J. Am. Chem. Soc. **2000,** *122,* 8007−8012

Electric Field Simulation of Substituents in Donor−Acceptor Polyenes: A Comparison with Ab Initio Predictions for Dipole Moments, Polarizabilities, and Hyperpolarizabilities

Bernard Kirtman,*,[†] Benoît Champagne,[‡] and David M. Bishop[§]

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106, Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix, rue de Bruxelles, 61, B-5000 Namur, Belgium, and Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5

Received September 7, 1999. Revised Manuscript Received May 19, 2000

Abstract: The treatment of dipole moments (μ), polarizabilities (α), and hyperpolarizabilities (β, γ) in push−pull systems using electric field simulation for the substituents is reanalyzed and tested by comparison with ab initio Hartree−Fock calculations on representative donor−acceptor (D/A) polyenes. Both vibrational and electronic contributions are properly taken into account. We find that the field simulation approach can be applied semiquantitatively to relate the odd-order (μ, β) properties only. Even for these properties, however, features such as the chain-length dependence cannot be reproduced due to the excessively delocalized description of the D/A substituents.

I. Introduction

Five years ago Marder et al.[1] introduced the idea of simulating the substituents in a donor−acceptor (D/A) polyene by means of a uniform electric field. They used this method as the basis for a unified description of electronic dipole moments (μ), polarizabilities (α), and hyperpolarizabilities (β and γ). Since then a number of papers have appeared[2−11] which have utilized the same approach to rationalize both the qualitative and quantitative behaviors of these properties.

There is no doubt as to the simplicity, intuitive appeal, and potential usefulness of the field simulation approach. As with any model, however, it is difficult to know, without adequate testing, the quantitative or qualitative extent to which it is reliable. Various treatments have been carried out using other models that provide some information in this regard. Chen and Mukamel,[12,13] for example, applied the Pariser−Parr−Pople (PPP) Hamiltonian to an N site, N electron π-system where the donor/acceptor is simulated by a single nucleus of charge $+2e/0$ and atomic energy $-\epsilon/\epsilon$. They concluded that the derivative relations, which are the essence of the unified description mentioned above, hold "only over a limited range of parameters" but they did not specifically address the connection with real molecules. On the other hand, Barzoukas et al.[14,15] utilized a two-state approximation, with parameters derived from electroabsorption measurements, to verify and further understand the structure/property correlations that emerge from the field simulation procedure. There are, however, no ab initio studies of these issues and the vibrational effects, which are known to be very important for the type of molecules considered here,[16−19] have never seriously been incorporated. With respect to the vibrational contribution, in particular, the two-state approximation is known[16] to be inadequate. For these reasons, we have undertaken ab initio calculations on a representative set of D/A polyenes simulated by imposing a variable electric field on octatetraene (primarily) and determined both the electronic and vibrational values of μ, α, β, and γ at the coupled perturbed Hartree−Fock (CPHF) 6-31G level. Using larger basis sets and adding electron correlation would certainly affect the ab initio results but not, as will be evident, the general conclusions that we have reached.

Although our work was motivated initially by field simulations, it also deals in large part with more general concerns. One of these is a re-interpretation of the derivative relations which takes vibrations, i.e., the effect of changes in geometry, properly into account. Another is the extent to which the π-bond order alternation, by itself, determines the separate electronic and vibrational contributions to α, β, and γ. In addition, we

---

[†] University of California.

[‡] Notre-Dame de la Paix.

[§] University of Ottawa.

(1) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Brédas, J. L.; Pierce, B. M. *Science* **1994**, *265*, 632.

(2) Meyers, F.; Marder, S. R.; Pierce, B. M.; Brédas, J. L. *Chem. Phys. Lett.* **1994**, *228*, 171.

(3) Meyers, F.; Marder, S. R.; Pierce, B. M.; Brédas, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 10703.

(4) Ravi, M.; Radhakrishnan, T. P. *J. Phys. Chem.* **1995**, *99*, 17624.

(5) Chen, G.; Mukamel, S. *J. Chem. Phys.* **1995**, *103*, 9355.

(6) Zuliani, P.; Del Zoppo, M.; Castiglioni, C.; Zerbi, G.; Marder, S. R.; Perry, J. W. *J. Chem. Phys.* **1995**, *103*, 9935.

(7) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 9714.

(8) Del Zoppo, M.; Castiglioni, C.; Gerola, V.; Zuliani, P.; Zerbi, G. *J. Opt. Soc. Am.* **1998**, *B15*, 308.

(9) Del Zoppo, M.; Tommasini, M.; Castiglioni, C.; Zerbi, G. *Chem. Phys. Lett.* **1998**, *287*, 100.

(10) Honda, Y.; Nakatsuji, H. *Chem. Phys. Lett.* **1998**, *293*, 230.

(11) Sheng, Y.; Giang, Y.; Wang, X. C. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 47.

(12) Chen, G.; Mukamel, S. *J. Am. Chem. Soc.* **1995**, *117*, 4945.

(13) Chen, G.; Mukamel, S. *J. Phys. Chem.* **1996**, *100*, 11080.

