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Mechanism for photogeneration of charge carriers in polyacetylene

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In light of new experimental observations, a mechanism for the photogeneration of charge carriers in *trans*-polyacetylene is presented. By way of introduction, we discuss the qualitative changes in the picture of charged-soliton photogeneration that are expected due to the inclusion of electron correlation effects. In addition, we point out the unique implications the soliton model has for the generation of photocarriers by impurity-induced photoabsorption. Experimentally, we report two types of observations which are relevant to this discussion. First, measurements of the relative efficiency for photocarrier generation, as a function of photon energy, are presented for samples of varying thickness and impurity content. Second, we compare the optical absorption spectra of photocarriers created by intrinsic and extrinsic photoabsorption. Finally, we present a model for the relaxation of photoexcited polyacetylene which attempts to account for these, as well as earlier, observations.

I. INTRODUCTION

Recent work on conducting polymers has focused on the nature of electronic excitations in the prototypical material, polyacetylene, $(CH)_x$.[1] Interest has been stimulated largely by the development of an elegant theory[2–4] for these elementary excitations. A starting point for this theory is the Hamiltonian proposed by Su, Schrieffer, and Heeger,[3] which includes the coupling of electrons to the lattice in a realistic way. The solutions of this Hamiltonian lead to the prediction of self-localized electronic excitations in $(CH)_x$ of two types, known as soliton[2–4] and polaron[5–8] states. Evidence for the existence of solitons has come from magnetic, transport, and optical measurements on both doped and photoexcited *trans*-$(CH)_x$.[1]

Although several predictions of the soliton picture have been borne out, the study of photoexcited $(CH)_x$ has revealed unexpected phenomena. Most important is that an overall neutral, as well as a charge-carrying, excitation is seen in photoinduced absorption[9–11] and photoluminescence[12] experiments. Currently, the nature of this neutral excitation and the branching process which determines the relative photoproduction of neutral versus charged states is not understood.

The purpose of this paper is to examine the branching process which leads to the photogeneration of charge carriers in *trans*-$(CH)_x$. In the remainder of the Introduction we discuss qualitatively two theoretical questions which are relevant to this process. First, we discuss the effect of electron-electron interaction on the nature of the lowest-lying photoexcitations in $(CH)_x$. Second, we point out the unique implications that the soliton picture has for the creation of carriers by intrinsic compared with extrinsic photoabsorption. In Sec. II we present new experimental findings concerning the creation of photocarriers in *trans*-$(CH)_x$. We have measured the relative efficiency for photogeneration of charge carriers as a function of photon energy for samples of varying thickness and purity. In addition we compare the photogeneration efficiency, and optical-absorption spectrum, of carriers created by intrinsic and impurity-induced absorption. Finally, in Sec. III a model is described which incorporates these results into a coherent picture of charge-carrier photogeneration in $(CH)_x$.

Recently there has been a growing awareness of the influence of electron-correlation effects on the nature of excitations in $(CH)_x$. This awareness has been stimulated by both photoexcitation[9–12] and magnetic resonance[13] experiments which indicate the necessity of going beyond a one-electron theory. Simultaneously there has been a recognition that quantum-chemical methods for treating the many-electron problem have successfully explained similar experimental results obtained in the study of polyenes, molecules which are short-chain analogs of $(CH)_x$.[14]

In describing the effect of the electron-electron interaction, it is necessary to distinguish its consequences on the ground-state structure from effects on the nature of excited states. Recent calculations, using valence-bond[15] and quantum Monte Carlo[16] methods, have investigated the electronic structure of the ground state in models which include correlation effects. These papers include Hubbard on-site (U) and nearest-neighbor (V) terms in a Hamiltonian which describes an electron-phonon coupled half-filled band. An important result is that the inclusion of U and V terms does not destroy the ground-state dimerization, but actually reinforces it for $U \lesssim 4t$, where t is the transfer-matrix element. As a consequence many of the qualitative properties of the one-electron approach survive in a more realistic Hamiltonian. In particular the neutral spin-$\frac{1}{2}$ soliton is maintained in the ground-state structure of a finite chain with an odd number of carbon atoms.[17,18]

The aspect of the problem in which a proper treatment of the electron-electron interaction *is* crucial is the excited states. The statement that neutral solitons exist in the ground state of a finite odd chain does not necessarily mean that neutral or charged solitons appear as photoexcitations of ideal chains. The existence of solitons as independent excitations depends critically on their mutual interaction since they must be created in pairs from the ground state. If their interaction is attractive, then the lowest-energy elementary excitation is not an isolated soliton but rather a bound state of a soliton-antisoliton pair.

The two dominant interactions in polyacetylene, electron-phonon and electron-electron, make contributions to the soliton-antisoliton interaction which are opposite in sign. This can be understood in the following way. In a one-electron theory with electron-phonon coupling, a distortion of the lattice takes place around electrons (and holes) which lowers the total energy. In *trans*-$(CH)_x$ this distortion takes the form of a topological kink or soliton in the $(CH)_x$ order parameter. For a photo- or thermally-induced electron-hole pair the lattice distortion around each particle interferes and the incipient pair of solitons can lower their energy by separating.[19] This net repulsion of two solitons is a direct consequence of the fact that in a theory without electron-electron repulsion, the gap is defined by the amplitude of the ground-state dimerization. However, if electron-electron interaction is more important the situation is quite different. Here the magnitude of the gap is determined largely by energy required to create a doubly occupied site, which is U. The energy required to create an electron-hole pair is significantly smaller than U if the pair remains close, that is, forms an exciton. In the Hubbard parametrization the exciton effect lowers the excitation energy to $U-V$. Thus we expect different excitations to be lowest in energy, depending on which interaction dominates; electron-phonon interaction leads to independent, charged solitons whereas correlation effects lead to an overall neutral bound state. For this reason the problem of identifying the charge state of the lowest-energy excitation is important in order to understand the basic physics of $(CH)_x$ in particular, and conducting polymers in general.

