[a] On leave from the University of Würzburg, D-8700 Würzburg, Federal Republic of Germany.

[1] L. Esaki and R. Tsu, IBM J. Res. Dev. 14, 61 (1970).
[2] W. Dobrowolski, M. von Ortenberg, J. Thielemann, and R. R. Galazka, Phys. Rev. Lett. 47, 541 (1981).
[3] J. Kossut, Solid State Commun. 27, 1237 (1978).
[4] M. Dobrowolska, W. Dobrowolski, R. R. Galazka, and A. Mycielski, Phys. Status Solidi (b) 105, 477 (1981).
[5] A. Mycielski, J. Kossut, M. Dobrowolska, and W. Dobrowolski, J. Phys. C 15, 3293 (1982).
[6] R. de L. Kronig and W. J. Penney, Proc. Roy. Soc. London, Ser. A 130, 499 (1930).
[7] W. Dobrowolski, private communication.

Photogenerated Gap States in Polyacetylene

Joseph Orenstein and G. L. Baker
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 4 March 1982)

This paper reports the first observation of photogenerated gap states in polyacetylene, $(\mathrm{CH})_x$. A transient optical absorption, at photon energies less than the band gap, is produced by photogeneration of electron-hole pairs. The spectrum of this absorption is measured in both *cis* and *trans* isomers of $(\mathrm{CH})_x$. From a comparison of these spectra with similar spectra seen in molecular analogs of $(\mathrm{CH})_x$, it is concluded that these gap states are intrinsic, self-localized excitations of the semiconductor chain.

PACS numbers: 71.38.+i, 72.80.Le, 78.50.Ge

The ability to synthesize polyacetylene, $(\mathrm{CH})_x$, in bulk or thin-film form[1] has inspired interest in the physics of a one-dimensional (1D) organic semiconductor. Of particular interest is the nature of electronic excitations responsible for charge and energy transport along the chains. Theoretical studies[2-8] of 1D models of $(\mathrm{CH})_x$ indicate that the lowest-energy electronic excitations are not free electrons and holes, but rather are self-localized states which have energy levels in the gap. Remarkably, the effective masses of these states, with their associated lattice distortions, are comparable to the free-electron value and therefore their in-chain mobility can be high.

In $(\mathrm{CH})_x$ the chain consists of a backbone of carbon atoms in a planar structure with alternating single and double bonds between them (see Fig. 1). The mobile distortion of this structure which has been discussed most extensively is a boundary between two segments of chain which differ by π in the phase of their bond alternation. Associated with this kink, or "soliton," is an electronic level of nonbonding character, located at the gap center. The most significant prediction of a simple 1D, one-electron model of $(\mathrm{CH})_x$, first described by Su, Schrieffer, and Heeger,[3] and by Rice,[4] is that in *trans*-$(\mathrm{CH})_x$ a pair of injected carriers is unstable to the formation of a pair of these midgap levels.

Generation of solitons has been invoked[3,9] to explain the unusual and dramatic effects of doping the polymer with strong oxidizing and reducing agents. However, the carrier added to the chain by this procedure is tightly bound to the dopant ion and may not represent an unperturbed excitation of the polymer chain. To attempt to create intrinsic gap states we have used photoexcitation to add electron-hole pairs to $(\mathrm{CH})_x$. We find that a transient optical absorption, at photon energies less than the band gap, is produced by photoexcitation. From a comparison of the spectrum of this transient absorption with similar spectra seen in molecular analogs of $(\mathrm{CH})_x$, we conclude that the gap states we observe are the intrinsic, self-localized excitations of the $(\mathrm{CH})_x$ chain.

The samples for this experiment were prepared according to the procedure first described by Ito, Shirakawa, and Ikeda.[1] The *cis*-$(\mathrm{CH})_x$ samples, polymerized at 196 K onto fused silica cover slips, were transferred directly to the cold cryostat. The *trans*-$(\mathrm{CH})_x$ was obtained from the as-grown *cis* isomer by a heat treatment of 180 °C for 2 min. The thickness of the samples was ~1000 Å.

In order to measure the transient optical absorption due to the excited state, a tungsten-halogen lamp and monochromator were used to provide a variable-wavelength probe beam. The $(\mathrm{CH})_x$ was photoexcited by a 10-Hz train of 10-ns pulses from a dye laser tuned to 2.2 eV, near the peak of the interband absorption. The transmission of the probe beam was monitored with a photodiode, either Si, Ge, or InAs, depending upon the wavelength range. After amplification, the signal from the photodiode was sent to a digital signal averager which was triggered on each laser pulse. For the measurements reported here the response time of the photodiode-amplifier combination was ~3 μs, and the signal averager time resolution was 10 μs.

