

# Contributions of anharmonics to the nuclear relaxation second hyperpolarizability of a push–pull polyene

Emilio Squitieri\*

Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Apartado 47102, Caracas 1020-A, Venezuela

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**ABSTRACT:** A theoretical study of the contributions of anharmonics to the nuclear relaxation second hyperpolarizability of  $\pi$ -conjugated push–pull polyenes by using an analytical evaluation of electrical properties method and a valence-bond–charge-transfer model was carried out. A relationship between nuclear relaxation and electronic contributions to the second hyperpolarizability is derived. It was found that the anharmonicity is essential in a numerical estimation of nuclear relaxation second hyperpolarizability. Copyright © 2004 John Wiley & Sons, Ltd.

**KEYWORDS:** nuclear relaxation; second hyperpolarizability; anharmonics; push–pull polyene

## INTRODUCTION

To study the effect of a uniform electric field on a molecule, the molecular potential energy,  $U(q, \varepsilon)$ , can be expanded in a Taylor series as

$$U(q, \varepsilon) = U(q, 0) - \sum_i \mu_i \varepsilon_i - (1/2!) \sum_{i,j} \alpha_{ij} \varepsilon_i \varepsilon_j - (1/3!) \sum_{i,j,k} \beta_{ijk} \varepsilon_i \varepsilon_j \varepsilon_k - (1/4!) \sum_{i,j,k,l} \gamma_{ijkl} \varepsilon_i \varepsilon_j \varepsilon_k \varepsilon_l - \dots \quad (1)$$

where  $U(q, 0)$  is the potential energy in the absence of the field,  $\varepsilon$ ,  $\mu_i$  is the  $i$ th Cartesian component of the dipole moment,  $\varepsilon_i$  are the  $x$ ,  $y$  and  $z$  components of the static electric field and  $\alpha_{ij}$ ,  $\beta_{ijk}$ ,  $\gamma_{ijkl}$  are the first-, second- and third-order polarizability tensor, respectively. In this expression, the potential energy  $U(q, \varepsilon)$  and the electrical properties  $\mu_i$ ,  $\alpha_{ij}$ ,  $\beta_{ijk}$  and  $\gamma_{ijkl}$  are calculated at the field-free equilibrium geometry,  $q_{\text{eq}}$ . However, under the stimulus of a uniform electrostatic field, the equilibrium geometry will relax to a new field-dependent equilibrium position,  $q_{\text{eq}}(\varepsilon)$ , and the same field alters the potential energy surface for nuclear motion about the new equilibrium position. These induced shifts in geometry and potential energy are recognized as nuclear relaxation (nr) and vibrational contribution, respectively.<sup>1,2</sup>

One important point to consider on the calculation of the nuclear contributions (nuclear relaxation and vibrational) to the hyperpolarizabilities is the effect of the electrical and mechanical anharmonicities associated

with the potential energy surface. When these anharmonicities are ignored, i.e. the so-called double harmonic approximation (DHA) hypothesis, the nuclear contribution is due entirely to the nuclear relaxation. In particular, Zuliani *et al.*<sup>3</sup> found experimentally an interesting similarity in magnitude between the nuclear relaxation and electronic contributions to the first,  $\beta_{zzz}$ , and second,  $\gamma_{zzzz}$ , molecular hyperpolarizability. Castiglioni *et al.*<sup>4</sup> later presented a theoretical explanation for the observed close comparison between the first-order electronic hyperpolarizability,  $\beta_{zzz}^e$ , and its nuclear relaxation contribution,  $\beta_{zzz}^{\text{nr}}$ , along the  $\pi$ -chain axis on a number of donor–acceptor polyconjugated molecules. Considering only the harmonic effects of the potential energy, Kim *et al.*<sup>5</sup> also applied the valence-bond–charge-transfer (VB–CT) model for push–pull molecules to obtain an analytic expression for  $\beta_{zzz}^{\text{nr}}$  and  $\gamma_{zzzz}^{\text{nr}}$ , and confirmed that their magnitudes are similar to  $\beta_{zzz}^e$  and  $\gamma_{zzzz}^e$ , respectively. As a result of the above studies, the vibrational spectra from IR, Raman and hyper-Raman measurements can be directly used to calculate  $\beta_{zzz}^{\text{nr}}$  and  $\gamma_{zzzz}^{\text{nr}}$  and also to estimate the magnitudes of  $\beta_{zzz}^e$  and  $\gamma_{zzzz}^e$ . Bishop *et al.*,<sup>6</sup> on the basis of the VB–CT model and DHA hypothesis, found several parameter-independent relations between nuclear relaxation and electronic hyperpolarizabilities. *Ab initio* computational tests show that these relations are not satisfied. As a byproduct result of the *ab initio* calculations, they found cases where  $\beta_{zzz}^{\text{nr}}$  is larger than  $\beta_{zzz}^e$ .

