Phonon spectroscopy in π-conjugated polymers; the role of the excited electronic states

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ABSTRACT

The Raman active vibrational modes in π-conjugated polymers are known to have different frequencies in different types of experiments. The best known examples are the resonant Raman scattering (RRS) and doping or photoinduced absorption infrared active vibrations (IRAV) measurements, in which the same modes appear at different energies. Other examples are the phonon side bands, accompanying the polarons, bipolarons, and solitons absorption bands, in which the same modes give rise to different side band energies. In this work we discuss RRS and IRAV measurements and correlate their experimentally observed frequencies with the relevant electronic state that is active in this type of experiment. We show that the IRAV frequencies are lower than those of RRS since the relevant energy levels of charged solitons and/or polarons are closer to the ground state than the optically allowed $1B_u$ state of the neutral polymer. Thus a new insight into the meaning of the "pinning" potential, which is associated with the lowest frequency IRAV mode is obtained.

Key words: π-conjugated polymers, Resonant Raman scattering, ir-active phonons

1. INTRODUCTION

It is well established that the vibrational frequencies in π-conjugated oligomers and polymers are very sensitive to the π-electron configuration due to the strong electron-phonon coupling in these materials. This electron-phonon interaction manifests itself by reducing the vibrational frequencies from their "bare" values (values that may be typical to non-conjugated systems) to their realistic magnitude as measured by various experimental techniques. It is pertinent for this work to realize that frequencies of the same vibrational modes, as extracted from different types of measurements, may differ depending on the state of the electronic excitation. For example, using resonant Raman scattering (RRS) techniques, the measured frequencies are those of the A_g vibrational modes (associated with the electronic ground state) which are the most strongly coupled to the excited electronic states. On the other hand, phonon side band frequencies measured by optical absorption, yield the mode frequencies corresponding to the optically allowed excited electronic state. Since the atomic and electronic configurations in the

ground and excited states are different, it is not surprising that the strongly coupled vibrational modes differ in their frequencies.

The importance of the vibration-electron coupling for the electronic structure in π-conjugated systems has been realized already in the pioneering works of Coulson, Longuet-Higgins and Salem [1, 2]. Since then, many models for the actual force fields in conjugated systems have been proposed in order to calculate the vibrational frequencies. One of the most notable examples in recent years is *trans*-polyacetylene, whose vibrational frequencies were analyzed by many different approaches [3]–[9]. Recently, a linear response theory including both the linear and quadratic electron-phonon coupling was introduced by Girlando, Painelli and Soos (GPS) in order to account for the RRS and infrared active vibrations (IRAV) mode frequencies of *trans*-polyacetylene [10, 11].They showed that their model resembles the amplitude modes microscopic picture, with the advantage of having realistic reference force field. In the GPS model the mode frequencies are determined by the bond order electronic susceptibility, $\chi = \sum_n a_n^2/(E_n - E_0)$, whose only non zero matrix elements, a_n, are those connecting the ground state, E_0, to an excited state, E_n, *having the same parity* [12]. Utilizing the GPS model, we have shown [13, 14] that the dispersion of the RRS frequencies in π-conjugated polymers, is determined by the dependence of the even parity (A_g) electronic states on the inhomogeneity caused, for instance, by the polymer conjugation length distribution, explaining thus the larger RRS dispersion in non-luminescent polymers, where the $2A_g$ level is the lowest excited state.

GPS have shown [10] that their linear response theory is applicable also to infrared active vibrations (IRAV) induced by chemical doping or photoexcitations. In this work we show that the IRAV frequencies in various π-conjugated polymers can be directly related to the excited states of either charged polarons, bipolarons or solitons. For example, in *trans*-polyacetylene we specifically relate the IRAV frequencies to the soliton energy levels rather than to a heuristic pinning potential [6].

2. THE GPS MODEL

There are two distinctive steps in the treatment of the π-electron phonon coupling made by GPS [10, 11]. The first one is the recognition that the quadratic contribution to the electron-phonon is important. The second is the description of the phonon frequency shifts, due to the π-electrons, in terms of an electronic susceptibility, whose only non-zero matrix elements are those connecting electronic states with the same parity.

