Confinement potential and π-electron delocalization in polyconjugated organic materials

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Frequency dispersions with chain length have been experimentally determined from Raman-scattering data published previously on a series of oligomers and polymers of paraphenylene, paraphenylene vinylene, thiophene, N-protected pyrrole, pyrrole, and furan. The dispersion behavior changes noticeably in the different series of compounds. Conformational flexibility and the confinement of π electrons within each aromatic ring are the two factors considered for the explanation of such an observation. The π-electron confinement is analyzed in terms of the effective conjugation coordinate theory which is related to the amplitude mode theory. *Ab initio* calculations performed on model compounds are used to support the experimental evidence of the competition between π-electron confinement within the rings and delocalization along the chain.

I. INTRODUCTION

The electrical conductivity,[1,2] very fast nonlinear optical responses,[3] and electroluminescence[4] of polyconjugated organic materials are the center of interest of basic and applied sciences for the development of new materials for new technologies. The reason for such interest is first the understanding of the physics of the phenomena in order to develop new materials with improved properties. Quantum-chemical calculations and empirical structure-property relationships are the ingredients for molecular engineering which helps chemists to synthesize new materials.[1,2]

The basic physical phenomenon which gives rise to the peculiar electrical and optical properties of polyconjugated molecules is the delocalization of π electrons along the chain backbone. Such delocalization (or conjugation) has been treated with a variety of theoretical tools ranging from the simplest Hückel theory applied to very simplified molecular models[5] through more elaborate semiempirical quantum-chemical treatments[6] ending with high-level *ab initio* calculations.[7] All approaches have given their contributions towards a better understanding of the physics and chemistry of these materials.

The main problem, very relevant in the field, but still unsolved, is the determination of the delocalization length or confinement length of π electrons in real samples. We present here some contributions from vibrational Raman scattering towards the solution of this problem. Several authors have used Raman spectra for the determination of bimodal and/or multimodal distribution of confinement lengths in polyacetylene.[8] In this work we do not address this problem, but try to highlight the relationship between frequency dispersion and changes of the delocalization length.

II. AMPLITUDE MODES AND EFFECTIVE CONJUGATION COORDINATE

It is presently a known fact that the Raman spectra of polyconjugated organic materials (oligomers and polymers) show peculiar and very characteristic features uniquely determined by the delocalization of π electrons.[9,10] In particular, Raman lines show selective intensity enhancement and frequency and intensity dispersion with conjugation length.[9–13] Let us take all-*trans*-polyacetylene (PA) as a paradigm; the concepts developed for PA have been extended to more complex molecular systems.[13] Infinite PA is described as a dimerized Peierl's distorted chain[5] (in the chemists' view it is a typical polyene chain).[14] Let d_{C-C} and $d_{C=C}$ be the bond lengths of C-C in PA. The degree of alternation along the chain is measured by the dimerization parameter u, where u is the difference between single- and double-bond lengths, projected on the chain axis direction (**k**) $[u = (d_{C-C} - d_{C=C}) \cdot \mathbf{k}]$. The plot of the electronic energy of PA as a function of u shows two equal minima separated by a relatively low barrier (at $u = 0$) which corresponds to the undimerized metallic state, Fig. 1(a).

The theory of the "amplitude mode" (AM) by Horovitz and co-workers[9,10] accounts for the observed Raman spectrum of PA in terms of a very large electron-phonon coupling which occurs in low-band-gap systems when atoms move along the dimerization coordinate. The relevant parameter in the AM theory is $\bar{\lambda}$ which is somehow related to the confinement of π electrons along the carbon chain. The frequency and intensity dispersion of the Raman spectra of polyacetylene and its oligomers have been ascribed to differences in delocalization length and have been accounted for in terms of variation of $\bar{\lambda}$; $\bar{\lambda}$ decreases when the conjugation length increases, i.e.,
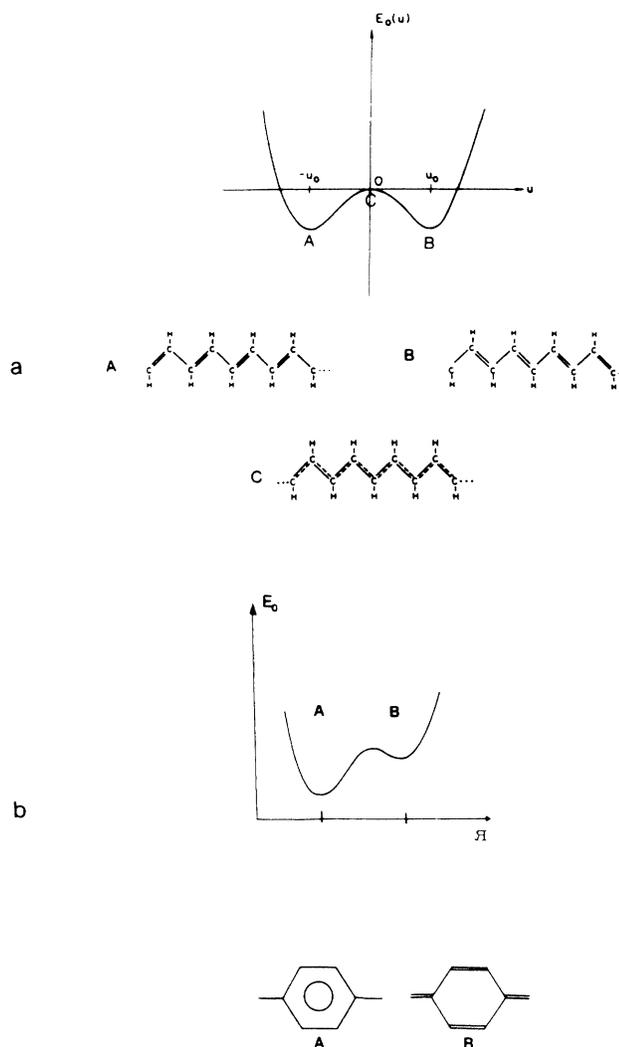
FIG. 1. (a) Electronic energy as a function of the dimerization u *trans*-polyacetylene. (b) Electronic energy as a function of the effective conjugation coordinate $\mathfrak{R}$ for systems with non-degenerate ground states.

