

Basis set and electron correlation effects on *ab initio* electronic and vibrational nonlinear optical properties of conjugated organic molecules

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We have studied how the calculation of electronic and vibrational contributions to nonlinear optical properties of three representative π -conjugated organic molecules is affected by the choice of basis set and the inclusion of electron correlation effects. The 6-31G basis does not always provide even qualitative accuracy. For semiquantitative accuracy a 6-31+G(*d*) basis is sufficient. Although, as compared to QCISD, a second-order Møller–Plesset (MP2) treatment often yields a substantial fraction of the electron correlation contribution, our MP2 results for the separate electronic and vibrational terms are not consistently of semiquantitative accuracy. Nevertheless, at the MP2 level the ratio between the vibrational and electronic contributions is satisfactorily reproduced. © 2003 American Institute of Physics. [DOI: 10.1063/1.1521725]

I. INTRODUCTION

There is increasing interest in materials with high nonlinear optical (NLO) properties due to their potential application in technologies such as telecommunications, information processing, surgery, metallurgy and holography. π -conjugated organic polymers are an excellent option because they are easily synthesized and chemically modified, have extremely fast switching times, and resist high intensity radiation. At the macroscopic level the relevant NLO properties are the second- and third-order nonlinear susceptibilities ($\chi^{(2)}$ and $\chi^{(3)}$), whereas their microscopic analogues are the first and second hyperpolarizabilities, $\beta(-\omega_\sigma; \omega_1, \omega_2)$ and $\gamma(-\omega_\sigma; \omega_1, \omega_2, \omega_3)$.

Although neglected in the past, the meaning and importance of the pure vibrational contribution to the hyperpolarizabilities, β^v and γ^v , is now fully established.^{1–8} Due to the high computational cost, electron correlation has rarely been included in *ab initio* calculations of the vibrational hyperpolarizability of medium size or large NLO organic molecules. In the few studies available, only the harmonic terms (i.e., *double harmonic* approximation)^{1,6,9} or the lowest order anharmonic terms (i.e., nuclear relaxation contribution, β^{nr} and γ^{nr})^{10–12} were computed. Recently, the authors of this paper performed a preliminary investigation of the initial convergence behavior of the perturbation series in anharmonicity for β^v and γ^v of typical π -conjugated NLO molecules.¹¹ In that work we found that including electron correlation yields drastic differences in the absolute and relative values of the electronic and vibrational contributions. In a few cases even the sign of the contribution changes. For example, for 1,1-diamino-6,6-diphosphino-hexa-1,3,5-triene the value of $\gamma_{zzzz}^{nr}(0;0,0,0)$ is -2.11×10^7 a.u. at the restricted Hartree–

Fock (RHF)/6-31G level and 8.4×10^6 a.u. at the second-order Møller–Plesset (MP2)/6-31G level. Contrary to what had been previously observed,¹⁰ we also found that the magnitude of the ratio P^{nr}/P^e is not systematically reduced by including correlation. In fact, a reduction occurs for only about half of the molecules studied.

The radical changes between the RHF/6-31G and MP2/6-31G methods made us doubt the reliability of our results. Thus, the main goal of this paper is to investigate the effect of basis set and electron correlation beyond the MP2 method on the electronic and vibrational hyperpolarizabilities of π -conjugated organic molecules. Ultimately we hope to determine the minimum level necessary to obtain quantitative or semiquantitative accuracy.

Bishop and Kirtman^{13–16} (BK) have developed a general perturbation theory approach to evaluate the vibrational hyperpolarizabilities at nonresonant frequencies. In the BK formalism the total hyperpolarizability can be written as

$$P = P^e + P^{zpv} + P^v, \quad (1)$$

where P^e is the pure electronic contribution at the equilibrium geometry, P^{zpv} is the zero-point vibrational averaging contribution, and P^v is the pure vibrational contribution. The sum of the last two contributions is usually considered to be the total vibrational contribution. Whereas P^{zpv} has its origin in the difference between the electronic contribution of a “frozen” molecule and a vibrating molecule, P^v comes from the dependence of the vibrational wave function on the external electric field. The BK perturbation theory formulas are expressed in terms of electrical property derivatives with respect to nuclear displacements as well as harmonic and anharmonic vibrational force constants. These formulas are organized into contributions of different “square bracket” types where the nomenclature used depends on the electrical properties involved and on the order of the derivatives or,

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equivalently, the order of electrical anharmonicity.¹⁶ It also depends on the order of mechanical anharmonicity. For instance, the expression for the pure vibrational contribution to the static second hyperpolarizability is given by

$$\begin{aligned} \gamma_{\alpha\beta\gamma\delta}^{\nu}(0;0,0,0) = & [\alpha^2]_{\omega=0}^0 + [\mu\beta]_{\omega=0}^0 + [\mu^2\alpha]_{\omega=0}^I \\ & + [\mu^4]_{\omega=0}^{II} + [\alpha^2]_{\omega=0}^{II} + [\mu\beta]_{\omega=0}^{II} \\ & + [\mu^2\alpha]_{\omega=0}^{III} + [\mu^4]_{\omega=0}^{IV} + [\alpha^2]_{\omega=0}^{IV} \\ & + [\mu\beta]_{\omega=0}^{IV} + [\mu^2\alpha]_{\omega=0}^V + [\mu^4]_{\omega=0}^{VI} \\ & + \dots, \end{aligned} \quad (2)$$

where the electrical properties involved are explicitly indicated. In Eq. (2) the terms of the same total order of anharmonicity (electrical+mechanical) have been grouped together and labeled with the corresponding superscript 0, I, II,...

