Photoexcitation Dynamics in Polyacetylene Probed by Transient Photoinduced Resonance Raman Scattering

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We have measured photoexcitation dynamics in the picosecond time domain in fully *trans* and partially isomerized $(CH)_x$ and $(CD)_x$ films with different *cis*/*trans* content ratios, using the technique of transient photoinduced resonant Raman scattering. Following the distinctively different decay kinetics of *cis* and *trans* resonantly enhanced vibrations, we observed an intersystem crossing of photoexcitations from *cis* to *trans* segments which is dominated by a diffusion process in the *cis* segments, with a time constant between 24 and 215 ps depending on the *cis*/*trans* ratio.

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The properties of polyacetylene $[(CH)_x]$ have been extensively studied in the last decade, in part because it is the simplest of conducting polymers, and hence, the easiest to compare with model calculations [1,2]. Based on the suggestion that the lowest lying electronic excitations in *trans*-$(CH)_x$ are topological defects, solitons with unusual quantum numbers [1], which can be photogenerated with above gap photon absorption [3], many of the recent experimental studies of $(CH)_x$ have focused on photospectroscopy [1,2]. In particular, picosecond transient photoinduced absorption (PA) measurements [4-6] have played a central role in the study of the formation and dynamics of soliton excitations.

$(CH)_x$ is unique in that two isomers, *cis* and *trans*, coexist in partially isomerized samples before complete isomerization to the more stable *trans* isomer is achieved by heat treatment at elevated temperature (~180 °C). Unlike the *trans* isomer, the *cis* isomer does not support soliton excitations because of a lack of degeneracy in its backbone structure [1]. It has been assumed, therefore, that photoexcitations in *cis* segments are self-trapped singlet excitons which quickly recombine, accompanied by a moderately strong photoluminescence at 1.96 eV [7]. Transient PA measurements in partially isomerized $(CH)_x$ samples show, however, a fast decay which stops at about 10 ps [4,8]. To explain this phenomenon, it has been suggested [9] that the PA is dominated by photoexcitations in *trans* segments and consequently the photoexcitation dynamics in *cis*-$(CH)_x$ have never been measured.

In this paper we introduce a novel technique, "two-color" transient photoinduced resonant Raman scattering (TPRRS) with picosecond resolution, in which the transient response of individual resonantly enhanced phonons in the system can be separately monitored with *different* pump-probe wavelengths. Since the strongly coupled resonant vibrations in *cis* and *trans* $(CH)_x$ have different frequencies and since their intensities in resonant Raman scattering (RRS) can be influenced separately by photoexcitations in *cis* and *trans* segments [10], respectively, the photoexcitation dynamics in *cis* can be obtained by monitoring the TPRRS response of the *cis*-$(CH)_x$ phonons. We observed, for the first time, a fast migration of photoexcitations from *cis* into *trans* segments, which is dominated by a diffusion process in the *cis* segements. Three partially isomerized $(CH)_x$ and $(CD)_x$ films with different *cis*/*trans* content ratios have been measured. We found that the fast exciton migration process exists in all of them, with a time constant between 24 and 215 ps, depending on the *cis*/*trans* content ratio in the film.

TPRRS spectra were excited using a mode-locked Nd:YAG laser which was frequency doubled and synchronously pumped two dye lasers (pump and probe) producing pulses typically with 2-ps time durations and 0.2-nJ energies at a repetition rate of 76 MHz. The time resolution of the system, as estimated by the cross correlation of the dye laser pulses in potassium dihydrogen phosphate, was about 5 ps. The pump and probe beams were focused onto the sample through a sapphire substrate using an achromatic lens, and complete overlap was assured by maximizing the PA signal. The Raman scattering was monitored in the forward direction using a triple spectrograph with 3-cm^{-1} resolution coupled to a multichannel charge-coupled device detector. Spectra were recorded [11] with different time delays τ between pump and probe.

The partially isomerized $(CH)_x$ and $(CD)_x$ thin films used in our measurements are summarized in Table I. The *cis*/*trans* content ratio has been estimated [10] by RRS measurements at 580 nm. $(CH)_x$ No. 1 was subsequently isomerized into fully *trans*-$(CH)_x$ by thermal annealing at 180°, and TPRRS measurements were repeat-

TABLE I. Fitting (τ_3) and observed (τ_0) time constants for the TPRRS decays in the partially isomerized $(CH)_x$ and $(CD)_x$ films.

