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Two Valence Bond State Model for Molecular Nonlinear Optical Properties. Comparison with Push−Pull Polyene Solution Measurements

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The (hyper)polarizabilities obtained from the two valence bond state model including nonequilibrium solvation are compared to experiment. Specifically, the values of $\mu_g^2\alpha_{zz}(0)$ and $\mu_g\beta_{zzz}(0)$ in different solvents calculated from the model are compared to experimental measurements for several push−pull polyene molecules in a range of solvents. The model calculations are in qualitative agreement with the experimental results, but quantitatively the results are mixed. Implications for the two valence bond state model are discussed.

I. Introduction

Push−pull polyenes—organic molecules consisting of electron donor and acceptor groups connected by a conjugated carbon chain—have attracted a great deal of interest because of their nonlinear optical properties.[1−16] In a recent paper (hereafter referred to as Paper I),[17] three of us have generalized the two valence bond (VB) state model[3−9] frequently used to describe the nonlinear optical properties of these molecules to include the effects of nonequilibrium solvation. (Other approaches may be found in refs 10−14.) The model consists of neutral and zwitterionic VB states—the zwitterionic form is obtained from the neutral by electron transfer from the donor group to the acceptor group—that are mixed to obtain the ground and excited electronic states. The VB states also differ in the spatial ordering of the single and double bonds in the intervening conjugated chain, which can be described by a bond length alternation (BLA) coordinate.[2−10] In the development of the model in Paper I, Thompson et al. explicitly considered two degrees of freedom: the BLA coordinate and a solvent coordinate. Equilibrium solvation of the ground electronic state was assumed; however, when the molecule is promoted to the first excited state, this Franck−Condon transition yields the solvent out of equilibrium with the excited-state charge distribution. Since nonlinear optical properties involve Franck−Condon transition energy gaps, this requires the consideration of nonequilibrium solvation.

In solution, the zwitterionic state is preferentially stabilized by the solvent relative to the neutral state. The electronic character of the electronically adiabatic ground and excited states, obtained from mixing the neutral and zwitterionic VB states, thereby changes with the solvent polarity. In this way, the solvent polarity can significantly affect the nonlinear optical properties of these molecules. One would accordingly like to be able to predict for a given molecule which solvent—and more generally which environment[18]—will give the largest hyperpolarizability.

Paper I presented calculations of the static (zero frequency) polarizabilities $\alpha_{zz}(0)$, $\beta_{zzz}(0)$, and $\gamma_{zzzz}(0)$ for several push−pull polyene molecules as a function of solvent dielectric constant. The purpose of the present paper is to compare the predictions of the two VB state model including nonequilibrium solvation with experimental measurements of the polarizabilities. Specifically, we compare the results from the model to those obtained from electric field induced second harmonic generation[19] (EFISH) measurements of $\mu_g\beta_{zzz}(0)$ and ellipsometry measurements[20] of $\mu_g^2\alpha_{zz}(0)$.[21] Here μ_g, $\alpha_{zz}(0)$, and $\beta_{zzz}(0)$ are the adiabatic ground-state dipole moment, and the first- and second-order static polarizabilities, respectively.

The organization of the remainder of this paper is as follows. The experimental procedures for measuring $\mu_g^2\alpha_{zz}(0)$ and $\mu_g\beta_{zzz}(0)$ are described in section II. A brief summary of the relevant features and equations of the two VB state models as developed in Paper I is given in section III. The predictions of the model are compared to experimental measurements in section IV for four push−pull polyene molecules, and the results are discussed. Concluding remarks are given in section V.

II. Experimental Section

The push−pull polyenic molecules investigated in the present work (see Scheme 1) were prepared by a Knoevenagel condensation[22] of an activated methylene derivative with an aldehyde precursor according to the synthetic methodology described in ref 23. After column chromatography on silica gel followed by recrystallization, pure compounds were obtained as assessed by NMR, elementary analyses, and mass spectra.[24] Electronic absorption spectra were recorded at 20 °C with a Beckmann DU 600 spectrophotometer. Solvatochromism was studied using analytical grade solvents. The nonlinear optical properties of each push−pull compound were investigated in a series of solvents of different polarity (i.e., CCl_4, toluene, dioxane, tetrahydrofurane, $CHCl_3$, and dimethylformamide). We have determined the products $\mu_g\beta_{zzz}(0)$ by using the electric field induced second harmonic (EFISH) generation experiment.[25] In this technique, the solution centrosymmetry is broken by a dc electric field, which partially aligns the push−pull molecules.

