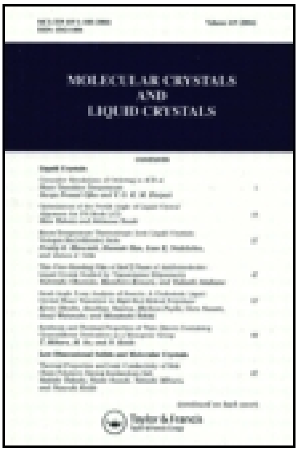

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# Delocalization Contributions to Polyacetylene Force Fields

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# DELOCALIZATION CONTRIBUTIONS TO POLYACETYLENE FORCE FIELDS

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Abstract

The force fields of *trans* and *cis*-polyacetylene(PA) are obtained in internal coordinates by combining linear-response analysis of the Raman and ir shifts due to $\pi$-electrons, molecular force-field methods, and the Hückel susceptibility of $k \neq 0$ phonons. We find transferable electron-phonon coupling constants, exponential transfer integrals $t(R)$, and coupling to CCC bends through the Coulomb potential $V(R)$. The electronic response of *cis*-PA is 56% of the *trans* susceptibility, indicative of reduced delocalization and an energy gap in the $A_g$ manifold due to third-neighbor $V(R)$ terms.

## 1. TRANSFERABLE ELECTRON-PHONON COUPLING CONSTANTS

Recent reviews explore the extensive vibrational spectroscopy of polyacetylene(PA)[1] and finite polyenes[2]. Vibronic coupling in conjugated systems goes back to seminal contributions[3,4,5] by Coulson, Longuet-Higgins, and Salem. A related issue is the Peierls instability of Hückel or tight-binding chains with transfer integral $t(R)$. The self-localized excitations obtained by Su, Schrieffer, and Heeger[6] are based on linear electron-phonon (e-ph) coupling $t'(R_o)$, where $R_o$ is the benzene bond length. The vibrational consequences of the SSH model were studied in *trans*-PA by Horovitz[7] and Mele[8] in terms of the amplitude mode(AM) formalism, with excellent results for Raman and ir-active modes. But early work[3,4] implicated both linear e-ph coupling $t'(R)$ and quadratic coupling $t''(R)$ and exponential rather than linear $t(R)$ is generally expected. Moreover, the AM parametrization forgoes such traditional tools of molecular spectroscopy as force fields. Considerably more information about delocalized polymeric states can be extracted from vibrational spectra.

Pecile and coworkers[9] have systematically analyzed the vibrational spectra of organic molecular crystals based on $\pi$-electron donors (D) and acceptors(A). Painelli and Girlando[10] pointed out that quadratic as well as linear e-ph contributions were necessary to define a reference state precisely and to obtain consistent results. For polymers, we introduce[11] a reference for force field $F_o$ that resembles butadiene[12] and includes quadratic e-ph coupling of $\pi$-electrons as well as all $\sigma$-electron contributions. The Raman and ir shifts of PA are then related to an electronic response $\chi$ and to linear e-ph coupling constants $g_i$.

We have recently fit[11,13] the Raman and ir shifts of both *cis* and *trans*-PA and their isotopes with a transferable set of $g_i$. As summarized in Section 2, a $\chi$ based on Hückel theory leads to $t'(R_d) = 6.4$ eV/A and $t'(R_s) = 4.1$ eV/A for double and single bonds, and indicates exponential rather than linear t(R) in PA. The *cis* $\pi$–system is shown in Section 3 to be far more localized, with $\chi = 0.56$ relative to *trans*. Since their idealized backbones have identical first and second neighbors, the reduced $\chi$ is evidence for long-range Coulomb interactions.

The empirical force field $F_o$ in Table 1 generates reference frequencies $\omega_i^o$ for all k = 0 in-plane vibrations of *trans*-PA. There are four $a_g$ modes, three coupled to $\pi$-electron fluctuations, while the high-energy CH stretch is not. The observed $a_g$ fundamental frequencies $\omega_i$ in the Resonance Raman spectrum determine the dimensionless e-ph coupling constants $\lambda_i = \chi g_i^2/\omega_i$. For p coupled modes, we obtain a system of p linear equations[10,11]

$$\sum_i \chi g_i^2 \prod_{j\neq i} [(\omega_j^o)^2 - \omega_i^2] = \prod_i [(\omega_i^o)^2 - \omega_p^2] \ . \qquad (1)$$

Different choices of $\chi$ fit the Raman and dopant- or photo-induced ir frequencies. The $g_i$ in symmetry (k = 0) coordinates are related to microscopic parameters such as $t'(R_d)$, $t'(R_s)$ or various[14] $V'(R_{pp'})$ in models with intersite interactions. The electronic response $\chi$ depends on the $\pi$-electron Hamiltonian $H_e$ and must be evaluated separately to obtain $g_i$ from the shifts. The polymer force field F is ultimately needed in the internal coordinates of Table 1 and requires knowledge of e-ph coupling for general k.