Luis *et al.*<sup>1</sup> applied an analytical method to evaluate nuclear contributions to the electrical properties of polyatomic molecules, the so-called analytical evaluation of electrical properties (AEEP) method. Expressions to compute the nuclear contributions are derived from a power series expansion of the energy potential. These contributions to the electrical properties are given in terms of the molecular energy derivatives with respect

\*Correspondence to: E. Squitieri, Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Apartado 47102, Caracas 1020-A, Venezuela.

E-mail: esquitier@strix.ciens.ucv.ve

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to normal coordinates, electric field intensity or both. Only one calculation of such derivatives at  $q_{\text{eq}}$  is required. The energy expansion considers the mechanical and electrical anharmonicities associated with the energy potential. Therefore, the AEEP method allows us to make calculations of the electrical properties clear of the hypothesis of DHA.

We applied the AEEP method to push–pull polyenes in order to study the nuclear relaxation contribution to the first hyperpolarizability.<sup>7</sup> As a result, a formal relationship between the nuclear relaxation and electronic contributions to the first hyperpolarizability ( $\beta_{zzz}$ ) was derived, which incorporates the anharmonic terms related to the ground-state potential energy. We found situations where the anharmonic and harmonic contributions are of the same order of magnitude. This result indicates that the anharmonicity is vital in a numerical evaluation of the nuclear relaxation contribution to  $\beta_{zzz}^{\text{nr}}$ .

In this paper, we make use of the AEEP method and VB–CT model to establish the effects of the electrical and mechanical anharmonicities on the nuclear relaxation second hyperpolarizability,  $\gamma_{zzz}^{\text{nr}}$ . The anharmonicity effect on the nuclear relaxation second hyperpolarizability is theoretically studied by replacing the analytical expression for  $q_{\text{eq}}(\varepsilon)$  in Eqn (1). The use of the AEEP method and VB–CT model enabled us to express in a clearer way a mathematical connection between the nuclear relaxation and electronic contribution to the second hyperpolarizability for push–pull polyenes without using the DHA hypothesis.

The theoretical background for the VB–CT model is summarized in the next section. The subsequent section deals with the basic elements of the AEEP method as applied to the VB–CT model, and we show how the nuclear relaxation contribution to  $\gamma_{zzz}$  is related to the



**Figure 1.** Valence-bond (VB) and charge-transfer (CT) structures of a push–pull molecule

$$\psi_{\text{gr}} = (1 - f)^{1/2} \psi_{\text{VB}} + f^{1/2} \psi_{\text{CT}} \quad (2)$$

where the base function,  $\psi_{\text{VB}}$ , corresponds to a neutral (VB) structure (no charge transfer from donor to acceptor) and  $\psi_{\text{CT}}$  to a charge-transfer (CT) structure. In the CT structure, one electron is completely transferred from the donor (D) to the acceptor (A) group, while readjusting the other bonds (see Fig. 1). The fraction  $f$  of the CT configuration in the ground state is determined by the relative energy of  $\psi_{\text{VB}}$  and  $\psi_{\text{CT}}$  on  $\psi_{\text{gr}}$ , the coupling between them, the change in dipole moments and the solvent polarity.

The Hamiltonian matrix describing a linear push–pull molecule with a relevant vibrational mode  $q$  is

$$H = \begin{pmatrix} \frac{1}{2}k(q - q_{\text{VB}}^{\circ})^2 & -t \\ -t & V_0 + \frac{1}{2}k(q - q_{\text{CT}}^{\circ})^2 \end{pmatrix} \quad (3)$$

where  $t$  represents the charge transfer integral ( $t$  is positive),  $V_0$  corresponds to the electronic energy gap between the CT and VB states evaluated at its corresponding equilibrium positions  $q_{\text{CT}}^{\circ}$  and  $q_{\text{VB}}^{\circ}$  (with  $q_{\text{VB}}^{\circ} = -q_{\text{CT}}^{\circ}$ ) and  $k$  represents the force constant appropriate for the polyene linkers.

From Eqns (2) and (3), the adiabatic potential energy surface of the ground state for the zero field case, i.e.  $\varepsilon = 0$ , is

$$U_{\text{gr}}(q) = \frac{V_0 + (k/2)[(q - q_{\text{VB}}^{\circ})^2 + (q - q_{\text{CT}}^{\circ})^2] - \sqrt{(V_0 + k\delta q)^2 + 4t^2}}{2} \quad (4)$$

electronic counterpart ( $\gamma_{zzz}^{\text{e}}$ ), when harmonic and anharmonic contributions associated with the potential energy are taken into consideration. Conclusions and some speculations about future work are presented in the last section.

