ARTICLES

Molecular first hyperpolarizability of push-pull polyenes: Relationship between electronic and vibrational contribution by a two-state model

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In this work we present a theoretical justification, based on a two-state model, of the recently observed close resemblance between the molecular first-order hyperpolarizability (β^e) obtained with traditional experimental or theoretical methods and the vibrational (or relaxation) contribution (β^r) for several classes of polyconjugated molecules. The vibrational hyperpolarizabilities have been evaluated according to a semiclassical model previously presented by the authors in which molecular polarizabilities are expressed in terms of vibrational (infrared and Raman) intensities. Here we prove that in the case of polyconjugated molecules, the analytic expressions of β^e and β^r are functions of the same physical parameters. This implies that β^e and β^r provide a measure of the same physical property.

I. INTRODUCTION

In the past ten years, under the driving force of the increasing interest in photonics and optoelectronics applications, many polyconjugated materials with large nonlinear optical (NLO) response have been synthesized.[1-3] It is a known fact that the vibrational spectra (infrared and Raman) of these compounds show common peculiar characteristics which can be ascribed to the presence of highly mobile and polarizable conjugated π electrons strongly coupled with particular nuclear displacements in the vibrational space. The above observation forms the basis of a method known as effective conjugation coordination (ECC) theory,[4,5] devel-

oped to treat in an analytic and compact way the vibrational problem of conjugated organic systems. This method offers a unified point of view for the interpretation of the vibrational spectra (both in frequencies and band intensities) of many different classes of polyconjugated oligomers and polymers.

Infrared and Raman frequencies and intensities are also the ingredients which determine the vibrational (or relaxation) contributions to molecular hyperpolarizabilities. Using a simple semiclassical model, we have shown, in the hypothesis of double (mechanical and electrical) harmonic approximation, that the vibrational hyperpolarizabilities (β^r and γ^r) can be obtained with the following expressions, in the limit of static applied electric fields:

$$\beta^r_{nmp} = \frac{1}{4\pi^2 c^2} \sum_k \left(\frac{1}{\nu_k^2}\right) \left[\left(\frac{\partial \mu_n}{\partial Q_k}\right)\left(\frac{\partial \alpha_{mp}}{\partial Q_k}\right) + \left(\frac{\partial \mu_m}{\partial Q_k}\right)\left(\frac{\partial \alpha_{np}}{\partial Q_k}\right) + \left(\frac{\partial \mu_p}{\partial Q_k}\right)\left(\frac{\partial \alpha_{nm}}{\partial Q_k}\right) \right], \tag{1}$$

$$\gamma^r_{nmps} = \frac{1}{4\pi^2 c^2} \sum_k \left(\frac{1}{\nu_k^2}\right) \left[\left(\frac{\partial \mu_n}{\partial Q_k}\right)\left(\frac{\partial \beta_{mps}}{\partial Q_k}\right) + \left(\frac{\partial \mu_m}{\partial Q_k}\right)\left(\frac{\partial \beta_{nps}}{\partial Q_k}\right) + \left(\frac{\partial \mu_p}{\partial Q_k}\right)\left(\frac{\partial \beta_{nms}}{\partial Q_k}\right) + \left(\frac{\partial \mu_s}{\partial Q_k}\right)\left(\frac{\partial \beta_{nmp}}{\partial Q_k}\right) + \left(\frac{\partial \alpha_{nm}}{\partial Q_k}\right)\left(\frac{\partial \alpha_{ps}}{\partial Q_k}\right) \right.$$

$$\left. + \left(\frac{\partial \alpha_{np}}{\partial Q_k}\right)\left(\frac{\partial \alpha_{ms}}{\partial Q_k}\right) + \left(\frac{\partial \alpha_{ns}}{\partial Q_k}\right)\left(\frac{\partial \alpha_{mp}}{\partial Q_k}\right) \right], \tag{2}$$

were ν_k are harmonic vibrational frequencies, $\partial \mu_n / \partial Q_k$ the derivatives of the molecular dipole moment with respect to the normal coordinate Q_k, $\partial \alpha_{nm} / \partial Q_k$ the derivatives of the molecular polarizability tensor, and $\partial \beta_{nmp} / \partial Q_k$ the derivatives of the molecular first hyperpolarizability. As already discussed in Refs. 7 and 8, the first four terms of Eq. (2), which contain hyper-Raman contributions, can be neglected in a number of cases.