The familiar plot of $a_g$ frequencies versus $\chi$ is shown in Fig. 1 for *trans*-PA. In the absence of coupling, the $\chi = 0$ solutions of (1) are the $\omega_i^o$. All modes shift to lower frequency with increasing $\chi$. The $\chi = 1$ fit for the Raman modes[15] of *trans*-PA is forced. The ir-active vibrations[15] of doped or photoexcited samples fall on the Fig. 1 curves with larger $\chi$, while the Raman modes[2,16] of finite polyenes are fit with smaller $\chi$. The red shifts arising from linear e-ph coupling in (1) are clearly shown without specifying either $\chi$ or the reference frequencies $\omega_i^o$ explicitly. Both of these quantities are amenable to analysis beyond the AM formalism, whose importance lies in the direct connection between the $g_i$ and observed spectra.

Table 1 Valence Force Fields of *cis* and *trans*-PA in Internal Coordinates.

| | Symbol[a] | *trans*-PA | *cis*-PA | $F_o$ (ref.) | butadiene[b] |
|---|---|---|---|---|---|
| Stretch | K(C=C) | 7.50 | 7.88 | 8.10 | 8.89 |
| | K(C-C) | 4.97 | 5.04 | 5.80 | 5.43 |
| | K(C-H) | 5.00 | 5.00 | 5.00 | 5.07 |
| Bend | H(CCC) | 0.859 | 0.530 | 0.891/0.550 | 0.691 |
| | H(CCH) | 0.531 | 0.530 | 0.533 | 0.519 |
| Interaction[c] (Stretch-stretch, at m unit cells of *trans*-PA separation) | | | | | |
| m = 0 | F(C=C,C-C) | 0.770 | 0.561 | 0.267 | 0.400 |
| m = 1 | F(C=C,C=C) | -0.289 | -0.111 | 0.0 | |
| | F(C-C,C-C) | -0.116 | -0.045 | 0.0 | |
| | F(C=C,C-C) | 0.081 | 0.021 | 0.0 | |
| m = 2 | F(C=C,C=C) | -0.064 | -0.011 | 0.0 | |
| | F(C-C,C-C) | -0.026 | -0.004 | 0.0 | |
| | F(C=C,C-C) | 0.021 | 0.002 | 0.0 | |
| m = 3 | F(C=C,C=C) | -0.019 | 0.0 | 0.0 | |
| | F(C-C,C-C) | -0.008 | 0.0 | 0.0 | |
| | F(C=C,C-C) | 0.007 | 0.0 | 0.0 | |

a. units are mdyn/A for K and F, mdyn/rad for H.
b. ref 12.
c. bend-stretch, bend-bend intercation constants for m = 0 are given in ref. 13.

Since $\chi$ depends on the $\pi$–$\pi^*$ spectrum, it cannot vary with isotopic substitutions. In contrast to adjustable $\omega_i^o$ in the AM formalism, $F_o$ yields $\omega_i^o$ for *trans*-$(CD)_x$ or $(^{13}CH)_x$ by standard GF methods[17] and no additional parameters are needed to fit[11] $\omega_i$ with $\chi = 1$ for pristine samples and the same relative $\chi > 1$ for doped or photoexcited samples. The combination of linear response and spectroscopic methods lead to transferable $g_i$ in (1). We can then develop a more complete microscopic picture of these polymers.

Polyenes and other conjugated hyrocarbons were the motivation for Hückel theory[5]. The discrete $\pi$–$\pi^*$ spectra of small molecules are satisfactorily fit without considering the distance dependence of t(R). But equal bond lengths in PA produce a half-filled, or metallic, $\pi$ band and the Peierls distortion to an insulator leads to $t(R_d) = t(1 + \delta)$, $t(R_s) = t(1 - \delta)$ for double and single bonds, respectively. The bandwidth 4t is ~10 eV. The optical gap $E_g$ = $4t\delta$ in the Hückel model of PA thus implies alternation $\delta \sim 0.18$. Smaller $\delta$ = 0.07 is used in PPP models[18], where $E_g$ also has correlation contributions.

