# Two Valence Bond State Model for Molecular Nonlinear Optical Properties. Nonequilibrium Solvation Formulation

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*Received: April 17, 1998; In Final Form: July 8, 1998*

The two valence bond state model frequently used to describe the nonlinear optical properties of push−pull polyenes and the effect of the bond length alternation (BLA) coordinate is generalized to include the effects of nonequilibrium solvation. It is shown how a polar solvent modifies, via the diabatic gap between the valence bond free energy surfaces, the character of the electronically adiabatic ground state and consequently the BLA and the (hyper)polarizabilities. The parameters characterizing a molecule in the model can be readily extracted from experimental measurements. The model is applied to the calculation of (hyper)polarizabilities for several molecules as a function of solvent polarity, and comparison is made with both experimental and previous theoretical results. Some directions for an improved description are discussed.

## I. Introduction

It has long been recognized that organic molecules consisting of electron donor and acceptor groups separated by a conjugated chain (sometimes referred to as push−pull molecules) can possess large optical (hyper)polarizabilities.[1] These molecules have thus attracted a great deal of attention for their possible use in a wide range of technological applications.[2] Recently, Marder and co-workers have discovered a relationship between the nonlinear optical properties of these molecules and the geometry of the alternating short and long bonds in the intervening chain,[3−6] which they quantify in terms of a bond length alternation (BLA) coordinate. Goddard and co-workers have used a two valence bond (VB) state model (consisting of a neutral and a zwitterionic form, which are mixed to produce the ground and excited electronic states) to describe the effect of the BLA on the hyperpolarizabilities.[7−9] Barzoukas, Blanchard-Desce, and co-workers have utilized a similar model,[10−13] but characterize the system in terms of a different parameter, MIX, which represents the degree of zwitterionic character in the electronic ground state and which can, in appropriate cases, be related to the BLA.[10] The applicability of the two VB state perspective, which is an attractive albeit comparatively simplified description, has been verified in a number of cases both by comparison with experiment and with (non-VB perspective) electronic structure calculations.[7,8,14]

As noted by several groups,[8,10,11,15−19] it is clear that the role of the solvent can be significant in determining the characteristics of these molecules. The solvent preferentially stabilizes the zwitterionic form altering the equilibrium value of the BLA coordinate in the ground state of the molecule and thereby changing its optical properties. Indeed, understanding the role of the solvent can be particularly important in the context of optimizing the nonlinear optical properties of a system. For example, one would like to be able to predict which solvent—or more generally, which environment—will produce the largest hyperpolarizability for a given molecule. An explicit formulation for the solution problem is required, since as shown in ref 18, attempted assessments of solvent effects via gas-phase calculations in external fields can be misleading.

There have been several studies of the effects of a solvent on the polarizabilities;[8,10,11,15−23] in the two VB state context, the solvation has been described in the equilibrium limit.[8,10] Here we present a nonequilibrium treatment of the solvent within the two valence bond state model, while including the BLA geometric coordinate; the nonequilibrium formulation is required because, while optical transitions occur from an equilibrium solvated ground electronic state, a nonequilibrium solvation state is produced in the transition by the Franck−Condon principle, and this feature is reflected in the various linear and nonlinear polarizabilities (aspects of nonequilibrium solvation have been included in the context of other solute electronic structure descriptions, e.g., refs. 16, 17, 19, 22, and 23). Using the solvated ground and excited electronic states with a proper accounting of solvation effects within a dielectric continuum framework, the nonlinear optical properties (in the form of the (hyper)polarizabilities) of the molecules in the two VB state description are generated as a function of the solvent polarity. In addition, we show how the parameters characterizing a molecule in the model can be conveniently extracted from experimental measurements of properties other than the polarizabilities.

The organization of the remainder of this paper is as follows. Section II presents an outline of the two VB state model and describes the BLA and solvent coordinates; this model has as its starting point a description of the electronically uncoupled free energy surfaces for the VB states in a general form familiar from electron-transfer theory.[24,25] We then derive the equations relevant to the calculation of the (hyper)polarizabilities. Application of the model to several representative molecules is made in section III using experimental measurements to determine the model parameters. The dependence of the (hyper)polarizabilities on the solvent dielectric constant is obtained and compared to the results from the model of Chen et al.[8] Concluding remarks are given in section IV.

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S1089-5647(98)01916-6 CCC: $15.00

**SCHEME 1**

## II. Theory

**A. Description of the Model.** To describe push−pull molecules, we consider two valence bond states, which we refer to as neutral (N) and zwitterionic (Z). What we call the neutral state actually consists of small charges, $\pm Q_{\mathrm{N}}$, on the electron donor and acceptor groups (in this fashion, the small but finite dipole moment[10−13] of the N state is taken into account; see below), while the zwitterionic state possesses significantly greater charge separation than the neutral resulting in charges $\pm Q_{\mathrm{Z}}$ on the donor and acceptor. In addition, the ordering of single and double bonds in the conjugated chain connecting the donor and acceptor groups in the N state is reversed in the Z state. The definitions of the N and Z states are illustrated in Scheme 1 for a general chain length represented by $n$, the number of double bond units.

We formulate the electronic structure problem in solution in terms of two coordinates: a geometrical one, the BLA, as discussed in the Introduction, and a solvent coordinate $s$. The definition of the BLA coordinate can vary depending on the molecular structure. However, it can generally be thought of as the difference between the long and short bond lengths in the conjugated chain connecting the donor and acceptor groups[3−9] (normalized so that it is independent of the number of bonds in the chain); such a coordinate has a long history.[18] The solvent coordinate $s$, as in a range of other solution problems involving electron transfer,[24,25] charge-transfer reactions involving bond making and breaking,[26] or time-dependent fluorescence,[27] is treated in the dielectric continuum approximation and is a measure of the comparatively slow nuclear, orientational polarization in the solvent (as opposed to the rapid electronic polarization of the solvent). Both coordinates are most conveniently defined in terms of the electronically diabatic valence bond states, which can then be used to describe the state of the solute molecular geometry and the solvent nonequilibrium orientational polarization for the electronically adiabatic ground and excited electronic states resulting from the electronic coupling of the VB states.

Following Goddard and co-workers,[7,8] we denote the vibrational coordinate (the BLA) by $q$ and assume it is harmonic. As in other problems,[24−27] the solvent coordinate $s$ can also be considered to be harmonic. Thus, the free energies of the uncoupled valence bond states are given by the two-dimensional harmonic surfaces

$$G_{\mathrm{N}}(q, s) = G_{\mathrm{N},0,0} + \frac{1}{2}k_q(q - q_{\mathrm{N}}^0)^2 + \frac{1}{2}k_s(s - s_{\mathrm{N}}^0)^2 \quad (2.1)$$

and

$$G_{\mathrm{Z}}(q, s) = G_{\mathrm{Z},0,0} + \frac{1}{2}k_q(q - q_{\mathrm{Z}}^0)^2 + \frac{1}{2}k_s(s - s_{\mathrm{Z}}^0)^2 \quad (2.2)$$

as illustrated in Figure 1, where $q_{\mathrm{N}}^0$ ($s_{\mathrm{N}}^0$) and $q_{\mathrm{Z}}^0$ ($s_{\mathrm{Z}}^0$) are the equilibrium values of the BLA (solvent) coordinate in the neutral and zwitterionic states, respectively, and $k_q$ and $k_s$ are the force constants for the BLA and solvent coordinates, respectively (assumed to be the same for both states). $G_{\mathrm{N},0,0}$ ($G_{\mathrm{Z},0,0}$) is the free energy of the neutral (zwitterionic) state when the BLA and solvent coordinates are at their equilibrium values for that VB state. Note that this includes a contribution from the equilibrium solvation by the electronic and orientational degrees of freedom of the solvent. In the Marcus−Born model of solvation,[25] this solvation energy can be expressed as

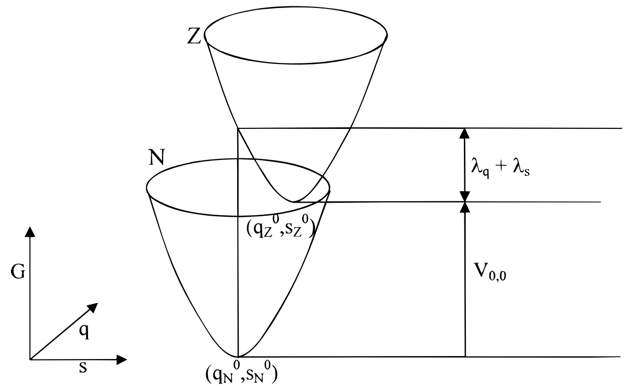


**Figure 1.** Schematic picture of the neutral and zwitterionic diabatic valence bond free energy surfaces in the vibrational ($q$) and solvent ($s$) coordinates. The reorganization energies $\lambda_q$ and $\lambda_s$ and the difference in equilibrium free energies $V_{0,0}$ are indicated. The picture shown is for the case where $V_{0,0} > 0$.

$$G_{\mathrm{N,Z};s}(\epsilon) = -\left(1 - \frac{1}{\epsilon}\right) Q_{\mathrm{N,Z}}^2 S_{\mathrm{F}} \quad (2.3)$$

where $\epsilon$ is the static dielectric constant of the solvent, $Q_{\mathrm{N,Z}}$ is the effective charge magnitude on the donor and acceptor groups in the neutral and zwitterionic states, respectively, and

$$S_{\mathrm{F}} = \frac{1}{2r_{\mathrm{D}}} + \frac{1}{2r_{\mathrm{A}}} - \frac{1}{R_{\mathrm{DA}}} \quad (2.4)$$

Here $r_{\mathrm{D}}$ and $r_{\mathrm{A}}$ are the radii of the electron donating and accepting groups and $R_{\mathrm{DA}}$ is the distance between their centers. (We note that the underlying geometric model[25] giving eq 2.4 is a quite simplified one for push−pull molecules; we will indicate in section II.C how this factor is effectively determined.)