Photoconductivity measurements show that photoinduced separation of charge does take place in *trans*-$(CH)_x$[20,21] as well as other polymeric semiconductors, notably the polydiacetylenes.[22] The mechanism for generation of charge carriers is crucial in distinguishing the strength of competing interactions. As a result, much attention has centered on the excitation spectrum for photocarriers. The excitation spectrum (ES) is the efficiency, per absorbed photon, of creating a charge carrier, measured as a function of the photon energy. The competing interactions discussed above are reflected in the ES in the following way. If the electron-phonon interaction dominates, then the lowest-energy photoexcitation is two well-separated charged solitons.[5] The threshold for optical absorption[23–25] occurs at twice the soliton creation energy, or $4\Delta/\pi$,[3,36] where 2Δ is the Peierls gap. Above this threshold a pair of photocarriers is created for each absorbed photon, i.e., the efficiency is unity. This should be contrasted with the prediction of models which incorporate the electron-hole interaction. In this case, the lowest frequency absorption creates an exciton. The efficiency of charge-carrier generation is therefore zero at threshold and increases with increasing photon energy as the probability of exciton ionization becomes larger. Measurement of the energy dependence of the excitation efficiency is, therefore, an important test of theoretical models.

There is another aspect of photocarrier generation in $(CH)_x$ which is equally relevant to understanding the nature of its electronic excitations. This is the question of photocarrier generation by absorption due to impurity-induced gap states. Here the topological nature of the soliton excitation leads to predictions which differ substantially from the conventional semiconductor picture.

According to current ideas,[3,4] doping in *trans*-$(CH)_x$ proceeds by generation of charged solitons. Experimentally, impurities which dope $(CH)_x$ also generate a new optical-absorption band with a peak near the midgap.[1,27] This optical transition has been interpreted as the promotion of an electron (or hole) from the gap state associated with a soliton to the continuum of delocalized states. If this electron transfers to a nearby chain, then it can contribute to photoconductivity. However, it cannot bring the soliton distortion along in this process. This is a consequence of the topological nature of solitons which dictates that they must be created in pairs. A single electron transferred to a neutral chain forms a one-dimensional polaron,[5–8] not a soliton. Within this picture, photoionization of a gap state should give rise to a carrier which is topologically, and spectroscopically, distinct from the soliton-antisoliton pair generated by above-gap excitation. It follows that a direct test of soliton photogeneration is to compare the carriers created by extrinsic and intrinsic photoabsorption.

II. EXPERIMENTAL RESULTS

The first set of experiments we will describe attempts to measure the efficiency ϵ for photogeneration of charge carriers as a function of photon energy $\hbar\omega$. Several measurements of ϵ versus $\hbar\omega$ have been reported based on photoconductivity measurements.[20,21,28,29] These papers report somewhat different results, indicating that the spectra appear to depend on sample thickness and impurity content.

The ability to detect the optical absorption from charge carriers offers the possibility of measuring ϵ more directly than in photoconductivity measurements. Recently the ES has been measured[30] in a thin film of $(CH)_x$ by monitoring photoinduced absorption (PA) at the frequency of a strong infrared (IR) active mode of the photocarrier (1360 cm^{-1}).[11] In this paper we present new ES data also obtained using the PA technique. For this measurement we have monitored the near-IR optical absorption of the photocarrier, which peaks at 0.45 eV.[11] The results illustrate the dependence of the ES on sample thickness and purity, as well as temperature.

The directly observed quantity in this technique is $\Delta T/T$, the fractional change in sample transmission caused by absorption due to photocarriers. This quantity yields the concentration of photocarriers integrated along the direction normal to the sample, N, through the relation $\Delta T/T = N\sigma$, where σ is the energy-dependent optical-absorption cross section of a photocarrier. The areal concentration is given in terms of the efficiency by

$$N=(1-R)\epsilon\Phi\tau(1-e^{-\alpha d}) , \tag{1}$$

where R,α are the photon-energy—dependent reflectivity and absorption coefficient of $(\mathrm{CH})_x$, Φ is the incident photon flux, d is the sample thickness, and τ is the photocarrier lifetime. In previous measurements with strongly absorbed ($\alpha d \gg 1$) above-band-gap excitation, ϵ was estimated to be $\sim 10^{-2}$.[11] In this work we plot the ES on an arbitrary scale—in all the present results the magnitude of the PA response for $\hbar\omega > 2$ eV is consistent with previously published data.