when π electrons are less confined.

AM theory, applicable to a simplified model of PA, could not be extended to explain the Raman spectra of larger low-gap polyconjugated systems with a very complex chemical and conformational structure. The exact concept of "dimerization amplitude" in chemically more complex systems is necessarily lost and $\tilde{\lambda}$ must be replaced by some other kind of parameter.

AM theory was later reformulated in terms of the effective conjugation coordinate (ECC) theory.[11−13] This approach, built on the concepts and formalism of classical molecular dynamics,[15] is based on the idea that in polyconjugated systems there exists a particular and unique vibrational coordinate strongly coupled with π electrons. This coordinate, referred to as $\mathfrak{R}$, in the case of polyene systems is exactly the dimerization amplitude oscillation of AM theory, but can easily be generalized in the case of other systems. Indeed, $\mathfrak{R}$ is chosen in such a way as to

describe a collective oscillation of the relevant molecular structural parameters in the direction of the path nuclei must follow in order to move from the geometry of the ground electronic state to the minimum geometry of the first electronic excited state. For instance, in polyaromatic systems, $\mathfrak{R}$ describes an oscillation from a more aromatic to a more quinoid structure.[13] In this case, the ground-state electronic energy vs $\mathfrak{R}$ is schematically given in Fig. 1(b). In the Raman spectra of polyconjugated systems of the very many normal modes of a finite chain (or of the very many phonons of an infinite one-dimensional polyconjugated polymer), only few bands have strong activity: the dynamical treatment shows that these strong bands originate from totally symmetric (TS) vibrational normal modes which contain a large contribution by the $\mathfrak{R}$ oscillation. In a number of cases, when the chain length of the oligomers increases and is accompanied by an increase of effective delocalization length, the strong TS bands which contain $\mathfrak{R}$ shift toward lower frequencies. These shifts are fully rationalized by ECC theory due the weakening of the force constant associated with the $\mathfrak{R}$ coordinate. Moreover, in all these cases, it is possible to extract a normal mode for which the observed Raman intensity is the largest and for which the frequency shift is particularly relevant. For this particular normal mode the $\mathfrak{R}$ content is the largest and, as a consequence, also the e-ph coupling is the most effective. For these reasons, in what follows we will refer to this normal mode as the $\mathfrak{R}$ mode.

The key parameter in ECC theory is the generalized diagonal force constant $F_{\mathfrak{R}}$. It has been shown that $F_{\mathfrak{R}}$ is related to $\tilde{\lambda}$ by the expression[11−13]

$$F_{\mathfrak{R}}^{0} - F_{\mathfrak{R}} = K(1 - 2\tilde{\lambda}) , \qquad (1)$$

where $F_{\mathfrak{R}}^{0}$ is the force constant of the reference molecule of the AM theory and K is the proportionality constant. It can be seen from Eq. (1) that the smaller $\tilde{\lambda}$ (notice that $0 < \tilde{\lambda} < \frac{1}{2}$), the larger the variation of the force constant associated with $\mathfrak{R}$. As a consequence, the evaluation of $F_{\mathfrak{R}}$ for a series of molecules gives a estimate of the degree of confinement of the π electrons. The degree of confinement is directly related to the effective conjugation length.

A more explicit correspondence between AM and ECC theories has recently been discussed by Girlando, Painelli, and Soos.[16] These authors present an approach which combines aspects from both formalisms.

To understand the reason why $F_{\mathfrak{R}}$ can be used as a measure of the effective conjugation length it is useful to consider its analytic expression in terms of bond-stretching valence force constants. In the case of an ideal infinite polymer

$$F_{\mathfrak{R}} = K^{0} + f^{0} + \sum_{s} f^{0,s} , \qquad (2)$$

where K^{0} is a combination of diagonal $C{=}C$ and $C{-}C$ stretching force constants of the central (zeroth) unit, f^{0} is a combination of the interaction force constants between C-C bonds within the central unit, and $\sum_{s} f^{0,s}$ is a

linear combination of force constants between C-C bonds of the central unit and the C-C bonds of the unit at a distance s from the central one along the one-dimensional lattice. Thus s defines the conjugation length as the threshold distance at which $f^{0,s}$ vanishes. The distance s is generally unknown, or poorly known.

