Quantum Chemical Calculations of the First- and Second-Order Hyperpolarizabilities of Molecules in Solutions

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A study of the effect of solute/solvent interactions on static and dynamic molecular hyperpolarizabilities (β and γ) of series of prototypical π-conjugated donor−acceptor chromophores is presented. The solvent effect was included via a recently proposed discrete quantum-mechanical Langevin dipoles/Monte Carlo method. The nonlinear optical properties (NLO) were computed using the INDO-like Hamiltonian based finite-field (FF) and sum-over-states (SOS) methods implemented in the GRINDOL code. The calculated $\beta(\gamma)$ values are compared with experimental data determined in solution phase EFISH(THG) measurements and other published theoretical works. Generally, a reasonable agreement between calculated and experimental data was obtained. Moreover, our results indicate that the QM/LD/MC model gives a correct description of the solvent effect on the nonlinear optical response of molecules. It suggests that this level of theory can be used as an effective tool for investigation of NLO properties in condensed phases.

I. Introduction

It is well established, both experimentally[1−16] and theoretically,[17−48] that the presence of environment strongly influences the nonlinear optical response for many polar and nonpolar molecules compared to the gas-phase. From the theoretical point of view, for a better understanding of the behavior of nonlinear optics in condensed phases, it is very useful to develop effective and reliable methods to reproduce the solvent effects on the nonlinear optical properties (NLO) of molecules. The effect of the solvent polarity is often discussed within the methods, which represent the solvent as a continuum medium of dielectric constant ϵ.[18−41,48] Most citations used the simple self-consistent reaction field methods (SCRF).[18−33,48] The SCRF methods are based on the reaction field theory, developed by Onsager[49] and Kirkwood.[50] These models have been used with reasonable success, although, there are important limitations. There is significant evidence that results of SCRF calculations are strongly dependent on cavity parameters.[22,26,30] Moreover, continuum models do not include specific interaction as hydrogen bonding, which can significantly perturb the structure of investigated molecules.[51]
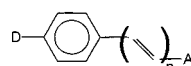
Among the classical continuum models, the polarized continuum models (PCM), first proposed by Miertus, Scrocco, and Tomasi,[52] are at present probably the most widely used for the description of solute/solvent interactions. This model utilizes more realistic solute cavity compared to the SCRF method, which is defined by the interlocking spheres centered on the solute nuclei.[34−39] Recently, Tomasi et al.[36] have shown that electrostatic interaction between solute and solvent is the most important effect on the nonlinear response of solute. Moreover, these authors have found a negligible effect due to dispersion and a substantial effect for Pauli repulsion.[36]

Figure 1. Compounds used in the present study.
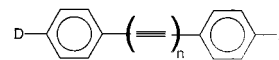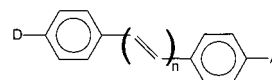
Donor-Acceptor Phenylpolyenes

1. D = OCH₃, A = COH, n = 1
2. D = OCH₃, A = COH, n = 2
3. D = OCH₃, A = COH, n = 3
4. D = N(CH₃)₂, A = NO₂, n = 1
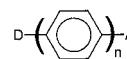
Donor-Acceptor Diphenylpolyenes

5. D = OCH₃, A = CN, n = 1
6. D = OCH₃, A = CN, n = 2
7. D = OCH₃, A = CN, n = 3
8. D = OCH₃, A = NO₂, n = 1
9. D = OCH₃, A = NO₂, n = 2
10. D = OCH₃, A = NO₂, n = 3
11. D = OCH₃, A = NO₂, n = 4
12. D = N(CH₃)₂, A = NO₂, n = 1
13. D = N(CH₃)₂, A = NO₂, n = 2
14. D = N(CH₃)₂, A = NO₂, n = 3
15. D = N(CH₃)₂, A = NO₂, n = 4

Donor-Acceptor Diphenylpolyines

16. D = NH₂, A = NO₂, n = 1
17. D = NH₂, A = NO₂, n = 2
18. D = NH₂, A = NO₂, n = 3

Donor-Acceptor Polyphenyls

19. D = NH₂, A = NO₂, n = 1
20. D = NH₂, A = NO₂, n = 2
21. D = NH₂, A = NO₂, n = 3
22. D = NH₂, A = NO₂, n = 3

In this article, the influence of the solvent effect on the static and time-dependent first- (β) and second-order (γ) hyperpolarizabilities is studied for series of large π-conjugated donor−acceptor compounds (see Figure 1). For this purpose, we apply a recently proposed quantum-mechanical Langevin dipoles/ Monte Carlo (QM/LD/MC) approach based on the discrete representation of the solvent.[53] In our opinion, the QM/LD/MC model gives the better description of the solute/solvent interac-

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tions compared to the continuum models. In our previous papers,[42−47] we considered the solvent effect on molecular (hyper)polarizabilities of selected compounds obtained from sum-over-states (SOS)[54] and finite-field (FF)[55−57] methods implemented in GRINDOL code (based on the INDO-like Hamiltonian).[58] The aim of the present work is to confirm that the QM/LD/MC model gives the qualitatively and quantitatively correct description of the solvent effect on β and γ for extended collections of compounds. The results of our calculations are compared with the available experimental electric-field-induced second harmonic generation (EFISH)[5,6,8] and third harmonic generation (THG) data.[5,6] The critical comparisons between GRINDOL-FF/QM/LD/MC and GRINDOL-SOS/QM/LD/MC results to publish ZINDO−SOS/SCRF[23] and ZINDO-TDHF/SCRF[25] calculated values of β were carried out in the gas phase and in the solvent.

