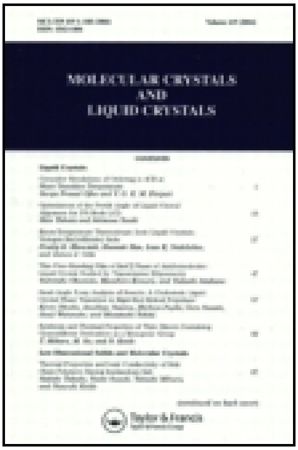

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Raman Probes of Photoexcited States in Polyacetylene

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To cite this article: D. B. Fitchen (1985): Raman Probes of Photoexcited States in Polyacetylene, Molecular Crystals and Liquid Crystals, 117:1, 411-420

To link to this article: http://dx.doi.org/10.1080/00268948508074659

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 411-420
0026-8941/85/1174-0411/$15.00/0

Printed in the United States of America

RAMAN PROBES OF PHOTOEXCITED STATES IN POLYACETYLENE

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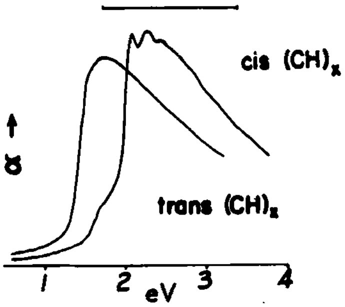
Abstract Efforts to characterize photoexcited states in polyacetylene in the frequency domain and in the time domain are briefly described. Recent evidence from Raman excitation profiles in cis $(CH)_x$ shows the importance of the inhomogeneously broadened exciton state near 2 eV, and suggests a comparable resonance should occur near 1.5 eV in trans $(CH)_x$. The formation and decay of photoexcited states is explored with time-resolved measurements using picosecond lasers.

Much of the emphasis in Raman studies of polyacetylene has been on characterization of the vibrational and structural properties of the ground state of the polymer. Here I describe very briefly two recent efforts to use Raman scattering techniques to probe photoexcited states in polyacetylene. The first is in the frequency domain, where we have determined the excitation profile for the Raman scattering in cis polyacetylene to identify the dominant intermediate state. The second is in the time domain, where we are using picosecond lasers to examine transient Raman scattering in photoexcited trans polyacetylene.

The optical absorption profiles for cis and trans polyacetylene are shown schematically in Fig. 1. Most of the Raman scattering experiments to date have used lasers in the range indicated by the bar at the top. Much of the interest has been in trans $(CH)_x$ even though these lasers do not span the important region at and below the absorption edge. On the other hand, these lasers do nicely span the region of the absorption edge and associated exciton structure in cis $(CH)_x$. We have just com-

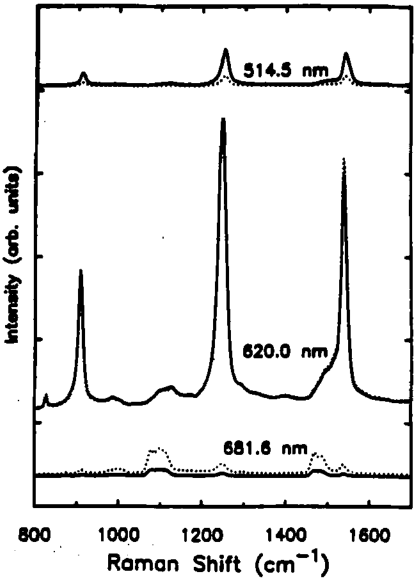
FIGURE 1. Schematic optical absorption of thin films of trans and cis polyacetylene. The bar at the top indicates the range of lasers usually used for Raman studies of $(CH)_x$.



pleted a comprehensive study of the resonance behavior of the Raman scattering in the vicinity of this cis absorption edge.[1]

Figure 2 shows an example of the Raman scattering due to the three principal cis backbone stretching modes at different laser wavelengths. The solid curves include the substantial corrections for absorption and reflection of the incident and scattered light, while the dotted curves do not. It is clear

FIGURE 2. Raman spectra of 96% cis $(CH)_x$ film measured at 77K at three laser wavelengths. The dotted curves show the relative yield of scattered photons per incident photon after correction only for instrument response. The solid curves show the relative quantum scattering efficiency after correcting also for absorption and reflection in the sample. (from Ref. 1)



that the scattered intensity goes through a pronounced maximum near 620 nm. However, in contrast to trans $(CH)_x$, these Raman profiles do not change dramatically with wavelength. On closer inspection there is some variation in the Raman profile for each of the cis modes as the laser is tuned through resonance. Fig. 3 shows this variation for the mode ν_2. The peak intensity has been normalized in each trace by multiplying by factors such as those at the right. There is an apparent shift of a few cm^{-1} near resonance, while the band becomes broader as one goes away from resonance. This change in the Raman bandshapes suggests that we have selective excitation of an inhomogeneous distribution of chains[2]. Local strain appears a more likely cause of this inhomogeneity than conjugation length.[3]