In the case of a finite molecule (oligomer) of length L (expressed as a number of chemical units) an expression similar to Eq. (2) can also be written for $F_{\mathfrak{R}}$. In this case $s \leq L$, i.e., the effective conjugation length does not necessarily correspond to the "real" chain length L. When $s < L$, increasing L does not affect the value of $F_{\mathfrak{R}}$. This corresponds to finding a saturation limit with L in the Raman dispersion of the $\mathfrak{R}$ mode. In most of the cases studied (with the exception of trans-polyenes) the dispersion reaches a plateau after relatively few repeating units, as will be discussed later in this paper.

Let us discuss the role played by the various terms in Eq. (2). It was suggested empirically by Crawford and Califano[17] and later proven by Kakitani[18] that the valence interaction force constants between conjugated C-C bonds must obey a precise sign rule. Let $f_{\mathrm{I}}, f_{\mathrm{II}}$, etc. be the interaction valence force constant between first, second, etc. neighbors C-C stretchings, respectively. The general rule states that interaction force constants with odd indices $(f_{\mathrm{I}}, f_{\mathrm{III}}, f_{\mathrm{V}}, \dots)$ are negative, and interaction force constants with even indices $(f_{\mathrm{II}}, f_{\mathrm{IV}}, f_{\mathrm{VI}}, \dots)$ are positive. In the case of polyene chains this means that the interaction force constants of any order between $C{=}C$ and $C{\equiv}C$, and $C{-}C$ and $C{-}C$ are negative and those between $C{=}C$ and $C{-}C$ are positive. Application of such a rule makes the second and third terms in Eq. (2) negative, as can be seen explicitly if one writes Eq. (2) for the specific case of polyacetylene:

$$F_{\mathfrak{R}} = \tfrac{1}{2}(K_{C=C} + K_{C-C}) - 2 \sum_{n=0,s-1} f_{2n+1} + \sum_{n=1,s} f_{2n} ,$$

(3)

where K are C-C stretching diagonal force constants and s is the number of the translational unit at which the interaction starts being negligible (see above).

The larger the absolute value of the sums in Eq. (3), the smaller the value of $F_{\mathfrak{R}}$, i.e., the larger is the effective conjugation and the smaller the π-electron confinement: both $\tilde{\lambda}$ and $F_{\mathfrak{R}}$ are thus a measure of the delocalization of the π electrons. Since the variation of $F_{\mathfrak{R}}$ with the delocalization length is reflected in the frequency shift of the $\mathfrak{R}$ mode, trends in the Raman shift also give a direct estimate of the "effective conjugation length."

III. EXPERIMENTAL DATA

ECC theory has been successfully applied to several classes of oligomers and polymers. The following materials have been studied: (i) polyenes and PA,[11,12] (ii) polyaromatic systems such as polyparaphenylene (PPP),[19,20] poly (paraphenylene vinylene) (PPV);[21] and (iii) polyheteroaromatic systems such as polythiophenes (PTh),[22–24] polypyrroles (PPy),[25–26] and polyfurans (PFu).[27]

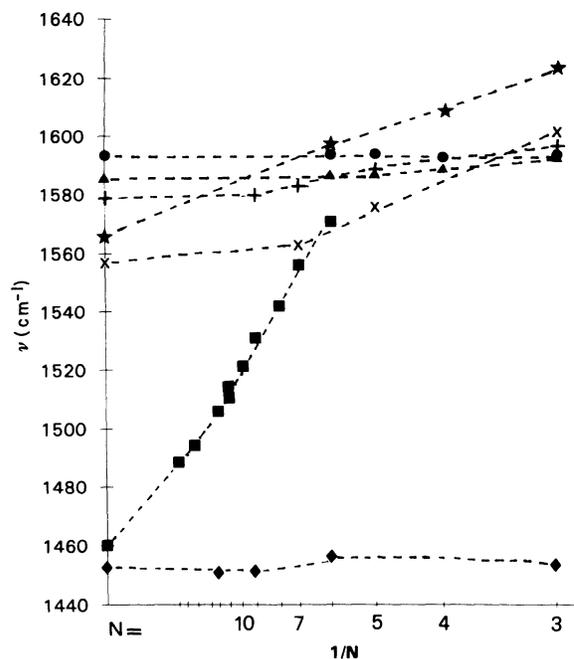The interpretation of the data on polythiophenes re-

FIG. 2. Experimental frequency dispersion of the $\nu_{\mathfrak{R}}$ mode vs the reciprocal of the number (N) of repeat units for polyconjugated oligomers. The frequency for the "polymers" is also reported in the plot ($\blacksquare$) polyenes; ($\blacktriangle$) phenylene vinylenes; ($\bullet$) phenylenes; ($\times$) pyrroles; ($+$) protected pyrroles; ($\blacklozenge$) thiophenes; ($\bigstar$) furans. The dashed lines are only meant as a guide for the eye.

ported and discussed in Refs. 22–24 has been recently reassessed based on an assignment of the $\mathfrak{R}$ mode supported by quantum-chemical calculations on the vibronic structure of the electronic transitions of oligomers of thiophene.[28] A more thorough discussion will be presented elsewhere together with experimental data on a large variety of thiophene derivatives and ab initio computed Raman spectra.[29]

The purpose of this work is to carry out a comparative study of the many data collected from Raman spectra of the oligomers and polymers mentioned above; we aim at giving a comprehensive rationalization of the different frequency dispersions of the $\mathfrak{R}$ mode observed for the series of materials studied. In so doing we will obtain some information on the mechanisms which are responsible, at the molecular level, for π-electron confinement within the various chemical groups.