In the AM formalism[7], the response $\chi$ in (1) is due to the modulation of the Hückel gap $E_g$ with $\delta$ and is related to $\partial^2E_o/\partial\delta^2$, where $E_o$ is the ground-state energy per site of $H_e$. Linear t(R) gives $t'(R_o)$ for both single and double bonds. The out-of-phase stretching of single and double bonds is the effective conjugation coordinate (ECC) introduced by Zerbi and coworkers[1] for vibrational analysis of PA and other conjugated polymers. Exact solution of alternating Hückel chains leads to[11]

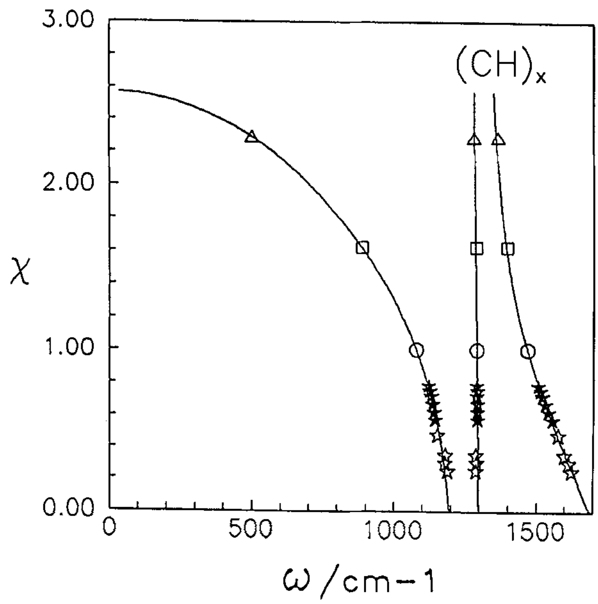


Fig. 1. Relative $\chi$ vs. $\omega$ curves, Eq. (1), for the $a_g$ modes of *trans*-PA. The data from ref. 15 are open circles for pristine samples, open squares for chemical doping, open triangles for photoexcitation; open and close stars are finite polyenes from refs. 2 and 16 ; (from ref. 11).

$$\chi_o(\delta) = \frac{4[(1 + \delta^2)K(q) - 2E(q)]}{\pi t\,(1 - \delta^2)^2} \quad (2)$$

with $q^2 = t_d t_s/(t_d + t_s)^2 = (1 - \delta^2)$ and complete elliptic integrals E and K. The Peierls instability at $\delta = 0$ is the $\ln\delta$ divergence of K. The numerical value of $\chi_o(0.18)$ is 0.617 $eV^{-1}$ for $t = 2.5$ eV.

Translational symmetry actually makes the electronic response $\chi_o(\delta)$ far simpler[8] than in finite polyenes. PA has two CC bonds per unit cell and hence two $k = 0$ stretches that can be combined into in-phase and out-of-phase vibrations of the partial single and double bonds. The latter gives $\chi_o(\delta)$ in (2), while the response of in-phase vibrations is $\delta^2\chi_o(\delta)$. Alternatively, we can use single and double bonds to obtain[13] $\chi_s$ and $\chi_d$ from the curvature of $E_o(t_d,t_s)$ along $t_s$ and $t_d$, respectively. The observed $\chi g_i^2$ for double and single bond stretches then yield[13] expressions for $t'(R_d)$ and $t'(R_s)$ without making any assumptions about the form of t(R):

$$t'(R_{s,d})\,(1 \pm \delta)\,[\chi_o(\delta)/2]^{1/2} = 2.675,\ 2.889\ eV^{1/2}/A \quad (3)$$

The Hückel value, $\chi_o(0.18) = 0.617$ $eV^{-1}$, gives $t'(R_d) = 6.4$ and $t'(R_s) = 4.1$ eV/A. Linear t(R) with constant t'(R) is a poor approximation, while exponential t(R) implies $t'(R_d)/t'(R_s) = (1 + \delta)/(1 - \delta) = 1.44$ at $\delta = 0.18$, close to the observed ratio 6.4/4.1 = 1.56. The Raman and ir-active modes of PA thus point to exponential rather than linear t(R) and to e-ph coupling with both $k = 0$ modes of the alternating chain.

