Photoexcitations of A Polydiacetylene

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PHOTOEXCITATIONS OF A POLYDIACETYLENE

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Abstract. Recent results of Photoinduced Absorption and Photoluminescence experiments on single crystals of a polydiacetylene are reviewed. These results are discussed in terms of the photoexcitations of a 1-d semiconductor.

A fundamental requirement for the development of conjugated polymers as a class of potentially useful semiconductors is an understanding of their electronic excitations. In this respect, polydiacetylenes are particularly attractive because of the availability of large, relatively defect-free single crystals. In this paper we review the results of Photoinduced Absorption (PA) and Photoluminescence (PL) experiments on single crystals of poly(2,4-hexadiyn-1,6-di-*p*-toluenesulphonate) (PTS). These results are compared with results of corresponding experiments on *cis*-$(CH)_x$, and are discussed in terms of the photoexcitations of a 1-d semiconductor with nondegenerate ground states.

PA experiments were carried out on thin single crystal platelets of PTS. Figure 1 shows the spectral dependence of the fractional change in transmission, $\delta t/t$, of a sample at 10 μs after exposure to a laser pulse of 3.48 eV photons. The absorption coefficient α parallel to the chains is also shown for comparison. For $\delta t/t \ll 1$, $\delta t/t$ is approximately $\delta\alpha/\alpha_o$, where α_o is the absorption coefficient at the laser excitation frequency. Thus, $\delta t/t$ as plotted in Fig. 1 is a direct measure of the absorption spectrum of the photoexcited state. In the range from 0.5 eV to 1.8 eV, the PA spectrum consists of a single, sharp asymmetric peak at 1.4 eV, strongly polarized along the direction of the polymer chains ($>10^2$ anisotropy). An analysis of the decay dynamics of the excited state is consistent with a monomolecular recombination mechanism, indicating that it is a photoexcitation which is neutral as

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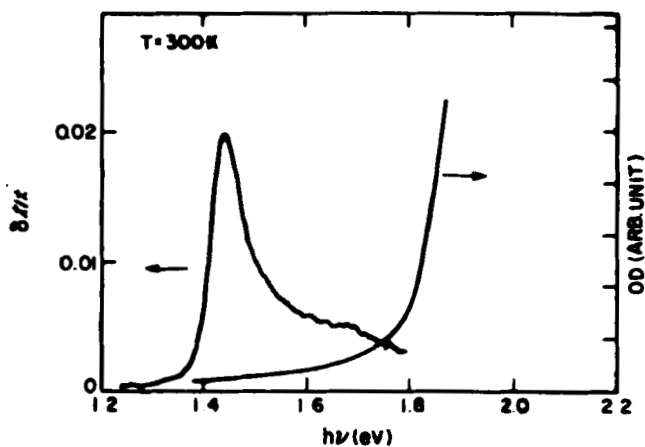
Figure 1. Fractional change in transmission $\delta t/t$ of a PTS crystal at 10 μs after a 3.48 eV laser pulse. T — 300K.

Figure 2. The Photoluminescnce and multiple order Raman lines from a PTS crystal using 2.41 eV laser excitation. T — 300K.

a whole [1]. The decay of the photoexcitation has a time constant of about 100 μs. The PA spectrum and decay rate obtained from polycrystalline films, similar in crystalline size to polyacetylene, are almost identical to those from single crystals

