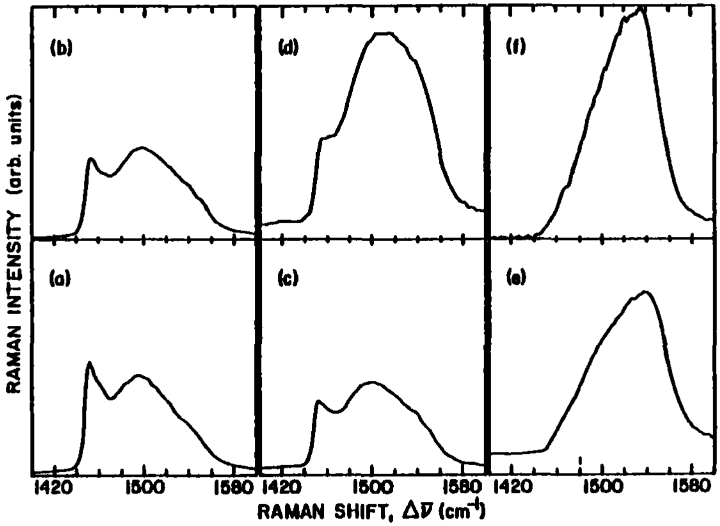

FIGURE 5 Sample dependence of Raman profiles in trans $(CH)_x$ (all excited at 457.9 nm). Curves (a) to (f) show the effect of increasing exposure to air and less than ideal isomerization conditions. (a) is "best", (f) "worst". (From Ref. 1)

alternatives have not yet been adequately developed. Some of the explanations proposed are these:

1) The Raman profile corresponds to an inhomogeneously-broadened band, a superposition of lines at slightly different frequencies reflecting some (presumably static) distribution of different polyacetylene chains in the sample. The dispersion is then due to selective excitation of different chains at different laser wavelengths.

2) The apparent dispersion is a nonlinear non-equilibrium effect caused by a background of photogenerated solitons. This background will be different at different laser wavelengths.

3) The Raman profile is a homogeneous lineshape. Its shape reflects the dynamical processes occuring as the photogenerated electron-hole pair decays very rapidly into a soliton-antisoliton pair.

The first alternative is the traditional alternative[3-6] and the one that I shall present in some detail. The latter two are intriguing, but seem to me unlikely to be the dominant effects. The second alternative, that the dispersion reflects some interference from a background of photogenerated solitons, seems to be ruled out by a recent two-beam experiment in our laboratory. We measured the Raman profile for red laser excitation with and without the presence of a blue laser beam throughout the same scattering volume. No change in the profile was detected. Nor has any change been seen when the laser intensity is varied by an order of magnitude. The third alternative is under active but fairly qualitative discussion and deserves further investigation. The question of how solitons affect optical lineshapes is one of fundamental interest. The solitons present in polyacetylene must have some effect on absorption and scattering spectra. My own impression is that the Raman profiles show too much sample dependence for this to be the dominant effect.

To return to the first alternative, we need to show that scattering from an inhomogeneous sample can give a self-consistent explanation for the data. From a series of excitation curves such as those in Figure 4, we can infer the relationship between a particular vibrational frequency ω and the laser frequency ν for which the scattering at ω has its greatest intensity. The relationship is approximately linear:

$$\{\nu(\mathrm{cm}^{-1}) - 14520\} = 119.6\ \{\omega(\mathrm{cm}^{-1}) - 1450\}$$

This relation corresponds quite closely to that observed for finite polyenes of different (short) lengths. Hence it has been customary to assign the variation in ν to differences in the effective conjugation length in different parts of the polyacetylene chain[4,6]. Shorter conjugation lengths have a higher vibrational frequency ω and are selectively excited at higher photon energy ν.