Sample	% *cis*	$10^{-2}\times(\% \, cis)^2$	τ_3 (ps)	τ_0 (ps)
$(CD)_x$	20	4	28	35
$(CH)_x$ No. 2	37	13.7	105	110
$(CH)_x$ No. 1	50	25	215	210

ed on the same film.

Collection of a single TPRRS spectrum at a fixed pump-probe delay τ required recording four data sets [10,11]: (1) RRS scattered intensity I_A excited by the pump beam alone; (2) I_B excited by the probe beam alone; (3) I_{A+B} excited by both beams simultaneously; and (4) I_C which measured the background spectrum without laser excitation. The TPRRS signal is the change ΔI in the probe RRS intensity I_B induced by the pump beam. The ΔI spectrum is then obtained [11] by subtracting: $\Delta I = I_{A+B} + I_C - (I_A + I_B)$. To obtain a satisfactory signal-to-noise ratio, between 4 and 10 spectra at each τ were averaged.

Typical room-temperature TPRRS spectra of the fully isomerized *trans*-$(CH)_x$ film are shown in Fig. 1 (top panel) for both pump and probe beams at 750 nm. Figure 1(a) is the cw RRS spectrum showing the two dominant resonantly enhanced vibrations of *trans*-$(CH)_x$ [10]: the C—C stretching mode at 1070 cm^{-1} and the C=C stretching vibration at 1450 cm^{-1}. Figures 1(b)-1(d) are normalized TPRRS (ΔI) spectra at $\tau = 0$, 20, and 100 ps, respectively. We note that $\Delta I < 0$, and its maximum value at $\tau = 0$ is $\Delta I/I \approx 2\%$ [10,11].

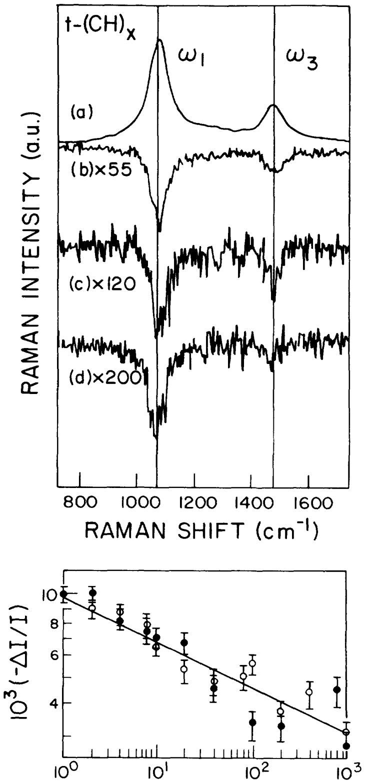

FIG. 1. Upper panel: (a) cw and (b)-(d) normalized transient photoinduced RRS spectra of *trans*-$(CH)_x$ at room temperature, excited and probed at 750 nm. The pump-probe delays are $\tau = 0$, 20, and 100 ps for spectra (b)-(d), respectively. Lower panel: TPRRS decays of the *trans*-$(CH)_x$ film excited at 580 nm. Solid circles are for probe at 580 nm; open circles are for probe at 750 nm. The line through the data is a power-law decay $\tau^{-\alpha}$ with $\alpha = 0.17$.