In the same model,[25] the solvent reorganization energy

$$\lambda_s = \frac{1}{2}k_s(s_{\mathrm{Z}}^0 - s_{\mathrm{N}}^0)^2 \quad (2.5)$$

which is the difference between the free energy of the zwitterionic nonequilibrium solvation free energy evaluated at $s = s_{\mathrm{N}}^0$ and $s = s_{\mathrm{Z}}^0$, is given by

$$\lambda_s = \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon}\right) \Delta Q^2 S_{\mathrm{F}} \quad (2.6)$$

$$\Delta Q = Q_{\mathrm{Z}} - Q_{\mathrm{N}}$$

where $\Delta Q$ is the effective charge transfer between the N and Z states and where $\epsilon_\infty$ is the high-frequency, optical, dielectric constant. Since the latter reflects the electronic polarization of the solvent, the combination of dielectric constants in eq 2.6 reflects the feature that the reorganizational energy and thus the solvent force constant are related to the orientational, nonelectronic nonequilibrium solvent polarization. By contrast, both the solvent electronic and orientational polarizations contribute to the equilibrium solvation free energy eq 2.3, so that only the static dielectric constant $\epsilon$ appears there. For any given value of the solvent coordinate $s$ in Figure 1, the electronic polarization of the solvent is separately equilibrated to each of the charge distributions of the N and Z VB states and so does not enter as an explicit variable coordinate, although it contributes to the equilibrium solvation free energies $G_{Z,N;s}(\epsilon)$. On the other hand, a given $s$ value in Figure 1 corresponds to a certain orientational polarization in the solvent, which in general is in equilibrium with neither of the VB N and Z charge distributions. Even if the $s$ value corresponds to the equilibrium orientational polarization for one of the VB states, say N, that $s$ value is not the equilibrium one for the other VB state, say Z, by the Franck–Condon principle; while the solvent electronic polarization follows the solute charge distribution change, the slow solvent orientational polarization does not.

In a similar vein, one can define a reorganization energy $\lambda_q$ for the vibrational coordinate $q$, defined to be the (free) energy difference of the zwitterionic VB state energy between the value $q = q_N^0$ appropriate for equilibrium in the neutral state and the value $q = q_Z^0$ appropriate for equilibrium in the zwitterionic state:

$$\lambda_q = \frac{1}{2}k_q(q_Z^0 - q_N^0)^2 \qquad (2.7)$$

The model equations above have the structure and general interpretation of those used in a variety of problems, especially in electron-transfer rate theory.[24,25] In those problems, the electronic coupling between two electronically diabatic states (here N and Z) is usually taken to be small. In the present problem, however, the electronic coupling is significant[7,8,10–13] and plays a major role in determining the molecular nonlinear optical properties; estimated couplings for various push–pull molecules are large—in the 1 eV range[7,8,10–13]—and in this framework, the solute molecular polarizability, for example, changes with solvent via the shifting mixture, in the ground electronic state, of the N and Z states allowed by the coupling. Before proceeding, it is important to immediately stress that couplings of this order of magnitude for the significant donor–acceptor distances typical of push–pull molecules are a signal that the two VB state description is an *effective* one,[28] a point made long ago in a related connection by Pauling[29] (for a general discussion, see ref 30); this is to say that the two VB states are those that, when mixed with a self-consistently determined coupling, produce the required properties of the ground and first excited electronically adiabatic states. We will return to this important point in the concluding section.

Thus, the neutral and zwitterionic valence bond (diabatic) states are electronically coupled, resulting in electronically adiabatic ground- and excited-state surfaces given by

$$G_{e,g}(q,s) = \frac{G_N(q,s) + G_Z(q,s)}{2} \pm \frac{1}{2}[V(q,s)^2 + 4t^2]^{1/2} \qquad (2.8)$$

Here $t$ is the electronic coupling between the neutral and zwitterionic states and is considered to be independent of both $q$ and $s$. We have defined the quantity

$$V(q,s) = G_Z(q,s) - G_N(q,s) \qquad (2.9)$$

which from eqs 2.1, 2.2, 2.5, and 2.7 can be written as

$$V(q,s) = G_{Z,0,0} - G_{N,0,0} + \lambda_q\frac{q_Z^0 + q_N^0 - 2q}{q_Z^0 - q_N^0} + \lambda_s\frac{s_Z^0 + s_N^0 - 2s}{s_Z^0 - s_N^0} \qquad (2.10)$$

and which we refer to as the diabatic gap.[31] The diabatic gap $V(q, s)$, which is the difference at a given $q$ and $s$ between the two free energy surfaces illustrated in Figure 1, is a fundamental quantity in all that follows. First, its equilibrium value characterizes the composition of the ground-state wave function $\Psi_g$, which can be expressed as[7,32]

$$\Psi_g = (1 - f_{eq})^{1/2}\psi_N + f_{eq}^{1/2}\psi_Z \qquad (2.11)$$

with

$$f_{eq} = \frac{1}{2} - \frac{1}{2}\frac{V_{eq}}{[V_{eq}^2 + 4t^2]^{1/2}} \qquad (2.12)$$

being the equilibrium fraction of zwitterionic character in the ground state. $f_{eq} = 0$ implies the ground state is purely neutral, $f_{eq} = 1$ purely zwitterionic, and $f_{eq} = {}^1/_2$ an equal mixture of the two. Alternatively, in the formulation of Barzoukas, Blanchard-Desce, and co-workers, the wave function can be expressed as[10]

$$\Psi_g = \cos\frac{\theta}{2}\psi_N + \sin\frac{\theta}{2}\psi_Z \qquad (2.13)$$

where $\theta$ is related to the equilibrium diabatic gap and coupling by $\tan\theta = 2t/V_{eq}$. $\theta$ can also be related to the parameter $\mathrm{MIX}_{eq}$ (a quantity analogous to $f_{eq}$) as[10]

$$\mathrm{MIX}_{eq} = -\cos\theta = -\frac{V_{eq}}{[V_{eq}^2 + 4t^2]^{1/2}} \qquad (2.14)$$

It is thus easy to see the relationship[10] between $f_{eq}$ and $\mathrm{MIX}_{eq}$

$$\mathrm{MIX}_{eq} = 2f_{eq} - 1 \qquad (2.15)$$

and that $\mathrm{MIX}_{eq}$ ranges from $-1$ to $+1$ with $\mathrm{MIX}_{eq} = -1$ corresponding to a completely neutral ground state, $\mathrm{MIX}_{eq} = 1$ a zwitterionic ground state, and $\mathrm{MIX}_{eq} = 0$ an equal mixture of the two; in the BLA language for push–pull polyene systems, the latter condition corresponds to equal bond lengths in the intervening chain, i.e., $\pi$ electron delocalization.[33]

The second aspect of the importance of the diabatic gap $V_{eq}$ is that, in the two-level approximation,[1,34] the various polarizabilities can be conveniently expressed in terms of it, localizing the $q$ and $s$ dependence. Expressed also in terms of $\mathrm{MIX}_{eq}$, the diagonal elements of the static (zero-frequency) first-, second-, and third-order polarizabilities are given by[7,10,35]

$$\alpha_{zz} = \frac{2t^2\mu_{CS}^2}{E_{gap}^3} = (1 - \mathrm{MIX}_{eq}^2)^{3/2}\frac{\mu_{CS}^2}{4t} \qquad (2.16a)$$

$$\beta_{zzz} = \frac{6V_{eq}t^2\mu_{CS}^3}{E_{gap}^5} = -\mathrm{MIX}_{eq}(1 - \mathrm{MIX}_{eq}^2)^2\frac{3\mu_{CS}^3}{8t^2} \qquad (2.16b)$$

$$\gamma_{zzzz} = \frac{24(V_{eq}^2 - t^2)t^2\mu_{CS}^4}{E_{gap}^7} = (1 - \mathrm{MIX}_{eq}^2)^{5/2}(5\mathrm{MIX}_{eq}^2 - 1)\frac{3\mu_{CS}^4}{16t^3} \qquad (2.16c)$$

where the charge shift dipole moment $\mu_{CS} = \mu_Z - \mu_N$, where $\mu_Z$ and $\mu_N$ are the dipole moments of the neutral and zwitterionic states[36] (the $z$-axis is chosen to lie along the dipole $\mu_{CS}$), $t$ is the electronic coupling, and

$$E_{\mathrm{gap}} = [V_{\mathrm{eq}}^2 + 4t^2]^{1/2} \tag{2.17}$$

is the gap[31] $G_e - G_g$ between the ground and electronic state surfaces at equilibrium in the ground state (cf. eq 2.8). We note that we have used the Taylor series convention[37] for the polarizabilities given here in which the total dipole moment is expressed as

$$\mu = \mu_0 + \alpha E + \frac{1}{2!}\beta E^2 + \frac{1}{3!}\gamma E^3 + ... \tag{2.18}$$

where $E$ is the applied electric field, $\mu_0$ is the permanent dipole moment, $\alpha$ is the polarizability, and $\beta$, $\gamma$, etc., are the hyperpolarizabilities.