When the quadratic contributions to the electron-phonon coupling is taken into account and linearized, the total Hamiltonian of the π-conjugated polymer is written as,

$$H = H_e + H_{ph}^{(\sigma+\pi)} + H'_{e-ph} , \tag{1}$$

where $H_{ph}^{(\sigma+\pi)}$ is the $\sigma + \pi$ "force field" including the quadratic corrections to the σ force field. The eigen frequencies, ω_ν^0, and the normal coordinates, $Q_\nu^{(0)}$, of $H_{ph}^{(\sigma+\pi)}$ are the reference frequencies and normal coordinates, respectively. The remaining e-ph coupling, H'_{e-ph}, is restricted to excited state mixing and is given by,

$$H'_{e-ph} = \sum_\nu G_\nu Q_\nu^0 \Theta_\nu , \tag{2}$$

where G_ν is a generalized linear e-ph coupling constant and Θ_ν is an electronic operator.

Using linear response theory, GPS then showed that for *trans*-polyacetylene, the m renormalized phonon frequencies, ω_i, are given by the solution of the following equation:

$$\sum_i^m \chi g_i^2/[(\omega_i^0)^2 - \omega^2] = 1 \,, \tag{3}$$

where g_i are the e-ph coupling constants for the mode i, and χ is the electronic susceptibility associated with the staggered bond order,

$$\chi = \frac{8}{N} \sum_n | < n| \sum_j (-1)^j p_j |0 > |^2/E_n \equiv \sum_n a_n^2/E_n \,, \tag{4}$$

where N is the conjugation length, p_j is the π bond order operator between site $j+1$ and j, and $|0 >$ and $|n >$ are the ground and excited π electron states with energies 0 and E_n, respectively.

It is worth emphasizing here that the GPS model is formally equivalent to the amplitude modes model, and in particular it obeys a similar "product rule" relation:

$$\prod_i^m (\omega_i/\omega_i^0)^2 = 1 - \chi \sum_i (g_i/\omega_i^0)^2 \equiv 2\tilde{\lambda}, \,. \tag{5}$$

where $\tilde{\lambda}$ is the "renormalization coupling parameter" defined previously in the amplitude modes theory [6, 7]. Note, however, that in the present model ω_i^0 in Eq. (5) include the quadratic corrections and could be calculated by force field models, whereas in the amplitude modes model, they are treated as free parameters.

3. APPLICATIONS OF THE GPS MODEL TO RRS AND IRAV MEASUREMENTS

3.1 RRS in luminescent and non-luminescent π-conjugated polymer

The GPS model was successfully applied to the RRS dispersion in disordered *trans*-polyacetylene or the blue shift of the RRS frequencies for shorter polyene chains [10]. As in the amplitude modes model, g_i and ω_i^0 were assumed to be transferable between infinite conjugation length *trans*-polyacetylene and finite chain *trans*-polyacetylene and/or polyenes. Thus, the RRS frequencies of different conjugation lengths and finite polyenes were accounted for by choosing different χ values (shorter conjugation length requires lower χ value), as shown schematically in Fig. 1. The advantage here over the amplitude modes model, is the smaller number of fitting parameters, since ω_i^0 can be determined separately.

In a recent work we have analyzed in detail the RRS dispersion in luminescent and non-luminescent π-conjugated polymers [13, 14]. If the parity of the ground state is even $(1A_g)$, as is the case for *trans*-polyacetylene and other centro-symmetric π-conjugated polymers, then χ is solely determined by the even parity electronic states, nA_g. Consequently, the RRS frequencies do not depend on the properties and dispersion of the odd parity nB_u states; and in particular

not on $1B_u$ (which is the optical gap, E_g). It is therefore evident that the RRS dispersion results only from the *distribution* of $E(nA_g)$ caused by inhomogeneity in the π-conjugated polymer films.
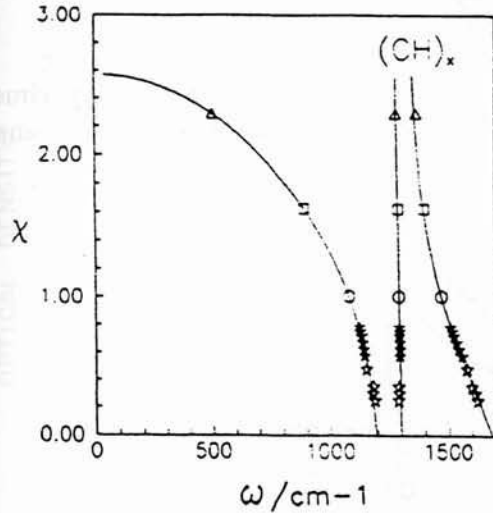

Fig. 1 χ vs ω curves for the three A_g modes of *trans*-polyacetylene χ is normalized to 1.0 for pristine *trans*-polyacetylene (open circles). $\chi < 1$ corresponds to finite polyenes, open squares and triangles correspond to chemically doped and photogenerated IRAV modes, respectively. From Girlando et. al., [10].