There exists an alternative approach to calculating the pure vibrational hyperpolarizability based on the changes in P^e and P^{zpva} generated by a static external electric field, including the effect of the distortion of equilibrium geometry (i.e., "nuclear relaxation") induced by this field.¹⁷⁻²¹ An expansion of the difference in P^e between its field-free value at the undistorted equilibrium geometry and its field-dependent value at the relaxed geometry as a power series in the static electric field vector components leads to expressions for the static and/or infinite optical frequency (see the following) nuclear relaxation (NR) contribution to the (hyper)polarizabilities, P^{nr} .¹⁸ The analogous expansion of P^{zpva} gives the remaining P^{c-zpva} contribution [cf. Eq. (4)] to P^{ν} .¹⁷

A comparison of the analytical expression for P^{nr} with the BK P^{ν} formula shows that the NR contribution contains the lowest-order BK term of each square bracket type.¹⁸ Thus, for example, the NR contribution to the static hyperpolarizability can be written as

$$\begin{aligned} \gamma_{\alpha\beta\gamma\delta}^{nr}(0;0,0,0) = & [\alpha^2]_{\omega=0}^0 + [\mu\beta]_{\omega=0}^0 + [\mu^2\alpha]_{\omega=0}^I \\ & + [\mu^4]_{\omega=0}^{II}. \end{aligned} \quad (3)$$

This leaves the higher order "square bracket" terms which constitute the so-called C-ZPVA contribution,

$$P^{\nu} = P^{nr} + P^{c-zpva}. \quad (4)$$

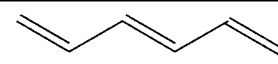
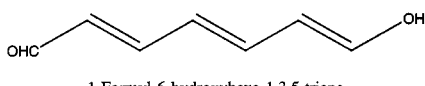
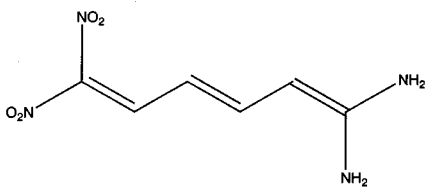
The order of anharmonicity included in calculations of P^{c-zpva} depends upon the order of anharmonicity included in the ZPVA expression from which this quantity is derived. Again using the static second hyperpolarizability as an example, one finds that the first-order P^{zpva} leads to¹⁷

$$\begin{aligned} \gamma_{\alpha\beta\gamma\delta}^{c-zpva(I)}(0;0,0,0) = & [\alpha^2]_{\omega=0}^{II} + [\mu\beta]_{\omega=0}^{II} + [\mu^2\alpha]_{\omega=0}^{III} \\ & + [\mu^4]_{\omega=0}^{IV}. \end{aligned} \quad (5)$$

Thus, the resulting static P^{ν} is correct through third order and contains one fourth-order term. In this paper, however, we will focus our attention on the leading perturbation terms which are contained in P^{nr} .

The main advantage of the alternative approach is that P^{nr} (and P^{c-zpva}) can be evaluated using either of two different computational methodologies: (i) through analytical

TABLE I. Structural formula of molecules studied in this paper.

Number	Formula/Structure
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

formulas¹⁷⁻¹⁹ based on field induced coordinates,²⁰ or (ii) numerical finite field (FF) techniques.^{10,21-23} On the other hand, in contrast with the general analytical BK method, P^{nr} (and P^{c-zpva}) are obtained only for the case where all optical frequencies are infinite (i.e., the infinite frequency approximation) or only a static field is present. Nevertheless, it has been shown²⁰⁻²⁵ that for typical laser optical frequencies the infinite frequency approximation does not lead to a significant loss of accuracy, although the error can increase rapidly when the optical frequencies approach the IR region.²⁰ For the medium size organic molecules studied in this paper, the derivatives required to evaluate the analytical expressions for P^{nr} at correlated levels of theory are beyond our computational resources. That is why all our calculations were performed using the alternative FF method and the infinite frequency approximation.

II. COMPUTATIONAL CONSIDERATIONS

The number of molecules investigated was limited by the computational resources available to us. We chose three molecules with different polarity and valence bond-charge transfer (VB-CT) features:²⁶ 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) (Table I); I is nonpolar, II is polar with a dominant VB ground state, and III is polar with a ground state that has mixed VB-CT character.

The longitudinal component of the various field-free and field-dependent P^e were calculated, in part, analytically using the GAUSSIAN 98 suite of programs.²⁷ The electronic properties that were determined in this way include μ^e , α^e , and β^e at the HF level, μ^e and α^e at the MP2 level, and μ^e at the QCISD level. All remaining higher-order properties (i.e., γ^e at the HF level; β^e and γ^e at the MP2 level; and α^e , β^e , and γ^e at the QCISD level) were obtained by numerical differentiation of the highest-order analytical P^e available with respect to an electric field. At the coupled-cluster single double (CCSD) level, all the electronic contributions to the (hyper)polarizability were calculated by numerical differentiation of the field-dependent electronic energy. For each molecule, property, and level of calculation, the numerical

TABLE II. Electronic and nuclear relaxation polarizabilities and second hyperpolarizabilities of molecule I calculated at the HF level. The quantity in parentheses is the relative error (in percent) with respect to the corresponding 6-311++G(3df,3pd) property; and the quantity in italics is the P^{nr}/P^e ratio. All quantities are in atomic units.