(14) Barzoukas, M.; Runser, C.; Fort, A.; Blanchard-Desce, M. *Chem. Phys. Lett.* **1996**, *257*, 531.

(15) Barzoukas, M.; Fort, A.; Blanchard-Desce, M. *New J. Chem.* **1997**, *21*, 309.

(16) Bishop, D. M.; Champagne, B.; Kirtman, B. *J. Chem. Phys.* **1998**, *109*, 9987.

(17) Champagne, B.; Kirtman, B. *Chem. Phys.* **1999**, *245*, 213.

(18) Kirtman, B.; Champagne, B. *Int. Rev. Phys. Chem.* **1997**, *16*, 389.

(19) Luis, J. M.; Duran, M.; Champagne, B.; Kirtman, B. *J. Chem. Phys.*, in press.

10.1021/ja993226e CCC: $19.00

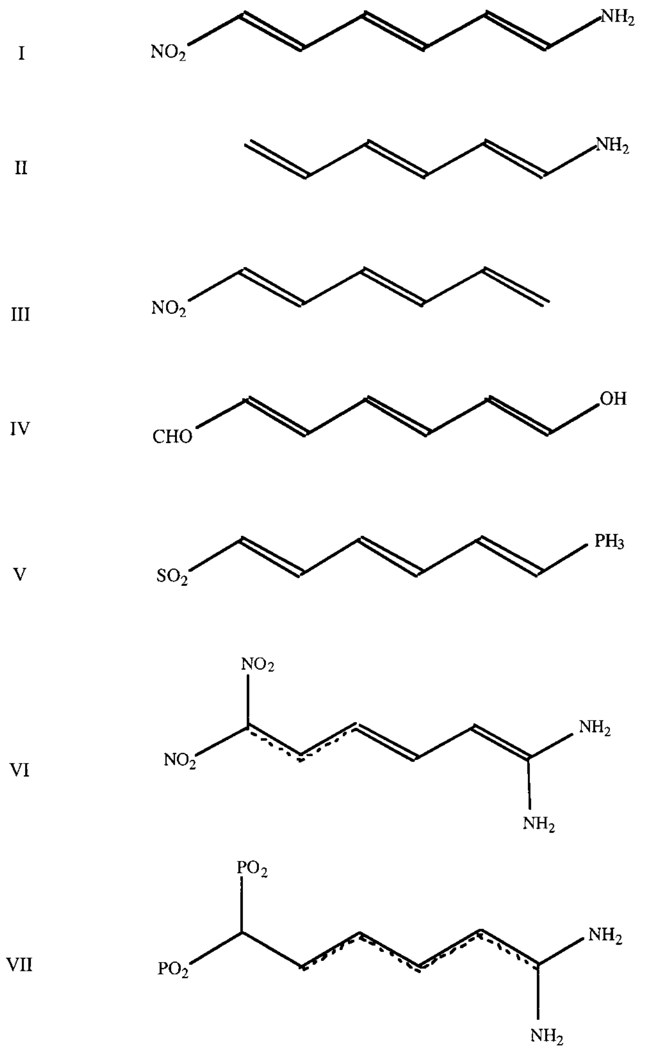

Figure 1. Representative set of molecules used for assessment of field simulation.

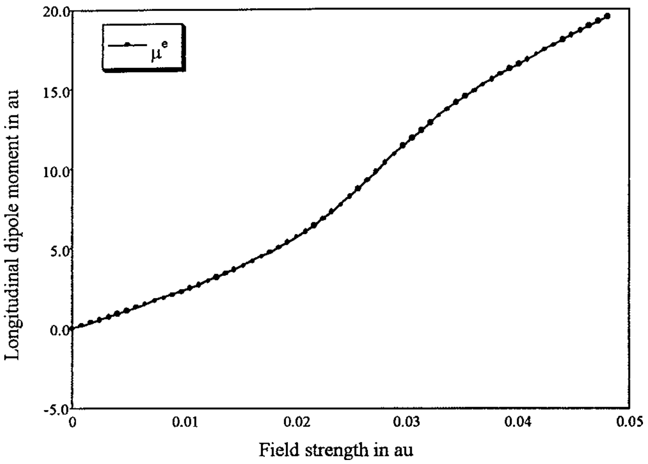

Figure 2. Electronic dipole moment of *all-trans*-octatetraene as a function of the simulation field strength.

examine whether a single field can be used to simulate the entire set of electrical properties for a given molecule. Although the results in this case are specific to field simulations, there are obvious implications for other simplified models. Finally, the dependence of the properties on the chain length of the polyene linker, for a fixed simulation field, allows us to gain quantitative information regarding the localization of substituent effects.

