Photogeneration of solitons in *trans*-$(CH)_x$: The reversed spin-charge relation of the photoexcitations

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High-sensitivity ESR studies of *trans*-$(CH)_x$ have been carried out during photoexcitation with $\hbar\omega > E_g$. The results set an upper limit on the number of photoinduced unpaired spins, which is more than 2 orders of magnitude smaller than the number of charged excitations photogenerated under the same experimental conditions. We conclude that the charged photoexcitations are spinless and therefore have the reversed spin-charge relation of solitons. The photogeneration branching ratio, neutral solitons to charged solitons, is less than 10^{-2}.

I. INTRODUCTION

The possibility that solitonlike excitations of the coupled electron-lattice system may play an important role in the physics of *trans*-$(CH)_x$ has recently stimulated considerable research activity. Such nonlinear excitations are of broad interest to the scientific community, ranging from chemistry (stabilized carbonium ion or carbanion) to particle physics and field theory as well as condensed matter physics. Consequently, the study of solitons in this prototype quasi-one-dimensional polymer offers a special opportunity.[1] In this paper, we demonstrate that the charged photoexcitations in *trans*-$(CH)_x$ are solitons, and we use electron-spin resonance (ESR) during photoexcitation to establish the unique reversed spin-charge relation predicted for such solitons.

Because of the electron-hole (e-h) symmetry of *trans*-$(CH)_x$, the creation of a bond-alternation domain wall in the polymer chain structure causes the formation of an associated localized electronic state at midgap.[2,3] The resulting soliton (structural domain wall plus localized electronic state) can be neutral with spin $\frac{1}{2}$ (one electron in the midgap level) or charged $+$ or $-$ with spin zero (zero or two electrons, respectively, in the midgap level). The reversed spin-charge relationship for solitons in *trans*-$(CH)_x$ is a direct manifestation of charge fractionalization discovered in the mathematical analysis of spinless fermion systems.[4] In *trans*-$(CH)_x$ the localized midgap state of the soliton derives from one-half a state removed from the occupied valence band and one-half a state removed from the empty conduction band *for each sign of spin.* Thus although the charge fractionalization is masked by the spin degeneracy in *trans*-$(CH)_x$, the resulting reversed spin-charge relation has the same physical origin.[2,5]

Soliton-antisoliton pairs can be generated on a *trans*-$(CH)_x$ chain either by charge-transfer doping or by photoexcitation. Transport,[6–8] optical,[9,10] infrared,[11–13] and magnetic[14–16] studies of *trans*-$(CH)_x$ at dilute doping levels have previously been shown to be consistent with the soliton-doping mechanism. However, because of the complications which arise from nonuniform doping, from uncertainty in the precise nature of the dopant species (e.g., AsF_5 and/or AsF_6^-), and from the addition of the Coulomb potential of the charged dopant ion, a variety of alternative explanations have been proposed.[17] In this context the possibility of photogeneration of soliton-antisoliton pairs is particularly attractive.

Su and Schrieffer[18] and Mele[19] have carried out molecular dynamics calculations which follow the time evolution of the displacement pattern on the $(CH)_x$ chain after the photoinjection of an electron-hole (e-h) pair. They found that the photoinjected pair evolves to a soliton-antisoliton pair in a time of the order of an optical phonon period, i.e., $\sim 10^{-13}$ sec. Subsequently, a number of photoinduced absorption experiments[20–23] were successfully carried out on *trans*-$(CH)_x$ with results which agree with the Su-Schrieffer theory.

The photoproduction of soliton-antisoliton pairs implies formation of states at midgap. Orenstein and Baker[20] used transient spectroscopy to observe absorption due to photogenerated intrinsic gap states. They found two peaks for *trans*-$(CH)_x$, one at 1.4 eV near the band edge and one deep in the gap at about 0.5 eV. Their time-resolved studies indicate relatively long decay times; the 0.5-eV absorption decays slowly, falling by only about a factor of 2 in a few milliseconds, whereas the 1.4-eV maximum decays more rapidly (~ 100 μsec), indicating that these two features are not related. This conclusion is consistent with their observation of a photoabsorption peak near the gap edge (but nothing near midgap) in *cis*-$(CH)_x$. From a more detailed analysis of their results,[21] they concluded that the 0.5-eV absorption is due to a charged excitation whereas the gap edge feature arises from a neutral excitation (i.e., an exciton on the polyene chain). Independent evidence of photogenerated gap states has been reported by Salaneck *et al.*[24] with the use of photoemission from photogenerated excited states.

