Environmental Effects on Nonlinear Optical Chromophore Performance. Calculation of Molecular Quadratic Hyperpolarizabilities in Solvating Media

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Abstract: The molecular quadratic hyperpolarizabilities of a wide series of π-conjugated, donor–acceptor chromophores in various solvation media are calculated using the INDO/S (ZINDO) sum over excited particle hole states formalism. The energy terms of the perturbation theory are corrected for solvent effects by means of a continuum Onsager cavity model, based on the reaction field model. Calculated hyperpolarizability values including solvent effects are in excellent agreement with experimental electric field induced second-harmonic generation data taken in solution. The calculations show that red shifts of the lowest energy electronic charge-transfer transition upon solvation are the most important feature altering hyperpolarizability values on passing from the gas phase to solution. A linear correlation found between the hyperpolarizability and the energy of the lowest charge-transfer transition demonstrates the general validity of the simple two-state model in predicting solvation trends in hyperpolarizability for donor–acceptor chromophores. The consistency of this model is probed by calculating chromophore hyperpolarizabilities in different solvents and for different fundamental laser frequencies.

Introduction

The current, intense research activity on nonlinear optical (NLO) materials has produced a wide variety of new chromophoric building blocks and molecular assemblies having sizable second-order NLO responses.[1–3] The understanding and rationalization of such NLO characteristics has greatly benefited from the development of various chemically oriented quantum mechanical formalisms[4] capable of accurately describing the NLO response and oriented toward the design and optimization of microscopic hyperpolarizability, $\beta(-2\omega;\omega,\omega)$.

Optimization of molecular response is important, but in actual applications, the characteristics of NLO responsive materials will depend crucially upon how the chromophore molecular response is affected by environment and the temporal characteristics of that environment. It thus becomes essential to understand bulk environmental effects on the NLO response of individual chromophore molecules. The simplest example of this phenomenon is represented by the effect of a dilute solvation environment in a fluid (or polymer host matrix) on molecular hyperpolarizability. Such effects are observed when comparing available experimental electric field induced second-harmonic generation (EFISH) hyperpolarizability data with molecular calculations. With the exception of rare cases, quantum chemically derived hyperpolarizability values invariably underestimate those obtained experimentally.[4–6] While the calculations describe gas-phase (isolated) molecules, experimental EFISH measurements are made in solution, and even when phenomenological "local field factors" are included in data analysis to account for solvent effects,[7,8] $\beta(-2\omega;\omega,\omega)$ values are strongly dependent upon the particular solvent.[9] It is also known that solvation effects influence many other properties of chromophoric solutes. For instance, one of the most obvious linear optical changes is solvatochromism associated with certain electronic transitions.[10] These observations suggest that any correct theoretical evaluation of hyperpolarizability and any meaningful comparison with experimental data must necessarily take into account the actual molecular environment. Such information is of relevance to understanding the role of environment/matrix on NLO chromophore performance and complements our previous studies on the effects of chromophore–chromophore intermolecular interactions on second-order optical nonlinearity.[11]

Among the various quantum mechanical approaches to the calculation of molecular hyperpolarizability,[4] the perturbative sum-over excited particle-hole-states (SOS) formalism,[12] implemented in various chemically oriented semiempirical codes,[4] has proven to be suitable for the description of hyperpolarizability of large donor–acceptor, π-conjugated chromophores.[4–6] Within

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the SOS formalism, the hyperpolarizability may be related to the molecular excited states in terms of energy, dipole moment, and transition probabilities associated with all possible molecular excitations. Clearly, the correct evaluation of these variables in the actual molecular environment would allow a quantitative description of "real world" NLO properties and, hence, a direct comparison with experimental data. Moreover, the quadratic dependence of hyperpolarizability on the energy ($\hbar\omega$) of the excited states ($\beta \sim 1/(\hbar\omega)^2$)[5] typically observed[4] raises the question of whether this is the most important environmentally related parameter influencing $\beta(-2\omega;\omega,\omega)$. In this case, the evaluation of solvent effects on the calculated energy of electronic transitions followed by perturbation theory with the corrected energy terms would be a straightforward task.

