Hot luminescence in *trans*-polyacetylene: A picosecond time-resolved study

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The picosecond time-resolved optical emission from *cis*- and *trans*-polyacetylene excited at 2.3 eV has been observed. The *trans* isomer shows an initial decay ≤ 5 psec followed by an exponential decay with a lifetime of 1200 ± 150 psec at 10 K. The spectrum of the observed emission is well above the band edge. The long-lifetime component, which contains over 90% of the integrated intensity, is interpreted to be hot luminescence. The *cis* isomer has principally a fast decay with a lifetime ≤ 15 psec.

Extensive studies have been conducted on the Raman spectroscopy of the isomeric forms of polyacetylene[1-6] [abbreviated $(CH)_x$]. The *trans* isomer emission spectrum is characterized by sharp features ($\simeq 50$ cm^{-1}) which change shape with the excitation frequency.[2,3,6] These changes have been interpreted variously as due to a chain length distribution resulting from inhomogeneous broadening of the optical absorption spectrum[2,3] and to hot luminescence.[6,7] A broad ($\simeq 3000$ cm^{-1}), weak background[1-6] is also evident. The spectrum for the *cis* isomer consists of relatively sharp lines with multiple overtones.[1,4] A broad emission is observed Stokes shifted to near the band edge (1.8 eV). Transient bleaching and absorption experiments have been conducted on a subpicosecond time scale by two different groups.[8,9] In one case transient bleaching was observed with both pump and probe optical energies of 2 eV.[8] The initial recovery was fit to a power law ($t^{-1/2}$) with the exponent changing to a smaller value for $t > 50$ psec. The bleaching depolarizes exponentially with a time constant of 1200 psec. These kinetics have been associated with a recovery mechanism involving thermalization of the initially generated excitations followed by carrier diffusion along the polyene chain.[8] Other measurements[9] were of transient absorption induced with 2-eV optical excitation and monitored with a subpicosecond continuum. These dynamical results were attributed to geminate recombination controlled by one-dimensional diffusion. Transient absorption experiments with microsecond resolution[10] have shown induced absorption in the band gap of *cis*- and *trans*-$(CH)_x$. Both isomers have a common spectral feature which is thought to arise from a self-localized state.[10] An additional absorption feature occurring in the *trans* isomer is suggested to result from a single carrier being added to a polyene chain.[10]

We report here the first observations of time-resolved emission from the $(CH)_x$ isomers. For *trans*-$(CH)_x$ we observe a very fast component (≤ 5 psec) and a long component comprising over 90% of the integrated emission intensity and having a decay time of 1200 psec. The integrated intensity is nearly independent of temperature over the range 10−300 K. Both of these decays occur from emission bands originating near the exciting laser line which is almost 1 eV above the band edge. The cw excited emission spectrum consists of sharp lines atop a broad background which contains over 90% of the integrated emission intensity. Their relative contributions to the respective spectra suggest that the broad emission decays with the long lifetime. Light emission occurring on a nanosecond time scale and nearly independent of temperature up to 300 K can only be due to a luminescence process.[11] Since the emission is well above the band edge, this represents a hot luminescence process.

The potential importance of this type of measurement is that time-resolved emission provides information about the radiative and nonradiative recombination pathways for the electron-hole pairs produced by optical excitation. Since transient absorption measurements are not necessarily sensitive to the populations of the emitting electronic states, luminescence dynamics provide information which is complementary to transient absorption data.

Films of *cis*-$(CH)_x$ approximately 75 μm thick were prepared in the usual way.[12] The samples were thoroughly washed to remove catalyst. They were kept *in vacuo* at −80 °C until used. *Trans* samples were prepared by heating the films in ampules at 207 °C for 30 min. Care was taken to avoid exposure

of the sample to air.

Picosecond time-resolved emission was measured on two different streak camera systems. Initial measurements were made using Nd-YAG excitation (30-psec pulses) and a streak camera system optimized for signal averaging of picosecond emission decays.[13] Subsequent measurements using Nd-glass excitation (7-psec pulses) and a streak camera system explored the luminescence out to 3 nsec. The time-resolved emission of *trans*-$(CH)_x$ is shown in Fig. 1(a). The initial decay follows the YAG laser pulse and is ≤ 5 psec. The long-time tail is about 0.2 times as intense and shows only a slight decay over the streak width. Figure 2 shows the decay on a slower sweep. The long-time tail decays exponentially with a lifetime of 1200 ± 150 psec.

