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Frequency dependence of linear and nonlinear optical properties of conjugated polyenes: An *ab initio* time-dependent coupled Hartree-Fock study

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Using a split-valence Gaussian 4-31G basis function augmented with diffuse p and d function and multiconfiguration self-consistent-field optimized geometries, the frequency-dependent polarizability α and second hyperpolarizability γ of ethylene, *trans*-butadiene, *trans*-hexatriene, and *trans*-octatetraene molecules have been calculated by the time-dependent coupled perturbed Hartree-Fock *ab initio* method. The calculated values of α and γ are in good agreement with the corresponding gas-phase experimental values at the same fundamental wavelength. The various γ values corresponding to different third-order processes exhibit marked difference in their dependence on the conjugation length. For a specific fundamental frequency, the calculated γ value exhibits the following order: $\gamma(-3\omega;\omega,\omega,\omega)>\gamma(-2\omega;0,\omega,\omega)>\gamma(-\omega;\omega,\omega,-\omega)>\gamma(-\omega;0,0,\omega)\approx\gamma(0;0,\omega,-\omega)$.

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I. INTRODUCTION

The observation of very large third-order nonlinear optical (NLO) susceptibility, $\chi^{(3)}$, of polydiacetylene [1-5] has created a great deal of interest in the optical properties of conjugated polyenes [6-8]. In particular, the NLO properties of finite-length conjugated polyenes have been a subject of many theoretical investigations [9-20]. Attention has been thereby focused on understanding the relationship between microscopic NLO properties and effective π-electron conjugation length along the molecular chain.

The dispersion of NLO effects, which is of paramount importance in the study of optical nonlinearity of conjugated polymers and their application to photonic devices, has received rather limited attention. A few semiempirical studies of the frequency-dependent hyperpolarizabilities, γ, restricted to a single optical wavelength have been reported [15,16]. Furthermore, these studies have been concerned with hyperpolarizability for a single NLO process such as the third-harmonic generation (THG) only and provide no information about the dispersion of hyperpolarizability for other processes, such as dc-electric-field-induced second-harmonic (EFISH) generation, optical Kerr effect (OKE), degenerate four-wave mixing (DFWM), etc. Thus, in view of growing interest in the NLO properties of conjugated polymers, accurate and reliable study of their dispersion effect is considered important and timely.

Recent advances in computational techniques [21,22] have enabled us to study the dispersion of NLO properties of large organic molecules by an *ab initio* method [23-26]. In this paper we report our study of the dispersion of molecular polarizability α and second hyperpolarizability γ for various third-order NLO processes for ethylene (ET), *trans*-butadiene (BD), *trans*-hexatriene (HT), and *trans*-octatetraene (OT) using the *ab initio* method in the framework of the time-dependent coupled perturbed Hartree-Fock (TDCPHF) approach for closed-shell molecules. The frequency-dependent α has been calculated at a series of optical wavelengths λ down to 301 nm and various γ's down to 602 nm.

A comparison between the quantum-chemical calculation and experimental measurements is often not reliable because the measurements are generally conducted in solution or solid phase while the calculations are made for isolated molecule. These condensed-phase measurements are complicated by the local-field effects derived from intermolecular interaction.

Fortunately, for ET, BD, and HT, experimental values of γ in the gas phase have been reported using EFISH measurements [27,28]. Therefore, it is possible to compare the rigorous quantum-chemical results directly with the gas-phase experimental values. Such a comparison in our previous studies on haloforms [23] and p-nitroaniline [24] was restricted because experimental data for NLO properties of these systems were available only for the condensed phase. Thus, the purpose of this work is twofold: (i) to test the predictive ability of our method with regard to NLO properties by comparing with the corresponding gas-phase experimental results, and (ii) to study the dispersion effects of molecular NLO susceptibilities in finite-length polyene homologs.

The paper is organized as follows: The underlying theory and computational details are briefly described in Sec. II. In Sec. III, the calculated results of α and γ for ET, BD, and HT are compared with the reported experimental results. The dispersion properties of α and γ for the four molecules are discussed in Sec. IV. The main findings of the present study and implications on future calculations are summarized in Sec. V.

II. THEORY AND COMPUTATIONS

The microscopic polarization $\underline{p}$ induced in a centrosymmetric molecule by an external electric field of amplitude $\underline{E}$ can be written as

$$\underline{p}=\underline{\alpha}\cdot\underline{E}+\underline{\gamma}\vdots\underline{E}\,\underline{E}\,\underline{E}+\cdots , \tag{1}$$

where $\underline{\alpha}$ is the linear polarizability tensor and $\underline{\gamma}$ is the nonlinear second hyperpolarizability tensor. The elements of $\underline{\alpha}$ and $\underline{\gamma}$ can be obtained from the dipole moment matrix $\underline{M}$ and density matrix $\underline{D}(\underline{E})$ as

$$\underline{\alpha}=-\mathrm{Tr}[\underline{M}\,\underline{D}^{(1)}(\underline{E})] , \tag{2}$$

$$\underline{\gamma}=-\mathrm{Tr}[\underline{M}\,\underline{D}^{(3)}(\underline{E})] , \tag{3}$$

where $\underline{D}^{(1)}(\underline{E})$ and $\underline{D}^{(3)}(\underline{E})$ are the first-order and the third-order perturbed density matrices, respectively. The method used to calculate the frequency-dependent polarizability $\alpha(\omega)$ is similar to that of Sekino and Bartlett [29]. The frequency-dependent γ values for various third-order processes are calculated using the $2n+1$ rule of perturbation theory [30]. The details of our method have already been given elsewhere [22]. The second hyperpolarizability for different processes are denoted as follows: $\gamma(-3\omega;\omega,\omega,\omega)$ for THG; $\gamma(-2\omega;0,\omega,\omega)$ for EFISH; $\gamma(-\omega;\omega,\omega,-\omega)$ for DFWM; $\gamma(-\omega;0,0,\omega)$ for OKE, and $\gamma(0;0,\omega,\omega)$ for dc-electric-field-induced optical rectification (EFIOR). It should be noted that the elements of $\gamma(-\omega;0,0,\omega)$ and $\gamma(0;0,\omega,-\omega)$ are related to each other by the general symmetry property of the third-order hyperpolarizability tensor. The Kleinman symmetry [31] for hyperpolarizability tensors as discussed in the following section is not assumed in our study.