As Eq. (1) indicates, to determine the relative variation of ϵ versus $\hbar\omega$ the photocarrier concentration must be corrected for the fraction of the incident photons which are actually absorbed. In practice, for the range of $\hbar\omega$ where the sample is optically thin ($\alpha d \lesssim 1$) this correction is not straightforward. By using transmission techniques alone, it is not possible to separate the loss of incident photons due to absorption from that due to reflection and scattering. There are two approaches to this problem: The first is to not explicitly correct for the $1-e^{-\alpha d}$ factor but instead increase d until the sample is optically thick ($\alpha d \gg 1$) in the region of interest. The second is to couple ES measurements with photoacoustic or photothermal measurements of α which are directly proportional to the quantity $1-e^{-\alpha d}$. In the present work we have combined both methods to develop an accurate picture of the ES. We have made measurements on samples of thickness 0.3, 0.4, and 24 μm. In addition we have used preliminary results of a measurement of $1-e^{-\alpha d}$ by Weinberger *et al.*,[31] using photothermal deflection spectroscopy (PDS).[32] In particular, the PDS results tell us, for a given thickness, the lowest value of $\hbar\omega$ for which all of the incident photons are absorbed in the sample. For photon energies greater than this value, N in Eq. (1) is directly proportional to ϵ, without additional correction.

The apparatus required to measure ES is similar to that previously described for PA experiments.[9,11] The continuously tunable excitation source for this measurement was a W lamp and monochromator. The flux of incident photons was determined using a pyroelectric detector whose response is independent of photon energy. The intensity at the sample was 20 mW/cm^2 at the peak of the lamp spectrum, 0.95 eV. To detect $\Delta T/T$ due to photocarriers, we measured the transmission of a beam from a second W lamp which overlapped the excitation beam at the position of the sample. A 2.4-μm-long pass filter and fused silica window restricted the range of probe energies which reached the InSb detector to 0.45—0.55 eV. The excitation beam was chopped at 400 Hz and $\Delta T/T$ was measured by phase-sensitive detection of the signal from the InSb detector. Typical values of $\Delta T/T$ were in the range 10^{-4}—10^{-5}. This is approximately an order of magnitude smaller than previously reported due to the combined effect of greater chopping frequency and lower excitation intensity.

Previous measurements have shown that $\Delta T/T$ depends sublinearly on Φ, approximately as $\Phi^{0.6}$.[11] We have verified this Φ dependence over the photon energy range of our experiments by repeating scans with a 25% transmitting filter in front of the excitation source. The resulting $\Delta T/T$ decrease was sample dependent,[33] varying from 2.5 to 3. To obtain a Φ-independent measure of the relative excitation efficiency, $\Delta T/T$ was normalized according to this sublinear dependence.

Figure 1 shows two scans of $\Delta T/T$ normalized in this manner for a *trans*-$(\mathrm{CH})_x$ sample of thickness 24 μm. The upper plot was recorded on "as-grown" film, prepared by the standard Shirakawa technique.[34] The other spectra was obtained after *in situ* exposure of the same sample to NH_3. Both spectra were measured at 25 K.

The ES clearly shows two distinct regions, above gap, $\hbar\omega > 1.4$ eV, and below gap, $\hbar\omega \lesssim 1.4$ eV. The as-grown sample shows a peak in $\Delta T/T$ below the gap, at approximately 0.85 eV. Notice that the magnitude of $\Delta T/T$ at this energy, when normalized by $\Phi^{0.6}$, is comparable to that obtained with $\hbar\omega > 2.0$ eV. *In situ* exposure of this sample to NH_3 dramatically reduces the subgap response yet has no effect for photon energies above ~ 1.4 eV. PDS measurements[31] of $1-e^{-\alpha d}$ indicate that this sample is optically thick for $\hbar\omega > 1.2$ eV. Therefore, in this range the variation in the yield of photocarriers depicted in Fig. 1 directly shows the variation of ϵ versus $\hbar\omega$. The spectra demonstrate that the relative efficiency for generating charge carriers decreases sharply as a function of decreasing photon energy in the tail of the intrinsic $(\mathrm{CH})_x$ absorption.

The response to excitation at 0.85 eV is due to exciting an electron or hole from a level in the semiconductor gap that is associated with either a defect or impurity. In fact, these films are known to contain both types of states. The best characterized defect is a neutral spin-$\frac{1}{2}$ state which is present at a concentration of $\sim 10^{19}$ cm^{-3}.[35] This is generally thought to be the S^0, or neutral soliton.[36] Also present are approximately 10^{18}-cm^{-3} charged states generated by inadvertent doping, probably by the polymeriza-

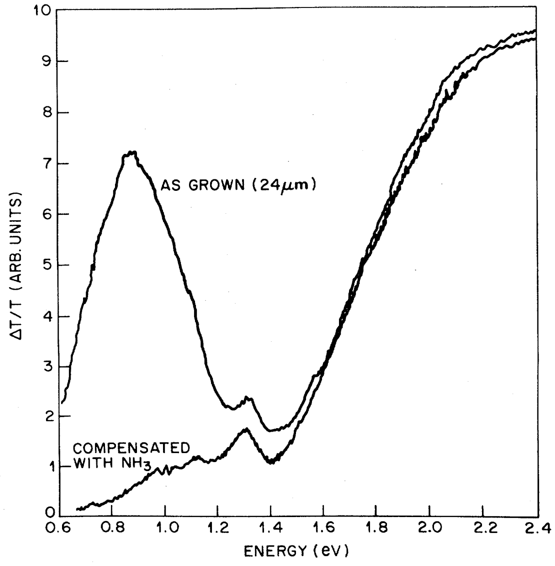

FIG. 1. Excitation spectra (ES) for photogeneration of charge carriers in a 24-μm-thick sample of $(\mathrm{CH})_x$. The two spectra compare the yield of photocarriers at 25 K, before and after exposure of the sample to NH_3 vapor.