The emission spectra as measured in the picosecond spectrometer using long-pass filters to isolate spectral regions are shown as inserts in Fig. 1. In *trans*-$(CH)_x$ both the long- and short-time components have similar spectral distributions. Thick films free of pinholes were mounted on either a

FIG. 2. The emission decay of *trans*-$(CH)_x$ at 10 K. The first spike is a timing reference pulse. The decay is the average of data from 20 laser shots. The insert is a logarithm plot of the data. The dashed line gives the best fit to the experimentally observed decay for $t > 400$ psec with an exponential time constant of 1200 ± 150 psec.

copper or quartz substrate. A signal was not observed for the quartz substrate without a sample. Estimates of the emission quantum yields were made by comparison with a fluorescence standard, the dye rhodamine 640. These estimates, good to within one order of magnitude, are for the short-time component 1×10^{-7} and for the long-time component 1.5×10^{-6}. The emission quantum yields are independent of YAG laser pulse intensity from $10^{14}-10^{16}$ photons/cm^2. The effective quantum yields decrease by less than a factor of 2 upon increasing the temperature from 10 to 300 K.

cw excited emission spectra were taken using a Spex Ramalog spectrometer with the sample immersed in liquid nitrogen. We observe a weak and broad luminescence component ($\simeq 4000$ cm^{-1}) which underlies the Raman spectrum and is present with both 5145- (shown in Fig. 3) and 4880-Å excitation. The band shapes of the sharp features change with the excitation wavelength in the expected
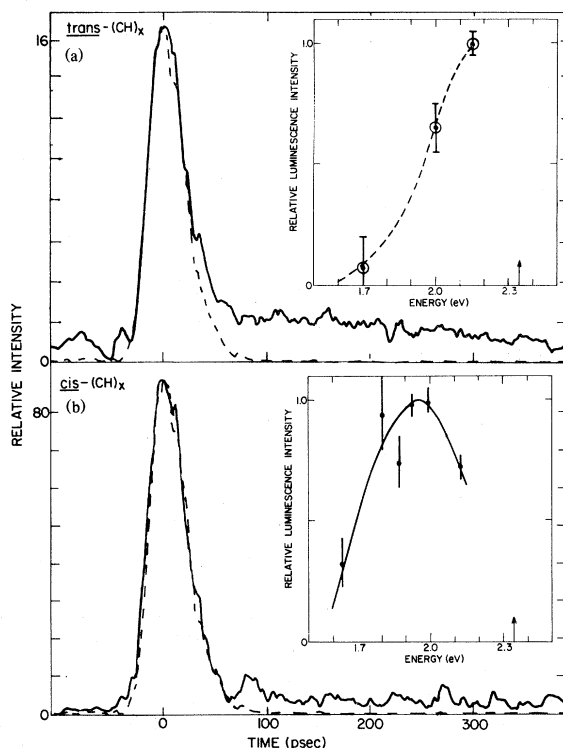

FIG. 1. The emission decay of (a) *trans*- and (b) *cis*-$(CH)_x$ at 10 K. The dashed line is the YAG laser pulse. The decays are the average of data from 300 laser pulses. The inserts are luminescence spectra for *cis*- and *trans*-$(CH)_x$ obtained with the picosecond spectrometer. The lines represent a suggested spectral shape. The arrow at 2.34 eV is the optical excitation energy.
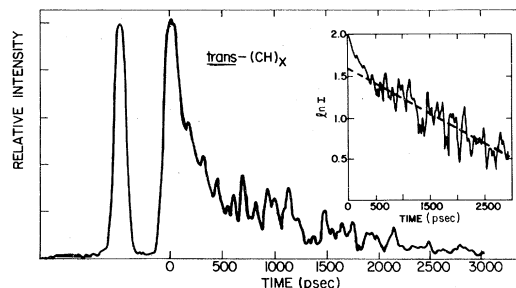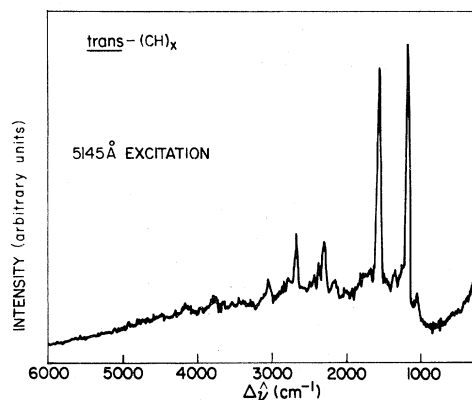

