An Attempt To Bridge the Gap between Computation and Experiment for Nonlinear Optical Properties: Macroscopic Susceptibilities in Solution†

Roberto Cammi,*,‡ Benedetta Mennucci,§ and Jacopo Tomasi§

*Dipartimento di Chimica Generale ed Inorganica, Università di Parma, Parco Area delle Scienze 1,
43100 Parma, Italy, and Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
via Risorgimento 35, 56126 Pisa, Italy*

Received: November 23, 1999; In Final Form: January 25, 2000

We present a new methodology, working within the framework of the Polarizable Continuum Model, that derives quantities directly comparable with data from nonlinear optical (NLO) experiments on liquid solutions through computed molecular properties. The procedure does not require any knowledge of preliminary experimental data (as do some semiempirical methods) but permits one to obtain the final molar property (specifically, the macroscopic susceptibilities) in terms of effective molecular dipoles and (hyper)polarizabilities. The latter are obtained through an ab initio description of the molecule of interest when it is mutually interacting with the surrounding medium, which is represented by a continuum dielectric. Numerical applications, and the related comparisons with experiments, are presented for refractive and permittivity first-order processes and for third-order EFISH (electric-field-induced second harmonic generation) experiments for 4-nitroaniline (pNA) and 3,5-dinitroaniline (3,5-DNA) in liquid dioxane at room temperature.

1. Introduction

The present paper focuses on the calculation of electric response functions that correspond to widely used nonlinear optical (NLO) processes for liquid solutions and on the connection between these calculations and the quantities that are actually measured by experiments.

The formal theory and the computational methodologies for obtaining the NLO properties of isolated molecules are well developed, and there is now a large body of numerical results for many classes of compounds. (For a very recent review, rich with references, see Bishop and Norman.[1]) On the contrary, although of major interest to experimentalists, the calculation of NLO properties for molecules in the condensed phase is much less advanced with respect to accuracy and reliability than that for molecules in the gas phase.

The classical approach to incorporating solution effects is to use the Onsager-Lorentz model[2] and to write the measured susceptibilities (the macroscopic equivalent of the linear and nonlinear optical molecular properties) in terms of the gas-phase molecular values multiplied by local field factors. For example, in the electric-field-induced second harmonic generation (EFISH) experiment, the third-order susceptibility for a pure liquid is generally expressed as

$$\chi^3(-2\omega;\omega,\omega,0) = Nf(2\omega)f^2(\omega)f(0)\bar{\gamma}(-2\omega;\omega,\omega,0) \quad (1)$$

where N is the number density of the molecules and $\bar{\gamma}$ is the averaged molecular second hyperpolarizability. The local field factors are usually given by the Lorentz expression, for the frequency-dependent part, and the Onsager expression, for the static part.[2]

In the past few years, different models have been proposed to improve this description. Most of these models are based on the concept of a solute in a cavity; within this framework, there have been several theoretical investigations of the interactions between solute and solvent molecules and the consequent changes in the solute properties. Frequently, solvent effects are established by the introduction of so-called reaction terms in the Hamiltonian (models that employ such terms are also called effective Hamiltonian, EH, approaches).[3] Applications of such models to NLO properties have been carried out by, among others, Willets and Rice,[4] Yu and Zerner,[5] Mikkelsen and co-workers,[6] and our group,[7,8] all applying different solvent models, as well as different levels of quantum theory.

The properties obtained through such models represent an intermediate step in the progression toward the real systems used in the experiments. First, the computed quantities are still molecular, or microscopic, and not macroscopic, exactly as are the corresponding quantities computed in vacuo, even though the molecular description has been modified by the solvent reaction field. In addition, even when the interactions between solute and solvent are incorporated into calculations, there still exists a need to take into account the modifications of the applied macroscopic fields at the local site of the solvated molecule (the phenomenon historically indicated as “local field effects”). The combination of these two modifications with respect to the gas-phase model leads to the definition of *effective* properties, which reflect the response of the solvated molecules to the applied field[9] and which are more directly comparable to the experiments.

In parallel, from the experimental point of view, the values reported in the literature are derived from a concentration series,

---

[†] Part of the special issue “Electronic and Nonlinear Optical Materials: Theory and Modeling”.

[*] Corresponding author. E-mail: chifi@unipr.it.

[‡] Università di Parma.

[§] Università di Pisa.

10.1021/jp994163p CCC: $19.00

and the data to be used in the comparison with the computed values must be suitably corrected for this fact. Actually, a protocol based on the general concept of partial and model molar polarizabilities[10,11] has been applied in a series of experiments,[12,13] thus producing sets of data that are more directly accessible for the theoretical chemist.

Pushed by the efforts made by experimentalists, we have formulated a new procedure that takes into account all of the complex features cited above so that one can obtain, in a single computational run, all of the components needed for a correct treatment of the computed results. This will lead to the definition of a quantity that is directly comparable with "pure", or almost pure, experimental data. In the next section, we comment in more detail on the protocol that gives the proper form of the experimental data to which the computational results should be compared and on the formal relations to be used in the treatment of the computed molecular properties. The following three sections are devoted to a description of the procedures that we have formulated, within the framework of the solvation model known as the Polarizable Continuum Model,[14,15] for including the effects of the medium, here treated as an infinite continuous dielectric, in all the aspects related to experimental measurements. Finally, in section 6, we present some numerical results, and the related comparisons with experiments, for two NLO model systems.

2. Macroscopic Susceptibilities and Molecular Effective Polarizabilities: General Expressions

The electric nth-order susceptibilities $\chi^{(n)}$ describe the polarization of a macroscopic portion of matter (for example, a dielectric medium) in the presence of an electric field.

If we consider an experimental situation in which a macroscopic (or Maxwell) field $\mathbf{E}(t)$ is generated in a medium by the superposition of a static and an optical component, that is

$$\mathbf{E}(t) = \mathbf{E}^0 + \mathbf{E}^\omega \cos(\omega t) \tag{2}$$

then the response of the medium can be represented by the dielectric polarization vector (dipole moment per unit volume) $\mathbf{P}(t)$, which, in terms of Fourier components, yields

$$\mathbf{P}(t) = \mathbf{P}^0 + \mathbf{P}^\omega \cos(\omega t) + \mathbf{P}^{2\omega} \cos(2\omega t) + ... \tag{3}$$

Each Fourier amplitude can be expanded as a power series with respect to the electric field, so that

$$\mathbf{P}^0 = \chi^{(0)} + \chi^{(1)}(0;0)\cdot\mathbf{E}^0 + \chi^{(2)}(0;0,0){:}\mathbf{E}^0\mathbf{E}^0 + \frac{1}{2}\chi^{(2)}(0;-\omega,\omega){:}\mathbf{E}^\omega\mathbf{E}^\omega + \chi^{(3)}(0;0,0,0)\vdots\mathbf{E}^0\mathbf{E}^0\mathbf{E}^0 + ... \tag{4}$$

$$\mathbf{P}^\omega = \chi^{(1)}(-\omega;\omega)\cdot\mathbf{E}^\omega + 2\chi^{(2)}(-\omega;\omega,0){:}\mathbf{E}^\omega\mathbf{E}^0 + 3\chi^{(3)}(-\omega;\omega,0,0)\vdots\mathbf{E}^\omega\mathbf{E}^0\mathbf{E}^0 + ... \tag{5}$$

$$\mathbf{P}^{2\omega} = \frac{1}{2}\chi^{(2)}(-2\omega;\omega,\omega){:}\mathbf{E}^\omega\mathbf{E}^\omega + \frac{3}{2}\chi^{(3)}(-2\omega;\omega,\omega,0)\vdots\mathbf{E}^\omega\mathbf{E}^\omega\mathbf{E}^0 + ... \tag{6}$$

where the argument in the parentheses of the susceptibility tensors $\chi^{(n)}$ describes the nature of the frequency dependence at the given order; in all cases, the frequency of the resulting wave (which from now on will be denoted ω_σ) is stated first, followed by the frequency of the incident interacting waves (two in a first-order process, three in the second-order analogue, and four in the third-order case).