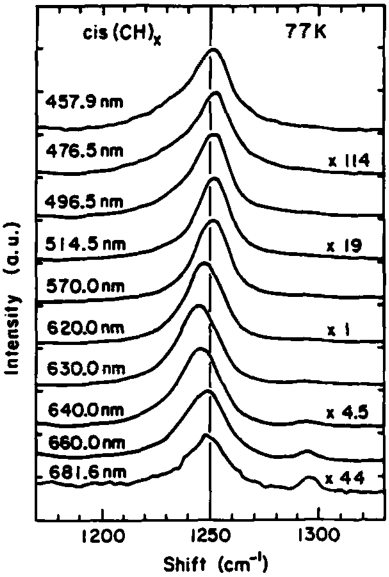


FIGURE 3. The normalized profile of the 1250 cm^{-1} Raman peak in cis $(CH)_x$ at 77K at ten laser wavelengths. (from Ref. 1)

When the corrected integrated intensity of each Raman peak is plotted versus laser photon energy one gets excitation profiles such as those shown in Fig. 4 for the fundamentals of cis

$(CH)_x$. The peak response in each case comes when the laser photon energy is close to the exciton peak (near 2.07 eV). The response at higher photon energies drops off much more quickly than the absorption (dotted curve). There is a suggestion of weak vibronic structure which is not well resolved. The peak in

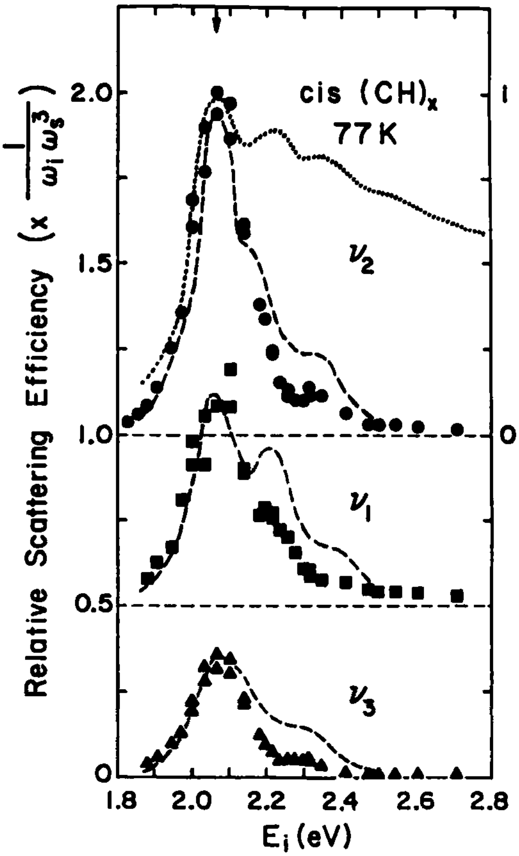


FIGURE 4. Raman excitation profiles for the three fundamental modes of *cis* $(CH)_x$ at 77K. Ordinate is relative quantum scattering efficiency (divided by $\omega_i \omega_s^3$ factor). Data points are from Ref. 1. Dashed curves are fits from Ref. 4.

the excitation profile is relatively broad. There is currently some controversy as to whether its breadth reflects homogeneous or inhomogeneous broadening processes. I believe that it is most likely inhomogeneous broadening, since it is still broad at low temperatures and since such a width could explain the variation in lineshape noted in Fig. 3.

The dashed curves in Fig. 4 show a fit to these profiles obtained very recently by Siebrand and Zgierski.[4] They find that the profiles can be fit reasonably well with the same Franck-Condon analysis and similar parameters as they used for β-carotene molecules in solution. Their fit was improved when they included a substantial (~310 cm^{-1}) inhomogeneous broadening for the exciton.

The fact that the Raman intensity peaks so strongly in the neighborhood of the exciton may have interesting implications for trans polyacetylene. Eckhardt[5] has pointed out that the intrinsic absorption edge in trans $(CH)_x$ may actually look much like that in cis $(CH)_x$, only displaced from 2 eV to about 1.5 eV. (The fact that the trans absorption appears broad and structureless in the usual thin film spectrum (c.f. Fig. 1) probably just reflects the fact that these samples are strained by the isomerization procedure.) If the absorption edge in trans $(CH)_x$ does have a prominent exciton peak near 1.5 eV, then there may well be a similar strong resonance enhancement of the Raman scattering for laser excitation near 830 nm. Much of the breadth and variation observed in the trans Raman lineshapes for visible laser excitation would then be a reflection of strongly perturbed segments excited far from the intrinsic resonance. Excitation near the exciton peak would give narrower lineshapes characteristic of unperturbed material. The preliminary experiments of Schott[6] reported at this conference are of much interest since they seem to confirm the presence of such a resonance in the infrared for trans $(CH)_x$.

