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Optical properties of one-dimensional semiconductors and conjugated polymers

C. Cojan, G. P. Agrawal,* and C. Flytzanis
Laboratoire d'Optique Quantique,† *Ecole Polytechnique, 91120-Palaiseau, France*

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We present a description of the optical properties of one-dimensional semiconductors within the one-electron tight-binding approximation. The case of conjugated carbon chains is explicitly considered; the influence of the bond alternation, superalternation, effective heteroatomicity and chain coupling on the optical properties of these systems is evaluated in terms of a simplified but exactly soluble model. It is found that the linear susceptibility in the transparency region of the semiconductor shows a square dependence on a parameter N_d which represents the extent of the electron delocalization. Further the peculiar structure observed in the low-temperature absorption spectrum of the polydiacetylenes is explained in terms of a short-range coupling between chains.

I. INTRODUCTION

One-dimensional systems are characterized by highly anisotropic optical, dielectric, conducting and mechanical properties.[1,2] This is because the valence electrons, responsible for these properties, are forced to move along linear chains of atoms or molecules with distances which are small enough to allow formation of energy states more or less delocalized in one direction; a similar delocalization, on the other hand, in the other two directions is hindered by a surrounding sea of stable saturated bonds which keeps the chains well apart. This confers these systems with an isolator type behavior in directions across the chains but a semiconducting or conducting behavior along the chains. The metallic state, on quite general grounds peculiar to the one-dimensional systems, is expected to be unstable in most cases.[3] The complete delocalization of the valence electrons along the chains is limited by different constraints like bond alternation[4] and superalternation,[5] heteroatomicity (atom alternation), chain coupling, electron repulsion,[6] and the system is mostly forced to be in a semiconducting state. This is the case for almost all polymers, in particular, the ones with carbon conjugated chains,[1] and many crystallized TCNQ (tetracyanoquinodimethane) and KCP (potassium cyano-platinide) complexes.[2,3]

The relative importance of the different constraints in forcing the semiconducting state is still a matter of controversy[7] as is the question of the characterization of the absorption spectrum of systems with conjugated carbon chains either in terms of exciton states or band-to-band transitions. The optical index of refraction and the optical nonlinear coefficients have their origin in the valence electrons and therefore are expected to be highly anisotropic and to reflect strongly the effect of the different constraints on the electron delocalization. The linear optical properties are the most easily accessible experimentally but nonlinear optical properties show some very interesting features pertinent to the electron delocalization and their now emerging[8,9] study seems promising.

In two following papers the nonlinear optical properties and the effects which arise from the formation of planar or three-dimensional arrays in such systems are discussed in detail. In the present one we give the theoretical background to be used there and we apply it here to the description of the linear optical properties. We mainly focus our attention on systems with conjugated carbon chains or similar ones with large π-electron delocalization and we use a one-electron tight-binding approach in a formulation equivalent to the Hückel molecular description of finite carbon chains.[10]

Some systems with characteristic one-dimensional structure are cursively described in Sec. II where the model is also set up and the polarization mechanism by an electric field of optical frequency is analyzed with due attention to local-field corrections. The delocalization concept is defined in Sec. III and in Sec. IV we give a description of the linear optical properties of an ideal one-dimensional chain; the effect of different constraints is discussed in detail within the one-electron tight-binding approximation. This is applied to actual systems in Sec. V. The modifications to be brought into the description when electron correlation is incorporated are discussed qualitatively in Sec. VI.

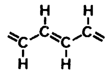
II. DESCRIPTION OF ONE-DIMENSIONAL SYSTEMS

A. Examples of one-dimensional systems

A strictly one-dimensional semiconductor in the sense described in the beginning of the introduction, namely formed by independent semiconducting chains immersed in a medium of saturated bonds, is seldom encountered in reality. All such systems because of cohesion and stability requirements possess a fully developed three-dimensional order; as a matter of fact, the fluctuations in this three-dimensional ordering probably are the agents for the onset of spectacular phase transitions from conducting to semiconducting state along the chains in some of these systems.[3] However, to the extent that the characteristic intrachain energies are much larger than the interchain coupling energy most of these systems satisfy the criteria of one dimensionality. This is the case of the polymers with long conjugated carbon chains like the polyenes, polyphenylacetylenes, polydiacacetylenes, polycumulenes, polyacenes, as well as the TCNQ or KCP salts.

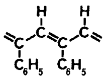
The characteristic valence four of the carbon atom is the origin of the enormous variety of these systems. Their common feature is that two of the four valence electrons are in hybridized *sp* orbitals and form saturated bonds with the neighboring carbon atoms; these so-called σ bonds stabilize the skeleton of the carbon chains. The remarkably different properties of the above systems are determined by the fate of the remaining two valence electrons per carbon atom.

(i) In *polyenes* where the constituent element is



one of these two electrons, by sp^2 hybridization with the previous two, forms a σ bond with a hydrogen atom thus forcing the skeleton in a zig-zag configuration with a 120° angle between carbon-carbon bonds; the fourth electron (or π electron), on the other hand, is placed in a band formed by the $2p_z$ orbitals of the carbon atoms where z lies perpendicular to the plane of the zig-zag chain. From the standpoint of the one-electron description to be adopted here the system is expected to stabilize in a configuration of alternatively long ("single") and short ("double") bonds[4]; this will be termed *bond alternation*.

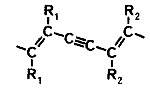
(ii) In polyphenylacetylenes the valence electron repartition is similar to the previous one except that now every other hydrogen atom along the chain is replaced by a C_6H_5 radical and the constituent element is thus



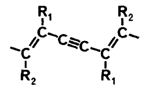
Because of the alternation of the side groups attached to the carbon atoms, successive carbon atoms are not equivalent and the chain probably acquires a heteroatomic character; this will be termed *atom alternation* or simply *heteroatomicity*. Clearly by replacing the hydrogen atoms with other appropriately chosen radicals a large variety of such chains can be obtained.

(iii) In polyacenes two parallel polyene chains are bonded together by replacing every other C-H bond of each chain with a C-C bond between the two chains; this is an extreme case of *short range interchain coupling*. More commonly this structure is described as a chain of benzene rings with neighboring benzene rings having one bond in common.

(iv) In polydiacetylenes[11] every other pair of successive C-H bonds of a polyene chain is replaced by an additional carbon-carbon bond along the chain; further there is a change of hybridization from sp^2 type to sp type on this pair of carbon atoms with corresponding stereochemical change of the chain. The constituent element now is

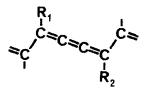


or



where for stability reasons the remaining two hydrogen atoms of the primary polyene chain have been replaced by appropriately chosen radicals R_1 and R_2 which may be identical. In the chain now appears an alternation of "double" and "triple" bonds separated by "single" bonds; this will be termed *bond superalternation*. Clearly more complicated structures can be obtained in this way still respecting the valency requirements of the carbon atom.

(v) In polycumulenes, formed like the polydiacetylenes, the constituent element is



from the standpoint of chemical resonance theory the actual system is said to resonate between these two structures, the polydiacetylene structure being by far the most dominant. Clearly here too more complex structures can be obtained.

More sophisticated one-dimensional structures which have been under active investigation recently[2,3] are the TCNQ and KCP salts. In the former class each site on a single chain does not contain a single atom as in the case of carbon chains but is composed on a molecular group or a charge-transfer complex; in the later class the delocalized states are formed from *d* states. To a lesser degree some features of genuinely three-dimensional compounds like the tetrahedral semiconductors can be ascribed to the one-dimensional delocalized electron states. In the following although we shall be using the terminology appropriate to materials composed of carbon chains, we should point out that the results are much more general and may as well be applied for more complex structures.

B. Model and underlying simplifications

We idealize the actual solid assuming that it consists of parallel linear chains extending along the x direction which will be taken to be a crystallographic axis as well (Fig. 1). The chains are embedded in a medium of localized σ bonds and other molecular groups dispersed in such a way that there is a symmetry of revolution around the chain axis; let σ be the number of such chains per unit area of the yz plane. For the present analysis we assume that the chains behave independently so that we can focus our attention to a single chain. We assume it to be sufficiently long so that the end effects are negligible. In fact we idealize the situation by considering the infinite chains.

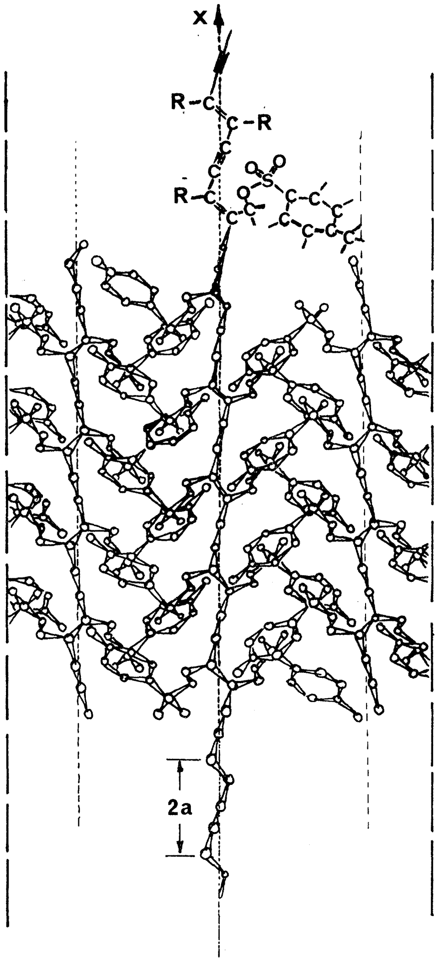


FIG. 1. Structure of the PTS-diacetylene polymer crystal [PTS, *bis* poly (Toluene Sulfonate); R, CH_2-SO_3-ϕ-CH_3] and the cavity used for the calculation of the local field.

The one-dimensional behavior, in these systems, has its origin in the distinctly different roles played by the π and σ electrons, respectively[10]; they are completely separated from each other with no direct interaction and because we are dealing with infinite systems they belong to different bands, the π and σ bands, respectively. The latter, however, are very narrow and deep lying and they may be more conveniently transformed to states localized on the σ bonds; transitions between these states make their appearance only in the far ultraviolet. Thus the contribution of these σ electrons to the optical and dielectric properties along and across the chains can be estimated by assigning to them bond polarizabilities which satisfy the additivity property. This σ bond additivity has been assumed previously too when discussing the optical properties of polymers with saturated bonds[12] and except for some finer details there is no serious reason to abandon it.