Properties	6-31G	6-31+G	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)	6-311++G(3df,3pd)
$\alpha_{zz}^e(0;0)$	1.44 × 10 ² (-6.5)	1.56 × 10 ² (1.4)	1.41 × 10 ² (-8.7)	1.53 × 10 ² (-0.7)	1.52 × 10 ² (-1.4)	1.53 × 10 ² (-0.6)	1.53 × 10 ² (-0.5)	1.53 × 10 ² (-0.5)	1.54 × 10 ²
$\alpha_{zz}^{nr}(0;0)$	3.13 × 10 ⁰ (-28)	3.28 × 10 ⁰ (-25)	3.80 × 10 ⁰ (-13)	3.87 × 10 ⁰ (-11)	4.03 × 10 ⁰ (-7.7)	4.14 × 10 ⁰ (-5.2)	4.43 × 10 ⁰ (1.4)	4.37 × 10 ⁰ (0.1)	4.37 × 10 ⁰
$\gamma_{zzzz}^e(0;0,0,0)$	5.22 × 10 ⁴ (-36)	9.88 × 10 ⁴ (21)	4.65 × 10 ⁴ (-43)	9.10 × 10 ⁴ (11)	8.26 × 10 ⁴ (1.2)	8.42 × 10 ⁴ (3.1)	8.31 × 10 ⁴ (1.8)	8.17 × 10 ⁴ (0.0)	8.17 × 10 ⁴
$\gamma_{zzzz}^{nr}(0;0,0,0)$	9.11 × 10 ⁴ (-28)	1.31 × 10 ⁵ (2.9)	9.09 × 10 ⁴ (-29)	1.29 × 10 ⁵ (1.7)	1.23 × 10 ⁵ (-3.2)	1.24 × 10 ⁵ (-2.1)	1.21 × 10 ⁵ (-4.4)	1.22 × 10 ⁵ (-4.3)	1.27 × 10 ⁵
$\gamma_{zzzz}^{nr}(-\omega; \omega, -\omega)_{\omega \rightarrow \infty}$	6.12 × 10 ⁴ (-23)	8.14 × 10 ⁴ (2.7)	5.98 × 10 ⁴ (-24)	8.03 × 10 ⁴ (1.4)	7.95 × 10 ⁴ (0.4)	8.07 × 10 ⁴ (1.9)	7.95 × 10 ⁴ (0.4)	7.98 × 10 ⁴ (0.7)	7.92 × 10 ⁴
$\gamma_{zzzz}^{nr}(-\omega; \omega, 0)_{\omega \rightarrow \infty}$	3.02 × 10 ⁴ (-23)	4.27 × 10 ⁴ (9.1)	2.92 × 10 ⁴ (-25)	4.20 × 10 ⁴ (7.3)	4.39 × 10 ⁴ (12)	4.26 × 10 ⁴ (8.7)	4.21 × 10 ⁴ (7.7)	3.94 × 10 ⁴ (0.6)	3.91 × 10 ⁴
$\gamma_{zzzz}^{nr}(-2\omega; \omega, \omega)_{\omega \rightarrow \infty}$	-5.15 × 10 ² (-16)	4.50 × 10 ² (-173)	-7.98 × 10 ² (30)	2.63 × 10 ² (-143)	4.12 × 10 ¹ (-107)	1.42 × 10 ¹ (-102)	-2.72 × 10 ² (-56)	-3.07 × 10 ² (-50)	-6.14 × 10 ² (-7.52)

differentiation was carried out for fields of ±0.0004, ±0.0008, ±0.0016, ±0.0032, and ±0.0064 a.u. Then, the smallest magnitude field that produced a stable derivative was selected using a Romberg method triangle.^{1,28}

The longitudinal component of the nuclear relaxation contribution to the static and infinite optical frequency (hyper)polarizabilities was calculated using the FF method of Bishop, Hasan, and Kirtman.²¹ In this treatment, as mentioned earlier, the P^{nr} are obtained from the coefficients of an expansion of the change in P^e [i.e., $\Delta P^e = P^e(\mathbf{R}_F, \mathbf{F}) - P^e(\mathbf{R}_0, 0)$] in a static electric field, \mathbf{F} :

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

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

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

where

$$a_{\alpha\beta}^{1,e} = \alpha_{\alpha\beta}^e(0;0) + \alpha_{\alpha\beta}^{nr}(0;0), \quad (9)$$

$$b_{\alpha\beta\gamma}^{1,e} = \beta_{\alpha\beta\gamma}^e(0;0,0) + \beta_{\alpha\beta\gamma}^{nr}(0;0,0), \quad (10)$$

$$g_{\alpha\beta\gamma\delta}^{1,e} = \gamma_{\alpha\beta\gamma\delta}^e(0;0,0,0) + \gamma_{\alpha\beta\gamma\delta}^{nr}(0;0,0,0), \quad (11)$$

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

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

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

In Eqs. (12)–(14) the subscript $\omega \rightarrow \infty$ refers to the infinite optical frequency limit and the subscripts α, β, γ , refer to the Cartesian axes.

The field-dependent geometry optimizations needed in order to calculate the NR contributions were carried out using our own program,²⁹ which rigorously enforces the Eckart conditions. As in the numerical determination of higher-order P^e , a Romberg method triangle for the electric fields ±0.0004, ±0.0008, ±0.0016, ±0.0032, and ±0.0064 a.u. was constructed to obtain the stable derivative with the smallest numerical error.

In our calculations we employed the 6-31G,³⁰ 6-31+G,^{30,31} 6-31G(d),^{30,32} 6-31+G(d),^{30–32} 6-311+G(d),^{31–34} 6-311++G(d,p),^{31–34} 6-311++G(2d,2p),^{31–35} 6-311++G(2df,2pd),^{31–35} and 6-311++G(3df,3pd)^{31–35} basis sets together with the HF, MP2, QCISD, and CCSD methods as implemented in the GAUSSIAN 98 suite of programs.²⁷ This choice allows us to proceed in a systematic manner without incurring excessive computational cost as would be the case using, for example, correlation consistent basis sets.³⁶

TABLE III. Electronic and nuclear relaxation polarizabilities and second hyperpolarizabilities of molecule I calculated at the MP2 level. The quantity in parentheses is the relative error (in percent) with respect to the corresponding 6-311+G(*d,p*) property; and the quantity in italics is the P^{nr}/P^e ratio. All quantities are in atomic units.

