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On the Electron Phonon Interaction in *Trans* Polyacetylene

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The effect of π conducting electrons on the lattice dynamics and on the Resonant Raman cross section in the simplest semiconducting polymer, *trans* polyacetylene, is discussed. Using the tight binding approximation and disregarding the electron correlation, explicit expressions for both delocalized force constants and Franck-Condon factors have been worked out as a function of the electron-phonon coupling constant.

Phonon frequencies and relative Resonance Raman intensities for the Raman active modes have been calculated and compared with the available experimental data for both *trans* $(CH)_x$ and $(CD)_x$.

INTRODUCTION

Significant progress has occurred in the past decade in the application of vibrational spectroscopy to a variety of different materials, ranging from simple molecules in the gas state to complex macromolecular and biological systems.

The two key developments were 1) improvement of the experimental techniques in the infrared region, 2) advances in the vibrational Resonance Raman (RR) spectroscopy, which carried the field beyond its initial stage of empirical correlations to improved levels of experimental and theoretical capability.

Indeed, the very large number of infrared spectra recorded with sophisticated equipments have provided a collection of reliable data on frequencies, linewidths and intensities. Once close agreement between theoretical and experimental IR data is achieved, a wealth of specified information becomes known regarding the ground electronic-state properties such as structure, intra-molecular and inter-molecular forces, types of structural defects and their distribution.

Information about molecular properties in the electronic excited states can be obtained from Resonance Raman spectroscopy. This effect occurs when the frequency of the exciting light in a Raman experiment is selected to be close to an electronic absorption band of the molecule of interest. The intensities of Raman bands associated with totally symmetric modes, which are strongly coupled to the electronic excited state responsible for that particular electronic absorption, may be largely enhanced. This technique

provides detailed information only about the chomophoric part of the scatterer. Indeed, this characteristic is one of the more fascinating features of RR spectroscopy, since it is usually the chromophore about which information is required.

In this paper we wish to report on recent results on the role played by the electron-phonon interaction in the lattice dynamics and in the Raman scattering of *trans* polyacetylene. Numerous discussions and papers[1-3] are available covering the various theoretical and experimental approaches used in studying the unusual properties of this polymer, which is considered the prototype of conducting polymers. Indeed, polymers with conjugated π electron backbones display unique properties, as compared to conventional polymers. They can be oxidized or reduced more easily than conventional polymers. Dopant agents affect this oxidation or reduction and convert the insulating polymer to a conducting polymer. It is this property that has stimulated the awareness of the potential importance of this class of new materials and attracted the interest of many scientists. Surely, the study of the simplest conjugated macromolecule, polyacetylene, has greatly benefited from the extensive literature on polyenic model compounds which has steadily grown in the past few years.[4]

There is considerable debate whether polyacetylene can be considered a Peierls or a Hubbard-Mott insulator, namely whether the effect of the electron-phonon interaction or of the electron correlation determines the optical energy gap. In the pioneering work of Su, Schrieffer and Heeger the role of the electron-phonon coupling was enphasized at the expense of the electron-electron interactions which were neglected.[5,6] On the other hand, Tavan and Schulten[7], in a recent study on the excitations of the polyenic chain, have concluded that the optical gap depends mainly on the electron correlation.

In the following text we will use the independent electron picture and, therefore, we will assume that the electronic energy gap between valence and conduction bands is strongly modulated by the vibrations of the carbon backbone skeleton. This coupling, which does not occur in insulating polymers because of their large energy gap, strongly affects the lattice dynamics and the Raman response of the polyenic chains. Indeed, the interaction between vibrational and π electron states gives rise to long-range forces between carbon atoms and enhances the Raman cross sections for the C—C and C=C stretchings.

Disregarding the electron correlation can be a possible source of error since it contributes to the energy gap which may then exist also in the undimerized chain.

LATTICE DYNAMICS

Several force fields have been so far proposed[8-11] to describe the phonon spectrum of the polyene chain, but, in general, too many parameters have been used to fit the few available experimental data. The main difficulty in dealing with conjugated systems arises from the fact that valence force constants are not additive and cannot be transferred from similar molecules as in the case of saturated hydrocarbons. As a matter of fact, in the case of conjugated systems force constants must include both a short range, directio-

nal contribution due to the σ electrons, and a long range, delocalized contribution arising from the deformation of the extended π electronic states.

