

Chapter 25

Valence Bond Charge Transfer Theory for Predicting Nonlinear Optical Properties of Organic Materials

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A simple theory (VB-CT) is developed for predicting nonlinear optical properties of organic materials. Application of this theory to donor-acceptor charge-transfer molecules leads to *analytic* formulae for the absorption frequency, hyperpolarizabilities, and bond length alternation. Derivative relationships between hyperpolarizabilities (with respect to bond length alternation) are derived. Using a continuum description of the solvent in the VB-CT framework leads to the VB-CT-S model which gives results for solvent shifts in good agreement with experiment. To predict the saturation behavior of polarizability and hyperpolarizability with respect to polymer length, we developed the VB-CTE model which is applied to nine polymeric materials.

There is a great deal of industrial interest in nonlinear optical (NLO) materials for use in

- (i) optical processing of data/images,
- (ii) optical storage of data/images,
- (iii) optically based telecommunications, and
- (iv) optically based computers.

The important properties for these applications are the hyperpolarizabilities. The effect on the energy (E) of applying an external electric field (\mathcal{E}) is

$$E = E_0 - \mu \cdot \mathcal{E} \quad (1)$$

where μ depends on \mathcal{E} as in (2)

$$\mu_z(\mathcal{E}) = \mu_{0z} + \alpha_{zz}\mathcal{E}_z + \beta_{zzz}\mathcal{E}_z^2 + \gamma_{zzzz}\mathcal{E}_z^3 + \delta_{zzzzz}\mathcal{E}_z^4 \quad (2)$$

The polarizability is defined as

$$\alpha_{zz} = \left(\frac{\partial \mu_z}{\partial \mathcal{E}_z} \right), \quad (3)$$

the first hyperpolarizability as

$$\beta_{zzz} = \frac{1}{2!} \left(\frac{\partial^2 \mu_z}{\partial \mathcal{E}_z^2} \right), \quad (4)$$

the second hyperpolarizability as

$$\gamma_{zzzz} = \frac{1}{3!} \left(\frac{\partial^3 \mu_z}{\partial \mathcal{E}_z^3} \right), \quad (5)$$

and the third hyperpolarizability as

$$\delta_{zzzzz} = \frac{1}{4!} \left(\frac{\partial^4 \mu_z}{\partial \mathcal{E}_z^4} \right), \quad (6)$$

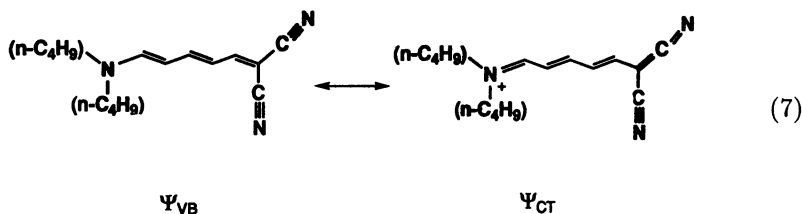
where each is evaluated at $\mathcal{E} = 0$.

The properties of most current interest are β and γ which control

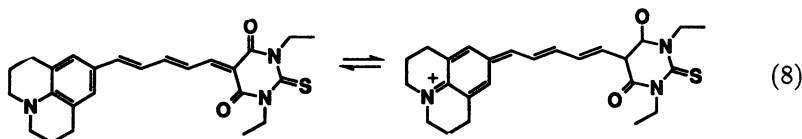
- (i) frequency doubling (better focus, more data),
- (ii) changes in refractive index (electro-optical switch for telecommunications), and
- (iii) frequency mixing.

Currently $LiNbO_3$ is the material of choice for such applications. However, polymers would provide great advantages in ease of processing and for tailoring the properties to match precise requirements.

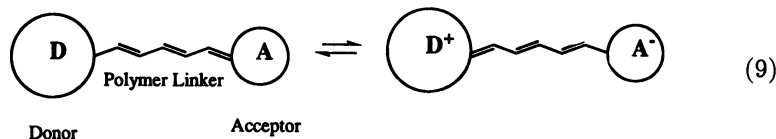
Recent advances in developing new high β , γ organic materials [S. Marder, J. Perry, and coworkers (3-5)] include the development of such materials as (4)



and (3)



The general pattern for good NLO organics is



We report here a simple method, VB-CT, for predicting the NLO properties of these materials (6-7).

A typical approach for predicting polarizabilities involves summing over intermediate states formed from molecular orbitals. Thus for a laser frequency