Properties	6-31G	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>)
$\alpha_{zz}^e(0;0)$	1.25×10 ² (-15)	1.40×10 ² (-4.1)	1.30×10 ² (-11)	1.45×10 ² (-0.6)	1.45×10 ² (-0.4)	1.46×10 ²
$\alpha_{zz}^{nr}(0;0)$	1.82×10 ⁰ (-32) <i>1.46×10⁻²</i>	1.95×10 ⁰ (-27) <i>1.39×10⁻²</i>	2.47×10 ⁰ (-7.4) <i>1.90×10⁻²</i>	2.55×10 ⁰ (-4.1) <i>1.76×10⁻²</i>	2.64×10 ⁰ (-0.9) <i>1.82×10⁻²</i>	2.66×10 ⁰ <i>1.83×10⁻²</i>
$\gamma_{zzzz}^e(0;0,0,0)$	1.56×10 ⁵ (-23)	2.53×10 ⁵ (25)	1.27×10 ⁵ (-37)	2.15×10 ⁵ (6.0)	2.01×10 ⁵ (-1.0)	2.03×10 ⁵
$\gamma_{zzzz}^{nr}(0;0,0,0)$	3.85×10 ⁴ (-47) <i>2.46×10⁻¹</i>	6.35×10 ⁴ (-12) <i>2.51×10⁻¹</i>	4.35×10 ⁴ (-40) <i>3.42×10⁻¹</i>	7.24×10 ⁴ (-0.2) <i>3.36×10⁻¹</i>	7.25×10 ⁴ (0.0) <i>3.60×10⁻¹</i>	7.25×10 ⁴ <i>3.57×10⁻¹</i>
$\gamma_{zzzz}^{nr}(-\omega;\omega,0,0)_{\omega\rightarrow\infty}$	1.45×10 ⁴ (-45) <i>9.28×10⁻²</i>	2.41×10 ⁴ (-9.0) <i>9.53×10⁻²</i>	1.69×10 ⁴ (-36) <i>1.33×10⁻¹</i>	2.75×10 ⁴ (3.8) <i>1.28×10⁻¹</i>	2.65×10 ⁴ (-0.1) <i>1.32×10⁻¹</i>	2.65×10 ⁴ <i>1.30×10⁻¹</i>
$\gamma_{zzzz}^{nr}(-2\omega;\omega,\omega,0)_{\omega\rightarrow\infty}$	2.26×10 ³ (-33) <i>1.45×10⁻²</i>	4.02×10 ³ (19) <i>1.59×10⁻²</i>	1.80×10 ³ (-47) <i>1.41×10⁻²</i>	3.53×10 ³ (4.2) <i>1.64×10⁻²</i>	3.27×10 ³ (-3.5) <i>1.62×10⁻²</i>	3.39×10 ³ <i>1.67×10⁻²</i>

III. RESULTS

Tables II–V, VI–VIII, and IX–X summarize the results obtained for the longitudinal component of the electronic and NR contributions to the NLO properties of molecules I, II and III, respectively. The computational cost of such calculations increases very rapidly with the number of basis functions. This explains why the level of treatment for molecule III is lower than for molecule I. Nevertheless, for all three molecules we were able to conduct a fairly systematic study of basis set and electron correlation effects on the electronic and vibrational contributions to NLO properties.

The 6-31G basis set has been used in many previous theoretical investigations of the NLO properties of organic molecules.^{1,8–12} Although it is well established that diffuse and polarization functions are required for a quantitative description of both the electronic and NR (hyper)polarizabilities of medium size organic molecules,⁶ it has been found in the past that the 6-31G basis is adequate to obtain semiquantitative results.^{37,38} This is the case for molecule II at the HF

(Table VI) and QCISD (Table VIII) levels where the magnitude of the errors relative to the HF/6-311+G(*d*) and QCISD/6-31+G(*d*) values lie in the range 1.0%–16%, and 5.2%–13%, respectively. However, the performance of the 6-31G basis set is poorer at the MP2 level (see Table VII) in which case the magnitude of the error with respect to MP2/6-311+G(*d,p*) varies from 2.6% to 32%. It is also poorer for molecule I at the HF, MP2, and QCISD levels; the magnitude of the error ranges from 6.5% to 36%, 15% to 47%, and from 15% to 54%, in comparison with HF/6-311++G(3*df*,3*pd*), MP2/6-311++G(*d,p*), and QCISD/6-311+G(*d*), respectively. Although the 6-31G results cannot be considered semiquantitative in these instances, they are still acceptable from a qualitative point of view. This is not true, however, for the 6-31G results of molecule III. At the HF level the magnitude of the error, with reference to the 6-311+G(*d*) value, varies from 4.0% to 297%; and, at the MP2 level, it varies from 1.5% to 77% with respect to MP2/6-31+G(*d*). Note that, for $\gamma_{zzzz}^e(0;0,0,0)$, the HF/6-

TABLE IV. Electronic and nuclear relaxation polarizabilities and second hyperpolarizabilities of molecule I calculated at the QCISD level. The quantity in parentheses is the relative error (in percent) with respect to the corresponding 6-311+G(*d*) property; and the quantity in italics is the P^{nr}/P^e ratio. All quantities are in atomic units.