tion catalyst.[37] These impurities give rise to the dark conductivity of these films, which is $\sim 10^{-5}$ $(\Omega\,\mathrm{cm})^{-1}$.[38]

To test which state, if either, gives rise to the subgap response in the ES of Fig. 1 we performed the experiment of compensating with NH_3 *in situ*. The exposure of as-grown $(CH)_x$ to NH_3 vapor is known to reduce conductivity of this p type material by many orders of magnitude.[38] At the same time the NH_3 has no effect on the concentration of unpaired spins.[36] To monitor this compensating effect, the sample was prepared with contacts (Electrodag) to measure the conductivity. After exposure to NH_3 at room temperature, the conductivity decreased by 4 orders of magnitude, from $\sim 10^{-5}$ to $\sim 10^{-9}$ $(\Omega\,\mathrm{cm})^{-1}$. Following this step, the sample chamber was evacuated and the temperature was reduced in a few minutes to 25 K in order to perform the ES measurement. As the results shown in Fig. 1 illustrate, the sub-band-gap peak is largely removed by the compensation while there is no effect on the photogeneration efficiency for $\hbar\omega > 1.3$ eV. This experiment proves that photoionization of charged, dopant-induced states in the gap gives rise to photoinduced absorption at 0.5 eV. In addition, it demonstrates that the efficiency of above-band-gap photocarrier generation is not dependent on the presence of dopant-induced gap states. Finally, there is no below-gap peak in the ES which can be clearly associated with photoionization of S^0 states, even though they are present in greater concentration than the dopant-generated states.

Excitation spectra of $\Delta T/T$ for the as-grown sample, measured at three temperatures, 25, 150, and 200 K, are shown in Fig. 2. The scans at 150 and 200 K have been multiplied by the indicated factors to enable comparison. The decrease of $\Delta T/T$ with increasing temperature reflects a reduction in the carrier lifetime. Figure 2 shows that the lifetime of carriers created by above-gap and below-gap excitation have a similar temperature dependence.

In Fig. 3 we summarize results obtained with samples of different thickness and purity. In general, we find that the ES below ~ 1.3 eV is strongly dependent on these factors while the response above this energy is intrinsic to $(CH)_x$. The three spectra in Fig. 3 show, in order of increasing subgap response, the data obtained for a 0.3 μm film, a 4 μm sample, and a 4 μm sample doped with I_2 to a concentration of approximately 0.05%. The concentration of electrically active dopant was determined by IR spectroscopy.[39] All three spectra were measured at 25 K.

The ES of the intentionally doped sample in Fig. 3 shows that photoionization of the dopant-generated gap state is a source of photocarriers, giving a response similar to that observed in the as-grown 24-μm sample. The origin of the two-peak structure of the ES in this sample is not understood at present, particularly since the absorption coefficient of doped samples has a single peak of 0.8 eV.[27] Future measurements of the ES as a function of dopant concentration should resolve this question. For now we wish to emphasize one important point—that excitation of extrinsic states in the semiconductor gap creates carriers with an efficiency which is comparable to that of the intrinsic process. The extrinsic response may be observed in as-grown thick films due to inadvertent impurities, or in thinner films which are deliberately doped. In either case the criterion is that αd, due to impurity-generated states, must be of order unity. Also shown in Fig. 3 is the ES for a much thinner film, of thickness 0.3 μm. This result is very similar to the ES obtained earlier by monitoring the photogenerated IR mode at 1360 cm^{-1}.[30] The spectrum for this film, in contrast to other samples, is monotonic. However PDS results show that samples of this thickness becomes optically thin for $\hbar\omega < 1.4$ eV.[31] For this range of energy, correction for the

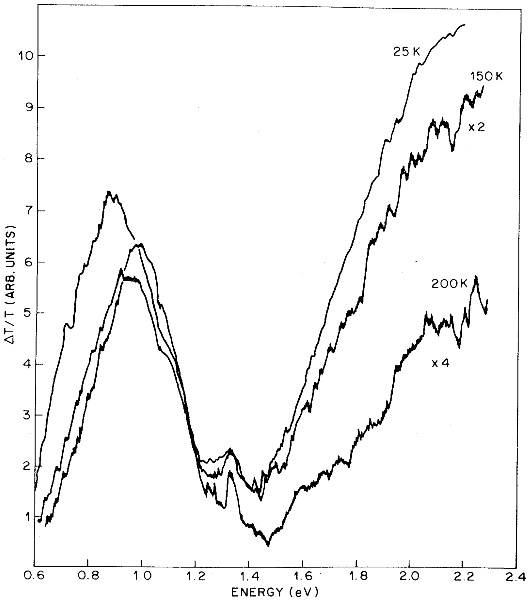

FIG. 2. ES for the as-grown sample of Fig. 1 measured at three temperatures, 25, 150, and 200 K. The spectra were multiplied by the indicated factors to aid in comparison.