II. Methods and Calculations

II.1. Molecular Hyperpolarizabilities. Calculations of first- (β) and second-order (γ) hyperpolarizability tensors of investigated molecules have been performed using SOS[54] and FF[55−57] methods. Both methods were implemented in our all-valence GRINDOL method[58] based on the INDO approximation. The method enables the calculation, within the unified parametrization scheme of ground- and excited-state properties (transition energies, oscillator strengths, and dipole moments) with acceptable agreement to relevant experimental studies for isolated molecules and molecular complexes.[42−47,53,58−60] Moreover, our group, as well as others, have shown that our GRINDOL methods gives β and γ which are comparable to ab initio methods (including electron correlation).[44,61]

Definitions and Conventions. In general, the total energy and dipole moment can be expanded as the Taylor series of the applied electric field:[62−64]

$$E(\bar{F}) = E(0) - \mu_i F_i - (1/2!)\alpha_{ij}F_i F_j - (1/3!)\beta_{ijk}F_i F_j F_k - \\ (1/4!)\gamma_{ijkl}F_i F_j F_k F_l - \ ... \ (1)$$

$$\mu_i(\bar{F}) = \mu_i(0) + \alpha_{ij}F_j + (1/2!)\beta_{ijk}F_j F_k + (1/3!)\gamma_{ijkl}F_j F_k F_l + ... \\ (2)$$

where $E(0)$ is the energy of the molecule in the absence of an electric field (F), $\mu_i(0)$ is its permanent dipole moment, α_{ij} is the dipole polarizability, and β_{ijk} and γ_{ijkl} are the first- and second-order hyperpolarizabilities tensors, respectively.

In the solution- and gas-phase experiments (isotropic systems), only invariant vector and scalar components of β_{ijk} and γ_{ijkl} are measured.[62−64] For β_{ijk}, the experimentally meaningful quantity (for the polar molecules in the EFISH experiment) is the vector quantity, β_μ, defined as

$$\beta_\mu = \frac{\bar{\mu} \cdot \bar{\beta}}{|\mu|} \quad (3)$$

with

$$\bar{\mu} \cdot \bar{\beta} = \sum_{i=1}^{3} \mu_i \beta_i \quad \text{and} \quad \beta_i = \beta_{iii} + \frac{1}{3}\sum_{j\neq i}(\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

$$i, j \in (x, y, z) \quad (4)$$

where μ is the ground-state molecular dipole moment.

The scalar part of γ, which can be compared with the solution-phase experimental value (in the THG experiment) is given by

$$\langle \gamma \rangle = \frac{1}{15}\sum_{ij}(2\gamma_{iijj} + \gamma_{ijji}) \qquad i, j \in (x, y, z) \quad (5)$$

In the case of static fields (including Kleinman symmetry relations[65]), eq 5 can be expressed as

$$\langle \gamma \rangle = \frac{1}{5}\{\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2[\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}]\} \\ (6)$$

Thr above relations show that there is no need for the calculation of all possible tensor components (27 for β_{ijk} and 81 for γ_{ijkl}) to obtain the isotropic quantities.

The so-called B convention or the perturbation series convention[64] for comparison between theoretically and experimentally determined values of hyperpolarizabilities was adopted in this work. In comparison to the molecular properties described in a Taylor series (eqs 1−2, T convention), the following relations hold: $\beta^T = 2\beta^B$ and $\gamma^T = 6\gamma^B$. The discussion about different conventions is very important problem in comparison between theory and experimental results.

Finite-Field Method. We have employed the FF method developed by Kurtz et al.[57] which was first used by Cohen and Roothaan[55] to calculate atomic polarizabilities based on the Hartree−Fock method. Equations 1 and 2 are the key equations for the calculation of molecular polarizabilities and hyperpolarizabilities by FF techniques because the tensor components are obtained by the numerical differentiation of the energy or dipole moment with respect to the perturbing electric field F. To calculate the energy and dipole moment in the presence of a uniform of electric field of strength F, an $-\vec{\mu}\vec{F}$ needs to be added to the unperturbed molecular Hamiltonian: $\hat{H} = \hat{H}^o - \vec{\mu}\vec{F}$. The β_{ijk} is obtained as the second derivative of the dipole moment (eq 2) with respect to the applied field or the third derivative of the energy (eq 1). The γ_{ijkl} is obtained as the third derivative of the dipole moment (eq 2) with the respect to the applied field, and so on. It should be noted that results obtained by eqs 1 and 2 are equivalent only if the Hellmann−Feynman theorem is satisfied.[66] The variational methods such as FF used in this work satisfy the theorem. The values of β_μ and $\langle\gamma\rangle$ were calculated with both energy and dipole expansions; however, only results obtained by dipole expansion are reported. It should be noted that no significant differences in β_μ and $\langle\gamma\rangle$ (both in the gas phase and in solution) values calculated by dipole and energy expansion were found for molecules investigated in this study. To avoid numerical errors, we used several minimum field strengths (usually 0.001 au). The SCF convergence criterion at the energy was set at 10^{-12} eV in all of the electronic structure calculations.

The FF method is limited to static fields. To compare with observed $\beta_\mu(-2\omega;\omega,\omega)$ values at different fundamental frequencies, the calculated FF values of $\beta_\mu(0;0,0)$ were transformed by the two-level model as follows (see, e.g., ref 64):

$$\beta_\mu(-2\omega;\omega,\omega) \approx \beta_{xxx}(-2\omega;\omega,\omega) = \\ \frac{\beta_\mu(0;0,0)}{(1 - \omega^2/E_{CT}^2)(1 - 4\omega^2/E_{CT}^2)} \quad (7)$$

The calculated static values of $\langle\gamma\rangle(0;0,0,0)$ were corrected to the frequency-dependent $\langle\gamma\rangle(-3\omega;\omega,\omega,\omega)$ values by using the following formula:[67]

$$\frac{\langle\gamma\rangle(-3\omega;\omega,\omega,\omega)}{\langle\gamma\rangle(0;0,0,0)} =$$

$$\frac{1}{4}\left[\frac{E_{CT}^3}{(E_{CT} - 3\omega)(E_{CT} - 2\omega)(E_{CT} - \omega)} + \right.$$

$$\frac{E_{CT}^3}{(E_{CT} + 3\omega)(E_{CT} + 2\omega)(E_{CT} + \omega)} +$$

$$\frac{E_{CT}^3}{(E_{CT} + \omega)(E_{CT} + 2\omega)(E_{CT} - \omega)} +$$

$$\left.\frac{E_{CT}^3}{(E_{CT} + \omega)(E_{CT} - 2\omega)(E_{CT} - \omega)}\right] \quad (8)$$

In the above expressions, E_{CT} is the transition energy between the ground and CT excited state and ω is the frequency of the applied electric field. It should be noted that eqs 7 and 8 are approximate. It is connected with the fact that the denominators in this equations contain the transition energy between the ground and CT excited state only. Hence, the extrapolated values should be considered as approximations to the true hyperpolarizabilities. It is worth noting that the two-level formula was successfully applied to calculations of extrapolated values of β for various donor−acceptor molecules.[62,66] Equation 8 was first applied by Goddard III et al.[67] in their study of the valence-bond charge-transfer solvation model for NLO properties of organic molecules in polar solvent. Nowadays, the time-dependent Hartree−Fock (TDHF) method is not implemented in the GRINDOL program. Therefore, it is not possible to make extrapolation by using high-level TDHF method.