The signal from the photodiode shows that absorption of the excitation pulse by the sample produces a sudden decrease in transmission. This excess absorption then decays, in a highly nonexponential manner, during the 100-ms interval between pulses. We observe no long-term darkening of the sample after prolonged exposure to the laser. The kinetics of the induced absorption decay will be presented in a subsequent publication; for now we concentrate on the spectra of the excitations. To measure these spectra we record ΔT, the difference in transmission during the 10-μs time bin coincident with the laser from that during the preceding one. This difference, when normalized to the total transmitted signal, T, is equal to the photoinduced change in the absorbance of the sample.

The magnitude of $\Delta T/T$ induced by a laser pulse of 10^{14} photons cm^{-2} (3.5×10^{-5} J cm^{-2}) is shown in Fig. 1, as a function of the probe photon energy. The energy resolution is approximately equal to the spacing between data points. The photodiode-amplifier noise was responsible for error in $\Delta T/T$ of order 10^{-5}, and typical variation in laser power during a scan was found to be less than 5%. Spectra recorded with ten times less laser power were the same as in Fig. 1, within our level of accuracy.

In both isomers, the dominant feature at low temperature is a narrow (~0.20-eV) peak at 1.35 eV in *trans*-$(\text{CH})_x$ and 1.55 eV in *cis*-$(\text{CH})_x$, close to the optical gap. In the *trans* isomer there is additional absorption at lower energy which appears to peak at 0.5 eV. In this region of the spectrum the induced absorption in *cis*-$(\text{CH})_x$ is monotonic, and is a factor of ~20 smaller than in *trans*-$(\text{CH})_x$ at 0.5 eV. The peak positions measured at greater time delays from the excitation pulse were not substantially different.

The higher-energy peaks occur in a region of the spectrum where $(\text{CH})_x$ is strongly absorbing ($\alpha \sim 10^4$ cm^{-1}). For this reason a concern is that $\Delta\alpha$, the induced change in absorption coefficient, results from a shift in the absorption edge due to inadvertent heating by the laser pulse. To check this we have measured the dependence of the optical absorption edge in $(\text{CH})_x$ on the temperature. We find that the optical gap *decreases* with cooling to 10 K by about 50 meV, an effect which is of the same magnitude but opposite in sign compared with most inorganic semiconductors. Therefore transient heating will result in an apparent photoinduced decrease in absorption, opposite to what we observe.

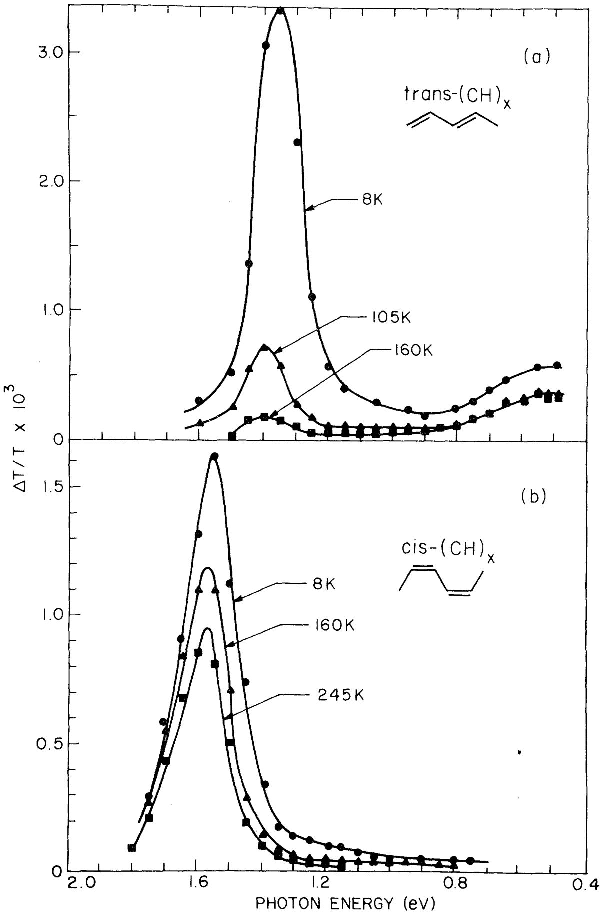

FIG. 1. Magnitude of $\Delta T/T$ in (a) *trans*-$(\text{CH})_x$ and (b) *cis*-$(\text{CH})_x$, as a function of probe photon energy for laser excitation at 2.2 eV.

At 8 K, the peaks present in both isomers are similar in magnitude, width, and position relative to the optical gap. In spite of this, they have dramatically different temperature dependences. The peak in *cis*-$(\text{CH})_x$ is relatively insensitive to temperature, decreasing by ~50% upon warming to 245 K. The 1.35-eV peak in *trans*-$(\text{CH})_x$, however, is strongly quenched by temperature. Preliminary measurements of the recombination kinetics indicate that the temperature dependence is due to a reduction in lifetime rather than photogeneration efficiency. The 0.5-eV peak is not thermally quenched and is the only feature observable at room temperature. This establishes that the two peaks in the spectrum of *trans*-$(\mathrm{CH})_x$ are not two transitions involving the same excited state.