To obtain force and interaction constants in internal coordinates, we need the electronic response $\chi(\delta,k)$ to phonons with all wavevectors k in the first Brillouin zone. In absence of experimental data, we evaluated[13] $\chi_o(\delta,k)$ for alternating Hückel chains. The partial derivatives of $E_o(\delta)$ with respect to individual $t_p$, $t_{p'}$ along the chains are the bond-bond polarizabilities $\pi_{pp'}$ introduced by Coulson and Longuet-Higgins[3], who emphasized their $-(-1)^r$ variation with $r = p - p'$. The $t'(R_{d,s})$ values from the $k = 0$ data and $\chi_o(\delta,k)$ lead to the force and interaction constants[13] listed in Table 1 for CC stretches. The C=C and C-C frequencies are significantly lowered, as expected, while interaction constants between stretches extend over about three unit cells.

In applying (1) to PA data, we also found[11] coupling to CCC and CCH bends, with $\sqrt{\chi}\,g = 0.357$ and 0.215 eV/rad, respectively. This is an order of magnitude less than for the stretches. CCC bends occur naturally in the

Pariser-Parr-Pople (PPP) model as the curvature of $E_0$ with respect to bond angles. Parameters[18] originally developed for $\pi$–$\pi^*$ spectra of small hydrocarbons lead to quantitative agreement[14] for $\pi$-electron coupling to CCC bends. Potential contributions $V'(R_{pp'})$ are consequently discernible in PA vibrations. Coupling to CC stretches remains comparable to the Hückel $\chi_0(0.18)$, although smaller $\delta = 0.07$ appropriate to polyenes is then used. We have found it useful[13,14] to combine Hückel results such as $\chi_0(\delta,k)$ for the dominant t(R) modulation with detailed PPP analyses of k = 0 vibrations.

## 3. *Cis*-PA AND LONG-RANGE CORRELATIONS

We have applied[13] the reference $F_0$ in Table 1 to *cis*-PA for a planar $D_{2h}$ structure with *trans*-PA bond lengths and bond angles of $2\pi/3$. Two minor changes are needed: an interaction constant of 0.02 mdyn/rad$^2$ for a nearest-neighbor CCH bends and a lowering of H(CCC) from 0.891 to 0.550 mdyn/rad$^2$ to fit the $b_{1u}$ v16 mode in the ir. The Raman spectrum now contains in-plane vibrations of $a_g$ and $b_{3g}$ symmetry, with strong $\pi$-electron coupling expected and found to involve three $a_g$ modes.

Figure 2 shows the fits for *cis*-$(CH)_x$ and *cis*-$(CD)_x$ for relative $\chi$ in (1) of 0.56. The *cis*-PA vibrations indicate far less delocalization than in the *trans* polymer, since comparable $\chi$'s are found in Fig. 1 for finite polyenes of 14 carbons. Hückel theory does not distiguish between the two polymers. The slightly larger (2.0-2.1 eV) optical gap of *cis*-PA increases $\delta_{cis}$ to 0.21 and

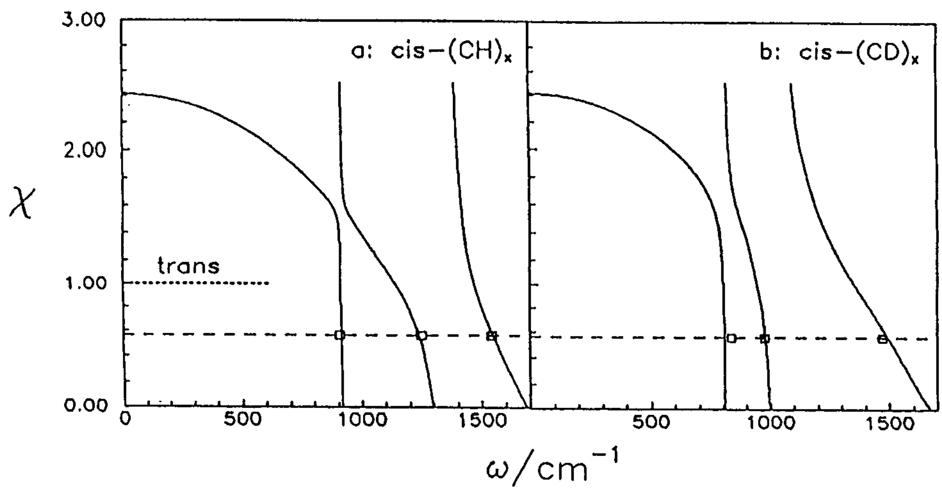


Fig. 2. Relative $\chi$ vs. $\omega$ curves for the $a_g$ modes of *cis*-PA. The open squares are Raman data from refs. 19 and 20; (from ref. 13).

lowers $\chi_o$in (2) by 10%. Although $\chi = 0.56$ in (2) gives an artificially high $\delta_{cis}$ of 0.36, the Hückel dispersion $\chi_o(0.36,k)$ and the *trans*-PA parameters $t'(R_{d,s})$ of 6.4 and 4.1 eV/A generate[13] a successful force field for *cis*-PA. As seen in Table 1, interaction constants for stretches are now restricted to two unit cells.