Various theoretical approaches[13] using continuum or semicontinuum (classical or quantum mechanical) electrostatic models, based on the reaction field[14–19] (RF) or statistical[20] models, have been proposed to evaluate solvent effects on linear optical absorption spectra. In the simplest formulation of the reaction field model, first proposed by Onsager,[21] the solvent is described by a homogeneous continuous medium characterized by its macroscopic dielectric properties. The solute molecule, embedded in a cavity (usually spherical), interacts with the surrounding dielectric medium through the reaction field. Refinements and improvements to this basic theory (including a more realistic description of the cavity, multipole expansion of the molecular charge distribution, and different formulations of the interaction potential), within a self-consistent quantum mechanical treatment of the reaction field interaction with the cavity molecules, have been successfully used[13] to predict solvent effects on conformation energies,[22] electron transfer,[23] and spectroscopic properties.[16–19,24] Recently, the reaction field model has also been applied to calculating the static hyperpolarizabilities of acetonitrile[25a] and *p*-nitroaniline[25b] in the liquid phase by ab initio techniques. The contribution by Mikkelsen et al.[25b] is particularly important in the context of the current discussion. Using reaction field linear response theory and a full reaction field model, with ab initio wave functions and extended basis sets, they show that, for the β response of *p*-nitroaniline, the charge and dipolar terms in the reaction field account for over 80% of the effect of the full reaction field in shifting the excitation energy.

In this paper we present a simple, efficient approach for calculating the second-order hyperpolarizabilities of various, prototypical π-conjugated, donor–acceptor (D–A) chromophores[26,27] of current interest[1–3] in solvent media.[28] This approach uses the RF model to account for solvent effects on the energy of excited states, and the efficient ZINDO-SOS formalism,[5] together with a correction to the energy of the SOS perturbation theory, to calculate molecular hyperpolarizability.

Theoretical Methods

Although the reaction field model can be formulated to include all multiple moments in the charge distribution, the chromophores of interest here have large dipole moments, so we will use only dipolar terms. Moreover, only spherical cavities will be explored in this initial study.

The reaction field, **R**, is the electric field felt by the solute due to the orientation and/or electronic polarization of the solvent (reaction) induced by the solute dipole. Its magnitude is proportional to the solute dipole moment μ,

$$\mathbf{R} = g\mu \tag{1}$$

The reaction field factor, g (the Onsager dipolar term),[21a] which gives the strength of the reaction field, depends on the dielectric constant of the medium, ϵ, and on the radius of the spherical cavity, a

$$g = \frac{1}{a^3}\frac{2(\epsilon - 1)}{(2\epsilon + 1)} \tag{2}$$

In MO theory,[30] the reaction field may be considered as an additional term, H_S, in the Hamiltonian of the isolated molecule, H_0

$$H = H_0 + H_S \tag{3}$$

The perturbation term, H_S, describes the coupling between the molecular dipole operator ($\hat{\mu}$) and the reaction field **R**

$$H_S = -\hat{\mu}\mathbf{R} \tag{4}$$

The Fock operator is then corrected by

$$\hat{F} = \hat{F}_0 - g\mu\langle\Psi|\hat{\mu}|\Psi\rangle \tag{5}$$

The total energy in the presence of the reaction field, E^S, is given by[22,30]

$$E^S = E_0 - \frac{1}{2}g\mu_g{}^2 \tag{6}$$

In eq 6, E_0 is the SCF reaction field (SCRF) energy, while the second term represents the electrostatic (stabilizing) contribution to the total energy of solvation. Note that μ_g is now the ground-state dipole moment as calculated self-consistently in the presence of the reaction field.

A proper description of solvent effects must consider solvent polarization. In fact, part of the energy gained from the stabilization of the solute dipole is invested in polarizing the solvent. The contribution to the orientational polarization, D', may be related to the bulk dielectric properties by the Clausius–Mosotti relationship[31]

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(27) The present choice of chromophores examined was limited by the available experimental EFISH data in the same solvent, sampled using the same laser frequency. Moreover, the comparison of our theoretical results to an internally consistent set of EFISH data from a single laboratory[26] should minimize deviations due to experimental conditions such as local-field models and data-reduction schemes.