The model then assumes that different conjugation lengths are present in the sample, with this length characterized by the number n of carbon double bonds between interruptions. The nature of these interruptions is not well specified, but is thought to include such things as crosslinks, bond defects, impurities, etc[7]). We calculate the optical absorption $\alpha_n(\nu)$ and the Raman cross section $\sigma_n(\nu,\omega)$ for an idealized conjugated segment of length n. This has been done most recently by Kuzmany[8] using the Franck-Condon approach to calculate these lineshapes.

We assume a distribution function P(n) for the conjugation lengths, where P(n) is the number of chains of conjugation length n. With this we can compute the total absorption coefficient

$$\alpha(\nu) = \sum_{n=1}^{\infty} P(n)\ \alpha_n(\nu)$$

and the total Raman profile at each laser frequency, ν_L,

$$\sigma(\nu_L,\omega) = \sum_{n=1}^{\infty} P(n)\ \sigma_n(\nu_L,\omega).$$

We iterate this procedure to find the distribution P(n) which gives the best fit to the measured spectra.

Figure 6 shows the sort of fits that are attainable, both from Kuzmany's recent treatment and from a simpler model in Lichtmann's thesis. In these fits, both the shape and relative intensity of the Raman profile at different ν_L are used as constraints.* The corresponding fit to the shape (but not the strength) of the optical absorption shown in Fig. 1 for trans $(CH)_x$ is reasonably good, but by no means exact.

Thus reasonably self-consistent solutions to the line-shapes can be found, but they have surprising implications for P(n). In order to fit the data, P(n) must have a very large contribution from segments of short conjugation length. Lichtmann[1] found the best fit for a distribution of the form $P(n) \propto 1/n^{2.3}$, while Kuzmany[8] chose a distribution which was the sum of two log normal distributions peaked at n = 5 and 40. The resultant distributions are not actually that different, and are probably not distinguishable with the present experimental data. But both distributions lead to the surprising conclusion that much of the material is in segments of short conjugation length. The particular choice of P(n) which gives the best fits corresponds to half the material being in conjugation lengths of about 30 double bonds or less. This result does not change appreciably for other possible fits. Thus this model clearly implies that there are interruptions in the conjugation occurring at short lengths which have so far not been detected with other probes.

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*In both treatments the breadth of the excitation curves in Fig. 4 implies a large width (~ 7000cm^{-1}) for the intermediate state in the scattering. One possible explanation is that the electron - hole pair created by the incident photon very rapidly decays into a soliton - antisoliton pair as suggested by the calculation of Su and Schrieffer[9].

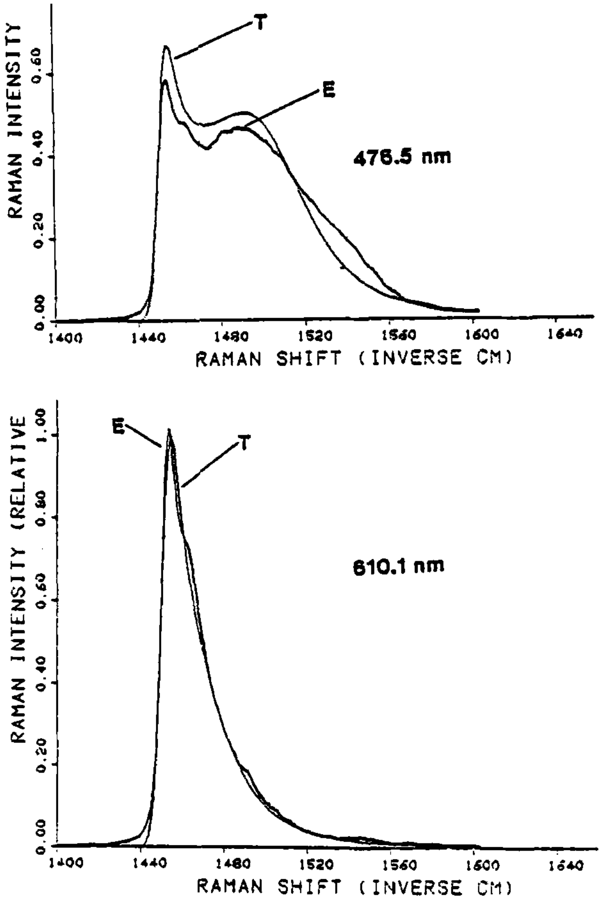

FIGURE 6 An example of calculated fits (T) to the measured Raman profiles (E) in trans $(CH)_x$ using a distribution function $P(n) \propto 1/n^{2.3}$. (From Ref. 1)