In Fig. 2 we report the experimental frequencies $\nu_{\mathfrak{R}}$ of $\mathfrak{R}$ mode vs the number of chemical repeating units (shown below) for the series of oligomers of PP (structure a), PV (structure b), Th (structure c), unsubstituted Py (structure d), protected Py (structure e), and Fu (structure f). The frequency dispersion for polyenes (structure g) is also reported in Fig. 2.

a   b   X = S, NH, NR, O   g

c   d   e   f
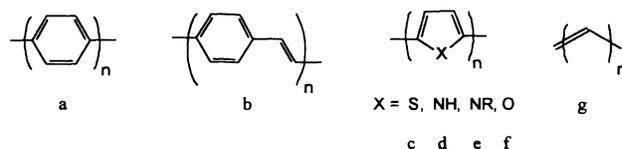
Let $\Delta\nu_{\mathfrak{R}}$ measure the frequency range (within each series) spanned by the experimental Raman data so far collected by us and by others; in Fig. 2 we can observe three different dispersion behaviors.

(i) In the case of PP, PV, and Th oligomers, practically no dispersion is observed with increasing N ($\Delta\nu_{\mathfrak{R}} \approx 0$); in the case of the polymers also $\nu_{\mathfrak{R}}$ remains unchanged.

(ii) In the case of polyenes $\mathfrak{R}$ frequencies change very rapidly along the series ($\Delta\nu_{\mathfrak{R}} = 166$ cm^{-1}) and no saturation has yet been observed for the chain lengths so far considered. The longest oligomer considered ($N = 19$) has an $\mathfrak{R}$ frequency of 1488 cm^{-1} to be compared with the 1460 cm^{-1} frequency of PA.

(iii) The other compounds considered show an intermediate behavior. Although frequency dispersion can be clearly seen, the range of variation of $\nu_{\mathfrak{R}}$ is much smaller than that observed in case (ii), namely, $\Delta\nu_{\mathfrak{R}}$ is 45 cm^{-1} in the case of Py and $\Delta\nu_{\mathfrak{R}}$ is 59 cm^{-1} in the case of Fu.

IV. ENERGY GAPS

The traditional way to obtain information on the dependence of π-electron delocalizaton on chain length is to plot the electronic energy gap vs $1/N$, where N is the number of chemical units in the chain. If one compares the gap dispersion (see Fig. 3) with the Raman frequency dispersion (Fig. 2) for the polyconjugated systems studied
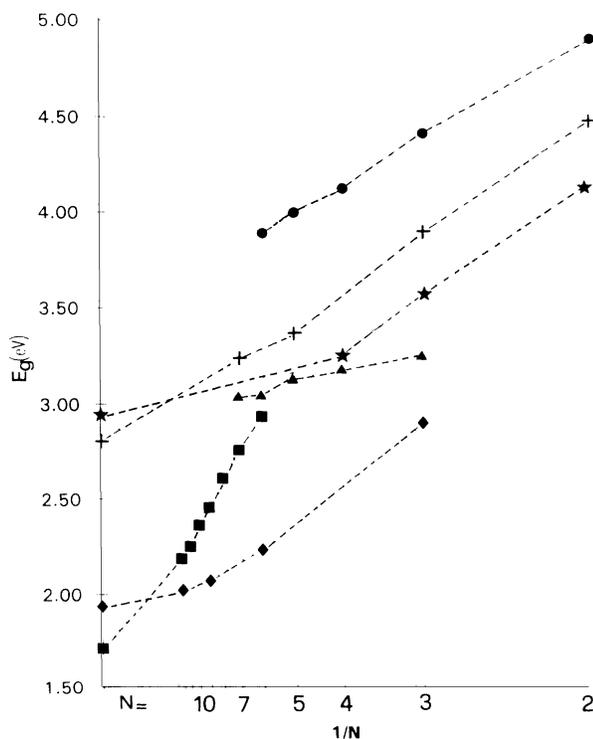
FIG. 3. Experimental energy gaps vs the reciprocal of the number (N) of repeat units for polyconjugated oligomers and polymers. (■) polyenes (λ_{max}, solid state); (▲) phenylene vinylenes (λ_{max}, solid state); (●) phenylenes (λ_{max}, solution); (+) protected pyrroles (λ_{max}, solution); (◆) thiophenes (λ_{onset}, solid state); (★) furans (λ_{max}, solid state). The dashed lines are only meant as a guide for the eye.

in this work, it becomes apparent that a direct correlation between the two phenomena does not necessarily exist. If the case of the oligomers of PP is taken as an example, an appreciable gap dispersion is observed while the $\mathfrak{R}$ mode does not show any frequency variation with N. The energy gaps for heteroaromatic oligomers (of Py, Th, and Fu) show trends similar to that of the oligomers of PP. Only polyenes behave in a remarkably different way, exhibiting a rapid decrease of E_g with increasing N. In all cases some kind of saturation effect in E_g becomes effective after a certain threshold value of N. It follows that additional information can be derived from $\nu_{\mathfrak{R}}$ vs $1/N$ with respect to that generally obtained from E_g vs $1/N$. This is precisely the issue to be discussed in this paper.

