Comment on "Photoexcitations in *trans*-$(CH)_x$: A Fourier-Transform Infrared Study"

In a recent Letter Blanchet *et al.*[1] have presented photoinduced absorption spectra of *trans*-polyacetylene which demonstrate that photogenerated charged solitons apparently are pinned. The pinning frequency is 500 cm^{-1} (0.06 eV). I remark that this observation has a natural interpretation in terms of solitonic exciton formation. If a potential well $V(R)$ with a minimum at a separation distance $R=R_0$ exists between the oppositely charged members (S^+ and S^-) of a photogenerated pair, the solitons will bind and oscillate with a frequency ω_0 about the equilibrium separation R_0. The following simple calculation correctly predicts the magnitude of ω_0 and leads to a rate for a photodecay process, $S^+S^- \rightarrow S^0S^0+h\nu$, which is consistent with the observed recombination time of the photogenerated species.

Lin-Liu and Maki[2] have calculated the interaction energy between two solitons for $R>2\xi_0$, where $2\xi_0=(4t_0/\Delta)a$ is the soliton width and where t_0 denotes the π-electron hopping integral, 2Δ the Peierls gap, and $2a$ the linear lattice constant. For the S^+S^- configuration their calculation may be trivially modified to allow for the correct (odd) parity[3] of the two-electron wave function describing the occupation of the split gap states. Consequently, the S^+S^- configuration is *repulsive*, and allowing for the Coulomb attraction, one has

$$V(R)=-(e^2/\epsilon R)+(8\Delta/\pi)\exp(-2R/\xi_0). \qquad (1)$$

Here ϵ is the static dielectric constant of the polymer. It follows immediately that R_0 is the solution of $\pi e^2/8\epsilon\xi\Delta=(R/\xi)^2\exp(-R/\xi)$, where $\xi\equiv\xi_0/2$, while

$$(\hbar\omega_0)^2=(2e^2\hbar^2/\epsilon R_0^{\,2}\eta M_s)(1-2\xi/R_0) \qquad (2)$$

in which M_s is the soliton translational mass. With use of the representative values $2\Delta=1.4$ eV, $t_0=3$ eV, $M_s=m_e$, $\epsilon=10$, and $a=1.2$ Å, we find $R_0=5.1\xi=26$ Å (i.e., $R_0/2\xi_0=1.28$) and $\hbar\omega_0=0.062$ eV. Allowing for zero-point motion, the dissociation energy of the bound pair is $k_BT_d\simeq V(R_0)+\hbar\omega_0/2$, giving $T_d\simeq 151$ K, consistent with the observed temperature for the onset of photoconductivity.[4]

The rate, $1/\tau$, for the spontaneous photodecay process $S^+S^-\rightarrow S^0S^0+h\nu$, where $h\nu=4\Delta\exp(-R_0/\xi_0)$ is equal to the splitting of the gap states, is, for $T=0$,

$$\hbar/\tau\simeq(2e^2/3\epsilon R_0)(4\Delta\epsilon^{1/2}R_0/c\hbar)^3 \times\exp(-3R_0/\xi_0) \qquad (3)$$

which yields $\tau\simeq 3\times10^{-6}$ sec.

The effects of electron correlation and the possibility of the formation of a three-dimensional ionic lattice of solitons with the (highly repulsive) S^+S^- configuration of even parity is presently under investigation.

I thank Graciela Blanchet and Curt Fincher for directly stimulating this Comment.

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Received 6 June 1983
PACS numbers: 72.80.Le, 72.15.Nj, 78.30.Cp

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