

Basis set and electron correlation effects on initial convergence for vibrational nonlinear optical properties of conjugated organic molecules

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Using three typical π -conjugated molecules (1,3,5-hexatriene, 1-formyl-6-hydroxyhexa-1,3,5-triene, and 1,1-diamino-6,6-dinitrohexa-1,3,5-triene) we investigate the level of *ab initio* theory necessary to produce reliable values for linear and nonlinear optical properties, with emphasis on the vibrational contributions that are known to be important or potentially important. These calculations are made feasible by employing field-induced coordinates in combination with a finite field procedure. For many, but not all, purposes the MP2/6-31+G(*d*) level is adequate. Based on our results the convergence of the usual perturbation treatment for vibrational anharmonicity was examined. Although this treatment is initially convergent in most circumstances, a problematic situation has been identified. © 2004 American Institute of Physics. [DOI: 10.1063/1.1667465]

I. INTRODUCTION

Materials that exhibit strong nonlinear optical (NLO) properties are of great importance due to potential applications in communications, medicine, optical computers, and holography. At the molecular level the NLO properties are determined by first and second hyperpolarizabilities. Organic oligomers formed from quasi-one-dimensional π -conjugated organic chains, which are capped with a donor group on one end and an acceptor group on the other, often have large hyperpolarizabilities and are of practical interest for that reason.^{1,2}

Using a clamped nucleus approximation³ the hyperpolarizability can be decomposed into electronic and vibrational contributions. The latter are often as large, or even larger, than their electronic counterparts.^{4–10} Bishop and Kirtman have developed a general perturbation treatment of vibrational hyperpolarizabilities at nonresonant frequencies using a normal coordinate power series expansion for all terms that depend on nuclear geometry.^{11–13} Within the Bishop–Kirtman (BK) method the vibrational hyperpolarizabilities may be separated into pure vibrational (P^v) and zero-point vibrational average (P^{zpv}) components. The P^{zpv} component is defined, as usual, to be the difference between the averaged electronic property in the vibrational ground state and the electronic property evaluated at the equilibrium geometry, whereas P^v includes all other vibrational effects. Based on their power series expansion Bishop and Kirtman organized the expressions for P^v and P^{zpv} into “square bracket”-type terms, which denote the electrical properties involved and the total order of electrical and mechanical anharmonicity. Successively higher-order anharmonic terms involve successively higher-order derivatives (or combinations

of derivatives) of the electrical properties and the pure vibrational potential energy with respect to normal coordinates.

The bottleneck in computing BK vibrational hyperpolarizabilities is the calculation of the higher-order derivatives. In fact, it is computationally prohibitive for medium/large organic molecules to go beyond the lowest-order square bracket terms using flexible basis sets and/or accurate *ab initio* techniques. Fortunately, there exists an alternative approach that avoids explicit determination of the derivatives.^{14–17} It can be shown that the pure vibrational contribution is given exactly by the sum of a so-called nuclear relaxation (NR) term P^{nr} and a so-called C -ZPVA term, P^{c-zpva} :¹⁵

$$P^v = P^{nr} + P^{c-zpva}, \quad (1)$$

where P^{nr} contains the lowest order nonvanishing anharmonicity contributions of each square bracket type and P^{c-zpva} includes all higher-order anharmonicity terms (hence all the higher-order derivatives). The alternative methodology, known as the finite field (FF) method, involves carrying out a geometry optimization for the molecule in the presence of a static electric field. By numerical differentiation of the field-dependent change in the electronic properties due to the shift in equilibrium geometry one can obtain an accurate approximation (see below) for P^{nr} . In an analogous manner the change in P^{zpv} yields an accurate approximation for P^{c-zpva} .

It is of interest at this point to describe the relationship between the various molecular vibrational contributions defined above and the corresponding quantities that occur in the modern solid-state physics literature of nonlinear static field and dynamic electro-optical properties. In the latter discipline it is usual to invoke a classical approximation, which neglects the zero-point vibrational averaging term P^{zpv} . Then the remaining pure vibrational contribution is factored

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into an ionic term and a piezoelectric term.¹⁸ The piezoelectric term is associated with strain and accounts for the acoustic modes that have zero frequency in the infinite periodic solid. In a finite molecule, the analogous modes have nonvanishing frequencies and are treated in the same manner as all other vibrations (a detailed analysis of the role of acoustic modes in molecular calculations has been given elsewhere¹⁹). Although, in principle, the total pure vibrational contribution in periodic solids is included in the sum of the piezoelectric and ionic terms, practical calculations are currently limited to the nuclear relaxation component. This is primarily because of the difficulties in obtaining the higher-order derivatives.²⁰

It can be foreseen that advances made in molecular calculations, particularly with respect to FF treatments, will be transferred to solid-state physics in the not-too-distant future. Practical procedures for carrying out FF calculations in solids using periodic boundary conditions have just recently been presented.^{21–23} Furthermore, the nonclassical ZPVA computation can be made practical by taking advantage of the methodology described in Sec. II of this paper [see, particularly, Eq. (5)]. Although the *C*-ZPVA contribution may be obtained from a finite field treatment of the ZPVA term, it is important to bear in mind that the former (i.e., *C*-ZPVA) can be quite significant even when the latter is not as we will see in the current paper. For both ZPVA and *C*-ZPVA the leading term depends inversely on the square root of the mass, which tends to make the contribution smaller in solid-state oxides, for example, than it is in π -conjugated organic molecules that contain hydrogen. However, anharmonicity parameters can easily play a more decisive role than the mass effect and thus the importance of the ZPVA and *C*-ZPVA contributions needs to be investigated for both types of systems. Finally, there is an important distinction between quasilinear organic molecules and three-dimensional (3D) solids regarding the electronic structure treatment that is employed. Whereas density-functional theory (DFT) is the method of choice for 3D solids, it has been shown that conventional functionals lead to a dramatic overshoot of the (hyper)polarizabilities calculated for quasilinear organic molecules.^{24,25} There have recently been two new formulations of DFT that report a major improvement in the case of the linear polarizability,^{26,27} which leads to some optimism that a reasonably successful treatment of hyperpolarizabilities might not be too far in the future.

Focusing again on medium size organic molecules, we note that the FF method demands substantially less computational resources than are required to calculate the higher-order derivatives that appear in the analytical expressions for P^{nr} and, especially, $P^{(c-zpva)}$.^{28–30} There is a price to pay in accuracy, although it is ordinarily a small price. This is due to the fact that the FF values pertain to the case where all optical frequencies are infinite (i.e., the infinite frequency approximation) or only a static field is present. For typical laser optical frequencies it has been shown^{31–33} that the infinite frequency approximation does not lead to a significant loss of accuracy. However, the error can increase rapidly when the optical frequencies approach the IR region.³¹

It is well known that the perturbation series for the en-

ergy of a harmonic oscillator perturbed by cubic (quartic,...) terms will eventually begin to diverge at some order. Similarly it can be expected that the BK treatment will also fail since it is based on a power series expansion in the normal coordinates. For weakly bound systems, such as $\text{HF}^{34,35}$ or H_2O^{34} dimers, calculations reveal that the perturbation series diverges immediately, which means that this treatment cannot be used in its current form. On the other hand, for typical π -conjugated NLO molecules, it is usually found or assumed that the perturbation series is, at the least, initially convergent.² For a few π -conjugated molecules it turns out that the first- and second-order anharmonic terms make larger contributions to P^{nr} than the harmonic terms.^{10,29,36} However, P^{nr} terminates at second order. In order to monitor the convergence of P^v therefore it was suggested that the behavior of two distinct sequences—which add up to the total—should be separately examined:

$$\begin{aligned} \text{(A)} \quad & P^e, [P^{\text{zpva}}]^{\text{I}}, [P^{\text{zpva}}]^{\text{III}}, \dots, \\ \text{(B)} \quad & P^{\text{nr}}, P^{(c-zpva)(\text{I})}, P^{(c-zpva)(\text{III})}, \dots \end{aligned}$$

