

Anharmonic contributions to the nuclear relaxation first hyperpolarizability for push–pull molecules

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ABSTRACT: The nuclear relaxation first hyperpolarizability of a push–pull molecule was studied using the simple valence-bond charge-transfer model and analytical evaluation of electrical properties method. A relationship between the nuclear relaxation and electronic contributions to the first hyperpolarizability was derived, which incorporates the harmonic and anharmonic terms associated with the ground-state potential energy. We show that the anharmonic contribution is as important as that of the harmonic contribution and it follows the trend of the electronic contribution. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: anharmonics; nuclear relaxation; first hyperpolarizability; push–pull molecules; valence-bond charge-transfer model

INTRODUCTION

When a molecule is placed under the stimulus of a static electric field, its electronic cloud is modified, its equilibrium geometry will relax to a new field-dependent equilibrium position and the same field alters the potential energy for nuclear motion about the new equilibrium position.^{1,2} All these induced changes can be explained in terms of electronic, nuclear relaxation and vibrational contributions to the electric properties (polarizabilities).

The effect of an applied field on the potential energy of a molecule, $U(q, \varepsilon)$, can be expressed using the Taylor series:

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

where $U(q, 0)$ is the energy in the absence of the field, μ_i is the i th Cartesian component of the dipole moment, ε_i are the x , y and z components of the static electric field, ε , and α_{ij} , β_{ijk} and γ_{ijkl} are the first-, second- and third-order polarizability tensor, respectively.

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Theoretically, if the electrical and vibrational anharmonicities associated with $U(q, 0)$ are ignored, i.e. the so-called hypothesis of the double harmonic approximation (DHA),² the polarizabilities are due entirely to the electronic (e) and nuclear relaxation (nr) contributions.

Several authors have found experimental evidence^{3–5} of nuclear contributions to electrical properties. In particular, Castiglioni *et al.*³ presented a theoretical justification, based on a valence-bond and charge-transfer (VB–CT) model⁶ and the DHA hypothesis, for the recently observed close resemblance between the first-order electronic hyperpolarizability, β_{zzz}^e , and its nuclear relaxation contribution, β_{zzz}^{nr} , on several classes of π -polyconjugated molecules. Kim *et al.*⁷ also applied the VB–CT model for push–pull molecules and the DHA assumption to obtain a relationship between β_{zzz}^{nr} and β_{zzz}^e , to confirm that their magnitudes are similar. Consequently, IR and Raman measurements can be used directly to calculate β_{zzz}^{nr} and to estimate the magnitude of β_{zzz}^e . Bishop *et al.*⁸ found several parameter-independent relations between nuclear relaxation and electronic hyperpolarizabilities, based on the VB–CT model and DHA hypothesis. However, *ab initio* computational results are in disagreement with these parameter-independent relations. As a secondary result of the *ab initio* calculations, they have found cases where β_{zzz}^{nr} is larger than β_{zzz}^e .

A method to evaluate nuclear relaxation and vibrational contributions to the static electrical properties of polyatomic molecules was presented by Luis *et al.*¹ as applied to water and pyridine. The method, named analytical evaluation of electrical properties (AEEP), was deduced from a double power series expansion on the potential energy of a given chemical system with

respect to normal coordinates, field strength or both. Only one calculation of such derivatives in the field-free equilibrium geometry is required. This energy expansion also includes the mechanical anharmonicity associated with potential energy and electrical anharmonicity for dipole moment, polarizability, first hyperpolarizability, etc. The accuracy of the AEEP method is determined only by the quality of the wavefunction used to describe the molecular system. The method predicts the order of the necessary derivatives required to estimate a specific nuclear contribution (e.g. for the nuclear relaxation contribution to the polarizability, α_{ij} , only second derivatives are required). This interesting feature is exclusive to AEEP method and allows important savings in computational time. More recently, Luis *et al.*⁹ extended the AEEP method to consider the determination of frequency-dependent nuclear relaxation and vibrational hyperpolarizabilities for π -conjugated molecules.

In this work, we investigated how β_{zzz}^{nr} can be derived without using the DHA hypothesis by applying the AEEP method to push-pull polyenes. As a consequence, a relationship between the nuclear relaxation (harmonic and anharmonic) contribution and its electronic counterpart was obtained.