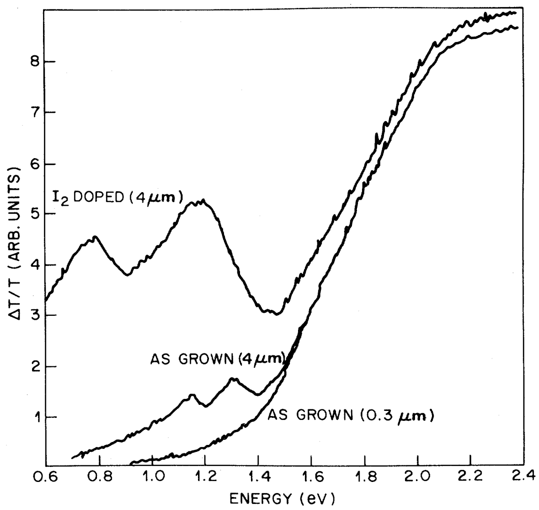

FIG. 3. Comparison of ES for two as-grown samples of thickness 0.3 and 4 μm, and a 4-μm sample doped to a level $\sim 0.05\%$. The spectra illustrate that the creation of photocarriers for $\hbar\omega < 1.4$ eV is strongly sample dependent whereas the response above this energy is intrinsic.

number of transmitted photons is necessary in order to obtain ϵ versus $\hbar\omega$.

Using the I_2-doped sample we were able to answer the question raised in the Introduction of whether carriers created by photoionization of gap states are the same as those created by above-gap excitation. The most direct method to compare the above- and below-gap generated carriers is to measure their optical-absorption spectra. In several papers, the optical absorption of photocarriers created in undoped $(CH)_x$ has been thoroughly characterized.[9,10,12,40] The absorption is of two types, a broad electronic transition with a peak of 0.45 eV, and three sharp lines in the infrared. In Figs. 4 and 5 we compare those results with spectra we have obtained by creating photocarriers in I_2-doped $(CH)_x$.

The curve labeled as-grown in Fig. 4 shows the near-IR optical-absorption spectrum of photocarriers created by above-gap (1.96 eV) excitation of undoped $(CH)_x$. In agreement with previous results, we observe a broad, asymmetric peak whose maximum is at 0.45 eV.[11] The curve labeled "I_2-doped" shows the spectrum obtained by exciting the doped sample at 1.0 eV, near the peak of its extrinsic response (see Fig. 3). Note that the two spectra are almost identical for energies below 0.5 eV. Above this energy the PA spectrum in the I_2-doped sample decreases much more rapidly and reverses sign at 0.58 eV. This observation can be interpreted in a straightforward way, if we note that the optical absorption of the dopant- and photo-induced carriers peaks at different energies. Excitation of the doped sample at 1.0 eV photoionizes a hole formerly bound in the vicinity of a dopant-ion (I_3^-). This results in a reduction, or bleaching, of the dopant-generated absorption which peaks at ~ 0.8 eV. The reversal in sign of $\Delta T/T$ seen in the I_2-doped spectrum of Fig. 4 is due to this photoinduced bleaching effect.

A fraction of the photoionized holes, of order 10^{-2}, manages to transfer to a neighboring $(CH)_x$ chain to give rise to long-lived photocarriers. In contrast to the prediction explained in Sec. I, they form the *same type of carrier* as created by above-gap excitation of undoped samples. This is clear from comparison of the two spectra of Fig. 4, which show the same peak position and low-energy cutoff.

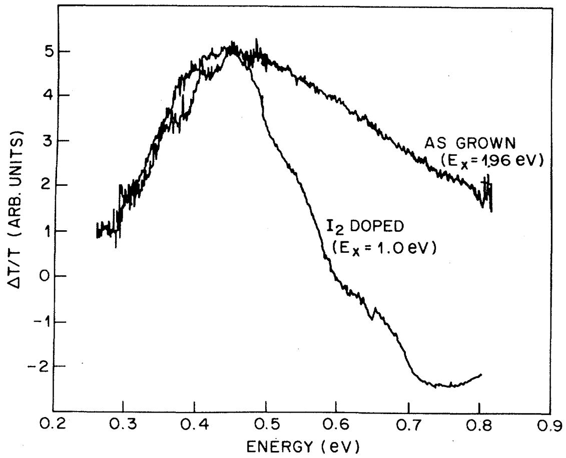

FIG. 4. Photoinduced changes in optical absorption in as-grown versus I_2-doped $(CH)_x$. Above-gap excitation of undoped $(CH)_x$ yields photocarriers whose optical absorption peaks at 0.45 eV. Excitation of doped $(CH)_x$ at 1.0 eV creates the same type of carrier by transferring charge out of impurity-induced states.