In the (A) series the Roman superscript refers to the total order in anharmonicity and the absence of even order reflects the fact that such terms vanish exactly. $P^{(c-zpva)(\text{I})}$ is derived from $[P^{\text{zpva}}]^{\text{I}}$ and contains the second lowest-order anharmonicity terms of each square bracket type in P^v ; $P^{(c-zpva)(\text{III})}$ is derived from $[P^{\text{zpva}}]^{\text{III}}$ and contains the third lowest-order BK terms of each square bracket type of P^v , etc. For typical π -conjugated NLO molecules, $[P^{\text{zpva}}]^{\text{I}}$ is usually small in comparison with P^e . In some instances it is over two-thirds as large^{9,29} but the sequence (A) has always been found thus far to be initially convergent. However, in a previous investigation of seven typical medium size NLO molecules this was not always true for sequence (B).²⁹ For infinite-frequency approximation dynamic hyperpolarizabilities the ratio $P^{(c-zpva)(\text{I})}/P^{\text{nr}}$ was never greater than 0.68, but for static hyperpolarizabilities it was sometimes larger than unity.

In the study just described we obtained very substantial differences between Hartree–Fock (HF)/6-31G and second-order Møller–Plesset perturbation theory MP2/6-31G results, not only for the individual values of the electronic and vibrational hyperpolarizabilities, but also for their relative values. The most pronounced differences were found for $[P^{\text{zpva}}]^{\text{I}}$ and $P^{(c-zpva)(\text{I})}$. This made us doubt the reliability of our MP2/6-31G results and motivated us to investigate the effect of basis set and level of correlation treatment on the calculated P^e and P^{nr} for three representative π -conjugated organic molecules.³⁰ It was found that the 6-31G basis set does not systematically provide even qualitative results. In a few cases even the sign of the contribution changes. However, semiquantitative accuracy was achieved using the 6-31+G(*d*) basis set, (maximum error 17%). Compared with quadratic configuration interaction with single and double excitations (QCISD), MP2 gives a significant fraction of the correlation correction, but does not provide semiquantitative accuracy for P^e or P^{nr} (errors up to 94%). The accuracy of MP2 is far better for the ratio P^{nr}/P^e , in which case the maximum error is 32% for the largest basis set considered. Differences between QCISD and coupled cluster with single

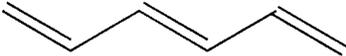
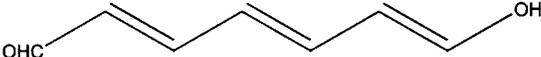
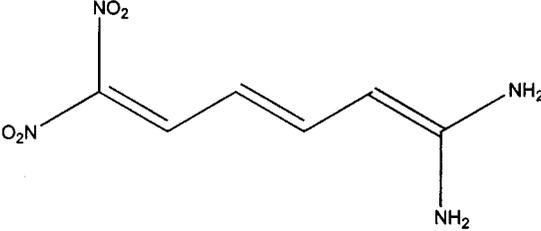
Number	Structure/Formula
I	 1,3,5-Hexatriene
II	 1-Formyl-6-hydroxyhexa-1,3,5-triene
III	 1,1-Diamino-6,6-dinitrohexa-1,3,5-triene

FIG. 1. Structural formula of molecules studied in this paper.

and double excitations (CCSD) values, calculated at the QCISD geometry, were always less than 8%.

From the results of Ref. 30 we know what level of *ab initio* theory we need to use to compute reliable values for P^e and P^{nr} . In order to assess the initial convergence of the two sequences above we also need reliable values of the first-order ZPVA and *C*-ZPVA contributions. Hence the goal of the present paper is to carry out a study of a similar type for $[P^{zpva}]^I$ and $P^{(c-zpva)(I)}$. The latter properties are far more computationally demanding to determine than P^e and P^{nr} . Nevertheless, by using field induced coordinates³⁷ (FIC's) to obtain P^{zpva} and the FF method of Kirtman, Luis, and Bishop¹⁴ to calculate $P^{(c-zpva)(I)}$ we were able to do these calculations. The FIC's constitute a minimum set of coordinates that allow the property to be obtained exactly.^{31,37} In contrast with normal coordinates their number does not increase with the number of the atoms of the system and there are far less than $3N-6$ of them for the molecules considered here. Consequently, this is the first time that the ZPVA and *C*-ZPVA(I) contributions to the hyperpolarizability have been calculated at an *ab initio* level beyond MP2/6-31G for a medium size organic molecule.

Our presentation is organized as follows: Section II summarizes the methodological and computational considerations. It is followed in Sec. III by a discussion of the results for P^e , $[P^{zpva}]^I$, P^{nr} , and $P^{(c-zpva)(I)}$ for three representative π -conjugated organic molecules. Finally, our conclusions are given in Sec. IV.

II. METHODOLOGICAL AND COMPUTATIONAL CONSIDERATIONS

The usual expression for $[P^{zpva}]^I$ is given by

$$[P^{zpva}]^I = \frac{\hbar}{4} \sum_i^{3N-6} \left(\frac{1}{\omega_i} \frac{\partial^2 P}{\partial Q_i^2} \right) - \frac{\hbar}{4} \sum_i^{3N-6} \left(\sum_j^{3N-6} \frac{F_{ijj}}{\omega_j} \right) \frac{1}{\omega_i^2} \frac{\partial P}{\partial Q_i}, \quad (2)$$

where ω_i is the harmonic vibrational frequency of mode i , Q_i is the corresponding mass-weighted normal coordinate, and F_{ijj} is the cubic vibrational force constant defined by $F_{ijj} = (\partial^3 V / \partial Q_i \partial Q_j^2)_{Q=0}$. The first term on the right-hand side of Eq. (2) is first order in electrical anharmonicity, since it involves second (as opposed to first) derivatives of the electrical property with respect to nuclear coordinates, but zeroth-order in mechanical anharmonicity. In the second term the orders are reversed. This term is second-order in mechanical anharmonicity because it contains third derivatives with respect to the vibrational potential energy, which is one order higher than the harmonic force constants (e.g., $F_{jj} = (\partial^2 V / \partial Q_j^2)_{Q=0}$). In either case anharmonicity introduces higher-order derivatives that become increasingly more tedious to determine as the number of normal modes of the chemical system increases.

If we regard the harmonic vibrational force constants as a function of the normal coordinates and the electric field, then Eq. (2) can be also be written as³⁷

$$[P^{zpva}]^I = \frac{\hbar}{4} \sum_i^{3N-6} \left(\frac{1}{\omega_i} \frac{\partial^n \mathcal{F}_{ii}}{\partial F^n} \right) - \frac{\hbar}{4} \sum_i^{3N-6} \left(\sum_j^{3N-6} \frac{1}{\omega_j} \frac{\partial \mathcal{F}_{jj}}{\partial Q_i} \right) \frac{1}{\omega_i^2} \frac{\partial P}{\partial Q_i}, \quad (3)$$

where n is 1 for the dipole moment, 2 for the linear polarizability, 3 for the first hyperpolarizability, and 4 for the second hyperpolarizability. For convenience, the designation of the

TABLE I. Electronic and vibrational polarizabilities and second hyperpolarizabilities of molecule I calculated at the HF level. All quantities are in a.u.