If one accepts this model for the Raman data, then it provides a convenient explanation for some of the sample - dependent changes which occur with different sample treatments. For instance, when the sample undergoes isomerization from cis to trans $(CH)_x$, the band profile changes in a way which implies that short trans segments are formed first, then longer ones, followed by eventual decrease in the long chains as degradation processes occur.[7]

CIS $(CH)_x$

The spectra of cis $(CH)_x$ are very different from those of trans $(CH)_x$. If a sample of as - prepared polyacetylene (containing about 90% cis and 10% trans $(CH)_x$) is excited with a visible laser, one obtains a spectrum of outgoing light such as that shown in Fig. 7. This consists of three Raman lines due to backbone vibrations at 909, 1250 and 1541 cm^{-1}, together with a long progression of overtones and combinations of these three modes. (The progression has the appearance of a single series, but in fact the peaks are in most cases superpositions of two or more lines since the frequencies of the three modes are approximately multiples of a single frequency.) In addition to these Raman features there are two broad luminescence bands, one at ~ 1.9 eV and another at ~ 1.3 eV.

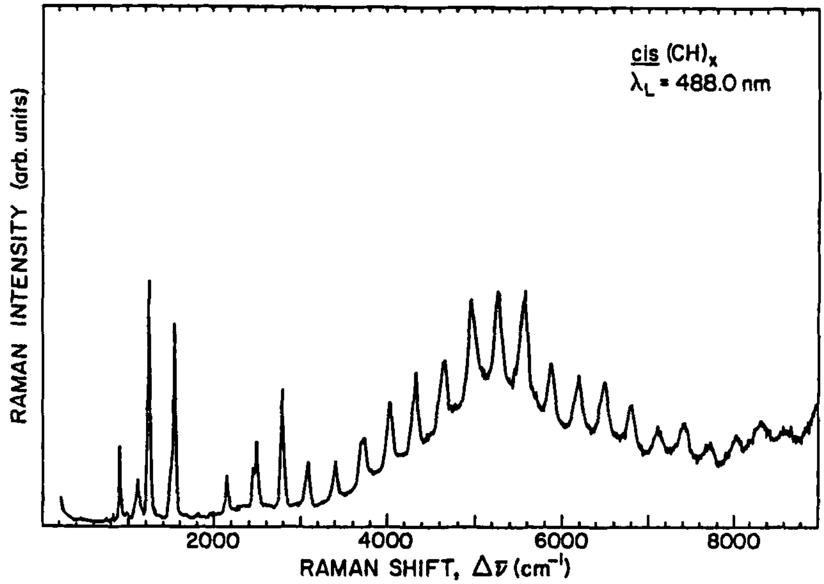

FIGURE 7 Spectrum of outgoing light from a sample of cis $(CH)_x$ at 78K. (From Ref. 1)

Figure 8 shows examples of the spectra for several different laser wavelengths. The Raman features shift with the laser, while the luminescence bands always appear at the same energy. In contrast to the trans spectra, the Raman fundamental bands show no appreciable dispersion in profile