(28) Previous studies accounting for solvent effects on calculated molecular second-order hyperpolarizability of π-chromophores include the following: solvent effects on hyperpolarizability dispersion of *p*-nitroaniline using a two-level model and experimental excitation energies;[29a,b] two-level (optical) model on solvent hyperpolarizability of *p*-(dimethylamino)benzonitrile;[29c] solvent effects on hyperpolarizability of some π-chromophores using empirical (spectroscopic) derived field relationships;[29d] and a self-consistent reaction field calculation using TDHF response in a ZINDO model.[29e]

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$$\frac{\epsilon - 1}{2\epsilon + 1} = \frac{D' - 1}{2D' + 1} + \frac{n_0^2 - 1}{2n_0^2 + 1} \tag{7}$$

in which n_0^2, the square of the solvent refractive index extrapolated to zero frequency, represents the electronic (inductive) polarization. Thus, the reaction field due to orientational polarization, $\mathbf{R}'$, is obtained as the difference between the field due to the total (electrostatic) polarization (eq 1) and that due to electronic polarization

$$\mathbf{R}' = g(\epsilon, n_0) \tag{8}$$

where

$$g(\epsilon, n_0) = \frac{2}{a^3}\left[\frac{(\epsilon - 1)}{(2\epsilon + 1)} - \frac{(n_0^2 - 1)}{(2n_0^2 + 1)}\right] \tag{9}$$

The total energy of the ground state is then given by

$$E^{S}_{g} = E_0 - \frac{1}{2}g(\epsilon, n_0)\mu_g^2 \tag{10}$$

The second term of eq 10 represents the energy of interaction between the permanent dipoles of the solvent and the solute molecule in the ground state.

The interaction energy of the excited state is similarly expressed. However, since the electronic excitation process is normally far more rapid than the reorientation time of the solvent dipoles, the induced dipole of the solvent molecule will respond to the changed solute dipole upon excitation, but the solvent permanent dipoles are frozen in their ground-state polarization. The interaction energy of the excited state, E^{S}_{n}, is thus given by[15b]

$$E^{S}_{n} = E_n - \frac{1}{2}g(\epsilon, n_0)\mu_n\mu_g - \frac{1}{2}g(n_0)\mu_n^2 \tag{11}$$

where

$$g(n_0) = \frac{1}{a^3}\frac{(n_0^2 - 1)}{(2n_0^2 + 1)} \tag{12}$$

The second term of eq 11 is the energy contribution due to the solvent permanent dipoles frozen in the ground-state polarization, i.e., the case of negligible dipole reorientation. The last term is the stabilizing energy contribution due to the solvent-induced dipoles.

Combining eqs 10 and 11, the energy of an electronic transition, $\hbar\omega_{\mathrm{ng}}$, in presence of the reaction field is given by

$$\hbar\omega_{\mathrm{ng}} = E^{S}_{n} - E^{S}_{g} = E_n - E_0 - \frac{1}{2}g(\epsilon, n)\mu_g(\mu_n - \mu_g) - \frac{1}{2}g(n)(\mu_n^2 - \mu_g^2) \tag{13}$$

The above expression may be applied to obtain transition energies of a molecule in various media on the basis of the macroscopic solvent properties, (ϵ, n), and for a given cavity radius. An implicit approximation of this procedure is that the molecular polarizability is assumed unchanged on passing from ground to excited states. Moreover, since evaluation of transition energies involves a configuration interaction (CI) treatment, the solution of eq 11 including the aforementioned electronic polarization is not straightforward. Thus, this term is often deleted from the SCRF procedure but is treated perturbatively as an additional energy term contribution.[16]

Equation 13 may be used to estimate solvent shifts even when the SCRF is not explicitly included in the calculation. In particular, using ground and excited dipole matrix elements calculated within the usual SCF procedure, the solvent shift, ΔE^{S}_{n}, may be obtained through finite differences and the calculated transition energies of the gas-phase molecule

$$\Delta E^{S}_{n} = -\frac{1}{2}g(\epsilon, n)\mu_g(\mu_n - \mu_g) - \frac{1}{2}g(n)(\mu_n^2 - \mu_g^2) \tag{14}$$

Although this approximation is not a rigorous solvent effect treatment, it allows a semiquantitative and computationally efficient estimation of solvent shifts (vide infra).