ω the polarizability and hyperpolarizabilities have the form (δ)

$$\alpha_{ij}(-w, w) = 2I_{-w, w} \left(\frac{e^2}{\hbar} \right) \sum'_n \frac{r_{gn}^i r_{ng}^j}{w_{ng} - w} \quad (10)$$

$$\beta_{ijk}(-w_\sigma; w_1, w_2) = 3K(-w_\sigma; w_1, w_2) \left(\frac{e^3}{\hbar^2} \right) I_{-\sigma; 1, 2} \sum'_{m, n} \left\{ \frac{r_{gn}^i \bar{r}_{nm}^j r_{mg}^k}{(w_{mg} - w_\sigma)(w_{ng} - w_1)} \right\} \quad (11)$$

$$\gamma_{ijkl}(-w_\sigma; w_1, w_2, w_3) = 4K(-w_\sigma; w_1, w_2, w_3) \left(\frac{e^4}{\hbar^3} \right) I_{-\sigma; 1, 2, 3} \left[\sum'_{m, n, p} \frac{r_{gp}^i \bar{r}_{pn}^j \bar{r}_{nm}^k r_{mg}^l}{(w_{pg} - w_\sigma)(w_{ng} - w_1 - w_2)(w_{mg} - w_1)} - \sum'_{mn} \frac{r_{gm}^i r_{mg}^j r_{gn}^k r_{ng}^l}{(w_{mg} - w_\sigma)(w_{ng} - w_1)(w_{ng} + w_2)} \right] \quad (12)$$

Here

- (i) g indicates the ground state and \sum' indicates that g is excluded from the sum over excited states.
- (ii) $\bar{r}_{kl}^i = r_{kl}^i - r_{gg}^i$, where r_{kl}^i is component i for the dipole matrix element between states l and k .
- (iii) $w_\sigma = \sum_i w_i$
- (iv) $K(-w_\sigma; w_1, w_2, w_3)$ is a numerical factor determined by the nature of the NLO process.
- (v) $I_{-\sigma; 1, 2, 3}$ denotes the average of all terms generated by permuting σ, w_1, w_2, w_3 .

Given a good description of the excited states this sum-over-states approach can be used to predict accurate values of α, β, γ . However there are two problems:

- (i) it rapidly becomes very complicated and expensive as system size increases
- (ii) there is no obvious relationship between α, β, γ or between these properties and other properties (D, A , linker length) of the system.

VB-CT Theory

We have developed a new approach (denoted VB-CT) (δ) for predicting NLO properties. Valence bond charge transfer (VB-CT) is based on a valence bond description, using only the two states, Ψ_{VB} and Ψ_{CT} , corresponding to the left and right sides of (7) or (8). VB-CT theory determines all NLO properties ($\alpha, \beta, \gamma, \delta$) and establishes relationships between them. It involves two main parameters t and V which can be extracted from the experimental λ_{max} (or from theory). It can be used to predict the solvent dependence and should be useful for designing new materials by tuning the donor (D), acceptor (A), polymer linkers, and solvent.

No Solvent. The VB-CT model assumes that the wavefunction of the molecule and all properties can be described as a linear combination

$$\Psi_{gr} = \sqrt{1-f} \Psi_{VB} + \sqrt{f} \Psi_{CT} \quad (13)$$

of the two valence bond configurations, Ψ_{VB} and Ψ_{CT} . The optimum charge transfer (CT) fraction, f , in (13) 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

$$H_0 = \begin{pmatrix} E_{VB} & -t \\ -t & E_{CT} \end{pmatrix}, \quad (14)$$

where

$$\langle \Psi_{CT} | \Psi_{VB} \rangle = 0, \quad (15)$$

$$-t = \langle \Psi_{CT} | \mathcal{H} | \Psi_{VB} \rangle, \quad (16)$$

and

$$V = E_{CT} - E_{VB}. \quad (17)$$

This leads to a bandgap of

$$E_g = \sqrt{V^2 + 4t^2} \quad (18)$$

and to a CT fraction of

$$f = \frac{1}{2} - \frac{V}{2\sqrt{V^2 + 4t^2}} = \frac{\partial E_{gr}}{\partial V}, \quad (19)$$

where E_{gr} is the energy of the ground state.

Bond Length Alternation. Since Ψ_{CT} and Ψ_{VB} involve alternate resonant descriptions of the intervening polyene unit, the increase of f from 0 to 1 will change each double bond ($R = 1.33\text{\AA}$) of the polyene to a single bond ($R = 1.45\text{\AA}$) and vice versa. Thus the bond length alternation (BLA) coordinate changes from $q = -0.12\text{\AA} = q_{VB}^0$ to $q = +0.12\text{\AA} = q_{CT}^0$ as the CT fraction f goes from 0 to 1, leading to a one-to-one relationship. The contributions to the Hamiltonian (14) are

$$E_{VB} = \frac{1}{2}k(q - q_{VB}^0)^2, \quad (20)$$

$$E_{CT} = V_0 + \frac{1}{2}k(q - q_{CT}^0)^2. \quad (21)$$

where V_0 is referred to as the *adiabatic* excitation energy.

The equilibrium structure q_{opt} obtained by solving

$$\frac{dE_{gr}}{dq} = 0 \quad (22)$$

leading to

$$q_{opt} = \frac{1}{2}(q_{VB}^0 + q_{CT}^0) + \frac{1}{2}(q_{VB}^0 - q_{CT}^0) \frac{V}{\sqrt{V^2 + 4t^2}} \quad (23a)$$

$$\begin{aligned} &= q_{VB}^0 - f(q_{VB}^0 - q_{CT}^0) \\ &= -0.12 + 0.24f \end{aligned} \quad (23b)$$

Thus f and q_{opt} are linearly related to each other.