The time scale for the photogeneration of the gap states and the resultant bleaching of the interband transition was investigated by Shank *et al.*[25] and Vardeny *et al.*[26] using subpicosecond time resolution. They demonstrated that the gap states and the interband bleaching are produced in less than 10^{-13} sec, consistent with the predictions of Su and Schrieffer.[18] Vardeny *et al.*[26] furthermore concluded from analysis of the decay of photoinduced anisotropy that the photogenerated carriers are highly mobile (at least on a time scale less than 10^{-9} sec).

Infrared spectroscopy studies of lightly doped *trans*-

$(CH)_x$ have identified both the midgap electronic transition which arises upon doping[9,10] and the associated infrared active modes[11–13] introduced by the local lattice distortion. Vardeny *et al.*[22] and Blanchet *et al.*[23] have observed these same features in photoinduced ir-absorption experiments. *These important results demonstrate that both the photoinduced spectroscopic features and those induced by doping are associated with the same charged state.* Moreover, the observed frequencies and line shapes are consistent with those expected for charged-soliton excitations. The 0.5-eV absorption is the midgap transition shifted down in energy from $E_g/2$ by about 0.25 eV due to the electron-electron Coulomb interaction. The mid-ir modes at 1370 and 1260 cm^{-1} are consistent with the calculations of Mele and Rice[27] and Horowitz,[28] which predict the appearance of ir-active internal vibrational modes between each of the Raman modes of pure *trans*-$(CH)_x$.

All of the photoinduced ir-absorption peaks show a similar dependence upon laser intensity, increasing as $\sqrt{I}$ at low powers and saturating at about $I \simeq 50$ mW/cm^2. By comparing the strengths of the midgap absorption[9,10] and the absorption[11] at 1370 cm^{-1} to previous data from doped *trans*-$(CH)_x$, Blanchet *et al.*[23] estimate that the saturation occurs at a density of charged photoexcitations equivalent to a concentration of $\rho_{ch} \simeq 10^{17}-10^{18}$ cm^{-3} (i.e., $10^{-5}-10^{-4}$ per carbon atom). In independent experiments Vardeny *et al.*[22] obtained $\rho_{ch} \simeq 5 \times 10^{17}$ cm^{-3} at saturation.

In order to unambiguously identify the photoexcitations in *trans*-$(CH)_x$ as charged solitons, the reversed spin-charge relation must be demonstrated. By studying the electron-spin resonance in *trans*-$(CH)_x$ during photoexcitation, we have set an upper limit on the number of photoinduced spins which is 2–3 orders of magnitude smaller than the number of photoinduced charge carrying excitations. The implied reversed spin-charge relation thus identifies the excitations as charged solitons.

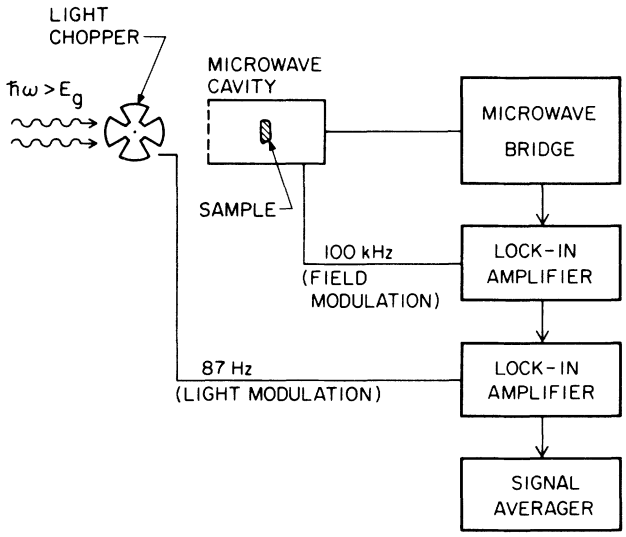

FIG. 1. Schematic diagram of experimental configuration for double modulation experiments.