Sum-over-States Method. In the SOS calculations, the transition dipole moments and transition energies are used in the equations (for β_{ijk} and γ_{ijkl}) derived from time-dependent perturbation theory of Orr and Ward.[54] In this paper, we do not include the results of $\langle\gamma\rangle$ calculations. It is connected with the fact that our configurations interaction (CI) calculations were performed with singly excited configurations only (SCI). This level of theory has been generally accepted to be adequate for computing first hyperpolarizability β. To obtain the correct sign of mean $\langle\gamma\rangle$ values, the excited states of molecular systems must be obtained from a single and double excitation CI (SDCI) method.[63] The SDCI method is more sophisticated compared to the SCI because it treats the repulsive interaction between a given pair of electrons. However, we found that values of $\langle\gamma\rangle$ for PNA molecule in aqueous solution (for high frequencies of external electric field) have a correct sign.[43] The relationship between the electronic structure of the molecule and the first molecular hyperpolarizability (β_{ijk}) tensor, as derived from time-dependent perturbation theory, is given by eq 9 (see, e.g., ref 64):

$$\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2) =$$

$$\frac{1}{\hbar^2}P(i,j,k;-\omega_\sigma,\omega_1,\omega_2)\sum_{l\neq0}\sum_{m\neq0}\frac{\langle0|\mu_i|l\rangle\langle l|\bar{\mu}_j|m\rangle\langle m|\mu_k|0\rangle}{(\omega_{0l} - \omega_\sigma)(\omega_{0m} - \omega_2)} \quad (9)$$

In eq 9, the matrix elements $\langle0|\mu_i|l\rangle$ and $\langle l|\bar{\mu}_j|m\rangle = \langle l|\mu_j|m\rangle - \langle0|\mu_j|0\rangle\delta_{lm}$ are the electronic transition moments, ω_{0l} (times $\hbar$) is the energy difference between the electronic ground and excited state l and $\omega_\sigma = \omega_1 + \omega_2$ is the polarization frequency (below electronic resonances). The superscripts i, j, and k refer to the molecular Cartesian coordinates x, y, and z. P is a permutation operator and indicates a summation over six terms obtained by permuting frequencies. The summations over

excited states used in the SOS expressions generated from CI calculations are in general infinite. In practice, one usually truncates these sums after apparent convergence has been reached. It is well-known that the first hyperpolarizability β converges rapidly with the number of singly excited states.[62] In our SOS calculations 200−250, the lowest CI energy states were included.

II.2. Solvent Model. In this work, we report a study of the effect of electrostatic solute/solvent interactions on the solute hyperpolarizabilities within our QM/LD/MC (quantum-mechanical Langevin dipoles/Monte Carlo) method.[53] The details of the QM/LD/MC method (with the discrete representation of solvent molecules) have been presented in previous works,[42−47,53,59,60] where it was successfully applied to calculations of solvation energies, solvatochromic shifts, nonlinear optical properties, and conformational problems. The QM/LD/MC method is a modification and extension of the LD model developed by Warshel and collaborators.[68−70] Solvent molecules are represented in the QM/LD/MC model by three-dimensional cubic grid of polarizable point dipoles constructed around the solute molecules. Each dipole (an ith solvent molecule) is polarized by the local field resulting from a set of charges, dipoles, and quadrupoles located on atoms of the solute molecules (CAMM; cumulative atomic multipole moments),[71] as well as from other solvent dipoles. In our calculations, we include the full (i.e., without dumping) Langevin formula for the polarization of solvent dipole moments and mutual polarization of the solute and solvent molecules.[53] The optimum position and orientation of the solute molecule, placed in a cubic grid of polarizable solvent molecules, was determined using the MC method.[72]

The effect of reaction field (electrostatic potential and electrostatic field on each atom of the solute molecule), produced by solvent, is introduced into the solute Hamiltonian by means of a perturbation operator V according to equation

$$H = H^o + V \quad (10)$$

where H^o is the Hamiltonian of isolated molecule. Hence, at the LCAO MO SCF method level, the Hartree−Fock−Roothaan operator is corrected by

$$F_{\mu\nu} = F_{\mu\nu}^o + \langle\mu|V|\nu\rangle \quad (11)$$

In our approach, the total potential V acting on the solute atoms is a sum of averaged (in the meaning of the MC method) potential due to the permanent (V_{perm}) and induced (V_{ind}) dipole moments of solvent molecules:[53]

$$V = V_{perm} + V_{ind} \quad (12)$$

Above averaged values of V are introduced into eq 10, and after SCF calculation, new CAMMs were obtained, which generate new V, which are then incorporated into eq 10 to give new CAMMs. By repeating these calculations, we obtain new V, etc., until self-consistency is reached.