Properties	6-31G ^a	6-31G(d)	6-31+G(d)	6-311+G(d)	6-311+G(d,p)	6-311++G(2d,2p)	6-311++G(2df,2pd)
$\alpha_{\alpha\beta}^e(0;0)^b$	1.42×10^2	1.41×10^2	1.53×10^2	1.52×10^2	1.53×10^2	1.53×10^2	1.53×10^2
$\alpha_{zz}^{zpv}(0;0)$	3.70×10^0	3.68×10^0	4.22×10^0	4.43×10^0	4.66×10^0	4.63×10^0	4.68×10^0
$\alpha_{zz}^{nr}(0;0)^b$	3.13×10^0	3.79×10^0	3.87×10^0	4.03×10^0	4.14×10^0	4.43×10^0	4.37×10^0
$\alpha^{(c-zpva)}(0;0)$	3.08×10^{-1}	3.52×10^{-1}	4.94×10^{-1}	4.36×10^{-1}	4.39×10^{-1}	3.91×10^{-1}	3.63×10^{-1}
$\gamma_{zz}^{zpv}(0;0,0)^b$	5.44×10^4	4.65×10^4	9.10×10^4	8.26×10^4	8.42×10^4	8.31×10^4	8.17×10^4
$\gamma_{zzz}^{zpv}(0;0,0,0)$	9.6×10^2	9.86×10^2	3.8×10^3	4.4×10^3	9.5×10^3	1.02×10^4	1.09×10^4
$\gamma_{zzz}^{nr}(0;0,0,0)^b$	9.14×10^4	9.09×10^4	1.29×10^5	1.23×10^5	1.24×10^5	1.21×10^5	1.22×10^5
$\gamma_{zzz}^{(c-zpva)}(0;0,0,0)$	1.16×10^4	1.27×10^4	1.41×10^4	1.42×10^4	1.23×10^4	1.20×10^4	1.5×10^4
$\gamma_{zzz}^{zpv}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}^b$	2.95×10^4	2.90×10^4	4.20×10^4	4.12×10^4	4.18×10^4	4.07×10^4	4.08×10^4
$\gamma_{zzz}^{(c-zpva)}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}^b$	3.3×10^3	3.26×10^3	3.68×10^3	3.6×10^3	2.7×10^3	3.3×10^3	2.8×10^3
$\gamma_{zzz}^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}^b$	-4.42×10^2	-7.98×10^2	2.64×10^2	3.92×10^1	1.43×10^1	-2.74×10^2	-3.07×10^2
$\gamma_{zzz}^{(c-zpva)}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}^b$	2.75×10^2	-8.09×10^1	-4.6×10^2	-6.1×10^2	-1.12×10^3	1×10^1	8×10^1
$\gamma_{zzz}^{nr}(-\omega; \omega, \omega, -\omega)_{\omega \rightarrow \infty}^b$	6.12×10^4	5.98×10^4	8.03×10^4	7.95×10^4	8.07×10^4	7.95×10^4	7.98×10^4

^aResults taken from Ref. 29 except for $\gamma_{zzz}^{nr}(-\omega; \omega, \omega, -\omega)_{\omega \rightarrow \infty}$.
^bResults were also calculated in Ref. 30 but using the FF method.

components of the electric field F has been suppressed. As shown in Eq. (3) the electrical anharmonicity terms can be computed by taking derivatives of \mathcal{F}_{jj} with respect to the finite field. For large molecules this is computationally cheaper than taking second derivatives of the property with respect to the normal coordinates. Furthermore, if one defines the harmonic FIC associated with the property P by the relation (again, $n=1$ corresponds to the dipole moment, $n=2$ to the linear polarizability, etc.)³⁶

$$\chi_{n,\text{har}} = \sum_{i=1}^{3N-6} \frac{1}{\omega_i^2} \frac{\partial P}{\partial Q_i} Q_i, \quad (4)$$

then Eq. (3) can be simplified to²⁰

$$[P^{\text{zpvva}}]^I = \frac{\hbar}{4} \sum_i^{3N-6} \left(\frac{1}{\omega_i} \frac{\partial^n \mathcal{F}_{ii}}{\partial F^n} \right) - \frac{\hbar}{4} \left(\sum_j^{3N-6} \frac{1}{\omega_j} \frac{\partial \mathcal{F}_{jj}}{\partial \chi_{n,\text{har}}} \right) \frac{1}{\omega_{\chi_{n,\text{har}}}^2} \frac{\partial P}{\partial \chi_{n,\text{har}}}, \quad (5)$$

where $\omega_{\chi_{n,\text{har}}}^2 = (\partial^2 V / \partial \chi_{n,\text{har}}^2)_{Q=0}$. The calculation of $[P^{\text{zpvva}}]^I$ using Eq. (5) requires evaluation of a single derivative of \mathcal{F}_{jj} with respect to the FIC instead of $3N-6$ derivatives with respect to the entire set of normal coordinates as in Eq. (2). In this work $[P^{\text{zpvva}}]^I$ and all the NR contributions except $\gamma_{zzz}^{nr}(0;0,0,0)$ have been computed analytically using harmonic FIC's.³⁶

The static and infinite optical frequency C -ZPVA (hyper)polarizabilities were calculated using the Kirtman–Luis–Bishop (KLB) method.¹⁴ In this treatment the P^{c-zpva} are obtained from the coefficients in a power series expansion of $\Delta P^{\text{zpvva}} = P^{\text{zpvva}}(\mathbf{R}_F, \mathbf{F}) - P^{\text{zpvva}}(\mathbf{R}_0, 0)$ as a function of a static electric field \mathbf{F} . Here \mathbf{R}_F denotes the equilibrium geometry in the presence of the electric field and the expansions may be written as

$$\Delta \mu_{\alpha}^{\text{zpvva}} = a_{\alpha\beta}^{1,\text{zpvva}} F_{\beta} + \frac{b_{\alpha\beta\gamma}^{1,\text{zpvva}}}{2} F_{\beta} F_{\gamma} + \frac{g_{\alpha\beta\gamma\delta}^{1,\text{zpvva}}}{6} F_{\beta} F_{\gamma} F_{\delta} + \dots, \quad (6)$$

$$\Delta \alpha_{\alpha\beta}^{\text{zpvva}} = b_{\alpha\beta\gamma}^{2,\text{zpvva}} F_{\gamma} + \frac{g_{\alpha\beta\gamma\delta}^{2,\text{zpvva}}}{2} F_{\gamma} F_{\delta} + \dots, \quad (7)$$

$$\Delta \beta_{\alpha\beta\gamma}^{\text{zpvva}} = g_{\alpha\beta\gamma\delta}^{3,\text{zpvva}} F_{\delta} + \dots, \quad (8)$$

where

$$a_{\alpha\beta}^{1,\text{zpvva}} = \alpha_{\alpha\beta}^{\text{zpvva}}(0;0) + \alpha_{\alpha\beta}^{c-\text{zpvva}}(0;0), \quad (9)$$

$$b_{\alpha\beta\gamma}^{1,\text{zpvva}} = \beta_{\alpha\beta\gamma}^{\text{zpvva}}(0;0,0) + \beta_{\alpha\beta\gamma}^{c-\text{zpvva}}(0;0,0), \quad (10)$$

$$g_{\alpha\beta\gamma\delta}^{1,\text{zpvva}} = \gamma_{\alpha\beta\gamma\delta}^{\text{zpvva}}(0;0,0,0) + \gamma_{\alpha\beta\gamma\delta}^{c-\text{zpvva}}(0;0,0,0), \quad (11)$$

$$b_{\alpha\beta\gamma}^{2,\text{zpvva}} = \beta_{\alpha\beta\gamma}^{\text{zpvva}}(0;0,0) + \beta_{\alpha\beta\gamma}^{c-\text{zpvva}}(-\omega; \omega, 0)_{\omega \rightarrow \infty}, \quad (12)$$

$$g_{\alpha\beta\gamma\delta}^{2,\text{zpvva}} = \gamma_{\alpha\beta\gamma\delta}^{\text{zpvva}}(0;0,0,0) + \gamma_{\alpha\beta\gamma\delta}^{c-\text{zpvva}}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}, \quad (13)$$

and

$$g_{\alpha\beta\gamma\delta}^{3,\text{zpvva}} = \gamma_{\alpha\beta\gamma\delta}^{\text{zpvva}}(0;0,0,0) + \gamma_{\alpha\beta\gamma\delta}^{c-\text{zpvva}}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}. \quad (14)$$

TABLE II. Electronic and vibrational polarizabilities and second hyperpolarizabilities of molecule I calculated at the MP2 and QCISD levels. All quantities are in a.u.