**B. Ground-State Equilibrium and the Diabatic Gap.** Having outlined the salient features of the two VB state model, we now proceed to find the equilibrium values of $q$ and $s$ on the electronic ground-state free energy surface. These are critical in the determination of the nonlinear optical properties of the molecule since they are related to the equilibrium electronic structure of the ground state and dictate the initial conditions in a Franck−Condon transition to the excited state. The equilibrium values, which we shall refer to as $q_{\mathrm{eq}}$ and $s_{\mathrm{eq}}$, satisfy the conditions

$$\frac{\partial G_g(q, s)}{\partial q} = 0, \quad \frac{\partial G_g(q, s)}{\partial s} = 0 \tag{2.19}$$

Solution of these two equations leads to the results

$$q_{\mathrm{eq}} = \frac{q_Z^0 + q_N^0}{2} + \frac{(q_Z^0 - q_N^0)}{2}\mathrm{MIX}(q_{\mathrm{eq}}, s) \tag{2.20}$$

and

$$s_{\mathrm{eq}} = \frac{s_Z^0 + s_N^0}{2} + \frac{(s_Z^0 - s_N^0)}{2}\mathrm{MIX}(q, s_{\mathrm{eq}}) \tag{2.21}$$

These equations indicate how the equilibrium molecular geometry[38] and equilibrium solvent orientational polarization vary between the limiting neutral and zwitterionic forms with the ground-state electronic structure measure MIX. (They are analogous to the equation connecting[10] the ground-state dipole moment $\mu_g$ to the VB state dipole moments $\mu_N$ and $\mu_Z$.) Note that the expression for $q_{\mathrm{eq}}$ depends on $s$ and, similarly, $s_{\mathrm{eq}}$ depends on $q$. Since the global minimum is located at ($q_{\mathrm{eq}}$, $s_{\mathrm{eq}}$), we wish to evaluate the above equations using MIX($q_{\mathrm{eq}}$, $s_{\mathrm{eq}}$) $\equiv$ MIX$_{\mathrm{eq}}$. This allows a relationship between $q_{\mathrm{eq}}$ and $s_{\mathrm{eq}}$ to be established, namely

$$\frac{s_{\mathrm{eq}} - s_N^0}{s_Z^0 - s_N^0} = \frac{q_{\mathrm{eq}} - q_N^0}{q_Z^0 - q_N^0} = f_{\mathrm{eq}} \tag{2.22}$$

where $f_{\mathrm{eq}}$ is the fraction of zwitterionic character in the equilibrium ground state. It is interesting to note that while we began with a description of the system in terms of $s$ and $q$ as independent variables, the values at the global minimum are, in fact, linearly related as just seen. It should be emphasized, however, that the determination of either equilibrium value requires the solution of one of the simultaneously valid nonlinear eqs 2.20 or 2.21.

We now find the key quantity, the diabatic gap evaluated at the minimum on the ground electronic state surface. In view of the above discussion, this gap[31] can be expressed in terms of $q_{\mathrm{eq}}$ alone (or, equivalently, $s_{\mathrm{eq}}$ alone). From eqs 2.10, 2.20, and 2.21, it is easily shown that

$$\begin{aligned} V(q_{\mathrm{eq}}) &= G_Z(q_{\mathrm{eq}}, s_{\mathrm{eq}}) - G_N(q_{\mathrm{eq}}, s_{\mathrm{eq}}) \\ &= V_{0,0} + \frac{1}{2}k_q\left(1 + \frac{\lambda_s}{\lambda_q}\right)(q_Z^0 - q_N^0)\,[q_Z^0 + q_N^0 - 2q_{\mathrm{eq}}] \end{aligned} \tag{2.23}$$

where

$$\begin{aligned} V_{0,0} &= G_{Z,0,0} - G_{N,0,0} \\ &= V_0 + G_{Z;s} - G_{N;s} = V_0 + \Delta G_s \end{aligned} \tag{2.24}$$

is the difference between the zwitterionic and neutral state free energies evaluated at their equilibrium positions, ($q_Z^0$, $s_Z^0$) and ($q_N^0$, $s_N^0$), respectively, neither of which in general is equal to the ground-state equilibrium location ($q_{\mathrm{eq}}$, $s_{\mathrm{eq}}$) via eqs 2.20 and 2.21. Here $V_0$ is the gas-phase difference between the zwitterionic and neutral state (free) energies evaluated at their equilibrium positions $q_Z^0$ and $q_N^0$, and $\Delta G_s = -(1 - 1/\epsilon)(Q_Z^2 - Q_N^2)S_F$ is the difference of the equilibrium solvation free energies eq 2.3.

The expression eq 2.23 for the diabatic gap bears a remarkable similarity to that found by Lu et al.[7] for the gas-phase case. Solvation effects are responsible for the several differences in eq 2.23 compared to that gas-phase diabatic gap expression. First, $V_{0,0}$ contains a contribution $\Delta G_s$ from the differential solvation of the zwitterionic and neutral states by the solvent. Second, the force constant for the $q$ vibrational degree of freedom becomes "renormalized" by the factor $(1 + \lambda_s/\lambda_q)$, owing to the presence of the solvent orientational degrees of freedom. Finally, the actual value of $q_{\mathrm{eq}}$ is different in solution than in the gas phase (since both eqs 2.20 and 2.21 must be simultaneously satisfied); equivalently, the electronic composition of the ground state differs from that in the gas phase.

The diabatic gap $V(q_{\mathrm{eq}})$ evaluated at the ground electronic state equilibrium configuration can be written in a useful and appealing form involving the equilibrium value of MIX by combining eq 2.23 with eq 2.20 evaluated at $s = s_{\mathrm{eq}}$ and the vibrational reorganization energy definition eq 2.7 to find

$$V(\mathrm{MIX}_{\mathrm{eq}}) = V_{0,0} - (\lambda_q + \lambda_s)\mathrm{MIX}_{\mathrm{eq}} \tag{2.25}$$

The content of this equation is the following. Consider first the limit that MIX$_{\mathrm{eq}}$ = −1, i.e., the ground adiabatic state is just the pure neutral VB state and so ($q_{\mathrm{eq}}$, $s_{\mathrm{eq}}$) = ($q_N^0$, $s_N^0$). Equation 2.25 then says that the equilibrium diabatic gap exceeds the difference $V_{0,0}$ of the equilibrium free energy values for the zwitterionic and neutral state by the sum of the reorganization energies; that this is correct is clear from Figure 1. As the ground state electronic structure progressively involves a contribution from the zwitterionic VB state and MIX$_{\mathrm{eq}}$ increases in magnitude toward zero, this excess in the diabatic gap over $V_{0,0}$ will progressively diminish, as is also clear from Figure 1; for example, when $V_{0,0} = 0$ so that MIX$_{\mathrm{eq}}$ = 0, the excess vanishes. This having been said, it needs to be emphasized that the formally linear eq 2.25 conceals very strong nonlinear effects: MIX$_{\mathrm{eq}}$ and $V(q_{\mathrm{eq}}) = V(\mathrm{MIX}_{\mathrm{eq}})$ are found by requiring that eqs 2.14 and 2.25 are simultaneously satisfied, and the former relation is highly nonlinear in the diabatic gap. Thus, for example, MIX$_{\mathrm{eq}}$ in eq 2.25 is not independent of $V_{0,0}$; as an illustration, if $V_{0,0} = 0$ then both MIX$_{\mathrm{eq}}$ and $V(\mathrm{MIX}_{\mathrm{eq}})$ must vanish.

An additional aspect of eq 2.25 is that this expression for the gap does not depend explicitly on the individual vibrational parameters $k_q$, $q_N^0$, or $q_Z^0$ but only their combination in the form of the vibrational reorganization energy. Thus, in principle a specific definition of the BLA coordinate is not required, but rather only a knowledge of $\lambda_q$. The situation is slightly different for the solvation aspects since the solvent is in a generalized sense providing an external field for the molecule: while only the solvent reorganization energy $\lambda_s$ enters the second term of the right-hand side of eq 2.25, the equilibrium solvation free energies for the two VB states enter into $V_{0,0}$, via eq 2.24. It can also be noted that the sum of reorganization energies in eq 2.25 is related directly to the Stokes shift $S$, the difference of the absorption and relaxed emission energies in the special case that $\mathrm{MIX}_{\mathrm{eq}} = -1$, so that the ground state is purely N and the excited state is purely Z (see also Figure 1), namely, $S = 2(\lambda_q + \lambda_s)$. This follows directly from the definition $S = [G_Z(q_N^0, s_N^0) - G_N(q_N^0, s_N^0)] - [G_Z(q_Z^0, s_Z^0) - G_N(q_Z^0, s_Z^0)]$ in that case.

Our treatment above differs from that of two other discussions[8,10] of solvent effects on nonlinear optical properties within a two VB state framework. Chen et al.[8] have presented an extension of the gas-phase results of Lu et al.[7] to account for solvent effects. The treatment is the same as in the gas phase with a single BLA coordinate (and no solvent coordinate) but with an extra term added to the gas-phase diabatic gap; the proposed gap with solvent effects included is[8] (in our notation)

$$V_s = V_{\mathrm{gp}} + f_{\mathrm{eq}} G_{\mathrm{Z};s}(\epsilon) \tag{2.26}$$

where $V_{\mathrm{gp}}$ is the gas-phase diabatic gap and $G_{\mathrm{Z};s}(\epsilon)$ is the equilibrium solvation free energy for the zwitterionic state defined in eq 2.3.[39] Barzoukas et al.[10,11] suggest a related inclusion of solvent effects via the equilibrium solvation free energy of point dipoles. These treatments correctly suggest that the solvent can influence the nonlinear optical properties by stabilizing the zwitterionic form and reducing the diabatic gap compared to the gas phase. However, they have the difficulty that for the gap between the diabatic curves—which, as we have noted previously, can be viewed in terms of a Franck–Condon transition between those curves at fixed $q$ and $s$ values—the electronic polarization of the solvent will adjust, while the orientational solvent polarization will not; the latter, as emphasized earlier, is then by definition out of equilibrium with the higher energy VB state. This fundamental nonequilibrium solvation aspect of the problem cannot be treated solely by the introduction of an equilibrium solvation free energy and requires the type of analysis that we have presented in this paper.[40]

The consequences of a nonequilibrium treatment compared to an equilibrium one can be clarified by examination of the simplified case where all vibrational effects are absent and there are charges on the donor and acceptor groups only in the zwitterionic VB state. In addition, we consider only the solution case, where the solvent dielectric constant $\epsilon$ is equal to or greater than $\epsilon_\infty$. With these simplifications, the difference $D = V(\mathrm{MIX}_{\mathrm{eq}}) - V_s$ between eqs 2.25 and 2.26 for the diabatic gap evaluated at equilibrium in the ground-state reduces to

$$D = -Q_Z^2 S_F\left(1 - \frac{1}{\epsilon_\infty}\right)(1 - f_{\mathrm{eq}}) - Q_Z^2 S_F\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon}\right) f_{\mathrm{eq}} \tag{2.27}$$

where we have used eqs 2.24, 2.3, and 2.6. Since the fraction of zwitterionic character $f_{\mathrm{eq}}$ is in the range 0–1, this difference is always negative. In the most common case where the ground adiabatic state is more neutral than zwitterionic in character (cf. section III), this means that the nonequilibrium treatment of the solvent lowers the diabatic gap more than the equilibrium treatment. This indicates that one can expect larger solvent effects in the nonequilibrium treatment than in the equilibrium solvation analogue.