Expressions for vibrational molecular hyperpolarizabili-

ties have been derived in the past by Flytzanis[9(a)] and Bishop[9(b)] on the basis of a completely independent and fully quantum treatment in the frame of perturbation theory: these expressions reduce to those given in Eqs. (1) and (2) if the anharmonic terms are neglected.

In previous works,[7,8,10,11] through Eqs. (1) and (2) using experimental spectroscopic data, we have measured β^r and γ^r for a variety of organic compounds known for their large NLO response. The molecules examined belong to different

chemical classes and were sythesized on the basis of different synthetic strategies aimed at optimizing the NLO responses. Among the compounds with large β values we have measured push-pull polyenes with different end groups and chain length,[10,11] aromatic push-pull systems such as p-nitroaniline,[10] octupolar compounds such as triamino-trinitro-benzene (TATB), and crystal violet.[8,10] As to compounds with large γ, we have measured and studied apolar and polar polyene systems and oligothiophenes.[7,8]

The values of β^r and γ^r which we have obtained were compared with their purely electronic counterpart β^e and γ^e. This study has been made following two completely independent routes:

(i) We have calculated theoretical *ab initio* infrared and Raman spectra. With these data, using Eqs. (1) and (2), we have evaluated theoretical $\beta^r(0;0,0)$ and $\gamma^r(0;0,0,0)$. The vibrational hyperpolarizabilities obtained have been compared with $\beta^e(0;0,0)$ and $\gamma^e(0;0,0,0)$ computed at the same level with standard derivative methods. Notice that these last values can be correctly interpreted as purely electronic in the limit of static applied field: indeed, during the calculation, nuclei are not allowed to relax under the action of the external static field.

(ii) Infrared and Raman absolute intensities of the samples have been measured, and experimental β^r and γ^r have been evaluated with Eqs. (1) and (2). These values have been compared with experimental β^e and γ^e reported in the literature. Values of β^e are usually obtained from electric-field-induced second-harmonic generation (EFISH) experiments or from hyper-Rayleigh harmonic light scattering (HLS) measurements; values of γ^e are obtained from third-Harmonic generation (THG) experiments.

Notice that all experimental β^e values obtained by EFISH or HLS are commonly assumed to be purely electronic in origin, since they are obtained by probing the samples with lasers in the visible or in the near infrared. From these experimental determinations it is also possible to extrapolate the static values $\beta^e(0;0,0)$ with a simple two-state model which allows us to take into account dispersion effects. These extrapolated values are the quantities which we compare (when available) with our vibrational β^r. It is more difficult to obtain a static limit value for γ^e, since the simple two-state model is inadequate for the description of the processes involved. However, the γ^e values (free from multiphoton resonances) obtained with laser at $1.9 \mu m$ are usually considered as good approximations for $\gamma^e(0;0,0,0)$.

All the comparisons we have carried out according to (i) and (ii) show a surprisingly close similarity (in trends and also in absolute values) between vibrational and electronic hyperpolarizabilities. In Table I some selected examples are shown. The striking similarity between data which are due, at least in principle, to two independent and different processes (nuclear relaxations and electronic excitations) suggests that a physical reason for this behavior must exist.

In previous papers[8,10] we have suggested that the origin of the large β^r and γ^r values of the systems studied has to be traced to the strong electron-phonon coupling which is a peculiar characteristic of these molecules. It follows that, since in the presence of large electron-phonon coupling a complete separation between nuclear and electronic motions becomes questionable, the separation between a purely electronic and

a purely nuclear (vibrational) contribution also becomes artificial. As a result we expect that the two quantities [hereafter referred to as $\beta^r(\gamma^r)$ and $\beta^e(\gamma^e)$], which were defined in the hypothesis of a complete separation, are no longer independent. As a consequence it may happen, in some limiting cases, that the two quantities coincide.

In what follows we present a simplified model which establishes in an analytic form a relation between β^e and β^r. This model proves that the observed similarity between β^e and β^r is not casual, but is a consequence of the peculiar physics of the systems studied. It will be shown below that these relevant physical characteristics can be modeled in terms of very few parameters. Moreover, it can be clearly seen that the key feature of the model is the occurrence of *one relevant structural parameter* strongly coupled with the electronic structure of the molecule.
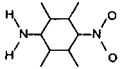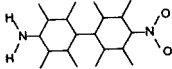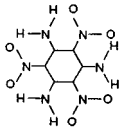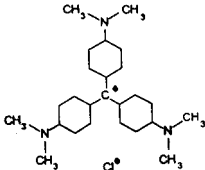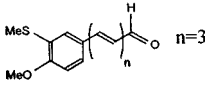
II. MODEL

The model we present here describes the case of push-pull polyenes, a particular class of compounds of great interest for their large β_{zzz} values (where z is in the direction of the charge-transfer axis). For this reason, in the model discussed only one relevant component of the β tensor is considered to be nonvanishing; therefore all equations are in the scalar form.