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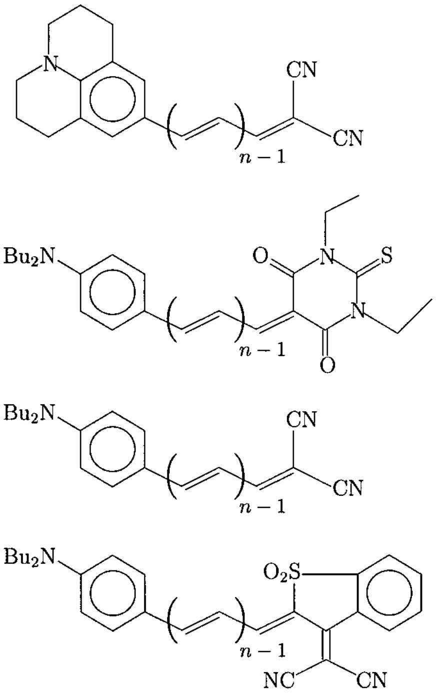
SCHEME 1



2[*n*]

3[*n*]

4[*n*]

5[*n*]

The second harmonic interference fringes were recorded, for solutions of increasing concentration, by using the wedge cell technique at the fundamental wavelength $\lambda = 1907$ nm.[26] From these measurements, we have derived the values of $\mu_g\beta_z(2\omega)$, where $\beta_z(2\omega)$ is the component projected along the ground-state dipole moment of the vector part of the $\beta_{ijk}(2\omega)$ tensor.[27] To a good approximation, $\beta_z(2\omega)$ reduces to $\beta_{zzz}(2\omega)$ for push−pull polyenes, and the static component $\beta_{zzz}(0)$ is related to $\beta_{zzz}(2\omega)$ via the two-level dispersion factor according to

$$\beta_{zzz}(0) = \frac{(\lambda^2 - 4\lambda_{\max}{}^2)(\lambda^2 - \lambda_{\max}{}^2)}{\lambda^4}\beta_{zzz}(2\omega) \tag{2.1}$$

where the frequency $\omega/2\pi$ corresponds to the optical wavelength λ and $\lambda_{\max}$ is the wavelength of the maximum of the charge-transfer absorption band. We have also determined in these solvents the products $\mu_g{}^2\alpha_{zz}(0)$ by using the field induced ellipsometric technique[20] and the EFISH data. The light source was a diode laser operating at $\lambda' = 785$ nm. The variations, induced by a dc electric field, of the transmitted ellipsometric light intensity were recorded for solutions of increasing concentration. From these measurements, we have derived the values of the sum $\mu_g{}^2\delta\alpha(\omega') + 2kTf_{\omega'}\mu_g\beta(\omega')$ (where the frequency $\omega'/2\pi$ corresponds to the optical wavelength λ', $f_{\omega'}$ is the local field factor for an optical electric field, and T is the room temperature). The first contribution in this sum arises from the orientational birefringence caused by the linear polarizability anisotropy $\delta\alpha(\omega')$, which to a good approximation equals $\alpha_{zz}(\omega')$ for push−pull polyenes.[21] The second contribution originates from the Pockels EO effect.[28] We have evaluated the values of this second term by using the two-level dispersion factor relating $\beta_{zzz}(\omega')$ to $\beta_{zzz}(0)$:

$$\beta_{zzz}(\omega') = \frac{\lambda'^2(3\lambda'^2 - \lambda_{\max}{}^2)}{3(\lambda'^2 - \lambda_{\max}{}^2)^2}\beta_{zzz}(0) \tag{2.2}$$

Finally, we have derived the values of the product $\mu_g\alpha_{zz}(0)$ from that of $\mu_g{}^2\alpha_{zz}(\omega')$ by taking into account the dispersion enhancement according to the two-level model:

$$\alpha_{zz}(0) = \frac{(\lambda'^2 - \lambda_{\max}{}^2)}{\lambda'^2}\alpha_{zz}(\omega') \tag{2.3}$$

III. Theoretical Considerations

In this section, we briefly summarize the key features of the two VB state model including the effects of nonequilibrium solvation. The reader is referred to Paper I[17] for the complete details of the theoretical treatment.

The two VB state model for push−pull polyene molecules considers neutral (N) and zwitterionic (Z) states. The neutral state actually consists of small charges, $\pm Q_N$, on the electron donor and acceptor groups to account for a small but finite dipole moment.[6−9] In the zwitterionic state, the corresponding charges $\pm Q_Z$, are significantly larger. The electronically adiabatic ground and excited states are obtained as a mixture of the neutral and zwitterionic configurations. Thus, the ground-state wavefunction is given by

$$\Psi_g = c_N\psi_N + c_z\psi_Z \tag{3.1}$$

where ψ_N and ψ_Z are the neutral and zwitterionic electronic wave functions and

$$c_N = \left[\frac{1 - \mathrm{MIX}_{eq}}{2}\right]^{1/2} \tag{3.2}$$

$$c_Z = \left[\frac{1 + \mathrm{MIX}_{eq}}{2}\right]^{1/2} \tag{3.3}$$

The parameter MIX_{eq} characterizes the mixture of neutral and zwitterionic components at equilibrium in the ground state and thus is a key quantity in the theory. It ranges in value from −1, corresponding to a purely neutral ground state, to +1, a purely zwitterionic ground state.