The theoretical background on the VB-CT model for push-pull is summarized in the next section. In the

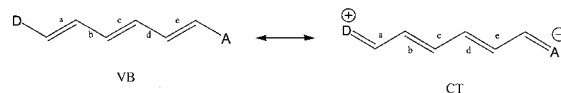


Figure 1. VB and CT structures for a push-pull molecule

CT configuration in the ground state is determined by the relative energy of Ψ_{VB} and Ψ_{CT} on Ψ_{gr} , the coupling between them, the change in dipole moments and the solvent polarity.

The Hamiltonian matrix describing a linear push-pull polyene with a relevant vibrational mode, q , is given by

$$H = \begin{bmatrix} (1/2)k(q - q_{VB}^0)^2 & -t \\ -t & V_0 + (1/2)k(q - q_{CT}^0)^2 \end{bmatrix} \quad (3)$$

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_{CT}^0 and q_{VB}^0 (with $q_{VB}^0 = -q_{CT}^0$) 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 is given by

$$U_{gr}(q) = \frac{V_0 + (k/2) \left[(q - q_{VB}^0)^2 + (q - q_{CT}^0)^2 \right] - \sqrt{(V_0 + k\delta q)^2 + 4t^2}}{2} \quad (4)$$

subsequent section, we present the AEEP method as applied to push-pull molecules. In the same section, we show how β_{zzz}^{nr} and β_{zzz}^e are related. Finally, the results of this work and some speculations about future work are summarized.

THE VB-CT MODEL FOR PUSH-PULL MOLECULES

The simple VB-CT model⁶ assumes that the electronic ground state wavefunction, Ψ_{gr} , the molecule and all its properties can be described using the linear combination of two orthogonal wavefunctions representing two valence-bond electronic configurations (or resonant structures):

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

where the base function Ψ_{VB} corresponds to a neutral (VB) structure (no charge transfer from donor to acceptor) and Ψ_{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, as shown in Fig. 1. The fraction f of the

where $\delta = q_{VB}^0 - q_{CT}^0$.

As assumed by several authors,^{3,6,7} we have considered that the relevant vibrational coordinate, q , is identical with that of the bond length alternation (BLA) coordinate, which is located along the π -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 Ψ_{VB} and Ψ_{CT} represent alternative resonant descriptions of the intervening polyene unit, the increase of f from 0 to 1 will change 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).⁶ Consequently, for the donor-acceptor hexatrienes the BLA changes from -0.12 to 0.12 Å as the CT fraction f goes from 0 to 1.

Using the expression for $U_{gr}(q, 0)$ in Eqn. (4), we can easily verify that the equilibrium BLA coordinate, q_{eq} , obtained by resolving the equation $dU_{gr}(q, 0)/dq = 0$ at q_{eq} , can be written as

$$q_{eq} = q_{VB}^0 - \delta f \quad (5)$$

where f is the squared coefficient corresponding to the Ψ_{CT} function in the electronic ground-state wavefunction, Ψ_{gr} , evaluated at q_{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, we derive the force constant of the adiabatic potential energy curve for the ground state, $U_{\text{gr}}(q, 0)$, from Eqn. (4):

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

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

It should be emphasized, however, that the VB–CT model makes drastic approximations in the description of the chemical–physical characteristics of the push–pull molecules. Consequently, the numerical results that the model render are not fully reliable and errors can be large for those molecules where the oversimplifications introduced in the model are more dramatic.⁸ However, in general, this model has been proven to be useful in the interpretation of several experimental findings concerning the non-linear optics behavior of push–pull molecules⁶ and its evolution in solvents of different polarity.⁵ Moreover, the VB–CT model clarifies the origin of the large nuclear relaxation (harmonic) contribution to β_{zzz} .⁷

THE AEEP METHOD APPLIED TO PUSH–PULL MOLECULES

In this section we apply the AEEP method to π -conjugated organic molecules. Since for push–pull molecules the CT state has a large dipole moment, μ_{CT} , compared with that in the VB state, it is safe to ignore the permanent dipole moment of the VB state. In consequence, and in order to consider the response of this polyene in the presence of an electrostatic field ε , the energy parameter V_0 in Eqn. (4) may be substituted by $V_0 - \mu_{\text{CT}}\varepsilon$.⁶ Thus, following the AEEP method, Eqn. (4) can be expanded as a double power series in terms of ε and the BLA coordinate along the π -chain axis (z direction):

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

The a_{nm} coefficients of the power series expansion are given by

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

and are evaluated in equilibrium geometry at zero field, $\varepsilon = 0$. Terms up to $n + m \leq 4$ are considered in the

expansion of the potential energy. For this case, $U_{\text{gr}}(q, \varepsilon)$ 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). Using this level of truncation for $U_{\text{gr}}(q, \varepsilon)$, we are able to obtain a complete evaluation of nuclear relaxation contribution to the first hyperpolarizability, β_{zzz} .

