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Citation: *The Journal of Chemical Physics* **101**, 5860 (1994);

View online: <https://doi.org/10.1063/1.467302>

View Table of Contents: <http://aip.scitation.org/toc/jcp/101/7>

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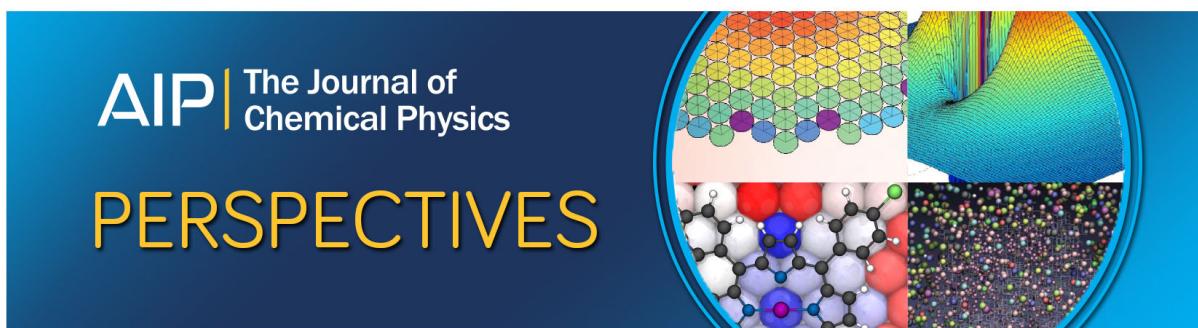
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Valence-bond charge-transfer solvation model for nonlinear optical properties of organic molecules in polar solvents

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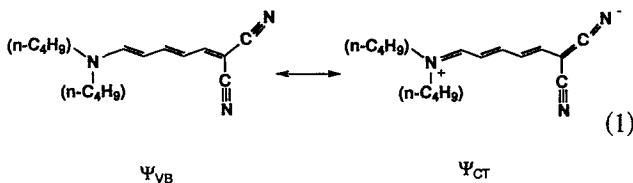
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(Received 23 March 1994; accepted 20 June 1994)

A simple model is developed for predicting solvation effects on the nonlinear optical properties of charge transfer organic materials such as 1,1 dicyano,6-(di-butyl amine) hexatriene. This model is based on the valence-bond charge-transfer (VB-CT) framework, using a continuum description of the solvent. The resulting VB-CT solvation model leads to analytic formulas for the absorption frequency (E_g), the polarizability (α), the hyperpolarizabilities (β, γ, δ), and the bond length alternation with only one solvent dependent parameter (ϵ , the dielectric constant of the solution). The theory involves just four solvent-independent parameters, V_0 , t , S_F , and Q which are related to the band gap, bandwidth, geometry, and dipole moment of the CT molecule [plus a length (R_{DA}) and force constant (k) derivable from standard force fields]. The results are in good agreement with experiment.

I. INTRODUCTION

Lu *et al.*¹ (denoted as Paper I) recently proposed the valence-bond charge-transfer (VB-CT) model to predict polarizability (α) and hyperpolarizabilities (β , γ , and δ) of charge-transfer conjugated molecules, such as 1,1 dicyano,6-(di-butyl amine) hexatriene, (1)



This simple model accounts for the dependence of the polarizabilities on the charge transfer energy (V) and shows that α , β , γ , and δ are all related to the bond-length alternation (BLA), which is in turn related to the fraction, f , of the wave function having CT character. This leads to a derivative relationship among α , β , γ , and δ . In Sec. II we start with the VB-CT model and employ the Marcus solvation model² to predict how solvation affects the polarizabilities of molecules such as Eq. (1). This leads to the valence-bond charge-transfer-solvation (VB-CT-S) model in which the solvent is described as a continuous medium with dielectric constant ϵ and the donor and acceptor groups are represented by two spheres of radius r_D and r_A , respectively (see Fig. 1). VB-CT-S describes how the absorption edge, BLA, and hyperpolarizabilities are related to the solvent properties.

In Sec. III VB-CT-S is employed to interpret and explain recent experimental observations by Marder, Perry, and co-workers³ on the effect of solvation on the second hyperpolarizability, γ . We also predict the values of α , β , and δ as a function of solvent polarity.