The dependence of MIX_{eq} (and thereby the coefficients c_N and c_Z) on the BLA coordinate, q, and the solvent coordinate, s, is explicitly considered. While the definition of the BLA coordinate depends on the molecule,[2b] it can generally be thought of as the difference in the single and double bond lengths of the conjugated chain, normalized for the number of bonds.[2] The solvent is described by a nonequilibrium dielectric continuum model, and the solvent coordinate describes the slow orientational polarization of the solvent (as opposed to the fast electronic polarization). Both coordinates are considered to be harmonic.[3,4,29−32] The equilibrium values of the coordinates in the ground electronic state, q_{eq} and s_{eq}, are important in determining the nonlinear optical properties in that they represent the initial conditions in a Franck−Condon transition to the excited state. These equilibrium values of q and s in the ground state are not, however, the equilibrium values for the excited state by the Franck−Condon principle; this is the origin of the nonequilibrium solvation effects, discussed in some detail in ref 17.

The quantity MIX_{eq} characterizing the electronic structure of the ground state is related to the diabatic gap, V_{eq}, and the electronic coupling between the VB states, t, by

$$\mathrm{MIX}_{eq} = -\frac{V_{eq}}{[V_{eq}{}^2 + 4t^2]^{1/2}} \tag{3.4}$$

The diabatic gap is the difference between the neutral and zwitterionic state (free) energies at $q = q_{\mathrm{eq}}$ and $s = s_{\mathrm{eq}}$. As indicated by this equation, $\mathrm{MIX}_{\mathrm{eq}}$ and V_{eq} are strongly related and the relevant quantities in the theory can be expressed in terms of either variable.

The equilibrium values of MIX and V in an arbitrary solvent of dielectric constant ϵ can be expressed in terms of $\mathrm{MIX}_{\mathrm{eq}}$ and V_{eq} in a "reference" solvent. The most convenient reference solvent is that with $\epsilon = \epsilon_\infty$, for which there is no orientational polarization. (ϵ_∞ is the high-frequency, or optical, dielectric constant.) This choice gives

$$V_{\mathrm{eq}}(\epsilon) = V_{\mathrm{eq}}(\epsilon_\infty) - \lambda_{\mathrm{s}}\left(\frac{Q_{\mathrm{Z}} + Q_{\mathrm{N}}}{Q_{\mathrm{Z}} - Q_{\mathrm{N}}}\right) - (\lambda_{\mathrm{q}} + \lambda_{\mathrm{s}})\mathrm{MIX}_{\mathrm{eq}}(\epsilon) + \lambda_{\mathrm{q}}\mathrm{MIX}_{\mathrm{eq}}(\epsilon_\infty) \quad (3.5)$$

where λ_q and λ_s are the BLA and solvent reorganization energies.[17] For a given solvent, eqs 3.4 and 3.5 combine to form a nonlinear equation which can be iteratively solved to find $\mathrm{MIX}_{\mathrm{eq}}(\epsilon)$ and $V_{\mathrm{eq}}(\epsilon)$.

The relevant parameters entering in the model can be obtained from experimental data as follows. The values of V_{eq}, t, μ_{N}, and μ_{Z} in a solvent such as dioxane ($\epsilon = 2.209$) are derived from the absorption and electrooptical absorption measurements[33] in low-polarity solvents, as described in ref 8 and 9. Here μ_{Z} and μ_{N} are the dipole moments of the neutral and zwitterionic states. It is assumed that the electronic coupling, t, and the dipole moments, μ_{Z} and μ_{N} are independent of the solvent.[17] The ratio $(Q_{\mathrm{Z}} + Q_{\mathrm{N}})/(Q_{\mathrm{Z}} - Q_{\mathrm{N}})$ is taken to be equal to the corresponding ratio with the charges replaced by the dipole moments, $(\mu_{\mathrm{Z}} + \mu_{\mathrm{N}})/(\mu_{\mathrm{Z}} - \mu_{\mathrm{N}})$. As described in detail in Paper I, the unknown factor in the solvent reorganization energy λ_s can be obtained from solvatochromic data giving the absorption energy in different solvents, a procedure that finesses any specification of any cavity model for the molecular solute. The values of MIX and the diabatic gap in the reference solvent, $\mathrm{MIX}_{\mathrm{eq}}(\epsilon_\infty)$ and $V_{\mathrm{eq}}(\epsilon_\infty)$, are obtained from the solvatochromic data using a linear fit to $E_{\mathrm{gap}}(\epsilon)$ vs $(1/\epsilon_\infty - 1/\epsilon)$. E_{gap} is the (free) energy difference between the electronically adiabatic excited and ground states at q_{eq} and s_{eq},