Next we determine the nuclear relaxation contribution to the first hyperpolarizability. As discussed in the first section, this contribution is due to the change in the equilibrium geometry induced by the applied field.^{2,3} Thus, from the stationary-point condition to $U_{\text{gr}}(q, \varepsilon)$, the following iterative solution to the equilibrium field-dependent BLA coordinate, $q_{\text{eq}}(\varepsilon)$, is obtained:¹

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

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, $U_{\text{gr}}[q_{\text{eq}}(\varepsilon), \varepsilon]$, evaluated at the new equilibrium coordinates, which includes both the electronic and nuclear (harmonic and anharmonic) contributions:

$$\begin{aligned} U_{\text{gr}}[q_{\text{eq}}(\varepsilon), \varepsilon] = & a_{00} + a_{01}\varepsilon + \left(a_{02} - \frac{a_{11}}{2} q \right) \varepsilon^2 \\ & + (a_{03} - a_{12}q_1 + a_{21}q_1^2 - a_{30}q_1^3) \varepsilon^3 + \dots \quad (11) \end{aligned}$$

Comparison between this equation and the Taylor series [Eqn. (1)] and subtraction of the purely electronic contribution to $\beta_{\text{zzz}}^{\text{e}}$, i.e. the $-6a_{03}$ term,¹ leads to a definition of the nuclear relaxation contribution to the first molecular hyperpolarizability, $\beta_{\text{zzz}}^{\text{nr}}$:

$$\beta_{\text{zzz}}^{\text{nr}} = 6(a_{12}q_1 - a_{21}q_1^2 + a_{30}q_1^3) \quad (12)$$

where the coefficients a_{20} , a_{11} and a_{12} are harmonic and a_{30} and a_{21} represent first-order anharmonic terms. In particular, $a_{20} = K/2$ and $a_{30} = [\partial^3 U_{\text{gr}}(q, \varepsilon) / \partial q^3]_{q_{\text{eq}}, \varepsilon=0}$ are mechanical terms of the potential energy, where as

$a_{11} = -(\partial\mu_z^e/\partial q)_{q_{\text{eq}},\varepsilon=0}$, $a_{22} = -(1/4)(\partial^2\alpha_{zz}^e/\partial q^2)_{q,\varepsilon=0}$, $a_{21} = (\partial K/\partial\varepsilon)_{q_{\text{eq}},\varepsilon=0}$ and $a_{12} = -(1/2)(\partial\alpha_{zz}^e/\partial q)_{q_{\text{eq}},\varepsilon=0}$ are molecular property derivatives.¹

From these expressions, we can write Eqn. (12) as

$$\begin{aligned} \beta_{zzz}^{\text{nr}} = & \frac{3}{K} \left(\frac{\partial\mu_z^e}{\partial q} \right)_{q_{\text{eq}},\varepsilon=0} \left(\frac{\partial\alpha_{zz}^e}{\partial q} \right)_{q_{\text{eq}},\varepsilon=0} \\ & - \frac{3}{K^2} \left(\frac{\partial\mu_z^e}{\partial q} \right)_{q_{\text{eq}},\varepsilon=0}^2 \left(\frac{\partial K}{\partial\varepsilon} \right)_{q_{\text{eq}},\varepsilon=0} \\ & - \frac{1}{K^3} \left[\frac{\partial^3 U_{\text{gr}}(q,\varepsilon)}{\partial q^3} \right]_{q_{\text{eq}},\varepsilon=0} \left(\frac{\partial\mu_z^e}{\partial q} \right)_{q_{\text{eq}},\varepsilon=0}^3 \end{aligned} \quad (13)$$

The last two terms are anharmonic contributions and are omitted when the DHA hypothesis is used.^{2,3,7,11} An interesting feature of Eqn. (13) is that the harmonic contribution (the first term) can be estimated by measuring the IR and Raman spectra and extracting information on $(\partial\mu_z^e/\partial q)_{q_{\text{eq}},\varepsilon=0}$ and $(\partial\alpha_{zz}^e/\partial q)_{q_{\text{eq}},\varepsilon=0}$ from them.^{2,7}