The π electrons, on the other hand, are mobile over the whole chain and their description in terms of delocalized band states is appropriate. However, because they are forced to move only along one direction, that of the chains, they feel the full impact of the different constraints there and the system is found to be in a semiconducting state. The exact origin of this semiconducting state is still controversial particularly owing to the wide gap observed in these materials. From global energy arguments one expects that either the static Peierls distortion[4] leading to bond alternation and/or the electronic repulsion[6] are responsible for this. This will clearly affect the choice of the description in terms of either one-electron or many-electron states, respectively. Here we favor the static Peierls distorsion and we adopt the one-electron approximation for the π electrons; we particularly emphasize the delocalized character of their states.

These π electrons move along a periodic array of atoms. Near each nucleus the potential field due to that nucleus by far swamps out the effect of the other nuclei in the chain and there the wave function ψ of the π electron looks very much like the atomic orbital ϕ of the atom; it is thus resonable to write the π states as linear combination of the atomic orbitals. This is the basis of the tight-binding or linear combination of atomic orbitals approximation[13]; choosing an appropriate unit cell we write

$$\psi(x) = \sum_{n=0}^{N=1} \sum_{i=1}^{s} c_{ns+i}\, \phi_{ns+i}(x), \tag{2.1}$$

where ϕ_{ns+i} is the atomic orbital corresponding to the ith site in the nth unit cell, s is the number of sites in a unit cell, and N is the number of unit cells and should tend to infinity for an infinite chain. The expansion coefficients c_{ns+i} are determined by minimizing the energy $\int \psi^* H \psi\, d\tau$ where H is the one-electron Hamiltonian and $d\tau$ is the volume element. Using the Bloch theorem

$$\psi(x + nd) = e^{iknd}\psi(x), \tag{2.2}$$

d being the unit cell length, it follows from Eq. (2.1) that the coefficients c_{ns+i} of the nth unit cell are related to those of the unit cell at the origin c_i,

$$c_{ns+i} = e^{inkd} c_i \quad (i = 1, \ldots, s), \tag{2.3}$$

using (2.1) and (2.3), the energy $\epsilon = \int \psi^* H \psi\, d\tau$ can be written

$$\epsilon = \sum_{n=1}^{N-1} \sum_{i=1}^{s} (\alpha_i c_i^* c_i + \beta_{i,i+1} c_i^* c_{i+1} + \beta_{i-1,i} c_{i-1}^* c_i + \text{c.c.}), \tag{2.4}$$

where the Coulomb integral $\alpha_i = \int \phi_i^* H \phi_i\, d\tau$ is the on-site energy and the resonance integral $\beta_{ij} = \int \phi_i^* H \phi_j\, d\tau$ $(j = i \pm 1)$ represents the hopping probabilities from the ith site to the neighboring left and right sites; all other integrals as well as all the overlap integrals $\int \phi_i^* \phi_j\, d\tau$ $(i \neq j)$ are assumed to vanish. Equations (2.1) and (2.4) together with the energy minimizing conditions

$$\frac{\partial \epsilon}{\partial c_i} = 0 \tag{2.5}$$

give the band energies $\epsilon_n(k)$ and wave functions $\psi_{nk}(x)$ for the π electrons. We are interested in the perturbation of these states by an external electric field of optical frequency ω.

C. Optical properties: Linear susceptibility

In an electric field E of optical frequency ω the system will respond through an induced polarization $\vec{P}(\omega) = \underline{\chi}^{(1)}(\omega) \cdot \vec{E}(\omega)$. Owing to the symmetry of revolution around the chain direction x, which also is a crystallographic axis, the symmetric second rank tensor of the linear susceptibility $\chi^{(1)}(\omega)$ has only two independent components, $\chi_\parallel^{(1)}$ and $\chi_\perp^{(1)}$, parallel and perpendicular to the chain axis or

$$P_\parallel(\omega) = \chi_\parallel^{(1)}(\omega) E_\parallel(\omega)$$

and

$$P_\perp(\omega) = \chi_\perp^{(1)}(\omega) E_\perp(\omega). \tag{2.6}$$

To $P_\parallel$ contribute the delocalized π electrons as well as the localized σ electrons while to P_L only the latter contribute; accordingly

$$\chi_\parallel^{(1)} = \chi_\pi^{(1)} + \chi_\sigma^{(1)} \tag{2.7}$$

and

$$\chi_\perp^{(1)} = \chi_{\sigma'}^{(1)}, \tag{2.8}$$

where $\chi_\pi^{(1)}$ is the contribution of the delocalized electrons of the π band along the chain and $\chi_\sigma^{(1)}$ and $\chi_{\sigma'}^{(1)}$ are the contribution of the localized σ electrons, respectively, along and across the chain direction.

At the microscopic level the contribution of the σ electrons will be expressed by a polarizability α per unit cell, equal to the sum of the σ-bond polarizabilities, where for simplicity we disregard any anisotropy variations; α is assumed a scalar. Its relation to $\chi_\sigma^{(1)}$ and $\chi_{\sigma'}^{(1)}$ will be provided through the local-field corrections.

In order to estimate the local-field corrections we use the cavity procedure[14] with due attention to the axial symmetry inherent in the material.[15] We consider a reference chain and the surrounding side groups and we enclose it in a cylindrical cavity of infinite axial extension and radius much smaller than the wavelength of the applied electric field but larger than the interchain spacing (Fig. 1). Then the local field E_L on the position on the reference chain and its side groups is

$$\vec{E}_L = \vec{E} + \vec{E}_{\text{cav}} + \vec{E}_d, \tag{2.9}$$

where E is the macroscopic field, $\vec{E}_{\text{cav}}$ is the field from the polarization charges on the surface of the cylindrical cavity cut (as a mathematical fiction) out of the specimen with the reference chain as axis, and $\vec{E}_d$ is the field due to the interactions between the induced charges inside the cavity.

We make the assumption

$$\vec{E}_d = 0.$$

This is consistent with the isotropic distribution of the σ bonds on the one side and the delocalized nature of the π electrons on the other side and will not be justified any further here. The field $\vec{E}_{\text{cav}}$ will be deduced from electrostatics. Indeed one finds that for the component perpendicular to the chain direction $E_{\perp\text{cav}}$ is equal to $2\pi P_\perp$ and from (2.9) the local field in this direction is

$$E_{\perp L} = \tfrac{1}{2}(\epsilon_\perp + 1)E. \tag{2.10}$$

Since by definition $P_\perp = [(\epsilon_\perp - 1)/4\pi] E_\perp$; expressing $P_\perp$ as the sum of the dipoles induced per unit volume, $P_\perp = N_c \alpha E_{\perp L}$, where N_c is the number of unit cells per unit volume, one has

$$2\pi N_c \alpha = (\epsilon_\perp - 1)/(\epsilon_\perp + 1) \tag{2.11}$$

or

$$\epsilon_\perp = (1 + 2\pi N_c \alpha)/(1 - 2\pi N_c \alpha). \tag{2.12}$$

On the other hand for the component parallel to the chain direction one easily finds $E_{\parallel \text{cav}} = 0$ and from (2.9) one obtains that the local field in this direction is equal to the macroscopic field, or

$$E_{\parallel L} = E_\parallel . \tag{2.13}$$

Then from (2.6), $\chi_\sigma^{(1)} = N_c \alpha$ and using (2.7) we obtain

$$\epsilon_\parallel(\omega) = 1 + 4\pi\chi_\parallel^{(1)} = 1 + 4\pi\chi_\pi^{(1)}(\omega) + 4\pi N_c \alpha, \tag{2.14}$$

where $\chi_\pi^{(1)}$ is the π-electron contribution and its expression will be given by band theory.

For our purposes it is convenient to use the expression derived by Genkin and Mednis[16]; there it is shown that

$$\chi_\pi^{(1)}(\omega) = \frac{2e^2}{V\hbar} \sum_n \sum_{n' \neq n} \sum_k f_n(k) \left(\frac{\Omega_{nn'}(k)\Omega_{n'n}(k)}{\omega_{nn'}(k) - \omega + i/\tau(k)} + \frac{\Omega_{nn'}(k)\Omega_{n'n}(k)}{\omega_{nn'}(k) + \omega - i/\tau(k)} \right) \tag{2.15}$$

where the factor 2 takes into account the number of the spin states, V is the crystal volume, $f_n(k)$ is the distribution function over the states prior to turning on the electric field, $\hbar\omega_{n'n}(k) = \epsilon_{n'}(k) - \epsilon_n(k)$, $\tau(k)$ is a relaxation time, and

$$\Omega_{n'n}(k) = \frac{1}{v} \int_{\text{u.c.}} U^*_{n'k}(x) \frac{\partial}{\partial k} U_{nk}(x)\, d\tau, \tag{2.16}$$

where U_{nk} is the unit cell periodic part of the Bloch wave function

$$\psi_{nk}(x) = e^{ikx} U_{nk}(x). \tag{2.17}$$

In the present case the volume of the unit cell is $v = d/\sigma$, where σ is the density of chains per unit cross area, and, since only the x dependence is relevant, Eq. (2.16) can be written

$$\Omega_{n'n}(k) = \frac{1}{d} \int U^*_{n'k}(x) \frac{\partial}{\partial k} U_{nk}(x)\, dx. \tag{2.18}$$

In (2.15) $V = Nd/\sigma$; replacing

$$\frac{2\pi}{Nd} \sum_k \to \int dk$$

for an infinite chain and using the zero-temperature distribution function $f_n(k) = 1$ for occupied (v, valence) bands and zero for nonoccupied (c, conduction) ones, Eq. (2.15) is transformed to

$$\chi_\pi^{(1)}(\omega) = \frac{2e^2\sigma}{\pi\hbar} \sum_v \sum_c \int_{-\pi/d}^{\pi/d} dk \frac{\omega_{cv}(k) |\Omega_{cv}(k)|^2}{\omega_{cv}^2(k) - (\omega - i/\tau)^2} . \tag{2.19}$$

This expression can be separated into its real and imaginary parts and, using expression (2.14), one can determine the dispersion and absorption of an electromagnetic field of frequency ω. In particular one can calculate the refractive index $n_\parallel(\omega)$ and the absorption coefficient $k_\parallel(\omega)$ defined by $\epsilon_\parallel(\omega) = \epsilon'_\parallel(\omega) + i\epsilon''_\parallel(\omega) = [n_\parallel(\omega) + ik_\parallel(\omega)]^2$ and the reflectivity $R = [(n_\parallel - 1)^2 + k_\parallel^2]/[(n_\parallel + 1)^2 + k_\parallel^2]$. An important quantity is

$$\chi_\pi^{(1)}(0) = \frac{2e^2\sigma}{\pi\hbar} \sum_v \sum_c \int_{-\pi/d}^{\pi/d} dk \frac{|\Omega_{cv}(k)|^2}{\omega_{cv}(k)}, \tag{2.20}$$

which appears when evaluating the index of refraction $n_\parallel = [\epsilon_\parallel(0)]^{1/2}$ in the transparency region of the crystal for fields polarized along the chains, namely

$$n_\parallel^2 = 1 + 4\pi\chi_\pi^{(1)}(0) + 4\pi N_c \alpha. \tag{2.21}$$

III. π-ELECTRON BAND STATES

We shall now derive within the one-electron tight-binding approximation the expressions of the Bloch energies and wave functions for the three ideal infinite chains defined in Sec. II.

