Theoretically predicted Drude absorption by a conducting charged soliton in doped polyacetylene

M. J. Rice
Xerox Webster Research Center, Webster, New York 14580
(Received 9 June 1981)

With the aid of a novel quantum theory of the charged soliton we conclude that the observation of a "discrete Drude absorption" would constitute an experimental verification of charged-soliton transport in doped polyacetylene.

The suggestion[1,2] that charged solitons may be generated in *trans*-polyacetylene $[(CH)_x]$ by light acceptor or donor doping has stimulated much subsequent experimental and theoretical interest in this subject.[3] A recent development of considerable interest has been the report by Ikekata *et al.*[4] of a range of dopant concentration for which the homogeneously doped polymer exhibits metallic conductivity with an essentially zero Pauli spin susceptibility. Although electron transport arising from a small but finite Fermi-level density of localized one-electron states cannot be ruled out,[5] the conclusion that the metallic-like dc conductivity results from the transport of charged solitons is seriously suggested for the first time. In order to conceive of an experiment that could distinguish between soliton and electron transport we have theoretically investigated the Drude absorption of a conducting charged soliton in $(CH)_x$. Remarkably, we find that in addition to the usual Drude absorption expected for a diffusing free carrier, the charged soliton's Drude absorption possesses a vibrational component which leads to a discrete absorption band at the frequency ω_i of the soliton's internal breathing mode.[6,7] This band is a consequence of the coupling of the internal and translational motions of the soliton which endows the *mobile* charged soliton with an oscillating electric dipole moment proportional to its mean velocity of translation. The observation of this "discrete Drude absorption" would constitute an experimental verfication of charged-soliton transport in doped $(CH)_x$.

In order to calculate the charged soliton's Drude absorption we employ the results of a quantum theory which we have developed for the charged soliton. The latter theory, which is planned to be published in an independent article,[8] is a straightforward extension to quantum mechanics of a classical Hamiltonian theory of the soliton recently introduced by Rice and Mele.[6] In the quantum theory the soliton is described by the wave function $\Psi(x,l)$ where $|\Psi(x,l)|^2\,dx\,dl$ determines the probability that the center of the soliton be found between the spacial points x and $x+dx$ with a length between l and $l+dl$. The frequency-dependent conductivity of the free-charged soliton, $\sigma(\omega)$, is

$$\sigma(\omega)=\lim_{q\to 0}\left[-i\omega\Omega^{-1}e^2\sum_{\alpha\gamma}P(E_\alpha)\left(\frac{2}{\hbar\omega_{\gamma\alpha}}\right)\times\frac{|v_{\gamma\alpha}(q)|^2}{\omega_{\gamma\alpha}^2-(\omega+i\delta)^2}\right], \tag{1}$$

where $\{E_\alpha\}$ denote the energy eigenvalues of the free soliton, $\hbar\omega_{\gamma\alpha}=E_\gamma-E_\alpha$, Ω denotes the volume of the system,

$$P(E_\alpha)=\exp(-\beta E_\alpha)\Big/\sum_\alpha\exp(-\beta E_\alpha)$$

is the probability of finding the soliton in the state with energy E_α at temperature $T=1/k_B\beta$, and $v_{\gamma\alpha}(q)$ is the matrix element

$$v_{\gamma\alpha}(q)=i\int_0^\infty dl\int_{-\infty}^\infty dx\,\Psi_\gamma^*(x,l)\,v(q,l)\,\Psi_\alpha(x,l)\ , \tag{2}$$

of the velocity fluctuation operator

$$v(q,l)=[1/2M_s(l)][p_x\exp(-iqx)+\exp(-iqx)p_x]\ . \tag{3}$$

In Eq. (3) $M_s(l)$ denotes the classical length-dependent *translational* mass of the soliton[6] and $p_x=-i\hbar\nabla_x$ is the soliton's translational momentum operator.

The energy eigenvalues of the free soliton are determined by the Schrödinger equation

$$H\Psi_\alpha(x,l)=E_\alpha\Psi_\alpha(x,l)\ , \tag{4}$$

where the Hamiltonian operator H is

$$H=\tfrac{1}{4}[M_i(l)^{-1}p_l^2+p_l^2M_i(l)^{-1}]+V_i(l)+\tfrac{1}{2}M_s(l)^{-1}p_x^2\ . \tag{5}$$

Here, $M_i(l)$ denotes the classical length-dependent *internal* inertial mass of the soliton,[6] $p_l=-i\hbar\nabla_l$ its internal momentum operator, and $V_i(l)=Al^{-1}+Bl$ its internal potential energy. A and B are positive constants which determine the formation energy E_s^0 and equilibrium length l_0 of the classical static soliton

according to the familiar relations $E_s^0 = 2\sqrt{AB}$ and $l_0 = \sqrt{A/B}$. If we denote by M_s and M_i the translational and internal inertial masses of the latter soliton, we have according to the classical Hamiltonian theory,[6] $M_i(l) = M_i l_0/l$ and $M_s(l) = M_s l_0/l$. An extension of Eqs. (4) and (5) to provide a quantal description of a charged soliton bound to an ionic dopant molecule is planned to be discussed elsewhere.[8]