## THE VB–CT MODEL FOR PUSH–PULL MOLECULES

We start by considering the VB–CT model.<sup>8,9</sup> In the VB–CT model, the electronic ground-state wavefunction,  $\psi_{\text{gr}}$ , of the push–pull polyene is described by using a linear combination of two orthogonal wavefunctions representing two resonant structures:

where  $\delta = q_{\text{VB}}^{\circ} - q_{\text{CT}}^{\circ} = -2q_{\text{CT}}^{\circ}$ . As assumed by Lu *et al.*,<sup>5</sup> the relevant vibrational coordinate  $q$  is identical with that of the bond length alternation (BLA) coordinate,<sup>3,4,8,9</sup> which is located along the  $\pi$ -chain axis. For the donor–acceptor hexatrienes under consideration, the BLA coordinate  $q$  corresponds to  $(b + d)/2 - (a + c + e)/3$  (Ref. 10) (see Fig. 1). Since  $\psi_{\text{VB}}$  and  $\psi_{\text{CT}}$  involve alternate resonant descriptions of the intervening polyene unit, an increase of  $f$  from 0 to 1 will shift each double bond (1.33 Å) of the polyene to a single bond (1.45 Å) and vice versa (these distances are based on the experimental observations of the average bond lengths of *trans*-1,3,5,7-octatetraene).<sup>8</sup> Consequently, the BLA coordinate changes from  $q_{\text{VB}}^{\circ} = -0.12$  Å to  $q_{\text{CT}}^{\circ} = 0.12$  Å as the CT fraction  $f$  goes from 0 to 1.

Using the above expression for  $U_{\text{gr}}(q)$ , it is straightforward to verify that the equilibrium BLA coordinate  $q_{\text{eq}}$  [obtained by solving  $dU_{\text{gr}}(q)/dq = 0$  at  $q_{\text{eq}}$ ] can be written as follows:

$$q_{\text{eq}} = q_{\text{VB}}^{\circ} - \delta f \quad (5)$$

with  $f$  as the square coefficient corresponding to the  $\Psi_{\text{CT}}$  function in the ground-state  $\psi_{\text{gr}} > q_{\text{eq}}$ :

$$f = \frac{1}{2} \left[ 1 - \frac{(V_0 + k\delta q_{\text{eq}})}{\sqrt{(V_0 + k\delta q_{\text{eq}})^2 + 4t^2}} \right] \quad (6)$$

Finally, the force constant (from  $d^2U_{\text{gr}}(q)/dq^2 = 0$  at  $q_{\text{eq}}$ ) for the ground-state  $U_{\text{gr}}$  at  $q_{\text{eq}}$  is

$$K = k \left\{ 1 - \frac{2t^2 k \delta^2}{[(V_0 + k\delta q_{\text{eq}})^2 + 4t^2]^{3/2}} \right\} \quad (7)$$

As can be seen from Eqn (7),  $K$  differs from  $k$  when the electronic structure does not correspond to either VB or CT.

## THE AEEP METHOD APPLIED TO PUSH-PULL MOLECULES

The AEEP method<sup>1</sup> has been derived from a double power series expansion on the potential energy of a given chemical system with respect to normal coordinates, field strength or both. Just a calculation of such derivatives at the field-free equilibrium geometry,  $q_{\text{eq}}$ , is required. This energy expansion also includes the mechanical anharmonicity associated with the potential energy and electrical anharmonicity for dipole moment, polarizability, first hyperpolarizability, etc. The accuracy of the AEEP method is only determined by the quality of the wavefunction used to describe the molecular system. With this method it is simple to obtain equilibrium field-dependent normal coordinates,  $q_{\text{eq}}(\varepsilon)$ , although some algebra is required. In the AEEP method we need just a calculation of the energy and its derivatives at  $q_{\text{eq}}$ , followed by trivial application of the related formulas. The method predicts the order of the derivatives required for a complete computation of a specific nuclear contribution (e.g. for nuclear relaxation to the polarizability,  $\alpha_{ij}$ , only second derivatives are required). This interesting advantage is exclusive to the AEEP method and allows important savings in computational time.

For linear  $\pi$ -conjugated systems such as that in Fig. 1, i.e. push–pull molecules, the hyperpolarizabilities are

dominated by the  $z$  component along the  $\pi$ -chain axis, so that all other components are ignored. Moreover, assuming that the CT state has a large dipole moment,  $\mu_{\text{CT}}$ , as compared with that found in the VB state, it is safe to ignore the permanent dipole moment of the VB state. As a result, in order to consider the response of a conjugated donor–acceptor polyene in the presence of an electric static field  $\varepsilon$ , along the  $z$  direction, the energy  $V_0$  in Eqn (4) can be substituted by  $V_0 - \mu_{\text{CT}}\varepsilon$ .<sup>8,9</sup>

We now start to apply the AEEP method to the push–pull molecules.  $U_{\text{gr}}(q)$  in Eqn (4) is expanded as a double power series in terms of  $\varepsilon$  and BLA coordinate,  $q$ , along the  $z$  direction:

$$U_{\text{gr}}(q, \varepsilon) = \sum_{n=0} \sum_{m=0} a_{nm} q^n \varepsilon^m \quad (8)$$

where

$$a_{nm} = \frac{1}{n!m!} \left[ \frac{\partial^{(n+m)} U_{\text{gr}}(q, \varepsilon)}{\partial q^n \partial \varepsilon^m} \right]_{q_{\text{eq}}, \varepsilon=0} \quad (9)$$

is the coefficient of the power series expansion evaluated in equilibrium geometry at zero field,  $q_{\text{eq}}$ .