Recently, the QM/LD/MC method has been constructed for water and chloroform solvent.[53,59]

II.3. Molecular Geometries. The ground-state structures of donor−acceptor diphenylpolyines and donor−acceptor polyphenyls molecules (see Figure 1) were optimized without any symmetry constraints on the basis of the AM1 Hamiltonian in the MOPAC package.[73] The molecular structure of donor−acceptor phenylpolyenes and donor−acceptor diphenylpolyenes were optimized assuming the planar geometries (i.e., dihedral

angels were not optimized for π-conjugated bridge). The convergence criterion for AM1 calculations of geometries was one hundred times greater (PRECISE option) than usually used. It should be noted that the chosen input geometry is an important issue in these molecules.[62] More details on the effect of input geometries on NLO properties are given by Ratner et al.,[24,62,74] Barzoukas et al.,[75,76] Dehu et al.,[26] Yu and Zerner,[25] Cheng et al.,[6] and Lipiński and Bartkowiak.[46] Our selection of input geometries is a consequence of results above investigations. In our studies, the solvent molecular geometries were not treated explicitly. Barzoukas et al.[76] have shown (for donor–acceptor stilbenes; molecule 5 and 12) that many rotational conformers can exist in a liquid solution, but for strong donor–acceptor interaction (NMe$_2$–NO$_2$) the planar geometry is favored. The above conclusion is supported by works of Skrabal et al.[88] and Enzumi et al.[89] These authors have reported (based on calculated and experimental UV spectrum) that 4-(dimethylamino)-4′-nitro-*trans*-stilbene (molecule 12) takes a nearly planar conformation in solutions. For planar conformations, increasing the value of the ground-state dipole moment are usually observed as compared to twisted conformers. Hence, the planar conformers are more stabilized in the polar solvent as compared to that in the gas-phase.[45,46] Moreover, Ratner et al.[23,62,74] chose bonds-alternating idealized (BAI) planar geometries, being a compilation of experimental (crystal structures) geometries for calculations of NLO properties of similar series donor–acceptor molecular chromophores. It should be noted that the AM1 method essentially reproduced these geometries (in this case dihedral angles were not optimized).[74] The crystal structure data show that molecules investigated here have planar structure (π-conjugated bridge).[6,7,74] However, AM1 calculations (the full geometry optimization) give highly twisted nonplanar structures. On the other hand, our experience shows that the PM3 calculations[73] (in the gas phase) give planar geometries. These results are supported by B3LYP/6-31G(d) calculations for phenylpolyenes and diphenylpolyenes derivatives with strong donor (NH$_2$) and acceptor (NO$_2$) for $n = 1$. On the other hand, the experimental results indicate that biphenyls (molecule 19) have not planar structure in the gas phase and solution phase.[5,6]

The effect of input geometries (SCRF calculations) on NLO properties was investigated for PNA (molecule **19**), ANB (molecule **20**), and ANS (molecule **12** with NH2 donor group) in our previous work.[46] The inclusion of solvent does not change the geometry significantly (from the chemical point of view; the maximum changes in the bond lengths are smaller than 0,02 Å). The values of NLO properties computed for AM1 geometries usually lie between values calculated for ab initio gas-phase and ab initio chloroform geometries. Additionally, we observed that AM1 optimized gas-phase geometries (for these molecules) are very similar to the chloroform-phase HF/6-31G(d) geometries obtained in the SCRF ab initio calculations. Hence, we conclude that our input geometries are accurate representation of molecular structures for calculation of NLO properties in the solution-phase.

III. Results and Discussion

In this paper, we study the influence of the solvent effect on the static and time-dependent first- (β) and second-order hyperpolarizabilities (γ) of series prototypical molecules contain electron-donating (D) and -withdrawing (A) groups at the opposite ends of an extended π-conjugated bridge (D–π–A). It is generally accepted that these types of molecules lead to large values of β.[5,6,62] The molecules chosen are shown in Figure 1. The simple donor–acceptor chromophores serve as important

model molecules for calculations and the experiments.[62,63] These compounds exhibit a large ground-state dipole moment, low-lying strongly allowed electronic transition (π–π*), and substantial change in dipole moment upon excitation. This lowest-energy electronic transition is often identified as due to the intramolecular CT occurring along the long axis of the molecule.[62,77–79] The donor–acceptor compounds investigated in this paper are one-dimensional NLO chromophores with only one significant component of β (in the direction of dipole moment).[62] Hence, the hyperpolarizabilities (β) are often described on the basis of the so-called two-state model originally proposed by Oudar and Chemla[80] in which only low-lying CT excited state in the summation is taken into consideration (see eq 9). In the two-level picture, $\beta_\mu \propto (E_{CT})^{-3} f \Delta\mu$, where f is oscillator strength, $\Delta\mu$ is difference in dipole moment between the ground state and the CT excited state. The solvent dependence of β can be understood in terms of a positive (red-shift) or negative (blue-shift) solvatochromic behavior of the predominant π–π* transition.[77–79] The increase of β is followed in general by red-shift of the CT absorption band and increase of $\Delta\mu$ (going from the gas-phase to the polar solvent).[17–21,23,27,43,46] In contrast, for chromophores displaying negative solvato-chromism, the solvent dependence of β shows opposite trends.[2,42,45] All of the investigated molecules in this paper displayed positive solvatochromism. It should be noted that the absolute values of β obtained in the two-level model are usually overestimated compared to full quantum chemical calculations.[62,64,46] Experimental as well as theoretical observations show a significant contribution of the CT state to γ.[5,44]