The fundamental question concerning the photogenerated absorption is the following: Is it due to an extrinsic gap state, associated with an impurity or point defect, or does it arise from an intrinsic excited state of the polymer chain? In many solid-state systems it is difficult to distinguish between these two possibilities. It turns out that for $(\mathrm{CH})_x$ there exists a unique source of information which can resolve this question, namely studies of finite-chain analogs of $(\mathrm{CH})_x$.[10-13] The excited states of these molecules, termed polyenes, have been studied extensively because of their role as primary photoreceptors in vision and photosynthesis. In particular, the optical absorption in the excited state, prepared by both laser pulse[10-12] and electron-beam irradiation[13] of molecules in solution, has been measured in polyenes with up to nineteen double bonds along the chain.

The electron-beam excitation produces an excited state due to an electron added to or removed from the polyene.[13] For each polyene studied two peaks are observed. In Fig. 2 the energy of these peaks is plotted as solid circles and squares as a function of N^{-1}, where N is the number of conjugated double bonds. Pulsed laser excitation of the polyenes produces a neutral excited molecule. The absorption due to this excited state has a single peak, whose energy is plotted as triangles in Fig. 2. Also indicated, as open circles, is the peak of the ground-state absorption spectrum of each of the polyenes.

For comparison, the arrows indicate the position of the spectral features we observe in *cis*- and *trans*-$(\mathrm{CH})_x$. The energies agree well with the extrapolation of the polyene data to the limit of the infinite chain. In addition to this spectroscopic information there are other striking similarities between the finite polyenes and $(\mathrm{CH})_x$ which lead us to assign a common origin to these peaks. First, the fractional width of the peaks, $\Delta\epsilon/\epsilon$, is the same for $(\mathrm{CH})_x$ as in the polyenes. Second, the lifetime of the neutral excited molecule is long, typically 1–10 μs. Finally, the decay channel of the excited state in both $(\mathrm{CH})_x$ and finite polyenes is nonradiative.[14]

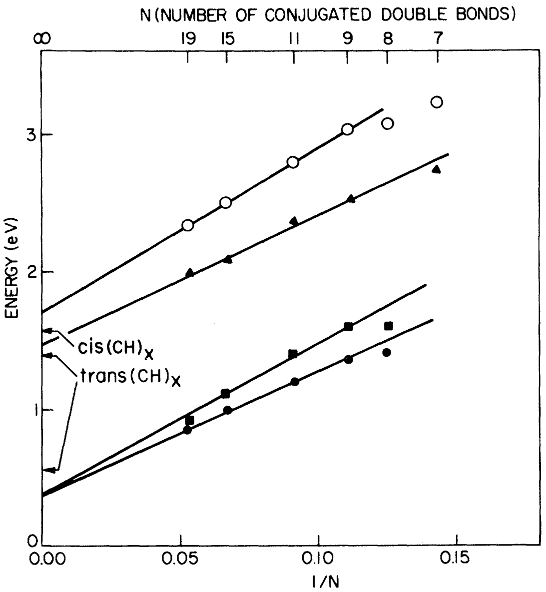

FIG. 2. Comparison of excited-state absorption spectra for finite polyenes with $(\mathrm{CH})_x$. Solid triangles indicate the absorption peak due to laser excitation of polyenes; squares and circles represent peaks which arise from electron-beam excitation. Open circles indicate the peak of the ground-state absorption.

On the basis of this link between $(\mathrm{CH})_x$ and finite analogs, we conclude that the data of Fig. 1 represent the spectrum of intrinsic excitations of the 1D chain. The two high-energy peaks are due to a self-localized state which results from an electron and hole added to a chain; the low-energy peak, present only in *trans*-$(\mathrm{CH})_x$, results from a single carrier added to a chain. Additional support for this assignment is the work of Lauchlan *et al.*,[15] who observed a photoconductive response ($\mu\tau \sim 10^{-8}$ cm^2 V^{-1}) in *trans*-$(\mathrm{CH})_x$ which was $\sim 10^3$ greater than the noise level, but no detectable signal in *cis*-$(\mathrm{CH})_x$.