In Eqn (8), the electronic contributions along the  $\pi$ -chain axis to the zero field case for dipole moment and polarizabilities<sup>1</sup> are represented by the terms  $\mu_z^e = -a_{01}$ ,  $\alpha_{zz}^e = -2a_{02}$ ,  $\beta_{zzz}^e = -6a_{03}$ ,  $\gamma_{zzzz}^e = -24a_{04}$ , while mechanical terms of the potential energy such as force constant,  $K$ , and first anharmonicity,  $f$ , are given by  $K = 2a_{20} = [d^2U_{\text{gr}}(q)/dq^2]_{q_{\text{eq}}, \varepsilon=0}$  [see Eqn (7)] and  $f = 6a_{30} = [d^3U_{\text{gr}}(q, \varepsilon)/dq^3]_{q_{\text{eq}}, \varepsilon=0}$ , respectively. Derivatives for molecular properties can also be obtained from the expansion coefficients, e.g.  $(\partial \mu_z^e / \partial q) = -a_{11}$ ,  $(\partial \alpha_{zz}^e / \partial q)_{q_{\text{eq}}, \varepsilon=0} = -2a_{12}$ ,  $(\partial K / \partial \varepsilon)_{q_{\text{eq}}, \varepsilon=0} = 2a_{21}$ ,  $(\partial^2 \alpha_{zz}^e / \partial q^2)_{q_{\text{eq}}, \varepsilon=0} = -4a_{22}$ ,  $(\partial f / \partial \varepsilon)_{q_{\text{eq}}, \varepsilon=0} = 6a_{31}$ ,  $(\partial \beta_{zzz}^e / \partial q)_{q_{\text{eq}}, \varepsilon=0} = -6a_{13}$  and  $g = [\partial^4 U_{\text{gr}}(q, \varepsilon) / \partial q^4]_{q_{\text{eq}}, \varepsilon=0} = 24a_{40}$ .

In order to take into account the nuclear relaxation second hyperpolarizability,  $\gamma_{zzzz}^{\text{nr}}$ , terms up to  $n+m \leq 4$  are considered in Eqn (8). In this case,  $\gamma_{zzzz}^{\text{nr}}$  includes first- and second-order mechanical anharmonicity ( $a_{30}$  and  $a_{40}$  terms), first- and second-order electrical anharmonicity of the dipole moment ( $a_{21}$  and  $a_{31}$  terms), first-order electrical anharmonicity of polarizability ( $a_{22}$  term) and the harmonicity approximation for the first hyperpolarizability ( $a_{13}$  term).

The problem is then to determine the nuclear relaxation contribution to the electrical properties arisen as consequence of the changes in the equilibrium geometry induced by the applied field. To do this, we begin considering the stationary-point condition to  $U_{\text{gr}}(q, \varepsilon)$  [Eqn (4)]. This property allows us to write an iterative solution to the related equilibrium field-dependent BLA coordinate,  $q_{\text{eq}}(\varepsilon)$ , as<sup>1,2</sup>

$$q_{\text{eq}}(\varepsilon) = -q_1\varepsilon + \left( \frac{a_{21}}{a_{20}}q_1 - \frac{3a_{30}}{2a_{20}}q_1^2 - q_2 \right)\varepsilon^2 + \left\{ \left[ \frac{a_{22}}{a_{20}} - \left( \frac{a_{21}}{a_{20}} \right)^2 \right]q_1 + \left( \frac{9a_{30}a_{21}}{2a_{20}^2} - \frac{3a_{31}}{2a_{20}} \right)q_1^2 + \left[ \frac{2a_{40}}{a_{20}} - \frac{9}{2} \left( \frac{a_{30}}{a_{20}} \right)^2 \right]q_1^3 + \left[ \frac{a_{21}}{a_{20}} - \frac{3a_{30}}{a_{20}}q_1 \right]q_2 - q_3 \right\}\varepsilon^3 + \dots \quad (10)$$

where  $q_1 = a_{11}/2a_{20}$ ,  $q_2 = a_{12}/2a_{20}$  and  $q_3 = a_{13}/2a_{20}$ .