$$E_{\mathrm{gap}} = [V_{\mathrm{eq}}^{\;2} + 4t]^{1/2} \quad (3.6)$$

In the calculations, we assume that $\epsilon_\infty = 2$; see Paper I for a discussion of this approximation. The final model parameter, the BLA reorganization energy λ_{q}, is more difficult to obtain. While it was noted in ref 17 that it can be derived from Stokes shift measurements in low polarity solvents, such experiments have not yet been carried out. To proceed then, we assume, as in Paper I, that $\lambda_q = 0.966$ eV and is the same for all the molecules; this is the λ_q value calculated by Chen et al. in ref 4.

The relevant dipole moments and hyperpolarizabilities can be expressed in terms of $\mathrm{MIX}_{\mathrm{eq}}$ (or equivalently V_{eq}). The adiabatic ground-state dipole moment is given in terms of the neutral and zwitterionic dipole moments by

$$\mu_{\mathrm{g}} = \frac{\mu_{\mathrm{Z}} + \mu_{\mathrm{N}}}{2} + \frac{\mu_{\mathrm{Z}} - \mu_{\mathrm{N}}}{2}\mathrm{MIX}_{\mathrm{eq}} \quad (3.7)$$

The diagonal elements of the static (zero frequency) first- and second-order polarizabilities in the Taylor series convention[34] are given by[3,6]

$$\alpha_{zz}(0) = \frac{2t^2\mu_{\mathrm{CS}}^{\;2}}{E_{\mathrm{gap}}^{\;3}} = (1 - \mathrm{MIX}_{\mathrm{eq}}^{\;2})^{3/2}\frac{\mu_{\mathrm{CS}}^{\;2}}{4t} \quad (3.8\mathrm{a})$$

$$\beta_{zzz}(0) = \frac{6V_{\mathrm{eq}}t^3\mu_{\mathrm{CS}}^{\;3}}{E_{\mathrm{gap}}^{\;5}} = -\mathrm{MIX}_{\mathrm{eq}}(1 - \mathrm{MIX}_{\mathrm{eq}}^{\;2})^2\frac{3\mu_{\mathrm{CS}}^{\;3}}{8t^2} \quad (3.8\mathrm{b})$$

where the charge shift dipole moment $\mu_{\mathrm{CS}} = \mu_{\mathrm{Z}} - \mu_{\mathrm{N}}$ and the z-axis is chosen to lie along the dipole μ_{CS}. We note that, in the calculation of $\mu_{\mathrm{g}}\beta_{zzz}(0)$ to compare with experimental measurements, an angle correction factor cos θ arises, where θ is the angle between the ground-state and transition dipole moments. Similarly, in the calculation of $\mu_{\mathrm{g}}^{\;2}\alpha_{zz}(0)$ to compare with experimental measurements, an angle correction factor $(3\cos^2\theta - 1)/2$ should be included. However, there is experimental evidence that these dipoles are almost parallel,[33] so the angle factor is assumed to be equal to unity here.[35]

To summarize, the procedure for calculating the hyperpolarizabilities for a given molecule is as follows. The electronic coupling, t, VB state dipole moments, μ_{N} and μ_{Z}, and the diabatic gap, V_{eq}, in dioxane are obtained from the absorption and electrooptical absorption measurements. (Note that these quantities are obtained from the experimental data using the two VB state model.) The ϵ-independent factor in λ_s is obtained from solvatochromic data as described in detail in Paper I; λ_q is taken to be 0.966 eV. $V_{\mathrm{eq}}(\epsilon_\infty)$ and $\mathrm{MIX}_{\mathrm{eq}}(\epsilon_\infty)$ are obtained from the solvatochromic data given the electronic coupling, t, as described above. Given this information, eqs 3.4 and 3.5 are solved self-consistently to find $\mathrm{MIX}_{\mathrm{eq}}(\epsilon)$ for a given solute molecule in a solvent with dielectric constant ϵ; the ground-state dipole moment, μ_{g}, and the polarizabilities, α_{zz} and β_{zzz}, are then calculated via eqs 3.7, 3.8a, and 3.8b, respectively.