In order to compare with the experimental results, the orientationally averaged scalar values of $\underline{\alpha}$ and $\underline{\gamma}$, respectively, are calculated as

$$\langle\alpha\rangle=\tfrac{1}{3}\sum_{i}\alpha_{ii},\quad i=x,y,z , \tag{4}$$

$$\langle\gamma\rangle=\tfrac{1}{15}\sum_{i,j}(\gamma_{iijj}+\gamma_{ijij}+\gamma_{ijji}) ,\quad i,j=x,y,z . \tag{5}$$

All calculations have been performed using the HONDO [21] *ab initio* molecular program package. Calculations have been performed in using a C_{2h} symmetry with z as the C_2 axis and the x axis along the molecular chain. The origin was taken at the center of symmetry for each molecule. For the components of α and γ tensors, we use a right-handed inertial axis of the molecules, as used earlier by Hurst *et al.* [19]. Thus, the Cartesian axes x,y,z for $\underline{\alpha}$ and $\underline{\gamma}$ refer to the inertial axes in the order of increasing moments of inertia.

The selection of proper basis functions is of paramount importance in the *ab initio* calculations of molecular NLO properties. In a recent basis-set study of static polarizability and second hyperpolarizability of ethylene, Chopra *et al.* [20] have noted that a sufficiently flexible valence Gaussian basis set, such as a 3-21G or 6-31G, augmented by diffuse p and d functions on carbon atoms is necessary for a proper description of various tensor components. These authors found the result of α and γ to be insensitive to the choice of the valence basis set, 3-21G or 6-31G, as also noted by Karna *et al.* [32] in the case of hexadine where a 4-31G basis essentially yields the same result as a 6-31G basis. In an effort to obtain an optimized basis set to be used for conjugated polyenes, Hurst *et al.* [19] have performed an extensive study of the influence of various polarization and diffuse functions on static (hyper)polarizabilities of trans-butadiene. In their study, the 6-31G basis set for butadiene was augmented by systematically adding polarization d and diffuse s, p, and d functions on carbon and polarization p and diffuse s and p functions on H. With a basis set (called K in Ref. [19]) which included one s, two p, and four d functions on carbon and one s function on hydrogen in conjunction with 6-31G, these authors were able to obtain nearly converged values of α and γ tensors. Further augmentation of basis K by adding three p functions on hydrogen (basis L of Ref. [19]) yielded negligible changes in all components of α and γ tensors, except an increase of $\sim 3\%$ in the value of γ_{zzzz} and a decrease of $\sim 5\%$ in the value of γ_{xxzz}. An optimized basis set that included a diffuse p (0.05) and a diffuse d (0.05) function on carbon, where the numbers in parentheses are the orbital exponents, in conjunction with a 6-31G basis, was found to yield values for α and γ within 0.1% of those obtained from a larger set (called J) composed of a 6-31G basis with C($1s1p1d$) and H($1s$) functions. The results obtained with the optimized basis set, which we will call 6-31G PD, are slightly overestimated with respect to their saturated basis sets K and L. In view of retaining reasonable accuracy as regards to basis-set saturation and yet being able to use consistently for all molecules considered in this study, we selected a 4-31G basis augmented by the optimized p and d diffuse functions on carbon as obtained by Hurst *et al.* [19]. Hurst *et al.* did not study the influence of f functions, however, a recent study by Karna *et al.* [33] on haloforms has shown that these functions, when used in conjunction with diffuse p and d functions on heavy atoms, have negligible effect on the calculated values of (hyper)polarizability tensors. In large polyatomic systems, the diffuse p and d functions on neighboring atoms play the role of higher angular momentum functions, thereby diminishing the need for their explicit inclusion. Therefore, the absence of f functions in our basis set is not supposed to introduce a discernible error. However, it should be pointed out that the results obtained by the present basis set may be slightly overestimated with respect to a better, nearly saturated basis set, as noted by Hurst *et al.* [19] in the case of *trans*-butadiene. The *ab initio* multiconfiguration self-consistent field (MCSCF) optimized geometry of Ayogi *et al.* [33] was used for each molecule. Calculations were performed on an IBM 3090 VF and a dedicated IBM RS/6000-520 machine.

III. RESULTS FOR ET, BD, AND HT

For the first two members, namely ET and BD, the experimental values of α are available in the literature [34,35]. Also, as noted earlier, the gas-phase experimental values of $\gamma(-2\omega;0,\omega,\omega)$ for ET, BD and HT at a fundamental wavelength of $\lambda=694.3$ nm are available [27]. For BD, a recent measurement of $\gamma(-2\omega;0,\omega,\omega)$ at

$\gamma = 1064$ nm has also been reported [28]. The experimental data along with the corresponding results obtained in the present study are listed in Table I. One notices that the calculated values of α are slightly smaller (8% for ET and < 1% for BD) than their experimental counterparts. Considering the uncertainties involved in the experimental measurement of α, the agreement between the theory and the experiment is good. Such agreement between calculated and experimental results for α has also been noted in our previous studies on other molecules [23-26].