From the viewpoint of the vibrational spectra, push-pull polyenes show very simple Raman spectra, with a typical pattern common to all polyene systems. The Raman spectra consists of few strong lines due to vibrational modes which involve the stretching of the conjugated CC bonds of the polyenic chain.[11] These modes are described by the ECC theory[4,5] as an oscillation of the dimerization amplitude of the polyenic chain dynamically coupled with other vibrational coordinates, e.g., CH waggings (the dimerization amplitude oscillation is exactly a vibration along the so-called effective conjugation coordinate $\mathcal{R}$, defined as the in phase stretching of all $C=C$ bonds and a simultaneous shrinking of all $C-C$ single bonds of the chain). It has been shown that, in polyene systems,[4,5] the extremely large Raman cross sections of the few observed Raman bands can be justified by the presence in the normal modes of a large contribution by the oscillation in the $\mathcal{R}$ direction; this oscillation is responsible for a large redistribution of the π electrons conjugated along the chain (i.e., large $\partial\alpha/\partial\mathcal{R}$). In the case of push-pull compounds the occurrence of different end groups (electron donor and electron acceptor) polarizes the delocalized π electrons. The lowering of the symmetry also makes the relevant Raman normal modes strongly active in the infrared. It has been shown that the presence of modes with large $\mathcal{R}$ content ($\mathcal{R}$ modes,) *simultaneously very intense in the Raman and in the infrared*, is responsible for the large β^r values of push-pull polyenes.[8,11]

Since the value of β^r is essentially determined by the contribution to the normal modes by the $\mathcal{R}$ oscillation,[7] in our simplified model we will consider *only one* vibrational normal mode (Q), exactly coincident with the dimerization amplitude oscillation, i.e., $Q \equiv \mathcal{R}$. In treating the electrons, we make use of the simple model recently proposed by Lu *et al.*,[13(a)] developed for the study of the hyperpolarizabilities of push-pull polyenes and solvent effects.[14(b)] The model of

TABLE I. Comparison between β and β^r values for some selected organic molecules obtained both theoretically (with *ab initio* 3–21-G basis set) and experimentally. β values are in units of 10^{-30} esu.

molecule		β_r^μ(3–21 G)	β^μ(3–21 G)	β_r^μ (exp)	β^μ (exp)
I		10.67	9.55	5.3	10[a]
II		28.24	30.96		24[b]
III		8.27	11.08		
IV				50	46[c]
V	n=1	11.6	10.2	10.2	3.8[d]
	n=3	34.7	32.0	34.6	39.8[d]
	n=4			50.9	42.1[d]

[a]From EFISH experiments, Ref. 1.
[b]β_{yyy}.
[c]From HLS experiments: Ref. 13.
[d]From EFISH experiments: Ref. 12.

Lu *et al.* starts from the observation that the first hyperpolarizability of these systems is well described by a perturbative development which considers only two relevant electronic states: the ground state and only one excited state. These two states are obtained by a suitable linear combination of two wave functions representing two ideal electronic configurations of the molecule (canonical structures). The basis functions are Ψ_{VB}, which corresponds to an ideal apolar, polyenelike structure, and Ψ_{CT}, corresponding to a zwitterionic structure where one electron is completely transferred from the donor to the acceptor group. Notice that the nuclear structures (geometries) which correspond to these ideal canonical forms are two chains both with alternated single and double bonds; the difference between the two structures is represented by the phase of the bond alternation which is completely reversed in going from the polyenic to the zwitterionic form.

The ground and excited states of the molecule are represented by two wave functions which are the linear combinations of Ψ_{VB} and Ψ_{CT} obtained from the diagonalization of the Hamiltonian matrix:

$$H = \begin{vmatrix} E_{VB} & -t \\ -t & E_{CT} \end{vmatrix},$$

where $E_{VB} = \langle \Psi_{VB}|H|\Psi_{VB}\rangle$, $E_{CT} = \langle \Psi_{CT}|H|\Psi_{CT}\rangle$, and $t = \langle \Psi_{VB}|H|\Psi_{CT}\rangle$.