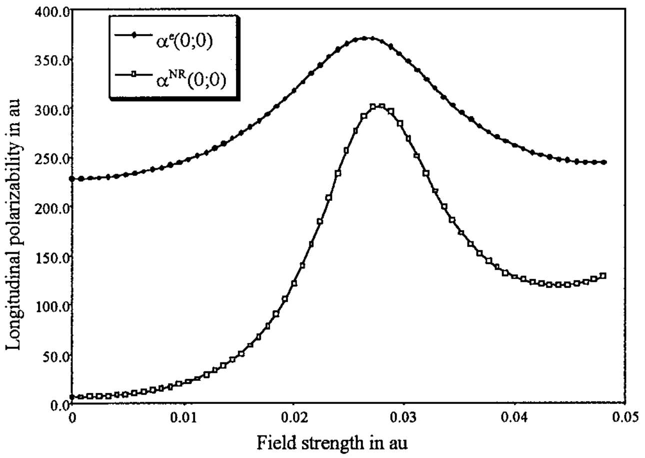

Figure 3. Electronic and nuclear relaxation polarizabilities of *all-trans*-octatetraene as a function of the simulation field strength.

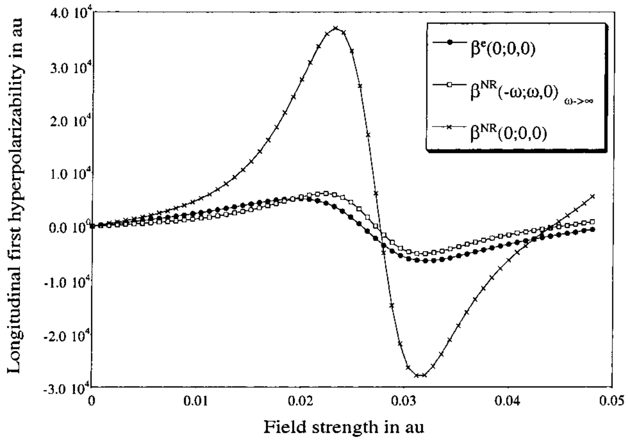

Figure 4. Electronic and nuclear relaxation first hyperpolarizabilities of *all-trans*-octatetraene as a function of the simulation field strength.

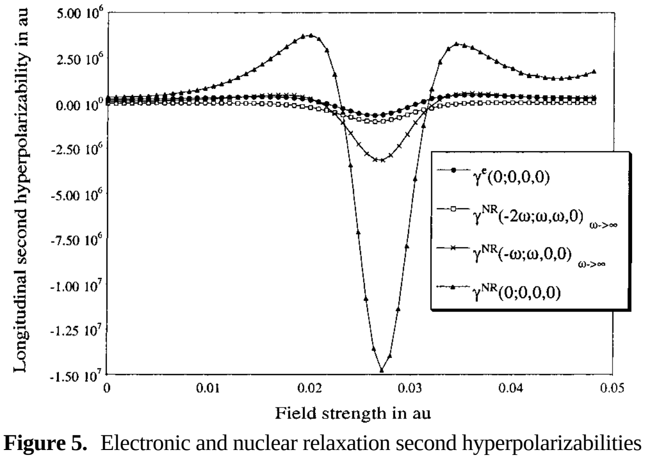

Figure 5. Electronic and nuclear relaxation second hyperpolarizabilities of *all-trans*-octatetraene as a function of the simulation field strength.

In the next section, we review the computational methods that have been employed and analyze, in detail, how the electronic and vibrational motions contribute to the calculated properties. Then, in section III, our results are presented and discussed with respect to the several issues raised above. Finally, section IV presents our conclusions and summarizes the circumstances under which the field simulation approach can be expected to yield useful information.

II. Computational Methods

We began by choosing a representative test set of seven molecules (Figure 1). Five of the seven were taken from a

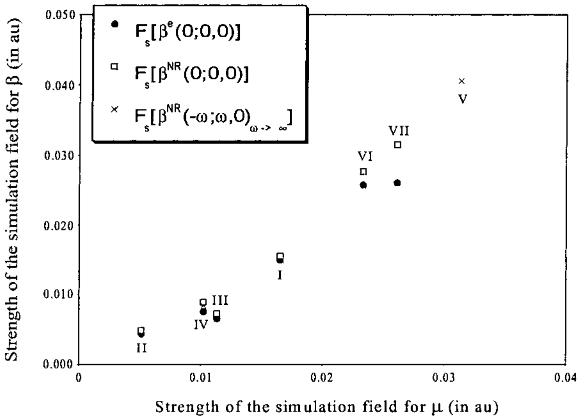

Figure 6. Relation between the F_s that reproduces μ^e vs the F_s that reproduces β^e, $\beta^{NR}(0;0,0)$, and $\beta^{NR}(-\omega;\omega,0)$. The straight line represents perfect correlation.

previous paper[16] dealing with the two-state valence-bond (VB) charge-transfer (CT) model for such molecules. They include cases where the VB structure is dominant (I, IV), where the CT structure is dominant (V), and where there is a large mixing (VI, VII) of the two structures. Molecules II and III were obtained from I by removing either the donor or the acceptor. The geometries of these molecules were optimized at the RHF/6-31G level using the Gaussian94 program[20] with the TIGHT optimization criterion. Our calculations focused on the longitudinal component of the electrical properties which is ordinarily dominant. For convenience, the longitudinal direction was defined to be along the line connecting the bond midpoints at the extremities of the backbone. μ^e, α^e, and β^e were obtained analytically by the CPHF scheme,[21] employing Gaussian94 and a 6-31G basis. γ^e was found by numerical differentiation of the field-dependent β^e; this is completely equivalent to an analytical CPHF calculation of the same quantity. The differentiation was carried out by the Romberg procedure[22] using fields of 8, 16, 32, and 64 × 10^{-4} au with two or three iterations to remove the higher-order hyperpolarizability contaminants. The use of the split-valence 6-31G basis set was dictated by the numerous studies that have shown it is adequate for obtaining semiquantitative electronic and vibrational first and second hyperpolarizabilities of π-conjugated systems.[23]