The evaluation of hyperpolarizability in a medium can thus be straightforwardly obtained by including the corrected energy terms for solvent shift ($\hbar\omega_{\mathrm{ng}}$, eq 13) in the SOS perturbative procedure[5,16]

$$\begin{aligned}
\beta_{ijk} + \beta_{ikj} = {} & -\frac{e^3}{4\hbar^2}\Bigg[\sum_{n\neq g}\sum_{\substack{n'\neq g\\ n'\neq n}}\Bigg\{(r^{j}{}_{gn'}r^{i}{}_{n'n}r^{k}{}_{gn} + r^{k}{}_{gn'}r^{i}{}_{n'n}r^{j}{}_{gn})\left(\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - \omega)}\right) + (r^{i}{}_{gn'}r^{j}{}_{n'n}r^{k}{}_{gn} + r^{i}{}_{gn'}r^{k}{}_{n'n}r^{j}{}_{gn}) \times \\
& \left(\frac{1}{(\omega_{n'g} + 2\omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)}\right) + (r^{j}{}_{gn'}r^{k}{}_{n'n}r^{i}{}_{gn} + r^{k}{}_{gn'}r^{j}{}_{n'n}r^{i}{}_{gn})\left(\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} + 2\omega)}\right)\Bigg\} + \\
& 4\sum_{n\neq g}\Bigg\{[r^{j}{}_{gn}r^{k}{}_{gn}\Delta r^{i}{}_{n}(\omega_{ng}^2 - 4\omega^2) + r^{i}{}_{gn}(r^{k}{}_{gn}\Delta r^{j}{}_{n} + r^{j}{}_{gn}\Delta r^{k}{}_{n}) \times (\omega_{ng}^2 + 2\omega^2)]\frac{1}{(\omega_{ng}^2 + \omega^2)(\omega_{ng}^2 - 4\omega^2)}\Bigg\}\Bigg]
\end{aligned} \tag{15}$$

where ω is the frequency of the applied electric field, $r^{i}{}_{mn} = \langle\Psi_m|r^i|\Psi_n\rangle$ is the matrix element of the displacement operator $r^{(i)}$ along the ith molecular axis between electronic states Ψ_m and Ψ_n, and $\Delta r^{i}{}_{n} = r^{i}{}_{nn} - r^{i}{}_{gg}$ is the dipole moment difference between the excited and ground state.

These corrections are zeroth-order wave functions in perturbation theory, whereas first-order wave functions are required for modification of the matrix (dipole moment) elements in the presence of the solvent reaction field. Moreover, if constant-frequency refractive indexes, n_D, are used in eqs 13 and 14, these corrections should yield (even at relatively low frequencies, i.e., at the frequencies usually employed in the EFISH experiments) the corrected frequency-dependent hyperpolarizability response. Frequency-dependent refractive indexes, n_ω, should be used in order to describe the complete dispersion of the NLO response at higher frequencies.[29b]

Computational Details

INDO/S calculations[4,5,11,32] and the monoexcited CI approximation, including the 130 lowest energy transitions in the CI mixing, were employed to calculate electronic transitions. Standard parameters and basis functions were used. The electronic transition energies thus obtained were corrected for solvent shift effects by means of the approximate formula of eq 14, using ground and excited dipole moment terms as calculated by the SCF procedure. Tabulated static dielectric constants and refractive indices (n_D) were used.[33] The cavity radius, a, was chosen from the solute molar volume (V_m)

$$V_m = \frac{4}{3}\pi a^3 = \frac{\mathrm{MW}}{d\mathrm{N}} \tag{16}$$

$$a = \left[\frac{3}{4\pi}\frac{\mathrm{MW}}{d\mathrm{N}}\right]^{1/3} \tag{17}$$

where MW is the molecular weight, d the mass density,[33,34] and N Avogadro's number. To the cavity radius thus obtained was added a constant term (0.5 Å) to account for the van der Waals radii of the surrounding solvent molecules.[22] This cavity radius choice allows, in all cases examined, a reasonable estimation of solvent effects (vide infra). Moreover, the present approximation gives linear optical results (for molecules in the same solvent and using the same cavity radius) in excellent agreement with those obtained by Karelson and Zerner,[16a] in which RF was included in the SCF calculation.