The TPRRS sign can be readily explained by a reduction in the RRS cross section associated with real photoexcitations which block the electronic transitions available in the absence of the pump beam. Similar bleaching of transitions occurs in the PA spectrum resulting in increased transmission: $\Delta T > 0$ [5,8]. For our sample $\Delta I/I$ ($\approx 2\times10^{-2}$) is larger than $\Delta T/T$ ($\approx 3\times10^{-3}$) [8,10,12] and this can be explained using the phase space filling (PSF) model [13] to describe $\chi^{(3)}$ response in resonance. Within this model $\chi^{(3)}$, which influences both TPRRS and transient PA signals, is proportional to the density ratio of the photoexcited excitons N_x and the excitons at saturation N_s ($\chi^{(3)} \sim N_x/N_s$) [13]. Using this form of $\chi^{(3)}$, we calculate for TPRRS $\Delta I/I = 2N_x/N_s$, whereas for PA $\Delta T/T = adN_x/N_s$, where ad is the optical density (OD) of the sample film. Consequently, $\Delta I/I = (2/\mathrm{OD}) \times \Delta T/T$, and since for our thin films OD < 0.2 at 750 nm, this explains the larger $\Delta I/I$ signal for the TPRRS. We also note in Fig. 1 that the TPRRS spectrum does not shift with τ, contrary to previous results [10]. Since we did observe a time-dependent shift of the TPRRS C=C stretching in other films, we conclude that this effect is sample dependent, possibly correlated with sample inhomogeneity [10].

For $\tau > 0$ ΔI decays. As shown in Fig. 1 (lower panel), in a fully isomerized *trans*-$(CH)_x$ film both "one color" and "two color" (pump at 580 nm, probe at 750 nm) TPRRS have the same relaxation kinetics: $\Delta I(\tau)$ has a power-law decay $\tau^{-\alpha}$ with $\alpha = 0.17$. This is in agreement with measurements of $\Delta T(\tau)$ in *trans*-$(CH)_x$ at $\tau > 30$ ps [5,8] for probe wavelengths where the contribution of the transient strain oscillations in ΔT is negligibly small [14].

The transient dynamics are more complicated in partially isomerized $(CH)_x$ and $(CD)_x$ films, since with laser excitation $\hbar\omega_L \gtrsim 2.1$ eV, photoexcitations in both *cis* and *trans* segments can be simultaneously generated. However, by separately monitoring the *cis* and *trans* resonantly enhanced vibrations using TPRRS at different laser wavelengths, we can separately follow the population decay in both isomers. This is demonstrated in Fig. 2 for the 50% partially isomerized $(CH)_x$ film. Figure 2(a) shows the cw RRS spectrum consisting of two *cis* lines (denoted by C) at 900 and 1250 cm^{-1}, respectively, and a *trans* line (denoted by T) at 1070 cm^{-1}. Figure 2(b) shows the TPRRS spectrum at $\tau = 0$ with both pump and probe beams at 580 nm. $\Delta I < 0$ for the vibrations of both isomers, but it is 2.5% for the *cis* lines and only about 1.2% for the *trans* line. This can be readily explained by the different *cis* and *trans* resonances. At 580 nm the *cis*-$(CH)_x$ lines are in full resonance, whereas the resonance of the *trans* lines is weaker; the *trans* lines in partially isomerized films become in full resonance only for $\lambda \gtrsim 750$ nm [15], where the *cis* RRS lines are not observed at all. We believe, therefore, that the *trans* line in

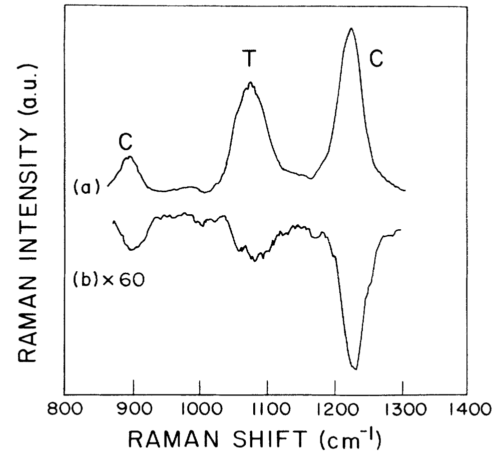

FIG. 2. (a) cw RRS and (b) normalized TPRRS at $\tau=0$ for a 50% partially isomerized $(CH)_x$ film, excited and probed at 580 nm. *cis* (*C*) and *trans* (*T*) Raman lines are indicated.

the TPRRS spectrum of partially isomerized $(CH)_x$ films at 580 nm does not properly reflect photoexcitation dynamics in the *trans* segments. In order to follow the photoexcitation dynamics in the *trans* segments we then used two color TPRRS with the pump at 580 nm and probe at 750 nm (in full resonance with *trans* segments). This also has the advantage that at 580 nm, photoexcitations are generated in both *cis* and *trans* segments enhancing the capability to observe a possible intersystem crossing process.