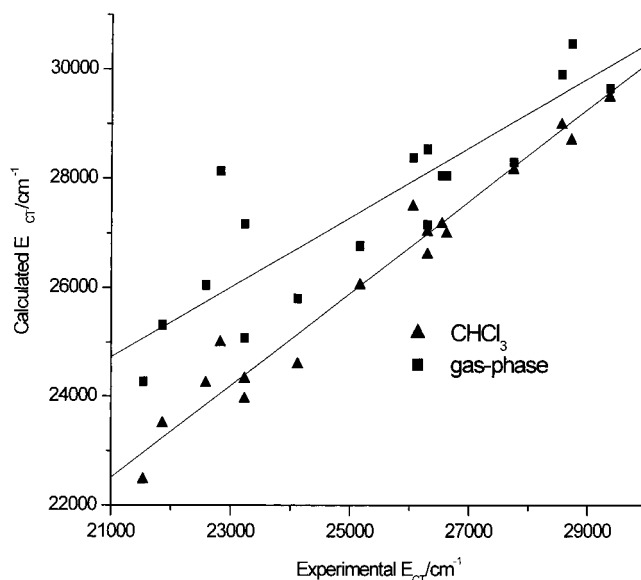The results of the FF and SOS calculations of static vector component $\beta_\mu(0;0,0)$ and time-dependent vector component $\beta_\mu(-2\omega;\omega,\omega)$ for second-harmonic generation (SHG) at $\omega = 0.650$ eV (and at $\omega = 1.17$ eV for molecule **19** (PNA)) in the gas phase and in solutions are presented in Table 1. These results are compared with available experimental data.[5,6,8] The calculated values of $\beta_\mu(-2\omega;\omega,\omega)$ in water solvent are compared with the experimental EFISH measurements made in more polar solvents than chloroform. It is connected with the fact that the QM/LD/MC method is constructed for the water and chloroform solvent only. Hence, the water solvent represents here polar solvents. To compare calculations with reported experimental values, the calculated $\beta_\mu(0;0,0)$ values (FF method) are transformed to experimental $\beta_\mu(-2\omega;\omega,\omega)$ values by using eq 7 for dispersion correction. The results of the FF calculations for $\langle\gamma\rangle$ with and without solvent effect are listed in Table 2, together with related experimental data.[5,6] No experimental static values of $\langle\gamma\rangle(0;0,0,0)$ are available for molecules investigated here. The THG measurements at $\omega = 0.650$ eV have been performed by Cheng at al.[5,6] The experimental values of $\langle\gamma\rangle(-3\omega;\omega,\omega,\omega)$ were extrapolated to static values by using eq 8. The transition energy, E_{CT} (see eq 8), between the ground an CT excited states were taken from experimental solution UV spectra.[5,6] It should be noted that the extrapolated values should be considered as approximation to the true static second-order hyperpolarizability. Moreover, the values of $\langle\gamma\rangle(-3\omega;\omega,\omega,\omega)$ obtained by using calculated (FF method) static values of $\langle\gamma\rangle(0;0,0,0)$ and utilizing eq 8 are presented in Table 2. In this case, the calculated values of E_{CT} (from the SCF CI/QM/LD/MC procedure) were used in eq 8. Good agreement between computed and experimental transition energies is generally observed when solvent effect is included (see Figure 2). The correlation coefficients (R values) of the least-squares fit are equal to 0.90 and 0.98 for the gas-phase and chloroform solvent. Including solvent effect provides better results of R. The QM/LD/MC method correctly predicts

TABLE 1: Calculated and Experimental Values of First-Order Hyperpolarizabilities β_μ (in 10^{-30} esu) for a Series of Investigated Donor−Acceptor Molecules in the Gas Phase and in Solvents

mol.	n	solvent	$\beta_\mu(0;0,0,)$ FF	SOS	ω [eV]	$\beta_\mu(-2\omega;\omega,\omega)$ FF[a]	SOS	expt[b]	expt[c]
			Donor−Acceptor Phenylpolyenes						
1	1	gas	6.7	6.2	0.650	7.7	7.7		
		CHCl₃	6.8	6.2	0.650	7.8	8.6	36	21
2	2	gas	9.0	8.1	0.650	10.6	10.3		
		CHCl₃	10.5	9.7	0.650	12.4	14.3	84	49
3	3	gas	26.5	24.5	0.650	31.9	31.3		
		CHCl₃	36.2	34.6	0.650	43.8	44.6	126	73
4	1	gas	23.7	27.6	0.650	28.7	34.6		
		CHCl₃	39.2	47.9	0.650	49.6	63.6	150	87
			Donor−Acceptor Diphenylpolyenes						
5	1	gas	8.1	8.1	0.650	9.6	9.9		
		CHCl₃	12.1	13.5	0.650	14.2	16.4	57	33
6	2	gas	12.8	12.2	0.650	15.3	15.4		
		CHCl₃	18.9	19.0	0.650	22.8	23.9	81	47
7	3	gas	17.3	16.4	0.650	21.1	20.9		
		CHCl₃	25.9	24.3	0.650	31.8	31.3	120	70
8	1	gas	28.7	31.5	0.650	34.5	39.8		
		CHCl₃	35.6	39.7	0.650	43.4	51.0	102	59
9	2	gas	44.4	43.3	0.650	54.5	56.8		
		CHCl₃	53.5	53.2	0.650	66.5	70.7	141	82
10	3	gas	60.8	48.0	0.650	76.0	63.6		
		CHCl₃	87.1	80.8	0.650	111.5	111.8	228	132
11	4	gas	76.1	64.6	0.650	96.5	88.7		
		CHCl₃	109.3	94.9	0.650	142.0	134.6	303	175
12	1	gas	41.3	43.2	0.650	50.4	55.5		
		CHCl₃	64.2	68.7	0.650	80.6	91.5	219	127
13	2	gas	59.3	56.5	0.650	73.7	74.6		
		CHCl₃	84.5	82.4	0.650	107.5	111.9	321	186
14	3	gas	77.7	69.2	0.650	98.0	93.2		
		CHCl₃	109.5	99.0	0.650	141.5	137.5	393	228
15	4	gas	105.8	85.6	0.650	136.4	118.7		
		CHCl₃	148.7	120.8	0.650	195.5	172.0	570	330
			Donor−Acceptor Diphenylpolyines						
16	1	gas	32.5	36.8	0.650	38.8	45.8		
		CHCl₃	48.0	55.3	0.650	59.1	71.2	72	42
		H₂O	66.3	76.6	0.650	83.8	101.1	120[d]	70
17	2	gas	38.9	41.7	0.650	46.7	51.9		
		CHCl₃	48.2	53.4	0.650	58.5	68.9	84	49
18	3	gas	46.2	47.2	0.650	55.6	58.7		
		CHCl₃	58.6	60.0	0.650	71.4	89.1		
			Donor−Acceptor Polyphenyls						
19	1	gas	7.6	10.6	1.17	13.6	20.3		
		CHCl₃	10.6	15.3	1.17	26.9	33.1	50.4	29.2
		H₂O	17.3	26.3	1.17	48.8	68.7	77.7[e]	45.1
					1.17			96.0[f]	55.7
					1.17			115.2[d]	66.8
		gas	7.6	10.6	0.650	8.9	12.7		
		H₂O	17.3	26.3	0.650	22.1	33.4	30[d]	17
20	2	gas	17.3	21.7	0.650	20.3	26.4		
		H₂O	41.6	54.2	0.650	52.9	71.3	72.0[d]	42
21	3	gas	21.8	24.2	0.650	25.6	29.8		
		H₂O	50.5	58.6	0.650	63.8	77.7	48.0[d]	28
22	4	gas	24.9	27.5	0.650	29.2	33.6		
		H₂O	49.5	55.2	0.650	61.4	71.6	33[d]	19

[a] Extrapolated to frequency-dependent values using two-state model (eq 7). [b] Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631. Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643. Stähelin, M; Burland, D. M.; Rice, J. E. *Chem. Phys. Lett.* **1992**, *191*, 245. [c] Experimental results based on new measurement of SHG coefficient (d_{11}) for quartz. [d] In NMP (*N*-methylpyrollidone). [e] In acetone. [f] In ethanol.