The various susceptibilities in eqs 4−6 can be obtained through specific experiments in linear and nonlinear optics. Thus, the first-order static susceptibility is related to the dielectric constant at zero frequency, $\epsilon(0)$, while $\chi^{(1)}(-\omega;\omega)$ is the linear optical susceptibility related to the refractive index n^ω at frequency ω. Moving to nonlinear effects, it is worth recalling that $\chi^{(2)}(-2\omega;\omega;\omega)$ describes the frequency doubling that is usually called second harmonic generation (SHG) and $\chi^{(3)}(-2\omega;\omega,\omega,0)$ describes the influence of an external field on the SHG process, which is of great importance, as we shall see in the following, for the characterization of second-order NLO properties in solution in electric-field-induced second harmonic generation (EFISHG).

If we consider, as a macroscopic sample, a liquid solution of different molecular components, each at a concentration c_J, then the effects of the single components are assumed to be additive, so that the global measured response becomes[10−12]

$$\chi^{(n)} = \sum_J \zeta_J^{(n)} c_J \tag{7}$$

where $\zeta_J^{(n)}$ are the nth-order molar polarizabilities of the constituent J. The values of the single $\zeta_J^{(n)}$ can be extracted from measurements of $\chi^{(n)}$ at different concentrations.

The molar polarizabilities can be interpreted microscopically in terms of the NLO response of a molecule to an electric field. By applying arguments of statistical classical mechanics, we obtain, for a general nth-order molar polarizability,[16]

$$\zeta_{ZZ...}^{(n)} = N_A \left(\frac{\bar{\mu}_Z(\omega_\sigma)}{E_Z E_Z ...}\right)_{E\to 0} \tag{8}$$

where we have introduced the Z space-fixed axes of the laboratory. The expression above implies the consideration of both rotation (or, classically, orientation) and thermal averaging over the populated rotational states. Classically, the component along the laboratory axes of the average dipole moment, $\bar{\mu}_Z(\omega_\sigma)$, of a single molecule of the species J at a temperature T and in the presence of the macroscopic field $\mathbf{E}(t)$ can be written as

$$\bar{\mu}_Z(\omega_\sigma) = \frac{\int_0^{2\pi}\int_0^{\pi} \tilde{\mu}_\alpha(\omega_\sigma) k_\alpha \exp(-w/kT) \sin\theta \, d\theta \, d\phi}{\int_0^{2\pi}\int_0^{\pi} \exp(-w/kT) \sin\theta \, d\theta \, d\phi} \tag{9}$$

where Einstein summation and the Boltzmann law are assumed; θ and ϕ are the usual spherical coordinates that define the molecular orientation with respect to X, Y, and Z; w is the angle-dependent part of the energy of the molecule in the presence of the electric field; k_α is the cosine of the angle between the molecular axis α and the laboratory axis Z; and the bar indicates an average over a statistical distribution of molecular orientations.

The molecular dipole $\tilde{\mu}(\omega_\sigma)$ can be related to the permanent dipole and the static and dynamic polarizabilities and hyperpolarizabilities of the molecules of the species J by exploiting the expressions of its Fourier amplitudes. Namely, we have (up to the second-order)

$$\tilde{\mu}_\alpha(0) = \tilde{\mu}^0_\alpha + \tilde{\alpha}_{\alpha\beta}(0)E^0_\beta + \frac{1}{2}\tilde{\beta}_{\alpha\beta\gamma}(0;0,0)E^0_\beta E^0_\gamma + \frac{1}{4}\tilde{\beta}_{\alpha\beta\gamma}(0;-\omega,\omega)E^\omega_\beta E^\omega_\gamma + \frac{1}{6}\tilde{\gamma}_{\alpha\beta\gamma\delta}(0;0,0,0)E_\beta{}^0 E_\gamma{}^0 E_\delta{}^0 + ... \quad (10)$$

$$\tilde{\mu}_\alpha(\omega) = \tilde{\alpha}_{\alpha\beta}(-\omega;\omega)E^\omega_\beta + \tilde{\beta}_{\alpha\beta\gamma}(-\omega;\omega,0)E^\omega_\beta E^0_\gamma + \frac{1}{2}\tilde{\gamma}_{\alpha\beta\gamma\delta}(-\omega;\omega,0,0)E^\omega_\beta E^0_\gamma E^0_\delta + ... \quad (11)$$

$$\tilde{\mu}_\alpha(2\omega) = \frac{1}{4}\tilde{\beta}_{\alpha\beta\gamma}(-2\omega;\omega,\omega)E^\omega_\beta E^\omega_\gamma + \frac{1}{4}\tilde{\gamma}_{\alpha\beta\gamma\delta}(-2\omega;\omega,\omega,0)E^\omega_\beta E^\omega_\gamma E^0_\delta + ... \quad (12)$$

where E^0_β and E^ω_β are the static and frequency-dependent components of the applied macroscopic (or Maxwell) field, respectively.

Such expansions, defining all of the properties involved in the various optical experiments, are well-known for isolated systems; however, in the condensed phase, some important specifications are required. The reaction of the solvent will surely induce changes in the charge distribution of the solute molecule, thus modifying its response functions. In addition, whereas in the gas phase, the applied macroscopic field and the field actually acting at the molecular position coincide, in solution, the presence of the environment introduces local modifications (in the past represented in terms of local-field factors). Both effects will contribute to a modification of the standard meaning of molecular properties; thus, to recover expansions with respect to the applied macroscopic field, such as those reported in eqs 10−12, we need to introduce *effective* (hyper)polarizabilities (the sum of both electronic and nuclear, or vibrational, components).[9,17] Here, the term "effective" indicates that the related property (denoted with a tilde) has been modified by the combination of the two different environmental effects mentioned above and, historically, has been represented in terms of "cavity" and "reaction" fields.[2,18]

In the past, explicit expressions for the effective properties were formulated by different authors in the case of a spherical solute molecule described classically (that is, formed by polarizable point dipoles). The original concept can be referred to the works of Brown for the static case;[19] more recently, the same idea has been generalized to frequency-dependent processes by Wortmann and Bishop.[9] Luo et al.[20] then proposed a generalization of similar concepts to a semiclassical model for properties of molecules in solution, and finally, Cammi et al.[17] introduced the evaluation of effective properties in the field of ab initio calculations for molecular solutes, although limiting the analysis to the static case only.

In parallel, the angle-dependent energy w of eq 9, which represents the energy of a molecule of the species J with respect to the orientation of the Maxwell field (here limited to its static component $\mathbf{E}^0$), must be modified as follows:

$$w = \mu^{*}\cdot\mathbf{E}^0 + \frac{1}{2}\alpha^{*}:\mathbf{E}^0\mathbf{E}^0 + ... \quad (13)$$

where the quantities with the asterisk correspond to derivatives of the energy of the system with respect to the static components of the Maxwell field; see refs 2, 18, and 19 for the original definition. More details on these quantities will be provided in section 4.