Figure 1 illustrates the dependence of the BLA on V_0 using

$$t = 1.1eV, \quad (24a)$$

a force constant in (20), (21) of

$$k = 33.55 \text{ eV}/\text{\AA}^2 = 773.7 \text{ kcal/mol}\text{\AA}^2 = 5.38 \text{ mdyn/cm}, \quad (24b)$$

from UFF (10), and $V_0 = 1 \text{ eV}$. This leads to $q_{opt} = -0.069\text{\AA}$. If VB and CT are degenerate ($V_0 = 0$) then $q_{opt} = 0$. Further stabilization of CT to $V_0 = -1 \text{ eV}$ reverses the BLA to $q_{opt} = +0.069\text{\AA}$.

Application of an Electric Field. For systems such as (7) and (8), the polarizability and hyperpolarizability are dominated by the z component (chain axis), and we will ignore all other components. Assuming that only Ψ_{CT} contributes to the dipole moment, we write

$$\mu_{CT} = QeR_{DA} \quad (25)$$

where Q (expected to be between 0.5 and 1.0) is the net charge transfer for Ψ_{CT} . In an applied external electric field, \mathcal{E} , the Hamiltonian (14) becomes

$$H = \begin{pmatrix} E_{VB} & -t \\ -t & E_{CT} - \mu_{CT}\mathcal{E} \end{pmatrix}. \quad (26)$$

Equations (13), (17) and (19) apply also for finite fields but with V replaced by

$$V_{\mathcal{E}} = V - \mu_{CT}\mathcal{E}. \quad (27)$$

In particular the change in f due to the applied field is

$$\frac{df}{d\mathcal{E}} = \frac{df}{dV_{\mathcal{E}}} \frac{dV_{\mathcal{E}}}{d\mathcal{E}} = \frac{2t^2\mu_{CT}}{(V_{\mathcal{E}}^2 + 4t^2)^{3/2}} = \frac{2t^2\mu_{CT}}{E_g^3}. \quad (28)$$

Polarizabilities. Given the dependence of the ground state energy on the external electric field, the dipole moment of the ground state, μ_z , is obtained from

$$\mu_z(\mathcal{E}) = -\frac{dE_{gr}}{d\mathcal{E}} = f\mu_{CT} \quad (29)$$

and the polarizability and hyperpolarizabilities are obtained from (3)-(6), leading to

$$\alpha_{zz} = -\mu_{CT}^2 \frac{df}{dV_{\mathcal{E}}} \Big|_{\mathcal{E}=0} = \frac{2t^2\mu_{CT}^2}{E_g^3} \quad (30)$$

$$\beta_{zzz} = \frac{\mu_{CT}^3}{2} \frac{d^2f}{dV_{\mathcal{E}}^2} \Big|_{\mathcal{E}=0} = \frac{3t^2\mu_{CT}^3V}{E_g^5} \quad (31)$$

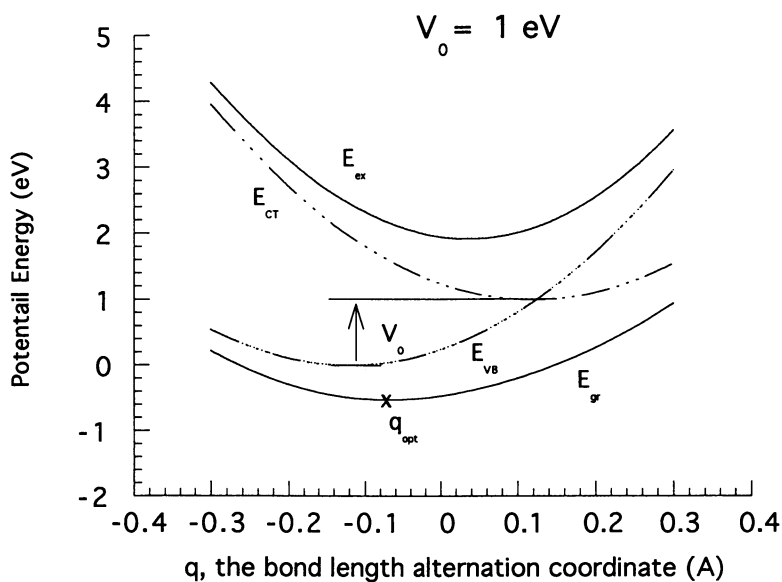


Figure 1. Relation between the energy curves for (i) pure VB and (ii) pure CT states for $V_0 = 1 \text{ eV}$. The ground state and excited state resulting from interaction of VB and CT. $E_{gap} = hc/\lambda_{max}$ is the observed transition energy.

$$\gamma_{zzzz} = -\frac{\mu_{CT}^4}{6} \frac{d^3 f}{dV_{\mathcal{E}}^3} \Big|_{\mathcal{E}=0} = \frac{4t^2 \mu_{CT}^4 [V^2 - t^2]}{E_g^7}, \quad (32)$$

$$\delta_{zzzzz} = \frac{\mu_{CT}^5}{24} \frac{d^4 f}{dV_{\mathcal{E}}^4} \Big|_{\mathcal{E}=0} = \frac{5t^2 \mu_{CT}^5 V [V^2 - 3t^2]}{E_g^9}. \quad (33)$$

(The following discussions will omit the z subscripts.)