Substituting  $q_{\text{eq}}(\varepsilon)$  into Eqn (8) (with  $n + m \leq 4$ ) leads to a field-dependent potential energy evaluated at the new equilibrium coordinates:

$$U[q_{\text{eq}}(\varepsilon), \varepsilon] = a_{00} + a_{01}\varepsilon + \left( a_{02} - \frac{a_{11}}{2}q \right)\varepsilon^2 + (a_{03} - a_{12}q_1 + a_{21}q_1^2 - a_{30}q_1^3)\varepsilon^3 + (a_{04} - a_{13}q_1 - \frac{a_{12}}{2}q_2 + a_{22}q_1^2 + 2a_{21}q_1q_2 - a_{31}q_1^3 - 3a_{30}q_1^2q_2 - \frac{a_{21}^2q_1^2}{a_{20}} + a_{40}q_1^4 + \frac{3a_{30}a_{21}q_1^3}{a_{20}} - \frac{9a_{30}^2q_1^4}{4a_{20}}) \varepsilon^4 \quad (11)$$

Comparison between Eqns (1) and (11) and subtraction of the purely electronic contribution to  $\gamma_{zzzz}$ , i.e.  $\gamma_{zzzz}^e = -24a_{04}$ , leads to a general definition of the nuclear relaxation second hyperpolarizability:

$$\gamma_{zzzz}^{\text{nr}} = 24 \left( a_{13}q_1 + \frac{a_{12}}{2}q_2 - a_{22}q_1^2 - 2a_{21}q_1q_2 + a_{31}q_1^3 + 3a_{30}q_1^2q_2 + \frac{a_{21}^2}{a_{20}}q_1^2 - a_{40}q_1^4 - \frac{3a_{30}a_{21}}{a_{20}}q_1^3 + \frac{9a_{30}^2}{4a_{20}}q_1^4 \right) \quad (12)$$

It is worth noting that in this expression  $\gamma_{zzzz}^{\text{nr}}$  is a function of the harmonic ( $a_{20}$ ,  $a_{11}$ ,  $a_{12}$  and  $a_{13}$ ) and anharmonics ( $a_{30}$ ,  $a_{21}$ ,  $a_{22}$ ,  $a_{31}$  and  $a_{40}$ ) coefficients. Therefore, the first two terms in Eqn (12) represents the harmonic contributions to  $\gamma_{zzzz}^{\text{nr}}$ , i.e. the so-called DHA assumption.

It is possible to obtain an explicit expression for the  $a_{nm}$  coefficients of  $\gamma_{zzzz}^{\text{nr}}$  in the VB-CT model by using Eqn (4), with  $V_0$  replaced by  $V_0 - \mu_{\text{CT}}\varepsilon$ :

$$a_{20} = \frac{k}{2} \left\{ 1 - \frac{2k\delta^2t^2}{[(V_0 + k\delta q_{\text{eq}})^2 + 4t^2]^{3/2}} \right\} \quad (13)$$

$$a_{30} = \frac{k^3\delta^3t^2(V_0 + k\delta q_{\text{eq}})}{\left[ (V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{5/2}} \quad (14)$$

$$a_{40} = \frac{k^4\delta^4t^2 \left[ t^2 - (V_0 + k\delta q_{\text{eq}})^2 \right]}{\left[ (V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{7/2}} \quad (15)$$

$$a_{11} = \frac{2\mu_{\text{CT}}k\delta t^2}{\left[ (V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{3/2}} \quad (16)$$

$$a_{21} = -\frac{3\mu_{\text{CT}}k^2\delta^2t^2(V_0 + k\delta q_{\text{eq}})}{\left[ (V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{5/2}} \quad (17)$$

$$a_{31} = -\frac{4\mu_{\text{CT}}k^3\delta^3t^2 \left[ t^2 - (V_0 + k\delta q_{\text{eq}})^2 \right]}{\left[ (V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{7/2}} \quad (18)$$

$$a_{12} = \frac{3\mu_{\text{CT}}^2t^2k\delta(V_0 + k\delta q_{\text{eq}})}{\left[ (V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{5/2}} \quad (19)$$

$$a_{13} = \frac{4\mu_{\text{CT}}^3t^2k\delta \left[ (V_0 + k\delta q_{\text{eq}})^2 - t^2 \right]}{\left[ (V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{7/2}} \quad (20)$$

and

$$a_{22} = -\frac{6\mu_{\text{CT}}^2k^2\delta^2t^2 \left[ (V_0 + k\delta q_{\text{eq}})^2 - t^2 \right]}{\left[ (V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{7/2}} \quad (21)$$

Substitution of these expressions in Eqn (12) allows us to identify each term in  $\gamma_{zzzz}^{\text{nr}}$  as a harmonic ( $T_i^{\text{har}}$ ) or anharmonic ( $T_i^{\text{anharm}}$ ) contribution:

$$T_1^{\text{har}} = 24a_{13}q_1 = \left( \frac{4}{K} \right) \left( \frac{\partial \beta_{zzz}^e}{\partial q} \right)_{q_{\text{eq}}, \varepsilon=0} \left( \frac{\partial \mu_z^e}{\partial q} \right)_{q_{\text{eq}}, \varepsilon=0} = 2\gamma_{zzzz}^e \bar{\gamma} \quad (22)$$

$$T_2^{\text{har}} = 12a_{12}q_2 = \left( \frac{3}{K} \right) \left( \frac{\partial \alpha_{zz}^e}{\partial q} \right)_{q_{\text{eq}}, \varepsilon=0}^2 = \gamma_{zzzz}^e \bar{\gamma} R \quad (23)$$