It is now well-known[16−19,24] that vibrational contributions to hyperpolarizabilities can be quite important for the type of molecules considered here. Indeed, the analysis presented in the original simulation paper[1] actually pertains to a combination of vibrational and electronic hyperpolarizabilities as recognized in general terms later on.[25] A more detailed treatment, which is needed for the purposes of this paper, now follows. The vibrational contributions can be evaluated at various levels of approximation.[26,27] Here we apply the finite field (FF) treatment of Bishop, Hasan, and Kirtman (BHK)[28] which yields the so-called nuclear relaxation (NR) vibrational hyperpolarizabilities in the infinite optical frequency limit. The NR hyperpolarizabilities contain the lowest-order terms of each "square bracket" type that appear in the complete perturbation treatment developed by Bishop and Kirtman.[27] This omits the zero-point vibrational averaging correction and higher-order terms[29] that arise from the effect of nuclear relaxation on this correction. It also only approximates[30] the true dispersion effect since the optical frequency is finite rather than infinite. Nonetheless, the most significant vibrational effects are included.

Table 1. Electronic Properties of the D/A Polyenes (in au)[a]

molecule	μ^e	α^e	β^e	γ^e
I	4.443	242.7	4084	32145 × 10
II	1.219	169.6	972	91518
III	2.812	189.2	1502	17122 × 10
IV	2.511	212.3	1774	19330 × 10
V	12.514	322.4	−6787	48630 × 10
VI	7.437	334.9	219	−23538 × 10
VII	9.164	322.4	−2889	−11140 × 10

[a] 1.0 au of dipole moment = 8.478358 × 10^{-30} C m = 2.5415 D; 1.0 au of polarizability = 1.6488 × 10^{-41} C^2 m^2 J^{-1} = 0.14818 $Å^3$; 1.0 au of first hyperpolarizability = 3.2063 × 10^{-53} C^3 m^3 J^{-2} = 8.641 × 10^{-33} esu; 1.0 au of second hyperpolarizability = 6.235377 × 10^{-65} C^4 m^4 J^{-3} = 5.0367 × 10^{-40} esu).

The first step in the BHK treatment is to optimize the geometry in the presence of a finite static "pump" field, F_p. It should be emphasized that F_p is unrelated to the simulation field, F_s, which is discussed later. To maintain the direction of F_p during the geometry optimization, particular care must be exercised[31] to satisfy the field-free Eckart conditions. In addition, the geometries must be obtained with high accuracy in order to limit errors in the subsequent fitting procedure. For this reason, it was necessary to lower the threshold on the residual atomic forces to 10^{-6} au along with an SCF threshold of 10^{-12} au. Given the optimized geometry, R_{F_p}, the next step is to evaluate μ^e, α^e, and β^e in the presence of the same field; this yields $\mu^e(F_p, R_{F_p})$, etc. If one subtracts $\mu^e(0,R_0)$, etc., then the difference may be written as an expansion in F_p:

$$\Delta\mu^e_\alpha(F_p,R_{F_p}) = \mu^e_\alpha(F_p,R_{F_p}) - \mu^e_\alpha(0,R_0) = a_1F_{p\beta} + \frac{1}{2}b_1F_{p\beta}F_{p\gamma} + \frac{1}{6}g_1F_{p\beta}F_{p\gamma}F_{p\delta} + \ldots \quad (1)$$

$$\Delta\alpha^e_{\alpha\beta}(F_p,R_{F_p}) = b_2F_{p\gamma} + \frac{1}{2}g_2F_{p\gamma}F_{p\delta} + \ldots \quad (2)$$

$$\Delta\beta^e_{\alpha\beta\gamma}(F_p,R_{F_p}) = g_3F_{p\delta} + \ldots \quad (3)$$

Although it may be obvious, we emphasize that the "probe" field used implicitly in the analytical evaluation of the lhs of

---

(20) Gaussian94, Revision B.1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Rhagavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

(21) Langhoff, P. W.; Karplus, M.; Hurst, R. P. *J. Chem. Phys.* **1966**, *44*, 505. Caves, T. C.; Karplus, M. *J. Chem. Phys.* **1969**, *50*, 3649. Dykstra, C. E.; Jasien, P. G. *Chem. Phys. Lett.* **1984**, *109*, 388. Sekino, H.; Bartlett, R. J. *J. Chem. Phys.* **1986**, *85*, 976; Karna, S. P.; Dupuis, M. *J. Comput. Chem.* **1991**, *12*, 487.

(22) Davis, P. J.; Rabinowitz, P. *Numerical Integration*; Blaisdell Publishing Co.: London, 1967; p 166. Jacquemin, D.; Champagne, B.; André, J. M. *Int. J. Quantum Chem.* **1997**, *65*, 679.