The eigenspectrum defined by Eqs. (4) and (5) and the latter stated l dependences of the classical masses, may be solved for exactly to yield the free-soliton eigenvalues

$$E_\alpha = E_{n,k} = [1 + (2/\kappa)(n + \tfrac{1}{2})](M_s^2 c_0^4 + c_0^2 \hbar^2 k^2)^{1/2} \quad , \tag{6}$$

where $n = 0, 1, 2, \ldots$, is an internal vibration quantum number and $\hbar k = \hbar(\pi/L)s$, with $s = \pm 1, \pm 2, \ldots$, specifies the quantization of the soliton's translational momentum along a chain of length L ($L \to \infty$). $M_s c_0^2 = E_s^0$ and $\kappa/2$ denotes the dimensionless parameter $\kappa/2 = (2M_i l_0 A/\hbar^2)^{1/2}$. The latter's magnitude specifies the extent to which the nature of the internal motion of the soliton is quantum mechanical. Clearly, in the limit $\kappa \to \infty$, Eq. (6) yields the classical energy spectrum of the soliton. For $(CH)_x$ we estimate $\kappa/2 \simeq 3$. The corresponding eigenfunctions are

$$\Psi_{n,k}(x,l) = L^{-1/2} \exp(-ikx)\psi_n(l/\lambda_k) \quad , \tag{7a}$$

where

$$\psi_n(y) = \exp\left(\frac{-y}{2}\right) y^{\kappa/2} \sum_{j=0}^{n} a_j y^j \quad , \tag{7b}$$

in which, for $j \neq 0$, the coefficients a_j are determined by the recurrence relation

$$a_{j+1} = -a_j(n-j)/[(j+1)(j+1+\kappa)]$$

and a_0 by the normalization of $\Psi_{n,k}(x,l)$. In Eq. (7a) λ_k denotes the characteristic length

$$\lambda_k = l_0 \kappa^{-1}[1 + (\hbar k/M_s c_0)^2]^{-1/2} \quad .$$

With the use of the relation $\kappa = 2E_s^0/\hbar\omega_i$, where $\omega_i = 2(B/2M_i l_0)^{1/2}$ is the classical *harmonic* frequency[6] of the internal breathing mode of the static soliton, Eq. (6) may be expanded for $\hbar^2 k^2/M_s << E_s^0$ to read

$$E_{n,k} = M_s c_0^2 + \hbar^2 k^2/2M_{sn} + (n + \tfrac{1}{2})\hbar\omega_i \quad , \tag{8}$$

where $M_{sn} = M_s \kappa/(\kappa + 2n + 1)$ may be regarded as the effective soliton translational mass in the vibrational subband n. We note that it follows from Eq. (7) that, for small k, the expectation value of the soliton length l is just $\langle l \rangle = l_0(\kappa + 2n + 1)/\kappa$ for the band n. This increase in $\langle l \rangle$ with vibrational excitation is responsible for the corresponding decrease in M_{sn}. The remarkable contrast between the simple harmonic nature of the vibrational eigenspectrum of Eq. (8) and the decidedly anharmonic nature of the associated wave functions (7b) is planned to be commented on in an independent publication.[8]

With the use of Eqs. (8), (7), and the assumption that E_s^0 and $\hbar\omega_i >> k_B T$, Eq. (1) for $\sigma(\omega)$ may be evaluated to yield

$$\sigma(\omega) = \sigma_0[(1 - i\omega/\Gamma)^{-1} + (k_B T/\hbar\omega_i)(l_{10}/l_{00})^2(-i\omega\Gamma)/(\omega_1^2 - \omega^2 - i\Gamma_i\omega)] \tag{9}$$

where

$$l_{nn'} = \int_0^\infty dl\, \psi_n(l)\, l\, \psi_{n'}(l) \quad ,$$

which, from Eq. (7), gives $l_{10}/l_{00} = -(1+\kappa)^{-1/2}$. In evaluating Eq. (1) we have introduced a phenomenological constant Drude lifetime $\tau = \Gamma^{-1}$ and a natural width Γ_i for the internal breathing mode of the soliton. σ_0 is the dc conductivity $\sigma_0 = \Omega^{-1} e^2 \tau/M_{s0}$ and the first term of Eq. (9) corresponds to the Drude absorption ordinarily expected for a diffusing free carrier. The second term is the discrete Drude absorption at ω_i arising from the coupling of the soliton's internal and translational motions. Its origin is clearly apparent from a classical interpretation of the soliton's velocity operator (3). Since, classically, l is oscillating about its equilibrium value l_0, the velocity $v = p_x/M_s(l)$ of the soliton in a state of constant translational momentum p_x has an oscillatory component. As the soliton is charged it consequently is endowed with an oscillating electric dipole moment which is proportional to its mean velocity of translation. The integrated oscillator strength of the discrete Drude absorption, $S_i = S_0(k_B T/\hbar\omega_i)(1+\kappa)^{-1}$, is therefore, understandably, proportional to the absolute temperature T. $S_0 = (\pi\Omega^{-1} e^2/2M_{s0})$ is the integrated oscillator strength of the ordinary Drude absorption.