$$T_3^{\text{anharm}} = -24a_{22}q_1^2 = -\left(\frac{6}{K^2}\right)\left(\frac{\partial^2 \alpha_{zz}^e}{\partial^2 q}\right)_{q_{\text{eq}}, \varepsilon=0}\left(\frac{\partial \mu_z^e}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0}^2 \\ = -\left(\frac{3}{2}\right)\gamma_{zzzz}^e \bar{\gamma}^2 \quad (24)$$

$$T_4^{\text{anharm}} = -48a_{21}q_1q_2 \\ = -\left(\frac{1}{2K^2}\right)\left(\frac{\partial \mu_z^e}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0}\left(\frac{\partial \alpha_{zz}^e}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0}\left(\frac{\partial K}{\partial \varepsilon}\right)_{q_{\text{eq}}, \varepsilon=0} \\ = -2\gamma_{zzzz}^e \bar{\gamma}^2 R \quad (25)$$

$$T_5^{\text{anharm}} = 24a_{31}q_1^3 = -\left(\frac{4}{K^3}\right)\left(\frac{\partial f}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0}\left(\frac{\partial \mu_z^e}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0}^3 \\ = \left(\frac{1}{2}\right)\gamma_{zzzz}^e \bar{\gamma}^3 \quad (26)$$

$$T_6^{\text{anharm}} = 72a_{30}q_1^2q_2 = -\left(\frac{6f}{K^3}\right)\left(\frac{\partial \mu_z^e}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0}^2\left(\frac{\partial \alpha_{zz}^e}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0} \\ = \left(\frac{1}{2}\right)\gamma_{zzzz}^e \bar{\gamma}^3 R \quad (27)$$

$$T_7^{\text{anharm}} = 24\left(\frac{a_{21}^2}{a_{20}}\right)q_1^2 = \left(\frac{12}{K^3}\right)\left(\frac{\partial K}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0}^3\left(\frac{\partial \mu_z^e}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0}^2 \\ = \gamma_{zzzz}^e \bar{\gamma}^3 R \quad (28)$$

$$T_8^{\text{anharm}} = -24a_{40}q_1^4 = -\left(\frac{g}{K^4}\right)\left(\frac{\partial \mu_z^e}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0}^4 = -\left(\frac{1}{2}\right)\gamma_{zzzz}^e \bar{\gamma}^4 \\ \quad (29)$$

$$T_9^{\text{anharm}} = -72\left(\frac{a_{30}a_{21}}{a_{20}}\right)q_1^3 \\ = \left(\frac{12f}{K^4}\right)\left(\frac{\partial K}{\partial \varepsilon}\right)_{q_{\text{eq}}, \varepsilon=0}\left(\frac{\partial \mu_z^e}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0}^3 \\ = -\left(\frac{1}{2}\right)\gamma_{zzzz}^e \bar{\gamma}^4 R \quad (30)$$

and

$$T_{10}^{\text{anharm}} = 54\left(\frac{a_{30}^2}{a_{20}}\right)q_1^4 = \left(\frac{3f^2}{2K^5}\right)\left(\frac{\partial K}{\partial \varepsilon}\right)_{q_{\text{eq}}, \varepsilon=0}\left(\frac{\partial \mu_z^e}{\partial q}\right)_{q_{\text{eq}}, \varepsilon=0}^4 \\ = \left(\frac{1}{2}\right)^4 \gamma_{zzzz}^e \bar{\gamma}^5 R \quad (31)$$

In the above expressions,  $\gamma_{zzzz}^e$  is the electronic contribution to the second hyperpolarizability for push-pull molecules obtained from the VB-CT model.<sup>8,9</sup>

$$\gamma_{zzzz}^e = \frac{24\mu_{\text{CT}}^4 t^2 \left[ (V_0 + k\delta q_{\text{eq}})^2 - t^2 \right]}{\left[ (V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{7/2}} \quad (32)$$

and the factors  $\bar{\gamma}$  and  $R$  correspond to

$$\bar{\gamma} = \frac{4kt^2 \delta^2}{\left\{ \left[ (V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{3/2} - 2kt^2 \delta^2 \right\}} \quad (33)$$

and

$$R = \left(\frac{9}{8}\right) \frac{(V_0 + k\delta q_{\text{eq}})^2}{\left[ (V_0 + k\delta q_{\text{eq}})^2 - t^2 \right]} \quad (34)$$