Figure 2. Correlation of calculated (in the gas phase and in CHCl₃ solvent) and measured (in CHCl₃ solvent) transition energies (E_{CT}) for molecules investigated in this work.

the solvent in the excited and ground state of the solute molecule by the solvent induced dipoles should be included (see eq 24 and discussion in ref 53). It is related to the fact that the solvation energy of the excited states is evaluated using the ground-state solvent configurations, because the absorption of light is faster than the orientation time of the permanent dipoles of the solvent and allowing only induced dipoles to be reoriented.[51,53,77−79] In our calculations of NLO properties based on eqs 7−9 which contain transition energies between ground and excited states above correction is not included.

It is important to note here that there are many difficulties in the comparison of absolute $\beta_\mu(-2\omega;\omega,\omega)$ values with experimental data. One is that there are two different values for the second harmonic generation coefficient (d_{11}) of the quartz (standard reference material for solution EFISH measurement), which differ by a factor of 0.58.[64,81] Chang et al.[5,6] and Rice et al.[8] in their experimental works have used older (larger) value of d_{11}. For comparison, in the last column of Table 1, we present the experimental $\beta_\mu(-2\omega;\omega,\omega)$ values based on more recent measurement for quartz. These values are about 40% less compared to the older experimental results (ninth column of Table 1). It is worth noting that the calculated values of $\beta_\mu(-2\omega;\omega,\omega)$ are in better agreement with experimental data based on more recent obtained values of d_{11} for quartz Moreover, the EFISH experiment measures $\mu\beta$ rather than β_μ (see eq 3). Hence, the EFISH method requires one to make an independent measurement of dipole moment (μ) in order to obtain β_μ.[1,3,5,6,8] Unfortunately, values of μ strongly depend on expressions used in calculations from experimental data.[13,82] Moylan and Walsh[82] have found that their dipole moments (for series of donor−acceptor diphenylpolyines) are greater that these measured by Chang et al.[6] The larger values of μ lead to decrease values of β_μ. The calculated values of the dipole moments in the chloroform solvent are larger by a factor 1.2−2.4 with the corresponding experimental values, but it should be noted that the GRINDOL method usually overestimates the experimental gas-phase dipole moments.

The next important problem of comparing experimental results in condensed phases with theoretical values is connected with the local field factors.[38,39,81,83] The most experimental values of β_μ and $\langle\gamma\rangle$ in solution (EFISH and THG measurements) are

solvatochromic shifts of electronic transitions for various molecules in polar solvent.[42,45,46,53,59] In the calculation of the electronic transition of solute molecule in a field of polarizable solvent molecules, the change of the energy necessary to polarize

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TABLE 2: Comparison of Theoretical and Experimental Second-Order Hyperpolarizabilities $\langle\gamma\rangle$ (in 10^{-36} esu) of Series Donor−Acceptor Molecules in Different Solvents

mol.	n	solvent	theory (FF)		expt.	
			$\langle\gamma\rangle(0;0,0,0)$	$\langle\gamma\rangle(-3\omega;\omega,\omega,\omega)^a$	$\langle\gamma\rangle(0;0,0,0)^b$	$\langle\gamma\rangle(-3\omega;\omega,\omega,\omega)^c$
			Donor−Acceptor Phenylpolyenes			
1	1	gas	3.7	5.8		
		CHCl$_3$	6.4	9.9	18	28
2	2	gas	13.4	22.5		
		CHCl$_3$	14.0	23.5	24	43
3	3	gas	37.0	66.9		
		CHCl$_3$	41.1	75.9	61	120
4	1	gas	14.3	26.3		
		CHCl$_3$	23.5	60.0		
			Donor−Acceptor Diphenylpolyenes			
5	1	gas	17.9	30.4		
		CHCl$_3$	19.0	32.3	32	54
6	2	gas	36.6	65.4		
		CHCl$_3$	38.5	69.3	66	122
7	3	gas	64.6	122.3		
		CHCl$_3$	67.6	129.1	117	234
8	1	gas	29.1	53.3		
		CHCl$_3$	35.2	66.2	47	93
9	2	gas	57.1	111.1		
		CHCl$_3$	66.2	134.3	60	130
10	3	gas	97.0	201.3		
		CHCl$_3$	127.0	285.2	98	230
11	4	gas	149.1	323.2		
		CHCl$_3$	191.0	454.1		
12	1	gas	40.1	76.0		
		CHCl$_3$	61.1	130.0	88	225
13	2	gas	73.2	146.2		
		CHCl$_3$	99.0	217.0		
14	3	gas	118.1	251.0		
		CHCl$_3$	156.2	363.0		
15	4	gas	192.1	442.2		
		CHCl$_3$	242.0	601.1		
			Donor−Acceptor Diphenylpolyines			
16	1	gas	31.2	55.2		
		CHCl$_3$	45.8	89.9	60	120
		H$_2$O	64.3	136.6	61	140^d
17	2	gas	45.6	81.4		
		CHCl$_3$	55.8	104.3	40	81
18	3	gas	64.3	116.7		
		CHCl$_3$	77.0	149.3		
			Donor−Acceptor Polyphenyls			
19	1	gas	3.3	5.4		
		H$_2$O	7.2	16.1	11 (8)	21 (15)^e
20	2	gas	12.3	20.5		
		H$_2$O	32.0	70.2	47	96
21	3	gas	21.5	36.1		
		H$_2$O	47.1	90.9	60	124
22	4	gas	32.6	53.9		
		H$_2$O	55.2	111.1	74	133