Although most other *ab initio* calculations [18-20] of α for polyenes have reported good agreement with experiment, the same is not true for γ, where a discrepancy of up to 50% between theory and experiment has been noted [19,20]. The basis-set inadequacy and lack of electron correlation in theoretical calculations among other factors have been suggested as the possible sources of this discrepancy. In the case of *trans*-butadiene, Hurst *et al.* [19] have shown that, in going from a modestly extended basis set including a *p* and a *d* diffuse function on *C* to a large one with one *s*, two *p*, and four *d* functions on *C* and one *s* and three *p* functions on *H*, the value of γ in the case of BD changes by less than 6%. Inclusion of electron correlation does improve the results, as has been noted by Perrin *et al.* [36] in the case of benzene, but these two effects alone cannot account for the large discrepancy between theory and experiment. Of course, the previous *ab initio* studies were performed at a zero optical frequency (static field), whereas the experimental measurements are done at a nonzero value of optical frequency which may cause substantial dispersion of γ, as will be discussed in the subsequent section. Therefore, the theoretical results could not correspond directly to the experimental values obtained from EFISH measurements. When calculated at the same frequency as the experiment, the theoretical results for $\gamma(-2\omega;0,\omega,\omega)$ of ET, BD, and HT show good agreement with their experimental counterparts, as can be seen from Table I. In fact, a small difference of about 6% between theoretical and experimental values of $\gamma(-2\omega;0,\omega,\omega)$ in the case of ET and BD decreases further to less than 2% in the case of HT, though the difference between theory and the experiment for the three molecules is not in the same direction. For example, the theoretical values of $\gamma(-2\omega;0,\omega,\omega)$ in the case of ET and HT are lower than the corresponding experiment values while the opposite is true in the case of BD. While a better agreement between the theoretical and the measured results is possible by further improving the basis set and including electron correlation in the wave function, the present study gives confidence in the *ab initio* TDHF method for predicting NLO properties of conjugated systems. The present study also indicates that a somewhat larger difference noted between the *ab initio* and measured values of γ of ET, BD and HT in previous studies [19,20] is mainly due to frequency-dependence (dispersion) of different third-order NLO processes not included in those works.

TABLE I. Calculated and experimental values of $\alpha(\omega)$[a] and $\gamma(-2\omega;0,\omega,\omega)$[b] for ethylene, *trans*-butadiene, and *trans*-hexatriene.

Molecule		Total energy (a.u.)	$\alpha(\omega)$ (10^{-24} cm^3)	$\gamma(-2\omega;0,\omega,\omega)$ (10^{-36} esu)
C_2H_4	Theory	−77.298 681	3.89	0.711
	Expt.		4.22[c]	0.758±0.017[d]
C_4H_6	Theory	−154.708 997	8.57	2.46
				1.74[e]
	Expt.		8.64[f]	2.30±0.13[d]
				1.69±0.013[e,g]
C_6H_8	Theory	−231.491 596	14.62	7.39
	Expt.			7.53±0.7[d]

[a] Theoretical value at λ=694.3 nm.

[b] Unless otherwise stated all γ values at λ=694.3 nm.

[c] Reference [34].

[d] Reference [27].

[e] At λ=1064 nm.

[f] Reference [35].

[g] Reference [28].

IV. DISPERSION OF POLARIZABILITY AND SECOND HYPERPOLARIZABILITY

As the second objective of this study, we now consider the dispersion of polarizability and the second hyperpolarizability for various processes.

A. Polarizability

The frequency-dependent polarizability calculated for ET, BD, HT, and TO are listed in Tables II–V.

One notices that, in each case, the component along the molecular chain direction (α_{xx}), is not only larger than the other components but increases more rapidly with the optical frequency. Furthermore, the difference between the component of α along the chain (α_{xx}) and other components increases with an increase in the number of carbon atoms. The dispersion behavior of the α_{xx} component of the four molecules are shown together in Fig. 1.

In order to get a clear idea of relative dispersion in each molecule, we define the dispersion of polarizability

TABLE II. Frequency dependence of polarizability $\alpha(\omega)$ of ethylene.

λ (nm)	$\hbar\omega$ (eV)	$\alpha(\omega)$ (10^{-24} cm^3) α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$
∞ (static)	0	5.23	3.33	2.80	3.79
1907	0.650	5.25	3.33	2.81	3.80
1064	1.165	5.30	3.35	2.83	3.83
9535	1.30	5.32	3.36	2.84	3.84
694.3	1.786	5.41	3.38	2.88	3.89
635.7	1.95	5.44	3.39	2.89	3.91
602	2.059	5.46	3.40	2.91	3.92
532	2.330	5.54	3.41	2.94	3.97
347.1	3.571	6.05	3.54	3.17	4.26
301	4.119	6.42	3.63	3.33	4.46

TABLE III. Frequency dependence of polarizability $\alpha(\omega)$ of *trans*-butadiene.