Returning to the general case, and following Barzoukas et al.,[10,11] we can relate the hyperpolarizabilities e.g., $\beta$, to the variation of lower order ones with solvent dielectric constant, e.g., $\partial\alpha/\partial\epsilon$. First, from eqs 2.16, the variation of $\mathrm{MIX}_{\mathrm{eq}}$ with $V$ in eq 2.14 and the fact that the $\epsilon$ variation of, e.g., $\alpha$, must arise from the $\epsilon$ dependence of $V$, one has

$$\alpha = F\,\mu_{\mathrm{CS}}\frac{\partial\mu_{\mathrm{g}}}{\partial\epsilon}$$

$$\beta = F\,\mu_{\mathrm{CS}}\frac{\partial\alpha}{\partial\epsilon}$$

$$\gamma = F\,\mu_{\mathrm{CS}}\frac{\partial\beta}{\partial\epsilon} \tag{2.28}$$

where $\mu_{\mathrm{g}}$ is the ground-state dipole moment and where $F$ is the factor

$$F = -\left(\frac{\partial V}{\partial\epsilon}\right)^{-1} = \left[-\frac{\partial V_{0,0}}{\partial\epsilon} + \frac{\partial\lambda_s}{\partial\epsilon}\mathrm{MIX}_{\mathrm{eq}}\right]^{-1}\left[1 + (\lambda_q + \lambda_s)\frac{\partial\mathrm{MIX}_{\mathrm{eq}}}{\partial V}\right] \tag{2.29}$$

where we have used eq 2.25 and the fact that $\mathrm{MIX}_{\mathrm{eq}}$ depends on $\epsilon$ only through the equilibrium diabatic gap.[41] The results in ref 11 (see also ref 10), based on an equilibrium solvation perspective, are equivalent to keeping only the term $-\partial V_{0,0}/\partial\epsilon$ in eq 2.29 (evaluated in ref 11 in a point dipole description). We have verified in model calculations that the additional terms in eq 2.29 accounting for nonequilibrium solvation effects (through the reorganization energy) and for the shifting electronic composition of the ground state (through $\partial\mathrm{MIX}_{\mathrm{eq}}/\partial V \propto \alpha$) are smoothly varying with $\epsilon$; thus, the basic qualitative conclusion of ref 11—that the shapes of $\alpha$, $\beta$, and $\gamma$ as a function of $\epsilon$ are similar to, though less symmetrical than, those obtained as a function of MIX—still applies.

**C. Diabatic Gap Referenced to a Nonpolar Solvent.** It is instructive to rearrange the formulas in a manner convenient for the introduction of experimental results. In particular, we are motivated by the experiments of Barzoukas, Blanchard-Desce, and co-workers who, from a combination of absorption and electrooptical absorption experimental data,[42] have been able to obtain the diabatic gap, the electronic coupling, and the neutral and zwitterionic dipole moments for a large number of molecules in low-polarity solvents.[12] Hence, we now proceed to show how one can use the knowledge of these quantities in a "reference" solvent to obtain the diabatic gap and equilibrium value of MIX in an arbitrary solvent. This procedure avoids difficulties associated with the application of simplified geometric model equations to molecules of some complexity, noted below eq 2.4, and with the charge difference $\Delta Q$ appropriate for an effective two VB state model (see discussion below eq 2.7). For convenience, we take the reference solvent to be that for which $\epsilon = \epsilon_\infty$, so that there is no orientational polarization (how this is dealt with in practice is discussed in section III). In what follows, we refer to the diabatic gap as a function of dielectric constant, $V(\epsilon)$, where it is implicit that this represents the gap at the global minimum on the ground electronic state surface.

For the case of a solvent with $\epsilon = \epsilon_\infty$, the diabatic gap can be written from eqs 2.24 and 2.25 as

$$V(\epsilon_\infty) = V_0 + \Delta G_s(\epsilon_\infty) - \lambda_q \,\mathrm{MIX}_{\mathrm{eq}}(\epsilon_\infty) \tag{2.30}$$

We have also noted that $\lambda_s$ is zero in this case, as can be easily seen from eq 2.6.[43] Analogously, for a solvent with a general static dielectric constant $\epsilon \neq \epsilon_\infty$, we have

$$V(\epsilon) = V_0 + \Delta G_s(\epsilon) - (\lambda_q + \lambda_s)\,\mathrm{MIX}_{\mathrm{eq}}(\epsilon) \tag{2.31}$$

Upon solving for $V_0$ in eq 2.30 and substituting into eq 2.31, we obtain

$$V(\epsilon) = V(\epsilon_\infty) + \Delta G_s(\epsilon) - \Delta G_s(\epsilon_\infty) - (\lambda_q + \lambda_s)\,\mathrm{MIX}_{\mathrm{eq}}(\epsilon) + \lambda_q \,\mathrm{MIX}_{\mathrm{eq}}(\epsilon_\infty) \tag{2.32}$$

It is easy to see from the definition of $\Delta G_s = G_{\mathrm{Z};s} - G_{\mathrm{N};s}$ and eq 2.3 that this reduces to

$$V(\epsilon) = V(\epsilon_\infty) - \lambda_s\left(\frac{Q_\mathrm{Z} + Q_\mathrm{N}}{Q_\mathrm{Z} - Q_\mathrm{N}}\right) - (\lambda_q + \lambda_s)\,\mathrm{MIX}_{\mathrm{eq}}(\epsilon) + \lambda_q \,\mathrm{MIX}_{\mathrm{eq}}(\epsilon_\infty) \tag{2.33}$$

This is a central result as it relates the diabatic gap and equilibrium value of MIX in an arbitrary solvent to the values in a reference solvent (here taken to be that with $\epsilon = \epsilon_\infty$). This equation and eq 2.14 form a nonlinear equation that can be solved in an iterative manner given a knowledge of $\lambda_q$ and $\lambda_s$.

The unknown reorganization factor in eq 2.6 for $\lambda_s$, $\Delta Q^2 S_\mathrm{F}$, can be derived for a molecule from solvatochromic data in which the absorption energy is measured in different solvents. The absorption energy is given by the electronically *adiabatic* gap, from which in the two VB state model the diabatic gap can be obtained from eq 2.17 as

$$V(\epsilon) = [E_{\mathrm{gap}}^2(\epsilon) - 4t^2]^{1/2} \tag{2.34}$$

With the absorption energy in the reference solvent $E_{\mathrm{gap}}(\epsilon_\infty)$ known, then measurement of $E_{\mathrm{gap}}(\epsilon_2)$ in a second solvent yields $V(\epsilon_2)$ and $\mathrm{MIX}_{\mathrm{eq}}(\epsilon_2) = -V(\epsilon_2)/E_{\mathrm{gap}}(\epsilon_2)$ (through eq 2.14). Solution of eq 2.33 for $\lambda_s$ leads to the following expression for $\Delta Q^2 S_\mathrm{F}$ in terms of the measured quantities and $\lambda_q$

$$\Delta Q^2 S_\mathrm{F} = \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_2}\right)^{-1} \times \left\{\frac{V(\epsilon_\infty) - V(\epsilon_2) + \lambda_q[\mathrm{MIX}_{\mathrm{eq}}(\epsilon_\infty) - \mathrm{MIX}_{\mathrm{eq}}(\epsilon_2)]}{(Q_\mathrm{Z} + Q_\mathrm{N})/(Q_\mathrm{Z} - Q_\mathrm{N}) + \mathrm{MIX}_{\mathrm{eq}}(\epsilon_2)}\right\} \tag{2.35}$$

The practical implementation of this will be discussed in section III. We note that here and in eq 2.33 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, namely, $(\mu_\mathrm{Z} + \mu_\mathrm{N})/(\mu_\mathrm{Z} - \mu_\mathrm{N})$.

The reorganization energy $\lambda_q$ associated with the BLA coordinate is perhaps the most challenging parameter to obtain. One could, for example, perform detailed molecular calculations for individual molecules along the lines of ref 7 to determine it. Another possibility is to extract it from Stokes shift $S$ measurements for the molecule in the $\epsilon = \epsilon_\infty$ solvent. Recall from the discussion of the very simplified case in section II.B that $S = 2(\lambda_q + \lambda_s)$, which is just $2\lambda_q$ when $\epsilon = \epsilon_\infty$; how this could work in the general case is discussed in ref 44.