^{a} Extrapolated using calculated static values of $\langle\gamma\rangle$ and utilizing eq 8. ^{b} Extrapolated to static values using eq 8. ^{c} Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631. Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643. ^{d} In NMP (*N*-methylpyrollidone). ^{e} In acetone.

obtained from the macroscopic optical susceptibilities ($\chi^{(3)}$). To obtain experimental values of β_μ and $\langle\gamma\rangle$, it is necessary to know the value of the microscopic static and frequency-dependent electric fields that molecule feels in solution.[5,6,8,81,83] The relation between the external applied and local (microscopic) fields, and consequently between β_μ ($\langle\gamma\rangle$) and $\chi^{(3)}$ is usually defined by the local field factors (f_0, f_ω, $f_{2\omega}$, and $f_{3\omega}$) based on Lorenz and Onsager theories.[81,83] Recently, it has been shown that the local field factors, based on above theories, used by experimentalists are not adequate to describe the effect of the solvent environment.[81] A general relation between microscopic (hyper)polarizability and macroscopic susceptibility tensors has been defined recently by Wortman and Bishop.[83] Moreover, Tomasi et al.[38,39] and Theodorou et al.[84] have proposed alternative strategies for

obtaining of the local field factors based on quantum chemical methods. Actually, investigations in this direction by different research groups are in progress. Furthermore, in the case of $\langle\gamma\rangle$, the comparison between theory and experiment is complicated by the presence of local field cascading process.[85] In this work, solvent effect on the NLO response of the solute molecules (microscopic quantities) is investigated by the introduction of reaction field operator in the Hamiltonian (eq 10). As was mentioned in the section II.2, in the QM/LD/MC approach, one can divide the total potential V, acting on the solute molecule, into two parts (the first one connected with permanent (V_{perm}) dipole moments of the solvent molecules and second one related to induced (V_{ind}) dipole moments of the solvent molecules). In Table 3, the calculated static values of β_μ and $\langle\gamma\rangle$ by the use of

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TABLE 3: Calculated Static Values of β_μ and $\langle\gamma\rangle$ as a Function of Hamiltonian Used in the QM/LD/MC Calculations (Equation 12)

		4-Nitroaniline (**19**)	
H^o	β_μ	$7.6\ (10.6)^a$	$7.6\ (10.6)$
	$\langle\gamma\rangle$	3.3	3.3
		CHCl$_3$	**H$_2$O**
$H^o + V_{perm}$	β_μ	8.8 (15.5)	14.7 (22.0)
	$\langle\gamma\rangle$	3.8	6.2
$H^o + V_{ind}$	β_μ	9.0 (12.9)	8.9 (12.8)
	$\langle\gamma\rangle$	3.9	3.8
$H^o + V_{perm} + V_{ind}$	β_μ	10.6 (15.3)	17.3 (26.3)
	$\langle\gamma\rangle$	4.5	7.2
		4-(Methoxy)-4′-nitrostilbene (**8**)	
H^o	β_μ	28.7 (31.5)	28.7 (31.5)
	$\langle\gamma\rangle$	29.1	29.1
		CHCl$_3$	**H$_2$O**
$H^o + V_{perm}$	β_μ	31.8 (35.2)	44.2 (49.9)
	$\langle\gamma\rangle$	31.6	42.7
$H^o + V_{ind}$	β_μ	31.9 (35.3)	31.5 (34.8)
	$\langle\gamma\rangle$	31.6	31.3
$H^o + V_{perm} + V_{ind}$	β_μ	35.6 (39.7)	49.5 (56.3)
	$\langle\gamma\rangle$	35.2	48.1

[a] Data in parentheses are the calculated β_μ values from the SOS method.

the SOS procedure as well as the FF method for compounds **8** and **19** are presented. The calculations were performed for three cases of Hamiltonian, apparently for the water and chloroform solutions, respectively. In the first case, we include in the Hamiltonian the potential related only to permanent dipole moments of the solvent molecules.

From the presented results for both compounds, it can be seen that values of β_μ and $\langle\gamma\rangle$ are almost twice as great in the case of water solution. It is so, because the water molecule has a greater permanent dipole moment than the chloroform one.[53] In the second case of the Hamiltonian, if one, doing the SCF calculations, takes into account the potential connected only with the induced dipole moments of the solvent molecules, this will result in a little bit greater values of β_μ and $\langle\gamma\rangle$ for the chloroform solution in comparison with water ones. This effect can be easily explained when it is taken into consideration that the chloroform molecule possesses greater polarizability than the water molecule. Comparing results of calculations for all three cases of Hamiltonians, it can be easily found that the values of hyperpolarizabilities obtained apparently for potential related to permanent (V_{perm}) as well as induced (V_{ind}) dipole moments, respectively, are not additive quantities.

It is important to compare our calculated results of the solvent effect on the molecular hyperpolarizabilities with related results obtained by another authors. In Table 4, comparison between our calculated $\beta_\mu(CHCl_3)/\beta_\mu(gas)$ ratios and ones obtained by Ratner et al.[23] and Yu and Zerner[25] is presented. These authors have used simple SCRF method based on spherical cavity implemented in the INDO/S Hamiltonian (ZINDO program).[23,25] In cited works, only dipolar terms in the description of the solute/solvent interaction have been included. The SOS and time-dependent coupled Hartree−Fock (TDCHF) formalism have been used for calculation of the first-order hyperpolarizabilities in the gas phase and in solution phase by Ratner et al.[23] and Yu and Zerner,[25] respectively. The INDO/S method has been mainly parametrized for the interpretation of UV spectra data.[86,87] This method is known to provide reliable trends in β values especially for large donor−acceptor molecules, but it should be noted that this method overestimates absolute values of β.[64] As we can see, the ratios $\beta_\mu(CHCl_3)/\beta_\mu(gas)$ found by us are very close to the ones computed by Ratner et al.