Properties	6-31G ^a	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)	6-311+G(<i>d</i>)	6-311++G(<i>d,p</i>)	6-311++G(<i>2d,2p</i>)	QCISD 6-31G
$\alpha_{zz}^e(0;0)^b$	1.25×10^2	1.40×10^2	1.30×10^2	1.45×10^2	1.45×10^2	1.46×10^2	1.48×10^2	1.18×10^2
$\alpha_{zz}^{zpv}^e(0;0)$	9.1×10^{-1}	1.68×10^0	1.28×10^0	2.01×10^0	2.31×10^0	2.76×10^0	2.95×10^0	1.64×10^0
$\alpha_{zz}^{nr}(0;0)^b$	1.82×10^0	1.95×10^0	2.47×10^0	2.55×10^0	2.64×10^0	2.67×10^0	2.89×10^0	1.52×10^0
$\alpha_{zz}^{(c-zpva)(I)}(0;0)$	1.64×10^{-1}	3.02×10^{-1}	1.14×10^{-1}	2.97×10^{-1}	3.09×10^{-1}	7.65×10^{-1}	c	1.61×10^{-1}
$\gamma_{zzzz}^e(0;0,0,0)^b$	1.56×10^5	2.53×10^5	1.27×10^5	2.15×10^5	2.01×10^5	2.03×10^5	1.93×10^5	1.05×10^5
$\gamma_{zzzz}^{zpv}^e(0;0,0,0)$	1.7×10^4	2.48×10^4	1.35×10^4	2.28×10^4	2.3×10^4	3.2×10^4	3.0×10^4	6.52×10^3
$\gamma_{zzzz}^{nr}(0;0,0,0)^b$	3.71×10^4	6.35×10^4	4.35×10^4	7.24×10^4	7.25×10^4	7.25×10^4	7.68×10^4	3.39×10^4
$\gamma_{zzzz}^{(c-zpva)(I)}(0;0,0,0)$	1.1×10^3	4.3×10^3	1.60×10^3	4×10^3	6×10^3	2.2×10^4	c	3.9×10^3
$\gamma_{zzzz}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}^b$	1.46×10^4	2.41×10^4	1.69×10^4	2.75×10^4	2.74×10^4	2.78×10^4	2.88×10^4	1.20×10^4
$\gamma_{zzzz}^{(c-zpva)(I)}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}^b$	5×10^3	1.98×10^3	5.3×10^2	4×10^2	1.8×10^3	1.0×10^4	c	2.3×10^3
$\gamma_{zzzz}^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}^b$	2.27×10^3	4.02×10^3	1.79×10^3	3.51×10^3	3.25×10^3	3.39×10^3	3.10×10^3	1.34×10^3
$\gamma_{zzzz}^{(c-zpva)(I)}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}^b$	-4.4×10^1	1.03×10^3	6.4×10^2	-7.4×10^2	1.9×10^3	2.9×10^3	c	3.0×10^2
$\gamma_{zzzz}^{nr}(-\omega; \omega, \omega, -\omega)_{\omega \rightarrow \infty}^b$	2.04×10^4	3.24×10^4	2.73×10^4	4.13×10^4	4.22×10^4	4.25×10^4	4.55×10^4	1.93×10^4

^aResults taken from Ref. 29 except for $\gamma_{zzzz}^{nr}(-\omega; \omega, \omega, -\omega)_{\omega \rightarrow \infty}$.

^bAll but 6-311++G(*2d,2p*) results were also calculated in Ref. 30 but using the FF method.

^cValue not calculated.

The subscripts α , β , γ , and δ in Eqs. (6)–(14) refer to the Cartesian axes whereas $\omega \rightarrow \infty$ indicates the infinite optical frequency limit. In our calculations we considered only the major component of each property, i.e., the diagonal component in the longitudinal direction. The field-free and field-dependent [P^{zpv}]^I terms needed to determine the *C*-ZPVA contribution were evaluated using Eq. (5) and the field-dependent geometry optimizations were carried out using our own program which rigorously enforces the Eckart conditions.³⁸ The first term on the right-hand side of Eq. (5) was calculated by numerical differentiation of the field-dependent harmonic vibrational force constants. All numerical differentiations with respect to the field necessary to obtain [P^{zpv}]^I and $P^{(c-zpva)(I)}$ were carried out using fields of ± 0.0001 , ± 0.0002 , ± 0.0004 , ± 0.0008 , ± 0.0016 , ± 0.0032 , ± 0.0064 , ± 0.0128 , and ± 0.0256 a.u. Then, the smallest magnitude field that produced a stable derivative was selected using the table generated by applying the Romberg method.^{2,39} Calculations were performed employing the HF, MP2, and QCISD models as implemented in the GAUSSIAN 98 suite of programs⁴⁰ together with the 6-31G,⁴¹ 6-31+G,^{41,42}

6-31G(*d*),^{41,43} 6-31+G(*d*),^{41–43} 6-311+G(*d*),^{42–45} 6-311++G(*d,p*),^{42–45} 6-311++G(*2d,2p*),^{42–46} and 6-311++G(*2df,2pd*)^{42–46} basis sets.

III. RESULTS AND DISCUSSION

In order to complement our previous investigation³⁰ concerning the effect of basis sets and electron correlation on the calculated P^e and P^{nr} we chose the same three representative molecules (see Fig. 1): 1,3,5-hexatriene (I), 1-formyl-6-hydroxyhexa-1,3,5-triene (II), and 1,1-diamino-6,6-dinitrohexa-1,3,5-triene (III). I is nonpolar; II is polar with a dominant valence bond ground state; and III is polar with a ground state that has mixed valence bond-charge transfer character.⁴⁷ Tables I–VI summarize the results obtained for the longitudinal component of P^e , [P^{zpv}]^I, P^{nr} , and $P^{(c-zpva)(I)}$ in the case of molecules I and II, respectively. Tables VII and VIII show corresponding quantities for molecule III except that $P^{(c-zpva)(I)}$ has been omitted because the large basis set calculations proved too time consuming. Even

TABLE III. Electronic and vibrational polarizabilities and first hyperpolarizabilities of molecule II calculated at the HF level. All quantities are in a.u.