Returning to the general expression in eq 8, we can now write the specific equations that give the molar quantities for each process of interest; in particular, to first-order (both static and frequency-dependent), we obtain[12,23]

$$\zeta^{(1)}(0;0) = N_A\left[\frac{\mu^{*}\cdot\tilde{\mu}}{3kT} + \tilde{\alpha}_{is}(0;0)\right] \quad (14)$$

$$\zeta^{(1)}(-\omega;\omega) = N_A\tilde{\alpha}_{is}(-\omega;\omega) \quad (15)$$

and for the third-order EFISHG process,[12] we obtain

$$\zeta^{(3)}_{ZZZZ}(-2\omega;\omega,\omega,0) = N_A\left[\frac{\tilde{\beta}(-2\omega;\omega,\omega)\cdot\mu^{*}}{15kT} + \tilde{\gamma}_s(-2\omega;\omega,\omega,0)\right] \quad (16)$$

where N_A is Avogadro's number. In eqs 14−16, $\tilde{\alpha}_{is}$ is $^1/_3$ the trace of the effective polarizability, and in eq 16, $\tilde{\gamma}_s(-2\omega;\omega,\omega,0)$ is the "scalar part" of the third-order polarizability. Parallel expressions for other NLO processes can be easily formulated, but they will not be reported here as they are not used in the numerical analysis.

As the molar polarizabilities $\zeta^{(n)}_J$ represent an easily available "experimental" set of data, the expressions above become important for the theoretical evaluation of molecular response properties; in fact, they represent the most direct quantities to compare with the computed results obtained by using a given model for the solvent effects.

In the following sections, we present a method for the evaluation of the effective molecular properties appearing in eqs 14−16 within the framework of the PCM continuum model. As said before, in this approach, the summation of eq 7 is reduced to two components only (a solute and the solvent). Of these two components, only the former is treated from a molecular point of view, whereas the latter is represented by an infinite continuum medium characterized by its dielectric constant and refractive index (this model can be associated with an infinitely dilute solution).

The present work, which can be seen as the natural extension to frequency-dependent processes of the theory originally formulated in ref 17 for the static case, is actually a development toward and a completion of a more direct and correct comparison between calculated and experimental results.

3. Effective Polarizabilities of PCM Solutes: The Electronic Component

The formal theory of PCM molecular solutes in the presence of external static and oscillating electric fields has been presented in previous papers[7,17,21] and then applied to different systems.[8] Here, we attempt to complete such a formulation by introducing all of the missing terms needed for a correct comparison with experimental results. The analysis will be partitioned into three separate sections, the first concerning the electronic component of the (hyper)polarizabilities, the second concerning the orientational energy w, and the last concerning the vibrational component of the same effective response properties.

For the electronic component of the effective polarizabilities, we adopt a different formulation than that presented in previous papers because the new formulation allows a simpler and more direct description and analysis of the effective properties.

In brief, the PCM model[14,15] represents the molecular solute as a quantum mechanical charge distribution contained in a volume (the so-called molecular cavity) of the proper shape; its form and dimension are determined by the number and the nature of the atoms constituting the molecule, as they define the position (the nuclei of selected atoms) and the radii of the interlocking spheres that yield the final cavity. The cavity is assumed to be immersed in a continuum dielectric characterized by the proper macroscopic properties (the permittivity and the refractive index at the frequencies of interest). When the dielectric is polarized by the solute, the induced separation of charges gives rise to a response field (*the reaction field*) that modifies the previous state of the solute charge distribution. Such mutual interaction is introduced in the Hamiltonian that describes the solute electronic charge (and that determines its wave function Ψ) through a perturbation operator $\hat{V}_{\mathrm{MS}}$, which contains a term linearly depending on Ψ. This operator is represented by the interaction of the solute potential with an apparent charge distribution, σ, spreading on the cavity surface and depending both on the solute field and on the macroscopic characteristics of the continuum solvent.

In the presence of a Maxwell field, the complete Hamiltonian can be thus written as

$$\hat{H} = \hat{H}^0 + \hat{V}_{\mathrm{MS}} + \hat{V}'(t) \tag{17}$$

where $\hat{H}^0$ is the Hamiltonian of the solute in vacuo and $\hat{V}_{\mathrm{MS}}$ is the electrostatic interaction between the solute and the solvent apparent charge, that is

$$\hat{V}_{\mathrm{MS}} = \int_\Sigma \sum_i \hat{V}(i;\, s)[\sigma^{\mathrm{N}}(s) + \sigma^{\mathrm{e}}(\Psi;\, s)]\, \mathrm{d}s \tag{18}$$

The summation runs over the solute electrons, and $\hat{V}(i;\, s)$ is the electronic potential operator calculated on the cavity surface Σ. In eq 18, we have partitioned the solvent response into its nuclear (that is, nuclei-induced) and electronic (that is, electron-induced) components, $\sigma^{\mathrm{N}}(s)$ and $\sigma^{\mathrm{e}}(\Psi;\, s)$, respectively, indicating the dependence of the latter on the solute wave function.

The remaining time-dependent perturbation $\hat{V}'(t)$ can be represented as

$$V'(t) = \sum_i \hat{\mu}_\alpha(i)[E_\alpha^\omega(\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{e}^{-\mathrm{i}\omega t}) + E_\alpha^0] + \int_\Sigma \sum_i \hat{V}(i;\, s)\left[\frac{\partial\sigma_\omega^{\mathrm{ex}}(s)}{\partial E_\alpha^\omega} E_\alpha^\omega(\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{e}^{-\mathrm{i}\omega t}) + \frac{\partial\sigma_0^{\mathrm{ex}}(s)}{\partial E_\alpha^0} E_\alpha^0\right] \mathrm{d}s \tag{19}$$

where Einstein summation on repeated indices is assumed.

In eq 19, a new apparent surface charge σ^{ex} has been introduced; it can be described as the response of the solvent to the external field (static or oscillating) when the empty molecular cavity is created in the bulk of the solvent. This effect must be summed up to the standard reaction field described by σ^{N} and σ^{e} in order to fully consider the effective reaction of the solvent on the combined action of the internal (due to the solute) and the external fields. More details on this point can be found in ref 17. Here, it can be useful to recall that the effects of σ^{ex} in the limit of a spherical cavity coincide with those of the cavity field factors historically introduced to account for the changes induced by the solvent molecules in the average macroscopic field (the Maxwell field) at each local position inside the medium.

Both σ and σ^{ex} are obtained from analytical expressions in terms of the acting fields (or equivalently the corresponding potentials), the intrinsic shape of the cavity, and the macroscopic characteristics of the solvent. In computational practice, the charge distributions are discretized into point charges by partitioning the cavity surface into K small portions (called tesserae) of known area a_k. To each tessera k is associated a point charge $q_k^x = a_k\sigma^x(s_k)$, which is placed at the representative point s_k (the geometrical center) of the tessera; this allows all of the surface integrals of eqs 18 and 19 to be reduced to finite summations over the K tesserae.

Approximate solutions of the time-dependent Schrödinger equation associated with the effective Hamiltonian[17] can be obtained by using the Frenkel variational principle, which, in the PCM method, can be cast in the form[7,22]

$$\delta\left\langle\Psi\middle|\hat{G} - \mathrm{i}\frac{\partial}{\partial t}\middle|\Psi\right\rangle = 0 \tag{20}$$

In eq 20, $\hat{G}$ represents the free energy operator

$$\hat{G} = \hat{H}^0 + \hat{V}_{\mathrm{MS}} + \hat{V}'(t) - {}^1/_2\hat{V}'_{\mathrm{MS}}(\Psi) \tag{21}$$

where $\hat{V}'_{\mathrm{MS}}(\Psi)$ indicates the wave-function-dependent component of the reaction potential $\hat{V}_{\mathrm{MS}}$ and where nonlinear medium response effects are discarded. In the static limit, the problem is reduced to a time-independent Schrödinger equation whose variational solution coincides with the stationary condition on the free energy functional $G = \langle\Psi|\hat{G}|\Psi\rangle$.