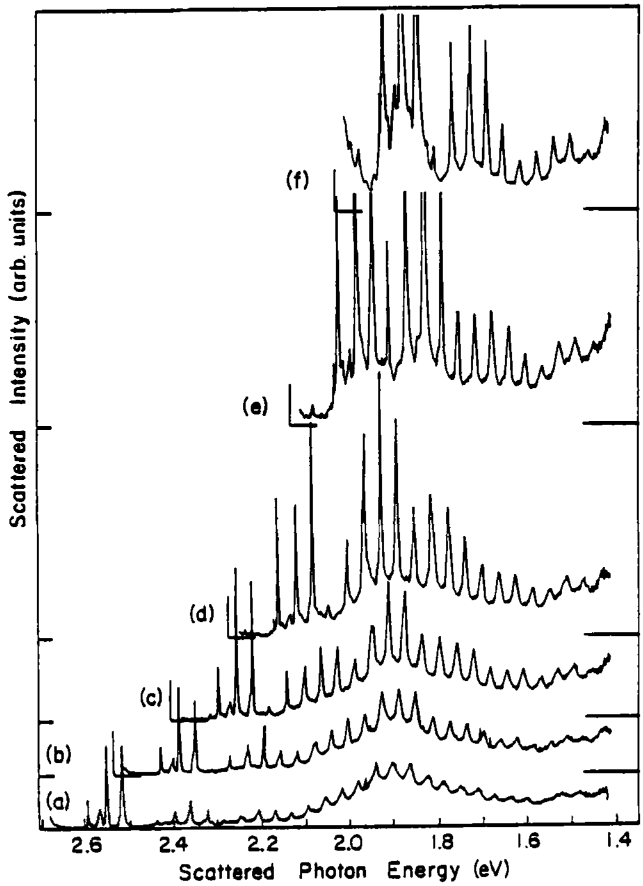

FIGURE 8 Spectra excited at five different laser wavelengths in cis $(CH)_x$. The broad luminescence band at 1.9 eV and the edge of another at 1.3 eV are apparent in each. Laser wavelengths: (a) 457.9 nm (b) 488.0 (c) 514.5 (d) 545.0 (e) 580.0 (f) 610.0 . (From Ref. 1)

and their integrated intensity does vary dramatically as the laser frequency is changed. This variation in intensity can be seen in excitation profiles measured by Lichtmann[1] for each of the principal Raman features at twenty different laser frequencies. For example, Fig. 9 shows the variation in scattered intensity for the fundamental at 1250 cm^{-1}. The resonance in this case occurs when the incident photon is close in energy to the first vibronic peak in the cis

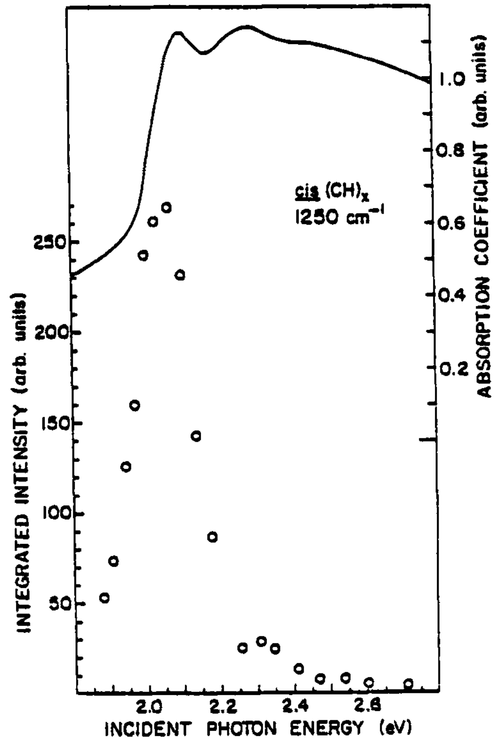

FIGURE 9 Excitation profile (open circles) for the intensity of the 1250 cm^{-1} Raman fundamental in cis (CH)$_x$. The upper curve shows the cis absorption band. (From Ref. 1)

absorption spectrum. The width of this resonance is about 1600 cm^{-1}, considerably less than the 7000 cm^{-1} width seen in trans (CH)$_x$.