A. Simply atom and bond alternated chain

There are two atoms per unit cell with Coulomb integrals α_1 and α_2 and the hopping integrals along the chain alternatively take the values β_1 and β_2 on the long and short bonds, respectively. The wave function is

$$\psi = \sum_{n=1}^{N} (c_{2n-1}\phi_{2n-1} + c_{2n}\phi_{2n}), \tag{3.1}$$

where the expansion coefficients c_i are determined by minimizing the energy

$$\begin{aligned}\epsilon = \sum_{n=1}^{N} [\, & \alpha_1 c^*_{2n-1} c_{2n-1} + \alpha_2 c^*_{2n} c_{2n} \\ & + (\beta_1 c^*_{2n-1} c_{2n} + \beta_2 c^*_{2n} c_{2n+1} + \text{c.c.})]\end{aligned} \tag{3.2}$$

Introducing the notation $\theta = ka$, where a is the unit-cell length, using the Bloch theorem (2.2) and the energy minimizing conditions (2.5) we obtain the following set of equations for the c_i's:

$$\begin{aligned}(\alpha_1 - \epsilon)c_1 + (\beta_1 + \beta_2 e^{-i\theta})c_2 &= 0, \\ (\beta_1 + \beta_2 e^{i\theta})c_1 + (\alpha_2 - \epsilon)c_2 &= 0,\end{aligned} \tag{3.3}$$

from which the following two-band solution for the Bloch energies and wave functions is derived (the parameters α_i and β_i are taken to be positive):

$$\epsilon_{c,v}(\theta) = \pm\beta_2(\mu^2 + 1 + \nu^2 + 2\nu\cos\theta)^{1/2} = \pm\beta_2\zeta, \tag{3.4}$$

$$\psi_{c,v}(\theta) = \frac{1}{(2N)^{1/2}} \sum_{n=1}^{N} e^{in\theta}[(1 \pm \mu/\zeta)^{1/2} e^{i\eta_\pm/2}\phi_{2n} + (1 \mp \mu/\zeta)^{1/2} e^{-i\eta_\pm/2}\phi_{2n-1}], \tag{3.5}$$

where "+" and "−" signs correspond to the conduction (c) and valence (v) bands, respectively, and we have introduced the following notations $\mu = (\alpha_2 - \alpha_1)/2\beta_2$, $\nu = \beta_1/\beta_2$ ($\nu < 1$), $\zeta = |\epsilon|/\beta_2$, and

$$e^{i\eta_\pm} = \pm[(1 + \nu e^{i\theta})/(1 + \nu e^{-i\theta})]^{1/2}, \tag{3.6}$$

and the band energies are measured from $\frac{1}{2}(\alpha_1 + \alpha_2)$. With one valence electron per site the valence band is filled and the conduction band empty, the system being thus in a semiconducting state. The smallest gap appears at the edge of the Brillouin zone ($\theta = \pi$)

$$E_g = 2\beta_2[\mu^2 + (1 - \nu)^2]^{1/2}, \tag{3.7}$$

and there the joint density of states is infinite; the largest gap appears at the center of the Brillouin zone, $\theta = 0$, and is

$$E_g' = 2\beta_2[\mu^2 + (1 + \nu)^2]^{1/2}.$$

One can define a Fermi energy by $2E_F = E_g'$. For the case of complete dimerization $\nu = 0$ and the two gaps are equal (flat bands).

For an homoatomic chain one obtains, with $\alpha_1 = \alpha_2$, the expressions

$$\epsilon_{c,v}(\theta) = \pm(\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2\cos\theta)^{1/2} = \pm\beta_2\zeta_0, \tag{3.8}$$

$$\psi_{c,v}(\theta) = \frac{1}{(2N)^{1/2}} \sum_{n=1} e^{in\theta}(e^{i\eta_\pm/2}\phi_{2n} + e^{-i\eta_\pm/2}\phi_{2n-1}), \tag{3.9}$$

which are identical with the ones of Ref. 17. The smallest gap (3.7) now becomes

$$E_g = 2(\beta_2 - \beta_1), \tag{3.10}$$

and the Fermi energy is $E_F = (\beta_2 + \beta_1)$.

B. Superalternated chain

The simplest case is the one representing the polydiacetylene chain with four atoms per unit cell whose length will be taken $2a$ (see Fig. 1); this structure is formally obtained from the simply alternated chain by periodically substituting every other β_2 with β_3. The wave function is

$$\psi = \sum_{n=1}^{N} (c_{4n}\phi_{4n} + c_{4n-1}\phi_{4n-1} + c_{4n-2}\phi_{4n-2} + c_{4n-3}\phi_{4n-3}), \tag{3.11}$$

and the energy (2.4) becomes

$$\epsilon = \sum_{n=1}^{N} [\alpha(c_{4n}^* c_{4n} + c_{4n-1}^* c_{4n-1} + c_{4n-2}^* c_{4n-2} + c_{4n-3}^* c_{4n-3}) + \beta_1(c_{4n-1}^* c_{4n} + c_{4n-3}^* c_{4n-2}) + \beta_2 c_{4n}^* c_{4n+1} + \beta_3 c_{4n-2}^* c_{4n-1}]. \tag{3.12}$$

The expansion coefficients c_i and the energy ϵ are determined from the following set of homogeneous equations:

$$(\alpha - \epsilon)c_1 + \beta_1 c_2 + 0 + \beta_2 e^{-2i\theta} c_4 = 0,$$
$$\beta_1 c_1 + (\alpha - \epsilon)c_2 + \beta_3 c_3 + 0 = 0,$$
$$0 + \beta_3 c_2 + (\alpha - \epsilon)c_3 + \beta_1 c_4 = 0,$$
$$\beta_2 e^{+2i\theta} c_1 + 0 + \beta_1 c_3 + (\alpha - \epsilon)c_4 = 0,$$

where the periodic boundary condition and the Bloch theorem have been incorporated and $\theta = ka$. One obtains the following four-band solution:

$$\epsilon = \pm\beta_2\{\nu^2 + \tfrac{1}{2}(1 + \nu'^2) \pm [\tfrac{1}{4}(1 - \nu'^2)^2 + \nu^2(1 + \nu'^2 + 2\nu'\cos 2\theta)]^{1/2}\}^{1/2} = \beta_2\xi, \tag{3.13}$$

$$\psi = \frac{C_0}{(4N)^{1/2}} \sum_n e^{2in\theta}[(\phi_{4n} \pm \rho e^{-i\eta_1}\phi_{4n-1}) + e^{-i\eta_2}(\rho\phi_{4n-2} \pm e^{-i\eta_1}\phi_{4n-3})], \tag{3.14}$$

where $\nu = \beta_1/\beta_2$, $\nu' = \beta_3/\beta_2$ and ρ, C_0, η_1, and η_2 are defined as follows:

$$\rho = [\xi^2 - \nu^2 - \nu'^2)/(\xi^2 - 1 - \nu^2)]^{1/2}, \tag{3.15}$$

$$C_{00} = \{(\xi^2 - 1 - \nu^2)/[\xi^2 - \nu^2 - \tfrac{1}{2}(1 + \nu'^2)]\}^{1/2}, \tag{3.16}$$

$$\eta_1 = \tan^{-1}\{\nu'\sin 2\theta/[(\xi^2 - \nu^2) + \nu'\cos 2\theta]\}, \tag{3.17}$$

$$\eta_2 = \tan^{-1}[\nu'\sin 2\theta/(1 + \nu'\cos 2\theta)]. \tag{3.18}$$

We number the four energy bands from 1 to 4 in order of increasing energy. In order to show better the effects of the superalternation on the band spectrum it is convenient to depict the bands in the extended Jones zone[18] (Fig. 2); each pair (1, 2) and (3, 4) can be viewed as arising by a discontinuity at the middle of the Brillouin zone of the simply alternated chain. With one electron per atom the two lower (valence) bands are filled and the two higher (conduction) bands are empty. Wilson[5] also derived approximate expressions of the energies and the wave functions by developing the coefficients in (3.12) in powers of $(2\beta_1 - \beta_2 - \beta_3)/(2\beta_1 + \beta_2 + \beta_3)$ and keeping only first-order terms with respect to this parameter.

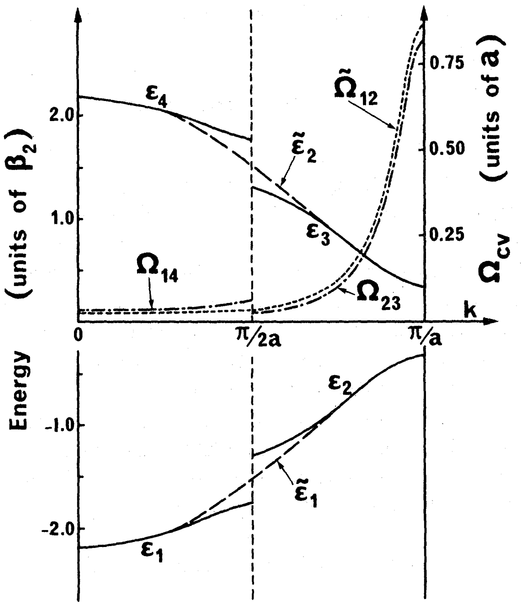


FIG. 2. Band structure and transition matrix elements for a bond superalternated chain (infinite polydiacetylene) and its equivalent bond alternated chain [infinite polyene (tilted quantities)] (see text). The values of the parameters β_i correspond to those adopted for the PTS-diacetylene ($\beta_2=3.2$ eV, $\beta_1/\beta_2=0.90$, and $\beta_3/\beta_2=1.50$); those of the equivalent bond alternated chain were calculated from expressions (3.20) ($\tilde{\beta}_1/\tilde{\beta}_2=0.75$, $\tilde{\beta}_2=4.0$ eV).