The restriction to a one-determinant wave function with orbital expansion over a finite basis set leads to the following time-dependent Hartree−Fock equation

$$\mathbf{F}'\mathbf{C} - i\frac{\partial}{\partial t}\mathbf{SC} = \mathbf{SC}\epsilon \tag{22}$$

with the proper orthonormality condition; $\mathbf{S}$, $\mathbf{C}$, and ϵ represent the overlap, the MO coefficient, and the orbital energy matrices, respectively.

In eq 22, the prime on the Fock matrix indicates that terms accounting for the solvent effects are included, that is,

$$\mathbf{F}' = \mathbf{h} + \mathbf{j} + \mathbf{G}(\mathbf{P}) + \mathbf{X}(\mathbf{P}) + \mathbf{m}_\alpha[E_\alpha^\omega(\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{e}^{-\mathrm{i}\omega t}) + E_\alpha^0] + \tilde{\mathbf{m}}_\alpha^\omega E_\alpha^\omega(\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{e}^{-\mathrm{i}\omega t}) + \tilde{\mathbf{m}}_\alpha^0 E_\alpha^0 \tag{23}$$

where $\mathbf{m}_\alpha$ is the matrix containing the dipole integrals along the three coordinates. The first two solvent-induced terms, $\mathbf{j}$ and $\mathbf{X}(\mathbf{P})$, indicate the constant and the wave-function-dependent (here represented by the one-electron density matrix $\mathbf{P}$) components of the reaction potential $\hat{V}_{\mathrm{MS}}$, while the last two solvent-induced terms, $\tilde{\mathbf{m}}_\alpha^\omega$ and $\tilde{\mathbf{m}}_\alpha^0$, are the matrices related to the apparent charge σ^{ex} induced by the external oscillating and static field, respectively; namely,

$$\tilde{\mathbf{m}}_\alpha^x = -\sum_k \mathbf{V}(s_k)\,\frac{\partial q_x^{\mathrm{ex}}(s_k)}{\partial E_\alpha^x} \tag{24}$$

where $\mathbf{V}(s_k)$ is the matrix containing the solute electronic potential integrals computed at the surface position s_k.

A more detailed analysis of all of the solvent-induced terms introduced in eq 23 can be found in refs 7 and 17; here, it suffices to recall that all of the related matrices account for the required details of the distribution of the frequency-dependent permittivity $\epsilon(\omega)$ within the range of frequencies associated with the resulting external field.

The solution of the time-dependent HF equation (eq 22) can be obtained within a time-dependent coupled HF (TDHF) approach by expanding all of the matrices involved in powers of the field components. For the sake of brevity, we report the detailed expressions only for the tensorial factors in the expansion of $\mathbf{F}'$ as explicitly modified by the solvent; the expansions of the other matrices $\mathbf{C}$, $\mathbf{P}$, and ϵ are exactly the same as in the case of the isolated system subject to the same external field. Limiting the analysis to third-order, we obtain

$$\mathbf{F}'_{\alpha}(-\omega;\omega) = \mathbf{G}[\mathbf{P}^{\alpha}(\omega)] + \mathbf{X}_{\omega}[\mathbf{P}^{\alpha}(\omega)] + \mathbf{m}_{\alpha} + \tilde{\mathbf{m}}_{\alpha}^{\omega}$$

$$\mathbf{F}'_{\alpha\beta}(-\omega_{\sigma};\omega_1,\omega_2) = \mathbf{G}[\mathbf{P}^{\alpha\beta}(\omega_1,\omega_2)] + \mathbf{X}_{\omega_{\sigma}}[\mathbf{P}^{\alpha\beta}(\omega_1,\omega_2)]$$

$$\mathbf{F}'_{\alpha\beta\gamma}(-\omega_{\sigma};\omega_1,\omega_2,\omega_3) = \mathbf{G}[\mathbf{P}^{\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)] + \mathbf{X}_{\omega_{\sigma}}[\mathbf{P}^{\alpha\beta\gamma}(\omega_1,\omega_2,\omega_3)]$$

where ω_x are the frequencies related to the external fields (eventually static and, thus, $\omega_x = 0$) and $\mathbf{P}^{\alpha\beta\cdots}(\omega_1, \omega_2, ...)$ are the perturbed density matrices at the various orders. The elements of the solvent-induced matrices $\mathbf{X}_{\omega_{\sigma}}$ depend twice on the frequency-dependent nature of the field, once in the density matrix $\mathbf{P}^{\alpha\beta\cdots}(\omega_1, \omega_2, ...)$ and again in the value of the dielectric permittivity at the resulting frequency $\omega_{\sigma} = \sum_x \omega_x$.

By applyication of standard iterative procedures, all of the perturbed density matrices can be analytically computed, and thus, also, the electronic component of the effective properties (eqs 10−12). Namely, we have

$$\tilde{\alpha}^{\mathrm{el}}_{\alpha\beta}(-\omega;\omega) = -\mathrm{tr}[\mathbf{m}_{\alpha}\mathbf{P}^{\beta}(\omega)] \tag{25}$$

$$\tilde{\beta}^{\mathrm{el}}_{\alpha\beta\gamma}(-\omega_{\sigma};\omega_1,\omega_2) = -\mathrm{tr}[\mathbf{m}_{\alpha}\mathbf{P}^{\beta\gamma}(\omega_1,\omega_2)] \tag{26}$$

$$\tilde{\gamma}^{\mathrm{el}}_{\alpha\beta\gamma\delta}(-\omega_{\sigma};\omega_1,\omega_2,\omega_3) = -\mathrm{tr}[\mathbf{m}_{\alpha}\mathbf{P}^{\beta\gamma\delta}(\omega_1,\omega_2,\omega_3)] \tag{27}$$

As shown by eqs 25−27, the procedure briefly sketched above allows one to account for all of the effects of the solvent, both those intrinsic, that is, due to the reaction potential, and those related to the presence of the external field, in a compact and self-consistent form. In this way, no a posteriori corrections, such as those usually introduced by cavity factors, are required. Rather, the computed properties can be used as they are and introduced into the expressions linking the microscopic properties to the macroscopic observables.

Let us now consider the two additional contributions necessary for obtaining the complete description, starting with the definition of the angle-dependent energy w[13] in the presence of the solvent effects.

4. Orientational Energy for a PCM Solute

In eq 13, we showed that the angle-dependent part of the energy in the presence of the externally applied field can be written in terms of the dipole μ^* (and, at higher order, the polarizability α^*). Classically, this expression can be obtained by expanding the Boltzmann potential energy in terms of the field (here appearing only through its static components); in the framework of the PCM solvation model, this energy must be replaced with the free energy analogue, specifically

$$G(\mathbf{E}^0) = G^0 + \mathbf{g}\cdot\mathbf{E}^0 + \frac{1}{2}\mathbf{H}{:}\mathbf{E}^0\mathbf{E}^0 + ... \tag{28}$$

where G^0 is the free energy of the solvated system in the absence of the field.

The components both of the gradient, $\mathbf{g}$, and of the Hessian, $\mathbf{H}$, must be computed at $\mathbf{E}^0 = 0$; in the framework of the CHF approach described above, they can be expressed in terms of the unperturbed density matrix and its derivative with respect to the static field. Specifically,

$$g_{\alpha} = \left(\frac{\partial G}{\partial E^0_{\alpha}}\right)^{0}_{\boldsymbol{E}=0} = -\mathrm{tr}[\mathbf{P}^0(\mathbf{m}_{\alpha} + \tilde{\mathbf{m}}^0_{\alpha})] \tag{29}$$

$$H_{\alpha\beta} = \left(\frac{\partial^2 G}{\partial E^0_{\alpha}\partial E^0_{\beta}}\right)^{0}_{\boldsymbol{E}=0} = -\mathrm{tr}[\mathbf{P}^{\beta}(\mathbf{m}_{\alpha} + \tilde{\mathbf{m}}^0_{\alpha})] \tag{30}$$

where $\mathbf{m}_{\alpha}$ and $\tilde{\mathbf{m}}^0_{\alpha}$ are the matrices introduced in eq 23.

