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INFRARED ACTIVITY OF PEIERLS SYSTEMS AND APPLICATION TO POLYACETYLENE

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The conductivity of added charge (e.g. solitons) to a dimerized Peierls condensate with N coupled phonon bands is considered. If the phonon frequencies are low compared with the Peierls gap and the charge extends over several atoms then: (a) The infra-red frequencies $\omega_n^\phi (n = 1, 2, \ldots, N)$ and their relative weights are independent of the charge configuration. (b) The product $\Pi_{n=1}^N(\omega_n^\phi/\omega_n^R)$, where ω_n^R are the Raman frequencies, is isotope independent. The results are valid even if electron–electron interactions are present and a pinning effect is included. The product rule (b) is in good agreement with data on *trans* $(CH)_x$ and $(CD)_x$. This data also yields the coupling constants and the pinning force.

THE DOPING PROCESS of polyacetylene and the nature of the charge transfer are of considerable recent interest [1]. In particular Fincher *et al.* have shown that lightly doped ($< 0.1\%$) polyacetylene $(CH)_x$ with a variety of acceptors or donors leads to the appearance of new infra-red (i.r.) active modes at 900 cm^{-1} (width of ~ 400 cm^{-1}) and at 1370 cm^{-1} (width of ~ 50 cm^{-1}). This i.r. activity is independent of the dopant type and is therefore evidence that charge has been transferred to the polyacetylene chain and its coupling with the polyacetylene vibrational normal modes causes the i.r. activity. Of additional interest is the i.r. data of $(CD)_x$ [3–5] where three lines appear with Na doping [5].

Undoped polyacetylene is a semiconductor with a gap of $2\Delta_0 \simeq 1.4$ eV [6]. This gap is maintained upon doping, so that the new i.r. modes are within the gap, at frequencies $\omega \ll \Delta_0$.

This behaviour is considered as an evidence [4, 7] for the soliton configuration in polyacetylene [8–11]. Here I show that this unusual behaviour is a universal result of the translation degree of freedom of the added charge, independent of its configuration.

Consider N phonon bands in an undimerized system whose bare frequencies at a zone boundary $q = \pi/a$ are ω_n^0 [a is the lattice constant, i.e. the c–c distance along the chain in $(CH)_x$] and their dimensionless electron–phonon coupling constants are $\lambda_n (n = 1, 2, \ldots, N)$. For trans $(CH)_x$ each C–H unit has 4 degrees of freedom for vibration within the polymer plane which may couple to the electronic charge, i.e. $N = 4$. Because of the polymer zig-zag shape two of these modes, associated with the carbon vibration, should be strongly coupled.

In the presence of dimerization the zone boundary (equivalent to the zone center) phonons have frequencies ω_n^R and are Raman active. These modes correspond to oscillations in the dimerization amplitude [12, 13] and their frequencies are known from Raman scattering [14–16].

When a unit charge is added to a dimerized chain a defect of length ξ in the dimerization pattern results and i.r. activity appears. We expect that $\xi \simeq \xi_0 \equiv v_F/\Delta_0$ where v_F is the Fermi velocity. There are two types of phonons [17]: extended modes, whose dispersion $\omega_n(q) = \omega_n^R(1 + \xi_0^2 q^2/12)^{1/2}$ is not affected by the defect, and localized modes with a discrete spectrum. In principal all modes become i.r. active since translation invariance is broken. However the contribution of the extended modes at the zone center and further than ξ^{-1} from the zone center are both vanishing. The spread of wavevectors in the range $(0, \xi^{-1})$ results in a spread in frequency of the order of $\omega_n^R/20$. Therefore, although the total contribution of the extended modes may be comparable to that of the localized modes it is less likely to be observed because of its much larger width. This is indeed confirmed by the numerical lattice calculation [7].

In the following I consider only the localized i.r. modes. A linear combination of these modes yields the time dependent center of mass $\phi(t)$; by solving the coupled set of equations of motion the i.r. frequencies $\omega_n (n = 1, 2, \ldots, N)$ are obtained as functions of ω_n^0 and λ_n.