From the field-dependent potential energy for push-pull molecules [Eqn. (4) with $V_0 \rightarrow V_0 - \mu_{\text{CT}}\varepsilon$], it is straightforward now to compute the coefficients in β_{zzz}^{nr} [Eqn. (12)]:

$$a_{11} = \frac{2\mu_{\text{CT}}k\delta t^2}{\left[(V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{3/2}} \quad (14)$$

$$a_{02} = -\frac{\mu_{\text{CT}}^2 t^2}{\left[(V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{3/2}} \quad (15)$$

$$a_{12} = \frac{3\mu_{\text{CT}}^2 t^2 k\delta (V_0 + k\delta q_{\text{eq}})}{\left[(V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{5/2}} \quad (16)$$

and

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

Using the above expressions for the a_{nm} coefficients, the β_{zzz}^{nr} component of the nuclear relaxation contribution to the first hyperpolarizability, β_{zzz} , is given by

$$\beta_{zzz}^{\text{nr}} = \beta_{zzz}^{\text{e}}\beta_{\text{total}} \quad (18)$$

where

$$\beta_{zzz}^{\text{e}} = \frac{6\mu_{\text{CT}}^3 t^2 (V_0 + k\delta q_{\text{eq}})}{\left[(V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{5/2}} \quad (19)$$

corresponds to the electronic first hyperpolarizability of push-pull polyenes calculated using the VB-CT model.⁶ The factor β_{total} in Eqn. (18) is found to be

$$\beta_{\text{total}}(q_{\text{eq}}) = B + \left(\frac{1}{3} \right) B^2 + \left(\frac{1}{27} \right) B^3 \quad (20)$$

where B is the harmonic part for β_{total} :

$$B = \frac{6kt^2\delta^2}{\left[(V_0 + k\delta q_{\text{eq}})^2 + 4t^2 \right]^{3/2} - 2kt^2\delta^2} \quad (21)$$

and the additional terms $B^2/3$ and $B^3/27$ are the anharmonic contributions. Using the AEEP method and VB-CT model, a simple equation is obtained to compute the nuclear relaxation contribution to the first hyperpolarizability of push-pull polyenes. Moreover, this equation shows that the nuclear relaxation contribution, β_{zzz}^{nr} , and its electronic counterparts, β_{zzz}^{e} , are related beyond the DHA supposition.

RESULTS

Equation (5) shows a linear relationship between q_{eq} and f . However, Eqn. (6) leads to a non-linear equation in q_{eq} that can be solved iteratively.⁶⁻⁹ Thus, given V_0 , k , t , δ , μ_{CT} and the initial value for q_{eq} , the self-consistent determination of the coordinate q_{eq} involves the following steps: (i) evaluate the function f according to Eqn. (6); (ii) calculate a value of q_{eq} by means of Eqn. (5); and (iii) repeat steps (i) and (ii) until convergence is achieved. From this iterated value of q_{eq} we calculate B , $(1/3)B^2$, $(1/27)B^3$, β_{total} , β_{zzz}^{e} and β_{zzz}^{nr} as a function of f . Calculations were carried out using the following parameters: $k = 33.55 \text{ eV \AA}^{-2}$, $t = 1.1 \text{ eV}$, $\delta = 0.24 \text{ \AA}$ and $\mu_{\text{CT}} = 32 \text{ D}$. These parameters are useful for treating molecules with electron donor and acceptor end-groups connected by a hexatriene chain.^{6,7}

Figure 2 displays the behavior of B , $(1/3)B^2$, $(1/27)B^3$ and β_{total} as a function of f . The maximum value of β_{total} is 4.67 and corresponds to the degenerate VB and CT states case, i.e. when $V_0 = 0$. It is important to emphasize that this result stems essentially from the contribution of B (harmonic) and $(1/3)B^2$ (anharmonic) terms. Therefore, the $(1/3)B^2$ term represents an important difference between to consider or not the anharmonic contribution to β_{zzz}^{nr} . Moreover, as can be seen in Fig. 3, the important anharmonic contribution to β_{zzz}^{nr} [$\beta_{\text{anhar},1} = (1/3)B^2\beta_{zzz}^{\text{e}}$] is of the same order of magnitude as the harmonic part ($\beta_{\text{har}} = B\beta_{zzz}^{\text{e}}$) and its electronic counterpart (β_{zzz}^{e}). Consequently, the vibrational spectra from IR and Raman measurements can be used directly to calculate β_{har} and to estimate the magnitudes of the anharmonic ($\beta_{\text{anhar},1}$) contribution and β_{zzz}^{e} .