The first attempt to describe phonons in *trans* polyacetylene by using a force field, which includes the electron-phonon interaction, has been proposed by Mele[12], who has shown that, for polymeric semiconductors, lattice vibrations modulate the electronic energies yielding an additional term (which is negligible for insulating systems) to the vibrational energy:

$$E'_{\text{rib}} = \frac{1}{2} \sum_{\mu,\nu} \partial R_\mu \partial R_\nu \sum_{K,K'} \frac{\langle v, K \mid \partial H/\partial R_\mu \, c, K' \rangle \langle c, K' \mid \partial H/\partial R_\nu \mid v, K \rangle}{E_c(K') - E_v(K)} \tag{1}$$

$\langle v, K \mid$ denotes the valence wave function at wave vector K, and $\langle c, K' \mid$ denotes the conduction wave function at wave vector K'.

We have developed a different model,[13-15] which is an extension to infinite polymers of Kakitani's theory for short polyenes.[16] This method allows to disentangle the contributions to the force field coming from localized σ electrons and from itinerant π electrons. As it has been shown[13], the π electron contribution to the bond-bond force constants can be written as:

$$F^{\pi}_{\text{ij, kl}} = \Pi_{\text{ij, kl}} \left(\frac{\partial \beta_{\text{kl}}}{\partial R_{\text{kl}}} \right)_0 \left(\frac{\partial \beta_{\text{ij}}}{\partial R_{\text{ij}}} \right)_0 \tag{2}$$

ij, kl label the atoms of the interacting bonds, and $\Pi_{\text{ij, kl}}$ is the bond-bond polarizability defined by:

$$\Pi_{\text{ij, kl}} = \frac{N^2}{(2\pi)^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \left\{ \frac{[C^*_{\text{vk}}(\Theta) C_{\text{cl}}(\Theta) + C^*_{\text{vl}}(\Theta) C_{\text{ck}}(\Theta')]}{E_v(\Theta) - E_c(\Theta')} \right. \tag{3}$$

$$\left. \cdot [C_{\text{vi}}(\Theta) C^*_{\text{cj}}(\Theta') + C_{\text{vj}}(\Theta) C^*_{\text{ci}}(\Theta')] + C.C. \right\} d\Theta \, d\Theta'$$

where $\Theta = K \cdot d$, d being the unit cell length (Figure 1), N is the number of atoms in the chain, C's are the coefficients of the tight binding wavefunctions in terms of the atomic $2p_z$ orbitals, c and v refer to conduction and valence band, respectively, $E_c(\Theta)$, $E_v(\Theta)$ are the corresponding energies and the integration is carried out over the entire Brillouin zone. In Hückel's approximation for the π electrons usually adopted, only matrix elements up to the nearest neighbours are considered, namely the Coulomb integral α and the transfer integrals β_1 and β_2 along the single and the double bond, respectively. These latter parameters are assumed to depend only on the bond distances, thus implying that only stretching coordinates and their interactions are affected by the existence of delocalized conduction electrons.

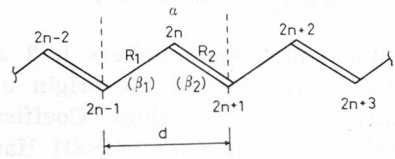

Figure 1. Unit cell of *trans*-polyacetylene.

By assuming a linear dependence of the resonance integral on the bond length, eq. 2 becomes:

$$F^{\pi}_{ij,kl} = \Pi_{ij,kl} \left(\frac{\partial \beta}{\partial R}\right)^2_0 \tag{4}$$

$(\partial\beta/\partial R)_0$ is the derivative of the transfer integral calculated at a value of R corresponding to the undimerized chain. This quantity plays a central role in determining the electronic properties of the conducting π electronic systems, as it appears in the expression of the skeletal bond-bond force constants and, as it will be discussed in the following chapter, in the Resonant Raman cross section. Moreover, it is related to the energy gap between valence and conduction band at the zone edge through the relation

$$E_g = 2\left(\frac{\partial \beta}{\partial R}\right)_0 |u| \tag{5}$$

where $u = R_{C=C} - R_{C-C}$ is the bond alternation. As discussed in the introductory section, this equation holds only if the electron correlation can be neglected.