We focus here on the implications of relative $\chi = 0.56$ for *cis*-PA vibrations in Fig. 2. Coulomb interactions $e^2/R$ are clearly important in atomic, molecular, or polymeric spectra. Within $\pi$–electron models, they lead[5,18] to spin-independent interactions $V(R_{pp'})$ between sites p and p'. Such potentials V(R) are added to the Hückel theory in PPP, extended Hubbard, and related models. Quite generally, then, the ground-state energy per site is $E_o[t(R_{d,s}),V(\{R\})]$ for nearest-neighbor transfer in alternating chains. Linear e-ph coupling constants appear in Herzberg-Teller (H-T) expansions[10] for $E_o(t_{d,s},V)$ as second partial derivatives with respect to $R_{d,s}$. These partials are formally equivalent to second-order perturbation theory[14] in $H' = (\partial H_e/\partial R_{d,s} - <\partial H_e/\partial R_{d,s}>)/\sqrt{2}$, where the ground-state expectation value of $H_e$ is indicated. The second-order correction entails a sum of over excited states $|F>$.

The electron-hole(e-h) symmetry of half-filled Hückel, Hubbard, or PPP models holds[18] for arbitrary spin-independent $V(R_{pp'})$ and nearest-neighbor $t(R_p)$. Since totally symmetric k = 0 modes are considered, the H-T expansion is restricted to the $^1A_g{}^+$ manifold containing the ground state. The regular Hubbard chain[21] has no gap in the $A_g$ manifold for any U/t, while a finite gap $E_g$ appears for any U > 0 to the $^1B_u{}^-$ state. The Peierls instability of $\delta = 0$ Hubbard or PPP chains reflects the gapless nature of the $A_g$ manifold and persists as the spin-Peierls instability for U >> t. Correlations do not lift the divergence of (2) in regular chains. Thus $\chi(0,t,V)$ diverges for an idealized *trans*-PA backbone with uniform $R_o$, since V(r) is constant for any r = p - p'. In idealized *cis*-PA with uniform $R_o$, on the contrary, V(r) alternates for r = 3,7, 11, .... The resulting gap in the $A_g$ manifold suppresses the divergence of $\chi$.

The qualitatively different susceptibilities of regular chains with long-range Coulomb interactions is lost in alternating chains, since $\delta > 0$ opens a gap[22] in the $A_g$ manifold of Hubbard as well as PPP models. We still expect a smaller gap and larger $\chi(\delta,t,V)$ for *trans* than *cis* when V(R) extends to third neighbors. Quantitative results for correlated models are currently restricted to oligomers and long-range interactions are difficult to extrapolate accurately. The reduced $\chi$ in Fig. 2 is direct evidence for Coulomb interactions in PA. Only part of the decrease is due to larger $E_g$ and $\delta$ in a slightly nonplanar structure.

Similar issues are encountered in the Peierls instability of correlated chains,[23] which goes as $\partial^2E_o/\partial\delta^2$ and takes the regular[6] chain as the reference. The half-filled $\pi$-band then overcomes any harmonic $\sigma$-potential. The $F_o$ reference used in Figs. 1 and 2 describes instead an alternating chain and large $\chi$ generates large frequency shifts. Thus *trans*-PA has the larger alternation for fixed restoring forces and also the larger red shifts for fixed alternation. As noted by Salem and Longuet-Higgins,[5] the equilibrium geometry imposes contraints on the $\pi$ and $\sigma$ force fields. A joint analysis consequently requires a full solution to the electronic structure of the polymer. Solid-state models emphasize instead the delocalized $\pi$-electrons of conjugated polymers. Different starting points are then indicated for the Peierls instability, with linear t(R) and a regular chain, and vibrational spectra, with exponential t(R) and alternating chains.

In summary, the explicit construction of PA force fields in internal coordinates provides a unified description of Raman and ir-active modes, confirms that e-ph coupling constants are transferable and that t(R) is exponential, and indicates far less delocalization in *cis* than in *trans*-PA. We are developing similar descriptions of other conjugated polymers and seeking more quantitative treatments of correlations.

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