Comparing eq 28 with eq 13 and introducing eqs 29 and 30, we can easily obtain the expressions for the previously introduced dipole and polarizability, namely,

$$\mu^*_{\alpha} = -\mathrm{tr}[\mathbf{P}^0(\mathbf{m}_{\alpha} + \tilde{\mathbf{m}}^0_{\alpha})] \tag{31}$$

$$\alpha^*_{\alpha\beta} = -\mathrm{tr}[\mathbf{P}^{\beta}(\mathbf{m}_{\alpha} + \tilde{\mathbf{m}}^0_{\alpha})] \tag{32}$$

These expressions are the PCM results for the evaluation of the orientational averaging required in eq 9.

5. Effective Polarizabilities of PCM Solutes: The Vibrational Component

In general, the vibrational contribution should contain two distinct effects,[25] the “curvature” that is related to the field dependency of the vibrational frequencies (that is, the changes in the potential energy surface in the presence of the external field) and that includes the zero-point vibrational correction and the “nuclear relaxation” that originates from the field-induced nuclear relaxation (that is, the modification of the equilibrium geometry in the presence of the external field). In the following analysis and in the related numerical results, however, only the nuclear relaxation will be considered. In addition, the following analysis will consider only the static limit; vibrational effects in the presence of frequency-dependent fields are, in fact, usually small, and they will be omitted completely here.

The nuclear-relaxation contribution (from now on just “vibrational”) to the static polarizabilities can be computed in the double harmonic approximation, that is, assuming that the expansions of both the potential energy and the electronic properties with respect to the normal coordinates can be limited to the quadratic and the linear terms (in other words, assuming both mechanical and electronic harmonicity).

As shown in the Appendix of ref 21, the double harmonic procedure can be analytically reformulated within the PCM model to obtain the analogues of the classical expressions in terms of summations of derivatives of dipoles and polarizabilities with respect to normal coordinates but with all of the properties computed in the presence of the solvent (that is, exploiting effective properties). Here, however, a new feature must be introduced as, in the analysis reported in ref 21, no considerations of the effects of the external field on the continuum dielectric were taken into account.

If we return to the analysis reported in the previous section (see eqs 28−32), then eqs 9 and 10 of the reference paper[21] must be modified by substituting the proper dipole and polarizability derivatives with the corresponding analogues in terms of the quantities defined in eqs 31 and 32. If each vibrational state is defined by the quantum numbers associated with each of the $3N - 6$ normal modes of the system, then the final expressions for the effective static vibrational polarizabilities and first hyperpolarizability become

$$\tilde{\alpha}^{\nu}_{\alpha\beta} = \sum_{a}^{3N-6} \left(\frac{\partial \tilde{\mu}_{\alpha}}{\partial Q_a}\right)_0 \left(\frac{\partial \mu^{*}_{\beta}}{\partial Q_a}\right)_0 / \omega_a^2 \tag{33}$$

$$\tilde{\beta}^{\nu}_{\alpha\beta\gamma} = \sum_{a}^{3N-6} \left[\left(\frac{\partial \tilde{\mu}_{\gamma}}{\partial Q_a}\right)_0 \left(\frac{\partial \alpha^{*}_{\alpha\beta}}{\partial Q_a}\right)_0 + \left(\frac{\partial \tilde{\mu}_{\beta}}{\partial Q_a}\right)_0 \left(\frac{\partial \alpha^{*}_{\alpha\gamma}}{\partial Q_a}\right)_0 + \left(\frac{\partial \tilde{\mu}_{\alpha}}{\partial Q_a}\right)_0 \left(\frac{\alpha^{*}_{\beta\gamma}}{\partial Q_a}\right)\right] / \omega_a^2 \tag{34}$$

where $\omega_a = 2\pi\nu_a$ is the circular frequency associated with the normal coordinate Q_a for the solvated molecule and each partial derivative is evaluated at the proper equilibrium geometry. We recall, in fact, that the equilibrium geometry and the vibrational frequencies, force constants, and normal modes are computed in the presence of the solvent interactions as derivatives of the free energy functional with respect to the nuclear coordinates.[26,27]

The derivatives of the asterisk quantities in eqs 33 and 34 can be obtained by including the contributions due to the external charge σ^{ex} in the expansion of G with respect to the field to be used in the derivation of the PCM double harmonic scheme (see Appendix 1 of ref 21), exactly as we did in the previous section to evaluate the orientational averaging. Specifically,

$$\left(\frac{\partial \mu^{*}_{\alpha}}{\partial Q_a}\right)_0 = -\mathrm{tr}[\mathbf{P}^{a}(\mathbf{m}_{\alpha} + \tilde{\mathbf{m}}^{0}_{\alpha}) + \mathbf{P}^{0}(\mathbf{m}^{a}_{\alpha} + \tilde{\mathbf{m}}^{a}_{\alpha})] \tag{35}$$

$$\left(\frac{\partial \alpha^{*}_{\alpha\beta}}{\partial Q_a}\right)_0 = -\mathrm{tr}[\mathbf{P}^{a,\beta}(\mathbf{m}_{\alpha} + \tilde{\mathbf{m}}^{0}_{\alpha}) + \mathbf{P}^{\beta}(\mathbf{m}^{a}_{\alpha} + \tilde{\mathbf{m}}^{a}_{\alpha})] \tag{36}$$

where $\mathbf{m}^{a}_{\alpha}$ and $\tilde{\mathbf{m}}^{a}_{\alpha}$ represent the derivatives with respect to the normal coordinate (and thus the nuclear motions) of the dipole matrix and the so-called external component of the solvent reaction, respectively. The matrix $\tilde{\mathbf{m}}^{0}_{\alpha}$ depends on the nuclear geometry through the form of the molecular cavity, and as a consequence, its variations with respect to the nuclear motions should be included. In the numerical results that we report in the following section, however, such geometry contributions are neglected, thus limiting eqs 35 and 36 to the first terms related to the density derivatives only. This approximation coincides with the limit of fixed cavities.

6. Numerical Results

In this section, we present some numerical results concerning molar polarizabilities of various orders for two model organic molecules whose optical properties are experimentally well-known: 4-nitroaniline (pNA) and 3,5-dinitroaniline (3,5-DNA) in liquid dioxane. In particular, we focus attention on two specific experimental processes from which data of first- and third-order molar polarizabilities have been extracted, namely, refractometric and EFISH measurements.

Details of the equations and the methods used in the evaluation of the refractometric and permittivity measurements have been described repeatedly.[23] Here, we only recall that the specific expressions to be used for the static and the frequency-dependent related properties are reported in eqs 14 and 15, respectively, where the exploited frequency is that corresponding to $\lambda = 589$ nm.