By using an internal coordinate space consisting of bond stretching and bond bendings, the dynamical matrix is written as:[17]

$$\mathbf{D}(q) = \mathbf{M}^{-1/2}\,\mathbf{B}^{+}(q)\,\mathbf{F}(q)\,\mathbf{B}(q)\,\mathbf{M}^{-1/2} \tag{6}$$

where q is the phonon wave vector, $\mathbf{B}(q)$ is the linear transformation matrix between the Fourier transformed internal and cartesian coordinates and $\mathbf{F}(q)$ is the sum of a localized short range part coming from the deformation of σ bonds and of a delocalized part coming from the deformation of the extended π electronic states:

$$\mathbf{F}(q) = \mathbf{F}^{\sigma}(q) + \mathbf{F}^{\pi}(q) \tag{7}$$

Using eq. 4 the elements of the Fourier transformed bond-bond interactions referring to the origin unit cell, namely single bond/single bond, $\mathbf{F}^{\pi}(q)_{ss}$, single bond/double bond $\mathbf{F}^{\pi}(q)_{sd}$, double bond/double bond $\mathbf{F}^{\pi}(q)_{dd}$ become:

$$\begin{aligned}
\mathbf{F}^{\pi}(q)_{ss} &= 2\left(\frac{\partial \beta}{\partial R}\right)^2_0 \sum_n \Pi_{1,2;\,2n-1,\,2n} \cos[(n-1)\,q\,d] \\
\mathbf{F}^{\pi}(q)_{sd} &= \left(\frac{\partial \beta}{\partial R}\right)^2_0 (1 + e^{-iqd}) \sum_n \Pi_{1,2;\,2n,\,2n+1}\, e^{i(n-1)qd} \\
\mathbf{F}^{\pi}(q)_{dd} &= 2\left(\frac{\partial \beta}{\partial R}\right)^2_0 \sum_n \Pi_{2,3;\,2n,\,2n+1} \cos[(n-1)\,qd]
\end{aligned} \tag{8}$$

where on the r.h.s. of the equations, numbers 1, 2 and 3 label the atoms which define the internal coordinates of the origin unit cell (see Figure 1) and n assumes only integer positive values. Coefficients Π evaluated for *trans* polyacetylene within the framework of SSH Hamiltonian are reported in Table I of ref. 13.

TABLE I

Force Field for Trans *Polyacetylene*

Symbol	Force constant[a]	Description
K_1	4.97 ± 0.01	C—H stretching
K_2	8.29 ± 0.19	C—C stretching
K_3	9.03 ± 0.14	C=C stretching
K_4	0.56 ± 0.15	C—Ĉ=C bending
K_5	0.52 ± 0.02	H—Ĉ=C and H—Ĉ—C bending
K_6	16.	$(\partial \beta/\partial R)_0^2$
K_7	0.51 ± 0.06	C—C/H—Ĉ—C interaction

[a] Stretching force constants are given in mdyne/Å; bending force constants in mdyne Å/rad²; $(\partial \beta/\partial R)_0^2$ is given in mdyne eV/Å; stretching-bending interaction in mdyne/rad.

The chain geometry, the extent of bond alternation and the energy gap (eq. 5) determine entirely the long range contribution to the dynamical matrix, which therefore does not contain any adjustable parameter. On the other hand, the short range force constants F^{σ}_{ij} have been adjusted to fit the available experimental IR and Raman data.

In Table I, the parameters of the force field are reported. The effect of the electron-phonon coupling on the phonon frequencies is shown in Figure 2. It can be noticed that the best fit between the model calculation and the most intense C=C and C—C stretching Raman frequencies for short polyenes is obtained with $(\partial\beta/\partial R)_0 = 10$ eV/Å. This value yields (eq. 5) $E_g = 1.4$ eV, in agreement with the value $E_g = 1.6$ eV given by Fincher[18].