II. EXPERIMENTAL TECHNIQUES

The experimental configuration is shown in Fig. 1. The spin resonance measurements were made with an IBM Instruments (Bruker) E-200D ESR spectrometer equipped with an optical access cavity. The signal-to-noise ratio was enhanced through the use of a Nicolet 1270 signal averager. The sample temperature was controlled by a variable temperature Helitran system. In order to minimize sample heating, helium gas was diffused into the sealed ESR tube.

The samples were semitransparent thin films (~ 0.1 μm) of *trans*-$(CH)_x$ which absorbed most of the incident light (optical denisty in the visible was greater than 2). The films were polymerized directly on the inner wall of an ESR tube as *cis*-$(CH)_x$ and subsequently isomerized to *trans*-$(CH)_x$ by heating to 180 °C for about 5 min. The dark signal corresponded to 3×10^{13} spins ($\sim 10^{19}$ cm^{-3}) with a linewidth at 300 K of about 1 G. Subsequent values for N_S used the dark signal as a secondary standard.

For illumination, we used the 2.41-eV line from an Ar-ion laser or the 1.96-eV line from a helium neon laser; both of these energies are larger than the band gap in *trans*-polyacetylene. The illuminated sample area was approximately 0.25 cm^2. The spin resonance was studied during illumination by searching for small changes in the ESR signal (laser on compared with laser off) and by using chopped light and a double-modulation technique. For the higher sensitivity double-modulation measurements, the standard derivative signal was detected with a lock-in amplifier at 100 kHz (output time constant of 1 msec) and the output was fed into a second lock-in set to detect at the chopping frequency. The resulting signal was then stored in the Nicolet 1270 for signal averaging. The laser light was chopped at 87 Hz. Vardeny *et al.*[22] measured the intensity of the photoinduced absorption at 0.5 and 0.17 eV as a function of laser-chopping frequency. They found that the response is flat until about 200 Hz, where the photoinduced absorption signal initially starts to roll off, falling to about one-half the initial value at about 10^3 Hz. Therefore, chopping at 87 Hz is sufficiently slow that any photoinduced ESR signal would follow the light intensity and be amplitude modulated by the chopped light. The sensitivity of the apparatus to photoinduced spins was verified through the observation of a spin resonance signal from spinach leaf in response to green laser light.

III. EXPERIMENTAL RESULTS

Measurements were made at 10 K, 100 K, and room temperature. At all three tempratures, the laser power on the sample was in the saturation regime (approximately equal to 20–100 mW/cm^2), where the photoinduced absorption signals are essentially independent of laser power.[22,23]

At room temperature and at 100 K, the double-modulation technique with signal averaging set upper limits on the number of photogenerated spins. Photoinduced ESR was not observed despite extensive signal averaging.

TABLE I. (a) Number of photoinduced spins (N_S) at $g=2$ (magnetic field sweeps at ±5 G about 3330 G), and (b) number of photoinduced triplets (N_t) (magnetic field sweeps ±60 G about $g=2$).

Temperature (K)	Laser intensity (mW/cm^2)	N_S(max)	ρ_S(max) (cm^{-3})
	(a)		
10	20	$\leq 3\times10^{10}$	$\leq 1\times10^{16}$
100	30	$<8\times10^{9}$	$<2.5\times10^{15}$
300	100	$<3\times10^{9}$	$<1\times10^{15}$
	(b)		
10	20	$<3\times10^{10}$	$<1\times10^{16}$
100	30	$<5\times10^{9}$	$<2\times10^{15}$
300	100	$<2\times10^{10}$	$<8\times10^{15}$