Two assumptions are made in the derivation:

(a) All phonon frequencies are small compared with internal electronic transition frequencies. The latter are of order Δ_0 and the conditions $(\omega_n^{\phi,R}/\Delta_0)^2 \ll 1$ are valid for polyacetylene. In the presence of a pinning potential, the electronic transition frequencies in this potential are also assumed to be large compared with the phonon frequencies.

(b) Lattice discreteness is neglected, i.e. $\xi \gg a$. This assumption is consistent with the metallic behaviour above 1% doping [6] and with the results below. This assumption justifies the use of dispersionless *bare* frequencies ω_n^0, the relevant ones being ξ^{-1} away from the zone boundary.

These two assumptions lead to the following conclusions:

(a) The i.r. frequencies and the ratio of their intensities are independent of the charge configuration. Thus the claim [4, 7] that the charged soliton configuration explains the i.r. data does not prove that solitons are indeed the charge carriers. The latter can be tested only if the electronic structure is involved, e.g. by comparing i.r. intensities with interband transitions or by measuring the dielectric constant.

(b) The zero frequency translation mode acquires a finite frequency if pinning is present, e.g. due to Coulomb interaction with the dopant ion in doped polyacetylene. The number of i.r. modes, *including* the pinned mode, equals the number of Raman modes, or the number of bare coupled phonons. This confirms that the pinned mode in polyacetylene is at 900 cm^{-1} [2], and not at a much lower frequency as claimed in [7].

(c) The product $\Pi_n(\omega_n^\phi/\omega_n^R)$ is isotope independent [see equation (21)]. The product rule is in good agreement with data of $(CH)_x$ and $(CD)_x$. This remarkable result in fact justifies the neglect of lattice discreteness.

(d) The results (a)–(c) are valid even if a direct electron–electron interaction is present. If, however, the latter is neglected, the parameter ω_n^0, λ_n and the pinning force can be determined, as summarized in Tables 1 and 2.

The approach to intra-gap i.r. activity, presented below, generalizes two known examples. The first one is the motion of an incommensurate charge density wave [13, 18]. The ion displacement at the mth site is $u(m) = u_0 \cos(q_0 ma + \phi)$ where u_0 is the displacement amplitude, $q_0 a/\pi$ irrational and the phase variable ϕ is the center of mass coordinate mentioned above. The second example is the i.r. activity of charged solitons in polyacetylene [7].

In a dimerized Peierls condensate, such as polyacetylene, $q_0 = \pi/a$ so that $u(m) = (-)^m u_0$; thus ϕ is not coupled to the ion displacement and there are no i.r. modes (except at high frequencies [19]). The addition of charge, e.g. by doping, restores the i.r. activity associated with the translation mode, as shown next.

The displacement pattern along the chain axis has the form $u_n(m) = (-)^m \Delta_n(ma)/4\alpha_n$, where $n = 1, 2, \ldots, N$ are the normal modes and α_n their couplings to the electrons as defined in [8]. The neglect of the lattice discreteness leads to a continuum model for $\Delta_n(x)$ [9–11]. The Δ_n dependent part of the Hamiltonian is

$$H\{\Delta_n\} = \int \mathrm{d}x \left\{ \sum_{n=1}^{N} (2\pi v_F \lambda_n)^{-1} [\Delta_n^2(x) + (\dot{\Delta}_n(x)/\omega_n^0)^2] + \Delta(x)C(x) \right\}, \qquad (1)$$

where $\lambda_n = 4\alpha_n^2 a/(\pi v_F K_n)$ with K_n the spring constants for distorting the undimerized system [8], $\dot{\Delta}_n$ the canonical momenta, $\Delta(x) = \Sigma_n \Delta_n(x)$ and $C(x)$ involves electron operators describing backscattering of electrons across the Fermi sea. All the relevant phonons near the zone boundary couple to the same electron scattering $C(x)$. The total Hamiltonian involves also the electron kinetic energy and direct electron–electron interactions. Here only the phonon equations of motion are relevant, and equation (1) yields

$$\Delta_n(x, t) + \ddot{\Delta}_n(x, t)/\omega_n^{02} = -\pi v_F \lambda_n C(x, t). \qquad (2)$$