Etemad et al[10] have suggested that the presence of luminescence here and its absence in trans (CH)$_x$ reflect the different decay channels for photo-generated solitons in the two isomers. In cis the solitons would not be mobile so there would not be the rapid dissociation proposed for trans. The difference in widths of the Raman resonances is in the right direction. On the other hand, these Raman and luminescence spectra of cis (CH)$_x$ are not unlike those observed for other conjugated molecules such as porphyrins[11] which cannot support solitons.

SHORT TRANS SEGMENTS IN AS-GROWN CIS $(CH)_x$

The as-grown cis $(CH)_x$ samples contain a small fraction of short trans segments, presumably formed during polymerization or subsequent handling, even when all operations are performed at low temperatures. The resonance behavior of these trans fragments is quite different: they show marked enhancement near 660 nm with strong overtone scattering. Fig. 10 shows the onset of this behavior in a sample of as-grown cis $(CH)_x$. The lower part (b) shows the normal cis fundamentals and first overtone peaks. The upper part (a) shows the enhancement of the formerly weak trans fundamental bands and the appearance of strong trans overtone bands when the laser is shifted further to the red, now corresponding the absorption edge in short trans segments. Nothing like this is seen at this wavelength in pure trans $(CH)_x$. It also appears that the second broad luminescence band in the as-grown samples may be associated with these fragments.

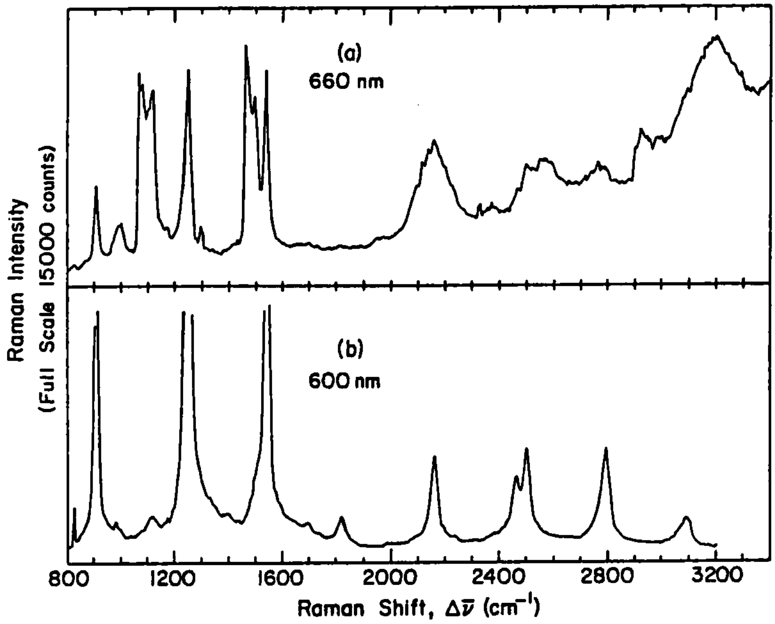

FIGURE 10 Resonance enhancement of the scattering from segments of trans $(CH)_x$ in as-grown cis $(CH)_x$, for two different wavelengths in the red. (From Ref. 1)

CONCLUSION

1) trans $(CH)_x$

Raman profiles at twenty laser frequencies and the optical absorption profile can be fit consistently by the inhomogeneous lineshape model provided there are many short conjunction lengths present. (About 50% of carbons are in conjugation lengths less than 30 carbons.) The strong variation in profile with isomerization conditions and sample treatment fits easily within this model.

2) cis $(CH)_x$

These spectra are very different from trans $(CH)_x$, but are not unlike spectra for other conjugated molecules (without solitons). Multiple-order Raman scattering, luminescence, and excitation profiles for many of the features have been measured.

3) Short trans Segments In As - Grown cis $(CH)_x$

Spectra here show a different behavior, with multiple order scattering strongly enhanced near the band edge.

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