In general, if one introduces a parameter f, which describes the amount of charge transfer (weight of Ψ_{CT} in the ground state, it is possible to write

$$\Psi_g = (1-f)^{1/2}\Psi_{VB} + f^{1/2}\Psi_{CT}, \tag{3}$$

and, using the orthogonality relationship between Ψ_e and Ψ_g,

$$\Psi_e = f^{1/2}\Psi_{VB} - (1-f)^{1/2}\Psi_{CT}. \tag{4}$$

It follows that f determines the molecular dipole moment in the ground and in the excited states [see Eqs. (12) and (13)]. The value of f depends on the characteristics of the system, i.e., the donor and/or acceptor strength and the degree of dimerization of the conjugated chain.
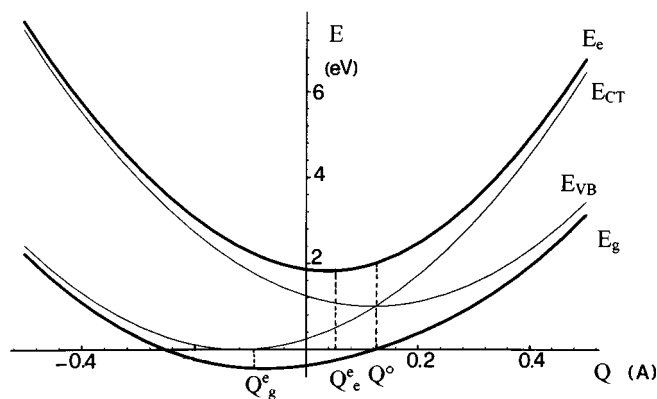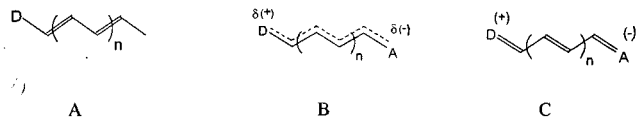
FIG. 1. Intramolecular potential wells (E_g and E_e) relative to the two relevant electronic states of a push-pull polyene. E_{VB} and E_{CT} (thin lines) are the harmonic potentials relative to the two canonical ''ideal'' structures (see text). The plots are obtained with the following parameters: $k = 33.55$ eV/Å^2, $Q^0_{VB} = -0.12$ Å, $Q^0_{CT} = 0.12$ Å, $V^0 = 1$ eV, and $t = 1$ eV.

It is then possible to modulate the value of f either by changing the end groups or the degree of bond alternation (the BOA parameter in the treatment of Ref. 13). If we recall that a change in BOA corresponds to moving the nuclei along the $\mathscr{R}$ coordinate, i.e., along the only normal coordinate Q, it turns out that f is modulated by Q. This observation is even clearer if one considers that in going from a polyenic structure ($f = 0$) to a zwitterionic one ($f = 1$), the bond alternation continuously changes from form A to C, going through the undimerized, cyaninelike structure B:

The nuclear structures in the ground and excited states (described by the equilibrium value of $\mathscr{R}$) are those which correspond to the minima of the potential curves relative to Ψ_g and Ψ_e. From the diagonalization of the Hamiltonian two potential curves [$E_g(Q)$ and $E_e(Q)$] which depend parametrically on the Q coordinate are obtained. The minima Q^{eq}_g and Q^{eq}_e determine the exact percentage of the charge-transfer character in the ground [$f(Q^{eq}_g)$] and excited states [$1 - f(Q^{eq}_e)$] in their respective equilibrium geometries.

Following Ref. 13, we describe the dependence of E_{VB} and E_{CT} from Q in a harmonic form, with an equal force constant k:

$$E_{VB} = \tfrac{1}{2}k(Q - Q^0_{VB}), \tag{5}$$

$$E_{CT} = \tfrac{1}{2}k(Q - Q^0_{CT}) + V^0. \tag{6}$$

Q^0_{VB} and Q^0_{CT} represent the equilibrium geometry of the two ideal canonical structures, and V^0 the energy difference between the two canonical structure in their respective equilibrium nuclear configurations.

In Fig. 1 are reported the plots of the two ''ideal'' potential wells E_{VB} and E_{CT}, and the ''real'' potential wells (E_g and E_e) which result from the interaction between Ψ_{VB} and Ψ_{CT} through the term t of the Hamiltonian: the choice of the

parameters t, V^0, k, Q^0_{VB}, and Q^0_{CT} has been made according to the data reported in Ref. 13(a). The form of the two potential wells (E_g and E_e) depends strongly on the choice of the parameters t and V^0 which characterize the molecule.