Thus VB-CT leads to *analytical equations* for all hyperpolarizabilities in terms of the atomistic parameters t and V ! This contrasts with the usual result (10)-(12).

Predictions of μ , α , β , and γ From VB-CT Theory. As f increases from $f = 0$ to $f = 1$, the VB-CT model leads to an alternation in which the polyene double bonds for Ψ_{VB} change to polyene single bonds in Ψ_{CT} and vice versa. Since there is a linear relation (23b) between f and q_{opt} [the change in bond length alternation (BLA)] and since f determines the polarizability and all hyperpolarizabilities, then a single BLA parameter, q_{opt} , determines the polarizability and all hyperpolarizabilities. This has been anticipated by Marder *et al.*, (9) who pointed out that BLA is a useful parameter for examining the structure-property relationships of NLO materials. They showed that the β and γ values can be tuned by varying BLA. In addition they carried out finite-field AM1 calculations (9) and showed the relationships of α , β and γ to q_{opt} . Their results provide a good test of VB-CT theory.

In order to illustrate the relationships, we used (19), (23), and (30)-(33) to calculate f , q_{opt} , α , β , γ , and δ as a function of V , all with the fixed values of t and k from (24). This allowed us to obtain α , β , γ , and δ as a function of f , Figure 2. The shapes of the polarizability curves are insensitive to the value t . Thus the salient factor for polarizability and hyperpolarizability is the bond length alternation.

General observations from these relations are as follows:

- (i) α has a maximum for $f = \frac{1}{2}$,
- (ii) β is the derivative of α with respect to f , leading to a maximum in $|\beta|$ at $f = 0.276$ and 0.724 and zero at $f = \frac{1}{2}$.
- (iii) γ is the derivative of β with respect to f , leading to the largest magnitude (a minimum) at $f = \frac{1}{2}$, with secondary maxima (1/4 the magnitude) at $f = 0.173$ and $f = 0.827$. Where $|\beta|$ is a maximum, $\gamma = 0$.
- (iv) δ is the derivative of γ with respect to f , leading to maxima in $|\delta|$ at $f = 0.357$ and $f = 0.643$ and secondary maxima at $f = 0.117$ and $f = 0.883$. Where $|\gamma|$ is a maximum, $\delta = 0$.

Special cases are:

- (a) When $V = 0$ (VB and CT states degenerate), we have

$$f = \frac{1}{2}, \quad q_{opt} = 0, \quad t = E_g/2. \quad (34)$$

At this point, α is a maximum, $\beta = 0$, $|\gamma|$ is a maximum, and $\delta = 0$.

- (b) When $|\dot{V}| = |t|$, we have

$$f = 0.276 \text{ or } 0.724, \quad q_{opt} = \pm 0.0538 \text{ \AA}, \quad t = \frac{E_g}{\sqrt{5}}. \quad (35)$$

Thus $|\beta|$ is a maximum and $\gamma = 0$.

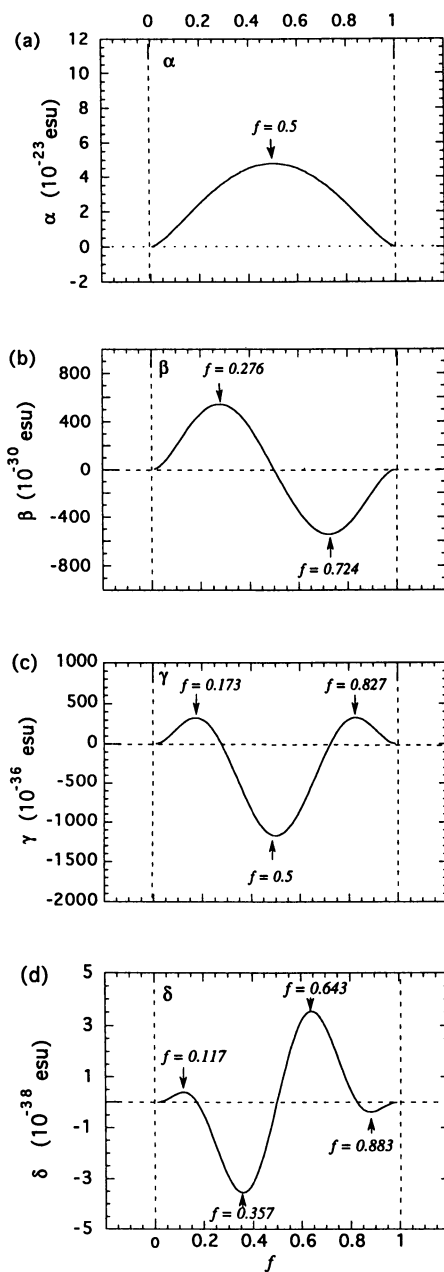


Figure 2. Predicted properties ($\alpha, \beta, \gamma, \delta$) as a function of CT fraction, f .

(c) When $|V| = \sqrt{3}|t|$, we have

$$f = 0.173 \text{ or } 0.827, \quad q_{opt} = \pm 0.0785\text{\AA}, \quad t = \frac{E_g}{\sqrt{7}}. \quad (36)$$

Thus $|\gamma|$ is a maximum and $\delta = 0$.