Properties	6-31G ^a	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)	6-311+G(<i>d</i>)	6-311++G(<i>d,p</i>)	6-311++G(<i>2d,2p</i>)	6-311++G(<i>2df,2pd</i>)
$\alpha_{zz}^e(0;0)^b$	2.11×10^2	2.24×10^2	2.02×10^2	2.15×10^2	2.13×10^2	2.14×10^2	2.14×10^2	2.14×10^2
$\alpha_{zz}^{zpv}^e(0;0)$	3.46×10^0	4.27×10^0	3.46×10^0	4.22×10^0	4.40×10^0	4.60×10^0	4.70×10^0	4.78×10^0
$\alpha_{zz}^{nr}(0;0)^b$	3.84×10^1	4.15×10^1	3.87×10^1	4.20×10^1	4.25×10^1	4.21×10^1	4.22×10^1	4.22×10^1
$\alpha_{zz}^{(c-zpva)(I)}(0;0)$	6.68×10^0	7.10×10^0	6.55×10^0	7.63×10^0	1.06×10^1	1.99×10^1	6.93×10^0	c
$\beta_{zzzz}^e(0;0,0,0)^b$	1.79×10^3	2.11×10^3	1.50×10^3	1.79×10^3	1.71×10^3	1.70×10^3	1.59×10^3	1.57×10^3
$\beta_{zzzz}^{zpv}^e(0;0,0,0)$	-8.78×10^1	-9.37×10^1	-8.1×10^1	-8.21×10^1	-9.88×10^1	-1.09×10^2	-7.99×10^1	-7.4×10^1
$\beta_{zzzz}^{nr}(0;0,0,0)^b$	3.96×10^3	4.64×10^3	3.81×10^3	4.50×10^3	4.52×10^3	4.43×10^3	4.34×10^3	4.36×10^3
$\beta_{zzzz}^{(c-zpva)(I)}(0;0,0)$	-1.1×10^3	-1.41×10^3	-1.25×10^3	-1.70×10^3	-3.45×10^3	-1.11×10^4	-1.31×10^3	c
$\beta_{zzzz}^{nr}(-\omega; \omega, 0)_{\omega \rightarrow \infty}^b$	1.11×10^3	1.29×10^3	1.04×10^3	1.22×10^3	1.21×10^3	1.19×10^3	1.16×10^3	1.17×10^3
$\beta_{zzzz}^{(c-zpva)(I)}(-\omega; \omega, 0)_{\omega \rightarrow \infty}^b$	8.32×10^1	7.6×10^1	8.54×10^1	9.16×10^1	7.64×10^1	1.09×10^2	5.63×10^1	c

^aResults taken from Ref. 29 except for $\beta_{zzzz}^{nr}(-\omega; \omega, \omega, -\omega)_{\omega \rightarrow \infty}$.

^b6-31+G, 6-31G(*d*), 6-31+G(*d*), and 6-311+G(*d*) results were also calculated in Ref. 30 but using the FF method.

^cValue not calculated.

TABLE IV. Electronic and vibrational second hyperpolarizabilities of molecule II calculated at the HF level. All quantities are in a.u.

Properties	6-31G ^a	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)	6-311+G(<i>d</i>)	6-311++G(<i>d,p</i>)	6-311++G (2 <i>d</i> ,2 <i>p</i>)	6-311++G (2 <i>df</i> ,2 <i>pd</i>)
$\gamma_{zzz}^e(0;0,0,0)^b$	1.96×10^5	2.38×10^5	1.59×10^5	1.95×10^5	1.85×10^5	1.84×10^5	1.74×10^5	1.71×10^5
$\gamma_{zzz}^{zpv}(0;0,0,0)$	-3.8×10^3	-7.6×10^3	-2.8×10^3	-5×10^3	-5.1×10^3	-8.22×10^3	-5.16×10^3	-4.0×10^3
$\gamma_{zzz}^{nr}(0;0,0,0)^b$	7.02×10^5	8.66×10^5	6.75×10^5	8.26×10^5	8.43×10^5	8.35×10^5	8.18×10^5	7.54×10^5
$\gamma_{zzz}^{(c-zpva)(I)}(0;0,0,0)$	1.2×10^6	1.2×10^6	7.50×10^5	1.31×10^6	3.1×10^6	1.24×10^7	1.1×10^6	c
$\gamma_{zzz}^{nr}(-\omega;\omega,0,0)_{\omega \rightarrow \infty}^b$	1.87×10^5	2.28×10^5	1.70×10^5	2.07×10^5	2.03×10^5	2.01×10^5	1.93×10^5	1.92×10^5
$\gamma_{zzz}^{(c-zpva)(I)}(-\omega;\omega,0,0)_{\omega \rightarrow \infty}$	1×10^4	7.2×10^3	-8.5×10^2	-1.1×10^3	7.8×10^3	-1.8×10^4	8.2×10^3	c
$\gamma_{zzz}^{nr}(-2\omega;\omega,\omega,0)_{\omega \rightarrow \infty}^b$	2.52×10^4	3.24×10^4	2.06×10^4	2.61×10^4	2.47×10^4	2.42×10^4	2.13×10^4	2.05×10^4
$\gamma_{zzz}^{(c-zpva)(I)}(-2\omega;\omega,\omega,0)_{\omega \rightarrow \infty}$	3.8×10^3	4.98×10^3	2.6×10^3	2.10×10^3	3.2×10^3	1.12×10^4	2.9×10^3	c
$\gamma_{zzz}^{nr}(-\omega;\omega,\omega,-\omega)_{\omega \rightarrow \infty}^b$	1.82×10^5	2.13×10^5	1.65×10^5	1.94×10^5	1.92×10^5	1.92×10^5	1.88×10^5	1.88×10^5

^aResults taken from Ref. 29 except for $\gamma_{zzz}^{nr}(-\omega;\omega,\omega,-\omega)_{\omega \rightarrow \infty}$.

^b6-31+G, 6-31G(*d*), 6-31+G(*d*), and 6-311+G(*d*) results were also calculated in Ref. 30 but using the FF method.

^cValue not calculated.

without $P^{(c-zpva)(I)}$ some useful conclusions can be drawn from the remaining data. A fairly systematic study of basis set and electron correlation effects on $P^{(c-zpva)(I)}$ was conducted for molecules I and II. The 6-31G results are taken from Ref. 29 while some of the smaller basis sets results for P^e and P^{nr} were also calculated in Ref. 30 but were obtained using the FF method as noted in the tables. For P^{nr} the difference between previous numerical FF calculations and the present analytical treatment using harmonic FIC's is small. Small deviations arise because of numerical errors in calculating the derivatives.

Let us begin by examining $\alpha_{zz}(0;0)$. Much of the following analysis for this property and all the others will be based on the relative magnitude of the various contributions compared to the total value indicated by a superscript *t*. For example, in the case of $\alpha_{zz}(0;0)$ the ratio $|\alpha^e/\alpha^t|$ is always greater than 0.94 for molecule I regardless of the basis set or level of calculation. We conclude that the electronic contribution is dominant for this molecule. While the electronic contribution remains the most important for molecules II and III, the NR contribution is also significant. The ratio $|\alpha^{nr}/\alpha^t|$ obtained at the highest level of calculation for II [MP2/6-311++G(*d,p*)] and III [MP2/6-31+G(*d*)] is 0.13 and 0.38, respectively. On the contrary, $|\alpha^{zpv}/\alpha^t|$ and $|\alpha^{zpv}|/\alpha^t|$ for molecule II are both less than about 0.03 at

the highest level of calculation [MP2/6-31+G(*d*)]. Clearly, the initial convergence is quite satisfactory for $\alpha_{zz}(0;0)$.

There are a couple of additional respects in which the results for $\alpha_{zz}(0;0)$ are worthy of notice. For any given basis set the HF and MP2 values may differ substantially with regard to the magnitude of the individual contributions to a total property value. They are similar to one another, however, as far as the relative importance of the various contributions, i.e., the fraction of the total property value, is concerned. The maximum difference in this fraction is 0.02, 0.07, and 0.15 for molecules I, II, and III, respectively. For molecule I we can also compare MP2/6-31G with QCISD/6-31G. While the maximum difference between the individual MP2 and QCISD contributions is 0.05, the difference in the relative contributions is always less than 0.01. Second, it is interesting to observe that the 6-31G and 6-31+G(*d*) basis sets give similar results for the relative importance of the various contributions at both the Hartree–Fock and MP2 levels. In fact, the largest absolute difference (in all cases at the MP2 level) is 0.01 for molecule I, 0.03 for molecule II, and 0.04 for molecule III.