III. CORRESPONDENCE BETWEEN β^r AND β^e

We now have all the ingredients necessary to the derivation of the analytic expressions for both β^r and β^e according to our simplified model. The well-known two-state expression for β^e is given by[14]

$$\beta^e = 6(\Delta M^{e-g}|M^{ge}|^2)/E_g^2. \tag{7}$$

From Eq. (2), the diagonal component of the β^r tensor is given by

$$\beta^r = 3/(4\pi^2 \nu_Q^2)(\partial \alpha / \partial Q)(\partial \mu / \partial Q). \tag{8}$$

It is possible to write the Raman term $\partial \alpha / \partial Q$ in terms of electronic observables by making use of Ting's formalism,[15] restricted to the case of a two-state model:

$$\partial \alpha / \partial Q = (8\pi^2 \nu_Q^2)(\Delta Q^{eg}|M^{ge}|^2)/E_g^2. \tag{9}$$

Expressions similar to Eq. (9) have already been used by Yaron and Silbey[16] to discuss the role of the vibrational contribution to the second-order hyperpolarizability of normal *trans*-polyenes. Inserting Eq. (9) into Eq. (8), we obtain

$$\beta^r = 6(\partial \mu / \partial Q)(\Delta Q^{eg}|M^{ge}|^2)/E_g^2. \tag{10}$$

A comparison between Eq .(10) and (7) indicates that β^e is equal to β^r if the equation

$$\Delta M^{eq} = (\partial \mu / \partial Q)(\Delta Q^{eg}) \tag{11}$$

is satisfied.

In other words, β^r is a good approximation of β^e, if the quantity $[(\partial \mu / \partial Q)(\Delta Q^{eg})]$ is a good approximation of the change of the molecule dipole moment in going from the ground to the electronic excited state. Notice that in the expression for β^e [Eq. (7)] the variation of the molecular dipole moment between the excited and ground states corresponds to the *direct* transition, without relaxation of the nuclei in the excited state: i.e., $\Delta M^{eg} = M_e(Q^{eq}_g) - M_g(Q^{eq}_g)$.

Using expressions (4) and (5) for the electronic wavefunction, we can write

$$M_g = f\mu_{CT}, \tag{12}$$

$$M_e = (1 - f)\mu_{CT}, \tag{13}$$

where μ_{CT} is the dipole moment associated with Ψ_{CT}, $\mu_{CT} = \langle \Psi_{CT}|M|\Psi_{CT}\rangle$.

As previously discussed, the value of f may be modulated by changing the BOA parameter, i.e., by moving the nuclei along $Q(\equiv \mathscr{R})$. Thus a special point exists along the Q axis (which we indicate as Q^0), where the value of f is such that $M_g = M_e$. Q^0 obviously corresponds to the choice: $f = \tfrac{1}{2}$. [see Eqs. (12) and (13)].

Another feature of Q^0 is that it represents a chain configuration where the energies associated with the two canonical

forms are identical, i.e., $E_{VB}(Q^0) = E_{CT}(Q^0)$. This can be easily proven by calculating the energy gap at Q^0:

$$E_{gap}(Q^0) = E_e(Q^0) - E_g(Q^0) = \langle \Psi_e(Q^0)|H|\Psi_e(Q^0)\rangle$$
$$- \langle \Psi_g(Q^0)|H|\Psi_g(Q^0)\rangle = 2t, \quad (14)$$

where $\Psi_e(Q^0)$ and $\Psi_g(Q^0)$ are the eigenfunction of Eqs. (3) and (4) with $f = \frac{1}{2}$.

Since the general forms for E_e and E_g are

$$E_e = \tfrac{1}{2}(E_{VB} + E_{CT}) + \tfrac{1}{2}[(E_{CT} - E_{VB})^2 + 4t^2]^{1/2}, \quad (15)$$

$$E_g = \tfrac{1}{2}(E_{VB} + E_{CT}) - \tfrac{1}{2}[(E_{CT} - E_{VB})^2 + 4t^2]^{1/2}, \quad (16)$$

we also obtain

$$E_{gap} = [(E_{CT} - E_{VB})^2 + 4t^2]^{1/2}. \quad (17)$$

By equating Eqs. (14) and (17), we obtain $E_{VB}(Q^0) = E_{CT}(Q^0)$. [In Fig. 1, Q^0 is exactly the intersection between the two parabolas $E_{VB}(Q)$ and $E_{CT}(Q)$.]