The experimentally determined upper limits at $g=2$ were $N_S(300\text{ K})<3\times10^{9}$ (1×10^{15} cm^{-3}) and $N_S(100\text{ K})<8\times10^{9}$ (2.5×10^{15} cm^{-3}). A series of broader sweeps (60 G above or below $g=2$) were carried out under continuous illumination to search for photogenerated triplets. Again, no signals were observed; upper limits on the number of triplets were set at less than 2×10^{10} (6×10^{15} cm^{-3}) at room temperature and 5×10^{9} (2×10^{15} cm^{-3}) at 100 K. At 10 K, the upper limits for N_S were not limited by the sensitivity of the spectrometer but rather by sample heating. Under the conditions described above (10 mW chopped light incident on the sample), a weak signal was observed with magnitude 10^3 smaller than the dark signal. Although this weak signal could result from photogenerated spins, the corresponding temperature change (due to sample heating by the absorbed laser light) needed to produce such a signal would be only about 10^{-2} K. Nevertheless, the observed signal set an upper limit of $N_S\leq3\times10^{10}$ (8×10^{15} cm^{-3}) on the number of photogenerated spins at $g=2$. Broader sweeps (60 G above or below $g=2$) also placed the limit for the number of photogenerated triplets at less than or equal to 2×10^{10} (6×10^{15} cm^{-3}). These results are summarized in Table I. Two principal assumptions were implied in the analysis leading to the upper limits presented above and in Table I:

(i) The spin-lattice relaxation time T_1 is sufficiently short for the photoinduced spins to come to thermal equilibrium before they decay, and (ii) the linewidth for the light-induced ESR would be comparable to that of the dark signal.

T_1 measurements based on both saturation[29] and on the electron-spin echo decay[30] have been reported. The saturation method yields an estimate at 77 K of $T_1\simeq70$ μsec. The values for T_1 obtained by spin echo increased from about 5 μsec at 300 K to about 10 μsec at 100 K. Transient measurements[31] provide a direct estimate of T_1 under the precise conditions of the experiment. We found that the rise time (~100 μsec) of transient heating signal was limited by instrumental resolution, so that $T_1\leq100$ μsec at 10 K, consistent with the above measurements. Since the characteristic decay time associated with the infrared signatures (0.5 and 0.17 eV) of the charged photoexcitations is about 10^{-3} sec,[22] any photoinduced spins would come to thermal equilibrium in times short compared to the decay of the excitation signal.

Extensive studies of the dark ESR have demonstrated that the linewidth is due to the hyperfine interaction narrowed by the delocalized nature of the spatial wave function and by the motion of the neutral soliton.[32,33] The linewidth of light-induced spin resonance would result from the same intrinsic hyperfine interaction. Since the neutral solitons are quasistatic at low temperatures (the solid-state effect in dynamic nuclear polarization studies[34]) the linewidth of light-induced spin resonance would be no greater than the 5-G width ($T=10$ K) of the dark signal. More extensive delocalization (e.g., an electron-hole pair) or more rapid motion would result in narrower lines and even more intense photogenerated signals.

IV. DISCUSSION

In an earlier series of experiments, Flood *et al.*[31] were able to set limits on the quantum efficiency for photoproduction of spins (and for the absolute number of photogenerated spins). These limits were several orders of magnitude below the estimated quantum efficiency (QE) for photoproduction of gap states and charged excitations. Thus Flood *et al.*[31] concluded that the photogenerated charge carriers are spinless and identified them as S-$\bar{S}$ pairs. Subsequently, Orenstein *et al.*[21] revised their earlier estimate[20] of the quantum efficiency for photoproduction of charged excitations. From a more detailed analysis,[21] they concluded that the QE was about 10^{-2} (rather than of order unity).

The uncertainty in the number of photoinduced charged excitations has been resolved through the photoinduced ir-absorption measurements[22,23] described in the Introduction. These data yield an estimate of $N_{ch}\simeq5\times10^{17}$ cm^{-3} (obtained from films with thickness of 0.5 μm) at the laser power levels used in the experiments described in Sec. III. Note, however, that for films sufficiently thick to absorb all the incident light, the total number of charged excitations in the sample per cm^2 of illuminated area at saturation is independent of sample thickness; $n_{ch}\simeq2\times10^{13}$ cm^{-2} of illuminated area. Thus, under the experimental conditions of Sec. III, $N_{ch}\simeq5\times10^{12}$ in the illuminated sample in the ESR cavity ($T\leq100$ K). This number involves no assumptions regarding the quantum efficiency; it was obtained directly from experiment under conditions essentially identical to those used in the ESR experiments.

By combining our data for the upper limit on the photoproduction of spins, N_S, with the saturation number of photogenerated charged excitations, we can calculate the experimental ratio

$$R=N_S/N_{ch}\ . \tag{1}$$

If $R=1$, the excitations have the common spin-charge relation of fermions; if $R=0$, the spin-charge relation is reversed. Using the 100-K data to set the tightest limits, we find

$$R_{expt}<2\times10^{-3}\ .$$

Even taking the most conservative limit for N_{ch} leads to $R<10^{-2}$.