Comparison with AM1 Calculations. The VB-CT results are compared with AM1 calculations (9) (dots) in Figure 3. In making these comparisons we used $Q = 0.69$ for α , γ , and δ but $Q = 0.51$ for β . The AM1 results for β and γ agree quite well with VB-CT theory. VB-CT has α go to zero as $f \rightarrow 0$ or 1, whereas AM1 calculations lead to about half the maximum. This is probably because the current VB-CT calculations ignore the polarizability for a fixed VB or CT structure (it could have been included).

Solvation Effects. Placing a CT molecule into a polar solvent leads to reorientation of both the solvent and solute molecules. This changes the relative energy of Ψ_{VB} and Ψ_{CT} , (17), which through (14) changes the optimum fraction, f , of CT character in the ground state (13). Assuming that only CT contributes, the dipole moment of the ground state becomes

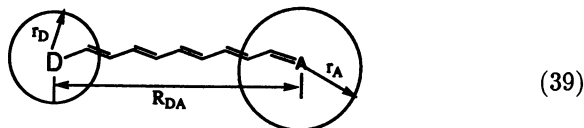
$$\mu = f\mu_{CT} = fQeR_{DA} = fQ\mu_{DA} \quad (37)$$

In the VB-CT-S model (7) 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, (17), due to the presence of solvent, and we write

$$V_S = V + \Delta V_S \quad (38)$$

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 (19) using V_S in place of V .

To evaluate ΔV_S we approximate (11) the donor and acceptor by two spheres of radius r_D and r_A with charges distributed symmetrically as in (39)



The net result is

$$\Delta V_S = -\frac{e^2}{4\pi\epsilon_0} \left(1 - \frac{1}{\epsilon}\right) fQ^2 S_F, \quad (40a)$$

where

$$S_F = \frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{R_{DA}}, \quad (40b)$$

depends only on the geometry.

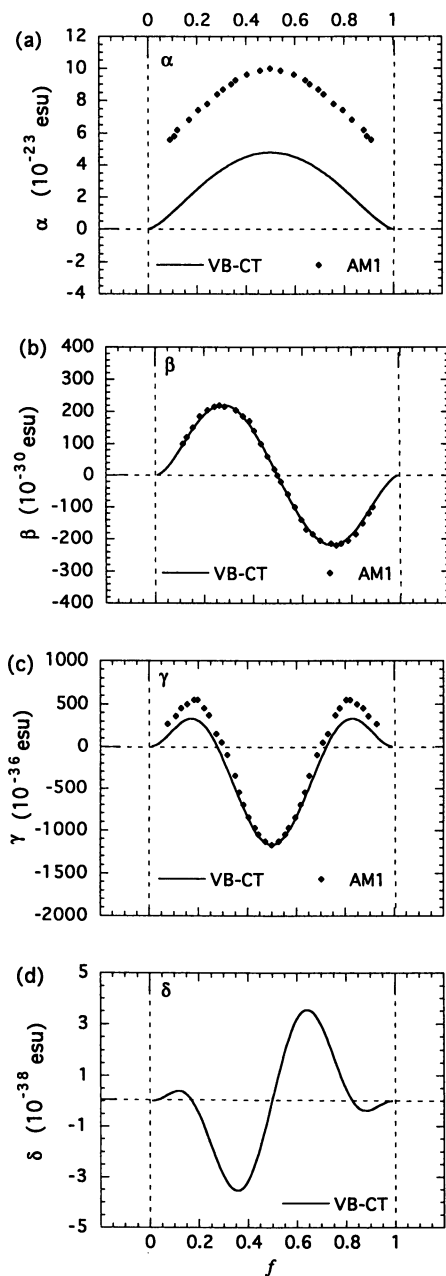


Figure 3. Comparison of predicted properties ($\alpha, \beta, \gamma, \delta$) with AM1 calculations (reference 9).

The polarizabilities have the form (30)-(33) where μ_{CT} is given by (37) and V is replaced by V_S , (38).

Measurements in solution lead to the rotationally averaged values of the polarizabilities,

$$\alpha = \frac{1}{3}\alpha_{zz} = \frac{2t^2\mu_{CT}^2}{3E_g^3} \quad (41)$$

$$\beta = \frac{\mu_z\beta_{zzz}}{\mu} = \frac{3t^2\mu_{CT}^3V}{E_g^5} \quad (42)$$

$$\gamma = \frac{1}{5}\gamma_{zzzz} = \frac{4t^2\mu_{CT}^4(V^2 - t^2)V}{5E_g^7} \quad (43)$$

Comparison with Experiment. The dots in Figure 4c show the experimental values (4) of the second hyperpolarizability γ for molecule (7) in a variety of solvents

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 (10) (UFF) in conjunction with Charge Equilibration theory (12) to predict the charges, we obtain

$$R_{DA} = 7.30\text{\AA} \quad (44)$$

for molecule (7). Similarly UFF (10) leads to the value of k in (24b). The remaining parameters t , V_0 , S_F , and Q are each intrinsic parameters of CT molecules and can be determined directly from experiment (4).