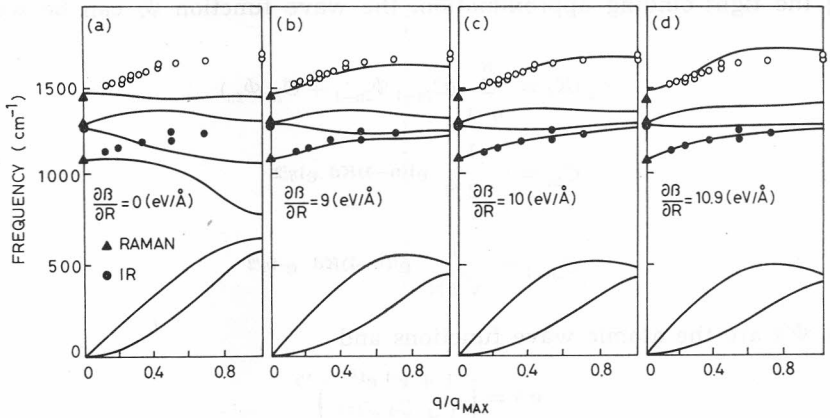

Figure 2. Calculated dispersion curves for *trans* $(CH)_x$ for selected values of $(\partial \beta/\partial R)$. ○ and ● refer to C=C and C—C stretching frequencies for short polyenes (Harada *et al.*, *J. Chem. Phys.* **73** (1980) 4746).

RESONANCE RAMAN SCATTERING

For a molecule, the vibronic coupling matrix element

$$f_i = \langle e \left| \frac{\partial H}{\partial Q_i} \right| e \rangle_o \tag{9}$$

responsible for the Raman enhancement of the totally symmetric mode[19] Q_i is related to the displacement δ_i between the ground and excited state potential minima (see Figure 3) by the relation:

$$\langle e \left| \frac{\partial H}{\partial Q_i} \right| e \rangle_o = K_e \, \delta_i \tag{10}$$

where K_e represents the force constant in the excited state, which, within the displaced harmonic oscillator approximation, coincides with the force constant in the ground electronic state.

For a crystal, the vibronic coupling matrix for the i-th phonon branch is given by:

$$f_i = \frac{1}{\sqrt{2\pi}} \sum_q f_i(K; q) \tag{11}$$

where q is the phonon momentum and

$$f_i(K; q) = \langle \psi_c(K) \left| \frac{\partial H}{\partial Q_i(q)} \right| \psi_c(K') \rangle \tag{12}$$

ψ_c is the wave function of the conduction band and K' is the electronic momentum after the interaction with the phonon. The momentum conservation law for wave-vectors within the first Brillouin zone requires that:

$$K' = K + q \tag{13}$$

Using the tight-binding approximation, the wave function ψ_c can be written as:[20]

$$\psi_c(K) = \sum_{n=1}^{N} (C_{2n-1} \Phi_{2n-1} + C_{2n} \Phi_{2n}) \tag{14}$$

$$C_{2n} = \frac{1}{\sqrt{2N}} e^{i(n-1)Kd} \, e^{i\eta/2}$$

$$C_{2n-1} = \frac{1}{\sqrt{2N}} e^{i(n-1)Kd} \, e^{-i\eta/2} \tag{15}$$

where Φ's are the atomic wave functions and

$$e^{i\eta} = \left(\frac{1 + \nu^{-1} e^{iKd}}{1 + \nu^{-1} e^{-iKd}} \right)^{1/2} \tag{16}$$

$\nu = \beta_1^\circ / \beta_2^\circ$, β_1° and β_2° being the transfer integrals evaluated at the equilibrium distances. Since the atomic wave functions can be considered independent

of the interatomic distances one has:

$$\langle \psi_c(K) \left| \frac{\partial H}{\partial Q_i(q)} \right| \psi_c(K') \rangle = \frac{\partial}{\partial Q_i(q)} \langle \psi_c(K) \mid H \mid \psi_c(K') \rangle \tag{17}$$