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II. THE VB-CT-S MODEL

A. No solvent

The VB-CT model of Paper I assumes that the wave function of the molecule and all properties can be described as a linear combination

$$\Psi_{\text{gr}} = \sqrt{1-f}\Psi_{\text{VB}} + \sqrt{f}\Psi_{\text{CT}} \quad (2)$$

of the two valence-bond configurations in Eq. (1), Ψ_{VB} and Ψ_{CT} . Here Ψ_{VB} is the wave function for the valence bond ground state (no charge transfer from donor to acceptor) while Ψ_{CT} describes the state in which an electron is moved from donor to acceptor while readjusting the other bonds. The optimum resonance fraction, f , in Eq. (2) is determined by the relative energy of Ψ_{VB} and Ψ_{CT} , the coupling between them, the change in the dipole moments, and the solvent polarity.

Without solvent the Hamiltonian is

$$H_0 = \begin{pmatrix} 0 & -t \\ -t & V \end{pmatrix}, \quad (3)$$

where Ψ_{CT} and Ψ_{VB} are assumed to be orthogonal

$$\langle \Psi_{\text{CT}} | \Psi_{\text{VB}} \rangle = 0. \quad (4)$$

Here

$$-t = \langle \Psi_{\text{CT}} | \mathcal{H} | \Psi_{\text{VB}} \rangle \quad (5)$$

is the charge transfer matrix element (t is positive), and

$$V = \langle \Psi_{\text{CT}} | \mathcal{H} | \Psi_{\text{CT}} \rangle - \langle \Psi_{\text{VB}} | \mathcal{H} | \Psi_{\text{VB}} \rangle \quad (6)$$

is the difference in energy between Ψ_{CT} and Ψ_{VB} . This leads to a band gap of

$$E_g = \sqrt{V^2 + 4t^2}. \quad (7)$$

Introducing the bond length alternation coordinate, q_{opt} , V is replaced by

$$V = V_0 + \frac{1}{2}k[(q - q_{\text{CT}}^0)^2 - (q - q_{\text{VB}}^0)^2], \quad (8)$$

and the bond length alternation can be written as

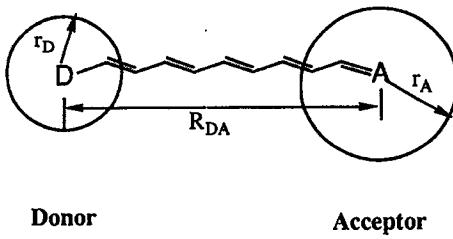


FIG. 1. The Marcus solvation model (Ref. 2). r_D and r_A are the radii of the donor and acceptor, respectively. R_{DA} is the distance between the donor and acceptor.

$$q_{opt} = (1-f)q_{VB}^0 + f q_{CT}^0 = q_{VB}^0 - f(q_{VB}^0 - q_{CT}^0), \quad (9)$$

where $q_{VB}^0 = -0.12 \text{ \AA}$ and $q_{CT}^0 = +0.12 \text{ \AA}$.

B. Solvation effects

Placing a CT molecule into a polar solvent leads to re-orientation of both the solvent and solute molecules. This changes the relative energy of Ψ_{VB} and Ψ_{CT} , Eq. (6), which through Eq. (3) changes the optimum fraction, f , of CT character in the ground state (2). Assuming that only CT contributes, the dipole moment of the ground state becomes

$$\mu = f\mu_{CT} = fQeR_{DA}, \quad (10)$$

where

$$\mu_{CT} = QeR_{DA}. \quad (11)$$

As shown in Paper I, the fraction of CT character in the ground state is

$$f = \frac{\sqrt{V^2 + 4t^2} - V}{2\sqrt{V^2 + 4t^2}} \quad (12)$$

$$= \frac{1}{2} - \frac{\sqrt{E_g^2 - 4t^2}}{2E_g}. \quad (13)$$

In the VB-CT-S model we assume that electronic states other than Ψ_{VB} and Ψ_{CT} have much higher energies and that t (the coupling between Ψ_{VB} and Ψ_{CT}) is independent of solvent. Thus quantitative evaluation of the solvation effects, requires only the change in relative energy, Eq. (6),

$$V_S = V + \Delta V_S \quad (14)$$

due to the presence of solvent. Here V is the energy difference between Ψ_{VB} and Ψ_{CT} without solvent and ΔV_S is the change in the relative energy caused by the addition of solvent. Including BLA the final V is obtained from Eq. (14) using V_S in place of V .