(23) Jacquemin, D.; Champagne, B.; André, J. M. *Int. J. Quantum Chem.* **1997**, *65*, 679. Jacquemin, D.; Champagne, B.; Hättig, C. *Chem. Phys. Lett.* **2000**, *319*, 327. Champagne, B.; Kirtman, B. In *Handbook of Advanced Electronic and Photonic Materials and Devices*; Nalwa, H. S., Ed.; Academic Press: San Diego, CA, 2000; references therein.

(24) Del Zoppo, M. Castiglioni, C.; Zerbi, G. *Nonlinear Opt.* **1995**, *9*, 73. Zuliani, P.; Del Zoppo, M.; Castiglioni, C.; Zerbi, G.; Marder, S. R.; Perry, J. W. *J. Chem. Phys.* **1995**, *103*, 9935.

(25) Gorman, C. B.; Marder, S. R. *Chem. Mater.* **1995**, *7*, 215.

(26) Bishop, D. M. *Adv. Chem. Phys.* **1998**, *104*, 1.

(27) Bishop, D. M.; Kirtman, B. *J. Chem. Phys.* **1991**, *95*, 2646.

(28) Bishop, D. M.; Hasan, M.; Kirtman, B. *J. Chem. Phys.* **1995**, *103*, 4157.

(29) Kirtman, B.; Luis, J. M.; Bishop, D. M. *J. Chem. Phys.* **1998**, *108*, 10008.

(30) Bishop, D. M.; Kirtman, B. *J. Chem. Phys.* **1998**, *109*, 9674.

(31) Luis, J. M.; Duran, M.; Andrés, J. L.; Champagne, B.; Kirtman, B. *J. Chem. Phys.* **1999**, *111*, 875.

Table 2. Vibrational Properties of the D/A Polyenes (in au)

molecule	$\alpha^{NR}(0;0)$	$\beta^{NR}(0;0,0)$	$\beta^{NR}(-\omega;\omega,0)_{\omega\to\infty}$	$\gamma^{NR}(0;0,0,0)$	$\gamma^{NR}(-\omega;\omega,0,0)_{\omega\to\infty}$	$\gamma^{NR}(-2\omega;\omega,\omega,0)_{\omega\to\infty}$
I	65.9	1299×10	2976	2690×10^3	5670×10^2	8288×10
II	18.6	178×10	509	237×10^3	739×10^2	724×10
III	18.6	295×10	836	555×10^3	1553×10^2	2258×10
IV	38.1	398×10	1119	707×10^3	1870×10^2	2482×10
V	242.0	-3983×10	-1333	107×10^5	-710×10^3	-2360×10^2
VI	334.9	-77×10	3256	-215×10^5	-326×10^4	-941×10^3
VII	241.2	-280×10^2	-2695	394×10^4	-1164×10^3	-5143×10^2

Table 3. Strength of Simulation Fields (au) That Reproduce a Given Electronic Property (1.0 au of Field = 5.1422×10^{11} V m^{-1})[a]

	F_s			
molecule	μ^e	α^e	β^e	γ^e
I	0.0165	0.0090	0.0150	0.0119
II	0.0051		0.0044	
III	0.0113		0.0066	
IV	0.0102		0.0076	
V	0.0313	0.0326		
VI	0.0233	0.0196	0.0258	0.0229
VII	0.0261	0.0326	0.0261	0.0302

[a] A blank space means that there is no F_s that gives the true value.

eqs 1−3 is different from F_p and F_s. In particular, the probe field is applied at fixed geometry. As shown in ref 28, theexpansion parameters can be related to the static and dynamic NR vibrational properties:

$$a_1 = \alpha^{e}_{\alpha\beta}(0;0) + \alpha^{NR}_{\alpha\beta}(0,0) \tag{4}$$

$$b_1 = \beta^{e}_{\alpha\beta\gamma}(0;0,0) + \beta^{NR}_{\alpha\beta\gamma}(0;0,0) \tag{5}$$

$$g_1 = \gamma^{e}_{\alpha\beta\gamma\delta}(0;0,0,0) + \gamma^{NR}_{\alpha\beta\gamma\delta}(0;0,0,0) \tag{6}$$

$$b_2 = \beta^{e}_{\alpha\beta\gamma}(0;0,0) + \beta^{NR}_{\alpha\beta\gamma}(-\omega;\omega,0)_{\omega\to\infty} \tag{7}$$

$$g_2 = \gamma^{e}_{\alpha\beta\gamma\delta}(0;0,0,0) + \gamma^{NR}_{\alpha\beta\gamma\delta}(-\omega;\omega,0,0)_{\omega\to\infty} \tag{8}$$

$$g_3 = \gamma^{e}_{\alpha\beta\gamma\delta}(0;0,0,0) + \gamma^{NR}_{\alpha\beta\gamma\delta}(-2\omega;\omega,\omega,0)_{\omega\to\infty} \tag{9}$$