Moreover,

$$\frac{\partial}{\partial Q_i(q)} \langle \psi_c(K) \mid H \mid \psi_c(K') \rangle = \sum_l L_{il}(q) \frac{\partial}{\partial R_l(q)} \langle \psi_c(K) \mid H \mid \psi_c(K') \rangle =$$

$$= \sum_l \mathbf{L}_{il}(q) \sum_n e^{i(n-1)qd} \frac{\partial}{\partial R_l} \langle \psi_c(K) \mid H \mid \psi_c(K') \rangle \tag{18}$$

where $\mathbf{L}(q)$ is the linear transformation matrix between normal and internal phonon coordinates[21]

$$R(q) = \mathbf{L}(q)\, Q(q) \tag{19}$$

The matrix element $\langle \psi_c(K) \mid H \mid \psi_c(K') \rangle$ on the r.h.s. of eq. (18) can be written explicitly using the wave function given by eq. (14)

$$\langle \psi_c(K) \mid H \mid \psi_c(K') \rangle = 1/N \sum_n e^{i(n-1)(K-K')d} \cdot [R\,e\,(e^{-i\eta/2+i\eta'/2})\,\alpha + R\,e\,(e^{i\eta/2+i\eta'/2})\,\beta_1 + \tag{20}$$

$$+ R\,e\,(e^{-iK'd+i\eta/2+i\eta'/2})\,\beta_2]$$

By introducing eq. (20) into eq. (18), an expression for $f_i(K; q)$ can be obtained in terms of parameters α and β of the Hückel theory. Moreover, since α is independent of the atomic displacements, β_1 and β_2 depend only on R_1 (C—C stretching) and R_2 (C=C stretching), respectively, eq. (18) can be rewritten as

$$f_i(K; q) = \frac{\partial}{\partial Q_i(q)} \langle \psi_c(K) \mid H \mid \psi_c(K') \rangle =$$

$$= R\,e\,(e^{i\eta/2+i\eta'/2}) \left(\frac{\partial \beta_1}{\partial R_1} \right)_o \mathbf{L}_{i1}(q) + R\,e\,(e^{-iK'd+i\eta/2+i\eta'/2}) \left(\frac{\partial \beta_2}{\partial R_2} \right)_o \mathbf{L}_{i2}(q) \tag{21}$$

where the momentum conservation law (eq. 13) has been taken into account.

Within the approximation that β depends linearly on the interatomic distance

$$\beta(R) = \beta_o + (\partial \beta / \partial R)_o \Delta R \tag{22}$$

where β_o is the transfer integral for the undimerized chain, one has:

$$(\partial \beta_1 / \partial R_1)_o = (\partial \beta_2 / \partial R_2)_o = (\partial \beta / \partial R)_o \tag{23}$$

The Raman active phonons of an infinite chain correspond to a phonon momentum $q = 0$. Therefore, $K' = K$. Eq. (21) becomes:

$$f_i(K; q = 0) = \left(\frac{\partial \beta}{\partial R} \right)_o \frac{1}{(1 + \nu^2 + 2\nu \cos K d)^{1/2}} \tag{24}$$

$$\cdot [(\nu + \cos K d)\, \mathbf{L}_{i1}(0) + (1 + \nu \cos K d)\, \mathbf{L}_{i2}(0)]$$

For excitations in the visible region, which correspond to values of K in the neighbourhood of π/d,[20] eq. (24) simplifies as:

$$f_i\,(K = \pi/d;\ q = 0) = (\partial\,\beta/\partial\,R)_o\,[-\mathbf{L}_{i1}\,(0) + \mathbf{L}_{i2}\,(0)] \tag{25}$$

It is apparent from eq. (25) that within the framework of first neighbours tight binding theory the electron-coupling constants depend on the same parameter $(\partial\beta/\partial R)_o$ which, as discussed in the previous section, is responsible for long range forces in a system with extended π electronic states. The phonon eigenvectors $\mathbf{L}$ appearing in eq. (25) are related to the solutions $\mathbf{L}_x$ of the eigenvalue equation:

$$\mathbf{D}\,(q = 0)\,\mathbf{L}_x\,(q = 0) = \Lambda\,(q = 0)\,\mathbf{L}_x\,(q = 0) \tag{26}$$

where $\mathbf{D}$ is the dynamical matrix discussed in the previous section, by the relation