From (35), γ is zero when $|V| = |t|$. Experimentally (4) $\gamma = 0$ for a solvent polarity of $\epsilon = 2.209$, leading to $E_g = 2.648$ eV for this polarity. Thus from $|V| = |t|$ and (7), we can evaluate t for (7),

$$t = E_g/\sqrt{5} = 1.184\text{eV}. \quad (45)$$

V_0 and S_F can be obtained by fitting absorption peaks in two different solvents. We chose dioxane ($\epsilon_1 = 2.209$ with absorption energy $E_{g1} = 2.648$ eV), with CH_3CN ($\epsilon_2 = 37.5$ and $E_{g2} = 2.604$ eV). This leads to two equation of the form

$$V_0 + \frac{1}{2}k \left[(q_i - q_{CT}^0)^2 - (q_i - q_{VB}^0)^2 \right] - \frac{e^2}{4\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_i} \right) f_i Q^2 S_F = \sqrt{E_{gi}^2 - 4t^2}, \quad (46)$$

where f_i depends on t and E_g . Solving equation (46) leads to

$$Q^2 S_F = 0.0373\text{\AA}^{-1} \quad (47)$$

$$V_0 = 0.833\text{eV} \quad (48)$$

To separate out Q from S_F , we can fit to the magnitude of γ at some ϵ . We chose to do this for CH_3CN ($\epsilon = 37.5$). The experimental value (4) is $\gamma_{static} = -35$ esu, whereas the calculated value would be $\gamma = -118$ esu for $Q = 1$. This leads to

$$Q^4 = 0.297, \quad (49a)$$

or

$$Q = 0.738, \quad (49b)$$

Substituting into (47) leads then to

$$S_F = 0.0685 \text{ \AA}^{-1} \quad (50)$$

Given t , V_0 , S_F , Q , R_{DA} , and k from (45), (48), (50), (49), (44), and (24b) we can calculate α , β , γ , and δ for all solvent polarities, ϵ . The resulting averaged values are shown in Figure 4.

Currently only γ is available from experiment, Figure 4c. Despite the simplicity of this model, VB-CT-S fits reasonably well with experiment (4). It will be valuable to measure the α and β for this molecule in various solvents in order to further test the model.

Use in Design and Prediction. The VB-CT-S model is quite simple. It involves

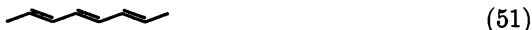
- i. two properties (k and R_{DA}) which can be obtained from the force field (spectroscopy or theory)
- ii. three electronic parameters (V_0 , t , Q) characteristic of the isolated molecule, which can be derived from theory or experiment on the isolated molecule or from experiment in solution [as illustrated in above]
- 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.

In designing new nonlinear 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). These in turn 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 (7) with other polymers is discussed below.

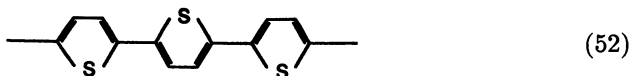
Linker Excited States

The VB-CT model assumes that all other excited states are much higher than the VB and CT states. In particular the resonant states involving the bridge or linker must be much higher. For octatetraene the absorption maxima is about 4 eV indicating that the resonance state of the linker in equation 51 is more than 4 eV above the VB state.



Since the donor-acceptor molecules considered here have the CT state about 1 eV above the VB state, neglect of the resonance state should be a good approximation. When the energy of the resonance structure is similar to those of VB and CT, the contributions from the linker resonance state must be included. This complicates the theory so that the results are no longer analytic.

To predict the dependence of α , β , γ on polymer length, we developed valence bond charge transfer exciton (VB-CTE) theory (8). Here the excited states are considered as charge transfer excitons with an electron removed from the HOMO on one monomer and added into the LUMO on another monomer p sites away. With some additional approximations this leads to an analytic result and to saturation behavior in good agreement with experiment. Thus for polythiophene (52) we obtain the results in Figure 5.