Paper I showed that the model is capable of reproducing the experimental measurements of the third-order hyperpolarizability, γ, of the particular push–pull polyene molecule considered in ref 4 as a function of the solvent dielectric constant. It is important to note the differences between the procedure used to obtain the parameters for those calculations and that described above and employed here (which is the same as that used for the other molecules in Paper I). Specifically, in ref 4 the measured value of γ for the molecule in acetonitrile was used to fit the value of the charge in the zwitterionic state, Q_{Z}, and thus the dipole moment μ_{Z} (it was assumed $Q_{\mathrm{N}} = 0$). The polarizability γ was also used to obtain the electronic coupling, t. Here, we are making a test of the model of ref 17, which is of a much more stringent character. The dipole moments and electronic coupling are determined from the absorption and electrooptical absorption measurements, and *no* experimental values of any polarizability are used to determine the parameters in the model.

IV. Comparison of Experimental and Calculated Polarizabilities

A. Results. In this section, we compare the $\mu_{\mathrm{g}}^{\;2}\alpha_{zz}(0)$ and $\mu_{\mathrm{g}}\beta_{zzz}(0)$ values obtained in a variety of solvents from the two VB state model and experimental measurements. Specifically, we consider the four push–pull polyenes shown in Scheme 1 with $n = 2$.

We will consider two primary quantities in the comparisons between the model calculations and experiments: the magnitudes of $\mu_{\mathrm{g}}^{\;2}\alpha_{zz}(0)$ and $\mu_{\mathrm{g}}\beta_{zzz}(0)$ and their variation over the range of solvent dielectric constant.

Figure 1 shows $\mu_{\mathrm{g}}^{\;2}\alpha_{zz}(0)$ as a function of the solvent dielectric constant ϵ for the molecules **2**[2] and **3**[2]. Focusing first on

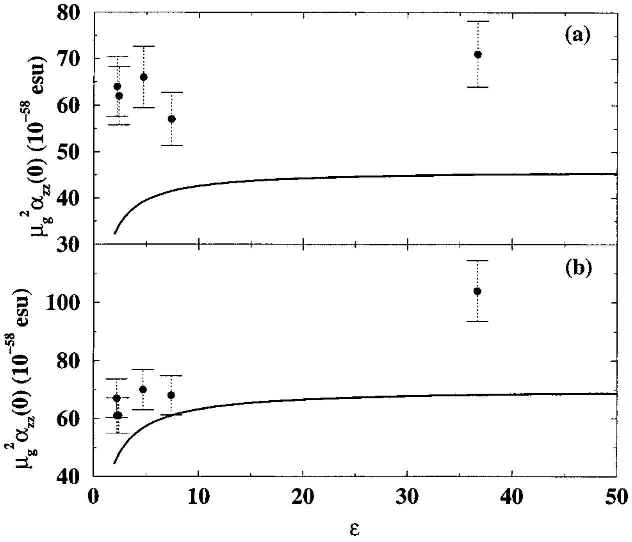


Figure 1. $\mu_g^2\alpha_{zz}(0)$ is plotted versus the solvent dielectric constant ϵ for the (a) **2**[2] and (b) **3**[2] molecules. Results are shown for the theoretical calculations (solid line) and the ellipsometry experiments (solid circles with error bars).

the overall magnitude, we note that for the **2**[2] molecule the two VB state model gives significantly lower values of $\mu_g^2\alpha_{zz}(0)$ than the ellipsometry experiments over the entire range of ϵ. Similarly, the model underestimates the experimental results for $\mu_g^2\alpha_{zz}(0)$ for the **3**[2] molecule, though the agreement is somewhat better for the low-polarity solvents.

Turning now to solvent variations, it is seen from Figure 1 that for both the **2**[2] and **3**[2] molecules the model predicts that $\mu_g^2\alpha_{zz}(0)$ increases with solvent dielectric constant. This is in agreement with the experimental values for the **3**[2] molecule; the two VB state model also correctly predicts the magnitude of the increase in $\mu_g^2\alpha_{zz}(0)$ for this case over the range of ϵ shown. However, for the **2**[2] molecule, the experimental values of $\mu_g^2\alpha_{zz}(0)$ are the same within the error bars for all the solvents used, and thus the model overestimates the magnitude of the change found in the experiments.

The results of the two VB state model calculations of $\mu_g\beta_{zzz}(0)$ for the **2**[2] and **3**[2] molecules as a function of solvent dielectric constant are shown in Figure 2 along with the values obtained from EFISH experiments. The magnitudes of $\mu_g\beta_{zzz}(0)$ for the **2**[2] molecule obtained from the model and from EFISH experiments are in quite reasonable agreement. The experimental variation of $\mu_g\beta_{zzz}(0)$ for the **2**[2] molecule with ϵ predicted by the model also agrees well with that observed in the experiments. However, the model predicts significantly larger values of $\mu_g\beta_{zzz}(0)$ for the **3**[2] molecule than found in the experiments. In addition, the change in $\mu_g\beta_{zzz}(0)$ with ϵ for the **3**[2] molecule obtained from the model is smaller than the experimental result, although it is in the same direction.