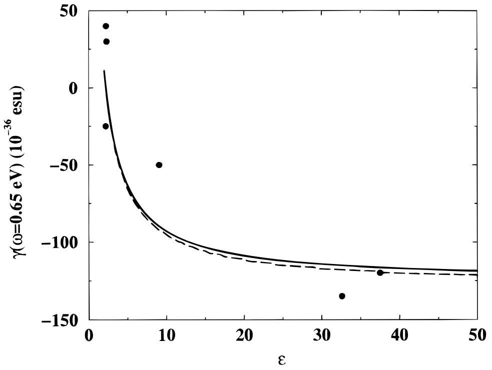


**Figure 2.** Comparison of $\gamma(\omega = 0.65\ \mathrm{eV})$ for the 1,1-dicyano-6-(dibutylamine) hexatriene molecule as a function of the solvent dielectric constant $\epsilon$ obtained from the present model (solid line), the model of Chen et al. (ref 8) (dashed lines), and the experimental results of Marder et al. (ref 3) (filled circles). Here $\gamma$ has been divided by a factor of 5 to compare with rotationally averaged experimental results.[3,8]

## III. Applications

In the present section, we apply our theoretical model to the hyperpolarizabilities of various push−pull polyenes for which at least some relevant solution data are available.

We first consider the application of the model described in section II to the 1,1-dicyano-6-(dibutylamine)hexatriene molecule treated by Chen et al.[8] These authors used their model for the inclusion of solvent effects to calculate the polarizabilities $\alpha$, $\beta$, $\gamma$, and $\delta$ as a function of solvent dielectric constant $\epsilon$. In particular, they compared their results for $\gamma$ to the third harmonic generation experiments of Marder et al.[3] and found good agreement.

Here we show that the present model is equally capable of reproducing the experimental polarizability, $\gamma$, if we obtain the necessary parameters from the model itself (as opposed to the alternative of using the parameters found by Chen et al. in the present model; the values of the parameters depend on the model used to interpret the experimental results). For this molecule we assume, as do Chen et al., that the neutral VB state has no dipole moment ($Q_\mathrm{N} = 0$). We adopt their values for $q_\mathrm{N}^0$, $q_\mathrm{Z}^0$, and $k_q$ giving $\lambda_q = 0.966$ eV as well as the electronic coupling, $t = 1.184$ eV. ($k_q$ is obtained from a quantum chemistry calculation[8] while $t$ is derived from experimental results.[3,8]) The value of $\Delta Q^2 S_\mathrm{F} = Q_\mathrm{Z}^2 S_\mathrm{F}$ is obtained from eq 2.35 (rather than from eq 2.26 as in ref 8) using the absorption energies in dioxane ($\epsilon_1 = 2.209$) with $E_{\mathrm{gap}}(\epsilon_1) = 2.648$ eV and acetonitrile ($\epsilon_2 = 37.5$) with $E_{\mathrm{gap}}(\epsilon_2) = 2.604$ eV; $E_{\mathrm{gap}}(\epsilon_\infty)$ is obtained from the linear relationship between $E_{\mathrm{gap}}(\epsilon)$ and $(1/\epsilon_\infty - 1/\epsilon)$ established from the values in dioxane and acetonitrile (see below for a discussion of the $\epsilon_\infty$ value). The reference diabatic gap, $V(\epsilon_\infty)$, and equilibrium value of MIX, $\mathrm{MIX}_{\mathrm{eq}}(\epsilon_\infty)$, can be obtained from the absorption energy $E_{\mathrm{gap}}(\epsilon_\infty)$ using eqs 2.34 and 2.14. Finally, we use the same dipole moment $\mu_{\mathrm{CS}} = \mu_\mathrm{Z} - \mu_\mathrm{N} = \mu_\mathrm{Z} = 25.9$ D found in ref 8 by matching the value of $\gamma$ in acetonitrile; this determination is independent of the model for the solvent as it only involves the magnitude of $\mu_{\mathrm{CS}}$.

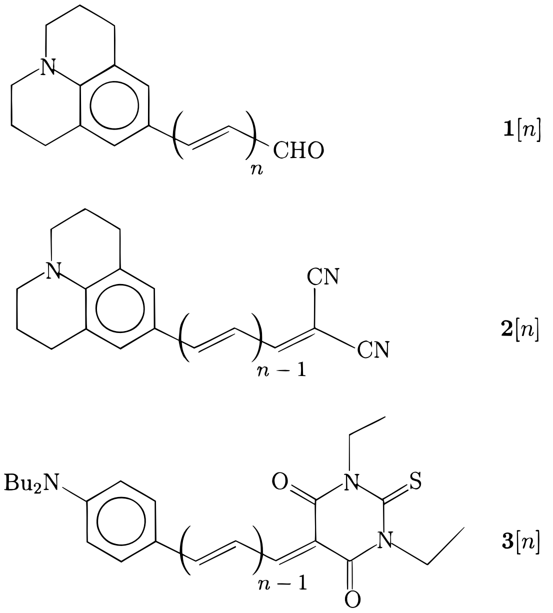
Figure 2 compares $\gamma(\omega = 0.65\ \mathrm{eV})$ versus the solvent dielectric constant for this molecule obtained from the present model, the model of Chen et al.,[8] and the experimental values of Marder et al.[3] (We have used the correction factor of ref 8 to obtain the values of $\gamma$ at $\omega = 0.65$ eV from the calculated static, $\omega = 0$, values of $\gamma$). Both models reproduce the experimental polarizability well. The particularly good agreement for $\gamma$ in acetonitrile is a natural result of using this solvent in determining $Q_Z^2 S_F$ and $\mu_{CS}$ as described above. That both models should exhibit the same solvent dependence in Figure 2 is initially surprising in view of our discussion around eq 2.27, where it was indicated that stronger solvent variation with the solvent was to be expected for the present model. The resolution of this seeming contradiction is that different values of the parameter $Q_Z^2 S_F$ in the two models result from the present type of fitting. In order to reproduce the experimental hyperpolarizability $\gamma$ in Figure 2, the model of Chen et al. requires $Q_Z^2 S_F = 0.536$ eV while the present model requires a value of almost a factor of 2 smaller, $Q_Z^2 S_F = 0.283$ eV. Thus the intrinsically stronger solvent dependence of the present model, carried in, e.g., the solvent reorganization energy eq 2.6, here proportional to $Q_Z^2 S_F$, must be muted by the smaller value of $Q_Z^2 S_F$ in the sort of fitting to experiment described above.

Having established that both models are capable of reproducing the experimental hyperpolarizability $\gamma$, we now turn to a closer examination of the properties of the models. To this end, we perform calculations in which the same parameters are input into both models. To this end, we perform calculations in which the same parameters are input into both models and compare the results as a function of solvent polarity. We consider molecules for which experimental absorption and electrooptical absorption measurements have been made in dioxane.[42] (For dioxane, $\epsilon$ is slightly greater than $\epsilon_\infty$,[45] so it cannot serve as the reference solvent for which $\epsilon = \epsilon_\infty$; the reference solvent information must instead be determined by extrapolation, as discussed below.[46]) These measurements give the diabatic gap in dioxane $V(\epsilon_1)$, the electronic coupling $t$, $\mathrm{MIX}_{eq}(\epsilon_1)$, and the dipole moments in the neutral and zwitterionic states, $\mu_N$ and $\mu_Z$, respectively; recall that the coupling $t$ is being treated as independent of the solvent.[47] Solvatochromic data $E_{gap}(\epsilon)$ will be used (see below) to obtain $\Delta Q^2 S_F$, which gives the solvent reorganization energy $\lambda_s$. As for the vibrational reorganization energy $\lambda_q$, the Stokes shift data necessary to implement the considerations of ref 44 is not currently available. Here we adopt the simple expedient of assuming that $\lambda_q = 0.966$ eV is the same as in ref 8 and the same for all the molecules.

Scheme 2 presents structures for the neutral-state configurations of the molecules studied.[42] Three series of push–pull phenylpolyenes bearing different D/A pairs have been examined. Series **1**[$n$] and series **2**[$n$] have a julolidine electron-donating group, whereas series **3**[$n$] presents a weaker, although more soluble *N*,*N*-dibutylaniline moiety. Three different electron-withdrawing groups of increasing acceptor strength have been investigated: carboxaldehyde for series **1**[$n$], dicyanomethylene for series **2**[$n$], and diethylthiobarbituric acid for series **3**[$n$]. (We have treated molecules with reasonably short chain lengths because the flexibility of the molecule[12] and the validity of the two-state model[30] both become issues for longer chains.) The various parameters from the dioxane measurements are collected in Table 1. The equilibrium values $\mathrm{MIX}_{eq}$ listed there for dioxane solvent indicate that, in this low-polarity solvent, the ground adiabatic state is predominantly neutral in character for all the molecules. In the remainder of this section, we will refer to the present model as NES (nonequilibrium solvation) and that of ref 8 as ES (equilibrium solvation) for convenience.

As indicated in section II.C, the solvatochromic data[48] is used to obtain $\Delta Q^2 S_F$ via eq 2.35. In principle, two solvents would suffice for this purpose. However, in practice, there is too much scatter in the experimental absorption energies in different solvents, and thus we fit the absorption energy versus $(1/\epsilon_\infty - 1/\epsilon)$ to a straight line (requiring that the line pass through the point for dioxane). The intercept from this linear fit gives $E_{gap}(\epsilon_\infty)$, which is used along with the electronic coupling, $t$, to obtain $V(\epsilon_\infty)$, eq 2.34, and $\mathrm{MIX}_{eq}(\epsilon_\infty) = -V(\epsilon_\infty)/E_{gap}(\epsilon_\infty)$, the values for the reference solvent as discussed in section II.C. Using the above linear fit to the absorption energies, any solvent with $\epsilon \neq \epsilon_\infty$ can be then be used in eq 2.35 to obtain $\Delta Q^2 S_F$ (the result is insensitive to the choice of the second solvent by virtue of the linear fit). The values obtained for $\Delta Q^2 S_F$ using this procedure are given in Table 1 for the molecules in Scheme 2.[49] The diabatic gap and $\mathrm{MIX}_{eq}$ for a given value of $\epsilon$ are found by solving eqs 2.33 and 2.14 self-consistently. The polarizabilities are then calculated using these values according to eqs 2.16. The same parameters are adapted to the ES model for purposes of comparison, that is, $V_0$ (see eq 2.24 and surrounding discussion) is chosen such that both models give the same diabatic gap in the reference solvent, $V(\epsilon_\infty)$, and the value of $\Delta Q^2 S_F = Q_Z^2 S_F$ used is obtained from eq 2.35 but assuming a dipole moment of zero in the neutral state.