Properties	6-31G	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)	6-311+G(<i>d</i>)
$\alpha_{zz}^e(0;0)$	1.18×10 ² (-15)	1.31×10 ² (-5.5)	1.25×10 ² (-9.9)	1.38×10 ² (-0.6)	1.39×10 ²
$\alpha_{zz}^{nr}(0;0)$	1.52×10 ⁰ (-41) <i>1.29×10⁻²</i>	1.64×10 ⁰ (-36) <i>1.25×10⁻²</i>	2.33×10 ⁰ (-9.3) <i>1.86×10⁻²</i>	2.42×10 ⁰ (-6.0) <i>1.75×10⁻²</i>	2.57×10 ⁰ <i>1.85×10⁻²</i>
$\gamma_{zzzz}^e(0;0,0,0)$	1.05×10 ⁵ (-25)	1.72×10 ⁵ (24)	8.94×10 ⁴ (-36)	1.51×10 ⁵ (8.1)	1.39×10 ⁵
$\gamma_{zzzz}^{nr}(0;0,0,0)$	3.39×10 ⁴ (-54) <i>3.24×10⁻¹</i>	5.32×10 ⁴ (-28) <i>3.09×10⁻¹</i>	4.48×10 ⁴ (-39) <i>5.01×10⁻¹</i>	6.39×10 ⁴ (-13) <i>4.24×10⁻¹</i>	7.36×10 ⁴ <i>5.27×10⁻¹</i>
$\gamma_{zzzz}^{nr}(-\omega;\omega,0,0)_{\omega\rightarrow\infty}$	1.23×10 ⁴ (-50) <i>1.17×10⁻¹</i>	1.95×10 ⁴ (-21) <i>1.13×10⁻¹</i>	1.59×10 ⁴ (-35) <i>1.78×10⁻¹</i>	2.42×10 ⁴ (-2.0) <i>1.60×10⁻¹</i>	2.47×10 ⁴ <i>1.77×10⁻¹</i>
$\gamma_{zzzz}^{nr}(-2\omega;\omega,\omega,0)_{\omega\rightarrow\infty}$	1.36×10 ³ (-32) <i>1.30×10⁻²</i>	2.57×10 ³ (28) <i>1.49×10⁻²</i>	9.92×10 ² (-51) <i>1.11×10⁻²</i>	2.21×10 ³ (10) <i>1.47×10⁻²</i>	2.01×10 ³ <i>1.44×10⁻²</i>

TABLE V. Electronic and nuclear relaxation polarizabilities and second hyperpolarizabilities of molecule I calculated at the CCSD level. The quantity in parentheses is the relative error (in percent) with respect to the corresponding 6-31+G(*d*) property. The quantity in italics is the P^{nr}/P^e ratio. All quantities are in atomic units.

Properties	6-31G	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)
$\alpha_{zz}^e(0;0)$	1.16×10^2 (-15)	1.29×10^2 (-5.5)	1.24×10^2 (-9.3)	1.36×10^2
$\alpha_{zz}^{nr}(0;0)$	1.50×10^0 (-37) <i>1.29 \times 10^{-2}</i>	1.61×10^0 (-32) <i>1.25 \times 10^{-2}</i>	2.30×10^0 (-3.5) <i>1.86 \times 10^{-2}</i>	2.38×10^0 <i>1.74 \times 10^{-2}</i>
$\gamma_{zzzz}^e(0;0,0,0)$	1.11×10^5 (-30)	1.79×10^5 (13)	8.93×10^4 (-44)	1.59×10^5
$\gamma_{zzzz}^{nr}(0;0,0,0)$	3.14×10^4 (-50) <i>2.83 \times 10^{-1}</i>	4.96×10^4 (-21) <i>2.78 \times 10^{-1}</i>	4.31×10^4 (-31) <i>4.82 \times 10^{-1}</i>	6.28×10^4 <i>3.96 \times 10^{-1}</i>
$\gamma_{zzzz}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}$	1.21×10^4 (-50) <i>1.09 \times 10^{-1}</i>	1.90×10^4 (-22) <i>1.07 \times 10^{-1}</i>	1.55×10^4 (-37) <i>1.73 \times 10^{-1}</i>	2.44×10^4 <i>1.54 \times 10^{-1}</i>
$\gamma_{zzzz}^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}$	1.24×10^3 (-62) <i>1.12 \times 10^{-2}</i>	3.27×10^3 (1.4) <i>1.83 \times 10^{-2}</i>	1.57×10^3 (-51) <i>1.76 \times 10^{-2}</i>	3.23×10^3 <i>2.03 \times 10^{-2}</i>

31G result has the wrong sign. We conclude that the 6-31G basis set cannot be systematically used to compute the NLO properties of medium size organic molecules.

As a computationally cheap first option for increasing the quality of the basis set we considered the addition of diffuse functions on the nonhydrogenic atoms. For molecule I, utilization of the 6-31+G basis leads to a meaningful decrease in the errors for $\alpha_{zz}^e(0;0)$, $\gamma_{zzzz}^{nr}(0;0,0,0)$, $\gamma_{zzzz}^{nr}(-\omega; \omega, \omega, -\omega)_{\omega \rightarrow \infty}$, and $\gamma_{zzzz}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}$ at all levels of calculation. However, the addition of diffuse basis functions does not improve the accuracy of P^e and P^{nr}

for the other two molecules. Next, we tried the 6-31G(*d*) basis set. This improves the results only for molecule III and is, therefore, not a good choice in general. On the other hand, the accuracy of the 6-31+G(*d*) basis is substantially better than that of 6-31G. In fact, with the exception of $\gamma_{zzzz}^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}$ for molecule I, which is a special case due to its small absolute value, the magnitude of the error obtained with the 6-31+G(*d*) basis is always less than 17% as compared to the largest basis set studied for each method and molecule. Indeed, in most cases the error is

TABLE VI. Electronic and nuclear relaxation polarizabilities, first and second hyperpolarizabilities of molecule II calculated at the HF level. The quantity in parentheses is the relative error (in percent) with respect to the corresponding 6-311+G(*d*) property; and the quantity in italics is the P^{nr}/P^e ratio. All quantities are in atomic units.