As can be seen in Fig. 2 or from (3.13) the smallest energy gap is

$$E_g=2\beta_2\{\nu^2+\tfrac{1}{2}(1+\nu'^2) - [\tfrac{1}{4}(\nu'^2-1)^2+\nu^2(1+\nu')^2]^{1/2}\}^{1/2} \qquad (3.19)$$

at the edge of the extended Jones zone (when reduced in the first Brillouin zone this gap appears at its center) where the joint density of states is infinite; the largest gap,

$$E_g'=2\beta_2\{\nu^2+\tfrac{1}{2}(1+\nu'^2) + [\tfrac{1}{4}(\nu'^2-1)^2+\nu^2(1+\nu')^2]^{1/2}\}^{1/2},$$

appears at the center of the Jones zone (edge of the first Brillouin zone). There are two other intermediate gaps; appear at the boundaries of the Brillouin zone and the joint density of states is infinite there. This is a typical behavior of one-dimensional systems.

For further reference it is convenient to determine the hopping integrals $\tilde{\beta}_1$ and $\tilde{\beta}_2$ of an alternated chain equivalent to the superalternated one so that the smallest and largest gaps are equal in both chains; one obtains

$$\tilde{\beta}_1=\tfrac{1}{4}(E_g'-E_g), \quad \tilde{\beta}_2=\tfrac{1}{4}(E_g'+E_g). \qquad (3.20)$$

From the formulas (3.13) and (3.18) one can derive the expression for the band energies and wave functions for the corresponding polycumulene chain by the following transformation: $\beta_2\rightarrow\beta_1$, $\beta_1\rightarrow\beta_2$, and *then* $\beta_3=\beta_2$. One obtains

$$\begin{aligned}\epsilon &= \pm\beta_2\{1+\tfrac{1}{2}(1+\nu^2) \pm[\tfrac{1}{4}(1-\nu^2)^2+(1+\nu^2+2\nu\cos 2\theta)]^{1/2}\}^{1/2}\\ &=\beta_2\xi\,. \end{aligned} \qquad (3.21)$$

The wave function is given by the same expression (3.14) where now ρ, c_0, η_1, and η_2 are given by

$$\rho=\xi/(\xi^2-1-\nu^2)^{1/2},$$

$$C_0=(\xi^2-1-\nu^2)^{1/2}/[\xi^2-1-\tfrac{1}{2}(1+\nu^2)]^{1/2},$$

$$\eta_1=\tan^{-1}[\sin 2\theta/(\xi^2-1+\cos 2\theta)],$$

$$\eta_2=\tan^{-1}[\sin 2\theta/(\nu+\cos 2\theta)].$$

The band structure of the monomers can also be obtained by interchanging β_1 and β_3 and putting $\beta_2=0$; the four bands reduce now to four localized states of energies (flat bands)

$$\epsilon_i=\pm[\beta_3^2+\tfrac{1}{2}\beta_1^2\pm\beta_1(\tfrac{1}{4}\beta_1^2+\beta_3^2)^{1/2}]^{1/2}. \qquad (3.22)$$

C. Two coupled bond alternated chains

We only consider the case of coupling between two identical simply bond alternated chains and denote by $2\beta'$ the coupling hopping integral (Fig. 3). There are four atoms per unit cell whose length in the direction of the chains is a. The

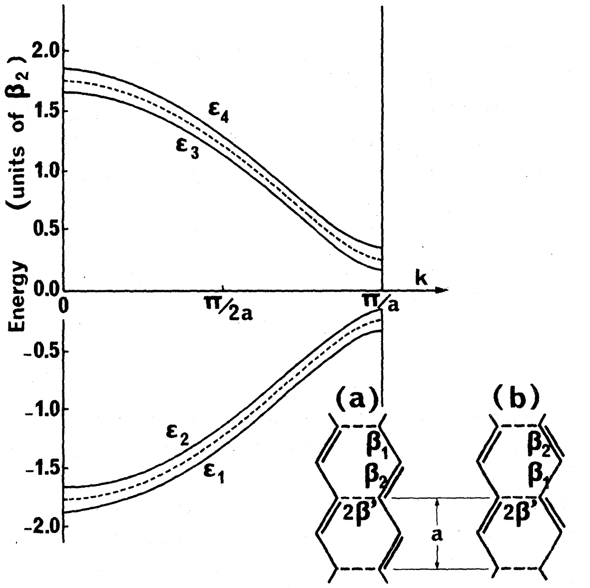


FIG. 3. Band structure for the two coupled bond alternated chain system (short-range coupling) in the centrosymmetric (a) and noncentrosymmetric (b) configurations. The band structure for zero coupling (single bond alternated chain) is represented with the dotted curves; the values of parameters are $\beta_1/\beta_2=0.75$ and $\beta'/\beta_2=0.10$.

wave function is

$$\psi = \sum_{n=1}^{N} (c_{2n-1}\phi_{2n-1} + c_{2n}\phi_{2n} + c'_{2n-1}\phi'_{2n-1} + c'_{2n}\phi'_{2n}).$$

As can be seen in Fig. 3, there are two possible configurations for the coupling, the centrosymmetric and the noncentrosymmetric.[19]

For the centrosymmetric case applying the periodic boundary conditions and the Bloch theorem for each chain one obtains

$$\begin{aligned}
&(\alpha-\epsilon)c_1 + (\beta_1+\beta_2 e^{-i\theta})c_2 + 0 + 0 = 0,\\
&(\beta_1+\beta_2 e^{i\theta})c_1 + (\alpha-\epsilon)c_2 + 0 + 2\beta' c'_2 = 0,\\
&0 + 0 + (\alpha-\epsilon)c'_1 + (\beta_2+\beta_1 e^{-i\theta})c'_2 = 0,\\
&0 + 2\beta' c_2 + (\beta_2+\beta_1 e^{i\theta})c'_1 + (\alpha-\epsilon)c'_2 = 0,
\end{aligned} \tag{3.23}$$

which has the following four band solution:

$$\epsilon_i = \pm[(\epsilon_0^2+\beta'^2)^{1/2} \pm \beta'] = \beta_2\zeta_i, \tag{3.24}$$

$$\psi_i = \frac{C_i}{(2N)^{1/2}} \sum_n e^{in\theta} \{[\phi_{2n} + (\zeta_0/\zeta_i)e^{i\eta}\phi_{2n+1}] \pm e^{-i\eta}[(\zeta_0/\zeta_i)\phi'_{2n} + e^{i\eta}\phi'_{2n+1}]\}, \tag{3.25}$$

where

$$\epsilon_0 = \beta_2\zeta_0 = (\beta_1^2+\beta_2^2+2\beta_1\beta_2\cos\theta)^{1/2},$$
$$e^{i\eta} = (\beta_1+\beta_2 e^{i\theta})^{1/2}/(\beta_1+\beta_2 e^{-i\theta})^{1/2},$$

and

$$C_i = \zeta_i/(\zeta_0^2+\zeta_i^2)^{1/2};$$

in Eq. (3.24) the "+" sign is for $i=3, 4$ and the "−" sign is for $i=1, 2$.

On the other hand, for the noncentrosymmetric case with the appropriate modifications in (3.23) one obtains the following four band solution:

$$\epsilon_i = \pm[(\epsilon_0^2+\beta'^2)^{1/2} \pm \beta'] = \beta_2\zeta_i,$$

$$\psi_i = \frac{C_i}{(2N)^{1/2}} \sum_n e^{in\theta} \{[\phi_{2n} + (\zeta_0/\zeta_i)e^{-i\eta}\phi_{2n-1}] \mp [\phi'_{2n} + (\zeta_0/\zeta_i)e^{-i\eta}\phi'_{2n-1}]\} \tag{3.26}$$

Thus in both cases the same band structure is obtained but the band wave functions are different. The variation of the band energies over the Brillouin zone is shown in Fig. 3. The difference between the two configurations in symmetry and wave functions is strikingly reflected in the absorption spectrum as will be shown below. In a forthcoming paper it will be shown that the nonlinear optical properties are strikingly different. The occurrence of one configuration rather than the other in any particular case will depend on many factors, energetic, chemical and structural; it is likely that the centrosymmetric one is the most common.

IV. TRANSITION MATRIX ELEMENTS: DELOCALIZATION

Before proceeding to the description of the linear optical properties and the way they are affected by the constraints along the chain, a preliminary insight into how these constraints restrict the extension of the π electrons can be gained by calculating the π-electron delocalization. This can be expressed in terms of the transition matrix elements between two bands $\langle nk|x|n'k'\rangle$ which are directly related to the quantities $\Omega_{nn'}(k)$ needed for the calculation of the linear susceptibility; there is a close relationship between this latter quantity and the delocalization. Following Blount[20] we have

$$\int \psi^*_{n'k'}x\psi_{nk}\,dx = i\left(\frac{\partial}{\partial k}\int \psi^*_{n'k'}\psi_{nk}\,dx + \Omega_{n'n}(k)\delta(k-k')\right). \tag{4.1}$$

The delocalization is most conveniently defined as the extension of the Wannier functions[20] associated to the valence band. The Wannier function centered on the nth unit cell is defined as

$$W_n^v(x) = \frac{1}{\sqrt{N}}\sum_k e^{-inka}\psi_{vk}(x). \tag{4.2}$$

Wannier functions belonging to different unit cells are orthogonal to each other. A measure to their extension is the mean square spread to the electron position coordinate in the Wannier function representation

$$\langle\Delta x^2\rangle \equiv \langle(x-\langle x\rangle)^2\rangle = \langle x^2\rangle - \langle x\rangle^2, \tag{4.3}$$

where the angular brackets $\langle\cdots\rangle$ denote the average over the Wannier states. One can easily show that for the valence-electron states

$$\langle\Delta x^2\rangle = \frac{2}{sN}\sum_{v,c}\sum_k |\Omega_{vc}(k)|^2,$$

where the factor 2 takes account of the two spin states. On transforming the summation to an integration and introducing $\theta' = kd$, where d is the unit cell length one has

$$\langle\Delta x^2\rangle = \frac{1}{\pi s}\sum_{v,c}\int_{-\pi}^{\pi} |\Omega_{vc}(\theta')|^2\,d\theta' = D^2. \tag{4.4}$$

Thus the calculation of D reduces to that of Ω_{vc} already defined by (2.18).