Figure 3 shows $\mu_g\beta_{zzz}(0)$ for the **4**[2] and **5**[2] molecules versus ϵ. The model predicts the magnitudes of $\mu_g\beta_{zzz}(0)$ in good agreement with experiment for the **4**[2] molecule but overestimates the magnitudes for the **5**[2] molecule. The variation in $\mu_g\beta_{zzz}(0)$ as a function of ϵ for the **4**[2] molecule obtained from the model appears to be in the same direction as obtained in the experiments, but with a smaller magnitude. (The comparison is not as clear for this molecule due to the large scatter in the experimental polarizabilities.) For the **5**[2] molecule the change in $\mu_g\beta_{zzz}(0)$ with ϵ observed in the model calculations is in good qualitative and quantitative agreement with the experimental measurements.

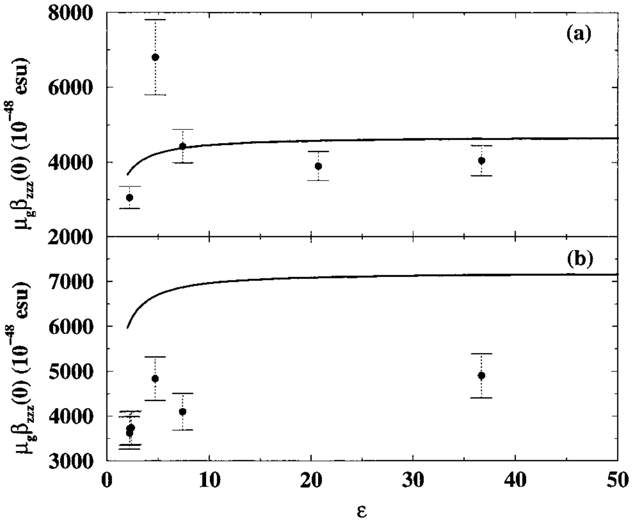


Figure 2. $\mu_g\beta_{zzz}(0)$ is plotted versus the solvent dielectric constant ϵ for the (a) **2**[2] and (b) **3**[2] molecules. Results are shown for the theoretical calculations (solid line) and the EFISH experiments (solid circles with error bars).

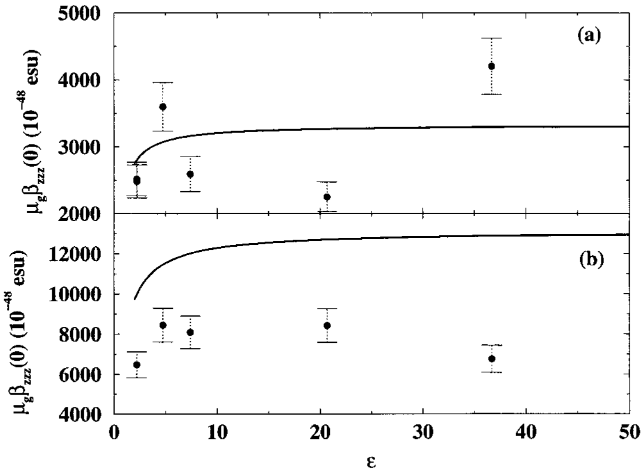


Figure 3. Same as Figure 2 but for the (a) **4**[2] and (b) **5**[2] molecules.

In summary, the two VB state model is in agreement with experimental measurements of the absolute magnitudes of $\mu_g\beta_{zzz}(0)$ for two of the molecules (**2**[2] and **4**[2]). However, for the other two molecules (**3**[2] and **5**[2]) the magnitudes of $\mu_g\beta_{zzz}(0)$ are overestimated. The magnitudes of $\mu_g^2\alpha_{zz}(0)$ obtained from the model are lower than those obtained from experiments for the **2**[2] and **3**[2] molecules.

A summary statement concerning the variation of the polarizabilities with solvent dielectric constant ϵ is that the model predictions are in good qualitative agreement with experimental measurements. Thus, the model accurately predicts which solvent gives the largest (hyper)polarizability for a given molecule. The quantitative predictions of the model of the change in $\mu_g\beta_{zzz}(0)$ with ϵ are in good agreement with experiment for the **2**[2] and **5**[2] molecules. However, for the **3**[2] and **4**[2] molecules, the model predicts a weaker variation with solvent polarity than found in the EFISH experiments. The model calculations and ellipsometry measurements find the same change in $\mu_g^2\alpha_{zz}(0)$ with ϵ for the **3**[2] molecule, while for the **2**[2] molecule the model overestimates the change with ϵ.