Assuming that the RRS dispersion arises from a distribution in the conjugation length N, we denote the susceptibility for conjugation length N by χ_ν (with $\nu \equiv 1/N$). We then write the product rule equation [Eq. (5)] as,

$$\prod_i^m (\omega_i(\nu)/\omega_{i0})^2 = 1 + C(\chi_0 - \chi_\nu) , \qquad (6)$$

where $\omega_i(\nu)$ and ω_{i0} are the observed RRS frequencies for conjugation lengths $N = 1/\nu$ and $N = \infty$, respectively, and $C = \sum (g_i/\omega_i^0)^2/[1 - \chi_0 \sum (g_i/\omega_i^0)^2]$. Note that C is independent of the conjugation length. We write for the energies E_{nAg} ($n \geq 2$) the dependence on ν [4, 15] as $E_{nAg}(\nu) = E_{nAg}^0 + \nu\beta_n$, where β_n are ν independent constants and E_{nAg}^0 is E_{nAg} at $\nu = 0$. Similarly, we write for $E_g(\nu) \equiv E_g^0 + \nu\beta$. Under resonance conditions, the laser exciting photon energy E_L is equal to the optical gap E_g, and consequently we find for the product (Eq. (6)),

$$\prod_{i=1}^m (\omega_i^L/\omega_{i0})^2 = 1 + D(E_L)(E_L - E_g^0) , \qquad (7)$$

where $\omega_i^L = \omega_i(\nu)$ is the ith phonon frequency for a conjugation length $N = 1/\nu$ which is at resonance with E_L, and the dispersion parameter $D(E_L)$ is given by,

$$D(E_L) = C \sum_{n \geq 2} \frac{\beta_n a_n^2}{\beta (E_{nAg}^0)^2} [1 + \frac{\beta_n (E_L - E_g^0)}{\beta E_{nAg}^0}]^{-1} . \qquad (8)$$

It is seen from Eq. (8) that for long chains where $\nu \ll 1$, $\beta_n(E_L - E_g^0/\beta E_{nAg}^0 = \beta_n\nu/E_{nAg}^0 \ll 1$ and thus $D(E_L)$ becomes E_L independent, given by the first part of Eq. (8):

$$D = C \sum_{n \geq 2} \frac{\beta_n a_n^2}{\beta(E_{nAg}^0)^2} \cdot \tag{9}$$

In this case, the product in Eq. (7) depends linearly on E_L, in agreement with the experiments [14]. Furthermore, it is seen from Eq. (9) that D is dominated by the ratio β_2/β and energy E_{2Ag}^0 of the lowest lying A_g exciton, namely the $2A_g$.
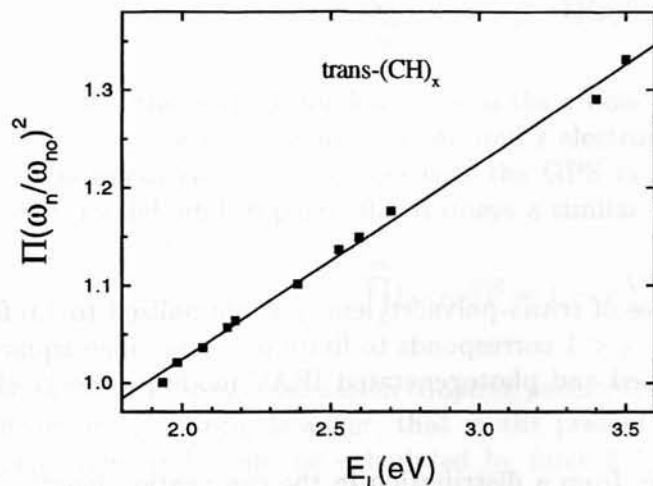

Fig. 2 Product rule relation vs E_L for *trans*-polyacetylene. The slope of the straight line is $D = 0.19$ eV^{-1}.