TABLE 4: Comparison of Calculated $\beta_\mu(CHCl_3)/\beta_{vec}(gas)$ Ratios ($\omega = 0.650$ eV) Obtained from Various Theoretical Methods

				GRINDOL (QM/LD/MC)		ZINDO (SCRF)	
mol.	D	A	n	FF	SOS	SOS^a	TDCHF^b
		Donor−Acceptor Phenylpolyenes					
1	OCH$_3$	COH	1	1.0	1.1	1.1	
2	OCH$_3$	COH	2	1.2	1.4	1.1	
3	OCH$_3$	COH	3	1.4	1.4	1.2	
4	N(CH$_3$)$_2$	NO$_2$	1	1.7	1.8	1.6	1.5
		Donor−Acceptor Diphenylpolyenes					
8	OCH$_3$	NO$_2$	1	1.3	1.3	1.2	1.6
9	OCH$_3$	NO$_2$	2	1.2	1.2	1.3	1.8
10	OCH$_3$	NO$_2$	3	1.5	1.8	1.3	2.1
11	OCH$_3$	NO$_2$	4	1.5	1.5	1.3	2.4
12	N(CH$_3$)$_2$	NO$_2$	1	1.6	1.7	1.4	1.7
13	N(CH$_3$)$_2$	NO$_2$	2	1.5	1.5	1.4	2.2
14	N(CH$_3$)$_2$	NO$_2$	3	1.4	1.5	1.5	2.2
15	N(CH$_3$)$_2$	NO$_2$	4	1.4	1.5	1.4	2.5
		4-Nitroaniline					
19	NH$_2$	NO$_2$	1	2.5^c	2.6^c		1.6^d

[a] Di Bella, S.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 4440. [b] Yu, J.; Zerner, M. C. *J. Chem. Phys.* **1994**, *100*, 7487. [c] In water. [d] In acetone.

(ZINDO−SOS/SCRF).[23] The ZINDO-TDHF/SCRF method predicts much greater solvent effect on β_μ. This discrepancy is probably connected with the of choosing of the cavity radius of solutes, but it should be noted that the reaction field has not been explicity included into the solute Hamiltonian (only transition energies (E_{CT}) have been corrected for solvent shift effects) in ref 23. On the other hand, Dehu et al.[26] have found that both a multipolar expansion of the interaction energy and the use of an ellipsoidal cavity shape in the SCRF calculations of β values for long donor−acceptor molecules are necessary. Moreover, recently obtained results indicate that the absolute values of $\langle\gamma\rangle$ very strongly depend on the continuum model of solvents included in the calculations.[41]

Finally, the following conclusion can be drawn from our quantum chemical calculations (Tables 1 and 2): (1) There is the large influence of solvent on the values of β_μ and $\langle\gamma\rangle$ for molecules investigated here. For example, the calculated values of $\beta_\mu(0;0,0)$ and $\langle\gamma\rangle(0;0,0,0)$ in solvents are larger by a factor of 1.2−2.5 and 1.1−2.6 than the corresponding calculated values in the gas phase. (2) The calculated ratios of $\beta_\mu(sol)/\beta_\mu(gas)$ hold the following relation: $\beta_\mu^{FF}(sol)/\beta_\mu^{FF}(gas) \approx \beta_\mu^{SOS}(sol)/\beta_\mu^{SOS}(gas)$ for all molecules. These results show that the FF and SOS methods (based on the same Hamiltonian) predict similar solvent effect on β_μ for donor−acceptor molecules. (3) For a small ($n \leq 2$) donor−acceptor phenylpolyenes and donor−acceptor diphenylpolyenes, $\beta_\mu^{SOS} \geq \beta_\mu^{FF}$ (both in the gas phase and in solvents). For larger molecules, when the chain between the D and A group is lengthened, the opposite relationship is observed. These results indicate that the electron correlation strongly influence the values of β_μ. For the remaining compounds (donor−acceptor diphenylpolyines and donor−acceptor polyphenyls), the effect of the electron correlation is weaker. (4) For most cases considered in this paper, the calculated ratio of $\langle\gamma\rangle^{sol}(0;0,0,0)/\langle\gamma\rangle^{gas}(0;0,0,0)$ is approximately equal to the $\beta_\mu^{sol}(0;0,0)/\beta_\mu^{gas}(0;0,0)$ ratio. This relation does not hold for molecules **1**, **5**, **6**, and **7** only. These results suggest that the lowest energy CT excited state give a significant contribution to the values of $\langle\gamma\rangle$ for donor−acceptor systems. (5) The computed values of $\beta_\mu(-2\omega;\omega,\omega)$ and $\langle\gamma\rangle(0;0,0,0)[\langle\gamma\rangle(-3\omega;\omega,\omega,\omega)]$ are in reasonable agreement with experimental data.

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IV. Conclusions

This paper presents a method for the calculation of solvent effect on the nonlinear optical properties of polar molecules in the polar solvents. The QM/LD/MC model (based on the discrete representation of the solvent molecules) was employed for the calculation of the static and time-dependent first- (β) and second-order (γ) hyperpolarizabilities of series of large donor–acceptor compounds in polar solvents. The values of β and γ were computed using FF and SOS methods implemented in the quantum chemical GRINDOL program based on the INDO-like Hamiltonian. In our opinion, the QM/LD/MC model is more sophisticated compared to the continuum models and gives correct values of β_μ and $\langle\gamma\rangle$ in solutions. In the future, our results should be compared to alternative quantum chemical methods including the solvent effect.

It should be noted that the calculated absolute values of β_μ and $\langle\gamma\rangle$ are usually underestimated compared with experimental results. In our opinion, it is connected with the fact that there are many difficulties in comparison of calculated absolute values of hyperpolarizabilities with experimental data. The method employed was found to produce correct trends for β_μ and $\langle\gamma\rangle$ values of donor–acceptor compounds in solutions. The results obtained in this work indicate that the QM/LD/MC model gives correct description of the solvent effect on the nonlinear optical response of molecules, and this suggests that this level of theory can be used as an effective tool for investigation of NLO properties in condensed phases.

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