In performing the integration over x in expression (2.18) the quantities $\int\phi_n^* x\phi_{n'}\,dx$ are needed; we adopt the Hückel approximation[10]

$$\int \phi_n^* x\phi_{n'}\,dx = \delta_{nn'}x_n, \tag{4.5}$$

where x_n is the site position where the orbital ϕ_n is located. In the following we assume that successive sites along the chain are equidistant and we disregard the variation of the intersite distances because of bond alternation; their main effect is already taken into account through the choice of alternating values of the hopping integrals β_i along the chain. The integration over x in (2.18) reduces thus to straightforward summations over site positions. In the following we give the expressions of Ω_{vc}, Ω_{vv}, and Ω_{cc} for the three ideal chains whose band structure was derived in Sec. III and we calculate D for each case separately.

A. Atom and bond alternated chain

$$\Omega_{vc} = -\Omega^*_{cv} = \frac{a}{2\zeta_0(\zeta_0^2+\mu^2)^{1/2}}\left(\frac{i(1-\nu^2)}{2} + \frac{\mu\nu\sin\theta}{(\zeta_0^2+\mu^2)^{1/2}}\right), \tag{4.6}$$

$$\Omega_{vv} = \tfrac{1}{2}ia - \Omega_{cc} = \tfrac{1}{4}ia\left(1 + \frac{\mu(\nu^2-1)}{\zeta_0^2(\zeta_0^2+\mu^2)^{1/2}}\right),$$

$$D = \left(\frac{1+\nu^2}{[(1+\nu)^2+\mu^2]^{1/2}[(1-\nu)^2+\mu^2]^{1/2}}\right)^{1/2}\frac{a}{4}\,. \tag{4.7}$$

For the homoatomic chain, $\mu = 0$, one has the simpler expressions

$$\Omega_{cv} = ia(1-\nu^2)/4\zeta_0^2, \quad \Omega_{vv} = \Omega_{cc} = \tfrac{1}{4}ia, \tag{4.8}$$

$$D = \tfrac{1}{4}a[(1+\nu^2)/(1-\nu^2)]^{1/2}. \tag{4.9}$$

Comparing (4.7) and (4.9) one sees that the heteroatomicity substantially reduces the delocalization; with no heteroatomicity and bond alternation D is infinite as expected. From (4.8) one also sees that the matrix elements $|\Omega_{cv}|$ which is a measure of the transition strength attains its maximum value at the edge of the Brillouin zone ($\theta = \pi$). Thus the band states are most delocalized at the edge of the Brillouin zone where the smallest energy gap also appears and the density of states is infinite; this is a general behavior of one-dimensional systems. For future reference it is convenient to define a dimensionless parameter

$$N_d = (4/a)|\Omega_{cv}(\theta=\pi)| = (1+\nu)/(1-\nu), \tag{4.10}$$

which we shall call delocalization parameter. It is normalized with respect to $a/4$ which is the half bond distance. For a dimer $\nu = 0$ and $N_d = 1$ indicating that the electron is localized within the bond. For any finite value of ν the electrons are delocalized over many bond lengths and N_d represents the extent of that delocalization. Note that D given by Eq. (4.7) represents an average delocalization length while N_d corresponds to the Brillouin-zone edge delocalization.

B. Superalternated chains

The matrix elements are

$$\Omega_{14,23} = \frac{ia}{4}\,\frac{(\nu^4-\nu'^2)+\xi_i^2[\frac{1}{2}(\nu'^2+1)-\nu^2]}{\xi_i^2[\xi_i^2-\nu^2-\frac{1}{2}(1+\nu'^2)]}, \tag{4.11}$$

$$\Omega_{22} = \Omega_{33}, \tag{4.12}$$

$$\Omega_{11} = \Omega_{44}. \tag{4.13}$$

In Fig. 3 we have depicted the variation of $\Omega_{14,23}$ over the Jones zone. It is easy to check that for $\nu' = 1$ all these expressions reduce to those of the simply bond alternated chain. The delocalization D has been calculated numerically from

$$D^2 = \frac{1}{\pi}\int_{-\pi/2}^{\pi/2} d\theta(|\Omega_{14}|^2 + |\Omega_{23}|^2) \tag{4.14}$$

for some characteristic values of ν and ν' and the results are depicted in Fig. 4 where for comparison the results for the simply bond alternated chain, expression (4.10), have been included. For $\nu' \simeq 1$ one obtains

$$D \simeq \frac{a}{4}\left(\frac{1+\nu^2}{1-\nu^2} - \frac{2\nu^2(\nu'-1)}{(1-\nu^2)^2}\right)^{1/2}, \tag{4.15}$$

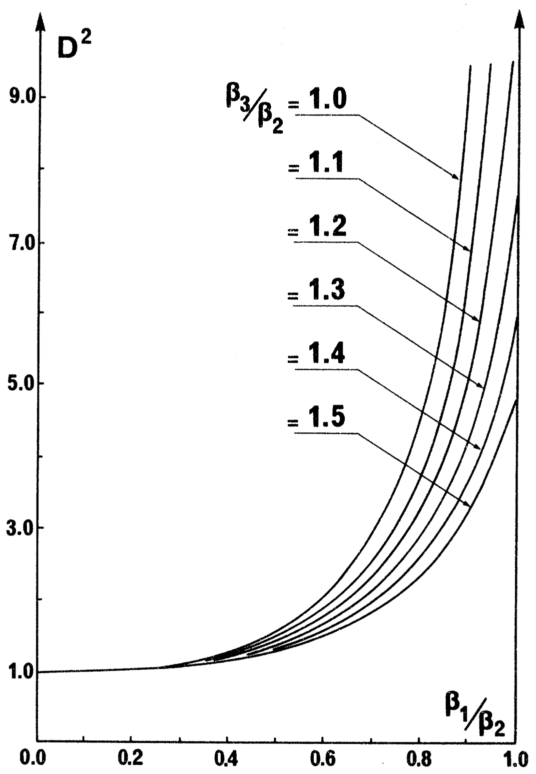


FIG. 4. Electron delocalization length D in units of $\frac{1}{4}a$ in a bond superalternated chain for six different values of β_3/β_2; the value $\beta_3/\beta_2 = 1$ corresponds to the bond alternated chain.

which shows that the superalternation further reduces the delocalization. Here also one can define the parameter $N_d = 4|\Omega_{23}(\theta=\pi)|/a$, and we have

$$N_d = \frac{(\nu^4 - \nu'^2) - \xi^2[\nu^2 - \frac{1}{2}(1+\nu'^2)]}{\xi^2[\xi^2 - \nu^2 - \frac{1}{2}(1+\nu'^2)]} . \tag{4.16}$$

C. Two coupled bond alternated chains

The two configuration, the noncentrosymmetric and the centrosymmetric ones, differ according to whether even sites of a chain are coupled to even sites or to odd sites, respectively, of the other chain. This is reflected in the wave functions which are in general of the form $\psi = \psi_1 + e^{i\phi}\psi_2$ ($\phi = 0$ for the noncentrosymmetric and $\phi = \eta$ for the centrosymmetric configuration), where ψ_1 and ψ_2 refer to the two chains of the pair. In the limit of no coupling this relative phase ϕ is irrelevant; hence, care should be taken while evaluating the transition matrix elements $\Omega_{nn'}$ so that with $\delta' = 0$ one recaptures the uncoupled chain results, Eqs. (4.6) and (4.9). With an appropriate modification in the Genkin-Mednis approach, discussed in detail in the forthcoming paper on nonlinear optical properties of one-dimensional semiconductors, we obtain the following expressions for $\Omega_{nn'}$ and D in the two configurations.

For the noncentrosymmetric configuration one has

$$\Omega_{13} = \Omega_{24} = \frac{a}{4}\left(\frac{i(1-\nu^2)}{\zeta_0(\zeta_0^2+\delta'^2)^{1/2}} + \frac{2\nu\delta'\sin\theta}{\zeta_0(\zeta_0^2+\delta'^2)}\right), \tag{4.17}$$

$$\Omega_{ii} = ia(1-\nu^2)/2(\zeta_0^2+\zeta_i^2) \quad (i = 1, 2, 3, 4),$$

all the other elements vanish. Thus in the noncentrosymmetric configuration the coupled bond alternated chains behave as two uncoupled atom and bond alternated chains with an effective heteroatomicity (atom alternation) $\delta' = \beta'/\beta_2$. The delocalization is

$$D_A = \frac{a}{4}\,\frac{(1+\nu^2)^{1/2}}{\{[(1+\nu)^2+\delta'^2]^{1/2}[(1-\nu)^2+\delta'^2]^{1/2}\}^{1/2}}, \tag{4.18}$$

and one sees that it behaves as (4.7).

For the centrosymmetric configuration one has

$$\Omega_{13} = \Omega_{24} = \tfrac{1}{4}a2\nu\delta'\sin\theta/\zeta_0(\zeta_0^2+\delta'^2), \tag{4.19}$$

$$\Omega_{12} = \Omega_{34} = 0, \tag{4.20}$$

$$\Omega_{23} = \Omega_{14} = \tfrac{1}{4}ia(\nu^2-1)/\zeta_0^2, \tag{4.21}$$

$$\Omega_{ii} = \frac{ia}{4}\left[-1 + \frac{1-\nu^2}{\zeta_0^2}\right]. \tag{4.22}$$

The reduction to two independent chains is not possible; transitions between any two bands are allowed. As will be seen below this strongly affects the one- and two-photon absorption spectrum and other nonlinear optical properties. The delocalization is

$$D_S^2 = \frac{1}{\pi}\int_{-\pi}^{\pi} d\theta\,(2|\Omega_{13}|^2 + |\Omega_{23}|^2 + |\Omega_{14}|^2)$$

$$= D_A^2 + \frac{2\delta'^2}{1-\nu^2}\left[-1 + 3\left(\frac{1+\nu^2}{1-\nu^2}\right)^2\right]\frac{a}{4}, \tag{4.23}$$

which shows that the absence of inversion symmetry reduces the electron delocalization.

V. OPTICAL PROPERTIES. DISPERSION AND ABSORPTION

We now proceed to calculate the contribution of the chains to the dielectric constant at optical frequencies. This contribution, $4\pi\chi_\pi^{(1)}(\omega)$, is given by (2.19). The σ-bond contribution can be incorporated according to (2.14) and will be considered in Sec. VI for some particular systems.