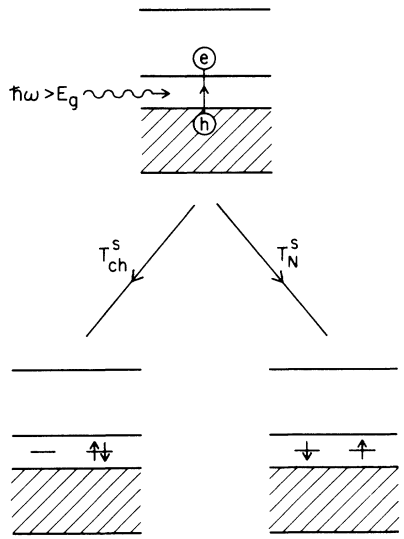

FIG. 2. Diagram showing two possible channels for photoproduction of solitons, charged and neutral.

The small value of R demonstrates that the charged photoexcitations are spinless and are identified as charged solitons. *The reversed spin-charge relation for the photoexcitations is therefore experimentally established.* Since the infrared signatures observed in the photoinduced absorption experiments[22,23] are in one-to-one correspondence with those generated by doping, the charges introduced onto the *trans*-$(CH)_x$ chain by charge transfer are accommodated in charged solitons. This conclusion is consistent with the theoretical analysis of Su, Schrieffer, and Heeger[2] (SSH) and Rice,[3] who demonstrated that within the coupled electron-lattice model, charged solitons would be the minimum energy configuration.

The experimental conclusion obtained from these and related data indicate that the photogenerated excitations are charged solitons, not neutral solitons. However, as noted in Fig. 2, it is not a *a priori* obvious whether the photoproduction of solitons should proceed through the charged channel T^S_{ch} or the neutral channel T^S_N, where the T's correspond to transition rates from the initial photoexcited state (an electron-hole pair) to the final photoexcited state (soliton-antisoliton pair). Our experiments indicate that the branching ratio strongly favors the charged-soliton channel

$$\frac{T^S_N}{T^S_{ch}} \leq 10^{-2} .$$

Ball *et al.*[35] have calculated the branching ratio for the two final configurations sketched in Fig. 2. Within the SSH model, they find for the branching ratio is zero (only charged solitons are produced) in the adiabatic approximation as a consequence of parity and the Pauli exclusion principle. They also proved that the branching ratio remains zero, at least to second order in the electron-phonon interaction, as a consequence of charge-conjugation symmetry.

V. CONCLUSION

In summary, we have carried out a series of ESR experiments on samples illuminated with light at photon energies $\hbar\omega > E_g$. From these studies, we have been able to set an upper limit on the number of photoinduced unpaired spins. Since $N_S/N_{ch} < 10^{-2}$, the charged excitations are spinless. Independent experiments carried out in the time domain have demonstrated that pumping with photons at $\hbar\omega > E_g$ leads to charged localized excitations which diffuse over substantial distances before recombination and that these excitations are generated instantaneously (less than 10^{-13} sec). Moreover, photoinduced absorption spectroscopy[20–23] has demonstrated that these excitations have both the infrared signature[11,12] and the midgap absorption[9,10] expected for charged solitons. These data, together with the reversed spin-charge relation demonstrated by the ESR studies, provide detailed experimental evidence of the rapid generation of S-$\bar{S}$ pairs after injection of e-h pairs, as predicted by Su and Schrieffer,[18] and by Mele.[19] Furthermore, these experimental results yield important additional information; the branching ratio (photoproduction of neutral solitons compared to photoproduction of charged solitons) is less than 10^{-2}. Ball *et al.*[35] have recently shown that this small branching ratio is a fundamental aspect of the soliton photoproduction process and can be understood from basic symmetry considerations. Finally, we note that the experimental demonstration that charged solitons are spinless is particularly interesting in a broader context. The reversed spin-charge relation is a direct manifestation of fermion charge fractionalization through soliton formation (charge $\frac{1}{2}$ for each sign of spin), a phenomenon first predicted in the mathematical physics of field theory.[4,5]

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