I now turn to the second experiment, in which we look at photoinduced transients in the Raman scattering on a picosecond time scale. This experiment, being carried out by David Weidman in my lab, is still in its early stages. It is an outgrowth of picosecond pump and probe techniques used to investigate transient photoinduced changes in optical transmission. These techniques were applied to polyacetylene by Vardeny et al[7] and Shank et al[8], and more recently by Weidman.[9]

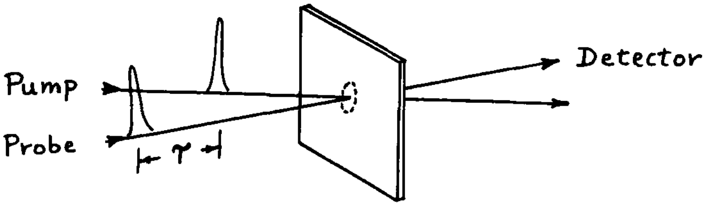


FIGURE 5. Schematic diagram of picosecond pump and probe experiment to detect transient photoinduced absorption.

The photoinduced absorption experiment is illustrated schematically in Fig. 5. A thin film of polyacetylene (~1000Å thick) is optically pumped and probed with laser pulses of picosecond or subpicosecond duration as shown. The pump pulses are focused on a small spot (~40μm dia.) and are of a wavelength to cause interband excitation throughout the illuminated volume. A non collinear beam of pulses probes this same region with each pulse delayed by a variable time τ after its pump pulse partner. The average transmitted intensity of the probe beam is monitored with a "slow" photodetector. Changes in this transmitted intensity are determined for different delay times, τ. Thus one is probing the illuminated region at various times after the pump excitation to see how the photoinduced changes decay.

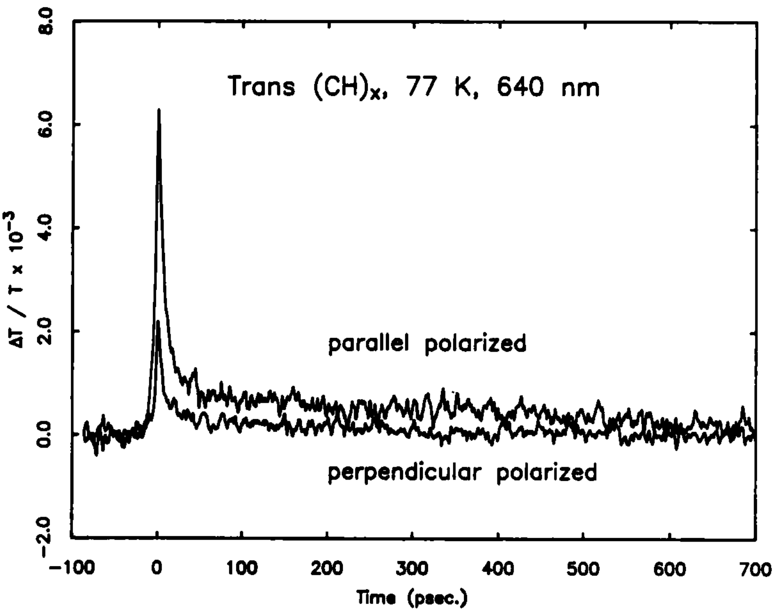


FIGURE 6. Example of transient bleaching in <u>trans</u> $(CH)_x$ measured as in Fig. 5. (from Ref. 9)

Fig. 6 shows an example of the sort of photoinduced change in transmission observed by Weidman[9] when pump and probe are both 3 ps pulses at the same wavelength. There is a very rapid rise in transmission at $\tau \sim 0$ to a peak value of a few parts in 10^3, after which this induced bleaching decays quickly. Most of the change is gone in a few ps, but relaxation continues for about 1 ns. The time behavior of this decay is close to the $t^{-1/2}$ dependence first noted by Vardeny,[7] who suggested geminate recombination is the dominant decay mode at short times.

Shank et al.[8] extended the experiment in several ways, using "white light" subpicosecond pulses to probe the induced changes at different wavelengths. They found that the photoinduced spectral changes in the picosecond regime were similar to those seen for the microsecond regime[10]. Namely, they found transient bleaching throughout the band and a new induced absorption band below the absorption edge, at about 1.35 eV in trans $(CH)_x$.