The second-order hyperpolarizability was calculated by means of the ZINDO-SOS formalism,[5] in which the corrected transition energy terms for solvent shifts were included in the perturbative

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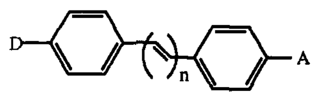
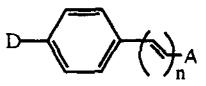
Chart 1



1, D = $N(CH_3)_2$, A = NO_2, n = 1
2, D = OCH_3, A = NO_2, n = 1
3, D = $N(CH_3)_2$, A = NO_2, n = 2
4, D = OCH_3, A = NO_2, n = 2
5, D = $N(CH_3)_2$, A = NO_2, n = 3
6, D = OCH_3, A = NO_2, n = 3
7, D = $N(CH_3)_2$, A = NO_2, n = 4
8, D = OCH_3, A = NO_2, n = 4



9, D = OCH_3, A = COH, n = 1
10, D = OCH_3, A = COH, n = 2
11, D = OCH_3, A = COH, n = 3
12, D = $N(CH_3)_2$, A = NO_2, n = 1

SOS procedure (eq 15). The details of the ZINDO-SOS-based method have been reported elsewhere.[5] Bonds-alternating idealized (BAI) geometries were chosen for all calculations as described elsewhere.[5a]

Results and Discussion

As already stated, perturbation SOS theory implies a sum over all excited states, and the quadratic dependence of $\beta(-2\omega;\omega,\omega)$ on $\hbar\omega_{ng}$ (eq 15) indicates that this is an important feature in determining the magnitude of $\beta(-2\omega;\omega,\omega)$ for a given class of D–A chromophores. In fact, it has been demonstrated that there is an essentially monotonic relationship between molecular hyperpolarizability determined by EFISH measurements and the energy of the lowest intramolecular charge-transfer (CT) transition. This relationship applies for a wide variety of D–A chromophores,[8,26,35] as well as for chromophores upon change of solvent polarity,[9c] i.e., undergoing solvatochromic shifts. These observations argue that the evaluation of $\hbar\omega_{ng}$ upon solvation is the crucial feature determining $\beta(-2\omega;\omega,\omega)$.

We have examined two series of second-order NLO organic chromophores[26,27] (Chart 1), having various donor and acceptor substituents dissolved in the same polar solvent, chloroform. This solvent is ideally suited to study solvation effects within the present model, since no specific, directed bonding interactions are expected. Often, more polar and protonic solvents can strongly and site-selectively interact with solute molecule substituents, e.g. by hydrogen bonding. Such specific interactions cannot be accommodated within the framework of a dielectric continuum model but will be discussed in a later contribution.

The origin and description of the second-order nonlinearities in the chromophores discussed here have already been analyzed.[5,26] These chromophores are characterized by strong, low-energy, CT transitions, involving a strong increase of the dipole moment along the dipolar axis in the excited state. As a consequence, solvent effects stabilize the excited state more than the ground state (eqs 13 and 14), with a red shift of the absorption bands associated with these transitions upon solvation. Moreover, since chloroform is characterized by a relatively low dielectric constant, the stabilization due to induced dipoles (the second term of eq 14) dominates the solvent shift contribution. The calculated energy shift on passing from the gas phase to chloroform ranges from ~800 to ~3200 cm^{-1} (Table 1), as typically observed for such CT transitions.[36] Good agreement between calculated vs experimental $\hbar\omega_{ng}$ values is generally found when solvent effects are included (Table 1). The accuracy of the calculated solvent shifts on passing from the gas phase to chloroform is most evident when comparing experimental λ_{max} data ($\lambda_{max} = 2\pi c/\omega$) vs the calculated values in the gas phase and including solvent-induced shifts (Figure 1). In particular, calculated values including solvent effects are associated both with a better correlation coefficient (R value) of the least-squares fit (0.98 vs 0.94) and with a slope nearer to unity (1.10 vs 0.79), compared to the calculated gas-phase $\hbar\omega_{ng}$ data. Note, however, that the present cavity choice generally gives rise to a slight overestimation of λ_{max} values compared to those obtained experimentally.