FIG. 3. The emission spectrum of *trans*-$(CH)_x$ at 77 K with 5145-Å excitation.

way.[2,3,5,6] Our spectrum is consistent with other reported spectra[1-6] though in Ref. 4 the background is attributed to the mounting substrate. By suspending the sample in liquid nitrogen rather than anchoring it to a substrate we feel that luminescence from the substrate or other extraneous sources, as suggested in Ref. 4, has been eliminated. The varying amount of fluorescence background[1-6] in other reported spectra is an indication that material preparation may be a key factor in determining the source of the broad emission. In particular, recent studies have shown a correlation between the intensity of the broad emission in this spectral region and the *cis* content of the films.[14] Our samples contain a residual *cis* double-bond content of 3%.[15]

Two aspects of the data support the assignment that the long-time decay is the result of a luminescence process. The first is that the quantum yield for this component is almost independent of temperature. Dephasing of the optical transition generates luminescence and causes a loss of Raman scattering intensity.[11] Typical sources of dephasing are population decay, phonon scattering, and defect scattering. The phonon scattering process arises from thermally populated phonons in the material and at temperatures near 300 K occurs on a subpicosecond time scale.[16] Second, in a material which can have efficient multiphonon decay, we would expect picosecond dephasing times even at low temperatures.[17] Therefore, nanosecond decay is expected to be associated with a hot luminescence process.

The carriers responsible for the long-time decay may be partially thermalized and associated with traps or other localized states distributed at all energies through the band. These localized states may be due to structural defects in the polyene chains. *Cis* double bonds are one type of defect we know to be present in our samples[15] and correlated with emission in this region.[14] Though for materials with such low quantum yields it is difficult to eliminate the possible contribution of impurity emission, we have seen no evidence for this in the five samples examined. The similarity of our cw and picosecond spectra to those reported by other groups[1-6,14] leads us to feel that our observations are intrinsic to polyacetylene.

Energy in excess of the band edge is usually rapidly converted to heat by a multiphonon emission on a picosecond time scale.[17] This path cannot be very efficient for the states emitting over many hundreds of picoseconds and containing energy more than 1 eV in excess of the band edge. The reason for the slow decay is presently the subject of speculation. At least two possibilities exist. The first is that there are dislocated chain segments that are not oriented properly for energy transfer to the bulk of the chains in the fibrils. Another possibility is that these states are of triplet multiplicity or for other reasons have a very small coupling to other levels resulting in transfer rates which are naturally smaller.

In recent work Lauchlin *et al.*[6] have attributed the sharp spectral components in the *trans*-$(CH)_x$ emission to hot luminescence.[7] Experiments of the type presented here could help to distinguish between Raman scattering and luminescence in these systems if enough time resolution were available to resolve the dephasing of the optical resonance.[18] Since at this time we do not have the required time resolution we cannot evaluate this interpretation from our experiments. Raman scattering and hot luminescence manifest different linewidths in general; therefore examination of the spectra and their temperature dependence may also have a bearing on this question.[11]