**SCHEME 2**



The results of the NES model presented in section II for the polarizabilities α, $\beta$, and $\gamma$ of the **1**[1] molecule as a function of solvent dielectric constant are shown in Figure 3, as are the values obtained from the ES model. We pause to note that in all the calculations presented here we assume a value for the high-frequency dielectric constant of $\epsilon_\infty = 2$. The choice of $\epsilon_\infty = 2$ may be considered somewhat arbitrary since the high-frequency dielectric constant varies with solvent and is not precisely 2. To test the consequences of this assumption we have repeated the calculation of the (hyper)polarizabilities α, $\beta$, and $\gamma$ for the **1**[1] molecule for each solvent for which solvatochromic data was available[48] using the individual $\epsilon_\infty$ values for each solvent. The results are shown in Figure 3, and the values obtained are within 2% of those where $\epsilon_\infty$ was taken to be 2 for all solvents for α and $\beta$ and within 1% for $\gamma$. In addition, the character of the results is the same in all cases and the approximation is therefore quite reasonable, especially for the present purposes.

Returning to the main thread, from Figure 3, it is immediately apparent that for the **1**[1] molecule, there are not large quantitative differences in the predictions of the NES and ES

**TABLE 1: Parameters for the Molecules Shown in Scheme 2 for Various Chain Lengths, *n*. Given Are the Dipole Moments in the Neutral and Zwitterionic VB States ($\mu_N$ and $\mu_Z$), the Electronic Coupling (*t*), the Equilibrium Diabatic Gap in Dioxane ($V_{eq}$), the Equilibrium Value of MIX in Dioxane ($MIX_{eq}$), and the Reorganization Parameter $\Delta Q^2 S_F$**

| molecule | $\mu_N$ (D)[a] | $\mu_Z$ (D) | *t* (eV) | $V_{eq}$ (eV) | $MIX_{eq}$ | $\Delta Q^2 S_F$ (eV)[b] |
|---|---|---|---|---|---|---|
| **1**[1] | 3.7 | 21.0 | 1.171 | 2.083 | −0.66 | 0.326 |
| **2**[1] | 5.2 | 22.4 | 1.223 | 1.337 | −0.48 | 0.270 |
| **3**[1] | 1.6 | 21.8 | 1.171 | 0.9639 | −0.38 | 0.492 |
| **3**[2] | 2.7 | 27.8 | 0.9432 | 1.171 | −0.52 | 0.473 |

[a] Parameters $\mu_N$, $\mu_Z$, *t*, and $V_{eq}$ are derived from electrooptical absorption data[42] as described in ref 12. [b] $\Delta Q^2 S_F$ is obtained by fitting solvatochromic data,[48] as detailed in section II.C.

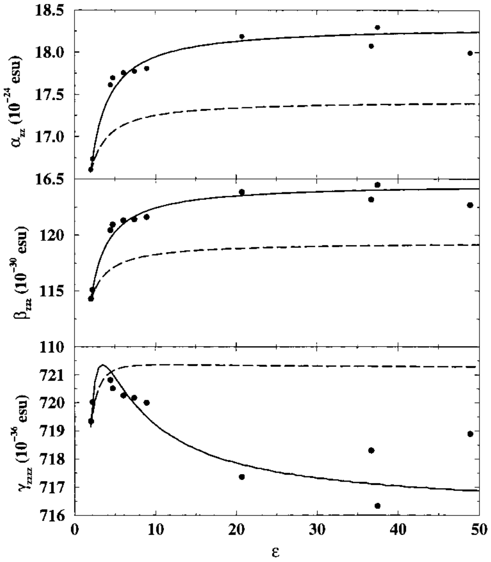


**Figure 3.** α, $\beta$, and $\gamma$ are shown versus the solvent dielectric constant, $\epsilon$, for the **1**[1] molecule. Results are shown for the present model (solid line) and the model of Chen et al. (ref 8) (dashed line). Also plotted (solid circles) are α, $\beta$, and $\gamma$ obtained by using the individual $\epsilon_\infty$ values specific to different solvents. (See the text.)

models for the absolute magnitudes of the polarizabilities. There are, however, significant quantitative differences in the model predictions for the variation of α and $\beta$ as a function of solvent polarity; the NES model predicts a significantly larger increase (by about a factor of 2) in α and $\beta$ over the range of $\epsilon$ shown. This is in line with the expectations discussed around eq 2.27.

Another interesting consequence of this difference in solvent influence in the two models is seen in Figure 3 in the plot of $\gamma$ versus $\epsilon$ for the **1**[1] molecule. The two models make qualitatively different predictions about which solvent should be used to generate the maximum hyperpolarizability. The NES model predicts that it should be a solvent with $\epsilon \approx 3.5$ while the ES model that it should instead be a high-polarity solvent. This difference arises as follows. The relationship between the polarizabilities and $q_{eq}$ (or $MIX_{eq}$) has been well documented:[7,8,10] changing the amount of zwitterionic character (which is related to the BLA coordinate[38]) in the ground state modifies the polarizabilities in a well-defined way described by eqs 2.16. For example, as $MIX_{eq}$ varies from −1 to 1 (or equivalently $f_{eq}$ from 0 to 1), $\gamma$ goes from zero, through a maximum at $MIX_{eq} = -(3/7)^{1/2}$, a deep minimum at $MIX_{eq} = 0$, another maximum at $MIX_{eq} = +(3/7)^{1/2}$, and back to zero. The solvent preferentially stabilizes the zwitterionic state relative to the neutral state, thereby increasing the zwitterionic character of the adiabatic ground state with increasing solvent polarity. In the case of the **1**[1] molecule in dioxane, $MIX_{eq} < -(3/7)^{1/2}$ and the NES model predicts that $MIX_{eq}$ increases with solvent polarity with $\gamma$ first increasing, then reaching a maximum and finally decreasing. On the other hand, the ES model, with a reduced influence of the solvent, finds that $\gamma$ only barely passes the maximum. Thus, the different qualitative predictions by the two models are due to a difference in the quantitative predictions of the change in $MIX_{eq}$ with the solvent polarity, with the NES model giving a significantly larger change in $MIX_{eq}$. Having said this, it has to be observed that, as a result of $\gamma$ being near its maximum, the numerical value for $\gamma$ does not change much with solvent polarity. That is, near the maximum, $\partial\gamma/\partial MIX_{eq}$ is small, resulting in only a slight change in the absolute value of the hyperpolarizability. Thus, while the qualitative predictions are quite different for the two models, the quantitative predictions of $\gamma$ are very similar.

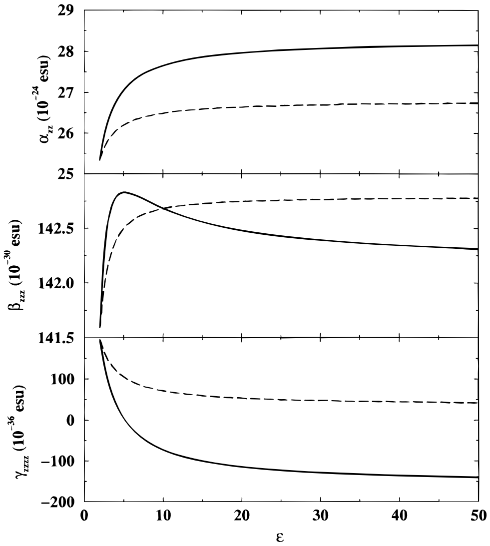


**Figure 4.** α, $\beta$, and $\gamma$ are shown versus the solvent dielectric constant, $\epsilon$, for the **2**[1] molecule. Results are shown for the present model (solid line) and the model of Chen et al. (ref 8) (dashed line).

Figure 4 shows the polarizabilities α, $\beta$, and $\gamma$ as a function of solvent dielectric constant for a different molecule, **2**[1]. Focusing first on α and $\gamma$, one sees that again the NES model predicts a stronger solvent variation than the ES model. In addition, significant differences in the magnitude and sign of $\gamma$ are predicted.

Figure 4 also shows, for the $\beta$ variation for the **2**[1] molecules, that the observation of different qualitative predictions for the **1**[1] molecule is not an isolated case, and it is not restricted to $\gamma$ (cf. Figure 3). Here, the NES and ES models predict qualitatively different behavior for $\beta$. Again, a small change in the magnitude of the hyperpolarizability is observed as a result of being near the maximum of $\beta$ as a function of $MIX_{eq}$ (which occurs at $MIX_{eq} = -(1/5)^{1/2}$. Comparison of the change in $\beta$ with solvent polarity for this molecule with that for the **1**[1] molecule emphasizes the small quantitative changes in the hyperpolarizabilities near a maximum. A similar comparison of $\gamma$ versus $\epsilon$ for these two molecules (**1**[1] and **2**[1]) reveals the same feature. Here again, significant differences in the magnitude of $\gamma$ are predicted between the NES and ES models.