The EFISH technique[24] is one of the techniques most often used to obtain information on the molecular hyperpolarizability, β; here, once again, we do not report any details but just some notes. The operating frequency is that corresponding to the fundamental beam of wavelength 1064 nm from a Q-switched, mode-locked Nd:YAG laser. A symmetry consideration shows that the third-order nonlinearity that is measured in the EFISH experiment for a medium that is isotropic in the absence of any external electric field has only two independent components. To determine these tensor elements, two EFISH measurements are usually performed for the two polarization conditions that have the electric field vector of the fundamental parallel (||) or perpendicular (⊥) to the external electric field $\mathbf{E}^0$. The frequency-doubled photons are detected with the polarization parallel to $\mathbf{E}^0$ in both cases. The exact expressions for the corresponding molar polarizabilities can be derived from the general expression in eq 16, by also taking into account the symmetry of the molecules under examination, which, in our case, is C_{2v}. In particular, if we identify the z axis of the molecule-fixed coordinate system with the C_2 axis and the x and y axes within and perpendicular to the molecular plane, respectively, then the resulting expressions are[12,16]

$$\zeta^{(3)}(||) = N_{\mathrm{A}}\left(\frac{[2\,^{2}\tilde{\beta} + {}^{1}\tilde{\beta}]\cdot\mu^{*}}{15kT} + \tilde{\gamma}_{||}\right)$$

$$\zeta^{(3)}(\perp) = N_{\mathrm{A}}\left(\frac{[2\,^{1}\tilde{\beta} - {}^{2}\tilde{\beta}]\cdot\mu^{*}}{15kT} + \tilde{\gamma}_{\perp}\right)$$

where

$$2\,^{2}\tilde{\beta} + {}^{1}\tilde{\beta} = 3\tilde{\beta}_{zzz}(-2\omega; \omega, \omega) + \tilde{\beta}_{zxx}(-2\omega; \omega, \omega) + \tilde{\beta}_{xxz}(-2\omega; \omega, \omega)$$

$$2\,^{1}\tilde{\beta} - {}^{2}\tilde{\beta} = \tilde{\beta}_{zzz}(-2\omega; \omega, \omega) - \tilde{\beta}_{zxx}(-2\omega; \omega, \omega) + 2\tilde{\beta}_{xxz}(-2\omega; \omega, \omega)$$

and

$$\tilde{\gamma}_{||} = [2\tilde{\gamma}_{\xi\xi\eta\eta}(-2\omega; \omega, \omega, 0) + \tilde{\gamma}_{\xi\eta\eta\xi}(-2\omega; \omega, \omega, 0)]/15$$

$$\tilde{\gamma}_{\perp} = [2\tilde{\gamma}_{\xi\eta\eta\xi}(-2\omega; \omega, \omega, 0) - \tilde{\gamma}_{\xi\xi\eta\eta}(-2\omega; \omega, \omega, 0)]/15$$

within the Einstein convention on repeated indices. Usually, the contributions of the field dependence of β, that is, $\tilde{\gamma}_{||}$ and $\tilde{\gamma}_{\perp}$, are neglected as much smaller (by at least one order of magnitude) than the other contributions.

All calculations have been done exploiting the implementation of the recently revised formulation of the PCM method known as IEF (Integral Equation Formalism)[28] in development versions of Gaussian[29] and GAMESS[30] codes. Dioxane solvent is represented by the two values of its permittivity, $\varepsilon(0) = 2.209$ and $\varepsilon(\infty) = 2.022$. The results refer to HF calculations with a Dunning double-ζ valence (DZV) basis set for geometry optimization,[31] to which d-orbital (0.2) functions for C, N, and O and a p-orbital (0.1) function for H have been added for the calculations of the properties;[32] the numbers in parentheses are the exponents of these extra functions.

The geometry of the two solutes was optimized in the presence of the solvent using the analytical PCM-IEF gradients[26] implemented in Gaussian. All of the effective electronic properties (both static and dynamic) were computed with the CPHF/TDHF procedure implemented in GAMESS and were properly modified to account for the solvent effects, whereas the vibrational contributions were obtained using the analytical PCM-IEF Hessians[27] implemented in Gaussian. The molecular cavity containing the solute was obtained in terms of interlocking spheres centered on the six carbons of the aromatic ring and on all of the nuclei of the external groups (globally, we have 6 + 6 and 6 + 9 spheres for pNA and DNA, respectively). The radii of the spheres were derived from the van der Waals radii multiplied by a scaling factor of 1.2, namely, $R_x = 1.2R_{\mathrm{vdw}}$. In this scheme, the radii centered on the aromatic carbons, and eventually including a hydrogen atom, were set equal to 2.28 Å, whereas those on the external atoms were derived from Bondi's R_{vdw}[33] to have the values $R_{\mathrm{N}} = 1.86$ Å, $R_{\mathrm{O}} = 1.824$ Å, and $R_{\mathrm{H}} = 1.44$ Å. A different choice, derived from the R_{vdw} values suggested by Pauling,[34] was also checked for the external groups (those actually in contact with the continuum dielectric, being the internal carbons almost completely buried). The calculations (limited to dipoles and static and dynamic polarizabilities) performed with this alternative set of radii gave results almost identical to those obtained with the first choice (that is, derived from Bondi), thus showing the stability of the model used. More details on this important aspect of all of the cavity-based solvation methods can be found in other preceding papers,[35] in which this and other types of properties (such as nuclear shielding constants, vibrational frequencies, etc.) have been systematically analyzed with respect to changes in the cavity size. These analyses clearly show that the solvation model does, indeed, depend on the choice of the cavity size but that this size dependence nevertheless preserves the stability of the results when reasonable ranges of variations are used; no assurance of equivalently reliable results can be given for cavities that are very unphysical in size.

In Tables 1−3, we report a collection of computed quantities for the two systems studied and a comparison with the experimental data reported by Wortmann et al.[12] All of the calculated molecular properties are in atomic units (au), whereas the molar polarizabilities are in SI units; the appropriate conversion factors are the following:

polarizability α :
$$1.6488 \times 10^{-41}\ \mathrm{C}^2\ \mathrm{m}^2\ \mathrm{J}^{-1} = 1\ \mathrm{au}$$

first-order molar polarizability $\zeta^{(1)}$:
$$10^{-16}\ \mathrm{C\ m}^2\ \mathrm{V}^{-1}\ \mathrm{mol}^{-1} = 9.9291 \times 10^{-18}\ \mathrm{au}$$

first hyperpolarizability β :
$$3.2064 \times 10^{-53}\ \mathrm{C}^3\ \mathrm{m}^3\ \mathrm{J}^{-2} = 1\ \mathrm{au}$$

second hyperpolorizability γ :
$$6.2354 \times 10^{-65}\ \mathrm{C}^4\ \mathrm{m}^4\ \mathrm{J}^{-3} = 1\ \mathrm{au}$$

third-order molar polarizability $\zeta^{(3)}$:
$$10^{-36}\ \mathrm{C\ m}^4\ \mathrm{V}^{-3}\ \mathrm{mol}^{-1} = 37.5496 \times 10^{-42}\ \mathrm{au}$$

The analysis of the results is usefully partitioned into two sections, according to the experimental process involved. Thus, in Table 1 we report the permittivity- and refractometric-related properties for both molecules.

TABLE 1: Effective Dipoles, Frequency-Dependent and Static Polarizabilities, and First-Order Molar Polarizabilities of pNA and 3,5-DNA in Dioxane[a]

	pNA		3,5-DNA	
	calc	exp[b]	calc	exp[b]
$\tilde{\mu}_z$	3.397		2.850	
μ_z^*	3.763		3.197	
$\tilde{\mu}\cdot\mu^*/3kT$	4517.03		3215.21	
$\tilde{\alpha}_{is}^{\mathrm{el}}(0)$	125.76		141.44	
$\tilde{\alpha}_{is}^{\mathrm{vib}}(0)$	49.89		39.21	
$\zeta^{(1)}(0)$	466	449 ± 7	337	367 ± 6
$\tilde{\alpha}_{is}^{\mathrm{el}}(\omega)$	129.99		144.21	
$\zeta^{(1)}(\omega)$	12.9	15.7 ± 0.5	14.3	17.3 ± 1

[a] All molecular properties are in au, whereas molar polarizabilities are in SI units (10^{-16} cm^2 V^{-1} mol^{-1}). The frequency corresponds to $\lambda = 589$ nm. [b] Ref 12.