Further Model Test. A further, somewhat more general, test of the model may be undertaken as follows. A relationship was derived in Paper I between the second-order polarizability, β and the variation of α with the solvent polarity,

$$\beta = -\left(\frac{\partial V_{\mathrm{eq}}}{\partial \epsilon}\right)^{-1} \mu_{\mathrm{CS}} \frac{\partial \alpha}{\partial \epsilon} \tag{4.1}$$

which holds for the two VB state model. The model can thus be tested by examining how the change in α with ϵ and the magnitude of β are predicted for a single molecule. That is, if the model correctly predicts the variation of α with the solvent dielectric constant, it should also correctly predict the magnitude of β, and vice versa. This should be equally true for $\mu_g{}^2\alpha_{zz}(0)$ and $\mu_g\beta_{zzz}(0)$.

For the **2**[2] molecule, the model predicts a larger change in $\mu_g{}^2\alpha_{zz}(0)$ with ϵ than observed in experiments. However, the model correctly predicts the magnitude of $\mu_g\beta_{zzz}(0)$ for this molecule. This is an inconsistency. On the other hand, the variation of $\mu_g{}^2\alpha_{zz}(0)$ with solvent polarity obtained from the model agrees with experiment for the **3**[2] molecule. But the experimental magnitude of $\mu_g\beta_{zzz}(0)$ is then significantly overestimated by the model for this molecule, again producing an inconsistency.

The fact that the relationship (4.1) is not observed to hold for the experimental measurements implies a difficulty with the two VB state model.

V. Concluding Remarks

We have calculated the polarizabilities $\mu_g{}^2\alpha_{zz}(0)$ and $\mu_g\beta_{zzz}(0)$ as a function of the solvent dielectric constant for four push–pull polyene molecules using the two VB state model accounting for nonequilibrium solvation effects.[17] The results of these calculations have been compared with $\mu_g{}^2\alpha_{zz}(0)$ and $\mu_g\beta_{zzz}(0)$ measured in ellipsometry and EFISH experiments, respectively, in a number of different solvents.

The two VB state model is in general qualitative agreement with experiment. However, the quantitative agreement between the model calculations and experimental results, while good for some molecules, is poor for others. The nature of the variations of $\mu_g{}^2\alpha_{zz}(0)$ and $\mu_g\beta_{zzz}(0)$ with the solvent dielectric constant is well predicted by the model. However, the size of the changes with ϵ obtained from the model calculations agrees with the experimental results for only three of six cases. The absolute magnitudes of $\mu_g\beta_{zzz}(0)$ given by the model calculations agree with experiment for two molecules, but are overestimated for the other two. The model underestimates the magnitude of $\mu_g{}^2\alpha_{zz}(0)$ for both molecules considered. In addition, inconsistencies appear when a certain internal relation [eq 4.1] is examined. The changes in the polarizabilities $\mu_g{}^2\alpha_{zz}(0)$ and $\mu_g\beta_{zzz}(0)$ with solvent polarity are reasonably small for the molecules considered here. It would be interesting to make a similar model calculation–experimental measurement comparisons of $\gamma_{zzzz}(0)$ for, e.g., molecules **2**[1], **3**[1], and **3**[2], for which the two VB state model predicts large changes in $\gamma_{zzzz}(0)$ with solvent polarity, including sign changes and magnitude changes by as much as a factor of 10.[17] Unfortunately this experimental data is not yet available.[36]

As noted in Paper I, the two VB state model is an effective one,[17] in which the two valence bond states have been chosen to reproduce the required properties of the ground and excited electronic states. This is carried out in the present formulation by the introduction of certain limited experimental measurements to parametrize the model, as described within. The present comparison of the two state VB model calculations and experimental measurements indicates that the model provides a good qualitative description of the nonlinear optical properties of push–pull polyenes in solution. However, the lack of quantitative agreement for some of the molecules considered here indicates that the model may not be adequate in all cases and implies a limitation of considering only two VB states and only one excited electronic state. Additional valence bond structures as well as contributions from higher excited states may therefore be necessary for a complete (quantitative) description of these systems, as noted previously.[17] Specifically, VB structures that have charge localized on the conjugated chain[37] may be required for a quantitative description of these molecules, as well as the possible role of other solute molecule coordinates. This issue is under study by both theoretical[38] and time-dependent spectroscopic[39] methods. It is important to note that this implication is found even though we have considered here molecules with relatively short conjugated chains connecting the electron donor and acceptor groups; the importance of additional VB structures is expected to increase with the length of the intervening chain.