Properties	6-31G	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)	6-311+G(<i>d</i>)
$\alpha_{zz}^e(0;0)$	2.11×10^2 (-1.0)	2.24×10^2 (5.1)	2.02×10^2 (-5.5)	2.15×10^2 (0.5)	2.13×10^2
$\alpha_{zz}^{nr}(0;0)$	3.84×10^1 (-9.5) <i>1.82 \times 10^{-1}</i>	4.15×10^1 (-2.2) <i>1.85 \times 10^{-1}</i>	3.87×10^1 (-8.9) <i>1.92 \times 10^{-1}</i>	4.20×10^1 (-1.0) <i>1.96 \times 10^{-1}</i>	4.24×10^1 <i>1.99 \times 10^{-1}</i>
$\beta_{zzz}^e(0;0,0)$	1.79×10^3 (4.7)	2.11×10^3 (23)	1.50×10^3 (-12)	1.79×10^3 (4.5)	1.71×10^3
$\beta_{zzz}^{nr}(0;0,0)$	3.96×10^3 (-12) <i>2.21 \times 10^0</i>	4.64×10^3 (2.8) <i>2.20 \times 10^0</i>	3.81×10^3 (-16) <i>2.54 \times 10^0</i>	4.50×10^3 (-0.4) <i>2.51 \times 10^0</i>	4.52×10^3 <i>2.64 \times 10^0</i>
$\beta_{zzz}^{nr}(-\omega; \omega, 0)_{\omega \rightarrow \infty}$	1.11×10^3 (-8.1) <i>6.21 \times 10^{-1}</i>	1.29×10^3 (6.3) <i>6.09 \times 10^{-1}</i>	1.04×10^3 (-14) <i>6.96 \times 10^{-1}</i>	1.22×10^3 (0.3) <i>6.80 \times 10^{-1}</i>	1.21×10^3 <i>7.08 \times 10^{-1}</i>
$\gamma_{zzzz}^e(0;0,0,0)$	1.96×10^5 (6.0)	2.37×10^5 (29)	1.59×10^5 (-14)	1.95×10^5 (5.7)	1.85×10^5
$\gamma_{zzzz}^{nr}(0;0,0,0)$	7.05×10^5 (-16) <i>3.60 \times 10^0</i>	8.66×10^5 (2.8) <i>3.65 \times 10^0</i>	6.75×10^5 (-20) <i>4.26 \times 10^0</i>	8.26×10^5 (-1.9) <i>4.24 \times 10^0</i>	8.43×10^5 <i>4.56 \times 10^0</i>
$\gamma_{zzzz}^{nr}(-\omega; \omega, \omega, -\omega)_{\omega \rightarrow \infty}$	1.82×10^5 (-5.4) <i>9.29 \times 10^{-1}</i>	2.13×10^5 (11) <i>8.97 \times 10^{-1}</i>	1.65×10^5 (-14) <i>1.04 \times 10^0</i>	1.94×10^5 (0.8) <i>9.94 \times 10^{-1}</i>	1.92×10^5 <i>1.04 \times 10^0</i>
$\gamma_{zzzz}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}$	1.87×10^5 (-8.3) <i>9.54 \times 10^{-1}</i>	2.27×10^5 (12) <i>9.57 \times 10^{-1}</i>	1.70×10^5 (-16) <i>1.07 \times 10^0</i>	2.07×10^5 (1.6) <i>1.06 \times 10^0</i>	2.04×10^5 <i>1.10 \times 10^0</i>
$\gamma_{zzzz}^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}$	2.51×10^4 (1.9) <i>1.28 \times 10^{-1}</i>	3.17×10^4 (29) <i>1.33 \times 10^{-1}</i>	2.06×10^4 (-17) <i>1.30 \times 10^{-1}</i>	2.60×10^4 (5.6) <i>1.33 \times 10^{-1}</i>	2.47×10^4 <i>1.34 \times 10^{-1}</i>

TABLE VII. Electronic and nuclear relaxation polarizabilities, first and second hyperpolarizabilities of molecule II calculated at the MP2 and QCISD levels. The quantity in parentheses is the relative error (in percent) with respect to the corresponding 6-311+G(*d*) property; and the quantity in italics is the P^{nr}/P^e ratio. All quantities are in atomic units.