To evaluate ΔV_S we approximate² the donor and acceptor by two spheres of radius r_D and r_A with charges distributed symmetrically as in Fig. 1. For charges of Ze and $-Ze$ on the donor and acceptor atoms, the electric displacement field \mathbf{D} is

$$4\pi\mathbf{D} = \frac{Ze}{|\mathbf{x}_s - \mathbf{x}_d|^3} (\mathbf{x}_s - \mathbf{x}_d) - \frac{Ze}{|\mathbf{x}_s - \mathbf{x}_a|^3} (\mathbf{x}_s - \mathbf{x}_a), \quad (15)$$

where \mathbf{x}_s , \mathbf{x}_d , \mathbf{x}_a are the displacement vectors for solvent, donor, and acceptor, respectively. Assuming the relaxation time of solvent molecules is much longer than the time scale of charge transfer, the induced dipole moment density of solvent is always equal to its equilibrium value \mathbf{P}_{eq} , which is readily expressed as

$$\mathbf{P}_{eq} = \left(1 - \frac{1}{\epsilon}\right) \mathbf{D}_{eq}, \quad (16)$$

where ϵ is the dielectric constant of the solvent, and \mathbf{D}_{eq} is the electric displacement field at equilibrium [i.e., $Z = fQ$ in Eq. (15)]. For a static electric field the energy is calculated as

$$E_e = \frac{1}{2} \int \mathbf{E} \cdot \mathbf{D} d^3r. \quad (17)$$

The energy change upon the adding the solvent is

$$\Delta E = -\frac{1}{2\epsilon_0} \int \mathbf{P}_{eq} \cdot \mathbf{D} d^3r. \quad (18)$$

Ignoring image charges, this leads to

$$\Delta V_S = -\frac{e^2}{4\pi\epsilon_0} \left(1 - \frac{1}{\epsilon}\right) fQ^2 S_F, \quad (19)$$

where

$$S_F = \frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{R_{DA}}, \quad (20)$$

depends only on the geometry.

From Eq. (20) we observe that strong solvation effects arise from: (1) large ϵ , (2) small radii of donor or acceptor, and (3) large R_{DA} .

Given Eqs. (14) and (19) expressing V in terms of V_0 , S_F , and ϵ , we can use Eq. (7) to determine the energy gap, E_g , as a function of solvent polarity. We assume that the energy gap is given by the absorption edge $\lambda_{max} = hc/E_g$.

The polarizabilities have the form (see Paper I)

$$\alpha_{zz} = \frac{2t^2\mu_{CT}^2}{E_g^3} = \frac{2t^2(\mu_{DA})^2 Q^2}{(V^2 + 4t^2)^{3/2}}, \quad (21)$$

$$\beta_{zzz} = \frac{3t^2\mu_{CT}^3 V}{E_g^5} = \frac{3t^2(\mu_{DA})^3 Q^3 V}{(V^2 + 4t^2)^{5/2}} = -\frac{1}{2} \mu_{CT} \frac{\partial \alpha_{zz}}{\partial V}, \quad (22)$$

$$\gamma_{zzzz} = \frac{4t^2\mu_{CT}^4(V^2 - t^2)}{E_g^7} = \frac{4t^2(\mu_{DA})^4 Q^4 (V^2 - t^2)}{(V^2 + 4t^2)^{7/2}} \\ = \frac{1}{3} \mu_{CT} \frac{\partial \beta_{zzz}}{\partial V}, \quad (23)$$

$$\delta_{zzzzz} = \frac{5t^2\mu_{CT}^5(V^2 - 3t^2)V}{E_g^9} \\ = \frac{5t^2(\mu_{DA})^5 Q^5 (V^2 - 3t^2)V}{(V^2 + 4t^2)^{9/2}} = -\frac{1}{4} \mu_{CT} \frac{\partial \gamma_{zzzz}}{\partial V}. \quad (24)$$