In eqs 4−9, we have used the standard notation, e.g., $\gamma(-\omega_\sigma; \omega_1, \omega_2, \omega_3)$, to designate the frequencies of the oscillating electric fields, $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$, and the subscript $\omega \to \infty$ to indicate the infinite optical frequency limit. The subscripts α, β, γ, and δ refer to Cartesian directions; in our calculations, only the longitudinal direction z is considered, i.e., $\alpha = \beta = \gamma = \delta = z$. Since the static electronic properties (hereafter denoted α^e, β^e, γ^e) are known from separate calculations, these equations are readily solved for $\alpha^{NR}(0;0)$, $\beta^{NR}(0;0,0)$, etc., once the coefficients in eqs 1−3 have been obtained. The latter, in turn, are found by using the Romberg technique with $F_p = 2^k F_{0p}$; $k = 0-3$; and $F_{0p} = 4 \times 10^{-4}$ or 8×10^{-4} au. For g_1 or, equivalently, $\gamma^{NR}(0;0,0,0)$, it is often necessary to include $k = 4$ as well.

To simulate the D/A polyenes we apply a uniform static field, F_s, to the corresponding unsubstituted molecule $CH_2{=}(CH{-}CH)_3{=}CH_2$. Then, with F_s fixed, the same procedures are employed as in the case of the "real" D/A molecule. Thus, for example, the lhs of eq 1 becomes

$$\mu^{e}(F_s + F_p, R_{F_s+F_p}) - \mu^{e}(F_s, R_{F_s}) \tag{10}$$

while the rhs is unaltered. Equations 2 and 3 are modified analogously. It should be evident that the derivative relations between the electrical properties of the simulated molecule are more complicated than at first envisioned. Marder et al.[1] defined the polarizability and hyperpolarizabilities as

$$\alpha_0 = \frac{\partial \mu_0}{\partial F} \qquad \beta_0 = \frac{\partial \alpha_0}{\partial F} \qquad \gamma_0 = \frac{\partial \beta_0}{\partial F} \tag{11}$$

where their F is our $F_s + F_p$ and the derivatives are evaluated at $F_p = 0$. The fact that each higher-order property is the derivative of the next lower-order property is the basis of their *unified* description of linear and nonlinear polarization. In the notation of this paper,

$$\alpha_0 = a_1 \qquad \beta_0 = b_2 \qquad \gamma_0 = g_3 \tag{12}$$

From eqs 4, 7, and 9, we see that the properties α_0, β_0, and γ_0 contain a vibrational contribution. Thus, one should not expect them to be the same as the *electronic* polarizability and hyperpolarizabilities evaluated at the R_{F_s} geometry, namely, $\alpha^e(F_s, R_{F_s})$, $\beta^e(F_s, R_{F_s})$, and $\gamma^e(F_s, R_{F_s})$, and the observed differences cannot simply be ascribed to errors in numerical differentiation[1]. Finally, we note that the alternative definitions for the hyperpolarizabilities (cf. eq 1):

$$\beta_0{}' = \frac{\partial^2 \mu_0}{\partial F^2} = b_1 \qquad \gamma_0{}' = \frac{\partial^3 \mu_0}{\partial F^3} = g_1 \qquad \gamma_0{}'' = \frac{\partial^2 \alpha_0}{\partial F^2} = g_2 \tag{13}$$

each include a vibrational contribution which is different from that given by eq 12. The reason for the difference is that the derivatives include contributions due to the geometry relaxation induced by F. As a result, the $\beta_0{}'$ given, for example, in eq 13 will contain terms that depend on the second derivative of μ_0 with respect to nuclear displacements whereas such terms are absent from the expression for β_0 in eq 12. This is just one way in which β_0 and $\beta_0{}'$ differ. There are other terms that are present in $\beta_0{}'$ but not in β_0; in addition, terms that are of the same form in both equations have different multiplicative coefficients.[18,26] A similar analysis pertains to the comparison among γ_0, $\gamma_0{}'$, and $\gamma_0{}''$.

III. Results and Discussion

In Figures 2−5 we plot the static electrical properties (μ, α, β, and γ, respectively) of $H(CH{=}CH)_4H$ as a function of the field, F_s, used to simulate the effect of replacing the terminal CH_2 groups by a donor (D) at one end and an acceptor (A) at the other. Except for the dipole moment, both electronic and vibrational contributions are shown on the same figure. For any given property, the electronic and vibrational curves are all *qualitatively* similar in shape to one another and to the corresponding π-bond order alternation (BOA) curve in ref 1. This confirms the key role of the BOA parameter as a descriptor for the variation of electrical properties as a function of field-induced intramolecular charge transfer. It also suggests a connection between the vibrational and electronic terms *insofar as* their response to a simulation field is concerned. It is

Table 4. Strength of Simulation Fields (au) That Reproduce a Given Vibrational Property[a]

molecule	F_s					
	$\alpha^{NR}(0;0)$	$\beta^{NR}(0;0,0)$	$\beta^{NR}(-\omega;\omega,0)_{\omega\to\infty}$	$\gamma^{NR}(0;0,0,0)$	$\gamma^{NR}(-\omega;\omega,0,0)_{\omega\to\infty}$	$\gamma^{NR}(-2\omega;\omega,\omega,0)_{\omega\to\infty}$
I	0.0166	0.0155	0.0150	0.0166		
II	0.0093	0.0049	0.0045			
III	0.0093	0.0073	0.0068	0.0069	0.0067	
IV	0.0136	0.0089	0.0085	0.0087	0.0084	
V	0.0243		0.0406	0.0546	0.0309	0.0319
VI		0.0277	0.0256			0.0252
VII	0.0316	0.0315	0.0286		0.0303	0.0302

[a] A blank space means that there is no F_s that gives the true value.