Analyzing in detail the RRS dispersion among luminescent as well as non-luminescent π-conjugated polymers [13, 14], we have shown that D is large for non-luminescent and small for luminescent π-conjugated polymers. Since the π-electron interaction renormalizes the RRS frequencies via an electronic susceptibility which contains only A_g states, then D is determined by the dependence of the A_g states on the inhomogeneity. The most dominant A_g state for RRS dispersion in non-luminescent polymers is $2A_g$, and therefore D serves as a useful spectroscopy for this state, which otherwise is only weakly detected in non-linear optical spectroscopies [16], because of its small dipole coupling to the B_u states. The large D in non-luminescent polymers is then explained as a result of the excited state ordering in these materials ($E_{2Ag} < E_g$), the small value of E_{2Ag} and its large variation with N.

As an illustration, we show in Fig. 2 the product rule relation for *trans*-$(CH)_x$ which is a non-luminescent π-conjugated polymer. As can be seen, the RRS dispersion slope is quite large: $D = 0.19$ eV^{-1}. Typical values for D for luminescent polymers are considerably smaller: $D \simeq 0.002 - 0.05$ (Ref. [14]). In particular, *cis*-$(CH)_x$ is practically non dispersive. One can understand such a behavior noting that for *trans*-$(CH)_x$ $E_{2A_g} \simeq 1.1$eV [17] while in the luminescent *cis*-$(CH)_x$, the $2A_g$ level is pushed above the optical gap at $\simeq 2$ eV, leading thus

to a significant decrease in D. A further decrease in D is caused by the different values of β_n: since the dimerization of $trans$-$(CH)_x$ is considerably smaller than that of cis-$(CH)_x$, $\beta_n(trans$-$(CH)_x) > \beta_n(cis$-$(CH)_x)$ thus enhancing the dispersion of $trans$-$(CH)_x$.
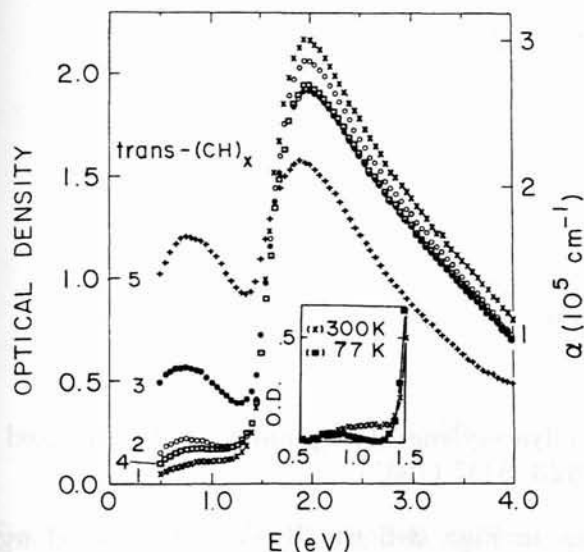

Fig. 3 Absorption coefficient of pristine (x) and AsF_5 doped (•) $trans$-polyacetylene. The positively charged soliton absorption is peaked at $\simeq 0.7$ eV. From Suzuki et. al., Phys. Rev. Lett., **45**, 1209 (1980).

3.2 Charge induced infrared active vibrations in $trans$-polyacetylene

Charged defects can be created by either doping or photoexcitation. Removing (or adding) charges from a π-conjugated polymer results in the formation of charged solitons (for degenerate ground state polymers like $trans$-polyacetylene) or singly charged polarons and doubly charged bipolarons [18]. The charged defects break the symmetry and induce infrared activity to the Raman active modes described in the preceding section, which consequently can then be detected by optical absorption [7]. The vibrational frequencies due to the motion of the center of mass of the charged defects were calculated first by Horovitz [6], who introduced a phenomenological "pinning" parameter, α, related to the defect center of mass motion. Formally, the role of α was shown to be equivalent to that of $2\tilde{\lambda}$ in Eq. (5). For all π-conjugated polymers it was found that $2\tilde{\lambda} > \alpha_{\text{dop}} > \alpha_{PG}$ (PG stands for photogeneration). In the present approach, these infrared active vibrations (IRAV) are treated similar to the ground state phonon modes, with the same eigen frequencies ω_ν^0 of the reference Hamiltonian, $H_{ph}^{\pi+\sigma}$. H'_{e-ph} is of the same form as in Eq. (2) but with an electronic operator adequate for the charged excited state. We then have a different χ in doped or photoexcited π-conjugated polymer, and this phenomenological change is related, in principle, to the electronic structure.
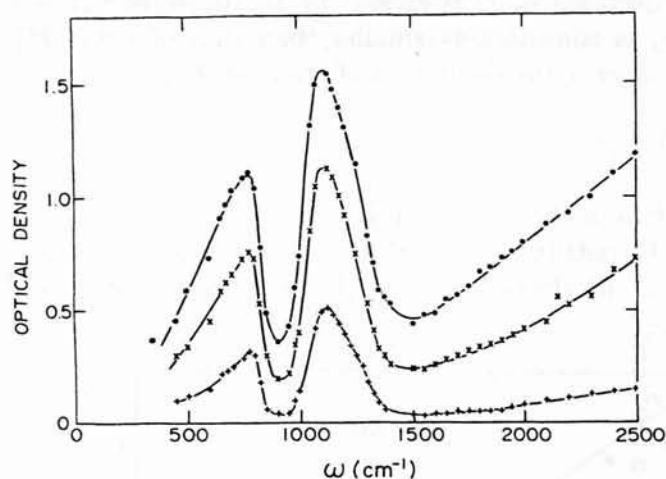
Fig. 4 Doping induced IRAV modes for *trans*-polyacetylene. The pinning mode is peaked at $\simeq 900$ cm^{-1}. From Etemad et. al., Phys. Rev., **B23**, 5137 (1981).