Due to symmetry, the longitudinal first hyperpolarizability vanishes for molecule I. For molecules II and III we first discuss the NR results. At the HF level $\beta_{zzz}^{nr}(0;0,0)$ yields the

TABLE V. Electronic and vibrational polarizabilities and first hyperpolarizabilities of molecule II calculated at the MP2 level. All quantities are in a.u.

Properties	6-31G ^a	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)	6-311+G(<i>d</i>)	6-311++G(<i>d,p</i>)
$\alpha_{zz}^e(0;0)^b$	2.09×10^2	2.31×10^2	2.15×10^2	2.36×10^2	2.36×10^2	2.35×10^2
$\alpha_{zz}^{zpv}(0;0)$	-2.89×10^{-1}	-9.60×10^{-1}	4.48×10^{-1}	8.53×10^{-1}	5.29×10^0	3.28×10^0
$\alpha_{zz}^{nr}(0;0)^b$	2.62×10^1	2.99×10^1	2.96×10^1	3.41×10^1	3.67×10^1	3.71×10^1
$\alpha_{zz}^{(c-zpva)(I)}(0;0)$	2.85×10^0	2.61×10^1	1.96×10^0	7.12×10^0	c	c
$\beta_{zzz}^e(0;0,0)^b$	5.05×10^3	6.08×10^3	4.24×10^3	5.12×10^3	4.91×10^3	4.81×10^3
$\beta_{zzz}^{zpv}(0;0,0)$	6.3×10^1	-9.4×10^1	8.9×10^1	6.2×10^1	5.09×10^2	2.4×10^2
$\beta_{zzz}^{nr}(0;0,0)^b$	2.90×10^3	3.73×10^3	3.29×10^3	4.20×10^3	3.34×10^3	2.82×10^3
$\beta_{zzz}^{(c-zpva)(I)}(0;0,0)$	-7.03×10^2	-2.31×10^4	-4.90×10^2	-2.47×10^3	c	c
$\beta_{zzz}^{nr}(-\omega;\omega,0)_{\omega \rightarrow \infty}^b$	9.49×10^2	1.21×10^3	1.06×10^3	1.33×10^3	1.39×10^3	1.37×10^3
$\beta_{zzz}^{(c-zpva)(I)}(-\omega;\omega,0)_{\omega \rightarrow \infty}$	7.00×10^1	8.1×10^2	3.62×10^1	1.55×10^2	c	c

^aResults taken from Ref. 29 except for $\gamma_{zzz}^{nr}(-\omega;\omega,\omega,-\omega)_{\omega \rightarrow \infty}$.

^bAll but 6-311++G(*d,p*) results were also calculated in Ref. 30 but using the FF method.

^cValue not calculated.

TABLE VI. Electronic and vibrational second hyperpolarizabilities of molecule II calculated at the MP2 level. All quantities are in a.u.

Properties	6-31G ^a	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)	6-311+G(<i>d</i>)	6-311++G(<i>d,p</i>)
$\gamma_{zzz}^e(0;0,0)^b$	6.13×10^5	7.58×10^5	4.59×10^5	5.70×10^5	5.42×10^5	5.38×10^5
$\gamma_{zzz}^{ZPVA}(0;0,0)$	2.3×10^4	1.2×10^4	2.2×10^4	1.7×10^4	4.3×10^4	5×10^4
$\gamma_{zzz}^{nr}(0;0,0)^b$	6.48×10^5	9.12×10^5	6.45×10^5	8.67×10^5	8.66×10^5	c
$\gamma_{zzz}^{(c-zpva)(l)}(0;0,0)$	2.9×10^5	3.9×10^7	1.6×10^5	1.9×10^6	c	c
$\gamma_{zzz}^{nr}(-\omega;\omega,0,0)_{\omega \rightarrow \infty}^b$	2.55×10^5	3.45×10^5	2.34×10^5	3.10×10^5	3.03×10^5	2.95×10^5
$\gamma_{zzz}^{(c-zpva)(l)}(-\omega;\omega,0,0)_{\omega \rightarrow \infty}^b$	-1×10^4	-6.64×10^5	9.5×10^3	-1.8×10^4	c	c
$\gamma_{zzz}^{nr}(-2\omega;\omega,\omega,0)_{\omega \rightarrow \infty}^b$	8.06×10^4	1.07×10^5	6.50×10^4	8.53×10^4	8.85×10^4	8.94×10^4
$\gamma_{zzz}^{(c-zpva)(l)}(-2\omega;\omega,\omega,0)_{\omega \rightarrow \infty}^b$	1.7×10^4	9.9×10^4	1.7×10^4	2.8×10^4	c	c
$\gamma_{zzz}^{nr}(-\omega;\omega,\omega,-\omega)_{\omega \rightarrow \infty}$	1.51×10^5	2.06×10^5	1.65×10^5	2.16×10^5	2.19×10^5	2.17×10^5

^aResults taken from Ref. 29 except for $\gamma_{zzz}^{nr}(-\omega;\omega,\omega,-\omega)_{\omega \rightarrow \infty}$.

^bAll but 6-311++G(*d,p*) results were also calculated in Ref. 30 but using the FF method.

^cValue not calculated.

major contribution to $\beta_{zzz}^t(0;0,0)$ [except for molecule II with the 6-311++G(*d,p*) basis which will be discussed later]. In addition, although the dynamic NR hyperpolarizability, $\beta_{zzz}^{nr}(-\omega;\omega,0)_{\omega \rightarrow \infty}$, is smaller than the static value (with the exception of molecule III in the 6-31G basis) it is still larger than $\beta_{zzz}^e(0;0,0)$ for molecule III and about $\frac{2}{3}$ as large as $\beta_{zzz}^e(0;0,0)$ for molecule II. There are major changes in the NR and/or electronic terms upon going from HF to MP2. Most notably, the relative value of β_{zzz}^{nr} with respect to the static β_{zzz}^e is reduced considerably. However, the qualitative picture is similar. Thus for molecule III at the MP2 level $\beta_{zzz}^{nr}(0;0,0)$ remains substantially larger than $\beta_{zzz}^e(0;0,0)$, while $\beta_{zzz}^{nr}(-\omega;\omega,0)_{\omega \rightarrow \infty}$ now becomes comparable in size. In the case of molecule II at the MP2 level, $\beta_{zzz}^{nr}(0;0,0)$ and $\beta_{zzz}^{nr}(-\omega;\omega,0)_{\omega \rightarrow \infty}$ become, respectively, about $\frac{2}{3}$ and $\frac{1}{4}$ as large as the static electronic term. Turning to the ZPVA and, particularly, C-ZPVA results we can see that, in general, they are much more sensitive to basis set than the NR values. Nonetheless, it is clear that $\beta_{zzz}^{ZPVA}(0;0,0)$ is very small compared to $\beta_{zzz}^t(0;0,0)$ and $\beta_{zzz}^e(0;0,0)$ regardless of the method or basis set. We conclude that the initial convergence for sequence (A) is rapid.