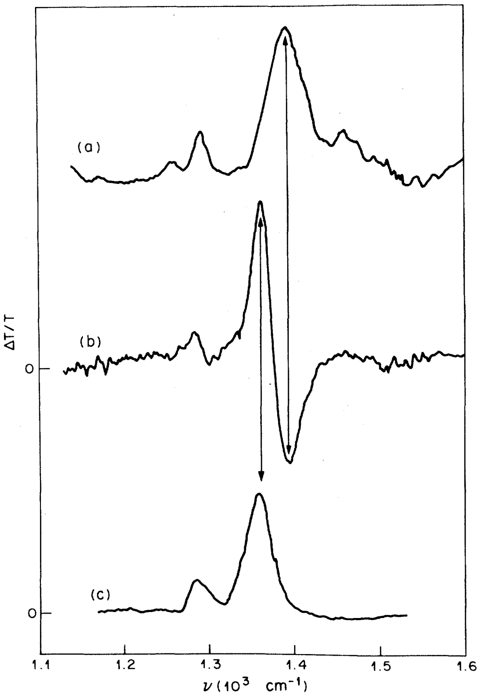

FIG. 5. Three spectra which illustrate the process of creation of charge carriers by extrinsic photoabsorption. Curve (a) shows the strong IR-active mode near 1390 cm^{-1} due to the presence of dopant-induced carriers bound to oppositely charged impurities. The spectrum labeled (c) shows the optical absorption in this spectral region of photocarriers generated in undoped $(CH)_x$. The middle spectrum, (b), results when doped $(CH)_x$ is photoexcited in the impurity-induced midgap absorption band.

This conclusion is reinforced by a comparison of the IR activity due to photocarriers in doped and as-grown samples. A measurement of this absorption tells us about the nature of the photocarrier and its local environment. For example, the oscillator strength of these IR modes is a direct measure of the polaronic mass of the charge carrier.[41,42] In addition their frequency is sensitive to the restoring force of a pinning center on or near the polymer chain.[42]

Shown in the top trace of Fig. 5 is the strong IR absorption at 1390 cm^{-1} which results from the presence of p-type carriers generated by I_2 doping.[39] Not shown is the lowest frequency mode at 900 cm^{-1}. The bottom trace shows the analogous IR absorption at 1360 cm^{-1} due to photocarriers, first observed by Vardeny, Orenstein, and Baker.[10] For these photocarriers, the lowest frequency mode, which is the most sensitive to the presence of a pinning potential, was observed by Blanchet, Fincher, and Heeger[40] to shift from 900 to 500 cm^{-1}. It appears that long-lived photocarriers in $(CH)_x$ are bound to pinning carriers whose restoring force is approximately 5 times weaker than that provided by a dopant ion.[43] The origin of this pinning is not as yet understood.

The middle trace, labeled (b), shows the spectrum obtained by photoexcitation of the I_2-doped sample with subgap photons of energy ~ 1.0 eV. While this result is analogous to the near-IR spectrum of Fig. 4, the sharpness of the IR features clarifies the process considerably. It is apparent that the IR absorption due to photocarriers is created at the expense of that associated with dopant-induced carriers. An important point is that the net change in absorption in spectrum (b) is less than 10%—consistent with no change given the experimental uncertainty. This demonstrates that the polaronic mass of the photocarrier is the same as that of the dopant-induced carrier. The peak position of the photocarrier absorption is also the same as observed previously. The 30 cm^{-1} shift of the photocarrier mode relative to the dopant-induced mode is nicely illustrated in this spectrum. The small shift reflects the weak dependence of this mode on the pinning force, as predicted theoretically.[42,43]

III. DISCUSSION

We have presented two important new findings. The first is excitation spectra for optically thick films which show that the intrinsic quantum efficiency decreases dramatically as the photon energy is lowered through the region of the absorption edge, from 2.0 to 1.3 eV. Second is the observation that carriers created by the photoionization of impurity-induced gap states are of the same type as those which result from photogeneration of an electron-hole pair. The point of this discussion is to describe a model which accommodates both of these results.

In Fig. 6, ϵ versus $\hbar\omega$ data from Fig. 1 for the compensated 24-μm film is replotted on a semilogarithmic scale. We compare this spectrum with $1-e^{-\alpha d}$, and α.[31] Previously it has been noted, for thinner samples, that ϵ begins to decrease at a smaller value of $\hbar\omega$ than does α. This has been interpreted[21,30] as evidence for direct photogeneration of charged solitons as prediced by one-electron theory.[5] However, to compare with theory ϵ should be more properly compared with $1-e^{-\alpha d}$. The model of soliton photogeneration predicts that ϵ should equal $1-e^{\alpha d}$, that is, a pair of photocarriers results from each absorbed photon. Instead, for all energies measured ϵ is much less than 1, and falls off more rapidly than $1-e^{-\alpha d}$ as $\hbar\omega$ decreases. This is direct evidence that the generation of photocarriers is the less likely outcome of a branching process which follows photoexcitation.

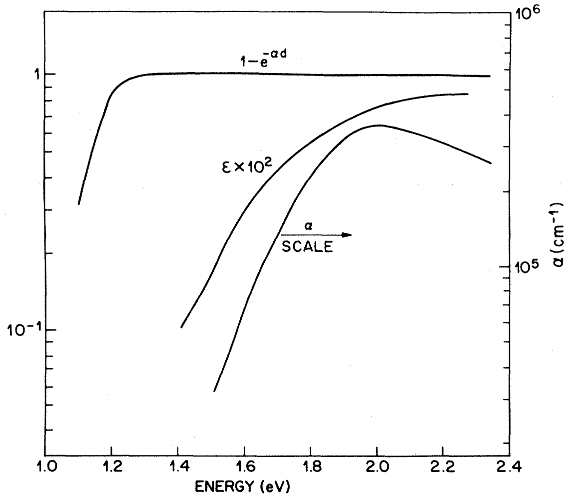

FIG. 6. Semilogarithmic plot of three quantities important to the photocarrier creation mechanism: absorption coefficient α, fraction of absorbed photons $1-e^{-\alpha d}$, and photogeneration efficiency ϵ. The curve of ϵ versus $\hbar\omega$ is the same as Fig. 1; however, only the intrinsic response is shown.