Table 5. $\mu^e(\beta^e)$ (in au) for F_s That Causes $\beta^e(\mu^e)$ To Vanish[a]

molecule	F_s	μ^e	β^e
I	0.0	4.443	4084
	−0.0190	0.0	−334
	−0.0169	0.457	0.0
IV	0.0	2.511	1774
	−0.0111	0.0	−147
	−0.0104	0.083	0.0
VI	0.0	7.437	219
	−0.0166	0.0	321
	−0.0187	−0.718	0.0

[a] The value of $\mu^e$and β^e for $F_s = 0.0$ is also given for comparison purposes.

interesting to note that, in every case, the oscillations in the vibrational curve are either larger or much larger than those in the corresponding electronic curve.

Ab initio values for the various electronic and vibrational polarization properties of the D/A polyenes that we seek to simulate are reported in Tables 1 and 2. Tables 3 and 4 list the fields that reproduce these properties. Looking at the electronic quantities in Table 3, we see that in many cases there is no F_s that will reproduce the static α^e or γ^e. The same is true for the vibrational contributions to the second hyperpolarizability as may be seen in Table 4.

It is clear, then, that the field simulation approach does not provide a *unified* description of the electronic or vibrational polarizability and hyperpolarizabilities of the D/A polyenes. On physical grounds, this is not too surprising since μ^e and β^e are a consequence of electronic asymmetry whereas α^e and γ^e are not. If we limit ourselves to the dipole moment and first hyperpolarizability, the situation is more favorable. A plot of the F_s that reproduces μ^e vs the F_s that reproduces β^e, $\beta^{NR}(0;0,0)$, and $\beta^{NR}(-\omega;\omega,0)_{\omega\to\infty}$ is shown in Figure 6. For a perfect correlation, the points would all fall on the same straight line with a slope of unity and an intercept of zero. We conclude that there is a semiquantitative correlation. No analogous figure can be made for the polarizability vs the second hyperpolarizability of the simulated D/A polyenes since there are so many cases where there is no F_s that will reproduce the true value.

As a further check on the validity of applying the field simulation approach in a semiquantitative manner to μ^e and β^e, the following calculations were performed. Starting with one of the real D/A polyenes, a simulating field was applied in such a direction as to reduce the dipole moment. That field was, then, increased in magnitude until the static μ^e was equal to zero. Hypothetically this should simulate the unsubstituted polyene and the static β^e should also vanish. In practice, the computed β^e is not zero and its magnitude is a measure of the error in the simulation method. One can also reverse the procedure by determining the field that causes β^e to vanish. In Table 5 three examples are given. For the most part, the magnitude of the "error" in μ^e or β^e is less than 10% of the zero field value. On the other hand, for $D = (NH_2)_2$ and $A = (NO_2)_2$ (VI) the discrepancy is over 100% in β^e when $\mu^e = 0$. This may be considered as a consequence of the small first hyperpolarizability of the D/A polyene. Thus, this particular test confirms the semiquantitative validity of the field simulation technique for μ^e and β^e except in cases where the static β^e of the D/A polyene has an unusually small magnitude.

Finally, we examined how the simulation field required to reproduce the ab initio μ^e, β^e, and β^{NR} depends on the chain length of the polyene linker. Table 6A gives the F_s values so obtained for $NH_2(CH{=}CH)_NNO_2$ with $N = 2-5$. For $N = 3-5$, there is only a small difference, as expected, between the β^e and β^{NR} fields. (It is surprising, however, that no F_s will yield the correct β^e when $N = 2$.) On the other hand, we see that the simulation field decreases rapidly with N for each property. An alternative way to represent the latter effect is to use a fixed F_s for all N and compare the calculated with the ab initio property value. To that end, we chose the set $F_s = 0.0096$, 0.0128, and 0.0160 au, which encompasses a reasonable range including the F_s that gives the ab initio μ^e and β^e for $N = 3-4$. Our results for $N = 2-5$ are presented in Table 6B−D. Looking at μ^e, one sees that field simulation leads to a much exaggerated increase with chain length and, in contrast to the ab initio values, shows no sign of saturation for $N \leq 5$. A similar excessive rate of increase with N occurs for both the electronic and vibrational first hyperpolarizabilities. This large overemphasis of the polarizing effect of the D/A pair, which occurs even for relatively short chains, is related to the fact that the effective potential due to the D/A pair is spatially more localized[32,33] than a uniform electric field. Another reflection of the localization is the fact that increasingly strong D/A pairs are required to reach a given bond length alternation value as molecules become longer.[25] Including a field gradient term would allow for a better description in this respect but would also complicate the treatment. The extent to which other more elaborate models[13,15] represent the correct D/A potential remains an open question. On the basis of the results in Table 6, and other ab initio calculations,[33] β^{NR} will usually behave like β^e as far as the chain length dependence is concerned. There will also be exceptions, and of course, the two do behave differently in other respects as we have already seen.