Figure 3 shows the cw RRS and TPRRS decays of two $(CH)_x$ films. From the cw RRS spectra we have obtained the *cis*/*trans* content ratios. It is 50% *cis* in film No. 1, whereas film No. 2 shows 37% *cis* with an uncertainty of about 7%. The TPRRS decays [Figs. 3(b) and 3(c), respectively] substantially deviate from the power-law decay observed in the 100% *trans* film (Fig. 1) or when excited and probed at 750 nm. $\Delta I(\tau)$ stops decaying after about 30 ps for both films, and contrary to expectation [4–8], it begins to increase forming an apparent peak at $\tau_0=210$ ps in $(CH)_x$ No. 1 and at 110 ps in $(CH)_x$ No. 2. We note that the TPRRS decay remains in the form of $\tau^{-\alpha}$ for both films, when *excited* and *probed* at 750 nm.

The same phenomenon occurs in partially isomerized $(CD)_x$ samples, as shown in Fig. 4, proving that the photoexcitation dynamics in partially isomerized films are isotope independent. From Fig. 4(a), which shows the cw RRS spectrum of the C=C stretching vibrations of *cis* and *trans* $(CD)_x$ at 580 nm, we determine this sample to have 20% *cis*. Figure 4(b) shows that the two color TPRRS decay pumped at 580 nm and probed at 750 nm also contains an apparent peak, now at $\tau_0=35$ ps (Table I).

Based on the TPRRS decays in Figs. 3 and 4, we believe that when excitations in both isomers are generated, a fast photoexcitation intersystem crossing occurs from *cis* to *trans* segments. This crossing is possible because

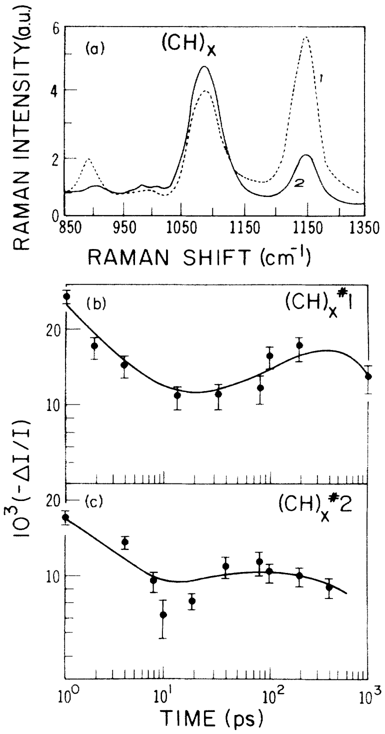

FIG. 3. (a) cw RRS spectra of partially isomerized $(CH)_x$ No. 1 and No. 2 (see Table I) excited at 580 nm. (b),(c) TPRRS decays of $(CH)_x$ No. 1 and No. 2, respectively, excited at 580 nm and probed at 750 nm. The line through the data is a theoretical fit, see text and Table I.

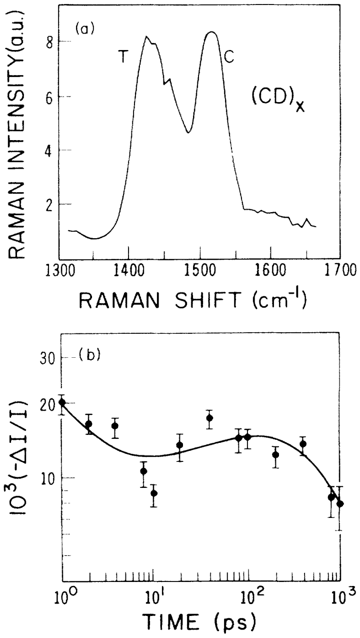

FIG. 4. (a) cw RRS spectrum of the C=C stretching vibration of *cis* (*C*) and *trans* (*T*) segments in partially isomerized $(CD)_x$ (Table I), excited at 580 nm. (b) TPRRS decay excited at 580 nm and probed at 750 nm. The line through the data is a theoretical fit to the data (see text and Table I).

trans segments have a lower energy gap (~1.8 eV) [16] than *cis* segments (≈ 2.1 eV) [9,10] and, therefore, are more energetically favorable. Consequently, exciton migration occurs into the *trans* segments. The decay of ΔI in the fully isomerized *trans*-$(CH)_x$ sample shown in Fig. 1, on the other hand, is a smooth power law regardless of the probe laser wavelength, in agreement with the lack of *cis* segments in this film.