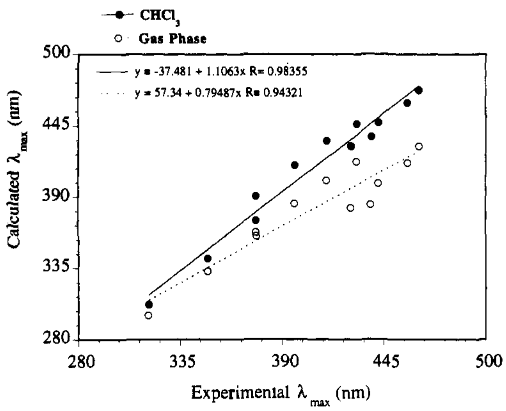


Figure 1. Plot of the computed chromophore first CT transition, λ_{max}, in the gas phase and in $CHCl_3$ solution vs experimental $CHCl_3$ solution values from ref 26 for a representative group of π-electron chromophores.

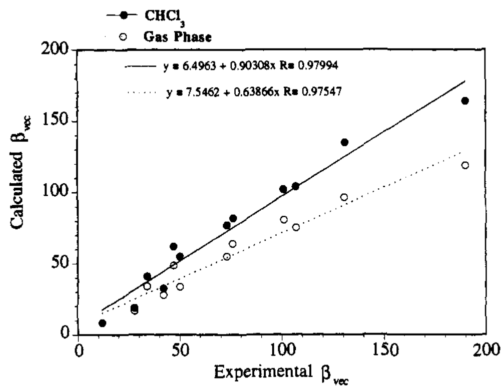


Figure 2. Plot of computed chromophore β_{vec} values in the gas phase and in $CHCl_3$ solvent vs experimental $CHCl_3$ solution values from ref 26. β_{vec} values are in units of 10^{-30} cm^5 esu^{-1}; $\hbar\omega$ = 0.65 eV.

It has been observed[5] that calculated hyperpolarizabilities generally underestimate experimental EFISH measurements made in solution. The inclusion of solvent effects on the energy of the perturbation sum leads, in the present investigation, to a substantial increase of calculated β_{vec}. The resulting β_{vec} values are now in excellent agreement with experimental data (Table 1). The plot of experimental vs calculated β_{vec} values (Figure 2) clearly indicates substantially better agreement when solvent effects are taken into account, with a slope of the least-squares fit near unity (0.90 vs 0.64 when solvent effects are not included). The difference between calculated hyperpolarizability values in $CHCl_3$ and in the gas phase ($\beta_{vec}(CHCl_3) - \beta_{vec}$(gas phase)) is appreciable and ranges from 0.5 × 10^{-30} to 42 × 10^{-30} cm^5 esu^{-1} (Table 1). This difference increases for larger β_{vec} values and parallels the energy of the associated low-energy CT transition, i.e., the $1/(\hbar\omega_{ng})^2$ value. In fact, a plot of calculated β_{vec} vs $1/(\hbar\omega_{ng})^2$ values for a series of α,ω-diphenylpolyenes (**1**–**8**) shows an excellent correlation of the least-squares fit (R = 0.98, Figure 3a). Interestingly, the slope of this least-squares fit (25.6) is almost identical to that obtained from a same plot using the experimental[26] data (28.2, Figure 3b).

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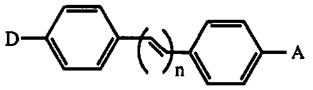
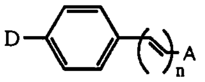
(35) Stiegman, A. E.; Graham, E.; Perry, K. J.; Khundkar, L. R.; Cheng, L.-T.; Perry, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 7658.

(36) Lalama, S. L.; Garito, A. F. *Phys. Rev. A* **1979**, *20*, 1179.