In Fig. 1 we have plotted the real and imaginary parts of $\sigma(\omega)/\sigma_0$ as a function of ω/ω_i for the representative choice of parameter values $\Gamma = \omega_i$, $\Gamma_i = \omega_i/5$, $k_B T = \omega_i/5$, and $\kappa = 2E_s^0/\omega_i = 6$. To date, an accurate microscopic calculation of ω_i for the charged soliton in $(CH)_x$ has not been undertaken. Following a phenomenological approach, Rice and Mele[6] have established the estimate $\omega_i \simeq 1280$ cm^{-1}, whereas Su *et al.*[7] have arrived at the result $\omega_i \simeq 780$

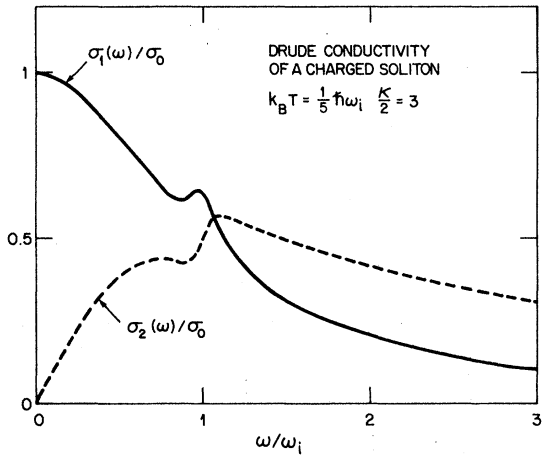

FIG. 1. Real and imaginary parts of $\sigma(\omega)/\sigma_0$ vs ω/ω_i computed from Eq. (9) for the parameter values stated in the text.

cm^{-1} on the basis of a simplified microscopic model of $(CH)_x$.

An experimental search for the discrete Drude absorption would be made difficult if the value of ω_i lies close to either of the two dopant-dependent intensely ir active modes already observed[9] for inhomogeneously doped $(CH)_x$ at 900 and 1370 cm^{-1}, respectively. The latter modes have been identified[10] as specific intrinsic structural vibrational excitations of the charged soliton. These necessarily arise in addition to the breathing mode ω_i as a consequence of the soliton's actual discrete atomistic structure. If, however, ω_i lies not too close to either the 900- or 1370-cm^{-1} mode the discrete temperature-dependent Drude absorption should be observable if charge transport is predominantly due to charged solitons.

It is hoped that this Communication will stimulate an experimental search for this possible absorption band.

Finally, it is interesting to note that the relatively small value of $\kappa/2$ for $(CH)_x$ implies that the bond alternation amplitude of nature's simplest polymer has the character of a quantum field. The relevance of the quantum-field-theory literature[11] to the present problem is therefore called to attention.

ACKNOWLEDGMENTS

We thank Gill Stengle, John Bardeen, and Eugene Mele for several useful discussions.

[1]M. J. Rice, Phys. Lett. 71A, 152 (1979).
[2]W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979).
[3]See, e.g., Proceedings of International Conference on Low-Dimensional Synthetic Metals Helsingor, Denmark, August 10–15, 1980 [Chem. Scr. (in press)].
[4]S. Ikekata, J. Kaufer, T. Woener, A. Pron, M. A. Druy, A. Sirak, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. Lett. 45, 1123 (1980): see, also, M. Peo, S. Roth, and J. Hocker, Ref. 3; A. J. Epstein, H. Rommelmann, M. A. Druy, A. J. Heeger, and A. G. MacDiarmid (unpublished).
[5]E. J. Mele and M. J. Rice, Phys. Rev. B 23, 5397 (1981); M. J. Rice and E. J. Mele, Chem. Scr. 17, 121 (1981).
[6]M. J. Rice and E. J. Mele, Solid State Commun. 35, 487 (1980).
[7]W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B 22, 2099 (1980).
[8]M. J. Rice and E. J. Mele (unpublished).
[9]C. R. Fincher, Jr., M. Ozaki, A. J. Heeger, and A. G. MacDairmid, Phys. Rev. B 19, 4140 (1979).
[10]E. J. Mele and M. J. Rice, Phys. Rev. Lett. 45, 926 (1980).
[11]R. Jackiw, Rev. Mod. Phys. 49, 681 (1977).