The different observed dispersions of E_g and $\nu_{\mathfrak{R}}$ can be rationalized in the following way. We notice that within the Hückel model a nonzero value of the hopping integral between two adjacent rings is sufficient for predicting a dispersion of E_g with N: the dispersion of E_g can be accounted for without the need to include interactions at distances larger than the first neighbor. On the contrary, the force constant $F_{\mathfrak{R}}$ [Eq. (3)] changes only if long-range interactions are introduced when the chain length increases. It follows that the dispersion of $\nu_{\mathfrak{R}}$ is a more direct probe of the changes of the electronic structure when N increases. The above concepts explain why the effective conjugation length as measured by the dispersion of $\nu_{\mathfrak{R}}$ or of E_g may differ.

We take as an example the case of PP oligomers and polymer. It will be shown that the observed lack of Raman dispersion (Fig. 2) can be ascribed to a very strong confinement potential within the benzene rings (see Sec. VI). The phenomenon of confinement of the p_z electrons within the ring opposes the delocalization of p_z along the molecular chain. The competition between these two effects determines the confinement length in polyconjugated aromatic and heteroromatic systems and hence the Raman dispersion. The fact that a sizable Raman dispersion is observed for Py and Fu indicates that the introduction of a heteroatom can reduce the confinement of π electrons within the ring.

V. DISCUSSION

Since, according to the concepts discussed in Sec. II, $\Delta\nu_{\mathfrak{R}}$ is related to the extent of π-electron delocalization with each series of molecules, the data reported in Fig. 2 provide experimental evidence that π electrons are most easily delocalizable along the chain in polyene systems, more confined in the case of PFu and PPy, and even more in the case of PTh, PPV, and PPP.

From a chemical viewpoint one could claim (and it has been claimed several times in the literature[30]) that electron confinement is caused by conformational distortions (conformational kinks, twistons, etc.) at the C-C bonds joining two units along the chain. The value of the exchange integral (β) between the two adjacent p_z orbitals of the C atoms forming the interunit C-C bond depends on the mutual orientation of these orbitals, being maximum or zero when the orbitals are parallel or orthogo-

nal, respectively.   The extent of π-electron delocalization along the molecular chain certainly depends on the value of the conformationally dependent exchange integral. However, as is shown below, we think that this is not the most important cause.

Detailed structural studies of some of these molecules in the solid state show that unsubstituted Th (Ref. 31) and Py (Ref. 32) oligomers and polymers[33] are almost planar; the benzene rings in a few oligomers of the PP series are twisted at an approximate angle of 13°.[34] No detailed structural studies are available for the PV series with the exception of the simplest model molecule, *trans*-stilbene, in which, in the crystalline state, the two benzene rings are twisted out of the plane of the —CH=CH— units by a torsional angle of approximately 5°.[35] These experimental data indicate that conformational distortion is not large enough to justify by itself the observed lack of frequency dispersion (PP, PV, Th). On the other hand, even in the case of protected Py oligomers, for which recent structural data measure a very large torsional angle of 74°[36] some $\mathcal{H}$-mode dispersion is observed ($\Delta\nu_{\mathcal{H}} = 18$ cm^{-1}), thus showing that π-electron delocalization along the chain takes place in spite of the large twisting of the molecular chain.

It has to be concluded that additional phenomena must take place. We focus our attention on the possibility of a different strength of the confinement potential on π electrons within the aromatic or heteroaromatic rings. The stronger the confinement in the ring, the smaller the delocalization length.

For the understanding of the discussion which follows let us first discuss at the molecular level the phenomena which may occur when π electrons are delocalized as in the case of the systems which are the subject of this work. Let us first consider one isolated chemical unit. It is a known fact that "aromatic" molecules are stabilized by the resonance energy since the actual ground-state electronic structure is hybrid between various resonating canonical structures.[37] The resonance energy is directly related to the aromaticity of the molecule.

Schematically the actual ground-state electronic structure of a single π-bonded molecule can be described by the wave function

$$\Psi_M = \sum_i a_i \psi_i , \tag{4}$$

where a_i are the coefficients of a linear combination of wave functions representing the canonical structures ψ_i. The coefficients a_i describe the weight of each canonical structure in the resonance hybrid.

I   II   III
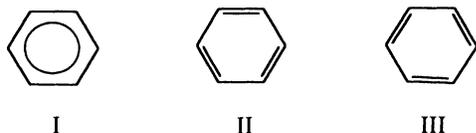
The real hexagonal structure of benzene (I) is the result of the resonance between the two canonical Kekulé structures (II) and (III) which contribute with equal weights to structure (I).