Table 1. Comparison of Experimental[a] and ZINDO-Derived Optical Absorption Maxima ($\hbar\omega_{ng}$, eV) and Molecular Second-Order Hyperpolarizabilities (β_{vec}, 10^{-30} cm^5 esu^{-1}; $\hbar\omega$ = 0.65 eV) of Various D–A Chromophores in Chloroform Solution[b]



molecule	D	A	n	a^c	$\hbar\omega_{ng}^{calc\ d}$	$\hbar\omega_{ng}^{expt}$	$\beta_{vec}^{calc\ e}$	β_{vec}^{expt}
1	$N(CH_3)_2$	NO_2	1	5.20	2.88 (0.36)	2.88	77.1 (21.6)	73
3	$N(CH_3)_2$	NO_2	2	5.40	2.77 (0.32)	2.80	104.4 (29.1)	107
5	$N(CH_3)_2$	NO_2	3	5.50	2.67 (0.30)	2.71	135.2 (39.3)	131
7	$N(CH_3)_2$	NO_2	4	5.65	2.62 (0.27)	2.67	162.0 (42.0)	190 ± 50
2	OCH_3	NO_2	1	5.15	3.17 (0.24)	3.30	41.3 (7.7)	34
4	OCH_3	NO_2	2	5.30	2.98 (0.23)	3.12	62.1 (13.5)	47
6	OCH_3	NO_2	3	5.45	2.85 (0.21)	2.99	82.9 (18.3)	76
8	OCH_3	NO_2	4	5.60	2.77 (0.19)	2.88	102.1 (21.5)	101



molecule	D	A	n	a^c	$\hbar\omega_{ng}^{calc\ d}$	$\hbar\omega_{ng}^{expt}$	$\beta_{vec}^{calc\ e}$	β_{vec}^{expt}
9	OCH_3	COH	1	4.50	4.03 (0.11)	3.90	8.9 (0.5)	12
10	OCH_3	COH	2	4.70	3.61 (0.12)	3.54	18.8 (1.8)	28
11	OCH_3	COH	3	4.90	3.33 (0.12)	3.30	32.6 (4.6)	42
12	$N(CH_3)_2$	NO_2	1	4.70	2.83 (0.40)	2.83	55.6 (21.7)	50

[a] Experimental data from ref 26. [b] ϵ = 4.806; n_D = 1.4459. [c] Cavity radius in Å. [d] Values in parentheses are the calculated shifts in eV (eq 14), on passing from the gas phase to chloroform. [e] Data in parentheses are the calculated $\beta_{vec}(CHCl_3)$ − β_{vec}(gas phase) values.

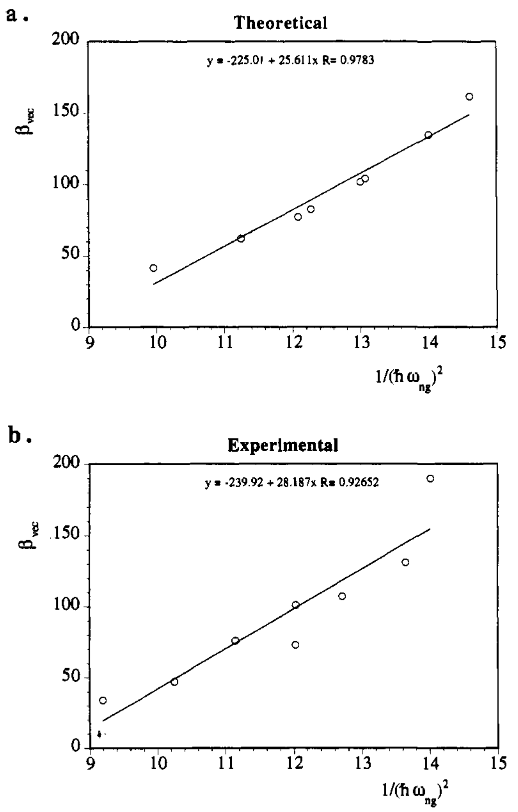
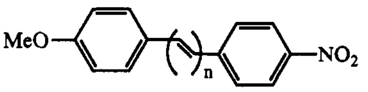


Figure 3. Plot of β_{vec} (in units of 10^{-30} cm^5 esu^{-1}; $\hbar\omega$ = 0.65 eV) values vs the inverse of the square of the first CT transition energy, $1/(\hbar\omega_{ng})^2$ (in eV × 10^2), for the series of α,ω-diphenylpolyenes **1**–**8**: (a) theoretical data calculated in $CHCl_3$ solution; (b) experimental $CHCl_3$ solution data from ref 26.