λ (nm)	$\hbar\omega$ (eV)	$\alpha(\omega)$ (10^{-24} cm^3) α_{xx}	α_{xy}	α_{yy}	α_{zz}	$\langle\alpha\rangle$
∞ (static)	0	13.25	−1.45	6.41	4.94	8.20
1907	0.650	13.36	−1.46	6.43	4.95	8.25
1064	1.165	13.60	−1.51	6.47	4.99	8.35
9535	1.30	13.69	−1.53	6.48	5.00	8.39
694.3	1.786	14.11	−1.61	6.54	5.07	8.57
635.7	1.95	14.29	−1.64	6.57	5.10	8.65
602	2.059	14.43	−1.67	6.59	5.12	8.72
532	2.330	14.81	−1.74	6.65	5.17	8.88
347.1	3.571	18.05	−2.37	7.03	5.55	10.21
301	4.119	21.04	−2.95	7.31	5.81	11.39

TABLE V. Frequency dependence of polarizability $\alpha(\omega)$ of *trans*-octatetraene.

λ (nm)	$\hbar\omega$ (eV)	$\alpha(\omega)$ (10^{-24} cm^3) α_{xx}	α_{xy}	α_{yy}	α_{zz}	$\langle\alpha\rangle$
∞ (static)	0	38.37	−5.05	12.42	8.73	19.84
1907	0.65	38.90	−5.15	12.46	8.75	20.04
1064	1.165	40.22	−5.38	12.56	8.81	20.53
935.5	1.30	40.72	−5.47	12.59	8.83	20.71
694.3	1.786	43.14	−5.90	12.75	8.93	21.61
635.7	1.95	44.25	−6.10	12.83	8.97	22.01
602	2.059	45.08	−6.24	12.88	9.00	22.32
532	2.330	47.56	−6.68	13.03	9.08	23.22
347.1	3.572	76.33	−11.83	14.43	9.64	33.47

at frequency ω as

$$d\alpha(\omega)=\frac{\Delta\alpha}{\alpha(\omega)}\times 100 \tag{6}$$

$$\Delta\alpha=\alpha(\omega)-\alpha(0)\ . \tag{7}$$

The quantity $\alpha(0)$ in Eq. (7) is the static polarizability. The dispersion $d\alpha(\omega)$ calculated for each molecule as a function of $\hbar\omega$ is shown in Fig. 2. It is clear that the dispersion of α increases with the number of carbon atoms as well as with the applied optical frequency.

The change in $\alpha(\omega)$ with the number of carbon atoms also can be seen from Fig. 1. With the limited number of molecules, as studied in this paper, $\alpha(\omega)$ is far from saturated and we did not make any attempt to fit the data to a power-law equation. However, it is evident that between C_2 to C_8 $\alpha(\omega)$ increases sharply.

B. Second hyperpolarizability

The frequency-dependent polarizability corresponding to EFIKE, DFWM, EFISH, and THG for ET, BD, HT, and OT are listed in Tables VI–IX. Given in the tables are only the long component (γ_{xxxx}) of the hyperpolarizability tensor, and the scalar value $\langle\gamma\rangle$. Other components that are much smaller than γ_{xxxx} in each case can be obtained from the authors upon personal request. Some interesting features of γ in polyenes emerge from the inspection of Tables VI–IX. One notes that there is large dispersion in the values of γ, which, as expected, increases with the size of the molecule. Thus, in going from the static limit to a fundamental optical wavelength $\lambda=6943$ nm ($\hbar\omega=1.786$ eV), the values of $\gamma_{xxxx}(-2\omega;0,\omega,\omega)$ and $\langle\gamma\rangle(-2\omega;0,\omega,\omega)$ in ET change (increase) by 44 and 42%, respectively. The corresponding increases in BD for the same process are 74 and 107%, respectively. For the higher two members, HT and OT, the value of $\gamma_{xxxx}(-2\omega;0,\omega,\omega)$ increases by factors of 2.7 and 3.7, respectively, while the scalar $\langle\gamma\rangle(-2\omega;0,\omega,\omega)$, increases by factors of 2.3 and 3.3, respectively, in going from static limit to $\lambda=694.3$ nm. It is also clear that the mean value of γ is dominated by γ_{xxxx}, the component along the chain direction. To illustrate this effect more clearly, the frequency-dependent values of γ_{xxxx} and $\langle\gamma\rangle$ corresponding to various third-order processes in the case of the smallest member ET are shown in Figs. 3 and 4, respectively. One notes that the characteristics of dispersion of $\langle\gamma\rangle$ are similar to γ_{xxxx}. The same behavior is shown for the other three molecules, as can be seen from the tables. The dominance of

TABLE IV. Frequency dependence of polarizability $\alpha(\omega)$ of *trans*-hexatriene.

λ (nm)	$\hbar\omega$ (eV)	$\alpha(\omega)$ (10^{-24} cm^3) α_{xx}	α_{xy}	α_{yy}	α_{zz}	$\langle\alpha\rangle$
∞ (static)	0	24.01	2.99	9.43	6.84	13.42
1907	0.65	24.27	3.04	9.46	6.86	13.53
1064	1.165	24.89	3.16	9.52	6.91	13.77
953.5	1.30	25.12	3.20	9.54	6.92	13.87
694.3	1.786	26.21	3.40	9.65	7.00	14.29
635.7	1.95	26.72	3.49	9.69	7.04	14.48
602	2.059	27.07	3.56	9.73	7.06	14.62
532	2.330	28.14	3.76	9.82	7.13	15.03
347.1	3.572	38.34	5.68	10.55	7.60	18.83
301	4.119	50.48	7.99	11.22	7.93	23.21

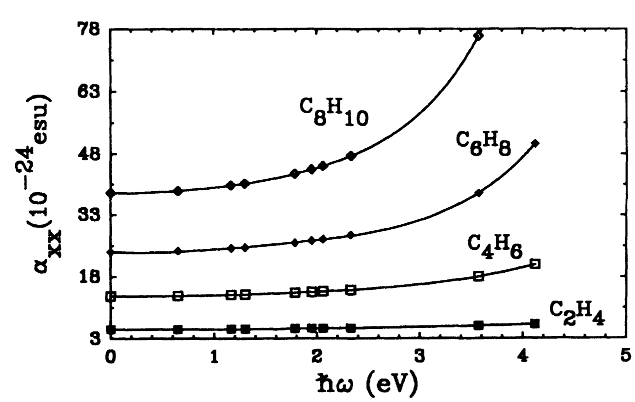

FIG. 1. Frequency dependence of the *xx* component of linear polarizability of ethylene, *trans*-butadiene, *trans*-hexatriene, and *trans*-octatetraene.