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(24) Molecules **3**[*n*] and **5**[*n*] have already been described in ref 23. NMR spectra were recorded with a Bruker AM 200 SY apparatus. Chemical shifts are given in ppm and coupling constants (*J*) in Hz. The vinylic protons are numbered along the polyenic chain starting from the donor end. The aliphatic and aromatic protons are indexed with respect to the donating nitrogen atom proximity. **2**[2]: (89%) (Found: C, 78.24; H, 6.08; N, 15.00. Calcd for $C_{18}H_{17}N_3$: C, 78.51; H, 6.22; N, 15.26) δ^H (200 MHz; $CDCl_3$) 1.96 (4 H, quin, b-CH_2), 2.74 (4 H, t, *J* 6.3, c-CH_2), 3.32 (4 H, t, *J* 5.8, a-CH_2), 6.93 (1 H, dd, *J* 11.0 and 14.6, 2-H), 7.05 (2 H, s, Ph-H), 7.07 (1 H, d, *J* 14.4, 3-H), 7.44 (1 H, d, *J* 11.0, 1-H); δ^C (50 MHz; $CDCl_3$) 160.13, 151.78, 146.92, 129.25, 121.21, 120.72, 116.00, 115.46, 113.60, 73.88, 50.00, 27.41, 21.03; λ_{max} 496 (cyclohexane), 500 (dioxane), 502 (diethyl oxide), 511 (ethyl acetate), 519 (tetrahydrofuran), 531 (dichloromethane), 520 (acetone), 524 (acetonitrile), 534 (dimethylformamide (DMF)), 540 (dimethyl sulfoxide (DMSO)). **4**[2]: (94%) (Found: C, 78.17; H, 8.23; N, 13.57. Calcd for $C_{20}H_{25}N_3$: C, 78.14; H, 8.20; N, 13.67) δ^H (200 MHz; $CDCl_3$) 0.94 (6 H, t, *J* 9.3, d-Me), 1.38 (4 H, sex., *J* 7.3, c-CH_2), 1.60 (4 H, m, b-CH_2), 3.35 (4 H, t, *J* 6.9, a-CH_2), 6.62 (2 H, d, *J* 9.0, a-H), 6.98 (1 H, dd, *J* 11.4 and 14.7, 2-H), 7.16 (1 H, d, *J* 14.7, 1-H), 7.45 (2 H, d, *J* 8.9, b-H) and 7.48 (1 H, d, *J* 11.3, 3-H); δ^C (50 MHz; $CDCl_3$) 160.34, 151.37, 151.30, 131.785, 121.09, 116.64, 115.09, 113.15, 111.615, 75.23, 50.78, 29.28, 20.12, 13.79; λ_{max} 481 (cyclohexane), 479 (dioxane), 480 (diethyl oxide), 486 (ethyl acetate), 494 (tetrahydrofuran), 503 (dichloromethane), 498 (acetone), 497 (acetonitrile), 507 (DMF), 513 (DMSO).

(25) The EFISH technique is described in ref 19. In these papers, the quadratic polarizabilities are given in the X convention of ref 34. The quadratic polarizability in the Taylor series convention, used in this work, is 4 times that of the X convention.

(26) The measurements were calibrated relative to a Quartz wedge ($d_{11}(2\omega) = 1.1 \times 10^{-9}$ esu at 1.907 μm).

(27) Away from resonance, $\beta_z(2\omega) = \beta_{xxz}(2\omega) + \beta_{yyz}(2\omega) + \beta_{zzz}(2\omega)$.

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(35) There is an additional issue, since eqs 3.8 assume that the *z*-axis lies along μ_{CS} while the experimental values are obtained by taking the *z*-axis along μ_g. Again, there is experimental evidence[33] that these dipole moments are close to parallel. Since we have no further information for these molecules concerning what the angle between μ_{CS} and μ_g may be, we make no accounting for these factors in the results presented here. However, it is useful to note that, according to an analysis within the context of the present model, none of the angle correction factors would exhibit a large change with the solvent dielectric constant. Thus, they cannot account for the differences in the variations of $\mu_g^2\alpha_{zz}(0)$ and $\mu_g^2\beta_{zzz}(0)$ with ϵ found in the model calculations and the experimental measurements found in section IV. In addition, any angle factor would reduce the calculated magnitude of the polarizabilities, and thus they can in no way account for the disagreements for $\mu_g^2\alpha_{zz}(0)$ observed in section IV. Also, consideration of the most severe possible case (of nonparallel μ_{CS} and μ_g) in the analysis referred to above indicates that the angle factors probably cannot account for the calculated and measured magnitude differences in the molecules **3**[2] and **5**[2] (cf. Section IV).

(36) In the present treatment, the phenyl rings in the Scheme 1 molecules are considered to be part of the electron-donating group. The effect of these aromatic groups[2b] on the nonlinear optical properties of the molecules may be accounted for in the effective VB treatment. Nevertheless, it would be interesting to examine molecules in which there is no such aromatic ring, to clearly assess its influence. See also: Hernandez, V.; Castiglioni, C.; Del Zoppo, M.; Zerbi, G. *Phys. Rev. B* **1994**, *50*, 9815 in this connection.

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