$$\mathbf{L} = \mathbf{B}\,\mathbf{L}_x \tag{27}$$

$\mathbf{B}$ is the linear transformation matrix between cartesian and internal coordinates. By introducing the values of $\mathbf{L}$ obtained by solving eqs. (26) and (27) into eq. (25), the electron-phonon interaction coupling constants can be computed. These constants are related to the Huang-Rhys factors S[22] by the relation

$$S_i = \frac{f_i^2}{8\,\pi^2\,h\,\mu_i\,c^3\,\omega_i^3} \tag{28}$$

where μ is the reduced mass, and ω the vibrational frequency in cm^{-1}. In Table II, these values are compared with those derived from the Resonance Raman excitation profiles and from the electronic absorption spectra of polyenes.[23] Even though these values are somewhat lower than the experimental ones, they are of the right order of magnitude.

TABLE II

Electron-vibrational Couplings for Trans-*Polyacetylene and Related Compounds*

	ω_α	ω_β	S_α	S_β	S^a
Soluble $(CH)_x$[b]	1080	1460	0.40	0.28	0.68
$(CH)_x$ film[c,d]	1070	1450	0.05	0.05	0.10
	1070	1460			0.85
β-carotene[e]	1155	1525	0.43	0.56	1.16
Poly(diacetylene)[f]					0.60
Theory[g]			0.27	0.11	0.41

[a] $S = \sum_n S_n$, n being the number of totally symmetric vibrations (n = 3 for β-carotene and polyacetylene and n = 4 for polydiacetylene). [b] Ref. 23. [c] Ref. 25. [d] Ref. 26. [e] Ref. 27. [f] Ref. 28. [g] This work.

Moreover, they predict the right relative intensities of the three Raman active skeletal modes of *trans* polyacetylene observed for excitation in the red region. Indeed, the highest intensity is calculated for the band at ~1100

cm^{-1}, while the band at ~ 1300 cm^{-1} is predicted with negligible intensity in agreement with experiment.[23]

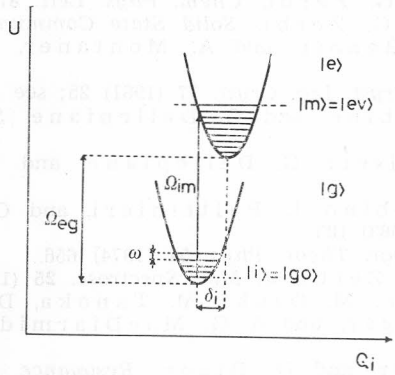

Fig. 3. Schematic diagram illustrating the dependence of the ground (g) and excited (e) state energies upon the normal coordinate Q_i.

The discrepancy can be probably ascribed to the oversimplifications of the Huckel's model adopted, which neglects all the interactions beyond the first neighbours, as well as the electronic correlation which, as shown in ref. 7, can indeed play a significant role. Furthermore, while the computed values are for an infinitely long polyenic chain, segments of finite conjugation length, with less extensive electronic delocalization and somewhat higher electron-vibrational interactions, are present in the actual polymer in solution.

The validity of the model here presented can be further checked by predicting the intensities of the Raman bands of *trans* $(CD)_x$ which exhibit three strong fundamental lines at about 840, 1200 and 1340 cm^{-1}. By inserting the eigenvectors of *trans* $(CD)_x$ into eq. (25), the following values for S are calculated:

$$\omega_1 = 840 \quad S_1 = 0.114$$

$$\omega_2 = 1200 \quad S_2 = 0.109$$

$$\omega_3 = 1340 \quad S_3 = 0.187$$

In fact, these values agree quite well with the relative intensities observed in *trans* $(CD)_x$ at 600 nm.[24]

REFERENCES

1. J. C. W. Chien, *Polyacetylene*, Academic Press, New York, 1984.
2. T. A. Skotheim, Ed., *Handbook of Conducting Polymers*, Dekker, New York, 1986, Vols. 1 and 2.
3. H. Kuzmany, M. Mehring, and S. Roth, Eds., *Electronic Properties of Polymers and Related Compounds, Springer Series in Solid State Science*, Verlag, Heidelberg, 1985.
4. B. Hudson and B. Kohler, *Ann. Rev. Phys. Chem.* **25** (1974) 437.
5. W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.* **42** (1979) 1698.
6. W. P. Su, T. R. Schrieffer, and A. J. Heeger, *Phys. Rev.* **B22** (1980) 2099; **28** (1983) 1138.