The case of the heteroatomic simply alternated chains is the simplest to deal with and allows one to gain a lot of insight on the role played by the different constraints. The expression of $\chi_\pi^{(1)}(\omega)$ is obtained by simple substitution of (3.4) and (4.6) in (2.10). The integration can be performed

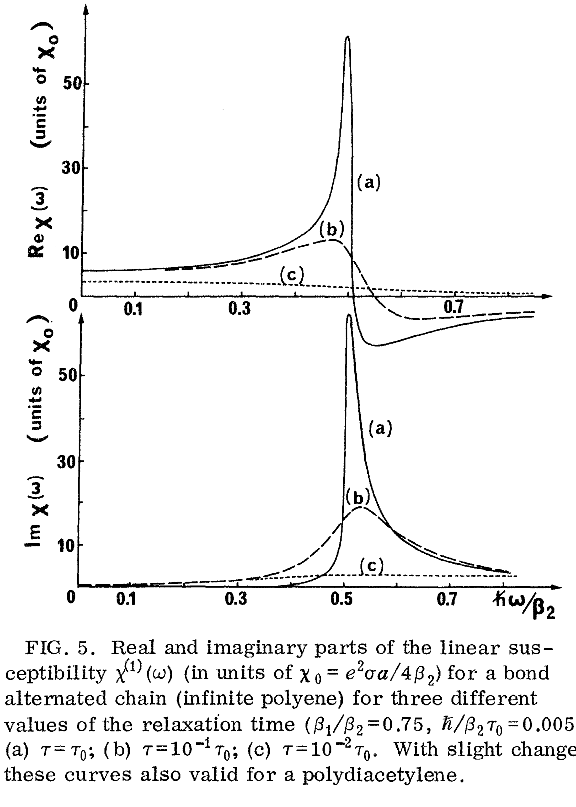


FIG. 5. Real and imaginary parts of the linear susceptibility $\chi^{(1)}(\omega)$ (in units of $\chi_0 = e^2\sigma a/4\beta_2$) for a bond alternated chain (infinite polyene) for three different values of the relaxation time ($\beta_1/\beta_2 = 0.75$, $\hbar/\beta_2\tau_0 = 0.005$). (a) $\tau = \tau_0$; (b) $\tau = 10^{-1}\tau_0$; (c) $\tau = 10^{-2}\tau_0$. With slight changes these curves also valid for a polydiacetylene.

by computing the real and the imaginary parts of $\chi_\pi^{(1)}(\omega)$ given by (2.19). In Fig. 5 we have shown the behavior of these two quantities for $\nu = 0.75$ and three different values of the relaxation time τ. The relaxation time τ was assumed to be k independent. Unless τ depends strongly on the wave vector k, only the value of τ near the edge of the Brillouin zone, where the density of states is infinite and the electrons are delocalized to their maximum extent, is relevant. In fact as can be seen from Fig. 5 the system behaves almost as a single oscillator of frequency $E_g/\hbar$. This appearance is sometimes used as an argument to support the hypothesis of this being an exciton state rather than band-to-band transitions.[21,22] There are no real crystals directly related to the case of simply bond alternated chains which can be used to estimate τ. But from other more complicated systems it can be inferred that $\tau \sim 10^{-13}$–10^{-14} sec at room temperature indicating an electron-electron scattering mechanism. For $\tau \to \infty$ one can obtain $\chi^{(1)}(\omega)$ in closed form in terms of elliptic integrals; one has

$$\chi_\pi^{(1)}(\omega) = \frac{e^2 a\sigma}{8\beta_2} \frac{2}{\pi W_0^2 c^2} \left[\frac{c^2 d^2 - W_0^2 \mu^2}{c^2 - W_0^2} \Pi\left(\frac{c^2 - d^2}{c^2 - W_0^2}, \frac{c^2 - d^2}{c^2}\right) - c^2 E\left(\frac{c^2 - d^2}{c^2}\right)\right], \tag{5.1}$$

where $E(k)$ and $\Pi(n, k)$ are the complete elliptic integrals of the second and third kind, respectively, $c^2 = \mu^2 + (1+\nu)^2$, $d^2 = \mu^2 + (1-\nu)^2$, and $W_0 = \hbar\omega/2\beta_2$.

Of particular interest is the quantity $\chi_\pi^{(1)}(0)$ given by (2.22), which is related to the refractive index n in the transparency region, $\omega \ll E_g/\hbar$. Again the integrals can be performed in terms of the first and second kind of elliptical functions and we obtain

$$\chi_\pi^{(1)}(0) = \frac{e^2 a\sigma}{8\beta_2} \frac{2}{3\pi} \frac{1}{[\mu^2 + (1+\nu)^2]^{1/2}} \left(\frac{\mu^2 + 4(1+\nu^2)}{\mu^2 + (1-\nu)^2} E(p) - F(p)\right), \tag{5.2}$$

where $p = \{4\nu/[\mu^2 + (1+\nu)^2]\}^{1/2}$. A case of specific interest corresponds to systems with no heteroatomicity ($\mu = 0$) and large delocalization ($\nu \simeq 1$); we expand the elliptical functions in powers of the delocalization parameter and keep the leading term with maximum contribution:

$$\chi_\pi^{(1)}(0) \simeq \frac{e^2 a\sigma}{12\pi\beta_2} N_d^2 = \frac{e^2 a\sigma}{3\pi\beta_2}\left(\frac{E_F}{E_g}\right)^2 \tag{5.3}$$

which shows the same dependence on the Energy gap E_g as one obtains in Penn's model,[23] the crudest band model used to estimate $\chi^{(1)}$ in a cubic semiconductor. This remarkably same square dependence on E_F/E_g obtained for a one-dimensional system in the tight-binding approximation as well as in the pseudopotential Penn's model indicates that the latter is in essence a one-dimensional model. This statement gets further support by the identical gap dependence in both models for the third-order susceptibility as well.[9]

Penn's model has been used as a starting point for the Phillips–van Vechten[24] dielectric description of the tetrahedrally coordinated heteropolar and homopolar semiconductors. For the case of an heteroatomic chain as well, the inverse-square dependence of the energy gap persists as long as the electrons are sufficiently delocalized so that ν is close to 1. Using (5.2) we obtain

$$\chi_\pi^{(1)}(0) \simeq \frac{e^2 a\sigma}{3\pi\beta_2} \frac{\mu^2 + 8}{(\mu^2 + 4)^{1/2}} \left(\frac{\beta_2}{E_g}\right)^2, \tag{5.4}$$

where now $E_g = 2\beta_2[\mu^2 + (1-\nu)^2]^{1/2}$. This is to be compared with the expression postulated by Phillips and van Vechten. We stress that the inverse-square dependence on E_g of $\chi_\pi^{(1)}(0)$ is a consequence of strong delocalization ($\nu \simeq 1$). Although delocalization introduces a band structure, the details of the latter are irrelevant, the oscillator strength being maximum at the Brillouin-zone edge, and the system can be approximately described by a single energy gap E_g as assumed in the Phillips–van Vechten theory. Their parameters E_h and C correspond to $2\beta_2(1-\nu)$ and $2\beta_2\mu$, respectively, in our case.

For the case of localized bonds, $\nu \simeq 0$, expression (5.2) becomes

$$\chi_\pi^{(1)}(0) \simeq \frac{e^2 a\sigma}{8\beta_2} \frac{1}{(1+\mu^2)^{3/2}} = \frac{e^2 a\sigma}{\beta_2}\left(\frac{\beta_2}{E_g}\right)^3. \tag{5.5}$$

This energy-gap dependence of $\chi^{(1)}$ is the same as the one obtained by[25] Harrison in his description of the tetrahedrally coordinated semiconductors. This is not totally surprising since his approach is a tight-binding one and the bands are constructed by coupling of four chains in the four directions of the bonds in the crystal. Moreover he computes the susceptibility by adding the bond polarizabilities ($\nu = 0$).

Thus these two descriptions can be viewed as limiting cases of the present one indicating their region of validity. It also gives an indication for the reason of their success in the case of the tetrahedrally coordinated semiconductors. The valence electrons there, despite the three-dimensional character of these systems, keep memory of their being bonded along the four 111 directions conveying thus to the system a one-dimensional character.

The case of the superalternated homoatomic chains is more interesting because it is directly related to polydiacetylene polymers; large defect-free crystals with good optical quality of such polymerized chains have been grown.[26] The expression of $\chi_\pi^{(1)}$ is quite involved algebraically to be given here; it contains four terms as indicated in (2.19) arising from transitions between the two valence and the conduction bands. The calculation shows that only the contribution from the pair of bands (1, 4) and (2, 3) are important and the other two have been neglected; between these two the contribution from the pair (2, 3) is by far the most important one. Viewed in the extended Jones zone this result can be easily understood when compared with the case of a simply conjugated chain. In Fig. 5 we have plotted $\mathrm{Re}\chi_\pi^{(1)}(\omega)$ and $\mathrm{Im}\chi_\pi^{(1)}(\omega)$. Again the details near the gap are strongly sensitive to the relaxation time τ and the conclusions drawn previously prevail here too. From Fig. 5 we find that both the real and imaginary parts are simply peaked and this has been observed experimentally too at room temperature. However, experiments show[27] that below a critical temperature both quantities, $\mathrm{Re}\chi_\pi^{(1)}(\omega)$ and $\mathrm{Im}\chi_\pi^{(1)}(\omega)$ consist of two peaks of roughly equal strength and form. The origin of this splitting will be discussed in the next section; it is ascribed to the chains being coupled in pairs.

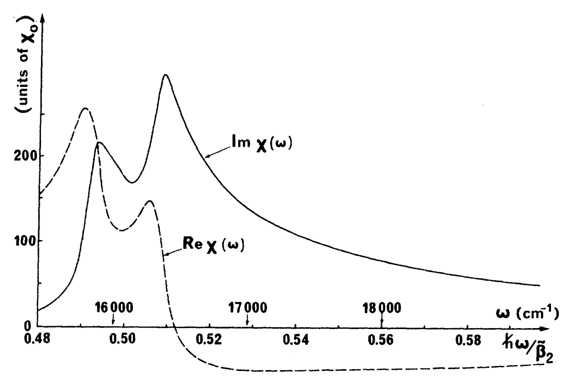


FIG. 6. Real and imaginary parts of the linear susceptibility $\chi^{(1)}(\omega)$ in units of $\chi_0 = e^2\sigma a/8\beta_2$) for two coupled bond alternated chains polymer in the centrosymmetric configuration ($\tilde{\beta}_2 = 4.00$ eV, $\tilde{\beta}_1/\tilde{\beta}_2 = 0.75$, $4\beta'/\tilde{\beta}_2 = 0.015$, and $\hbar/\tilde{\beta}_1\tau = 0.003$). The values of the parameters were chosen so that each chain is equivalent to a PTS-diacetylene chain (see text). The two peaks come from the 2 → 3 and 1 → 4 band-to-band transitions near the edge of the Brillouin zone.