TABLE VI. Frequency-dependent second hyperpolarizability γ (10^{-36} esu) of ethylene.

λ (nm) $\hbar\omega$ (eV)	∞[a] 0	1907 0.65	1064 1.165	694.3 1.786	602 2.059
$\gamma_{xxxx}(-\omega;0,0,\omega)$	0.274	0.278	0.288	0.307	0.319
$\langle\gamma\rangle(-\omega;0,0,\omega)$	0.500	0.504	0.520	0.553	0.575
$\gamma_{xxxx}(-\omega;\omega,\omega,-\omega)$	0.274	0.282	0.302	0.346	0.377
$\langle\gamma\rangle(-\omega;\omega,\omega,-\omega)$	0.500	0.512	0.546	0.621	0.679
$\gamma_{xxxx}(-2\omega;0,\omega,\omega)$	0.274	0.287	0.317	0.395	0.454
$\langle\gamma\rangle(-2\omega;0,\omega,\omega)$	0.500	0.519	0.574	0.711	0.815
$\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$	0.274	0.300	0.372	0.642	1.000
$\langle\gamma\rangle(-3\omega;\omega,\omega,\omega)$	0.500	0.543	0.670	1.129	1.736

[a]Static value.

TABLE VII. Frequency-dependent second hyperpolarizability γ (10^{-36} esu) of *trans*-butadiene.

λ (nm) $\hbar\omega$ (eV)	∞[a] 0	1907 0.65	1064 1.165	694.3 1.786	602 2.059
$\gamma_{xxxx}(-\omega;0,0,\omega)$	2.25	2.311	2.45	2.77	2.99
$\langle\gamma\rangle(-\omega;0,0,\omega)$	1.41	1.437	1.50	1.64	1.73
$\gamma_{xxxx}(-\omega;\omega,\omega,-\omega)$	2.25	2.38	2.70	3.52	4.16
$\langle\gamma\rangle(-\omega;\omega,\omega,\omega)$	1.41	1.46	1.61	1.99	2.28
$\gamma_{xxxx}(-2\omega;0,\omega,\omega)$	2.25	2.44	2.97	4.67	6.41
$\langle\gamma\rangle(-2\omega;0,\omega,-\omega)$	1.41	1.495	1.74	2.46	3.15
$\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$	2.25	2.67	4.17		
$\langle\gamma\rangle(-3\omega;\omega,\omega,\omega)$	1.41	1.60	2.25		

[a]Values listed in the column are for the static case.

TABLE VIII. Frequency-dependent second hyperpolarizability γ (10^{-36} esu) of *trans*-hexatriene.

λ (nm) $\hbar\omega$ (eV)	∞[a] 0	1907 0.65	1064 1.165	694.3 1.786	602 2.059
$\gamma_{xxxx}(-\omega;0,0,\omega)$	9.46	9.81	10.67	12.66	14.06
$\langle\gamma\rangle(-\omega;0,0,\omega)$	3.19	3.27	3.50	4.02	4.39
$\gamma_{xxxx}(-\omega;\omega,\omega,-\omega)$	9.46	10.15	11.93	16.83	20.88
$\langle\gamma\rangle(-\omega;\omega,\omega,-\omega)$	3.19	3.37	3.86	5.17	6.26
$\gamma_{xxxx}(-2\omega;0,\omega,\omega)$	9.46	10.54	13.68	25.56	41.19
$\langle\gamma\rangle(-2\omega;0,\omega,\omega)$	3.19	3.40	4.32	7.39	11.26
$\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$	9.46	11.80			
$\langle\gamma\rangle(-3\omega;\omega,\omega,\omega)$	3.19	3.82			

[a]Static value.

TABLE IX. Frequency-dependent second hyperpolarizability γ (10^{-36} esu) of *trans*-octatetraene.

λ (nm) $\hbar\omega$ (eV)	∞[a] 0	1907 0.65	1064 1.165	694.3 1.786
$\gamma_{xxxx}(-\omega;0,0,\omega)$	30.00	31.36	34.76	43.07
$\langle\gamma\rangle(-\omega;0,0,\omega)$	7.61	7.88	8.99	10.44
$\gamma_{xxxx}(-\omega;\omega,\omega,-\omega)$	30.00	32.04	39.96	61.39
$\langle\gamma\rangle(-\omega;\omega,\omega,-\omega)$	7.61	8.19	9.48	14.60
$\gamma_{xxxx}(-2\omega;0,\omega,\omega)$	30.00	36.04	47.60	110.96
$\langle\gamma\rangle(-2\omega;0,\omega,\omega)$	7.61	8.90	11.32	25.280
$\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)$	30.00	39.49		
$\langle\gamma\rangle(-3\omega;\omega,\omega,\omega)$	7.61	9.71		

[a]Static case.