There are, of course, several possibilities for such a process. The range of possibilities narrows, however, when we consider the other experimental finding in this work—the generation of photocarriers by extrinsic absorption. To be definite we start with the assumption that the extrinsic state is a charged soliton bound to an oppositely charged dopant-ion, as suggested by a body of experiments.[1] Photoexcitation of this center promotes an electron out of a state deep in the gap. The fact that some photocarriers live for milliseconds[10,21] indicates that a fraction of the excitations manage to transfer to neighboring chains. If not, then we expect retrapping at the charged center to be very rapid. This single electron (or hole) added to a nearby chain is predicted to form a one-dimensional (1D) polaron rather than a soliton pair.[5–8] However, the evidence of Figs. 4 and 5 shows that this is not the case. The PA spectra point instead to the conclusion that carriers created by extrinsic photoabsorption form the same type of localized state. There is only one way to reconcile this conclusion with the assumption that the dopant-generated state is a charged soliton; *the long-lived photocarriers created by extrinsic absorption must be due to photoionized holes (for p-type doping) which become trapped at neutral soliton sites.* The net change upon photoexcitation is, therefore, to go from a strongly pinned charged soliton to one which is less tightly bound.

The generation of charged solitons by extrinsic absorption has approximately the same low efficiency per absorbed photon as does the super-band-gap process (see Figs. 1 and 3). In addition, the lifetimes of photocarriers created by these two processes have a similar temperature dependence. These observations lead us to propose that the mechanism by which intrinsic and extrinsic absorption give rise to photoinduced absorption is essentially the same. For the intrinsic process as well the generation of charged solitons occurs by capture of the photoexcited electron and hole at neutral solitons. In order for this to happen, the electron and hole must first separate to different chains before the pair is localized by a large 1D lattice deformation. Once the separation takes place the photocarriers will form polarons which can propagate readily from chain to chain. Evidence for this motion is found in observations of transient photoconductivity ($\tau < 2$ nsecs),[44] which is not correlated with the photoinduced absorption at 0.45 eV.[45] This initial transport mechanism is terminated rapidly by recombination and by trapping of polarons at neutral soliton sites. The charged solitons thus created are then detected as long-lived photocarriers through their optical absorption. The mechanism is reminiscent of the efficient trapping at dangling bonds that take place in amorphous Si:H alloys.

This picture is consistent with several additional features of the photoinduced-absorption data. The long lifetime of photocarriers in *trans*-$(CH)_x$, which extends to milliseconds even at room temperature, follows from the deep trapping of carriers at S^0 states. In addition we expect that the maximum concentration of these long-lived photocarriers should not exceed the S^0 concentration. This is indeed the case; in typical films grown with the Shirakawa method the saturated photocarrier concentration is $\sim 3\times 10^{17}$ cm^{-3} (Ref. 10) as compared to $\sim 10^{19}$ cm^{-3} for S^0's.[35,36] This maximum photocarrier concentration is sample dependent, which also implicates defect states. In particular in polyacetylene-polystyrene block copolymers, in which the unpaired-spin concentration is a factor ~ 100 smaller than in Shirakawa films, the magnitude of photoinduced absorption is smaller by ~ 10. For these samples both unpaired spins and long-lived photocarriers are present at the same, extremely small, concentration of $\sim 3\times 10^{16}$ cm^{-3}.

In Fig. 7 we illustrate a model for the relaxation pathway of $(CH)_x$ following above-gap photoexcitation suggested by both the above arguments and by consideration of earlier photoinduced absorption results. The model tries to account for the evidence that a branching process takes place after photoexcitation which yields a neutral bound state as well as charged photocarriers. In Fig. 7 the ground and excited states are depicted in a manner which emphasizes the effect of the on-site repulsion energy U. The ground state is shown schematically as an array of singlet pairs, a picture which is strictly valid for $U \gg 4t$. For $U \sim 4t$, as is applicable to $(CH)_x$, configurations with double occupancy are mixed into the ground state. Nevertheless, these diagrams are useful in describing the structure of photoexcited states in a system where correlation effects are important.