For the refractive index of the polydiacetylenes, in the transparency region, $E_g/\hbar \gg \omega$, the quantity of interest is $\chi_\pi^{(1)}(0)$. An analytic expression like in the case of polyene chains could not be obtained. However, by plotting this quantity versus D^2 or N_d, given by (4.15) and (4.16), respectively, a square dependence is again obtained; the dependence on the gap E_g, given by (3.19), on the other hand, seems more involved except for $\nu' \simeq 1$ where one obtains the results of the simply alternated chain. For crystallized monomers with $\beta_2 = 0$ and interchanging β_1 and β_3 one obtains the result which can also be obtained by adding their polarizabilities.

The case of the two coupled simply alternated chains and polyacenes, shows some very interesting features. The noncentrosymmetric configuration is the simplest to deal with since it reduces to two uncoupled heteroatomic bond alternated chains. Indeed the expression of $\chi^{(1)}(\omega)$ for this case has the same behavior as the one in Fig. 5 and for $\tau = \infty$ is given by the same expression (5.1) provided we replace μ by the effective heteroatomicity δ'.

Far more interesting is the case of the centrosymmetric configuration. In this case transitions between any two bands are allowed and $\chi^{(1)}(\omega)$ is given by the sum of three terms, as follows:

$$\chi_\pi^{(1)}(\omega) = \frac{2e^2\sigma}{\pi\hbar a} \int_{-\pi}^{\pi} d\theta \left(\frac{\omega_{32}(\theta) |\Omega_{32}(\theta)|^2}{\omega_{32}^2(\theta) - (\omega - i/\tau)^2} + \frac{\omega_{41}(\theta) |\Omega_{41}(\theta)|^2}{\omega_{41}^2(\theta) - (\omega - i/\tau)^2} + \frac{2\omega_{31}(\theta) |\Omega_{31}(\theta)|^2}{\omega_{31}^2(\theta) - (\omega - i/\tau)^2} \right). \tag{5.6}$$

Clearly the main contribution to each of the three terms comes from the edge of the Brillouin zone $\theta = \pi$ where the joint density of states of each pair of bands is infinite. However not all three terms contribute equivalently. Because $\Omega_{13} = \Omega_{24}$ vanishes there, the contribution of the third term in (5.6) is completely masked by that of the other two; both $\mathrm{Im}\chi^{(1)}(\omega)$ and $\mathrm{Re}\chi^{(1)}(\omega)$ show each two peaks corresponding to the gaps E_{23} and E_{14}, respectively. The distance $\Delta\omega$ between the two peaks in $\mathrm{Im}\chi^{(1)}(\omega)$ is $\Delta\omega \sim 4\beta'/\hbar$ and for $\beta' \to 0$ the two peaks emerge to the one expected for a simply bond alternated chain. In Fig. 6 we have plotted the behavior of $\mathrm{Im}\chi^{(1)}(\omega)$ and $\mathrm{Re}\chi^{(1)}(\omega)$ for the special case of $4\beta'/\tilde{\beta}_2 = 0.015$ using the relaxation time $\hbar/\tilde{\beta}_2\tau = 0.003$ for the two peaks. As we shall see such a behavior in the absorption spectrum has been seen in polydiacetylenes and is a general feature of coupled systems. In a forthcoming paper it will be shown that this has some important implication on the two-photon spectrum as well.

VI. SPECIAL CASE: POLYDIACETYLENE POLYMERS

We shall specialize the parameters of the previous models to treat some particular one-dimensional systems. In doing so the idealizations and simplifications incorporated there should be clearly borne in mind. The most crucial ones are the neglect of the electron-electron correlation and the assumption of independent and infinite chains. The interpretation to be given to the parameters α and β as well as their computation strongly depend on these assumptions. This is because these parameters are obtained either by fitting empirically a physical property (optical spectrum, delocalization and ionization energies) or by semiempirical calculations.[10]

These different methods quite often yield different set of values for α or β for a given substance. For the carbon-carbon bonds in the aromatic substances there have been fairly detailed studies[10] for the values of β and empirical relations between β and the bond length have been proposed. These values, however, cannot be used for the linear carbon chains like the polyenes or polydiacetylenes; there it seems that higher values for β must be used[26,5] than those adopted for aromatic substances. Further in the case of the linear carbon chains the choice of the values of β is drastically affected by the assumption made about the electron-electron repulsion[21,22]; when electron-electron repulsion is neglected in order to reproduce the main features of the optical spectrum the appropriate values of β and the ratio $\nu=\beta_1/\beta_2$ are much lower than those used when electron-electron repulsion is included. It is clear for instance from (5.3) that even small changes in the ratio β_1/β_2 can lead to order of magnitude changes in the computed values for $\chi^{(1)}$.

There are difficulties in synthetizing polymers with polyene chains or other simply bond alternated chains and there are no data concerning optical properties of such systems. Polydiacetylenes is a more convenient class of materials where the considerations of Sec. I–V can be applied. This is because many such polymers have been grown[11,27] as large defect free crystals of good optical quality so that reliable measurements can be performed. In Table I we give a list of some polydiacetylenes differing from each other by the attached molecular sidegroups R_1 and R_2. Because of the mesomeric and inductive effects[10] of the sidegroups on the chain electrons there is an apparent heteroatomicity along the chains, in Secs. I–V this heteroatomicity has been altogether neglected because it was found that it affects only slightly the linear optical properties. As will be seen in a subsequent publication this approximation is not justified in some cases when it comes to reproduce the nonlinear optical properties. Further because of the overlap of the sidegroups of neighboring chains short range coupling between the chains seems to play an important role in some of these polymers as will be discussed below.

TABLE I. Optical coefficients for polydiacetylenes. The energy gap E_g is calculated from (3.19). The values $\beta_2=3.2$ eV and $\beta_3/\beta_2=1.50$ are used for all polydiacetylenes, those of β_1/β_2 are given in column seven. The dielectric constants $\epsilon_\parallel(0)$ and $\epsilon_\perp(0)$ are calculated from (2.21) and (2.12), respectively. In column five we give the values of the polarizability α needed for the calculation of $\epsilon_\parallel(0)$ and $\epsilon_\perp(0)$; they are calculated by adding the average polarizabilities that form the two radicals R_i per unit cell (see Fig. 1) (those of the four C-C σ bonds per unit cell of the chain backbone are not included). The volume of the unit cell $v=N_c^{-1}=2a/\sigma$, where $2a$ (=4.9 Å) is the unit cell length along the chain (see Fig. 1) and σ is the density of chains per unit cross-sectional area; the values of σ for the PTS [*bis*-poly(toluene sulfonate)]- and TCDU [*bis*(phenylurethane) of 5,7-dodecadyine-1,2-diol]-diacetylenes are known experimentally (Refs. 27 and 30), those of the other polydiacetylenes listed in column six are computed by assuming that α/v is a constant, equal to its value for the TCDU-polydiacetylene. The adopted simplifications and uncertainty in the choice of the appropriate values for the bond polarizabilities given in Table II introduce an over-all uncertainty of 10% in the calculated values.

	Calculated						Experimental		
Poly-R_i-diacetylene	E_g (eV)	$\epsilon_\parallel(0)$	$\epsilon_\perp(0)$	α (10^{-22} cm^3)	σ (10^{14} cm^{-2})	β_1/β_2	E_g (eV)	$\epsilon_\parallel(0)$	$\epsilon_\perp(0)$
CH_2-O-CO-ϕ	2.02	3.95	2.7	0.284	1.26	0.90			
CH_2-O-CO-NH-ϕ	2.02	3.85	2.7	0.312	1.17	0.90			
CH_2-O-SO_2-ϕ-CH_3 (PTS)	2.02	3.70	3.0	0.372	1.05	0.90	2.02	3.53	2.5
$(CH_2)_3$-O-CO-NH-ϕ	2.27	3.20	2.7	0.384	0.92	0.86			
$(CH_2)_4$-O-CO-NH-ϕ (TCDU)	2.27	3.10	2.7	0.420	0.86	0.86	2.27	3.24	2.72
CH_2-O-CO-NH-ϕ-C_2H_5	2.02	3.4	2.7	0.388	0.92	0.90			
$(CH_2)_3$-O-CO-NH-ϕ-C_2H_5	2.27	3.1	2.7	0.464	0.78	0.86			

TABLE II. Values of the average polarizabilities for the different bonds and molecular groups used for the calculation of the R_i-polarizabilities α given in Table I; the values are taken from Tables 18 and 19 of Ref. 12. The value of the SO-bond polarizability is uncertain.

Bonds or molecular group	C-H	C-C	C-O	C=O	C-N	N-H	S-O	$-CH_2$	$-CH_3$	$-\phi$	$-\phi-CH_3$	$-\phi-C_2H_5$
Polarizability (10^{-23} cm^3)	0.066	0.050	0.057	0.130	0.069	0.070	(0.141)	0.171	0.200	1.00	1.20	1.37

In Table I we give the values of $\epsilon_{\parallel}(0)$, $\epsilon_{\perp}(0)$, and $\Delta\epsilon$ for some polydiacetylene polymers differing from each other with respect to the attached molecular sidegroups R_i. The contribution of the latter to the dielectric constant was evaluated using (2.12) and (2.14); an isotropic polarizability was assigned to each molecular group and the additivity assumption way used. The values of the polarizabilities for different molecular groups are given in Table II. The contribution of the π electrons along the chain direction was evaluated along the lines of the previous section. The agreement with existing measured values is good. In Table I we also give the values of the optical gap E_g as calculated from (3.19).

For all the polydiacetylene chains the same values for β_2 was used. This value was chosen to be 3.2 eV for a "double" bond of length 1.36 Å. Further the same value, 1.5, for the ratio β_3/β_2 was chosen irrespective of the attached sidegroups R_i; the effect of the latter was included by using different values for the ratio β_1/β_2 and these values are given in Table I. The same value for α was used for all four carbon atoms in the unit cell. Clearly this is an approximation since the four carbon atoms of a unit cell are not all in the same environment. The band states can be explicitly obtained even when two different values are used for α for the two pairs of carbon atoms; no attempt, however, was made to compute the dielectric properties in this case because of difficulties in assigning *a priori* values to α.