γ_{xxxx} in $\langle\gamma\rangle$ becomes more pronounced as the number of carbon atoms increases as shown in Fig. 5 for $\gamma(-2\omega;0,\omega,\omega)$ at $\lambda=1064$ nm. The γ_{xxxx} also rises more quickly than other components with increase in optical frequency. Furthermore, it is noted from the tables that, at a given optical wavelength λ, the calculated values of γ for different third-order NLO processes show the following order: γ(THG) > γ(EFISH) > γ(DFWM) > γ(EFIKE) as also shown in Fig. 6 at $\lambda=1907$ nm. The values of γ_{xxxx} and $\langle\gamma\rangle$ for the process of EFIOR are the same as the corresponding values for EFIKE and, therefore, not given in the tables. Such an order in the γ for various third-order processes have also been noted in other classes of systems such as haloforms [23], *p*-nitroaniline [24], linear chain molecules, hexapentaene, hexadiyne, and divinylacytylene [25], and benzene [26]. Thus, in the context of the present study, the above ordering in γ bears an important consequence that the chain-length dependence of different NLO processes in conjugated polymers is different. Since our study is limited to only the lowest four members of the polyene series,

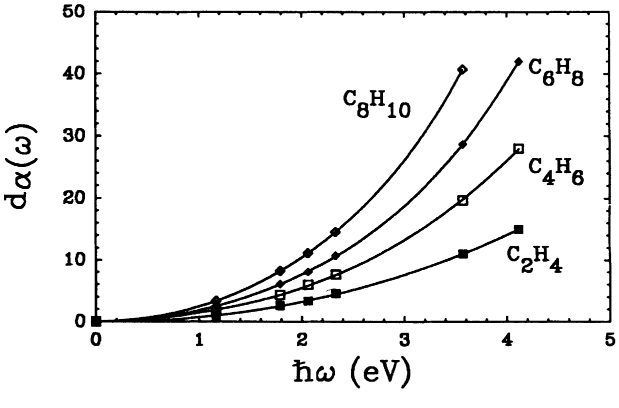

FIG. 2. Relative dispersion of linear polarizability of ethylene, *trans*-butadiene, *trans*-hexatriene, and *trans*-octatetraene.

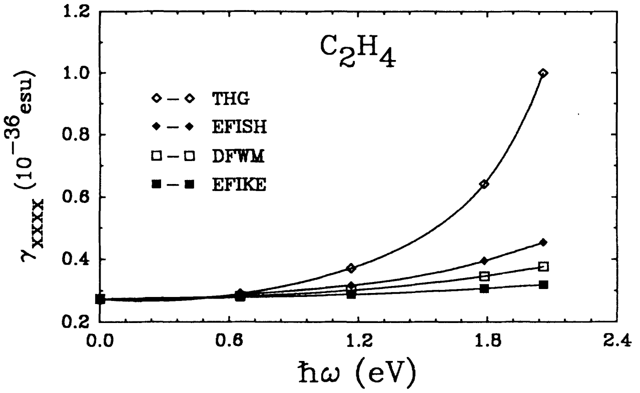

FIG. 3. Frequency dependence of the long component of γ for ethylene.

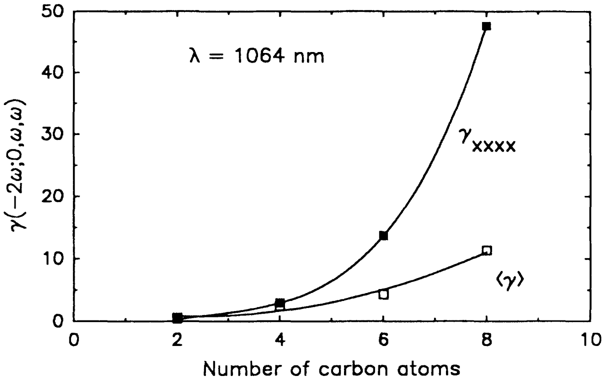

FIG. 5. Chain-length dependence of $\gamma_{xxxx}(-2\omega;0,\omega,\omega)$ and $\langle\gamma\rangle(-2\omega;0,\omega,\omega)$ at a fundamental wavelength of 1064 nm.

we are unable to establish an empirical relation of the type $\gamma = f(N)$, where N is the number of carbon atoms (or the number of double bonds) in the polyene chain. However, if one assumes that the second hyperpolarizability γ increases as a power n of the chain length N, then the value of n is much higher for THG than for EFISH, which, in turn, is higher than that for DFWM and EFIKE (or EFIOR) in that order. In other words, the same power law cannot explain the chain-length dependence of different third-order processes.

C. The Kleinman symmetry

A major issue in the study of dispersion of higher order NLO effects is the symmetry relationships among the elements of the hyperpolarizability tensors. The symmetry considerations become important for two reasons: (i) the number of elements of the hyperpolarizability tensors is equal to 3^N where N is the rank of the particular tensor. Thus, in the case of γ, which is a fourth-rank tensor, there are 81 individual elements. A knowledge of the symmetry relationship between the individual elements can save considerable computational time. (ii) The scalar quantity $\langle\gamma\rangle$ is dependent upon the individual elements of the tensor. Thus, an accurate knowledge of the redundant elements of the tensor is important for a correct calculation of the observable $\langle\gamma\rangle$.