From Table I we see that the secondary peak in $\Delta I(\tau)$ occurs at different τ_0 which actually depends on (% *cis*)^2 in the film, and is isotrope independent. This is consistent with an intersystem crossing dominated by a photoexcitation diffusion process in the *cis* segments: $(\bar{l})^2 \cong D\tau_0$, where $\bar{l}$ is the average length of the *cis* segments and D is the exciton diffusion constant, and $\bar{l}$ is proportional to the *cis/trans* ratio (% *cis*).

For a more quantitative description of our data we assume that the photoexcitation dynamics in the *trans* segments arise from initial photogeneration with density $n_1(t)$ and from the intersystem crossing from the *cis* segments with density of $n_2(t)$, and $n = n_1 + n_2$. The decay of n_1, arising from geminate recombination in the *trans* segments [4], varies according to $n_1(t) = n_1(0)\mathrm{erf}(-t/\tau_1)$ with $\tau_1 \approx 0.1$ ps [4]. The intersystem crossing term n_2, however, is subject to generation (G) from the *cis* segments and monomolecular recombination:

$$\frac{dn_2(t)}{dt} = G(t) - \frac{n_2(t)}{\tau_2}. \tag{1}$$

$G(t)$ in Eq. (1) is determined by the dynamics of the photoexcitations $N(t)$ in the *cis* segments. For $N(t)$ we consider 1D exciton diffusion along the *cis* segments towards the chain ends [17-19]. For this case $N(t) = N(0) \times \exp[-(t/\tau_3)^{1/2}]$ [17-19], where τ_3 is the average diffusion time, $\tau_3 \sim (\bar{l})^2$. Since the exciton recombination rate at the ends of the *cis* segments is equal to the generation rate into the *trans* segments, $G(t)$ can be obtained from $dN(t)/dt$:

$$G(t) = \frac{N(0)}{[2(\tau_3 t)^{1/2}]} \exp\left[-\left(\frac{t}{\tau_3}\right)^{1/2}\right]. \tag{2}$$

The solution of Eqs. (1) and (2) is

$$n_2(t) = n_2(0)\left(\frac{\tau_2}{\tau_3}\right)^{1/2}\left\{F(\varepsilon)\exp\left[-\left(\frac{t}{\tau_3}\right)^{1/2}\right] + F(\mu)\exp\left(-\frac{t}{\tau_2}\right)\right\} \tag{3}$$

with $\varepsilon = (t/\tau_2)^{1/2} - \mu$, $\mu = \frac{1}{2}(\tau_2/\tau_3)^{1/2}$, and F is the Dawson integral. We have fitted the $\Delta I(\tau)$ decays in Figs. 3 and 4 using Eqs. (1) and (3), the *cis/trans* content ratio from Table I, $\tau_1 = 0.5 \pm 0.3$ ps, and $\tau_2 = 1500$ ps for all samples. With different τ_3 for each sample as given in Table I, the fit to the various ΔI decays is good except for τ just before the secondary peaks (Figs. 3 and 4). We note that the parameter τ_3 scales with (% *cis*)^2 similar to τ_0 in the experimental curves.

In conclusion, we have demonstrated a new technique for studying photoexcitation dynamics in conducting polymers, the two color TPRRS method, in which the photoinduced changes in each resonantly enhanced phonon can be separately monitored. We have applied this technique to thin films of *trans*-$(CH)_x$ and partially isomerized $(CH)_x$ and $(CD)_x$ and showed that TPRRS is more sensitive to photoexcitation kinetics than transient PA. We have followed for the first time photoexcitation dynamics in *cis* segments and showed that fast exciton migration into the more energetically favorable *trans* segments takes place, which involves diffusion in the *cis* segments.

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