The ground state of the dimerized system is uniform $\Delta(x) = \Delta_0$. The addition of charge leads to an x dependent solution

$$\Delta_n(x) = -\pi v_F \lambda_n C(x) = \Delta(x) \cdot \lambda_n/\lambda, \qquad (3)$$

where $\lambda \equiv \Sigma_n \lambda_n$. Consider now a solution of the form $\Delta[x - \phi(t)]$, i.e. the static solution with time dependent center of mass. Each normal mode has its own center of mass variable $\phi_n(t)$ satisfying $\Delta(x - \phi) = \Sigma_n \Delta_n(x - \phi_n)$. Expanding to first order in ϕ_n yields $\phi(t) = \Sigma_n \phi_n(t)\lambda_n/\lambda$.

The main ingredient in the derivation is that the electronic part, $C(x, t)$, follows adiabatically the ion displacement, which is justified for $(\omega/\Delta_0)^2 \ll 1$. Thus $\Delta(x - \phi) = -\pi v_F \lambda C(x, t)$ and to first order in $\phi(t)$, $\Delta'(x)\phi = \pi v_F \lambda \delta C$. Expansion of equation (2) to first order in ϕ_n yields

$$\phi_n(t) + \ddot{\phi}_n(t)/\omega_n^{02} - \phi(t) = 0. \qquad (4)$$

These equations correspond to the Lagrangian

$$L\{\phi_n\} = \tfrac{1}{2} M_c N_c \Omega_0^2 \times \left\{ \sum_n [-\phi_n^2 + (\dot{\phi}_n/\omega_n^0)^2] \lambda_n/\lambda + \phi^2 \right\}, \qquad (5)$$

where N_c is the number of unit charges,

$$\Omega_0^{-2} = \sum_n \frac{\lambda_n}{\lambda} (\omega_n^0)^{-2} \qquad (6)$$

and M_c the kinetic mass per unit charge. To see this consider a uniform motion with velocity v, i.e. $\phi_n = \phi$, $\phi_n = v$ so that $L = \tfrac{1}{2} M_c N_c v^2$.

The mass M_c can be identified from the kinetic term in equation (1) where $\dot{\Delta}_n(x-\phi) = -\dot{\phi}\Delta'_n(x)$ to first order in ϕ; hence

$$M_c = \int \Delta'^2(x)\,\mathrm{d}x/(\pi\lambda v_F\Omega_0^2 N_c) \tag{7}$$

For the single soliton solution $\Delta(x) = \Delta_0 \tanh (x\Delta_0/v_F)$ equation (7) yields the known result [8, 10] $M_s = 4\Delta_0^3/(3\pi\lambda v_F^2\Omega_0^2)$. In the incommensurate limit (i.e. high density of the soliton lattice [20]) $\Delta(x) = \Delta_0 \exp(i2k_Fx)$ + h.c. where k_F is the Fermi wavevector. Equation (7) now yields the mass $M_c = M_F$ where $M_F/m = 4\Delta_0^2/\lambda\Omega_0^2$, and $m = k_F/v_F$. M_F is just the Fröhlich mass of an incommensurate charge density wave [12, 21] if $\Omega_0^2 \ll \Delta_0^2$.

If ρ is the average charge density, $\rho = N_c/L$, then motion of the center of mass implies an electric current

$$j(t) = e\rho\frac{\partial\phi(t)}{\partial t}. \tag{8}$$

The charge is assumed to move rigidly with the center of mass, which is again justified for low frequencies $(\omega/\Delta_0)^2 \ll 1$. As an example, a linear response analysis for the soliton solution [9–11] yields

$$j(\omega) = ie\rho\omega\phi(\omega)[1 + (\pi^2/12)(\omega/\Delta_0)^2 + 0(\omega/\Delta_0)^4].$$