Analogously, for the case of heteroaromatics the actual structure is a resonance at least between (IV), (V), and

(VI) where the contributions by (V) and (VI) are certainly smaller than the dominant contribution by (IV) and change on changing the heteroatom X.

IV   V   VI
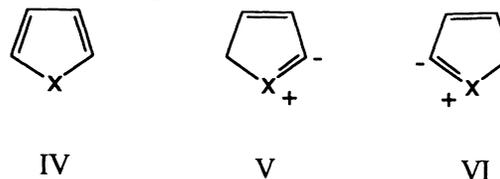
A measure of the aromaticity of the simplest heteroaromatics considered in this work is given by their measured resonance energies which are reported as 27.7, 24.5, and 22.2 kcal/mol for thiophene, pyrrole, and furan, respectively.[38] The larger the contribution of structures (V) and (VI), the larger is the resonance energy and the larger is the aromaticity of the system.

When the aromatic units are joined to form a polyconjugated oligomer or polymer, additional canonical structures enter the resonance stabilization. In particular, the quionoid structure (not included in the case of the monomers because of its very high energy) plays a more relevant role when the length of the chain increases. This is shown by recent calculations on the low-energy electronic excited states of oligoaromatics.[1,28] The electronic structure of the polymer in its ground state may be written schematically as

$$\Psi_{pol} = c \Psi_{arom} + d \Psi_{quin} , \tag{5}$$

where Ψ_{arom} and Ψ_{quin} are the wave functions which correspond to structures (VII) (aromatic) and (VIII) (quinoid) as sketched below in the case of polyparaphenylene.

VII   VIII

Many other canonical structures can be written, some of which should occur in Eq. (5) with negligibly small coefficients.

The weights c and d in Eq. (5) can be estimated by calculation or with direct experimental determination of the bond lengths (and bond orders) of the inter-ring C-C bonds. The difference in energy between the states described by Ψ_{arom} and Ψ_{quin} decreases with increasing chain length, since the energy gap between the prevalently aromatic ground state and the prevalently quinoid excited state closes when delocalization increases.

With the above definitions it becomes easier to understand the contribution by vibrational spectroscopy through the ECC theory for the estimate of the weights [such as c and d of Eq. (5)] of the resonating structures. We make use here of the concepts developed by ECC theory to understand and to rationalize this phenomenon in terms of $F_{\mathcal{H}}$.

The second order term in the Taylor expansion about the absolute minimum of the vibrational potential energy as a function of $\mathcal{H}$ (see Fig. 1) is the quadratic force constant $F_{\mathcal{H}}$ ($F_{\mathcal{H}} = [\partial^2 V / \partial^2 \mathcal{H}]_{eq}$) associated with the small displacements of the nuclei along the $\mathcal{H}$ coordinate which

describes the oscillation between the aromatic and the quinoid structures. $F_{\mathfrak{R}}$ is the measure of the curvature of the potential energy function at $\mathfrak{R} = \mathfrak{R}_{eq}$ and gives an estimate of the work to be done to displace electrons together with nuclei from the equilibrium ground-state structure toward the more quinoid structure characteristic of the first excited state. It is then to be expected that, in the case of molecules for which the ground state has a larger contribution from the quinoid form, the work to be done (and hence $F_{\mathfrak{R}}$ to reach the structure of the first excited state will be smaller.

VI. AB INITIO CALCULATIONS OF $F_{\mathfrak{R}}$

We have then decided to calculate by *ab initio* methods the parameter $F_{\mathfrak{R}}$ for the simplest aromatic and heteroaromatic molecules which model the structural units present in the polyconjugated chains under study. *Ab initio* calculations are the most reliable for a description of the intramolecular potential.[39] We have chosen a 6-31G** basis set as a better compromise between reliability of the results and feasibility of the computation. As is usually done in vibrational calculations based on quantum-chemical methods, one can rely on the trends shown by the calculated values of a series of molecules more than on each single value. In these calculations no scaling procedures were applied.

We use *ab initio* calculated $F_{\mathfrak{R}}$ for the model molecules to obtain an estimate of the confinement of the π elec-

trons within the rings, i.e., a measure of the work to be done during the deformation from the aromatic to the quinoid structures. For the calculation of $F_{\mathfrak{R}}$, the following procedure has been followed:

(i) determination of the *ab initio* minimum-energy geometry,

(ii) calculation of the quadratic force constants $F_{ij}^x = (\partial^2 V / \partial x_i \partial x_j)_{eq}$ in Cartesian displacement coordinates (x_i),

(iii) definition of vibrational internal displacement coordinates (R_i),[15] and transformation from F^X to F_R, and

(iv) definition of the $\mathfrak{R}$ coordinate and calculation of $F_{\mathfrak{R}}$.

Calculations were done on two series of molecules: benzene (Bz), furan (Fu), thiophene (Th), pyrrole (Py), and 1,3-cylopentadiene (CyP); biphenyl (Bz$_2$), 2,2'-bifuran (Fu$_2$), 2,2'-bithiophene (Th$_2$), 2,2'-bipyrrole (Py$_2$), and 2,2'-bi(1,3-cyclopentediene) (CyP$_2$). The molecules are sketched in Fig. 4 with the definition of their $\mathfrak{R}$ coordinates. The extreme case of 1, 3-cyclopentadiene (a nonaromatic molecule) and its dimer is considered for a more complete understanding of the issue treated in this paper.