The story for sequence (B) is not as simple. In the case of molecule II $\beta_{zzz}^{(c-zpva)(l)}(0;0,0)$ is smaller in magnitude than $\beta_{zzz}^{nr}(0;0,0)$ in most of the calculations. This is not true, however, at the MP2/6-31+G level. We believe that this egregious 6-31+G result is unreliable because the basis set contains relatively too many diffuse functions. In calculating properties other than the energy with a limited basis, the importance of using a “balanced” basis set is well known. For the same reason the HF/6-311+G(*d*) and 6-311++G(*d,p*) values for $\beta_{zzz}^{(c-zpva)(l)}(0;0,0)$ may be considered as spurious. Although these values are correct for the given basis set, we consider the results spurious because they depart so much from the values obtained with the largest basis sets. In this connection we note the utility of the 6-31+G(*d*) basis which appears to be well balanced (by virtue of the generally good agreement with the largest basis sets) and, at the same time, is fairly compact. Using the latter basis the MP2 ratio $|\beta_{zzz}^{(c-zpva)(l)}(0;0,0)/\beta_{zzz}^{nr}(0;0,0)|$ is 0.59. This is considerably larger than the HF result (0.38) because correlation increases the magnitude of the C-ZPVA contribution while keeping the NR contribution essentially the same. With or without correlation, however, an initially convergent (B)

TABLE VII. Electronic and vibrational polarizabilities, first and second hyperpolarizabilities of molecule III calculated at the HF level. All quantities are in a.u.

Properties	6-31G ^a	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)	6-311+G(<i>d</i>)	6-311++G(<i>d,p</i>)	6-311++G(2 <i>d,2p</i>)
$\alpha_{zz}^e(0;0)^b$	3.13×10^2	3.35×10^2	2.75×10^2	2.94×10^2	2.89×10^2	2.91×10^2	2.88×10^2
$\alpha_{zz}^{ZPVA}(0;0)$	1.87×10^0	1.45×10^0	6.18×10^0	7.26×10^0	7.05×10^0	7.09×10^0	6.78×10^0
$\alpha_{zz}^{nr}(0;0)^b$	3.35×10^2	3.77×10^2	3.16×10^2	3.44×10^2	3.22×10^2	3.22×10^2	2.90×10^2
$\beta_{zz}^e(0;0,0)^b$	2.20×10^2	3.09×10^2	2.27×10^3	2.56×10^3	2.37×10^3	2.32×10^3	2.36×10^3
$\beta_{zz}^{ZPVA}(0;0,0)$	-5.04×10^1	-7.8×10^1	-4.00×10^2	-4.85×10^2	-4.18×10^2	-4.23×10^2	-3.53×10^2
$\beta_{zz}^{nr}(0;0,0)$	5.20×10^2	9.87×10^3	9.07×10^4	1.12×10^5	9.95×10^4	9.73×10^4	8.50×10^4
$\beta_{zz}^{nr}(-\omega;\omega,0)_{\omega \rightarrow \infty}^b$	3.25×10^3	3.83×10^3	6.86×10^3	8.26×10^3	7.69×10^3	7.71×10^3	7.41×10^3
$\gamma_{zzz}^e(0;0,0,0)^b$	-2.36×10^5	-2.57×10^5	7.13×10^4	9.98×10^4	1.20×10^5	1.26×10^5	1.48×10^5
$\gamma_{zzz}^{ZPVA}(0;0,0,0)$	7.3×10^4	7.8×10^4	-3.3×10^4	-3.7×10^4	-3.7×10^4	-3.4×10^4	-2.4×10^4
$\gamma_{zzz}^{nr}(0;0,0,0)$	-2.11×10^7	-3.2×10^7	3.9×10^7	5.64×10^7	4.78×10^7	4.41×10^7	c
$\gamma_{zzz}^{nr}(-\omega;\omega,0,0)_{\omega \rightarrow \infty}$	-3.25×10^6	-4.28×10^6	8.33×10^5	1.20×10^6	1.19×10^6	1.15×10^6	1.29×10^6
$\gamma_{zzz}^{nr}(-2\omega;\omega,\omega,0)_{\omega \rightarrow \infty}$	-9.42×10^5	-1.17×10^6	-1.89×10^5	-2.33×10^5	-1.81×10^5	-1.85×10^5	-1.37×10^5
$\gamma_{zzz}^{nr}(-\omega;\omega,\omega,-\omega)_{\omega \rightarrow \infty}^b$	1.82×10^5	2.12×10^5	4.83×10^5	6.08×10^5	5.77×10^5	5.79×10^5	5.84×10^5

^aResults were from Ref. 29 except for $\gamma_{zzz}^{nr}(-\omega;\omega,\omega,-\omega)_{\omega \rightarrow \infty}$.

^b6-31+G, 6-31G(*d*), 6-31+G(*d*), and 6-311+G(*d*) results were also calculated in Ref. 30 but using the FF method.

^cValue not calculated.

TABLE VIII. Electronic and vibrational polarizabilities, first and second hyperpolarizabilities of molecule III calculated at the MP2 level. All quantities are in a.u.

Properties	6-31G ^a	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)
$\alpha_{zz}^e(0;0)^b$	3.75×10^2	4.10×10^2	3.35×10^2	3.69×10^2
$\alpha_{zz}^{c-zpva}(0;0)$	6.85×10^0	8.1×10^0	8.13×10^0	9.9×10^0
$\alpha_{zz}^{nr}(0;0)$	2.79×10^2	2.84×10^2	2.15×10^2	2.34×10^2
$\beta_{zzz}^e(0;0,0)^b$	1.32×10^4	1.58×10^4	9.10×10^3	1.08×10^4
$\beta_{zzz}^{c-zpva}(0;0,0)$	4.2×10^1	3.7×10^2	1.51×10^2	1.4×10^2
$\beta_{zzz}^{nr}(0;0,0)$	6.56×10^4	6.13×10^4	5.52×10^4	6.88×10^4
$\beta_{zzz}^{nr}(-\omega; \omega, 0)_{\omega \rightarrow \infty}$	1.26×10^4	1.43×10^4	8.74×10^3	1.03×10^4
$\gamma_{zzzz}^e(0;0,0,0)^b$	7.15×10^4	3.36×10^5	1.85×10^5	3.13×10^5
$\gamma_{zzzz}^{c-zpva}(0;0,0,0)$	-4.8×10^4	-9×10^3	-6.7×10^4	-3×10^4
$\gamma_{zzzz}^{nr}(0;0,0,0)$	8.4×10^6	5.8×10^7	1.65×10^7	2.72×10^7
$\gamma_{zzzz}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}$	1.17×10^6	1.59×10^6	1.30×10^6	1.82×10^6
$\gamma_{zzzz}^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}$	-3.88×10^5	-2.51×10^5	-8.73×10^4	-1.34×10^5
$\gamma_{zzzz}^{nr}(-\omega; \omega, \omega, -\omega)_{\omega \rightarrow \infty}$	1.87×10^6	2.38×10^6	1.10×10^6	1.39×10^6

^aResults taken from Ref. 29 except for $\gamma_{zzzz}^{nr}(-\omega; \omega, \omega, -\omega)_{\omega \rightarrow \infty}$.

^bResults were also calculated in Ref. 30 but using the FF method.

sequence is obtained. As we have seen in the past, for dynamic processes such as the Pockels effect [i.e., $\beta(-\omega; \omega, 0)$] the initial convergence of sequence (B) is much improved over the static case. Indeed, for molecule II the ratio $|\beta_{zzz}^{(c-zpva)(l)}(-\omega; \omega, 0)_{\omega \rightarrow \infty} / \beta_{zzz}^{nr}(-\omega; \omega, 0)_{\omega \rightarrow \infty}|$ is 0.12 at the MP2/6-31+G(*d*) level and even smaller at the HF/6-31+G(*d*) level since correlation affects the dynamic properties in much the same way as the static properties. In connection with the MP2 calculations it is apparent that the smaller [than 6-31+G(*d*)] basis set results are not reliable.