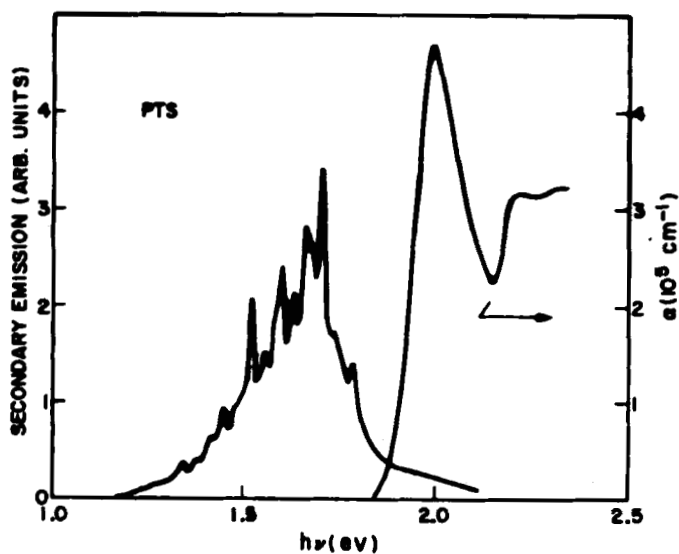The spectral dependence of the luminescence from PTS is shown in Fig. 2 for excitation with 2.41 eV photons. The absorption coefficient [2] is shown for comparison. A comparison of the results of experiments at different excitation energies shows that the spectrum of Fig. 2 consists of sharp, multiple order Raman lines superimposed on a relatively broad PL peak. After correcting for the response of the spectrometer, the PL peak is found at 1.7 eV, corresponding to a Stokes shift of about 0.3 eV. The absolute quantum efficiency for PL is of the order of 10^{-4}, and the PL decay constant appears to be faster than 10 ns. Very little change in the PL spectrum results from changing the temperature from 4K to 300K. We were unable to detect ($<10^{-5}$) any Optically Detected Magnetic Resonance (ODMR) signal, indicating that the PL peak is associated with a singlet state.
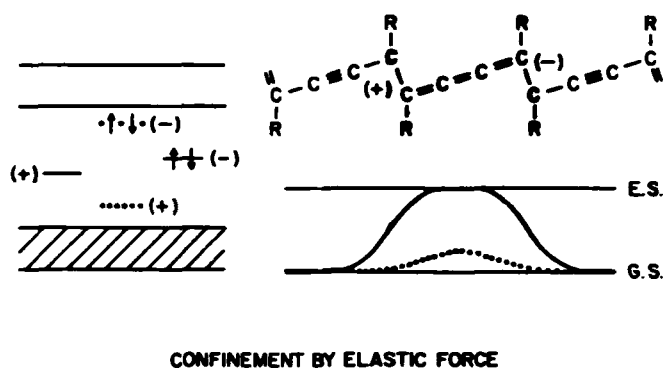

CONFINEMENT BY ELASTIC FORCE

Figure 3. Schematic drawing of a the order parameter and the electronic states of a confined soliton-antisoliton pair for weak (−) and strong (...) confinement.

There are striking similarities between the PL and PA results from PTS and those from *cis*-polyacetylene [3,4]. In PTS, the vinyl acetylene structure (G.S. in Fig. 3) for the unsaturated polydiacetylene backbone has a lower energy than the isomeric butatriene structure (E.S. in Fig. 3) [5]. Thus a domain wall defect or soliton-like excitation (S) would separate non-degenerate regions, as schematically shown in Fig. 3. In this respect also, PTS is similar to *cis*-$(CH)_x$. Associated with

each soliton-like excitation are electronic states inside the 1-d gap, whose positions are determined by the difference between the energy of the two isomers [6,7]. These states can be neutral or charged depending upon their occupancy.

If Coulomb effects can be ignored, the PL results in PTS can be interpreted in terms of the recombination of a confined soliton-antisoliton (SS*) pair, similar to the case of *cis*-(CH)$_x$ [6,7]. In analogy to *cis*-(CH)$_x$, absorption of a photon by PTS would generate a local lattice distortion, similar to a 1-d polaron. This excitation could spread, forming an SS* pair separated by a section of the less stable butatriene isomer (Fig. 3). Note that only in the case of weak confinement (see Fig. 3) a well defined butatriene segment is formed. The generation of this higher energy segment limits the separation of the SS* pair, causing them to be confined. As a result, they are forced to recombine and the resulting PL spectrum is related to the position of the electronic states inside the gap. We note that confinement by elastic forces (see Fig. 3) is an alternative mechanism to the formation of an intrachain exciton that can explain the absence of photoconductivity in the presence of strong absorption in PTS [8].

A recent analysis of the optical absorption of charged and neutral solitons in *trans*-(CH)$_x$ indicates that Coulomb effects are important [9]. As a result, Coulombic forces can contribute to the confinement of charged SS* pairs, analogous to excitons in a rigid lattice. However, since the presence of a Stokes shift implies a lattice relaxation following the absorption of a photon, the origin of the PL must be a polaronic exciton. In this analysis we have assumed that the PL peak inside the gap is intrinsic to PTS; i.e., it does not arise from defect states such as chain ends. Further experiments on PL from samples of different crystalline quality is necessary to substantiate this suggestion.

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