For an easier understanding of what follows the expression for $F_{\mathfrak{R}}$ [Eq. (2)] worked out for long-chain oligomers and polymer can be readjusted in the present study of small molecules in the following way. For the monomers
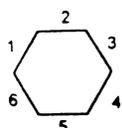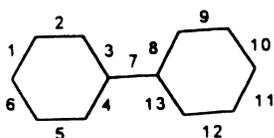

$$\mathfrak{R} = 1/\sqrt{6}(R_1 - R_2 + R_3 + R_4 - R_5 + R_6)$$
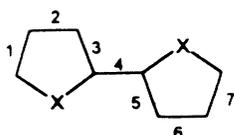
$$R = 1/\sqrt{6}(R_1 - R_2 + R_3 - R_4 + R_5 - R_6)$$
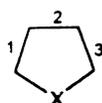
X = O, S, NH, CH$_2$

$$\mathfrak{R} = 1/\sqrt{3}(R_1 - R_2 + R_3)$$

$$\mathfrak{R} = 1/\sqrt{13}(R_1 - R_2 + R_3 + R_6 - R_5 + R_4 - R_7 + R_8 - R_9 + R_{10} + R_{13} - R_{12} + R_{11})$$

X = O, S, NH, CH$_2$

$$\mathfrak{R} = 1/\sqrt{7}(R_1 - R_2 + R_3 - R_4 + R_5 - R_6 + R_7)$$

FIG. 4. Structural formulas and definition of the effective conjugation coordinate $\mathfrak{R}$ for the model molecules considered.

TABLE I. Generalized force constants $F_\mathfrak{R}(\mathrm{mdyn}/\mathring{A})$ for some model molecules, obtained with *ab initio* calculations at 6-31 G** level. Also partial intra- and inter-ring contributions to $F_\mathfrak{R}$ are reported (see text).

Monomer	Intra-ring contributions	$F_\mathfrak{R}$	Dimer	Intra-ring contributions	Inter-ring contributions	$F_\mathfrak{R}$
Pyrrole	K = 8.3098 f = -1.1861	7.1237	Bipyrrole	K = 7.0519 f = -1.0156	K = 0.8881 f = -0.2145	6.7099
Thiophene	K = 8.5733 f = -1.2016	7.3717	Bithiophene	K = 7.3025 f = -1.0497	K = 0.8616 f = -0.2792	6.8352
Furan	K = 8.8184 f = -1.0704	7.7480	Bifuran	K = 7.4807 f = -0.9430	K = 0.9190 f = -0.2766	7.1801
1,3-cyclo-pentadiene	K = 9.0198 f = -0.7281	8.2917	Bi(1,3-cyclo-pentadiene)	K = 7.6059 f = -0.6711	K = 0.8648 f = -0.3705	7.42921
Benzene	K = 7.8768 f = +0.4727	8.3495	Biphenyl	K = 7.2182 f = 0.3716	K = 0.4310 f = -0.2965	7.7243

		F_R
Benzene	K = 7.8768 f = -4.0784	3.7984

$$F_\mathfrak{R} = K(\mathrm{diag}) + f(\mathrm{off\text{-}diag}) . \qquad (6a)$$

For the dimers

$$F_\mathfrak{R} = K(\mathrm{intraring,diag}) + f(\mathrm{intraring,off\text{-}diag})$$

$$+ K(\mathrm{interring,diag}) + f(\mathrm{interring,off\text{-}diag}) . \qquad (6b)$$

The calculated numbers reported in Table I refer to the various terms of Eqs. (6a) and (6b). The normalization of $\mathfrak{R}$ coordinates according to the definitions given in Fig. 4 allows a direct comparison among the values reported in Table I for the different molecules.

VII. RESULTS

According to the discussion in Sec. II, the interaction terms in the expression for $F_\mathfrak{R}$ [Eq. (3)] are negative and tend to decrease the positive value of $F_\mathfrak{R}$. Indeed, the calculations performed on the model monomers (see Table I) show that this is verified in all cases but benzene. The rationale behind this result is that in the case of benzene there exists a favorable delocalization path within the ring which is the result of the full aromaticity of the system. According to this observation, we can define an additional cooperative coordinate (R) (see Fig. 4) which describes the oscillation between two resonant Kekulé structures of the benzene ring (structures II and III in Sec. V). From the results in Table I we see that the contribution of the interaction term $f(\mathrm{intraring,off\text{-}diag})$ to the generalized diagonal force constant F_R is negative and very large. This means that the R coordinate plays within the ring the same role played by the $\mathfrak{R}$ coordinate defined for the other systems; the interaction terms are indeed very effective in softening the generalized force constant associated with R vibration. The presence of highly conjugated π electrons within the ring acts against the formation of a quinoid structure (interaction terms