The Lagrangian (5) describes a frictionless motion of the charge. The dopant ions however provide a pinning potential for the charge on the polyacetylene chain. For a charge distribution $\rho[x-\phi(t)]$ the pinning interaction is

$$V_{\mathrm{pin}} = -e^2\int V(x)\rho[x-\phi(t)]\,\mathrm{d}x.$$

Expansion to second order in ϕ yields

$$V_{\mathrm{pin}} = -E_B - \tfrac{1}{2}e^2\phi^2(t)\int V''(x)\rho(x)\,\mathrm{d}x, \tag{9}$$

where

$$E_B = e^2\int V(x)\rho(x)\,\mathrm{d}x$$

is the binding energy. The effective Lagrangian in the presence of an external electromagnetic potential $A(t)$ in the chain direction becomes

$$L_{\mathrm{eff}} = \tfrac{1}{2}M_cN_c\Omega_0^2 \left\{\sum_n [-\phi_n^2 + (\dot{\phi}_n/\omega_n^0)^2]\lambda_n/\lambda + (1-\alpha)\phi^2\right\} - e^2N_cA(t)\dot{\phi}(t) \tag{10}$$

where

$$\alpha = -e^2\int V''(x)\rho(x)\,\mathrm{d}x/(M_cN_c\Omega_0^2).$$

The equations of motion for $\phi_n(\omega)$ are now

$$(1-\omega^2/\omega_n^{02})\phi_n(\omega) - (1-\alpha)\phi(\omega) = -e^2E(\omega)/(M_c\Omega_0^2) \tag{11}$$

where $E(\omega)$ is the electric field. Equation (11) is easily solved for the field $\phi(\omega)$ and equation (8) yields the conductivity

$$\sigma(\omega) = i\omega\frac{\rho}{M_c\Omega_0^2}\,\frac{D_0(\omega)}{1+(1-\alpha)D_0(\omega)} \tag{12}$$

where

$$D_0(\omega) = \sum_n \frac{\lambda_n}{\lambda}\,\frac{\omega_n^{02}}{\omega^2-\omega_n^{02}}. \tag{13}$$

The poles of equation (12) yield the i.r. frequencies ω_n^ϕ. For $\alpha = 0$ there is a pole at $\omega = \omega_1^\phi = 0$ which corresponds to the Fröhlich type superconductivity [12] $\operatorname{Re}\sigma(\omega) = \delta(\omega)\pi\rho/M_c$ for $\omega < \omega_2^\phi$ [ω_2^ϕ is the next pole of equation (12)]. For $\alpha \neq 0$ translation invariance is lost and the Fröhlich mode becomes a pinned mode at frequency $\omega_1^\phi \neq 0$. The function $D_0(\omega)$ is plotted in Fig. 1 for a 3 phonon system. Its intersections with the value $-1/(1-\alpha)$ (line *a* in Fig. 1) determine the frequencies ω_n^ϕ. For $\alpha < 1$, $\omega_1^\phi < \omega_1^0$ and there is an additional solution in each interval $(\omega_n^0, \omega_{n+1}^0)$. For $\alpha > 1$ there is a solution at $\omega > \omega_N^0$ instead of the solution at $\omega < \omega_1^0$. There are always N solutions, i.e. the number of i.r. modes, *including* the pinned mode, equals the number of coupled bare modes.

Some properties of the conductivity equation (12) are worth discussing. First note that the information on the nature of the charge, i.e. if it is a soliton, a polaron [22], a soliton lattice [20] or any other configuration, is contained in the single parameter M_c. In fact, the conductivity in the incommensurate limit (or high soliton density) has been calculated [13, 18] and it coincides with equation (12) when $(\omega/\Delta_0)^2 \ll 1$, ρ is the total charge and $M_c = M_F$ the Fröhlich mass. Thus the i.r. frequencies, as well as their relative weights, are independent of the charge configuration, as long as $(\omega_n^\phi/\Delta_0)^2 \ll 1$. The value of M_c can be derived by comparing the i.r. intensities with the total intensity which includes electronic interband transitions. For this comparison one needs the conductivity sum rule [23]

$$\int_0^\infty \operatorname{Re}\sigma(\omega)\,\mathrm{d}\omega = e^2v_F. \tag{14}$$