TABLE 2: Effective Frequency-Dependent and Static Polarizabilities and First-Order Molar Polarizabilities of pNA and 3,5-DNA in Dioxane at the DFT Level[a]

	pNA		3,5-DNA	
	calc	exp[b]	calc	exp[b]
$\tilde{\alpha}_{is}^{\mathrm{el}}(\omega)$	151.36		161.44	
$\zeta^{(1)}(\omega)$	15.0	15.7 ± 0.5	16.0	17.3 ± 1

[a] All molecular properties are in au, whereas molar polarizabilities are in SI units (10^{-16} cm^2 V^{-1} mol^{-1}). The frequency corresponds to $\lambda = 589$ nm. [b] Ref 12.

TABLE 3: Effective SHG Hyperpolarizabilities, EFISHG Second Hyperpolarizabilities, and Third-order Molar Polarizabilities of pNA in Dioxane[a]

	calc	exp[b]
$1\tilde{\beta}$	3554.67	
$2\tilde{\beta}$	3634.16	
$(2\,{}^2\tilde{\beta} + {}^1\tilde{\beta})\cdot\mu^*/15kT$	2.877673	
$(2\,{}^1\tilde{\beta} - {}^2\tilde{\beta})\cdot\mu^*/15kT$	0.923999	
$\tilde{\gamma}_{\parallel}$	0.061139	
$\tilde{\gamma}_{\perp}$	0.028079	
$\zeta^{(3)}(\parallel)$	110	120 ± 11
$\zeta^{(3)}(\perp)$	36	39 ± 4

[a] Computed molecular properties are reported in 10^6 au, whereas molar polarizabilities are in SI units (10^{-16} cm^2 V^{-1} mol^{-1}). The frequency corresponds to $\lambda = 1064$ nm. [b] Ref 12.

Here, the relative errors are 2−6% for $\zeta^{(1)}(0)$ and 13−15% for $\zeta^{(1)}(\omega)$. These diescrepancies between computed $\alpha_{is}^{\mathrm{el}}$ and experimental $\zeta^{(1)}$ values, in our opinion, are due to an inadequate quantum mechanical (QM) description in which no electronic correlation is introduced. A comparison of the different accuracies obtained for the static and dynamic properties seems to confirm this opinion. The HF description usually overestimates dipole values and underestimates polarizabilities. Thus, for the static quantity $\zeta^{(1)}(0)$, which depends on both the effective dipoles and the polarizability, there can be a partial compensation, thereby reducing the error. On the contrary, such compensation is not active for the dynamic quantity $\zeta^{(1)}(\omega)$, which only depends on polarizability. We then repeated the calculation of both properties at the density functional level of theory using the B3LYP hybrid functional and the same basis set. The results obtained in this case appear to confirm our prediction, leading to an increase of 12−16% in the value of $\alpha_{is}^{\mathrm{el}}(\omega)$ with respect to HF and thus making the molar polarizability much closer to the experimental values. The DFT results are reported in Table 2.

In Table 3, we report the EFISH-related properties for pNA in dioxane.

The most evident aspect to note in the results is the much better agreement between computed third-order molar polarizabilities and experimental EFISH data compared to first-order results; both the computed $\zeta^{(3)}(\parallel)$ and $\zeta^{(3)}(\perp)$ values are well within the experimental error. This very good result, if compared with the previous results, confirms the difficulty in the analysis of the eventual errors affecting our model. Roughly, one could say that the complex nature of the final property (a combination of the effects of dipoles and first and second hyperpolarizabilities) is characterized by some compensation of errors leading to an almost exact result. Actually, the contribution given by the second hyperpolarizability $\tilde{\gamma}$ can be neglected, as it is at least an order of magnitude smaller that the $\tilde{\beta}\cdot\mu^*$ term (as usually observed by the experimentalists). Thus, an attempted explanation could be based, once again, on the different performances of HF approaches in the calculations of dipoles and higher-order properties. Here, no help from more accurate QM descriptions, such as that provided by DFT polarizabilities, can be exploited. For the moment, in fact, no DFT SHG hyperpolarizabilities can be obtained with the computational codes with which the PCM model has been implemented.

7. Conclusion

We have presented a formal methodology for a well-known continuum solvation model (the PCM-IEF model) that allows one to obtain, from purely computational results (that is, without the help of any experimental data), complex NLO properties that can be directly compared with the outcome of experimental measurements. Actually, the experimental data we have used do require some manipulations, mainly to extract concentration-independent values; however, such manipulations, performed directly by experimentalists, do not imply any modeling assumptions that, at the end, would lead to a certain “corruption” of the data. Within this synergic scheme, requiring efforts from both experimentalists and theoreticians in order to find a point of contact, the results we have obtained, even if limited to two single-molecule systems and a few NLO processes, can be considered encouraging.

Clearly, many important improvements can be introduced. In the previous section, we emphasized the limits of the QM calculation used in the numerical applications, both in the choice of the basis set and in the level of the QM description. In this direction, the few results obtained using a DFT/B3LYP approach show the evident improvements one can obtain with limited efforts.

However, other, completely different, sources of errors, or of an incomplete description, should also be taken into account, such as the omission of some interactions among solute and solvent molecules. The PCM approach, as presented in the previous sections, accounts for electrostatic solvent effects only; on the contrary, it is well-known that other forces of a dispersive and/or repulsive nature always act in liquid solutions. Extensions of PCM that include these nonelectrostatic terms in the QM description, and thus in the evaluation of molecular response properties, have been already presented[36] and also applied to the calculation of static (hyper)polarizabilities.[37] For the moment, however, they have not yet been reformulated for frequency-dependent processes or generalized to the scheme we have presented in the previous sections; efforts in this direction are certainly required.

Other interesting aspects to consider in future developments are related to the limits of a purely continuum treatment of the solvent. In some solute−solvent′ pairs, and for some molecular properties, it is known that specific interactions (such as hydrogen-bonding), not completely described by a continuum model, can affect the general behavior of the system and of the molecular property under scrutiny. In these cases, the considerations of small clusters that include only a few solvent molecules can represent a good solution.[38] However, for the solvent considered in the present paper (the apolar and aprotic dioxane at room temperature), a very strong, specific effect, acting at very short range, is rather unlikely; the good results obtained with a pure continuum method seem to confirm this prediction.

Despite the clear limits characterizing the numerical applications reported in the previous section, the theoretical model we have formulated presents many important potentialities. First, as has already been mentioned, this model is completely generalizable to any kind of QM description. It is also easily extended to include more detailed descriptions of the solvent (specifically, through the consideration of interactions of a different nature and the inclusion of explicit molecules in the QM system). In addition, the model allows complex effects that previous semiclassical models cannot describe to be taken into account. In particular, the use of specific operators representing the effects of the external field on the dielectric (see eq 19) permits the description of possible inhomogeneities in the field acting at the local molecular site, a feature that the more standard local field factors cannot reproduce.

As a last remark, it is worth noting that the theoretical methodology presented here only for permittivity and refractometric measurements at first order and the EFISH process at third order can be extended to other, still widely used NLO processes, such as the electro-optical Kerr effect (OKE) and the intensity-dependent refractive index (IDRI). Progress in this direction will soon be presented.

All of the considerations above can, thus, be summarized by saying that this paper represents an attempt to bridge the still-large gap between experiments and calculations in the sense that, on one hand, it tries to provide a sufficiently simple computational tool to also be used by non-theoreticians and, on the other hand, it presents an incentive for experimentalists to share an increasingly greater amount of data that is clear in origin and simple in analysis.

Acknowledgment. R.C. acknowledges the Italian CNR (Consiglio Nazionale delle Ricerche: Progetto Finalizzato “Materiali Speciali per Tecnologie Avanzate II”) and MURST (Ministero dell’Università e della Ricerca Scientifica e Tecnologica: “Cofinanziamento 97”) for financial support.