Table 2. Comparison of Experimental[a] and ZINDO-Derived Optical Absorption Maxima ($\hbar\omega_{ng}$, eV) and Molecular Second-Order Hyperpolarizabilities (β_{vdc}, 10^{-30} cm^5 esu^{-1}; $\hbar\omega$ = 1.17 eV) of α-(p-Methoxyphenyl)-ω-(p-nitrophenyl)polyenes in 1,4-Dioxane Solution[b]



molecule	n	a^c	$\hbar\omega_{ng}^{calc\ d}$	$\hbar\omega_{ng}^{expt}$	$\beta_{vec}^{calc\ e}$	β_{vec}^{expt}
2	1	5.15	3.23 (0.18)	3.45	87.7 (22.1)	81 ± 8
4	2	5.30	3.05 (0.17)	3.16	154.2 (43.3)	135 ± 14
6	3	5.45	2.92 (0.15)	2.99	243.5 (70.3)	274 ± 22
8	4	5.60	2.82 (0.14)	2.88	357.6 (109.5)	367 ± 73

[a] Experimental data from ref 37. [b] ϵ = 2.209; n_D = 1.4224. [c] Cavity radius in Å. [d] Values in parentheses are the calculated shifts in eV (eq 14), on passing from the gas phase to 1,4-dioxane. [e] Data in parentheses are the calculated β_{vec}(1,4-dioxane) − β_{vec}(gas phase) values.

Taken together, these results further confirm the general qualitative validity of the two-state model[1] in predicting trends in hyperpolarizability values for a series of substituted D–A second-order NLO chromophores, even in polar solvent media. We note, however, that the calculated red shift of the low-energy CT transition upon solvation is expected to give larger overestimated two-level $\beta(-2\omega;\omega,\omega)$ values compared to those calculated without the present solvent corrections.[5] Thus, even though the two-state model is a useful first approximation for the design of efficient new second-order molecular architectures, a quantitative estimation of nonlinearity must necessarily consider a complete SOS treatment.

In order to probe the general applicability of the present approach, we have examined the series of α-(p-methoxyphenyl)-ω-(p-nitrophenyl)polyenes (**2**, **4**, **6**, **8**) in a different solvent (1,4-dioxane) and have computed the hyperpolarizability at a different laser frequency, 1.064 μm ($\hbar\omega$ = 1.17 eV). These results are then compared with the available experimental data.[37] Excellent agreement between calculated values and experimental data, in terms of energy of the lowest CT transition as well as of β_{vec} values, is observed when solvent effects are included (Table 2). Note that, although solvent effects lead to relatively modest calculated solvent shifts (~1200 cm^{-1}), the difference between calculated β_{vec} values in 1,4-dioxane and the gas phase is large (e.g., 109.5 × 10^{-30} cm^5 esu^{-1} for **8**). This indicates that even for a relatively nonpolar solvent, such as dioxane, solvation can have dramatic effects on the molecular hyperpolarizability, especially at higher laser frequencies (closer to resonance).

Conclusions

This contribution illustrates the suitability of the ZINDO-SOS formalism in predicting second-order hyperpolarizabilities of various π-conjugated D–A chromophores in solvation media, when perturbation theoretical energy terms are corrected for solvent effects by means of a reaction field based on the Onsager

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[37] Huijts, R. A.; Hesselink, G. L. J. *Chem. Phys. Lett.* **1989**, *156*, 209.

continuum cavity model. Despite the approximations of the present approach (no explicit inclusion of the SCRF in the calculations, choice of spherical cavities, and use of only dipolar terms in the charge distribution), the calculated hyperpolarizability values including solvent effects are in excellent agreement with available experimental EFISH data made in the same solvents. The calculated red shifts of the lowest energy electronic CT transition upon solvation are the most important feature determining the increased hyperpolarizability values on passing from gas phase to solution. This becomes particularly evident for higher laser frequencies. In these cases, dramatic increases in β_{vec} values are observed, even in relatively nonpolar solvents. The linear correlation between hyperpolarizability and the inverse squared energy of the lowest CT transition further evidences the general validity of the two-state model in predicting trends in hyperpolarizability values for organic π-electron D–A chromophores. The results of this study indicate that this approach should be of wide applicability and should aid in tuning the architectures of guest–host combinations for maximum bulk NLO response.

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