From Eq. (17), recalling Eqs. (5) and (6), it is possible to obtain the explicit expression for Q^0:

$$Q^0 = V^0/[k(Q^0_{CT} - Q^0_{VB})] + \tfrac{1}{2}(Q^0_{CT} + Q^0_{VB}), \quad (18)$$

which reduces to the first term with a proper choice of the origin of the Q axis: that is, as the mean position between the two limiting ideal structures $[\tfrac{1}{2}(Q^0_{CT} + Q^0_{VB}) \equiv 0]$.

We can now expand the molecular dipole moment (in the ground and excited states) around Q^0:

$$M_g(Q) = M_g(Q^0) + (\partial M_g/\partial Q)_{Q^0}(Q - Q^0) + \cdots, \quad (19)$$

$$M_e(Q) = M_e(Q^0) + (\partial M_e/\partial Q)_{Q^0}(Q - Q^0) + \cdots. \quad (20)$$

If the hypothesis of electrical harmonicity holds in the range of reasonable Q values, Eqs. (19) and (20) can be truncated after the first two terms, and we can drop the index Q^0 in the derivatives of the dipole. Making use of Eqs. (12) and (13), we can also write

$$\partial M_g/\partial Q = \partial f/\partial Q \mu_{CT} \equiv - \partial M_e/\partial Q. \quad (21)$$

Since, following the definition of Q^0, $M_g(Q^0) = M_e(Q^0)$, combining Eqs. (19), (20), and (21) we obtain

$$\Delta M^{eg}(Q^{eq}_g) = M_e(Q^{eq}_g) - M_g(Q^{eq}_g)$$
$$= 2(\partial f/\partial Q)\mu_{CT}(Q^0 - Q^{eq}_g) = 2(\partial M_g/\partial Q)\Delta Q^{0g}, \quad (22)$$

or, using the symbols which appear in Eq. (10),

$$\Delta M^{eg}(Q^{eq}_g) = 2(\partial \mu/\partial Q)\Delta Q^{0g}. \quad (22')$$

Inserting this expression into Eq. (7), one obtains

$$\beta^e = 12(\partial \mu/\partial Q)(\Delta Q^{0g}|M^{ge}|^2)/E^2_g, \quad (23)$$

which coincides with the expression for β^r [Eq. (10)] provided that $2\Delta Q^{0g} = \Delta Q^{eg}$. A more detailed discussion on this coincidence is reported in the next paragraph.

A first look at Eq. (23) immediately shows an extremely important result, namely that the ingredients which determine β^e are the same as those which determine β^r. This is a consequence of the fact that the extent of charge transfer in the electronic structure of the molecule can be modulated both by direct excitation of the electrons and by nuclear displacements along the Q direction. In the model this property is reflected by the dependence of f from the parameter Q.

IV. DISCUSSION

According to the result presented above, in all the cases where the physical situation is well described in terms of a two state model based on VB and CT canonical wave function, β^r is certainly a meaningful projection (in the vibrational space) of the electronic hyperpolarizability.

A comparison between Eqs. (23) and (10) shows that the similarity observed between β^r and β^e can be justified in an analytical form. It is also evident that this similarity can be observed only for a specific class of compounds whose electronic structure can be modulated by nuclear displacements. This is evident looking at Eq. (11), which states that the same state of polarization described by M_e (Q^{eq}_g) can be reached by electronic excitation across the gap as well as by vibrational excitation (ΔQ^{eg}) in the ground state provided that ΔQ^{eg} is exactly the path of geometry variation which describes the transition between the two minima structures of the ground and of the excited state.

From the discussion above it is concluded that the coincidence between experimental β^r and β^e in organic conjugated materials is certainly not fortuitous; the measure of β^r can then be proposed as a reliable tool for the characterization of the NLO response of organic compounds in all those cases for which the direct measure of the electronic observable (β^e) is difficult or questionable.