References and Notes

(1) Bishop, D. M.; Norman, P. In *Handbook of Advanced Electronic and Photonic Materials*; Nalwa, H. S., Ed.; Academic Press: San Diego, CA; in press.

(2) (a) Böttcher, C. J. F. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1973; Vol. I. (b) Böttcher, C. J. F.; Bordewijk, P. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1978; Vol. II.

(3) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

(4) Willets, A.; Rice, J. E. *J. Chem. Phys.* **1993**, *99*, 426.

(5) Yu, J.; Zerner, M. C. *J. Chem. Phys.* **1994**, *100*, 7487.

(6) (a) Mikkelsen, K. V.; Jorgensen, P.; Aa Jensen, H. J. *J. Chem. Phys.* **1994**, *100*, 6597. (b) Mikkelsen, K. V.; Sylvester-Hvid, K. O. *J. Phys. Chem.* **1996**, *100*, 9116. (c) Sylvester-Hvid, K. O.; Mikkelsen, K. V.; Jonsson, D.; Norman, P.; Ågren, H. J. *Chem. Phys.* **1998**, *5576*, 109. (d) Sylvester-Hvid, K. O.; Mikkelsen, K. V.; Jonsson, D.; Norman, P.; Ågren, H. J. *J. Phys. Chem. A* **1999**, *103*, 8375 and references to other applications therein.

(7) (a) Cammi, R.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1996**, *104*, 4611. (b) Cammi, R.; Cossi, M.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1996**, *105*, 10556.

(8) (a) Cammi, R.; Cossi, M.; Mennucci, B.; Tomasi, J. *J. Mol. Struct.* **1997**, 436−437, 567. (b) Mennucci, B.; Cammi, R.; Cossi, M.; Tomasi, J. *J. Mol. Struct. (THEOCHEM)* **1998**, *426*, 191. (c) Champagne, B.; Mennucci, B.; Cossi, M.; Cammi, R.; Tomasi, J. *Chem. Phys.* **1998**, *238*, 153. (d) Mennucci, B.; Amovilli, C.; Tomasi, J. *Chem. Phys. Lett.* **1998**, *286*, 221. (e) Tomasi, J.; Cammi, R.; Mennucci, B. *Int. J. Quantum Chem.* **1999**, *75*, 784. (f) Mennucci, B.; Cammi, R.; Tomasi, J. *Int. J. Quantum Chem.* **1999**, *75*, 768.

(9) Wortmann, R.; Bishop, D. M. *J. Chem. Phys.* **1998**, *108*, 1001.

(10) (a) Liptay, W.; Becker, J.; Wehning, D.; Lang, W.; Burkhard, O. *Z. Naturforsch., A* **1982**, *37*, 1396. (b) Liptay, W.; Wehning, D.; Becker, J.; Rehm, T. *Z. Naturforsch., A* **1982**, *37*, 1369.

(11) Singer, K. D.; Garito, A. F. *J. Chem. Phys.* **1981**, *75*, 3572.

(12) Wortmann, R.; Krämer, P.; Glania, C.; Lebus, S.; Detzer, N. *Chem. Phys.* **1993**, *173*, 99.

(13) (a) Steybe, F.; Effenberg, F.; Beckmann, S.; Krämer, P.; Glania, C.; Wortmann, R. *Chem. Phys.* **1997**, *219*, 317. (b) Wortmann, R.; Glania,

C.; Krämer, P.; Matschiner, R.; Wolff, J. J.; Kraft, S.; Treptow, B.; Barbu, E.; Längle, D.; Görlitz, G. *Chem. Eur. J.* **1997**, *3*, 1765. (c) Wolff, K.; Längle, D.; Hillenbrand, D.; Wortmann, R.; Matschiner, R.; Glania, C.; Krämer, P. *Adv. Mater.* **1997**, *9*, 138.

(14) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.

(15) Cammi, R.; Tomasi, J. *J. Comput. Chem.* **1995**, *16*, 1449.

(16) Bishop, D. M. *Rev. Mod. Phys.* **1990**, *62*, 343.

(17) Cammi, R.; Mennucci, B.; Tomasi, J. *J. Phys. Chem. A* **1998**, *102*, 870.

(18) Wolfe, J. J.; Wortmann, R. *Adv. Phys. Org. Chem.* **1999**, *32*, 121.

(19) Brown, W. F. In *Encyclopedia of Physics*; Flügge, S., Ed.; Springer: Berlin, 1956.

(20) Luo, Y.; Norman, P.; Ågren, H. J. *J. Chem. Phys.* **1998**, *109*, 3589.

(21) Cammi, R.; Mennucci, B.; Tomasi, J. *J. Am. Chem. Soc.* **1912**, *34*, 8834.

(22) Cammi, R.; Tomasi, J. *Int. J. Quantum Chem.* **1996**, *60*, 297.

(23) (a) Liptay, W.; Wortmann, R.; Schaffrin, H.; Burkhard, O.; Reitinger, W.; Detzer, N. *Chem. Phys.* **1988**, *120*, 429. (b) Wortmann, R.; Elich, K.; Lebus, S.; Liptay, W.; Borowicz, P.; Grabowska, A. *J. Phys. Chem.* **1992**, *96*, 9724.

(24) (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers*; Wiley: New York, 1991. (b) Levine, B. F.; Bethea, C. G. *J. Chem. Phys.* **1977**, *66*, 2664. (c) Singer, K. D.; Sohn, J. E.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, C. W. *J. Opt. Soc. Am. B* **1989**, *6*, 1339.

(25) (a) Martí, J.; Andrés, J. L.; Bertán, J.; Duran, M. *Mol. Phys.* **1993**, *80*, 625. (b) Martí, J.; Bishop, D. M. *J. Chem. Phys.* **1993**, *99*, 3860. (c) Bishop, D. M.; Kirtman, B. *J. Chem. Phys.* **1991**, *95*, 2646. (d) Bishop, D. M.; Kirtman, B. *J. Chem. Phys.* **1992**, *97*, 5255.

(26) (a) Cancès, E.; Mennucci, B. *J. Chem. Phys.* **1998**, *109*, 249. (b) Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1998**, *109*, 260.

(27) Mennucci, B.; Cammi, R.; Tomasi, J. *J. Chem. Phys.* **1999**, *110*, 6858.

(28) (a) Cancès, E.; Mennucci, B. *J. Math. Chem.* **1998**, *23*, 309. (b) Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032. (c) Mennucci, B.; Cancès, E.; Tomasi, J. *J. Phys. Chem. B* **1997**, *101*, 10506.

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, C. S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, C. A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 99*, revision A.10 (development version); Gaussian,Inc.: Pittsburgh, PA, 1999.

(30) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(31) Karna, S. P.; Prasad, P. N.; Dupuis, M. *J. Chem. Phys.* **1991**, *94*, 1171.

(32) Daniel, C.; Dupuis, M. *Chem. Lett.* **1990**, *171*, 209.

(33) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(34) *Handbook of Chemistry and Physics*; Weast, R. C., Ed.; Chemical Rubber: Cleveland, OH, 1981.

(35) (a) Ref 7a. (b) Cammi, R.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1999**, *110*, 16. (c) Cappelli, C.; Mennucci, B.; da Silva, C. O.; Tomasi, J. *J. Chem. Phys.* In press.

(36) Amovilli, C.; Mennucci, B. *J. Phys. Chem. B* **1997**, *101*, 1051.

(37) Mennucci, B.; Amovilli, C.; Tomasi, J. *Chem. Phys. Lett.* **1998**, *286*, 221

(38) Ref 35c.