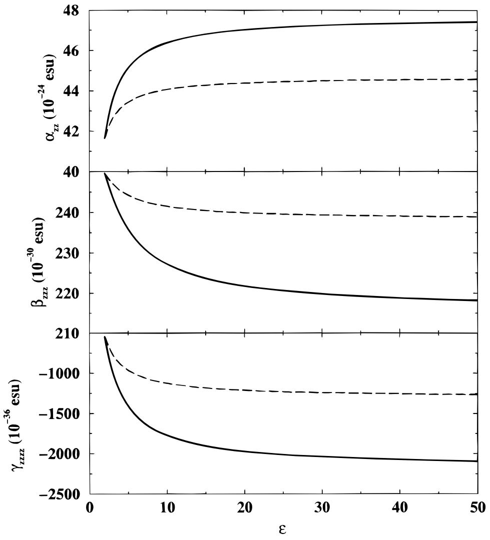


**Figure 5.** Same as Figure 4 but for the **3**[1] molecule.

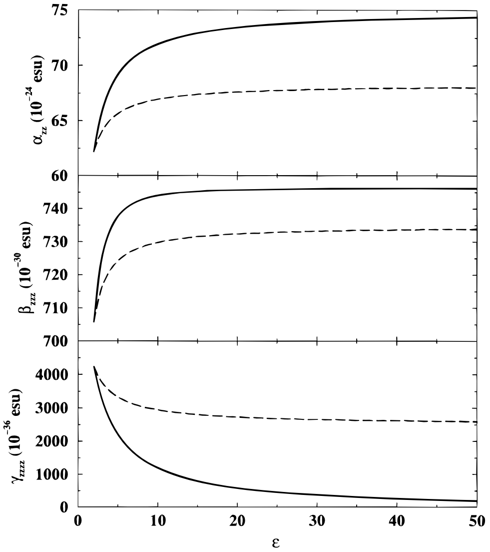


**Figure 6.** Same as Figure 4 but for the **3**[2] molecule.

Note that the maximum in $\beta$ occurs at the same value of $\mathrm{MIX}_{eq}$ that gives $\gamma = 0$.[10]

Figures 5 and 6 show calculated α, $\beta$, and $\gamma$ values versus $\epsilon$ for the **3**[1] and **3**[2] molecules. For these molecules, the predicted solvent trends are monotonic, since $\mathrm{MIX}_{eq}$ is not immediately near any value for which the (hyper)polarizabilities are extrema. Compared to the ES model, the NES model predicts a more rapid variation with solvent, and for the $\gamma$ values significant differences in magnitude, especially for the longer chain case $n = 2$.

Unfortunately, experimental data for the nonlinear optical parameter variation with solvent polarity do not yet exist for the molecules of Scheme 2, so that the above calculations serve as predictions. Since experimental uncertainty in $\beta$ measurements is not expected to ascertain unambiguously the solvent treatment (ES or NES) for the previous molecules, further experimental efforts are underway to test the predictions. In particular, improvement can be anticipated either by focusing on push−pull molecules showing more pronounced $\beta$ dependencies[50−52] or on examination of the solvent dependence of the cubic hyperpolarizabilities (work in progress).

## IV. Concluding Remarks

We have developed a treatment of push−pull molecules that, within a two VB state model, accounts for both the bond length alternation coordinate and a nonequilibrium solvent description, generalizing earlier equilibrium solvation treatments in this context.[8,10,11] We derived expressions for the quantities ($V(\epsilon)$ and $\mathrm{MIX}_{eq}(\epsilon)$) necessary for the calculation of the nonlinear optical properties, namely, the (hyper)polarizabilities, of this class of molecule. All the model parameters characterizing a given molecule, except the vibrational reorganization energy $\lambda_q$, can be obtained in a straightforward manner from experimental measurements; when Stokes shift measurements become available, $\lambda_q$ can also be obtained.[44] In particular, the extraction of relevant parameters for the nonlinear optical property problem via experimental (linear) solvatochromic data avoids difficulties and ambiguities both with charge parameters in the effective two VB state model and with the application of simplified cavity models[8,10,11,15−18,20] to the complex push−pull molecules of interest (though perhaps more sophisticated cavity models[19,21−23,53] might also play a useful role here).

We applied this formulation to the calculation of the first three polarizabilities (α, $\beta$, and $\gamma$) for a number of molecules with different electron donor and acceptor groups and varying chain lengths. We found both qualitative and quantitative differences with the results from the equilibrium solvation model of Chen et al.,[8] which displays a weaker influence of the solvent on the polarizabilities.

The present formulation could in principle be applied for push−pull molecules immersed in more general environments. Here the challenge will be to find useful ways to characterize the analogues of the solvation contributions to the free energies and the solvent reorganization energy.[54] In particular host−guest polymeric materials that are interesting for photonic materials (such as low-$T_g$ polymeric systems for photorefractive applications)[55] could be amenable to similar treatment. This is of particular interest since controlling the environment can be a very effective way of tuning the linear and nonlinear responses.

The present treatment can be generalized in a number of ways. We have treated the electronic polarization of the solvent in the Born−Oppenheimer approximation, and in general this approximation needs generalization[56] when the electronic coupling is large. Estimates[57] indicate that corrections would not be large for the sorts of molecules discussed in the present work, where the ground electronic state does not approach a fifty−fifty mixture of the two VB states; in those cases where the ground state can be so mixed, these corrections could be necessary[56] for an accurate description.

We have employed throughout a two VB state perspective, whose validity has been supported in certain contexts[7,8,14] (although as noted in section II.A, this is an effective description). Nontheless, it is certainly possible that, especially for longer conjugated chains, a description involving more such localized states will be required.[30] The recent multistate formulation of Lu et al.[58] is particularly attractive in this connection, and the necessary formalism for describing such multiple states in a solution context is in place.[59] One test for the necessity of further states would be experimental scrutiny of the predictions of the present model for molecular nonlinear optical properties as a function of solvent polarity; these are in progress.[50] Another experimental probe would be studies of excited electronic state dynamics of the push−pull molecular systems discussed within. With the model parameters listed in Table 1 we have confirmed that there will be a single minimum in the excited electronic state for the Scheme 2 molecules in solution, so that dynamics subsequent to a Franck−Condon transition from the equilibrated ground electronic state would result in a simple time-dependent fluorescence Stokes shift as relaxation to equilibrium in the excited state proceeds;[60] involvement of more than two VB states could lead instead to more complex dynamics involving the transition between the states.[61] Experiments to probe the dynamics are underway.[62]

**Acknowledgment.** This work was supported in part by the U.S. National Science Foundation through Grant CHE-970049 (J.T.H.). A portion of this work was performed in May−June 1997, when J.T.H. was Professor Invité at ENS, and he thanks the members of the Département de Chimie for their hospitality. J.T.H. also gratefully acknowledges receipt of a University of Colorado Research and Creative Work Fellowship (1997−98) in support of this work. The Centre National de la Recherche Scientifique is acknowledged for financial support.

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(32) Zichi, D. A.; Ciccotti, G.; Hynes, J. T.; Kapral, R. *J. Phys. Chem.* **1989**, *93*, 6261.

(33) This is an oversimplification; see ref 18 and the discussion around eq 2.20.

(34) The two-level expression of (hyper)polarizabilities are easily derived using the quantum-perturbed expressions given in: Ward, J. F. *Rev. Mod. Phys.* **1965**, *37*, 1.

(35) These expressions assume[10] that the “bare” transition moment $\langle N|\mu|Z\rangle$ vanishes, an assumption recently investigated by Cave and Newton (*Chem. Phys. Lett.* **1996**, *249*, 15). In addition, the transition moment $\mu_{eg} = \langle g|\mu|e\rangle$ can be readily related[10] to $\mathrm{MIX}_{eq}$, so that the developments within apply equally to $\mu_{eg}$.

(36) Equations 2.16 are derived[34] in terms of a molecule in a constant external electric field of infinite wavelength, such that the dipole moment can be used to characterize the molecule. On the other hand, a point dipole description of the solute molecule in interaction with polarization fields in the solvent is not expected to be very accurate for solutes the size of the push−pull polyenes and is avoided in the present treatment.

(37) Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.* **1992**, *97*, 7590.

(38) One should notice from eq 2.20 that the condition MIX = 0 (and thus that $\beta = 0$ from eq 2.16b) is not the same as the condition $q_{eq} = 0$ (e.g., equal bond lengths in the intervening chain; with the usual definition of BLA, this is the “cyanine limit”[3,5,12]). It is only when the special mirror condition $q_Z^0 = -q_N^0$ holds that the two conditions coincide. Note also that when the mirror condition holds MIX becomes proportional to BLA. See also ref 18 for a related discussion.

(39) It was assumed in ref 8 that the neutral state carries no dipole moment, but this is a detail irrelevant for the main point made in the text.

(40) These considerations are relevant even in the case that the ground state is purely neutral, $f_{eq} = 0$, $\mathrm{MIX}_{eq} = -1$: an equilibrium solvation based relation such as eq 2.26 will predict no solvent effect, whereas the nonequilibrium solvation based eq 2.25 predicts a solvent influence on the diabatic gap (see also Figure 1).

(41) $\mathrm{MIX}_{eq}$ and $\partial \mathrm{MIX}_{eq}/\partial V$ can be readily expressed respectively in terms of $\mu_g$ and $\alpha$.[11]

(42) Blanchard-Desce, M.; Alain, V.; Midrier, L.; Wortmann, R.; Lebus, S.; Glania, C.; Krämer, P.; Fort, A.; Muller, J.; Barzoukas, M. *J. Photochem. Photobiol. A* **1997**, *105*, 115.

(43) It is interesting to note that, with the simplifications given above eq 2.27, when the solvent dielectric constant is the nonpolar solvent value $\epsilon = \epsilon_\infty$, the nonequilibrium eq 2.25, or equivalently eq 2.30 with $\lambda_q = 0$, for the equilibrium diabatic gap becomes independent of the zwitterionic fraction $f_{eq}$, while instead eq 2.26 predicts a dependence on $f_{eq}$. That there should in fact be no $f_{eq}$ dependence follows from the fact that, when $\epsilon = \epsilon_\infty$, the orientational polarization coordinate $s$ completely disappears, and there is only solvent electronic polarization, whose equilibrium solvation contribution to the zwitterionic VB state $-(1 - 1/\epsilon_\infty)\, Q_Z^2 S_F$, is always the same, independent of what the composition of the ground adiabatic state might be: in a Franck−Condon transition between two VB states, the solvent electronic polarization adjusts instantly.