To have an idea of the limits of applicability of the vibrational method for the study of NLO responses, we can use the model discussed in Sec. II. Within this model it is possible to obtain in an analytical way a relationship which shows that β^r can be, at best, $\beta^e/2$; this happens when the equilibrium geometry displacement between ground and excited states (ΔQ^{eg}) is exactly ΔQ^{0g}. Indeed, equating to zero the derivative of the electronic energy E_e with respect to Q one obtains an implicit expression for the equilibrium geometry Q^{eq}_c. Keeping in mind Eqs. (5) and (6) the definition of the energy gap given in Eq. (17) one can write

$$Q^{eq}_e[(Q^0_{CT} - Q^0_{VB})V_0][k(Q^0_{CT} - Q^0_{VB})^2 + 2E_g(Q^{eq}_e)]. \quad (24)$$

Since $Q^0 = V_0/[k(Q^0_{CT} - Q^0_{VB}]$ [from Eq. (18), where the origin is chosen as $0 = \tfrac{1}{2}(Q^0_{CT} + Q^0_{VB})$] one can immediately see from Eq. (24) that Q^{eq}_e coincides with Q^0 coincides with Q^0 only if $E_g(Q^{eq}_e) \cong 0$. Since E_g is by definition [see Eq. (17)] a positive quantity, Eq. (24) states that the inequality $Q^{eq}_e < Q^0$ always holds. A particular case where an exact correspondence between Q^0 and Q^{eq}_e is realized, can be found when the minimum energies of the two canonical forms are equal, i.e., $V^0 = 0$ [see Eqs. (5) and (6)].

In this case we obtain the following.

(a) $Q^0 = 0$ [see Eq. (18)]: Q^0 coincides with the mean value between the optimum geometry relative to ψ_{VB} and that relative to ψ_{CT}.
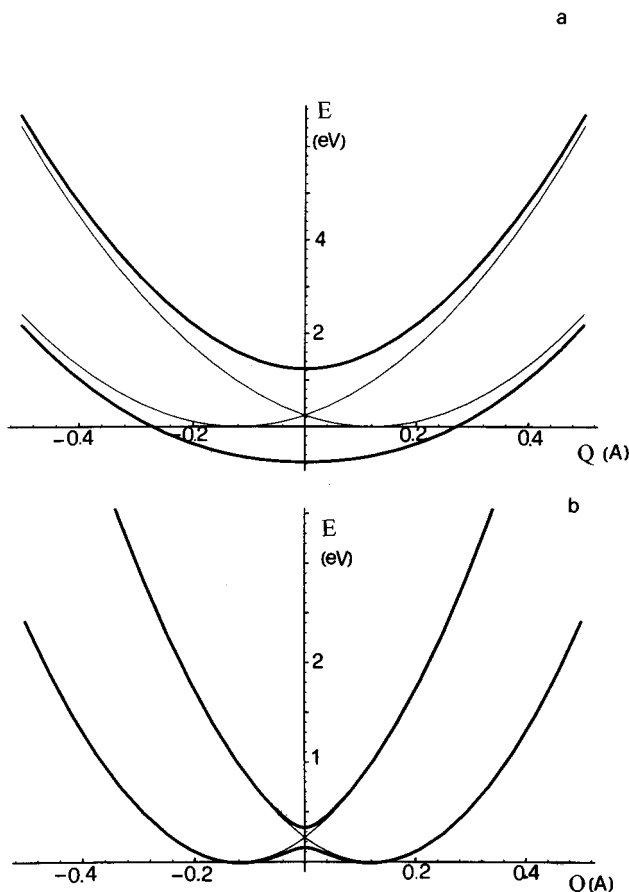
C. CASTIGLIONI, M. Del ZOPPO, AND G. ZERBI

FIG. 2. Intramolecular potential wells (E_g and E_e) relative to the two relevant electronic states of a push-pull polyene in the degenerate case with $V^0 = 0$. Case (a) $t = 1$ eV. Case (b) $t = 0.1$ eV. All other parameters are fixed at the same values used in the plots of Fig. 1.

(b) If we evaluate the derivatives of the potential energy of the excited and of the ground state,

$$\partial E_e / \partial Q = kQ + \tfrac{1}{2}k^2(Q_{CT}^0 - Q_{VB}^0)^2 [k^2(Q_{CT}^0 - Q_{VB}^0)^2 Q^2$$
$$+ 4t^2]^{1/2}Q, \qquad (25)$$

$$\partial E_g / \partial Q = kQ - \tfrac{1}{2}k^2(Q_{CT}^0 - Q_{VB}^0)^2 [k^2(Q_{CT}^0 - Q_{VB}^0)^2 Q^2$$
$$+ 4t^2]^{1/2}Q, \qquad (26)$$

we see that $Q = 0 = Q^0$ is a stationary point both for the ground and for the excited state. In the excited state Q^0 is always a minimum, since the second derivative of E_e with respect to Q is always positive in $Q = 0$. In the case of the ground state we can have either a minimum or a maximum according to the inequalities

Case A (minimum): $\partial^2 E_g / \partial Q^2]_0 > 0 \Rightarrow t > \tfrac{1}{4}k(Q_{CT}^0 - Q_{VB}^0)^2$,

Case B (maximum): $\partial^2 E_g / \partial Q^2]_0 < 0 \Rightarrow t < \tfrac{1}{4}k(Q_{CT}^0 - Q_{VB}^0)^2$.