Another possibility for determining M_c is by measuring the dielectric constant

$$\epsilon(0) = 1 + 4\pi\rho e^2/(\alpha M_c\Omega_0^2). \tag{15}$$

If the experimental values for $\epsilon(0)$ can be corrected

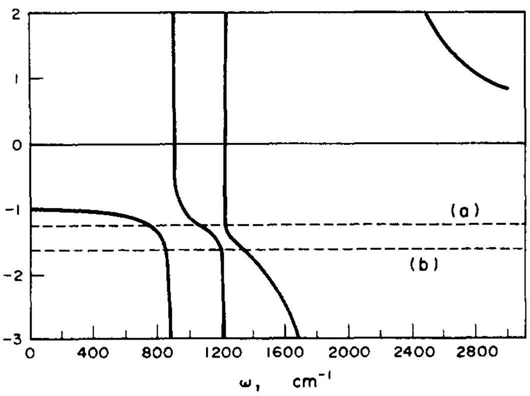

Fig. 1. The function $D_0(\omega)$ [equation (13)] with the parameters of Table 2. The intersections with the value $-1/(1-\alpha) = -1.26$ (line a) give the i.r. frequencies ω_n^ϕ, while the intersections with the value $-1/(1-2\lambda) = -1.62$ (line b) give the Raman frequencies ω_n^R.

for local field effects, the term linear with ρ should yield the value of M_c. Note that $\epsilon(0)$ does not determine a dynamic property such as M_c. It is the combined information of $\alpha\Omega_0^2$ from i.r. data with $\epsilon(0)$ which determines M_c.

Another feature of equation (12) is a "product rule" of the frequencies ω_n^ϕ. The denominator in equation (12) can be written as $\Pi_n(\omega^2-\omega_n^{\phi 2})/(\omega^2-\omega_n^{02})$. By comparing values at $\omega = 0$ the product rule is obtained

$$\sum_{n=1}^{N} (\omega_n^\phi/\omega_n^0)^2 = \alpha. \tag{16}$$

In order to test equation (12) with experimental data the frequencies ω_n^0 are needed. Since the available calculations of ω_n^0 [24] neglect interchain coupling, I use instead another set of data which is directly measurable, i.e. the Raman frequencies of the dimerized (undoped) system. The Raman frequencies correspond to amplitudes oscillations around Δ_0 [12, 13]. If $-N(0)E_i(\Delta)$ is the interaction energy of forming a gap $\Delta = \Sigma_n\Delta_n$ and $N(0) = 2/\pi v_F$, then the effective Lagrangian is

$$L_{\text{eff}}\{\Delta\} = N(0)\left\{\sum_n \frac{1}{4\lambda_n}\left[-\Delta_n^2 + (\dot{\Delta}_n/\omega_n^0)^2\right] + E_i(\Delta)\right\}. \tag{17}$$

$E_i(\Delta)$ is independent of $\dot{\Delta}$ since the dynamics are dominated by the phonon terms. This is the same adiabatic principle used above which is valid for $\omega \ll \Delta_0$.

The ground state is $\Delta_0 = 2\lambda E_i'(\Delta_0)$ while small oscillations with amplitude $\delta_n(t)$ satisfy

$$\delta_n(t) + \ddot{\delta}_n(t)/\omega_n^{02} = 2\lambda_n\delta(t)E_i''(\Delta_0), \tag{18}$$

where $\delta = \Sigma_n\delta_n$. The eigenfrequencies of equation (18) solve the equation

$$D_0(\omega) = -1/(1-2\tilde{\lambda}), \tag{19}$$

where $D_0(\omega)$ was defined in equation (13) and $1 - 2\tilde{\lambda} = 2\lambda E_i''(\Delta_0)$.

The interaction energy $E_i(\Delta)$ depends on both electron–phonon and electron–electron interactions. For the Peierls model (no electron–electron interactions) $E_i(\Delta) = \frac{1}{4}\Delta^2 + \frac{1}{2}\Delta^2 \ln(2E_c/\Delta)$ [21] where E_c is the electron cutoff energy. Thus $\Delta_0 = 2E_c \exp(-1/2\lambda)$ and in equation (19) $\lambda = \tilde{\lambda}$. This coincides with the Raman frequencies in the incommensurate limit [13] except that λ is replaced by 2λ [11].

Equation (19) is identical to the equation for ω_n^ϕ except α is replaced by $2\tilde{\lambda}$. Therefore it has N solutions for the Raman frequencies ω_n^R; for $2\tilde{\lambda} < 1$, $\omega_1^R < \omega_1^0$ and there is one additional solution in each interval $(\omega_n^0, \omega_{n+1}^0)$ (see Fig. 1).