In solution one measures the rotationally averaged values of the polarizabilities,

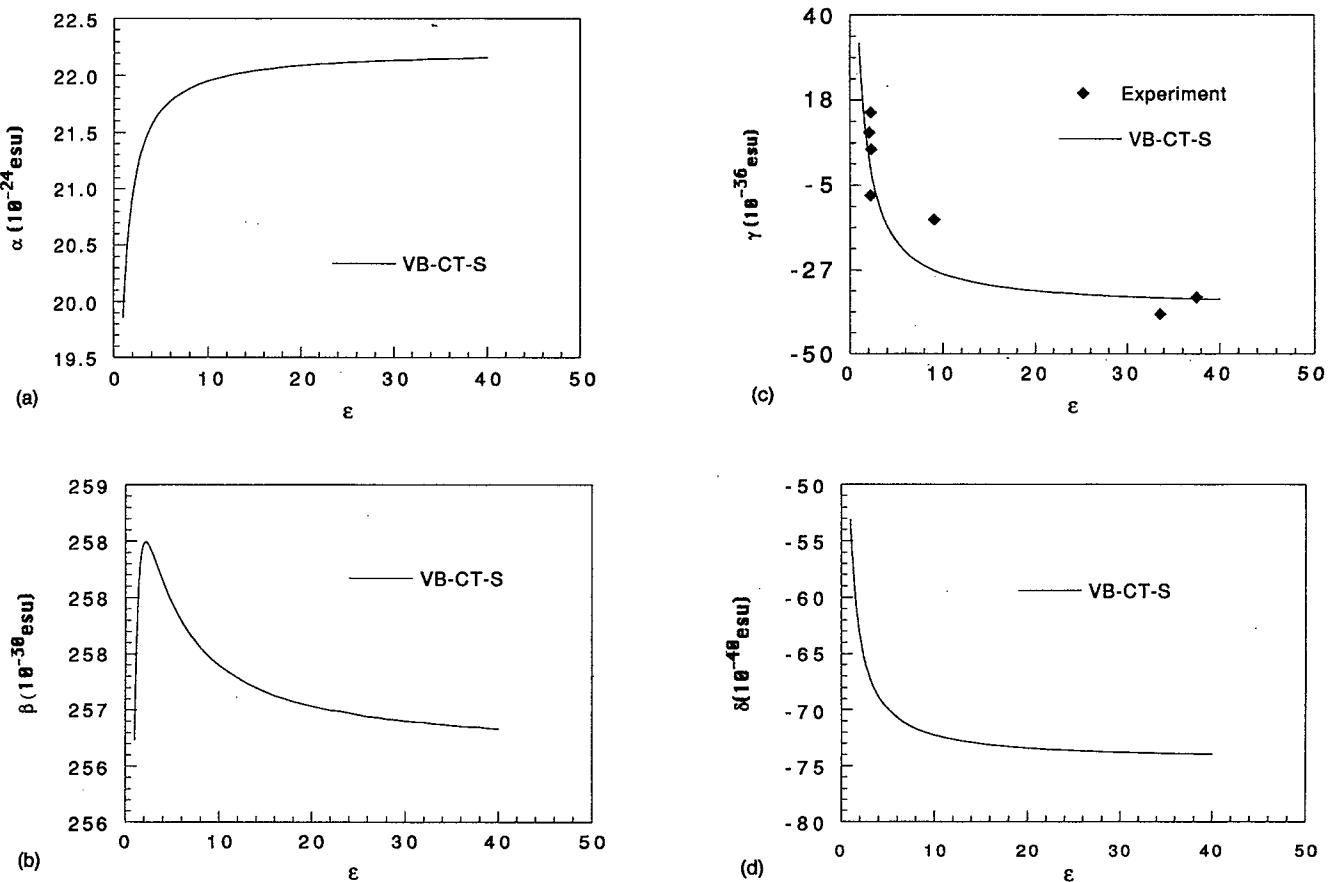


FIG. 2. The predicted dependence of polarizabilities on solvent polarity (expressed in terms of the static dielectric constant ϵ). (a) Polarizability, α , from Eq. (28). (b) Hyperpolarizability, β , from Eq. (29). (c) Second hyperpolarizability, γ , from Eq. (30). (d) Third hyperpolarizability, δ_{zzzz} , from Eq. (24). The values plotted are the static averaged values. The parameters used are: $V_0 = 0.833$ eV, $S_F = 0.0685 \text{ \AA}^{-1}$, $t = 1.184$ eV, $R_{DA} = 7.30 \text{ \AA}$, $Q = 0.738$, $k = 33.55 \text{ eV/\AA}^2$. For γ in (c) a comparison is made between theory (solid line) and experiment (dots). Here the experimental results were corrected to static values using Eq. (41).