The vibrational contributions are also of key importance in determining the second hyperpolarizability of the molecules in this study. In order to compute $\gamma_{zzzz}^{nr}(0;0,0,0)$ both harmonic and anharmonic FIC's are needed.³⁶ As a result the FF method¹⁷ utilizes less computational resources (just as it does in the C-ZPVA calculation) and thus it has been used to calculate $\gamma_{zzzz}^{nr}(0;0,0,0)$. Our calculated results (see Tables VII and VIII) show that for molecule III $\gamma_{zzzz}^{nr}(0;0,0,0)$ is two orders of magnitude larger than $\gamma_{zzzz}^e(0;0,0,0)$. The dynamic γ_{zzzz}^{nr} (infinite frequency approximation) values for the optical Kerr effect $\gamma_{zzzz}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}$ (OKE) and the intensity dependent refractive index $\gamma_{zzzz}^{nr}(-\omega; \omega, -\omega, \omega)_{\omega \rightarrow \infty}$ (IDRI) are both larger than $\gamma_{zzzz}^e(0;0,0,0)$ as well, while the dc-second harmonic generation $\gamma_{zzzz}^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}$ (dc-SHG) is about the same magnitude, even though all three properties are much reduced from the static NR value. For molecules I and II the situation is not as extreme, although NR is quite important in a number of instances. Thus, at the MP2/6-31+G(*d*) level, $|\gamma_{zzzz}^{nr}(0;0,0,0) / \gamma_{zzzz}^e(0;0,0,0)|$ is 1.52 for molecule II and 0.34 for molecule I, replacing the static NR with its dynamic counterpart reduces this ratio to less than 0.55 in all cases.

Although the static ZPVA contribution appears to be about $\frac{1}{3}$ as large as the static electronic term for molecule III, it is less important for the other two molecules and we can certainly say that sequence (A) is initially convergent for static γ . Sequence (B) is also well behaved, for both the static and dynamic processes, with one important exception: the ratio $|\gamma_{zzzz}^{(c-zpva)(l)}(0;0,0,0) / \gamma_{zzzz}^{nr}(0;0,0,0)|$ for molecule II is 1.6 at the HF/6-31+G(*d*) level and 2.2 at the MP2/6-31

+G(*d*) level. For larger basis sets the HF ratio remains either about the same or increases, but the corresponding MP2 calculations were not done. Thus the effect of correlation on the ratio is a bit uncertain. Nevertheless, we see that the initial convergence of sequence (B) can be problematic for the static second hyperpolarizability. This situation is not signaled by either the covalent versus ionic character of the ground state or by the relative magnitude of the NR hyperpolarizability in comparison with the electronic term.

Correlation always increases $\gamma_{zzzz}^e(0;0,0,0)$ while $\gamma_{zzzz}^{nr}(0;0,0,0)$ either decreases or remains essentially the same. The effect on the relative importance of these two contributions is substantial. For instance, in the case of molecule I, the HF/6-31+G(*d*) NR term is about $\frac{4}{3}$ the electronic term whereas, at the MP2 level the same ratio becomes about $\frac{1}{3}$. For the dynamic γ_{zzzz}^{nr} vs $\gamma_{zzzz}^e(0;0,0,0)$ the general trend is the same, though not as pronounced. At this point it is worthwhile to remark on the comparison between MP2 and QCISD based on the calculations done for molecule I using the 6-31G basis. Except for a couple of small terms (<10% of the total property) QCISD is less than 50% different from MP2. The QCISD values are generally smaller with the result that the relative importance of the various contributions is more accurately maintained. Thus, for example, the ratio $|\gamma_{zzzz}^{nr}(0;0,0,0) / \gamma_{zzzz}^e(0;0,0,0)|$ changes from 0.25 for MP2 to 0.32 for QCISD whereas $\gamma_{zzzz}^e(0;0,0,0)$ itself changes from 1.56×10^5 to 1.05×10^5 . We tentatively conclude that MP2 is adequate for investigating the relative importance of the different contributions and for obtaining a reasonable estimate of the total.

It is important to observe that, for molecule III at the HF level, the 6-31G and 6-31+G values often have the wrong sign. This is true for all contributions to the static second hyperpolarizability as well as the NR contribution to the OKE. In contrast, as already noted the 6-31+G(*d*) basis set appears to be fairly well balanced, and in almost all cases it gives values that are similar to those obtained for the much larger 6-311++G(2*d*,2*p*) basis. Although there are some glaring exceptions, overall the (hyper)polarizability values

for the individual electronic and vibrational components exhibit fair convergence with respect to increasing the size of the basis set beyond $6-31+G(d)$. Most often the exceptions occur when the particular component in question is small compared to the major contribution to the property value so that the discrepancy is not very significant. In fact, the difference between the $6-31+G(d)$ value for any one component and the value obtained for the largest basis set considered is almost always less than 9% of the total property value [assuming that the dynamic γ_{zzzz}^e is greater than or equal to $\gamma_{zzzz}^e(0;0,0,0)$]. The unique exception is $\gamma_{zzzz}^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}$ of molecule III. In that case the difference between the two basis sets for the NR property is relatively large (about 40%), and the effect is magnified by the fact that the electronic and NR contributions tend to cancel one another.

IV. CONCLUSIONS

We have investigated the level of *ab initio* theory that is necessary to compute reliable values for the static and dynamic (hyper)polarizabilities of three representative medium size π -conjugated organic NLO molecules. The various contributions that were taken into account include the electronic term, P^e ; the first-order ZPVA correction, $[P^{zpva}]^I$; the nuclear relaxation term, P^{nr} ; and the nuclear relaxation correction to the $[P^{zpva}]^I$ term, i.e., $P^{(c-zpva)(I)}$. $[P^{zpva}]^I$, and $P^{(c-zpva)(I)}$ were calculated for the first time at a level beyond MP2/6-31G by taking advantage of *field-induced coordinates* and the finite field procedure of Kirtman, Luis, and Bishop. Although these terms are much more sensitive to the choice of basis set than the NR terms, the $6-31+G(d)$ basis provides satisfactory accuracy (with one special exception) for the total property value and the relative importance of the various contributions.

In order to obtain reasonable values for the various individual contributions to the (hyper)polarizability it is necessary to include electron correlation. Rough qualitative results for the *relative* importance of these contributions can be obtained at the HF level, but beyond that correlation must be included for this purpose as well. A comparison for molecule I between MP2/6-31G and QCISD/6-31G indicates that the MP2 method adequately reproduces the effect of correlation on the relative magnitude of the various contributions to each property and gives a reasonable prediction for the individual values. However, higher level methods are necessary to obtain quantitative estimates for the latter. In general, correlation decreases the magnitude of the NR contribution to the static hyperpolarizabilities while increasing the magnitude of the electronic and ZPVA terms.

As in previous work we have found that, in comparison with the static electronic value, NR contributions to the hyperpolarizabilities are larger in magnitude, or comparable in size, whereas the ZPVA contributions are always smaller despite an increase in their relative weight from α to γ . Thus the current study agrees with earlier calculations showing that perturbation series (A) is initially convergent. In most instances we have found that perturbation series (B) is also initially convergent, but that is not the case for the

static second hyperpolarizability of molecule II since $|\gamma_{zzzz}^{(c-zpva)(I)}(0;0,0,0)/\gamma_{zzzz}^{nr}(0;0,0,0)|$ is larger than unity. This means that for $\gamma_{zzzz}(0;0,0,0)$ of II the higher-order anharmonicity contributions of each square bracket type are, *in toto*, large compared to the lowest-order contributions. Dynamic properties behave better than static properties in this regard because the divergence is due to large vibrational anharmonicities occurring in perturbation terms that tend to zero as the frequency of the optical field increases. Low harmonic frequencies indicate the possibility that series (B) may be nonconvergent. In future work we will try to establish more definitive criteria for predicting when this problem will occur. We are also developing a new finite field procedure for calculating vibrational (hyper)polarizabilities that does not rely on the usual perturbation expansion and, in principle, will produce reliable results for highly anharmonic systems.

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