Following the derivation of equation (16) the Raman frequencies ω_n^R satisfy the product rule

$$\prod_{n=1}^{N} (\omega_n^R/\omega_n^0)^2 = 2\tilde{\lambda}. \tag{20}$$

The ratio of equations (16) and (20) gives

$$\prod_{n=1}^{N} (\omega_n^\phi/\omega_n^R)^2 = \alpha/2\tilde{\lambda}. \tag{21}$$

The significance of this result is that the left-hand side involves measurable data while the right-hand side is isotope independent since α and $\tilde{\lambda}$ involve only electronic properties.

It should be emphasized that the product rule equation (21) as well as the conductivity equation (12) are of general validity – the effects of electron–electron interactions are contained in the parameters M_c and $\tilde{\lambda}$.

From the data on $(CH)_x$ and $(CD)_x$ (see Tables 1 and 2) the left-hand side of equation (21) is 0.61 for $(CH)_x$ and 0.55 for $(CD)_x$. In view of the experimental uncertainty (ω_1^ϕ has a width of ~ 400 cm^{-1}) these numbers are consistent with each other. Considering the large frequency shifts between $(CH)_x$ and $(CD)_x$ and the change in the number N of modes the result that the product rule remains unchanged is quite remarkable.

Consider now the calculation of Mele and Rice [7] on the i.r. activity of solitons. They claim that two normal modes are responsible for the observed i.r. modes at 900 and 1370 cm^{-1}, and for a third, as yet unobserved pinned mode at lower frequencies. This is inconsistent with the conclusion from equation (12) that the number of i.r. modes is equal to the number of

Table 1. Parameters of trans (CH)$_x$: i.r. (ω_n^ϕ), *Raman* (ω_n^R) *and bare* (ω_n^0) *frequencies in* cm^{-1}, *coupling constants* λ_n, ($\lambda = \Sigma_n \lambda_n = 0.19$) *and relative weight* W_n *in the sum rule [equation* (14)] *in units of* $\rho/M_c v_F$

ω_n^ϕ [2, 5]	ω_n^R [13, 14]	ω_n^0	λ_n/λ	W_n
900	1075	1210	0.08	1.2
1370	1470	2110	0.92	0.5

Table 2. Parameters of trans (CD)$_x$. *Notations as in Table 1*

ω_n^ϕ [5]	ω_n^R [13, 15]	ω_n^0	λ_n/λ	W_n
760	850	890	0.04	1.6
1070	1200	1220	0.007	2.0
1240	1340	2040	0.953	0.3

coupled bare modes. A third phonon is not involved in their calculation [7] since the lowest bare frequency is $\omega_1^0 \simeq 1100$ cm^{-1} and there can be only one i.r. solution with $\omega < \omega_1^0$. Thus the ~ 900 cm^{-1} mode in their calculation should be ω_1^ϕ, i.e. the pinned mode. The only pinning mechanism in their calculation comes from the lattice discreteness. This effect corresponds to a binding energy of ~ 16 cm^{-1} [8] and may lead to a rather high pinning frequency in view of the very light soliton mass [8]. Thermal and quantum fluctuations however can easily overcome the low binding energy of ~ 16 cm^{-1} and the pinning from lattice discreteness is not relevant to actual experiments.

Lattice pinning seems to be the only mechanism which may explain the results of [7]. Thus discrete lattice calculations at zero temperature for normal modes involving delocalized charge (e.g. a soliton) are misleading – they are sensitive to lattice pinning which is irrelevant.

The 900 cm^{-1} mode must be the pinned mode also in view of the Raman data. Since $\omega_1^R < \omega_1^0$ and the lowest Raman frequency [14, 15] is 1075 cm^{-1} (or the very weak line at 1015 cm^{-1}) ω_1^0 is at a higher frequency and $\omega_1^\phi = 900$ cm^{-1} $< \omega_1^0$ cannot be but the pinned mode.