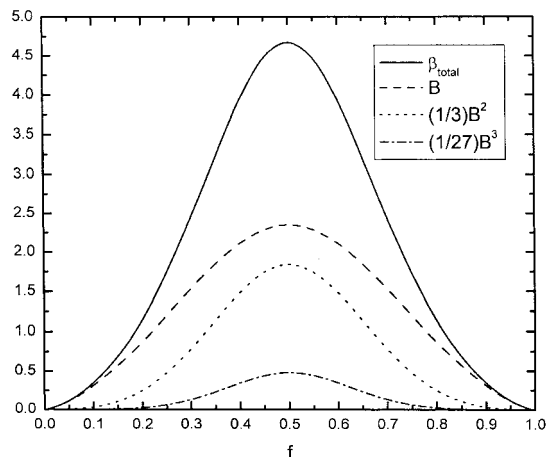


Figure 2. B , $(1/3)B^2$, $(1/27)B^3$ and β_{total} as a function of CT character f

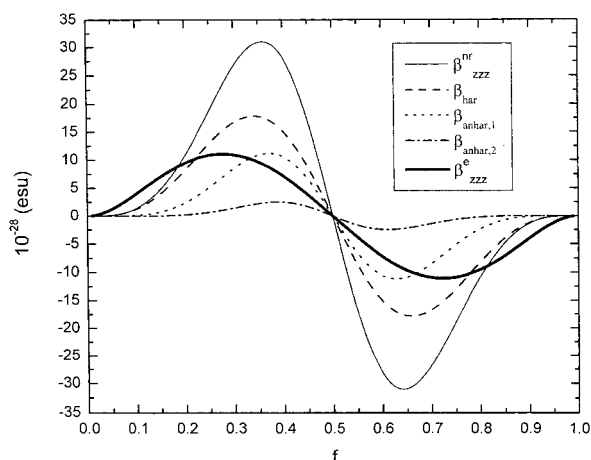


Figure 3. $\beta_{\text{har}} = B \beta_{\text{zzz}}^e$, $\beta_{\text{anhar},1} = (1/3)B^2 \beta_{\text{zzz}}^e$, $\beta_{\text{anhar},2} = (1/27)B^3 \beta_{\text{zzz}}^e$, β_{zzz}^e and $\beta_{\text{zzz}}^{\text{nr}}$ as a function of CT character f

In summary, from these figures we conclude that the most important result of this work is the indication that anharmonicity may play a relevant role in the nuclear relaxation contribution to the first hyperpolarizability.

CONCLUSIONS

We applied the AEEP method to push–pull molecules in order to obtain an analytical expression for $\beta_{\text{zzz}}^{\text{nr}}$. This expression includes the anharmonicity (mechanical and electrical) associated with the nuclear relaxation contribution, which is introduced in the AEEP method through the equilibrium field-dependent BLA coordinate, $q_{\text{eq}}(\varepsilon)$. The results obtained here provide evidence that the anharmonicity is essential in a numerical evaluation of

the nuclear relaxation contribution to $\beta_{\text{zzz}}^{\text{nr}}$. We hope that this paper contributes to clarifying the role of nuclear relaxation in the non-linear optics response of organic molecules. The analytical treatment described in this paper can be also regarded as a useful starting point for further investigations.

The mathematical expression of anharmonic terms in the Eqn. (13), i.e. $-(3/K^2)(\partial\mu_z^e/\partial q)_{q_{\text{eq}},\varepsilon=0}^2 (\partial K/\partial\varepsilon)_{q_{\text{eq}},\varepsilon=0}$ and $-(1/K^3)[\partial^3 U_{\text{gr}}(q,\varepsilon)/\partial q^3]_{q_{\text{eq}},\varepsilon=0} (\partial\mu_z^e/\partial q)_{q_{\text{eq}},\varepsilon=0}^3$, needs to be explored further in connection with theoretical and experimental measurements^{2,7} to verify the results here reported concerning to the anharmonic contribution on $\beta_{\text{zzz}}^{\text{nr}}$.

Finally, the total nuclear contribution to the molecular first hyperpolarizability requires the vibrational contribution at the equilibrium BLA coordinate. This vibrational contribution is a direct consequence of the curvature associated with the potential energy, as originally pointed out by Kern and Matcha.¹¹ In order to calculate this contribution it will be necessary to obtain an expression to fifth-order in the potential energy expansion.¹ Work on this aspect is in progress.

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