$$\alpha \equiv \langle \alpha \rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \quad (25)$$

$$\mu\beta \equiv \langle \mu \cdot \beta \rangle = \sum_{i,j} \beta_{ijj} \mu_i, \quad (26)$$

$$\begin{aligned} \gamma \equiv \langle \gamma \rangle &= \frac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} \\ &\quad + 2\gamma_{xxzz}). \end{aligned} \quad (27)$$

Assuming only the z components are nonzero, Eqs. (25)–(27) lead to

$$\alpha = \frac{1}{3} \alpha_{zz} = \frac{2t^2 \mu_{CT}^2}{3E_g^3}, \quad (28)$$

$$\beta = \frac{\mu_z \beta_{zzz}}{\mu} = \frac{3t^2 \mu_{CT}^3 V}{E_g^5}, \quad (29)$$

$$\gamma = \frac{1}{5} \gamma_{zzzz} = \frac{4t^2 \mu_{CT}^4 (V^2 - t^2) V}{5E_g^7}. \quad (30)$$

All quantities in Eqs. (21)–(24) are defined except Q , which is the ratio of the actual solvent-free dipole moment of the CT state to the ideal value assuming that the CT state has one

electron transferred from the donor to the acceptor. This can be obtained by comparing to the absolute value of one of the quantities in Eqs. (21)–(24) at some value of ϵ .

III. COMPARISON WITH EXPERIMENT

A. Application to 1,1 dicyano, 6-(di-butyl amine) hexatriene, (1)

The dots in Fig. 2(c) show the experimental values³ of the second hyperpolarizability γ for molecule (1) for a variety of solvents [$C_6H_6-n-C_6H_{14}$ ($\epsilon=2.087$), dioxane ($\epsilon=2.209$), CCl_4 ($\epsilon=2.238$), C_6H_6 ($\epsilon=2.284$), CH_2Cl_2 ($\epsilon=9.08$), CH_3OH ($\epsilon=32.6$), and CH_3CN ($\epsilon=37.5$)]. We will compare the predictions of VB-CT-S theory with these experimental results.

To compare VB-CT-S theory with experiment, we must evaluate six parameters: t , V_0 , S_F , R_{DA} , Q , and k . Using the universal force field^{4,5} (UFF) in conjunction with charge equilibration theory⁶ to predict the charges of Eq. (1) in vacuum, we obtain

$$R_{DA} = 7.30 \text{ \AA} \quad (31)$$

for molecule (1). Similarly UFF⁴ leads to

$$k = 773.7 \text{ kcal}/\text{\AA}^2 = 33.55 \text{ eV}/\text{\AA}^2 = 5.38 \text{ mdyn/cm.} \quad (32)$$

The remaining parameters t , V_0 , S_F , and Q are each intrinsic parameters of CT molecules and can be determined directly from experiment.³

According to Paper I, γ is zero when $|V|=|t|$. Experimentally³ $\gamma=0$ for a solvent polarity of $\epsilon=2.209$, leading to $E_g=2.648$ eV for this polarity. Thus from $|V|=|t|$ and Eq. (7), we obtain

$$t = E_g / \sqrt{5} = 1.184 \text{ eV.} \quad (33)$$

V_0 and S_F can be obtained by fitting absorption peaks in two different solvents. We choose dioxane ($\epsilon_1=2.209$ and⁷ absorption energy $E_{g1}=2.648$ eV), and CH₃CN ($\epsilon_2=37.5$ and⁷ $E_{g2}=2.604$ eV). This leads to the following equations:

$$V_0 + \frac{1}{2} k[(q_1 - q_{CT}^0)^2 - (q_1 - q_{VB}^0)^2] - \frac{e^2}{4\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_1}\right) \times f_1 Q^2 S_F = \sqrt{E_{g1}^2 - 4t^2}, \quad (34)$$

$$V_0 + \frac{1}{2} k[(q_2 - q_{CT}^0)^2 - (q_2 - q_{VB}^0)^2] - \frac{e^2}{4\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_2}\right) \times f_2 Q^2 S_F = \sqrt{E_{g2}^2 - 4t^2}, \quad (35)$$

where f_i depends on t and E_g [as given in Eq. (13)] and the BLA coordinate, q_i , can be obtained from Eqs. (8) and (9). Solving Eqs. (34), and (35), leads to

$$Q^2 S_F = 0.0373 \text{ \AA}^{-1} \quad (36)$$

and

$$V_0 = 0.833 \text{ eV.} \quad (37)$$

To separate out Q from S_F , we can fit to the magnitude of γ at some ϵ . We choose to do this for CH₃CN ($\epsilon=37.5$). The experimental value³ is $\gamma_{\text{static}}=-35$ esu whereas the calculated value would be $\gamma=-118$ esu for $Q=1$. This leads to

$$Q^4 = 0.297 \quad (38)$$

or

$$Q = 0.738. \quad (39)$$

Substituting into Eq. (36) leads then to

$$S_F = 0.0685 \text{ \AA}^{-1}. \quad (40)$$

Given t , V_0 , S_F , Q , R_{DA} and k from Eqs. (31), (32), (33), (37), (39), and (40), we can calculate α , β , γ , and δ for all solvent polarities, ϵ . The resulting averaged values are shown in Fig. 2.

Currently only γ is available from experiment, Fig. 2(c). We see that VB-CT-S fits reasonably well with experiment³ despite the simplicity of this model. It will be valuable to measure the α and β for this molecule in various solvents in order to further test the model.

B. Frequency dependent correction for hyperpolarizations

In Fig. 2(c) the experimental third harmonic generation (THG) results are corrected to the static values by using the following formula:

$$\begin{aligned} \frac{\gamma_{\text{THG}}}{\gamma_{\text{static}}} = & \frac{1}{4} \left(\frac{E_g^3}{(E_g - 3\omega)(E_g - 2\omega)(E_g - \omega)} \right. \\ & + \frac{E_g^3}{(E_g + 3\omega)(E_g + 2\omega)(E_g + \omega)} \\ & + \frac{E_g^3}{(E_g + \omega)(E_g + 2\omega)(E_g - \omega)} \\ & \left. + \frac{E_g^3}{(E_g + \omega)(E_g - 2\omega)(E_g - \omega)} \right), \end{aligned} \quad (41)$$

where E_g is the band gap and ω is the frequency used in the experiment ($\omega=0.65$ eV). Similarly when experiments are available, the α and β will be corrected by using

$$\frac{\beta_{\text{SHG}}}{\beta_{\text{static}}} = \frac{E_g^4}{(E_g^2 - 4\omega^2)(E_g^2 - \omega^2)} \quad (42)$$

and

$$\frac{\alpha_\omega}{\alpha_{\text{static}}} = \frac{E_g^2}{E_g^2 - \omega^2}. \quad (43)$$

IV. DISCUSSION

A. Summary of VB-CT-S

The VB-CT-S model is quite simple. It involves the following.

- (i) Two properties (k and R_{DA}) which can be obtained from the force field (spectroscopy or theory).
- (ii) Three electronic parameters (V_0, t, Q) characteristic of the isolated molecule that can be derived from theory or experiment on the isolated molecule or from experiment in solution (as illustrated in Sec. III A).
- (iii) One solvent independent parameter, S_F , which must be obtained from an experimental value of the α , β , or γ in a polar solvent.

Given these six parameters one can predict the properties [λ_{max} , α , β , γ , δ , and q_{opt}] as a function of solvent polarity.