In the absence of any external conditions, certain identities among the elements of the hyperpolarizability tensor may exist due to the symmetry of the molecule. Additionally, the hyperpolarizability tensors have an intrinsic symmetry, according to which, the indices $ijkl$ in $\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$ may be freely interchanged provided that the corresponding optical field amplitudes are also interchanged. In our study, we only consider the above-mentioned two symmetries. An extension of the intrinsic symmetry that has been extensively used in the study of NLO effects in inorganic solids and is frequently used in experimental and theoretical studies of organic solids is known as the Kleinman symmetry [31]. According to this symmetry, at an optical frequency far away from any resonances, the indices $ijkl$ of $\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$ can be freely interchanged without interchanging the frequency arguments. Although a good approximation at lower frequency which makes the calculations of NLO susceptibilities in solids tractable, it does not hold true in general, as the frequency of optical field increases. Deviation from Kleinman's symmetry has

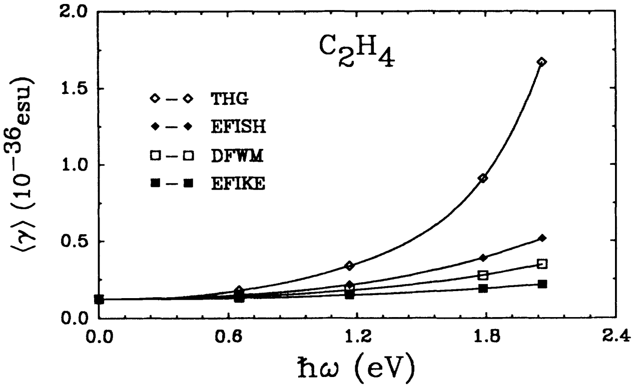

FIG. 4. Frequency dependence of $\langle\gamma\rangle$ for ethylene.

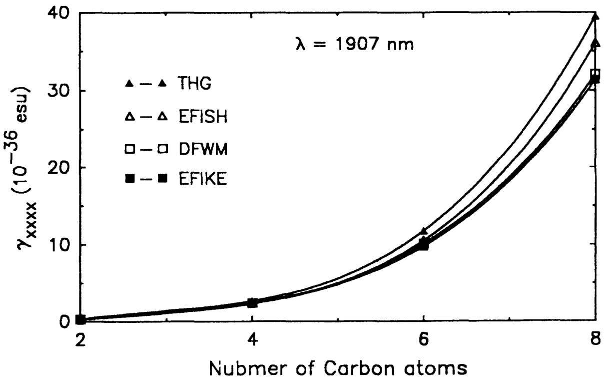

FIG. 6. Chain-length dependence of the long component of γ for various third-order effects at a fundamental wavelength of 1907 nm.

TABLE X. Components of γ (10^{-36} esu) of hexatriene calculated at a fundamental wavelength $\lambda = 1907$ nm.

Components	$\gamma(-\omega;0,0,\omega)$	$\gamma(-\omega;\omega,\omega,-\omega)$	$\gamma(-2\omega;0,\omega,\omega)$	$\gamma(-3\omega;\omega,\omega,\omega)$
xxxx	9.813	10.151	10.545	11.798
xxyy	0.255	0.264	0.276	0.302
xxzz	1.470	1.509	1.577	1.761
xyyx	0.260	0.272	0.266	0.302
xzzx	1.468	1.521	1.572	1.761
yxxy	0.258	0.268	0.261	0.266
yyxx	0.260	0.262	0.268	0.266
yyyy	0.774	0.781	0.790	0.815
yyzz	0.410	0.413	0.423	0.438
yzzy	0.410	0.414	0.420	0.438
zxxz	1.460	1.516	0.331	1.641
zyyz	0.409	0.417	0.421	0.442
zzxx	1.465	1.507	1.537	1.641
zzyy	0.409	0.414	0.423	0.442
zzzz	1.509	1.551	1.551	1.622

already been noted for different classes of molecules [23-26].

To illustrate the applicability of Kleinman's symmetry, we have listed in Table X the important elements of $\gamma(-\omega;0,0,\omega)$, $\gamma(-\omega;\omega,\omega,-\omega)$, $\gamma(-2\omega;0,\omega,\omega)$, and $\gamma(-3\omega;\omega,\omega)$ for hexatriene calculated at a fundamental wavelength $\lambda = 1907$ nm ($\hbar\omega = 0.65$ eV). It is evident from the table that even at such a low optical frequency, the elements of γ for different processes do not obey the Kleinman symmetry, though the deviation is fairly small. The deviation, of course, increases, as the value of $\hbar\omega$ increases (not listed in the table). Thus, where quantitative accuracy is needed, one has to be careful in using Kleinman's approximation.

V. SUMMARY AND CONCLUSION

The goal of the present study was to test the predictive ability of the *ab initio* method with regard to the NLO properties of organic molecules by comparing with the experimental gas-phase (close to isolated molecule limit) data and to study the dispersion properties of the linear and various nonlinear optical processes in polyenes. To study the frequency-dependent (hyper)polarizability we used the recently developed time-dependent coupled perturbed Hartree-Fock technique in the *ab initio* method. By using the previously optimized basis functions and geometry, we were able to show that the *ab initio* TDCPHF method indeed yields results for α and γ that are in good agreement with the gas-phase experimental results. A large discrepancy between the theoretical and the experimental values of γ of polyenes in the previous *ab initio* studies is attributed to the dispersion effect, not considered in those studies.

Here the *ab initio* results of frequency-dependent hyperpolarizabilities in large organic molecules have been directly compared with the gas-phase experimental data; we are hopeful that in other cases, where unambiguous measured results are available, a similar agreement would be obtained between theory and experiment. The good accord noted between the calculated and the experimental values in this study also leads us to believe that the *ab initio* TDHF results can be used to test and calibrate approximate quantum-chemical methods for predicting NLO effects in yet larger and complicated organic structures.