We are now in a position to obtain an interesting connection between nuclear relaxation and electronic contributions to the second hyperpolarizability. By replacement of the terms  $T_i^{\text{har}}$  and  $T_i^{\text{anharm}}$  in Eqn (12), and after some algebraic manipulation, we found that  $\gamma_{zzzz}^{\text{nr}}$  for push-pull molecules can be written as a sum of one harmonic ( $\gamma_{\text{har}}^{\text{nr}}$ ) and an anharmonic ( $\gamma_{\text{anharm}}^{\text{nr}}$ ) part, i.e. as a function of the contributions  $\gamma_{\text{har}}^{\text{nr}} = \gamma_{zzzz}^e \bar{\gamma} \{2 + R\}$  ( $T_i^{\text{har}}$  terms) and  $\gamma_{\text{anharm}}^{\text{nr}} = \gamma_{zzzz}^e \bar{\gamma}^2 \{C + R(2 + \bar{\gamma}C)\}$  ( $T_i^{\text{anharm}}$  terms), respectively. We can also write  $\gamma_{zzzz}^{\text{nr}}$  in a form more instructive that stresses the physical nature of our work, the relationship between  $\gamma_{zzzz}^{\text{nr}}$  and  $\gamma_{zzzz}^e$ :

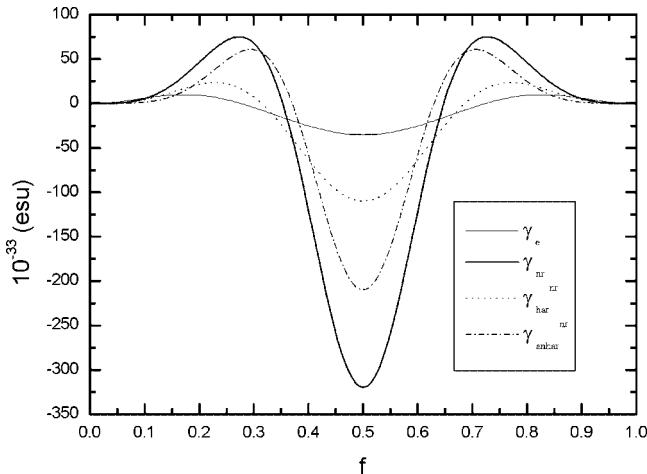
$$\gamma_{zzzz}^{\text{nr}} = \gamma_{zzzz}^e \bar{\gamma} \{2 + R + \bar{\gamma}[C + R(2 + \bar{\gamma}C)]\} \quad (35)$$

where  $C$  is given by

$$C = \left[ \left(\frac{3}{2}\right) + \left(\frac{1}{2}\right)\bar{\gamma} + \left(\frac{1}{2}\right)^4 \bar{\gamma}^2 \right] \quad (36)$$

In summary, by means of Eqn (35), a numerical estimation of the contributions of anharmonics to the nuclear relaxation second hyperpolarizability can be easily carried for  $\pi$ -polyconjugated push-pull molecules.

At this stage, it should be emphasized, however, that the result presented above is only valid when two electronic states are taken into account to calculate the second hyperpolarizability,  $\gamma_{zzzz}$ . Thus, we should expect that Eqn (35) is qualitatively acceptable within the two-state model approximations to the sum-over-state calculations. Therefore,  $\gamma_{zzzz}$ , whose sum-over-state expression contains two-photon contribution so that at least three different electronic states should be included, is expected to deviate from the theoretical predictions of this work in some molecular parameter regions.

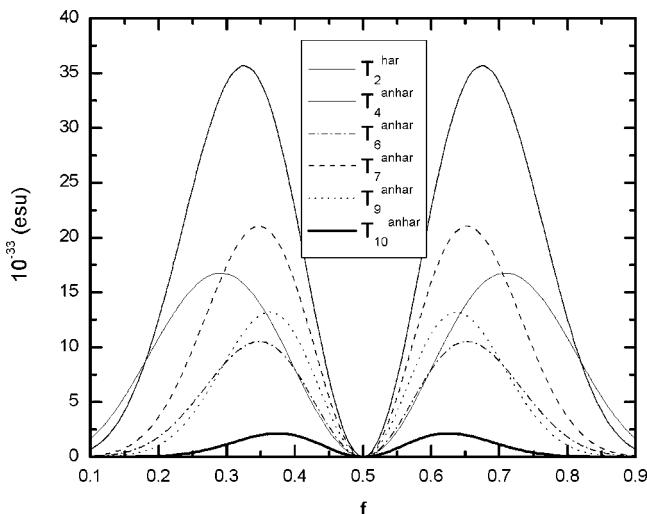


**Figure 2.**  $\gamma_{zzzz}^{nr}$ ,  $\gamma_{har}^{nr}$ ,  $\gamma_{anhar}^{nr}$  and  $\gamma_{zzzz}^e$  as a function of CT character  $f$