B. Estimation of molecular based properties

In designing new nonlinear optical materials, one might consider replacement of the donor, of the acceptor, or of the linker. The value for V_0 should depend strongly on the ionization potential (IP) of donor (D) and the electron affinity (EA) of acceptor (A) which might be related to the change in redox potentials for some solvent. Similarly the differential charge transfer, Q , can be estimated from IP_D and EA_A . The effect of changing the length of the linker or of replacing the polyene linker in Eq. (1) with other polymers is more difficult. In an earlier paper,⁸ we discussed the dependence of λ_{max} , α , β , and γ on polymer chain length based on a valence-bond charge-transfer-exciton (VB-CTE) model of the polymer chain. The combination of the VB-CT-S descrip-

tion of donor accepter systems with the VB-CTE model for polymer linker character and length leads to a three state description that is no longer analytic. This will be considered in a later paper.⁹

C. Estimation of solvent properties

In comparing to experiment we used the *static* dielectric constant for the solvent. This assumes that the relaxation time of the solvent is much longer than the time scale of charge transfer (that is, of the excitation process). This is true in polar solvents where the dielectric contribution is dominated by the orientation of the polar molecule. For nonpolar solvents, the contribution of the induced electronic dipole moment to the total dielectric constant is not negligible, and its response to the change of electric field may have a time scale similar to the charge transfer. In this case we should use the frequency dependent dielectric constant, ϵ_ω . This may account for the poorer fit of γ to experiment³ for the nonpolar solvents.

D. Estimation of solvation energy

In estimating the effect of solvent on the energy separation V_S [Eqs. (14)–(20)], we employed the Marcus solvent model used for predicting electron transfer rates.² This leads to the specific form (20) for the geometric parameter S_F in which r_A and r_D should be about the size of the van der Waals radii of the donor and the acceptor. Assuming that $r_A = r_D$, Eq. (42) leads to $r_A = 4.87 \text{ \AA}$ for molecule (1), see Fig. 1. This is a plausible value, but we may also treat S_F as a characteristic shape parameter of the CT molecule. The induced dipole density of the solvent is proportional to $1/\epsilon$. Therefore, ΔV_S in Eq. (19) should be proportional to $(1 - 1/\epsilon)$ and f regardless of the structure of solvent molecule. Hence Eq. (19) may be generalized to an arbitrary geometry of the CT molecule (rather than Fig. 1).

More rigorous ways to calculate solvation effects are available. Thus Warshel *et al.*¹⁰ used an explicit representation of the solvent (the SCAAS model, surface constrained all atom solvation) to treat the effect of solvent on the empirical valence bond (EVB) description of an S_{N^2} reaction.¹¹ To treat S_{N^1} ionic dissociation in a liquid, Kim and Hynes¹¹ used a nonlinear Schrödinger equation formulation. Alternatively, the solvation energy could be evaluated with the DelPhi Poisson–Boltzmann continuum solvent procedure of Honig *et al.*¹² The charges for such calculations could be obtained using charge equilibration (QE).⁶ Indeed, Friesner *et al.*¹³ have developed an interface between pseudospectral-generalized valence bond (PS-GVB)¹⁴ and DelPhi¹² that does the quantum mechanics self-consistently within the self-consistent reaction field of the solvent.¹³

V. SUMMARY

We find that the simple VB-CT-S model provides a quantitative explanation of the dependence of hyperpolarizabilities β and γ on solvation. The theory agrees well with the experimental results by Marder *et al.*³ for the γ of Eq. (1), the only system for which a hyperpolarizability has been measured for a wide range of solvents. The VB-CT-S theory employs a continuous dielectric description of the solvent and leads to analytic formulas for λ_{\max} , α , β , and γ in different solvents. Because of its simplicity, this theory should be of use in designing new nonlinear optical materials.

ACKNOWLEDGMENTS

We wish to thank Dr. Seth Marder of the Beckman Institute and Dr. Joseph Perry of JPL for helpful discussions. The research was funded by the National Science Foundation (No. CHE 91-100289). The facilities of the MSC/BI used in this research are also supported by grants from DOE-AICD, NSF-ASC, Allied-Signal Corp., Asahi Chemical, Asahi Glass, Chevron Petroleum Technologies, BF Goodrich, Hughes Research, Teijin Ltd., Vestar, and Beckman Institute. Some calculations were carried out on the JPL Cray and at the NSF Supercomputer Center in Pittsburgh.

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- ¹⁵This is available as PS-GVB/Solvate from Schrödinger Inc., Pasadena, CA.