The relative dispersion of α increases with the increase of the optical frequency in each system studied. Also, for a given frequency, α and its relative dispersion increases with the chain length. The γ values for each molecule at a given frequency have the following order: $\gamma(\mathrm{THG}) > \gamma(\mathrm{EFISH}) > \gamma(\mathrm{DFWM}) > \gamma(\mathrm{EFIKE}) \approx \gamma(\mathrm{EFIOR})$. Again, like α, the various γ values increase with the chain length. The relative dispersion of γ for different third-order processes have different chain-length dependence. Therefore, a single empirical relationship cannot explain the chain-length dependence of different third-order NLO processes.

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[1] P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers* (Wiley Interscience, New York, 1991).
[2] C. Sauteret, J. P. Hermann, R. Frey, F. Pradere, J. Ducuing, R. M. Baughman, and R. R. Chance, Phys. Rev. Lett. **36**, 956 (1976).
[3] M. Sinclair, D. Moses, A. J. Heeger, K. Wilhelonsson, B. Valk, and M. Salour, Solid State Commun. **61**, 221 (1987).
[4] A. J. Heeger, D. Moses, and M. Sinclair, Synth. Met. **17**, 343 (1987).
[5] F. Kajzar, S. Etemad, G. L. Baker, and J. Messier, Synth. Met. **17**, 563 (1987).
[6] F. Kajzar and J. Messier, Polym. J. **19**, 275 (1987).
[7] B. S. Hudson, B. E. Kohler, and B. K. Schulten, in *Excited States*, edited by C. E. Lim (Academic, New York, 1982), Vol. **6**, pp. 1–95, and references therein.
[8] B. E. Kohler, C. W. Spangler, and C. Westerfield, J. Chem. Phys. **94**, 908 (1991).
[9] K. C. Rustagi and J. Ducuing, Opt. Commun. **10**, 258 (1974).
[10] H. F. Hameka, J. Chem. Phys. **67**, 2935 (1977).
[11] E. F. McIntyre and H. F. Hameka, J. Chem. Phys. **68**, 3481 (1978); **69**, 4814 (1978).
[12] O. Zamani-Khamiri, E. F. McIntyre, and H. F. Hameka, J. Chem. Phys. **71**, 2215 (1979); **72**, 5906 (1980); **73**, 5693 (1980).
[13] M. G. Papadopoulous, J. Waite, and C. A. Nicolaides, J. Chem. Phys. **77**, 2527 (1982).
[14] C. P. deMelo and R. Silbey, Chem. Phys. Lett. **140**, 537 (1987); J. Chem. Phys. **88**, 2567 (1988).
[15] Z. G. Soos and S. Ramasesha, J. Chem. Phys. **90**, 1067 (1989).
[16] J. R. Heflin, K. Y. Wong, O. Zamani-Khamiri, and A. F. Garito, Phys. Rev. B **38**, 1573 (1988).
[17] B. Kirtman, Chem. Phys. Lett. **143**, 81 (1988).
[18] J.-M. Andre, C. Barbier, V. Bodart, and J. Delhalle, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by D. S. Chemla and J. Zyss (Academic, London, 1987), Vol. 2, pp. 137–158.
[19] G. J. B. Hurst, M. Dupuis, and E. Clementi, J. Chem. Phys. **89**, 385 (1988).
[20] P. Chopra, L. Carlacci, H. F. King, and P. N. Prasad, J. Phys. Chem. **93**, 7120 (1989).
[21] M. Dupuis, A. Farazdel, S. P. Karna, and S. A. Maluendes, in *Modern Techniques in Computational Chemistry*, edited by E. Clementi (Escom Science, Leiden, 1990), pp. 277–342.
[22] S. P. Karna and M. Dupuis, J. Comput. Chem. **12**, 487 (1991).
[23] S. P. Karna and M. Dupuis, Chem. Phys. Lett. **171**, 201 (1990).
[24] S. P. Karna, P. N. Prasad, and M. Dupuis, J. Chem. Phys. **94**, 1171 (1991).
[25] S. P. Karna, G. B. Talapatra, Z. Laskowski, and P. N. Prasad, J. Phys. Chem. **95**, 6508 (1991).
[26] S. P. Karna, G. B. Talapatra, and P. N. Prasad, J. Phys. Chem. Phys. **95**, 5873 (1991).
[27] J. F. Ward and D. S. Elliott, J. Chem. Phys. **69**, 438 (1978).
[28] D. P. Shelton, Phys. Rev. A **42**, 2578 (1990).
[29] H. Sekino and R. J. Bartlett, J. Chem. Phys. **85**, 976 (1986).
[30] S. T. Epstein, Chem. Phys. Lett., **70**, 311 (1980).
[31] D. A. Kleinman, Phys. Rev. **126**, 1977(1962).
[32] S. P. Karna, M. Dupuis, E. Perrin, and P. N. Prasad, J. Chem. Phys. **92**, 7418 (1990).
[33] M. Aoyagi, I. Ohmine, and B. E. Kohler, J. Chem. Phys. **94**, 3922 (1990).
[34] N. J. Bridge and A. D. Buckingham, Proc. R. Soc. London, Ser. A **295**, 334 (1966).
[35] *Handbook of Chemistry and Physics*, 66th ed., edited by R. C. Weast, M. J. Astle, and W. H. Beyer (CRC, Boca Raton, 1985), p. E-70.
[36] E. Perrin, P. N. Prasad, P. Mougenot, and M. Dupuis, J. Chem. Phys. **91**, 4728 (1989).