(44) When $\epsilon = \epsilon_\infty$, there is no solvent reorganization $\lambda_s = 0$, and eq 2.8 for the adiabatic surfaces $G_{e,g}$ can be expanded up to quadratic order about the equilibrium positions $q_{e,g}$ for the vibrational coordinate as $G_{e,g} = G_{e,g;eq} + k_{e,g}(q - q_{e,g})^2/2$ with a Stokes shift (difference of the absorption energy $E_-$ at $q_g$ and emission energy $E_+$ at $q_e$) given by $S = (q_e - q_g)^2(k_e + k_g)/2$. The equilibrium positions and force constants are found by expansion of eq 2.8, with eqs 2.1, 2.2, and 2.7, to be

$$q_{e,g} = \frac{q_Z + q_N}{2} \pm \frac{\sqrt{E_\pm^2 - 4t^2}}{E_\pm}\,\frac{(q_Z - q_N)}{2}$$

$$k_{e,g} = k_q\left[1 \pm \lambda_q \frac{4t^2}{E_\pm^3}\right]$$

where the adiabatic state force constants involve the polarizabilities of the states. These can be inserted into the expression for $S = E_- - E_+$, giving

a means to determine $\lambda_q = k_q(q_Z - q_N)^2/2$, given that $E_+$, $E_-$, and $t$ are known. We have confirmed, for the molecules in Scheme 2 of section III, that this is accurate to within 7%, i.e., an input $\lambda_q$ is recovered from the approximate $S{-}\lambda_q$ connection above to within 7%. If desired, a more accurate relation involving anharmonic terms in $G_{e,g}$ can be developed.

(45) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*; CRC Press, Inc.: Boca Raton, FL, 1983.

(46) It would be convenient to have $V(\epsilon)$, $t$, and $\mathrm{MIX}_{\mathrm{eq}}$ available for the Scheme 2 molecules in cyclohexane, for which $\epsilon$ is very close to $\epsilon_\infty$;[45] unfortunately, for most of the molecules solubility requirements for the various polarizability measurements rule this out.

(47) Manipulations similar to those used to derive eq 2.33 can be used to support this assumption. From eqs 3.33 and 3.35 of ref 56, the renormalized coupling $t_s$ due to solvent interaction, without any vibrational contribution, is approximately

$$t_s = t - [\Delta V_{\mathrm{solv}}(\epsilon) - \Delta V_{\mathrm{solv}}(\epsilon_\infty)]\frac{E_{\mathrm{ex}}}{E_\Delta}$$

where $t$ is the coupling in a solvent with $\epsilon = \epsilon_\infty$, $\Delta V_{\mathrm{solv}}$ is the solvent contribution to the equilibrium diabatic gap for a given dielectric constant, and $E_{\mathrm{ex}}/E_\Delta$ is the ratio of the vacuum exchange field (the field when the charge distribution is governed by $2\psi_N\psi_Z$) to the difference field ($E_Z - E_N$) where $E_{Z,N}$ are the fields associated with the charge distributions governed by $|\psi_Z|^2$ and $|\psi_N|^2$, respectively. With the same manipulations used to obtain eq 2.33 this gives

$$t_s = t + \lambda_s\left[\frac{Q_Z + Q_N}{Q_Z - Q_N} + \mathrm{MIX}_{\mathrm{eq}}(\epsilon) - \mathrm{MIX}_{\mathrm{eq}}(\epsilon_\infty)\right]\frac{E_{\mathrm{ex}}}{E_\Delta}$$

In the dipole approximation, $E_{\mathrm{ex}} = 0$ since there is no transition moment in the VB description used herein,[7,8,10,11] and in general $E_{\mathrm{ex}}$ is small compared to the difference field. Thus $t_s \approx t + \lambda_s c$, where $c$ is small compared to unity (the term in brackets is of order unity). Anticipating the results of section III, since $t$ in dioxane is (cf. Table I) of order 1 eV and $\lambda_s$ is at most ~0.25 eV, $t_s = t$ to a very good approximation.

(48) Alain, V.; Blanchard-Desce, M. Unpublished results. Absorption wavelengths (in nm) for the Scheme 2 molecules in different solvents:

**1**[1]. $\lambda_{\max}$: 389 (cyclohexane); 396 (dioxane); 397 (diethyl oxide); 397 (ethyl acetate); 399 (tetrahydrofurane); 410 (dichloromethane); 402 (acetone); 406 (acetonitrile); 407 (dimethylformamide (DMF)); 414 (dimethyl sulfoxide (DMSO)).

**2**[1]. $\lambda_{\max}$: 435 (cyclohexane); 445 (dioxane); 443 (diethyl oxide); 449 (ethyl acetate); 451 (tetrahydrofurane); 459 (dichloromethane); 453 (acetone); 458 (acetonitrile); 464 (DMF); 464 (DMSO).

**3**[1]. $\lambda_{\max}$: 479 (cyclohexane); 486 (dioxane); 486 (diethyl oxide); 494 (ethyl acetate); 497 (tetrahydrofurane); 504 (dichloromethane); 500 (acetone); 502 (acetonitrile); 507 (DMF); 513 (DMSO).

**3**[2]. $\lambda_{\max}$: 546 (cyclohexane); 556 (dioxane); 556 (diethyl oxide); 569 (ethyl acetate); 572 (tetrahydrofurane); 584 (dichloromethane); 578 (acetone); 581 (acetonitrile); 591 (DMF); 598 (DMSO).

(49) One reason for the (comparatively small) values of $\Delta Q^2 S_F$ (which leads to comparatively small solvent reorganization energies via eq (2.6) is likely to be that the effective charge transfer $\Delta Q$ between the N and Z states is less than a full electron. For example, for molecule **1**[1], the estimated distance from the nitrogen to the oxygen is 8.9 Å. With the dipole moment change $\mu_Z - \mu_N = 17.3$ D from Table 1, this gives $\Delta Q = 0.40e$. (See also ref 28.)

(50) Muller, J.; Fort, A.; Barzoukas, M.; Alain, V.; Blanchard-Desce, M. Work in progress.

(51) As noted in refs 44, 47, 52, and 57, refinements can be made within the basic two VB state description presented herein.

(52) According to estimates (see: Castiglioni, C.; Del Zoppo, M.; Zerbi, G. *J. Raman Spectrosc.* **1993**, *24*, 485), the frequency of the BLA vibration $q$ is in the 1000−1600 cm$^{-1}$ range, so that there are quantized vibrational levels for this coordinate, not treated explicitly in the present work. Any quantization of $q$ should be effected after the two VB states are mixed by the coupling $t$ (vibrations slow compared to electrons), so that there are $q$ vibrational levels for each of the adiabatic ground (g) and excited (e) electronic states. This aspect will influence various energy gaps in the problem, and an estimate of its influence in altering gaps can be gained by considering the case where the adiabatic state energy gap (ignoring vibration) is the smallest, i.e., when $\mathrm{MIX}_{\mathrm{eq}} = 0$ and the equilibrium adiabatic gap (ignoring vibration) is $2t$. Quantized $q$ vibration will add to the gap $2t$ the difference $\delta$ in the zero-point energies in the e and g states. From the e and g state force constant expressions in ref 44, this is approximately $\delta = (\hbar\omega_q/2)(\lambda_q/2t)$, where $\omega_q$ is the $q$ frequency in either of the diabatic N and Z states. Since $\lambda_q$ is about 1 eV (see text) and $t$ is about 1 eV (see Table 1), even if $\omega_q$ is taken as the high end value 1600 cm$^{-1}$, the fractional change in the gap, $\delta/2t$, is less than 3%. It should also be noted that aspects of the $q$ quantized vibrations are already included in an effective way when $\mathrm{MIX}_{\mathrm{eq}}$, $V_{\mathrm{eq}}$, and $t$ are extracted from experiment in low-polarity solvents, and that the practice in the present work of referencing quantities to the low-polarity case includes them as well.

(53) Klamt, A. *J. Phys. Chem.* **1996**, *100*, 3349.

(54) As an illustration for an environment somewhat more complex than simple solutions, one could consider the environment of an electrolyte solution (van der Zwan, G.; Hynes, J. T. *Chem. Phys.* **1991** *152*, 169), in which dissolved ions contribute to the "solvation" ingredients.

(55) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian. *Nature* **1997**, *28*, 845.

(56) Kim, H. J.; Hynes, J. T. *J. Chem. Phys.* **1992**, *96*, 5088.

(57) The relevant quantity here is $\rho = 2t/\hbar\omega_{\mathrm{el}}$, where $\omega_{\mathrm{el}}$ is the characteristic frequency of the solvent electronic polarization, which can be approximated by the solvent electronic absorption energy. The Born−Oppenheimer limit for the solvent electronic polarization is given by $\rho \to 0$. For the molecules and solvents considered here $\rho < {}^2/_3$. See Appendix C of ref 56 for the relevant equations.

(58) Lu, D.; Chen, G.; Goddard, W. A., III. *J. Chem. Phys.* **1994**, *101*, 4920.

(59) Bianco, R.; Juanos i Timoneda, J.; Hynes, J. T. *J. Phys. Chem.* **1994**, *98*, 12103. Bianco, R.; Hynes, J. T. *J. Chem. Phys.* **1995**, *102*, 7864, 7885.

(60) This assumes that vibrational relaxation is rapid compared to solvation dynamics proper, which is not guaranteed. In addition, the excited-state charge distribution will evolve from that reached in the Franck−Condon transition to that appropriate to equilibrium; such a feature is not included in standard descriptions, which assume, e.g., a fixed dipole moment in the excited state. This feature is incorporated in the present description.

(61) Such experiments could also indicate if other geometrical coordinates (e.g. cis−trans isomerization) are necessary beyond the BLA coordinate.

(62) Plaza, P.; Martin, M.; Laage, D.; Barbosa, E.; Alain, V.; Blanchard-Desce, M. Work in progress.