Having established that these states are intrinsic excited states of the $(\mathrm{CH})_x$ chain, it is worthwhile to discuss these results in terms of recent theoretical treatments. Independent of the details of the distortion, these one-electron, 1D models predict that the self-localized states have length $\xi \sim (W/\Delta)a$,[7,8] where a is the distance between C atoms measured along the chain, and W/Δ is the ratio of the electronic band width to the band-gap parameter. We use a result from these calculations to estimate an important quantity, the quantum efficiency, y, for photogeneration. This result is the integrated cross section for optical absorption by the gap state, given by

$$\int \sigma\, d\epsilon \equiv \Sigma \simeq (\alpha/n)\xi^2\Delta, \qquad (1)$$

where α is the fine-structure constant and n is the index of refraction of $(CH)_x$.[9,16,17] For $\xi = 7a$,[3] and $\Delta = 0.8$ eV,[3] Eq. (1) gives $\Sigma \simeq 10^{-17}$ cm^2 eV. With this value for Σ, we estimate that $y \gtrsim 0.5$ for *trans*-$(CH)_x$ and $y \gtrsim 0.3$ for *cis*-$(CH)_x$. The result that y is of order unity is additional strong evidence for the intrinsic nature of these states. The lower bound for y results from the fact that the measurement is not sensitive to states which have lifetimes shorter than 10^{-5} s. Experiments are currently in progress to attempt to resolve the smallest time contants for recombination.

According to current models for self-localized states in $(CH)_x$, a photogenerated electron-hole pair in the *trans* isomer can give rise to a pair of isolated bond-alternation kinks.[5,6] Associated with each kink is a midgap level. In *cis*-$(CH)_x$, the kinks are thought to be confined after photogeneration because of the lower symmetry of the C backbone.[6,18] In this case the levels are split by their interaction to produce bonding and antibonding levels displaced from the gap center. In comparison of our observations with these ideas, the 0.5-eV peak immediately suggests the isolated kink, which is unique to the *trans* isomer. The higher-energy peaks are consistent with a close pair of kinks which has energy levels near the conduction and valence band edges. Two difficulties with this straightforward interpretation present themselves: First, the 0.5-eV peak is not at the gap center, but at least 0.2–0.3 eV below; second, the 1.35-eV peak in *trans*-$(CH)_x$ should have a significantly shorter lifetime than the corresponding peak in *cis*-$(CH)_x$ since in the *trans* isomer the kink pair is free to dissociate. In fact, at 8 K the lifetimes are almost the same. However, whereas in *cis*-$(CH)_x$ the lifetime is temperature independent, in *trans*-$(CH)_x$ it is smaller by $\sim 10^2$ at 295 K.

We suggest that the explanation of these observations requires going beyond one-electron models for the self-localized gap states. In particular, an isolated charged kink, being doubly occupied, should have a smaller binding energy than the neutral midgap level. In the case of the 1.35-eV peak, the Coulomb attraction could be sufficient to bind the kink pair in *trans*-$(CH)_x$ at sufficiently low temperature. A firm identification of these excitations must, however, await a determination of their spin and charge in addition to their absorption spectrum and lifetime.

---

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

[2] J. A. Pople and S. H. Walmsley, Mol. Phys. 5, 15 (1962).

[3] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979).

[4] M. J. Rice, Phys. Lett. 71A, 152 (1979).

[5] W. P. Su and J. R. Schrieffer, Proc. Natl. Acad. Sci. U.S.A. 77, 5626 (1980).

[6] S. A. Brazovskii and N. N. Kirova, Pis'ma Zh. Eksp. Teor. Fiz. 33, 4 (1981) [JETP Lett. 33, 6 (1981)].

[7] H. Takayama, Y. R. Lin-Liu, and K. Maki, Phys. Rev. B 21, 2388 (1980).

[8] D. K. Campbell and A. R. Bishop, Phys. Rev. B 24, 4859 (1981).

[9] N. Suyuki, M. Ozaki, S. Etemad, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. Lett. 45, 1209 (1980).

[10] T. G. Truscott, E. J. Land, and A. Sykes, Photochem. Photobiol. 17, 43 (1973).

[11] P. Mathis and J. Kleo, Photochem. Photobiol. 18, 343 (1973).

[12] R. S. Becker, R. V. Bensasson, J. Lafferty, T. G. Truscott, and E. J. Land, J. C. S. Faraday Trans. 2 74, 2246 (1978).

[13] J. Lafferty, A. C. Roach, R. S. Sinclair, and T. G. Truscott, J. C. S. Faraday Trans. 1 73, 416 (1977).

[14] A weak fluorescence (quantum efficiency $\sim 10^{-5}$) has been observed in *cis*-$(CH)_x$. See L. Lauchlan, S. Etemad, T. C. Chung, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B 24, 3701 (1981); L. S. Lichtmann, A. Sarhangi, and D. B. Fitchen, Solid State Commun. 36, 869 (1980).

[15] Lauchlan *et al.*, Ref. 14.

[16] K. Maki and M. Nakahara, Phys. Rev. B 23, 5005 (1981).

[17] J. T. Gammel and J. A. Krumhansl, to be published.

[18] A. J. Heeger, Comments Solid State Phys. 10, 53 (1981).