7. P. Tavan and K. Schulten, *Phys. Rev.* **B36** (1987) 4337.
8. F. Inagaki, M. Tasumi, and T. Miyazawa, *J. Raman Spectrosc.* **3** (1975) 335.
9. G. Zannoni and G. Zerbi, *Chem. Phys. Lett.* **87** (1982) 50.
10. G. Zannoni and G. Zerbi, *Solid State Commun.* **47** (1983) 213.
11. M. Galtier, C. Benoit, and A. Montaner, *Mol. Cryst. Liq. Cryst.* **83** (1982) 109.
12. E. J. Mele, *Mol. Cryst. Liq. Cryst.* **77** (1981) 25; see also Chapt. 23 in ref. 2.
13. L. Piseri, R. Tubino, and G. Dellepiane, *Solid State Commun.* **44** (1982) 1589.
14. R. Tubino, L. Piseri, G. Dellepiane, and P. Piaggio, *J. Phys. (Paris)* **C3** (1983) 329.
15. L. Piseri, R. Tubino, L. Paltrinieri, and G. Dellepiane, *Solid State Commun.* **46** (1983) 183.
16. T. Kakitani, *Progr. Theor. Phys.* **51** (1974) 656.
17. L. Piseri and G. Zerbi, *J. Mol. Spectrosc.* **25** (1968) 254.
18. C. R. Fincher, Jr., M. Ozaki, M. Tanaka, D. Peebles, L. Lauchlan, A. J. Heeger, and A. G. MacDiarmid, *Phys. Rev.* **B20** (1979) 1589.
19. D. N. Batchelder and D. Bloor, *Resonance Raman Spectroscopy of Conjugated Macromolecules,* in: R. J. H. Clark and R. E. Hester, Eds., *Advances in Infrared and Raman Spectroscopy,* Vol. 11, Wiley, New York, 1984; see also references cited therein.
20. C. Cojan, G. P. Agrawal, and C. Flytzanis, *Phys. Rev.* **B15** (1977) 909.
21. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations,* McGraw Hill, New York, 1955.
22. Yu. E. Perlin, *Sov. Phys. Ups.* **6** (1964) 542.
23. R. S. Cataliotti, G. Paliani, G. Dellepiane, S. Fuso, S. Destri, L. Piseri, and R. Tubino, *J. Chem. Phys.* **82** (1985) 2223.
24. L. S. Lichtmann, A. Sarhangi, and D. B. Fitchen, *Solid State Commun.* **36** (1980) 869.
25. D. Moses, A. Fidblum, E. Ehrenfreund, A. J. Heeger, T. C. Chung, and A. G. MacDiarmid, *Phys. Rev.* **B26** (1982) 3361.
26. H. Kuzmany, E. A. Imhoff, D. B. Fitchen, and A. Sarhangi, *Phys. Rev.* **B26** (1982) 109.
27. W. Siebrand and M. Z. Zgierski, *J. Chem. Phys.* **71** (1979) 3561.
28. D. N. Batchelder and D. Bloor, *J. Phys.* **C15** (1982) 3005.

SAŽETAK

O interakciji elektron-fonon u *trans*-poliacetilenu

Giovanna Dellepiane, Riccardo Tubino i Carla Cuniberti

Razmatra se efekt π-vodljivih elektrona na dinamiku rešetke i na rezonantni Ramanov presjek u najjednostavnijemu poluvodljivom polimeru, *trans*-poliacetilenu. Primjenom aproksimacije čvrstog vezanja i zanemarivanjem elektronske korelacije, izvedeni su eksplicitni izrazi za delokalizirane konstante sile te su izračunani Franck-Condonovi faktori kao funkcija konstante sprege elektron-fonon.

Proračunane su fononske frekvencije i relativni rezonantni Ramanovi intenziteti za Raman-aktivne vibracije, te uspoređeni s raspoloživim eksperimentalnim podacima za *trans* $(CH)_x$ i $(CD)_x$.