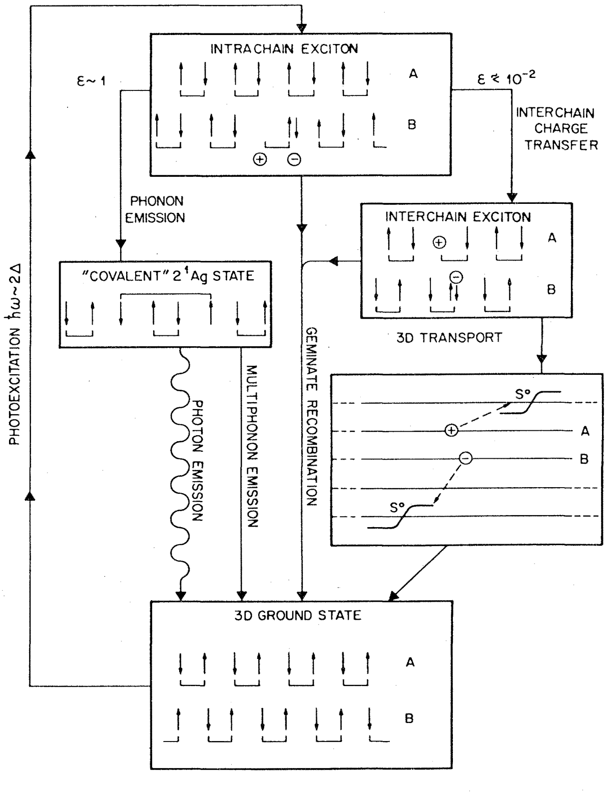

FIG. 7. A model for the relaxation of photoexcited $(CH)_x$.

In this highly correlated picture photoexcitation creates an intrachain exciton with energy $\sim(U-V)$. The dominant single-chain relaxation pathway is phonon emission to a state which, like the ground state, contains no doubly occupied sites in the larger U limit. This state, known as the 2^1Ag level in molecular notation, is found to lie below the exciton in calculations performed for finite polyenes.[14] Although in the 2^1Ag state there are no doubly occupied sites, its energy is above that of the ground state by $\sim t^2/U$ because it contains configurations with non-nearest-neighbor singlet pairs. The evidence for the importance of this excitation in $(CH)_x$ comes from both photoluminescence and photoinduced absorption experiments and will be described in detail in a subsequent publication.

As a consequence of correlation, the lowest-energy excitation in $(CH)_x$ does not carry a net charge. This is corroborated by Fig. 6 which shows that the efficiency of charge-carrier photogeneration decreases with decreasing photon energy. The path to the creation of charge carriers is shown by the right-hand-side branch of Fig. 7. In this picture the formation of a pair of photocarriers requires that an intrachain transfer take place before the excitation sinks into the 2^1Ag state. This probability increases with excitation energy, reflecting the energy required to separate electron and hole. In addition it must be at least as high as 10^{-2} in order to account for the observed yield of photocarriers.

A simple argument shows that a value of $\epsilon \sim 10^{-2}$ is plausible. We imagine that the photon energy is sufficiently large so that the intrachain excitation is resonant with the charge-transfer exciton. If after photoexcitation the electron-hole pair is initially localized on a chain labeled B then the probability amplitude for a carrier to appear on a neighboring chain labeled A is given by

$$\langle B \mid \psi(t)\rangle = \langle B \mid e^{iHt/\hbar} \mid A\rangle = \left[\frac{t_\perp}{\hbar}\right] t \qquad (2)$$

for sufficiently small time t.

In Eq. (2), $t_\perp$ is the interchain transfer integral whose value has been estimated between 25—100 meV.[46,47] After the onset of a strong 1D lattice relaxation the hopping probability is strongly reduced by the factor e^{-S}, where S is the Huang-Rhys parameter describing the strength of the electron-phonon coupling. If the 1D distortion requires a time τ_{rel}, then the probability for interchain charge transfer is $(t_\perp \tau_{rel}/\hbar)^2$. It is interesting that τ_{rel} has been determined directly in computer simulations performed by Mele.[48] In that work the quantum-mechanical overlap between the distorted lattice and the ground-state structure is calculated as a function of time following photoexcitation. Mele finds that this overlap decays with an effective $\tau_{\rm rel}$ of $\sim 3\times 10^{-15}$ sec. Substituting $\tau_{\rm rel}$ in the above relation demonstrates that an interchain charge-transfer efficiency $\sim 10^{-2}$ is consistent with estimates of $t_{\perp}$.

Once the interchain transfer takes place it is possible that the electron and hole will hop back together, leading to geminate recombination (GR). Evidence against the importance of this process in $(CH)_x$ is that ϵ versus $\hbar\omega$ is not strongly temperature dependent as is predicted in the Onsager formulation of GR.[49] This means that the creation of photocarriers is limited by the probability of the initial interchain transfer and that the energy dependence of this process gives rise to the observed dependence of ϵ on $\hbar\omega$.

After the electron and hole separate to different chains they will propagate as polarons until they encounter a $(CH)_x$ segment which contains an S^0. Subsequent trapping at the S^0 converts it to an S^+ or S^- state. We emphasize that this mechanism is strongly suggested by our results since it is the only way that the appearance of charged solitons by extrinsic absorption can be rationalized.

The model we have presented can account for experimental observations on photoexcited $(CH)_x$ to this point. Several predictions of this model can be subjected to experimental test in the future. In particular we do not expect to observe a large photoinduced absorption transient at 0.45 eV in sub-picosecond measurements, as is observed for the neutral excitation.[50] Instead a smaller response, consistent with excitation efficiency much less than unity, is predicted. It might be possible to resolve a rise time corresponding to the delay before trapping at S^0 sites. Additionally it is important to measure excitation efficiency spectra for photoproduction of the neutral bound state. According to the model we have described, ϵ for this state should decrease less rapidly with $\hbar\omega$ than is the case for photocarriers. Finally, we hope that the qualitative picture presented here will help to stimulate future theoretical work on the nature of excited states in 1D systems where effects of electron-electron and electron-phonon interactions are of comparable importance.

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