Interchain solitonic excitons in *trans*-polyacetylene

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We consider a pair of oppositely charged solitons on neighboring chains. The electrostatic attraction between them gives rise to a finite pinning frequency. This result can account for the photoinduced infrared absorption peak near 500 cm^{-1}.

Photoinduced absorption[1-3] has proved to be a unique tool to probe the dynamical properties of some low-lying excitations in *trans*-polyacetylene. Among the various photoinduced absorption peaks observed, the one at 0.45 eV has been attributed to the absorption of photogenerated charged solitons.[4] Photogenerated neutral solitons have been invoked to explain the 1.35-eV peak.[5,6] It has also been demonstrated that the infrared absorption peaks are signatures of charged solitons. The absence of a zero-energy peak (the Goldstone mode) implies that the charged solitons are pinned. The nature of the pinning force has remained unknown.

Rice[7] proposed an intrachain soliton exciton model. The repulsive force between two overlapping solitons and the Coulomb attraction between them lead to an equilibrium separation. Small oscillations about this separation can cause infrared absorption, Rice argued. He also estimated the binding energy of the exciton to be 0.014 eV and the pinning frequency to be about 0.06 eV.

Such an explanation suffers at least two objections. First, it was pointed out by Mele[8] that the vibrational motion of this overall neutral exciton is not infrared active. Second, the potential well is too shallow to contain any bound excited state. The lowest absorption energy would be the dissociation energy 0.014 eV rather than the vibrational quantum energy 0.06 eV.

In this paper we consider the possibility that a pair of oppositely charged solitons on two neighboring chains form an exciton. The binding potential is simply the Coulomb attraction. From the unit-cell structure determined by x-ray scattering[9] the nearest chain-chain spacing is $d = 4.2$ Å and the next-nearest interchain distance is $d = 7.3$ Å. We assume that the charge-density profile of the solitons is not affected by the attractive Coulomb interactions. It is then proportional to the probability distribution of the gap state[10]

$$| \phi_0(x = na) |^2 = \frac{1}{\zeta/a} \operatorname{sech}^2[(x - n_0 a)/\zeta] \cos(n\pi) , \qquad (1)$$

where $\zeta = 6a$ is the soliton width and $a = 1.23$ Å is the lattice constant.

Now imagine a soliton S_1 fixed on a chain A and another oppositely charged soliton S_2 free to move about an equilibrium point P on chain B. The electrostatic energy of the system as a function of the distance of the center of S_2 from P can be easily evaluated. Let s be this distance. The energy is given by

$$E(s) = -\frac{e^2}{\epsilon_\perp} \sum_m \sum_n | \phi_0(na)\phi_0(ma - s) |^2 / [(ma - na)^2 + d_{eff}^2]^{1/2} , \qquad (2)$$

where $d_{eff} = d(\epsilon_{||}/\epsilon_\perp)^{1/2}$ is the effective chain-chain separation. It is not the same as the actual chain-chain separation d because the static dielectric constant along the chain axis $\epsilon_{||}$ differs from the perpendicular dielectric constant $\epsilon_\perp$.[11,12]

Numerical values of the dielectric constants have been determined by Kahlert and Leising[13] experimentally. Using these values ($\epsilon_{||} = 7.1$ and $\epsilon_\perp = 1.8$) the potential energy $E(s)$ is plotted versus the soliton displacement s for $d = 4.2$, 7.3, and 12.0 Å in Fig. 1. The spring constants estimated from the potential energy curves are $K = 0.0025$, 0.001, and 0.000 37 eV/Å^2.

The vibrational quantum of the relative motion is given by $\hbar\omega = \hbar(2K/m_s)^{1/2}$, m_s being the soliton kinetic mass. In the original Su-Schrieffer-Heeger (SSH) paper[10] m_s
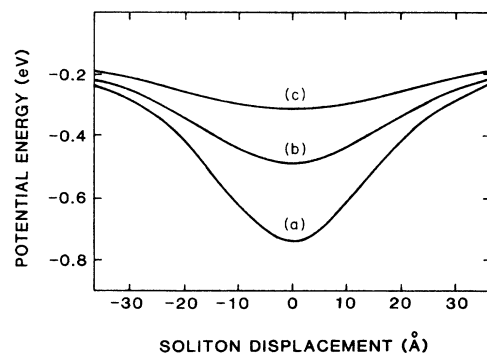

FIG. 1. Exciton potential energy curves for interchain spacing (a) $d = 4.2$ Å, (b) $d = 7.3$ Å, and (c) $d = 12.0$ Å.

was calculated to be $6m_e$. However, since the dimerization amplitude u_0 used there is slightly larger than the experimental value, we here adopt a somewhat smaller value of $m_s = 4m_e$. This also brings the theoretical values closer to the experimental numbers.[13,14] With the above choice of the parameters, $\hbar\omega$ equals 0.09, 0.06, and 0.04 eV for $d = 4.2$, 7.3, and 12.0 Å, respectively. The second number, 0.06 eV, is very close to the energy of the observed lowest infrared peak. Also notice that the potential wells are deep enough to hold several bound states. So it makes sense to talk about the absorption of a vibrational quantum.

The exciton considered above is stable in the absence of interchain coupling. Due to the existence of a finite transverse bandwidth of about 0.2 eV, an electron in the gap state of a negatively charged soliton can hop to the gap state of a positively charged soliton on a nearby chain. This process converts two charged solitons into two neutral solitons. This, being an exothermic reaction, can occur with the emission of a phonon. Therefore, for an interchain exciton to be stable, the soliton-soliton separation should be comparable to or larger than 7.3 Å so that the overlap of the two gap states is sufficiently small.

Although a direct electronic hop does not take place in a well-separated soliton pair, it can occur indirectly through the Kivelson mechanism.[15] In other words, the electron in the gap state of the negatively charged soliton can successively hop to the gap state of neutral solitons on chains in between the charged solitons. Since the Kivelson mechanism is fairly temperature sensitive, it is conceivable that above 200 K all the charged solitons are converted into neutral ones. This, in turn, can facilitate photoconduction through the Kivelson mechanism.

In the Rice model the onset of photoconductivity is attributed to thermal dissociation of the charged solitons. This would imply the existence of higher-energy infrared features and the absence of the pinning mode at the same time. Experimentally, however, all the photoinduced infrared features show the same dependence on temperature and laser intensity. The latter is consistent with our present scenario.

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