The *cis*-$(CH)_x$ emission decay is shown in Fig. 1(b). The principal decay follows the laser pulse and is ≤ 15 psec.[19] The estimated quantum yield is 1.5×10^{-6}. The spectrum of the *cis* isomer taken with the picosecond spectrometer is consistent with the reported cw excited emission spectra[2-4] and is dominated by emission from the band edge. For *cis*-$(CH)_x$ the dominant features of the time decay appear more straightforward. Both the relaxed band-edge luminescence and the Raman scattering decay very rapidly. We estimate the oscillator strength of the emitting state near the band edge to be ≥ 0.1 from the measured quantum yield of 10^{-6} and upper limit on the lifetime. This means that if this emission is due to a polaronlike state it has an unexpectedly large transition moment.[20] The present measurement suggests that the emission arises from the interband transition. Further studies to place a lower limit on the luminescence lifetime could give higher limits on the oscillator strength of the transition. The long-time component observed in the *cis* isomer could have a source similar to that in the *trans* isomer. Further studies of this type can have bearing on the nature of the emitting states and the relaxation pathways leading to the conducting states.

Our results for the luminescence in *trans*-$(CH)_x$ have in common with the reported picosecond transient absorption experiments[8,9] both fast time-scale decay and a long-time component lasting on the order of 1 nsec. Since we cannot resolve the emission decay at the shortest times it is possible that this unresolved component follows other than exponential decay kinetics. The long-time tail is best fit by an exponential decay. Exponentially decaying luminescence is not expected from recombination of carriers which have sampled a distribution of sites[8] or undergone a 1D random walk[9] but supports the conclusion that this emission arises from trapped or otherwise immobilized excitations inside the band. The common exponential decay time constant of 1200 psec reported here and for the bleaching depolarization[8] suggests that at least part of the observed transient absorption may originate from the "hot" states which give rise to the luminescence.

[1]H. Shirakawa and S. Ikeda, Polym. J. 2, 231 (1971); H. Shirakawa, T. Ito, and S. Ikeda, *ibid.* 4, 460 (1973); I. Harada, M. Tasumi, H. Shirakawa, and S. Ikeda, Chem. Lett. 12, 1411 (1978).

[2]L. S. Lichtman, D. B. Fitchen, and H. Temkin, Synth. Met. 1, 139 (1979/1980).

[3]H. Kuzmany, Phys. Status Solidi (b) 97, 521 (1980).

[4]L. Lauchlan, S. Etamad, T.-C. Chung, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B 24, 3701 (1981).

[5]D. B. Fitchen, Mol. Cryst. Liq. Cryst. 83, 95 (1982).

[6]L. Lauchlan, S. P. Chen, S. Etemad, M. Kletter, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B 27, 2301 (1983).

[7]E. J. Mele, Solid State Commun. 44, 827 (1982).

[8]Z. Vardeny, J. Strait, D. Moses, T.-C. Chung, and A. J. Heeger, Phys. Rev. Lett. 49, 1657 (1982).

[9]C. V. Shank, R. T. Yen, R. L. Fork, J. Orenstein, and G. L. Baker, Phys. Rev. Lett. 49, 1660 (1982).

[10]J. Orenstein and G. L. Baker, Phys. Rev. Lett. 49, 1043 (1982).

[11]R. M. Hochstrasser and C. A. Nyi, J. Chem. Phys. 70, 1112 (1979).

[12]T. Ito, H. Shirakawa, and S. Ikeda, J. Polym. Sci. Polym. Chem. Ed. 12, 11 (1974).

[13]W. Knox and G. Mourou, Opt. Commun. 37, 203 (1981).

[14]E. A. Imhoff, D. B. Fitchen, and R. E. Stahlbush, Solid State Commun. 44, 329 (1982).

[15]H. Gibson, S. Kaplan, R. Mosher, W. Prest, and R. Weagley (unpublished).

[16]C. B. Harris, J. Chem. Phys. 67, 5607 (1977).

[17]D. von der Linde, J. Kuhl, and R. Lambrich, in *Picosecond Phenomena II,* edited by R. M. Hochstrasser, W. Kaiser, and C. V. Shank (Springer, New York, 1980), p. 275.

[18]J. M. Friedman and R. M. Hochstrasser, Chem. Phys. 6, 155 (1974).

[19]Experimental uncertainty in the position of $t = 0$ for cis-$(CH)_x$ forces the larger limit on the fast decay.

[20]S. Etemad, A. Feldblum, A. J. Heeger, T.-C. Chung, A. G. MacDiarmid, A. R. Bishop, D. K. Campbell, and K. Fesser (unpublished).