The two cases are represented in Fig. 2. In case A [Fig. 2(a)] the minima of the ground and the excited states are both found at Q^0 (undimerized, cyaninelike structure): it follows

that $\Delta M^{eg} (Q_g^{eq}) \equiv \Delta M^{eg}(Q^0) \equiv 0$, i.e., $\beta^e = 0$, but also $\beta^r = 0$ since $\Delta Q^{ge} = 0$. This is a limiting but trivial case.

In case B [Fig. 2(b)], $\Delta Q^{ge} \neq 0$ and $\Delta Q^{g0} = \Delta Q^{ge}$: this implies $\beta^e = \beta^r$. The occurrence of two minima in the ground state, symmetric with respect to the equilibrium geometry of the excited state, would imply the occurrence of two, equally stable, molecular structures whose β is equal in value but opposite in sign. The result would then be a vanishing value of the macroscopic observable (χ^2): i.e., cases A and B are in practice indistinguishable.

In general the limiting degenerate case ($V^0 = 0$) discussed above is not to be expected because asymmetric end groups of push-pull polyenes tend to stabilize one of the two canonical electronic structures; this implies $V^0 \neq 0$. The degenerate limiting case corresponds to a cyanine structure only recently obtained in the case of asymmetric push-pull compounds.[17] These compounds are very interesting for the study of solvent effects in NLO response and show promising and large negative-γ values.

The more general case with nonvanishing V^0 is the case of interest. According to the discussion above we predict $\beta^r \neq 0$ with $|\beta^r| < |\beta^e|2$.

On the contrary, the examination of the results reported in Table I shows that the agreement is always much better. Indeed, both the experimental and the theoretical data reported indicate that the projection of β^e on the vibrational space is in many cases larger than one-half of its value.

This contradictory result can be acribed to two different sources of error. On one hand it must be remembered that the NLO measurements are generally affected by large experimental errors and also the quantum chemical "*ab initio*" values suffer from severe limitations due to basis set restrictions and computational approximations. On the other hand, the model presented is certainly too simple: in particular it is important to remind that the effect of structure modulation is contained only in the quadratic dependence of E_{VB} and E_{CT} from the normal coordinate Q [Eqs. (5) and (6)]. The interaction integral is instead fixed to a constant value, independent from Q. This is certainly an oversimplification since the explicit introduction of the electron-phonon interaction in the Hamiltonian would lead to a Q dependence (at least linear) of the t integral. In this case it is no longer possible to write to minimum geometry of the excited state in the form of Eq. (24). Moreover, it is known (18), at least in the case of polyenes, that an explicit introduction of vibronic coupling between ground and excited state will produce an appreciable change in the minimum structure of the excited state.

Finally, another possible weakness in our treatment arises from the hypothesis that electrical harmonicity [Eqs. (19) and (20)] holds in the range of Q values considered.

Indeed ΔQ^{eg} (and ΔQ^{0g}) certainly exceeds the values typical of the "small oscillations" hypothesis, generally assumed to justify electrical and mechanical harmonicity in the classical treatment of vibrational dynamics and intensities.

These observations seem to suggest that our model might be improved to obtain a more quantitative justification of the observed coincidence between β^r and β^e.

V. CONCLUSIONS

In this paper a very simple two-state model is presented for the explanation of the observed similarity between vibra-

tional and electronic β values measured for a series of organic polyconjugated compounds. The model establishes in an analytical way that the observed correspondence is not casual, but that the relevant factors which determine the response of the electrons (β^e) are the same which determine its vibrational counterpart (β^r). This is made possible by the existence of a preferential structural parameter which modulates the electronic structure of the molecule, i.e., by the existence of an important mechanism of electron-phonon coupling which determines the physical behavior of such compounds.

The use of vibrational spectroscopy as an alternative (or complementary) tool with respect to direct optical measurements of the first molecular hyperpolarizability is then justified. Further work is in progress for the discussion of the correspondence between vibrational and electronic second hyperpolarizabilities.

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