IV. Conclusions

We have calculated the electrical properties μ, α, β, and γ for a representative set of D/A polyenes by both ab initio methods and electric field simulation starting with the corresponding unsubstituted polyene. Vibrational and electronic contributions have been considered. It is shown that, for each property, the field simulation yields a particular combination

---

(32) Tretiak, S.; Chernyak, V.; Mukamel, S. *Chem. Phys. Lett.* **1998**, *287*, 75.

(33) Champagne, B.; Perpète, E. A.; Jacquemin, D.; van Gisbergen, S. J. A.; Baerends, E. J.; Soubra-Ghaoui, C.; Robins, K. A.; Kirtman, B. *J. Phys. Chem. A* **2000**, *104*, 4755.

Table 6.

(A) Simulation Field (in au) That, When Applied to $CH_2{=}(CH{-}CH)_N{=}CH_2$, Reproduces the Ab Initio CPHF/6-31G Dipole Moment and First Hyperpolarizability of $NH_2{-}(CH{=}CH)_N{-}NO_2$[a]

N	μ^e	β^e	$\beta^{NR}(0;0,0)$	$\beta^{NR}(-\omega;\omega,0)_{\omega\to\infty}$
2	0.0238		0.0231	0.0226
3	0.0165	0.0150	0.0155	0.0150
4	0.0123	0.0104	0.0110	0.0107
5	0.0096	0.0077	0.0082	0.0080

Dipole Moment and First Hyperpolarizability Obtained by Applying a Simulation (Sim) Field to $CH_2{=}(CH{-}CH)_N{=}CH_2$ vs the Ab Initio (AI) CPHF/6-31G Value Calculated for $NH_2{-}(CH{=}CH)_N{-}NO_2$

	μ^e		β^e		$\beta^{NR}(0;0,0)$		$\beta^{NR}(-\omega;\omega,0)_{\omega\to\infty}$	
N	Sim	AI	Sim	AI	Sim	AI	Sim	AI
(B) Simulation Field, $F_s = 0.0096$ au								
2	1.4153	3.8718	539	1494	103 × 10	484 × 10	281	1103
3	2.3451	4.4427	2328	4084	451 × 10	130×10^2	1336	2976
4	3.5499	4.8393	7348	8223	1697 × 10	245×10^2	4581	5792
5	5.1070	5.1173	1977 × 10	1356 × 10	6315 × 10	375×10^2	1486 × 10	9103
(C) Simulation Field, $F_s = 0.0128$ au								
2	1.9115	3.8718	736	1494	154 × 10	484 × 10	420	1103
3	3.2314	4.4427	3333	4084	795 × 10	130×10^2	217 × 10	2976
4	5.0953	4.8393	1125 × 10	8223	401×10^2	245×10^2	915 × 10	5792
5	8.0466	5.1173	3064 × 10	1356 × 10	266×10^3	375×10^2	4090 × 10	9103
(D) Simulation Field, $F_s = 0.0160$ au								
2	2.4312	3.8718	942	1494	222 × 10	484 × 10	593	1103
3	4.2354	4.4427	4400	4084	140×10^2	130×10^2	3429	2976
4	7.1964	4.8393	1363 × 10	8223	970×10^2	245×10^2	1675 × 10	5792
5	13.9546	5.1173	−1326 × 10	1356 × 10	-181×10^3	375×10^2	−1773 × 10	9103

[a] A blank space means that there is no F_s that gives the true value.

of vibrational and electronic terms. When these two terms are plotted vs F_s (the simulating field), the resulting curves are similar in shape. In addition, the curve for α, β, and γ has the general shape dictated by the derivative of the next lower-order property.

Although one particular F_s can approximately reproduce the ab initio μ and β (both electronic and vibrational) for a given D/A polyene, the same field does not reproduce either α or γ. In fact, we have found that there is in general no field that will do so. This leads us to conclude that the field simulation approach can only be used to provide a unified description of the odd-order properties (i.e. μ, β, ...) and that field nonuniformity and/or specific bonding interactions are important to reproduce the complete D/A effect. With this limitation, the results are semiquantitative, but one must be careful to avoid properties that depend strongly on the localized character of the substituent effect such as the dependence of μ and β on the chain length of the linker. Although only the linear polyene linker has been studied here, our analysis of the chain-length dependence strongly suggests that field simulation will not be useful for studying effects due to changing the linker in push−pull molecules.

Acknowledgment. D.M.B. thanks the Natural Sciences and Engineering Research Council of Canada for financial support. B.C. thanks the Belgian National Fund for Scientific Research for his Research Associate position. The calculations have been performed on the IBM SP2 of the Namur Scientific Computing Facility (Namur-SCF) for which the authors gratefully acknowledge the financial support of the FNRS-FRFC and the “Loterie Nationale” for the convention No. 2.4519.97.

JA993226E