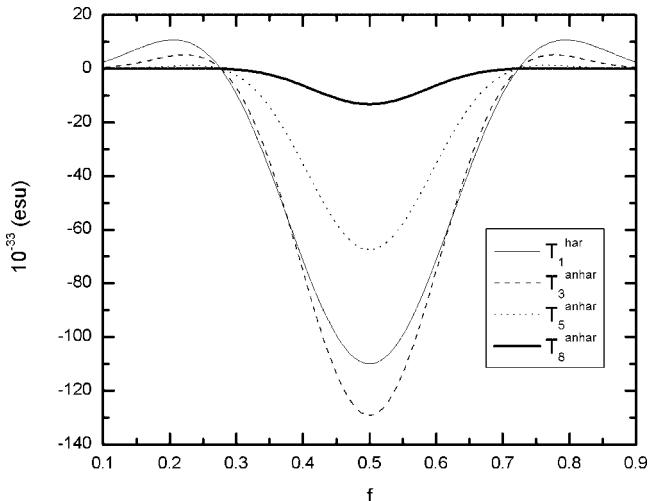
## RESULTS

Equation (5) shows that  $q_{eq}$  and  $f$  are linearly related to each other. Given  $V_0$  and values for the parameters  $k = 33.55 \text{ eV } \text{\AA}^{-2}$ ,  $t = 1.1 \text{ eV}$ ,  $\delta = 0.24 \text{ \AA}$  and  $\mu_{CT} = 32 \text{ D}$ , Eqn (6) leads to a non-linear equation which is solved iteratively for  $q_{eq}$ . These parameters  $k$ ,  $t$ ,  $\delta$ , and  $\mu_{CT}$  are useful for treating molecules with electron donor and acceptor end groups connected by a hexatriene chain.<sup>5,8,9</sup> From the iterative solution, we found that  $q_{eq} = 0$  and  $f = \frac{1}{2}$  when  $V_0 = 0$ , i.e. for the case of degenerate VB and CT states.

The expressions of  $\gamma_{zzzz}^{nr}$ ,  $\gamma_{har}^{nr}$ ,  $\gamma_{anhar}^{nr}$ , and  $\gamma_{zzzz}^e$  are plotted in Fig. 2 as a function of CT character  $f$ . We observe that the results obtained are further proof that contributions (both harmonic and anharmonic) from nuclear relaxation are far from negligible for push-pull polyenes and correlate well (qualitatively) with their electronic



**Figure 3.**  $T_2^{\text{har}}$ ,  $T_4^{\text{anhar}}$ ,  $T_6^{\text{anhar}}$ ,  $T_7^{\text{anhar}}$ ,  $T_9^{\text{anhar}}$  and  $T_{10}^{\text{anhar}}$  terms as a function of CT character  $f$



**Figure 4.**  $T_1^{\text{har}}$ ,  $T_3^{\text{anhar}}$ ,  $T_5^{\text{anhar}}$  and  $T_8^{\text{anhar}}$  terms a function of CT character  $f$

counterpart. In general, we found the result  $|\gamma_{anhar}^{nr}| \sim |\gamma_{har}^{nr}| > |\gamma_{zzzz}^e|$ .

In order to clarify the origins of  $\gamma_{zzzz}^{nr}$ , we also plot  $T_i^{\text{har}}$  and  $T_i^{\text{anhar}}$  terms separately in Figs 3 and 4. As can be seen, the terms  $T_2^{\text{har}}$ ,  $T_4^{\text{anhar}}$ ,  $T_6^{\text{anhar}}$ ,  $T_7^{\text{anhar}}$ ,  $T_9^{\text{anhar}}$  and  $T_{10}^{\text{anhar}}$  (which are proportional to the factor  $R$  and tend to zero at  $f = \frac{1}{2}$ ) are important in the wing region of  $\gamma_{zzzz}^{nr}$ , whereas the  $T_1^{\text{har}}$ ,  $T_3^{\text{anhar}}$ ,  $T_5^{\text{anhar}}$  and  $T_8^{\text{anhar}}$  terms dominates around  $f = \frac{1}{2}$ .

## CONCLUSIONS

We have presented an exact analytical expression of  $\gamma_{zzzz}^{nr}$  for push-pull molecules obtained from the AEEP method beyond the hypothesis of the double harmonic approximation. The results obtained show that anharmonicity plays a relevant role in determining the nuclear relaxation contribution to  $\gamma_{zzzz}$ . A numerical estimation (for the case of hexatriene chain) shows that this contribution is of the same order of magnitude as for the purely harmonic situation and larger than for the electronic case.

Note that the  $T_1^{\text{har}}$  term contains both the IR (derivatives of  $\mu_z^e$ ) and hyper-Raman (derivatives of  $\beta_{zzz}^e$ ) terms, whereas the  $T_1^{\text{har}}$  term is associated with Raman intensity (Herzberg-Teller terms) only. Therefore, the contributions to  $\gamma_{zzzz}^{nr}$  are of two kinds: one comes from simultaneous activity of a band in IR and hyper-Raman spectra, the second from simple Raman activity.<sup>2,7</sup> These spectroscopic measurements may be used to obtain an estimate of the  $T_i^{\text{anhar}}$  terms related to  $\gamma_{anhar}^{nr}$  [Eqns (24)–(31)].

Finally, this paper is a contribution to the debated problem of the relative importance of electronic and nuclear contributions to molecular hyperpolarizabilities in organic conjugated molecules. We hope that the analytical treatment described in this paper may be regarded as a useful starting point for further investigations.

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