The experiment which we are doing looks for picosecond changes in Raman scattering using a similar geometry. The sample is illuminated with two trains of laser pulses as before, with a variable time τ between pump and probe. In fact the same photoinduced absorption measurement is performed in situ to monitor the changes in the illuminated region. The pump and probe pulses both excite Raman scattering. We collect the back-scattered light from both with a lens and pass it through a monochromator to a "slow" multichannel diode array detector to analyze the spectrum of the scattered light. In our preliminary version, both pump and probe pulses are at the same wavelength. When the pulses are well separated in time we expect to see the superposition of two identical Raman spectra. When the pulses are close in time, the Raman spectrum of the probe is affected by the prior photoexcitation of the pump. This may appear either as new Raman peaks associated with transient excited states, or as decreased scattering due to the picosecond transient bleaching.

Figure 7 shows an example of our preliminary results.[9] The Raman spectrum in the upper panel is that due to widely separated picosecond pulses. It is similar to that obtained for these thin trans films using low power cw excitation, even though the peak powers differ by more than four orders of magnitude.

The transient changes in the Raman spectrum (at $\tau \sim 0$) are shown in the lower panel. There is a reduction in intensity of the two strong Raman bands by about 2%, under the same conditions which cause a transient bleaching of a few parts in 10^3. This change seems to decay rapidly, so that it is mostly gone for $\tau \sim 10$ps. No new induced Raman peaks are detected at this noise level.

We hope to repeat the experiment at other wavelengths where induced absorption would suggest that we might see resonant Raman scattering from the transient photoexcited states.

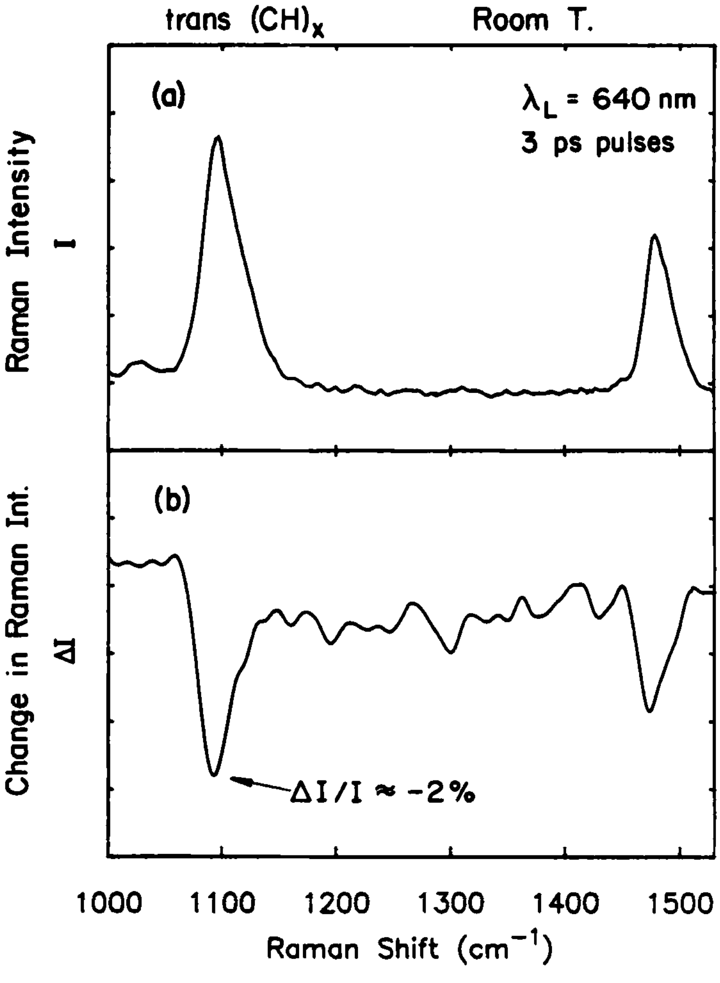


FIGURE 7. Picosecond Raman spectra of <u>trans</u> $(CH)_x$ at 300K, for 3ps pulses at 640 nm. a) Intensity with well separated pulses, τ - 1000 ps. b) Change in intensity relative to (a) for coincident pulses, τ - 0.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the people actually responsible for most of this work: L.S. Lichtmann, E.A. Imhoff and A. Sarhangi in the *cis* polyacetylene study, and D.L. Weidman in the picosecond experiments. The thin film samples were provided by H.W. Gibson (Xerox). Work at Cornell was supported by the National Science Foundation through the Materials Science Center.

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