The reflectivity of the PTS [*bis*-poly(toluene sulfonate)]-polydiacetylene is depicted in Fig. 7 where the absorption and dispersion curves are also included and compared with the experimental results of Bloor *et al.*[28] at room temperature. The agreement is satisfactory. A constant relaxation time $\tau = 10^{-13}$ sec was used for all band states. This is rather drastic approximation in view of the singular character of the density of states near the edges of the Brillouin zone. The appearance of the curves is extremely sensitive to the values of τ and in particular to its dependence on the wave vector k along the Brillouin zone. The theoretical curve for the reflectivity, with a constant relaxation time, independent of the wave vector, seem to fall off much slower past the main peak at $\omega_g = E_g/\hbar \simeq 16\,300$ cm^{-1} (=2.02 eV) than the experimental curve. The two weaker peaks in the experimental results, situated a distance $\Delta\omega = 2100$ cm^{-1} and $\Delta\omega \simeq 1500$ cm^{-1}, respectively, from the main peak correspond to the expected[29] frequencies of the vibrational modes of the $C\equiv C$ and $C=C$ bonds; These peaks cannot appear in our calculated curves because we have altogether neglected coupling of electronic and lattice motion. This would clearly affect the fall off of the calculated curves.

Wilson[5] has also performed a calculation of the optical properties of a polydiacetylene; besides the unnecessary approximation to compute the Bloch states stated previously, this author introduces a drastic assumption concerning the matrix elements of $\langle nk | p_x | n'k \rangle$, where p_x is the electron momentum operator and which amounts in assuming an explicit form for the atomic orbitals ϕ_j in order to compute quantities like

$$\int \phi_j^* \frac{\partial}{i\partial x} \phi_j \, dx ;$$

in our opinion this is not justified within the Hückel approximation and as we show here this is not necessary when the Genkin-Mednis[16] expression for the linear susceptibility is used. The advantages of this approach are particularly transparent when one considers nonlinear properties

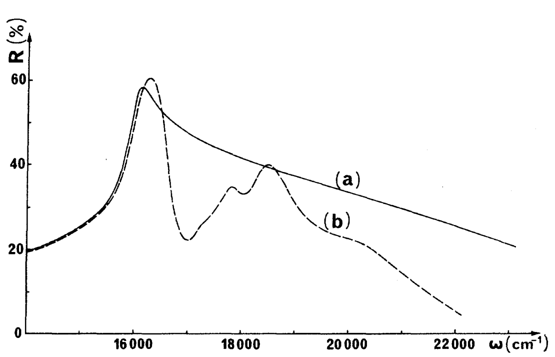


FIG. 7. Reflectivity of a PTS-diacetylene polymer crystal along the chain direction: (a) calculated curve (b) experimental curve from Bloor *et al*. (Ref. 28). In the calculation the following values were used $\beta_2 = 3.2$ eV, $\beta_1/\beta_2 = 0.9$, $\beta_3/\beta_2 = 1.50$, $\sigma = 0.86 \times 10^{14}$ cm^{-2}, $2a = 4.9$ Å, $\hbar/\beta_2\tau = 0.002$.

as will be shown in a subsequent publication.

The above used experimental results of the optical properties of the polydiacetylene polymers were obtained at room temperature. The picture drastically changes at lower temperature; it has been found by Bloor *et al.*[28] that the absorption spectrum of the PTS-polydiacetylene polymer at 4 °K has two main peaks ~500 cm^{-1} (0.062 eV) apart and of comparable strength. When the temperature is raised the spacing between the two peaks diminishes, the two peaks moving simultaneously, and at ~160 °K they emerge to each other to a single peak, namely the main peak at $\omega_g = 16\,300\ \mathrm{cm}^{-1}$ observed at room temperature.

This behavior of the spectrum of the PTS-polydiacetylene polymer at low temperatures is similar to the one predicted for two coupled chains in the centrosymmetric configuration (see Fig. 6) and indicates that in this polymer at low temperatures the chains are coupled in pairs. This chain pairing may be due to hydrogene bonding, van der Waals forces, or direct interaction through the sidegroups of two neighboring chains; the separation of the two peaks is a measure of the coupling of the two chains. We should point out that the coupling takes place between the two chains of the neighboring unit cells along the crystallographic a axis. Although x-ray studies[27,30] indicate that there are two chains per unit cell along the c axis, these chains can be assumed to be essentially independent at low temperatures. This chain pairing should result in the doubling of the a-direction unit-cell parameter and the recent observation of such a phase transition below 160 °K supports our point of view. In order to obtain an idea about the magnitude and the effect of this coupling at 4 °K let us replace each polydiacetylene chain by an equivalent simply bond alternated (polyene) chain with interchain resonances energies $\tilde{\beta}_1$ and $\tilde{\beta}_2$ defined by (3.20) and let us suppose that these chains are coupled in pairs in a symmetric configuration forming a "polyacene"-type chain. For such a system the results of Sec. III C give the absorption spectrum depicted in Fig. 6 which is strikingly similar to the one obtained by Bloor *et al.* for PTS-polydiacetylene at 4 °K; in particular the absorption spectrum clearly shows two peaks of equal strength. According to (3.24) and the bands structure shown in Fig. 4 these peaks arise from transitions at the edge of the Brillouin zone between the bands $1\rightarrow 4$ and $2\rightarrow 3$ and are $4\beta'$ apart where $2\beta'$ is the coupling strength between the two chains. The experimental value of the separation of the peaks at 4 °K is 500 cm^{-1} ($\simeq 0.062$ eV) which gives $\beta' \simeq 0.015$ eV. In order to account for the temperature dependence of the separation of the two peaks the actual origin of this coupling must be clarified and the statistical mechanics of the coupling must be worked out. Because of the low value of β' we can safely rule out the hydrogen bonding between the chains in favor of a short range coupling through the side groups of two neighboring chains. Further the fact that the double peak appears once the polymerization starts and that this behavior is independent of the degree of polymerization indicates that *the* chains start polymerizing in pairs.

The previous considerations refer to two coupled simply bond alternated chains and not to the actual coupled polydiacetylene chains; the main features and order of magnitude of β', however, should prevail even there. Further experimental study of the temperature dependence of the one- and two-photon absorption spectrum together with resonant Raman effect will be needed before a more detailed theoretical study of the realistic system can be undertaken.

VII. DISCUSSION AND CONCLUSION

In concluding this work some comments are called upon the assumptions inherent in the model. As stated in Sec. VI we have totally disregarded electron-electron repulsion and on the same token any excitonic structure in the optical spectrum of these systems; further we have assumed that the chains are independent and infinite.

The main effects of a short-range coupling between two chains have been treated in the present work and the ones expected when the assumption of independent chains is abandoned and a long-range, two- or three-dimensional ordering is established will be considered in a forthcoming paper. The main modifications that are expected when the chains are of finite extent have also been discussed elsewhere.[9,31] An important aspect, treated therein, is to what extent the main characteristics of the optical properties for an infinite chain pertain to a finite one; this is a crucial point since chains in many one-dimensional systems because of impurities or other defaults, break down to a succession of chains of finite and variable length N while others have never been synthetized with a very long length. In Refs. 9 and 31 it is shown that for simply bond alternated chains (e.g., finite polyenes) within the present one-electron tight-binding approximation as long as $N_d < N$, where N_d is the delocalization parameter of the infinite chain, then the electron in the finite chain with same values for the parameters α and β doesn't feel the end points of the chain and behaves as in an infinite chain; in particular the linear polarizability for a finite chain shows a square dependence on the delocalization parameter and for a given N_d one obtains only slight changes in the optical properties by increasing the chain length N as long as $N_d < N$. Similar conclusions were obtained when superalternation or short-range coupling is included.

The effects arising when allowance of the electron-electron repulsion is made are much more difficult to evaluate and they are expected to be quite drastic. In fact the whole picture changes when the electron-electron repulsion energy on one site γ is comparable to the intrachain hopping (resonance) energies β. As a first step instead of the tight-binding one-electron Hamiltonian used here one should proceed from the Hubbard Hamiltonian[32] and use an approximation scheme in order to obtain the electron states; the Hartree-Fock approximation[6,7] or the somewhat more involved Parr-Pariser-Pople approximation[10] are the most often used. In such a scheme the lower states are interpreted as exciton[21,22] states. From the existing studies along these lines it seems that the effects arising from electron-electron repulsion are negligible as long $2\gamma/\beta_0 \ll 1$, where β_0 is the mean value of the intrachain hopping energies along the chain, and this is the situation adopted in the present work. Consequently the narrow peaks in the optical spectrum were attributed to band-to-band transitions. To our opinion because of the discrepancies in the choices of values of β and because of the involved theoretical background needed to describe excitonic states no clear cut argument can be given in favor or against the present description. The agreement with the experimental results is good and as will be seen the present description allows one to satisfactorily account for the nonlinear optical properties, as well. We remark that the absence of photoconductivity[33] at the absorption peak has been used as a strong argument in favor of the exciton theory. However such a behavior is expected even in band picture and owes to the one-dimensionality of these materials. The absorption peak occurs at the Brillouin zone edge as there the dipole transition strength shoots up at a dramatic rate. At the same point, however, the joint density of electronic states J is infinite leaving the electrons totally immobile (electron velocity $v \sim J^{-1}$). Alternatively we may say that the effective mass of the electrons is infinite and at the absorption peak they cannot respond to the external voltage. The ability of the band theory to quantitatively account for most of the experimental observations in a simple and unified way and the lack of such a quantitative support for the exciton theory puts the former on a more firm basis.

Although our description was intended for the one-dimensional systems we were able to obtain a connection with the Phillip van Vechten theory[24] as well as the Harrison's bond orbital model[25] both developed for the dielectric characterization of the tetrahedrally coordinated semiconductors. It turned out that in a certain sense these two treatments are extreme cases of the present one. This is due to the characteristic singularity in the moint density of states at the edge of the Brillouin zone in one-dimensional systems.

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*Present address: Dept. of Physics, City College of New York, 139 St. & Convent Ave., N. Y., N. Y. 10031.

†Laboratoire Propre du Centre National de la Recherche Scientifique.

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