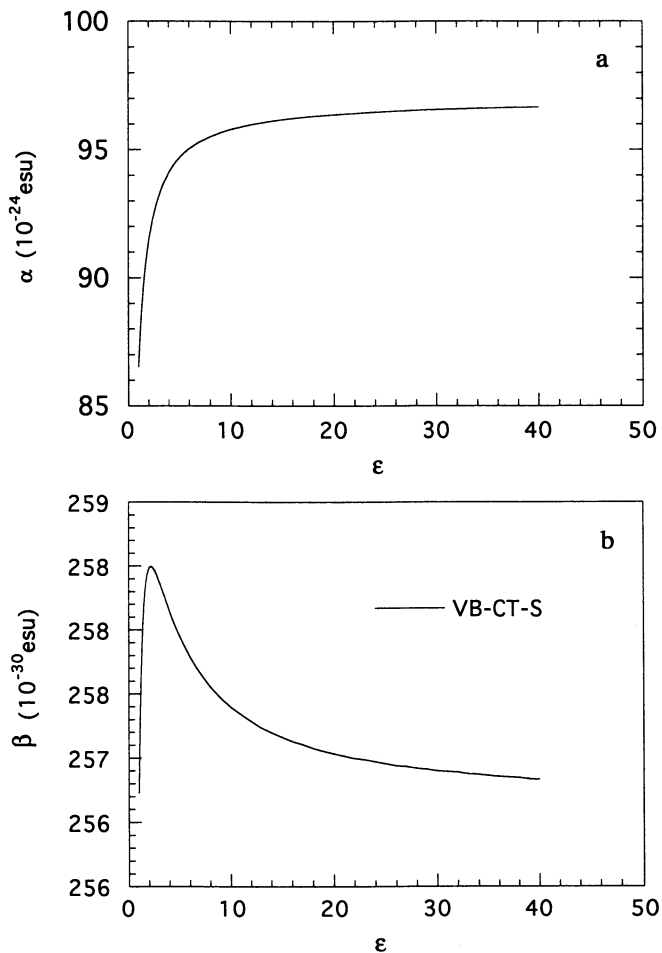


Figure 4. The predicted dependent of polarizability on solvent polarity (expressed in terms of the static dielectric constant ϵ). (a) Polarizability, α . (b) Hyperpolarizability, β . (c) Second hyperpolarizability, γ . (d) Third hyperpolarizability, δ_{zzzzz} . The values plotted are the static averages values. For γ in (c) a comparison is made between theory (solid line) and experiment (dots).

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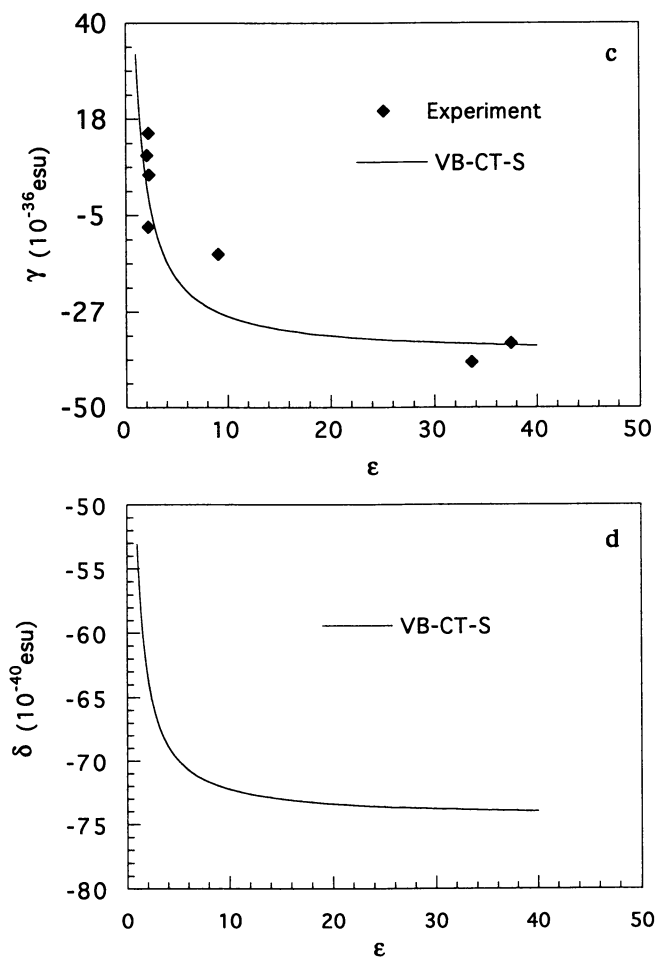


Figure 4. Continued.

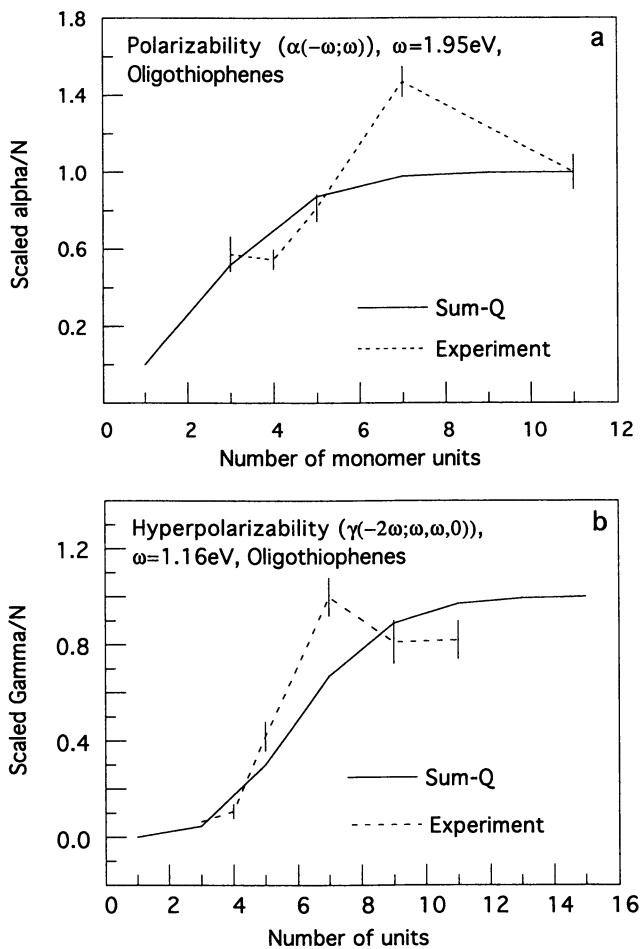


Figure 5. Comparison of theory and experiment for the saturation behavior of oligothiophenes. (a) Polarizability α ($\omega = 1.95 \text{ eV}$) and (b) hyperpolarizability γ ($\omega = 1.16 \text{ eV}$). The dashed line connects experimental data (with error bars). The solid line connects theoretical predictions.