Properties	6-31G	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)	6-311+G(<i>d</i>)	QCISD 6-31G
$\alpha_{zz}^e(0;0)$	2.09×10^2 (-11)	2.31×10^2 (-2.2)	2.15×10^2 (-9.0)	2.36×10^2 (-0.0)	2.36×10^2	1.87×10^2
$\alpha_{zz}^{nr}(0;0)$	2.62×10^1 (-24) 1.25×10^{-1}	2.99×10^1 (-13) 1.30×10^{-1}	2.96×10^1 (-14) 1.38×10^{-1}	3.41×10^1 (-1.3) 1.44×10^{-1}	3.45×10^1 1.46×10^{-1}	2.31×10^1 1.23×10^{-1}
$\beta_{zzz}^e(0;0,0)$	5.05×10^3 (2.7)	6.08×10^3 (24)	4.24×10^3 (-14)	5.12×10^3 (4.1)	4.91×10^3	3.50×10^3
$\beta_{zzz}^{nr}(0;0,0)$	2.90×10^3 (-32) 5.75×10^{-1}	3.73×10^3 (-12) 6.14×10^{-1}	3.29×10^3 (-23) 7.76×10^{-1}	4.20×10^3 (-1.2) 8.20×10^{-1}	4.25×10^3 8.64×10^{-1}	2.04×10^3 5.82×10^{-1}
$\beta_{zzz}^{nr}(-\omega; \omega, 0)_{\omega \rightarrow \infty}$	9.49×10^2 (-29) 1.88×10^{-1}	1.21×10^3 (-9.5) 1.99×10^{-1}	1.06×10^3 (-22) 2.49×10^{-1}	1.33×10^3 (-0.5) 2.60×10^{-1}	1.34×10^3 2.72×10^{-1}	6.59×10^2 1.88×10^{-1}
$\gamma_{zzzz}^e(0;0,0,0)$	6.13×10^5 (13)	7.58×10^5 (40)	4.59×10^5 (-15)	5.70×10^5 (5.1)	5.43×10^5	5.11×10^5
$\gamma_{zzzz}^{nr}(0;0,0,0)$	6.65×10^5 (-23) 1.08×10^0	9.12×10^5 (5.3) 1.20×10^0	6.45×10^5 (-25) 1.41×10^0	8.67×10^5 (0.1) 1.52×10^0	8.66×10^5 1.60×10^0	4.86×10^5 9.52×10^0
$\gamma_{zzzz}^{nr}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}$	2.55×10^5 (-16) 4.17×10^{-1}	3.45×10^5 (13) 4.55×10^{-1}	2.34×10^5 (-23) 5.10×10^{-1}	3.10×10^5 (1.4) 5.44×10^{-1}	3.06×10^5 5.63×10^{-1}	1.71×10^5 3.34×10^{-1}
$\gamma_{zzzz}^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}$	8.06×10^4 (-2.6) 1.31×10^{-1}	1.07×10^5 (30) 1.41×10^{-1}	6.50×10^4 (-21) 1.42×10^{-1}	8.52×10^4 (3.0) 1.49×10^{-1}	8.27×10^4 1.52×10^{-1}	5.24×10^4 1.03×10^{-1}

smaller than 8%. Thus, the 6-31+G(*d*) basis set seems to be an appropriate choice for studying the NLO properties of medium size conjugated organic molecules, although other molecules should be studied to corroborate this statement.

One might have expected that the P^{nr}/P^e ratio would be less sensitive to the choice of basis set than the individual electronic or NR contributions. However, the results presented in this paper do not bear that out. The errors in the P^{nr}/P^e ratios tend to be about the same magnitude as the errors in P^{nr} and P^e . The 6-31G(*d*) basis constitutes an exception to this general behavior. For that basis the errors in the ratios are two to five times smaller than the errors in the separate electronic and NR contributions.

As mentioned in Sec. I, we have shown previously that P^e and P^{nr} computed at the MP2/6-31G level can be very different¹¹ from the HF/6-31G value for the type of molecule studied in this paper. Although, in general, these differences tend to decrease slightly as the basis set is improved, even with the largest basis sets considered here the MP2 correla-

tion effect remains quite large. A major objective of the current work is to determine whether or not the MP2 method adequately characterizes the correlation contribution. For that purpose we compare MP2 with QCISD, which we prefer to CCSD because analytical evaluation of the QCISD gradient and dipole moment are implemented in GAUSSIAN 98. Tables IV and V show that, at least for molecule I, the difference between the QCISD and CCSD values calculated at QCISD geometries is always less than 8% for both P^e and P^{nr} with the exception of $\gamma_{zzzz}^{nr}(-2\omega; \omega, \omega, 0)_{\omega \rightarrow \infty}$ which, as noted previously, can be explained as a special case. At this point we do not know what would be the effect of adding noniterative triples excitations to the QCISD or CCSD calculations.

In order to see the effect of electron correlation and how well it is described at the MP2 level we compare both MP2 and HF to QCISD. The HF results for P^e and P^{nr} , obtained with the largest basis set considered here, differ from the corresponding QCISD values by 9.5%–98% for molecule I and by 9.2%–94% for molecule II. In general, whenever the correlation contribution given by QCISD is relatively small or large, the MP2 treatment will yield a correction that is correspondingly either small or large and in the same direction. Although we could give the percentage error in the correlation contribution, it is more relevant to compare MP2 directly with QCISD. The difference between MP2 and QCISD for molecule I lies between 1.4% and 63% whereas, for molecule II, it lies in the range from 12% to 54%. While a significant part of the large correlation effect is accounted for by MP2, there is also a substantial part that is not [see for instance $\gamma_{zzzz}^{nr}(0;0,0,0)$ and $\gamma_{zzzz}^e(0;0,0,0)$ of I]. For molecule III only P^e was computed at the QCISD level. In this

TABLE VIII. Electronic static polarizabilities, first and second hyperpolarizabilities of molecule II calculated at the QCISD. The quantity in parentheses is the relative error (in percent) with respect to the corresponding 6-31+G(*d*) property. All quantities are in atomic units.

Properties	6-31G	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)
$\alpha_{zz}^e(0;0)$	1.87×10^2 (-13)	2.06×10^2 (-3.8)	1.96×10^2 (-8.5)	2.14×10^2
$\beta_{zzz}^e(0;0,0)$	3.50×10^3 (-12)	4.35×10^3 (9.5)	3.23×10^3 (-19)	3.97×10^3
$\gamma_{zzzz}^e(0;0,0,0)$	5.11×10^5 (-5.2)	6.59×10^5 (22)	4.25×10^5 (-21)	5.39×10^5

TABLE IX. Electronic and some nuclear relaxation polarizabilities, first and second hyperpolarizabilities of molecule III calculated at the HF level. The quantity in parentheses is the relative error with respect to the corresponding 6-311+G(*d*) property, and the quantity in italics is the P^{nr}/P^e ratio. All quantities are in atomic units.