are responsible for a stiffening of the generalized diagonal force constant $F_\mathfrak{R}$). It follows that, when two or more aromatic benzene rings are linked in a chain, the conjugation within the rings is competitive with the delocalization of π electrons between rings along the chain, i.e., with the possibility of obtaining chains with some quinoid character. This is confirmed by the *ab initio* results on biphenyl (Table I), where, although the negative contribution to $F_\mathfrak{R}$ increases because of the interactions, $f(\mathrm{inter\text{-}ring,off\text{-}diag})$, this contribution is not large enough to balance the positive intra-ring contribution $f(\mathrm{intraring,off\text{-}diag})$. The effects of the different off-diagonal contributions to $F_\mathfrak{R}$ in Bz and Bz$_2$ are summarized in the total $F_\mathfrak{R}$ values, which turn out to be the largest of the series of monomers and of the dimers, respectively (see Table I).

The theoretical results obtained for Bz and Bz$_2$ justify the absence of frequency dispersion for the $\mathfrak{R}$ mode observed in the Raman spectra of the oligomers of paraphenylene and paraphenylene vinylene [class (i)] in Sec. III, which must be interpreted as due to the existence of a relatively small inter-ring conjugation caused by the opposing confinement of π electrons within the aromatic rings.

According to the above considerations, we can infer that the rings most suitable for obtaining polyaromatic systems with electrons highly mobile along the chain are those with the lowest degree of aromaticity. To check this statement, we have performed calculations also on 1,3-cyclopentadiene and its dimer, which are known to be nonaromatic. The very large value of $f(\mathrm{inter\text{-}ring,off\text{-}diag})$ in the dimer seems to indicate that the conjugation along the chain is very large. Further support should come from calculations on longer oligomers.

In the case of heteroaomatic systems the values reported in Table I suggest that these compounds form a class on their own: the numerical values of the off-diagonal

contributions to $F_{\mathfrak{R}}$ both in the monomers and in the dimers, are practically equal, within the reliability of the calculations, for the three models considered. From these results we would expect similar dispersion behavior in the Raman spectra of oligofurans, oligopyrroles, and oligothiophenes. On the contrary, according to the experimental data on $\mathfrak{R}$ dispersions, oligomers of furan and pyrrole belong to the same class but oligothiophenes do not show any $\mathfrak{R}$ dispersion, as in the case of oligophenylenes and oligo(phenylene vinylenes).

A closer look at the experimental data (Fig. 2) shows that the dispersion of the $\mathfrak{R}$ mode of oligofurans is not equal to that of oligopyrroles (as suggested by *ab initio* results) but is larger in the case of oligofurans. This fact can be correlated with the degree of aromaticity of the monomers: according to the above discussion on benzene, a high degree of aromaticity corresponds to a strong confinement potential for the π electrons within the ring. This idea suggests that the extent of the Raman dispersion ($\Delta\nu_{\mathfrak{R}}$ should decrease in the order

$$\Delta\nu_{\mathfrak{R}}(\text{Fu}) > \Delta\nu_{\mathfrak{R}}(\text{Py}) > \Delta\nu_{\mathfrak{R}}(\text{Th})\Delta\nu_{\mathfrak{R}}(\text{PP}) \ .$$

For this reason at least a small dispersion should be expected also in the case of oligothiophenes. The lack of experimental $\nu_{\mathfrak{R}}$ dispersion in oligothiophenes seems to indicate that when conjugation is not very large the use of $\Delta\nu_{\mathfrak{R}}$ as a measure of conjugation length reaches its limit of applicability. Independent evidence suggests that the dispersion behavior (with chain length) of the Raman intensity of the $\mathfrak{R}$ mode could be a more sensitive probe of π-electron delocalization. Further work, both experimental and theoretical, is in progress on this subject.[29]

VIII. CONCLUSIONS

In this paper we have shown that for low-band-gap polyconjugated organic molecules the totally symmetric and selectively enhanced Raman-active mode which mostly involves electron-phonon coupling ($\mathfrak{R}$ mode) shows different frequency dispersion depending on the chemical units which make up the chain. We have ascribed such differences to the fact that π electrons experience different degrees of confinement within the structural units, thus affecting the electron delocalization along the chain. In the framework of the effective conjugation coordinate theory, the parameters $F_{\mathfrak{R}}$ have been calculated by *ab initio* methods for each of the aromatic repeat units making up the simplest chains: these parameters measure the degree of confinement of π electrons within the rings. The result presented support the observation that the strongest confinement potential occurs within the benzene ring while the weakest of the series occurs for furan. Moreover, we have demonstrated, from the analysis of the experimental frequency dispersion of the $\mathfrak{R}$ mode in the case of oligomers and the polymer of pyrrole, that in polyaromatics the conformational flexibility of the systems is an additional, but not the most relevant, factor in determining the confinement of π electrons in a polyconjugated chain.

Materials science for these systems involving the electrical conductivity (intermolecular and/or intramolecular hopping), nonlinear optics, and electroluminescence should incorporate more carefully the phenomenon of electron localization, which we have shown can be estimated by experimental Raman spectroscopy and/or calculated by quantum-chemical methods. The choice of the materials for the improvement of one of the above physical properties should not neglect the phenomenon of the intraring confinement of the π electrons.

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