VB-CT-E theory involves just two parameters t and $V = IP - EA$. They are related to bandwidth B and bandgap E_g by (53) and (54),

$$B = 4t \quad (53)$$

$$E_g = V - 2t \quad (54)$$

The saturation length for polarizability is (55),

$$L_\alpha \sim 1 + 20 \frac{t}{V} \quad (55)$$

and the saturation length for second hyperpolarizability is (56),

$$L_\gamma \sim 1 + 38 \frac{t}{V}. \quad (56)$$

Thus applying VB-CT-E to other polymers require only two pieces of information, say a bandwidth and a bandgap. Table I shows the predictions for the polymers in Figure 6.

Table I. Saturated values for α and γ and saturation lengths (L_α, L_γ) predicted from VB-CT-E theory. These values assume $\omega = 0$.

Quantity	Band Width B	Band Gap ^a E_g	t^b	V^b	Saturation Length		α_{zz}/N	γ_{zzzz}/N
Polymer	(eV)	(eV)	(eV)	(eV)	L_α	L_γ	(10^{-23} esu)	(10^{-34} esu)
6a	3.9	2.1	1.0	4.1	5.8	10.1	2.41	11.3
6b ^c	3.5	3.4	0.9	5.1	4.4	7.5	1.13	2.54
6c	2.8	3.0	0.7	4.4	4.2	7.1	2.49	15.9
6d	3.8	3.2	0.95	5.1	4.8	8.2	1.13	2.55
6e	2.5	2.2	0.6	3.4	4.6	7.8	3.88	44.9
6f	3.3	3.3	0.8	5.0	4.2	7.1	0.40	0.51
6g	2.7	5.4	0.7	6.8	3.0	4.8	0.083	0.020
6h	1.3	3.1	0.3	3.8	2.6	4.0	1.09	3.45
6j	-	2.77	0.83	4.09	5.0	9.0	1.77	6.87
6i	-	1.8	0.83	2.85	6.8	12.0	5.65	82.1

^aFrom theory.

^bFrom experiment values of B, E_g .

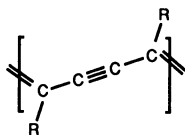
^cTwisted (22°).

First Principles Prediction of Solvent Effects

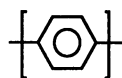
We are using PS-GVB/SOLV (13,14) to predict *ab initio* solvation effects for molecules such as (7) and (8). PS-GVB/SOLV considers that there is a dielectric continuum with dielectric constant ϵ surrounding the molecule as in Figure 7. Here the interface is the van der Waals surface around each atom. The procedure is as follows:

1. The PS-GVB program (14) is used to calculate the HF or GVB wavefunction and the optimum orbitals are used to determine the electron density.
2. The density from step 1 is converted to point charges (using electrostatic potential derived charges).

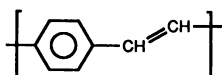
a Polydiacetylene(Acetylenic)



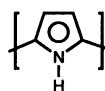
b Polyparaphenylene



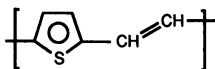
c Polyparaphenylene vinylene



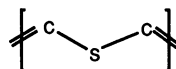
d Polypyrrole



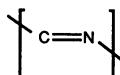
e Polythiophene vinylene



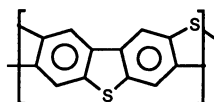
f Polyvinylene sulfide



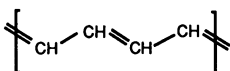
g Polymethineimine



h Polybenzothiophene



i Polyacetylene (trans)



j Polythiophene

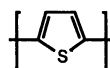


Figure 6. Polymers considered in Table I.

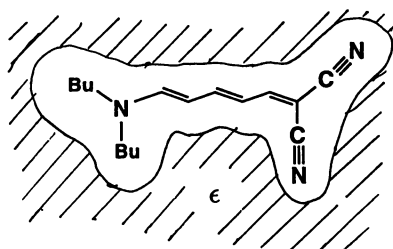


Figure 7. Illustration for PS-GVB/SOLV calculations.

3. DelPhi (from B. Honig of Columbia) calculates the solvent response to the charges from step 2, using the Poisson-Boltzmann equation. The net result is a set of charges at the interface representing the effects of the polarized solvent.
4. The interface charges from step 3 are input to PS-GVB which solves for a new HF or GVB wavefunction consistent with the solvent polarization.
5. The results in step 4 are used in step 2 and the process is iterated until convergence.

The net result is a wavefunction and structure self-consistently adjusted to the solvent. This should provide the ability to consider entirely new systems.

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Some calculations were carried out on the NSF-Pittsburgh supercomputer and on the JPL CRAY.

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 14. PS-GVB and PS-GVB/SOLV are from Schrödinger Inc. (Pasadena, California).

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