Properties	6-31G	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)	6-311+G(<i>d</i>)
$\alpha_{zz}^e(0;0)$	3.13×10^2 (8.3)	3.35×10^2 (16)	2.75×10^2 (-5.0)	2.94×10^2 (1.5)	2.89×10^2
$\alpha_{zz}^{\text{nr}}(0;0)$	3.35×10^2 (4.0) 1.07×10^0	3.77×10^2 (17) 1.12×10^0	3.16×10^2 (-1.8) 1.15×10^0	3.44×10^2 (6.9) 1.17×10^0	3.22×10^2 1.11×10^0
$\beta_{zzz}^e(0;0,0)$	2.20×10^2 (-91)	3.09×10^2 (-87)	2.27×10^3 (-4.5)	2.56×10^3 (7.9)	2.37×10^3
$\beta_{zzz}^{\text{nr}}(-\omega; \omega, 0)_{\omega \rightarrow \infty}$	3.25×10^3 (-58) 1.48×10^1	3.83×10^3 (-50) 1.24×10^1	6.86×10^3 (-11) 3.03×10^0	8.26×10^3 (7.5) 3.22×10^0	7.69×10^3 3.24×10^0
$\gamma_{zzzz}^e(0;0,0,0)$	-2.36×10^5 (-297)	-2.57×10^5 (-314)	7.13×10^4 (-40)	9.98×10^4 (-17)	1.20×10^5
$\gamma_{zzzz}^{\text{nr}}(-\omega; \omega, \omega, -\omega)_{\omega \rightarrow \infty}$	1.82×10^5 (-68) -7.72×10^{-1}	2.12×10^5 (-63) -8.25×10^{-1}	4.83×10^5 (-16) 6.77×10^0	6.08×10^5 (5.4) 6.09×10^0	5.77×10^5 4.82×10^0

case the electron correlation error (HF versus QCISD) lies in the range 9.4%–120%. At the MP2 level the values obtained differ from the corresponding QCISD results by 8.3%–94%. Clearly, for the medium size conjugated organic molecules in this study, the MP2 treatment does not consistently yield semiquantitative accuracy.

It is interesting to observe that, for the second hyperpolarizabilities of molecule I, the performance of MP2 is far better for P^{nr} than it is for P^e , which is the opposite of what one finds at the HF level. While the magnitude of the errors in the HF $\gamma_{zzzz}^e(0;0,0,0)$, $\gamma_{zzzz}^{\text{nr}}(-\omega; \omega, \omega, -\omega)_{\omega \rightarrow \infty}$ and $\gamma_{zzzz}^{\text{nr}}(-\omega; \omega, 0, 0)_{\omega \rightarrow \infty}$ are 41%, 67%, and 78%, respectively, the corresponding errors at the MP2 level are 44%, 1.4%, and 7.5%. This illustrates the fact that one cannot extrapolate relative errors in P^{nr} versus P^e from one level of treatment to another. In fact, we find that the accuracy of the MP2 P^{nr}/P^e ratio with respect to the QCISD ratio is far better, on average, than the corresponding HF value. For the largest basis set considered here the maximum error at the MP2 level for all cases is 32% whereas this error can be as large as 278% at the Hartree–Fock level. Thus, the MP2 treatment does appear to give semiquantitative accuracy for P^{nr}/P^e , though not for the individual values of the numerator and denominator.

IV. CONCLUSIONS

Electron correlation makes a major contribution to the hyperpolarizabilities and, hence, the NLO properties of π -conjugated organic molecules. For a representative set of three medium size molecules we have investigated how the calculation of this contribution is affected by the choice of basis set and level of electron correlation treatment. Both the pure electronic and the nuclear relaxation vibrational hyperpolarizabilities (P^e and P^{nr}) were considered. It was found that the often used 6-31G basis does not systematically provide semiquantitative, or even, qualitative results. Semiquantitative accuracy was achieved, however, for the 6-31+G(*d*) basis. In that case, the basis set error was typically less than 8% with a maximum of 17%. As compared to QCISD, a MP2 treatment often yields a significant fraction of the electron correlation contribution. MP2 also gives semiquantitative accuracy (maximum error=32%) for the ratio P^{nr}/P^e but not for P^e and P^{nr} individually. It still remains to be established, of course, that QCISD can be trusted to provide at least semiquantitative accuracy for the individual properties. Although the C-ZPVA contribution is computationally expensive to determine, we hope that in the near future we will be able to extend the present investigation to

TABLE X. Electronic static polarizabilities, first and second hyperpolarizabilities of molecule III calculated at the MP2 and QCISD levels. The quantity in parentheses is the relative error (in percent) with respect to the corresponding 6-31+G(*d*) property. All quantities are in atomic units.

Properties	6-31G	6-31+G	6-31G(<i>d</i>)	6-31+G(<i>d</i>)	QCISD/6-31G
$\alpha_{zz}^e(0;0)$	3.75×10^2 (1.5)	4.10×10^2 (11)	3.35×10^2 (-9.2)	3.69×10^2	3.46×10^2
$\beta_{zzz}^e(0;0,0)$	1.32×10^4 (22)	1.58×10^4 (46)	9.10×10^3 (-16)	1.08×10^4	1.79×10^4
$\gamma_{zzzz}^e(0;0,0,0)$	7.16×10^4 (-77)	3.39×10^5 (7.8)	1.85×10^5 (-41)	3.14×10^5	1.18×10^6

this contribution using field induced coordinates.¹² Finally, all of our results are for isolated molecules. In order to compare with experiment one also needs a satisfactory treatment of environmental effects in the condensed phase.

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