As an illustration of this concept we present in Figs. 3–5 the IRAV spectra of charged solitons in chemically doped and photogenerated *trans*-$(CH)_x$, together with the respective optical absorption δS in the electronic region. The lowest frequency IRAV, the "pinning" mode, is the most sensitive to changes in χ, since, in principle, it may shift down to zero frequency. Indeed we see that whereas for doping induced charged solitons, the pinning mode frequency is $\simeq 900$ cm^{-1} (Fig. 4), it red shifts to $\simeq 450$ cm^{-1} for photogenerated solitons (Fig. 5). Similarly, the charged soliton absorption in chemically doped *trans*-$(CH)_x$, δS_{dop} is observed to be at $\simeq 0.7$ eV (Fig. 3), whereas for photogenerated solitons, δS_{PG} is at $\simeq 0.45$ eV (Fig. 5). The higher energy soliton transition in chemically doped *trans*-$(CH)_x$ is due to the screening of the electron–electron Coulomb interaction by the charged dopants. In the absence of such dopants in photoexcited neutral polymer, the Coulomb repulsion pushes the charged soliton levels towards the respective HOMO/LUMO levels, thus decreasing δS_{PG}. Consequently, we can relate the behavior of the pinning mode to that of the electronic transition. Since the electronic transition for the photogenerated charged soliton is lower than that of the doping induced soliton, the electronic susceptibility is higher for photoinduced *trans*-$(CH)_x$ (see Fig. 1 and Eq. (4)), and hence the pinning mode frequency is lower. Referring to Fig. 1, we see that $\chi_{\text{PG}}/\chi_{\text{dop}} \simeq 1.4$; this is comparable to the ratio of the chemically doped to PG charged soliton transitions (Figs. 3 and 4): $\delta S_{\text{dop}}/\delta S_{\text{PG}} = 0.7/0.45 = 1.55$, in close agreement with the relation $\chi = \sum_n a_n^2/(E_n - E_0)$ (where n=PG or dop). With this interpretation of the IRAV frequencies, the heuristic pinning parameter of the amplitude modes formalism [6], can now be understood in terms of the charged soliton energy levels.
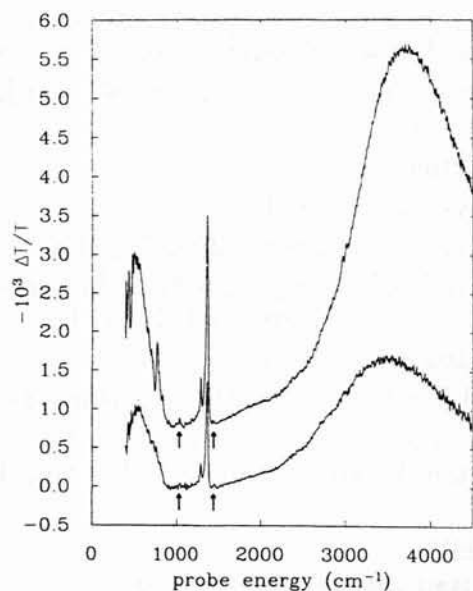
Fig. 5 Photoinduced absorption of *trans*-polyacetylene in the range 100–4500 cm^{-1}. The charged soliton peak appears at 0.45 eV and the pinning mode at $\simeq$500 cm^{-1}. From Schaffer et. al., Phys. Rev., B36, 7537 (1987).

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