Consider now the Peierls model ($\lambda = \tilde{\lambda}$); from data on $\Delta_0/2E_c$ λ is obtained and the i.r. and Raman frequencies yield $2N$ equation for the $2N$ unknowns ω_n^0, λ_n/λ and α. For polyacetylene $2E_c = 10$ eV, $\Delta_0 = 0.7$ eV [6] so that $\lambda = 0.19$. Note also that in resonance Raman scattering the intensity of phonons which are coupled to the extended π electrons is strongly enhanced. Thus in (CH)$_x$ there are two coupled modes while in (CD)$_x$ there are three modes [14–16]. This implies that the coupling of a CD bending mode with the electrons is stronger in (CD)$_x$ than that of the corresponding mode in (CH)$_x$ [4]. The i.r. data shows indeed two ω^ϕ modes in (CH)$_x$ [2] and three ω^ϕ modes in (CD)$_x$ [5]. The three modes in (CD)$_x$ appear, however, only upon doping with Na. Doping (CD)$_x$ with AsF$_5$ or I$_2$ shows [3–5] only two modes, but the higher frequency mode is much wider than ω_2^ϕ of (CH)$_x$ and should therefore be considered as two overlapping i.r. modes.

Tables 1 and 2 summarize the experimental data; the i.r. modes of (CD)$_x$ are those with Na doping [5]. Using $\lambda = 0.19$ the values of ω_n^0 and λ_n/λ are obtained, as shown in the tables. Also shown are the weights W_i of the i.r. modes relative to the conductivity sum rule [equation (14)] in units of $\rho/M_c v_F$. The intensity ratio is in reasonable agreement with experimental estimate [4] $W_1/W_2 \simeq 1.5$ for (CH)$_x$ and $W_1/(W_2 + W_3) \simeq 0.7$ for (CD)$_x$.

The weight W_n of a particular mode is affected by the coupling of all higher frequency modes, and not just by its own coupling λ_n/λ. Thus in (CH)$_x$ $\lambda_1/\lambda_2 \simeq 0.1$ but $W_1/W_2 \simeq 2.2$ while in (CD)$_x$ the mode with $\lambda_2/\lambda = 0.007$ has the strongest intensity. Note also that although the pinning force α is isotope independent, the pinned frequency ω_1^ϕ is isotope dependent as it is determined by the balance of all masses in the system.

The mean frequency of equation (6) is $\Omega_0 = 1960$ cm^{-1} for (CH)$_x$ and $\Omega_0 = 1880$ cm^{-1} for (CD)$_x$. The corresponding soliton masses are $M_s/m_e = 2.7; 2.9$.

Finally consider derivations of the mass M_c. If the pinning ion is at distance d from the chain it leads to a pinning potential $V(x) = \epsilon_0^{-1}(x^2 + d^2)^{-1/2}$. For a unit charge localized along a distance of 2ξ, the value of $\alpha = 0.23$ yields

$$\epsilon_0 \xi^3 M_c/m_e \simeq 8 \times 10^3 \tag{22}$$

for $\xi \gg d$ and ξ is measured in Å. For $\epsilon_0 = 2–5$ [2, 8] and $\xi = 5–10$ Å [8], equation (22) yields $M_c/m_e = 2–25$.

Since the distance d can be different for each dopant, there is a distribution of α values which affects mainly the width of the pinned mode ω_1^ϕ. This is consistent with the relatively large width of ~ 400 cm^{-1} for this mode [2].

The most reliable method of determining M_c is from the intensity ratio W_n/W_T where W_T is the total band absorption [equation (14)]. Using [2] $W_2 = (2–3) \times 10^7$ ρa cm^{-2} and $W_T = (1–4) \times 10^9$ cm^{-2} for (CH)$_x$, the result in Table 1 yields $M_c/m_e = 15–100$. This is considerably larger than the soliton or polaron masses. It seems that effects of interchain coupling or electron–electron interactions are needed to account for the experimental data.

In conclusion, I have shown that i.r. and Raman frequencies can determine the microscopic parameters of an electron–phonon system. Further data on the weights W_n and the dielectric constant $\epsilon(0)$ can determine the mass M_c of the charge on the polyacetylene chain, which in turn can determine the dopant ion pinning potential.

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