Vibrational Characteristics and Vibrational Contributions to the Nonlinear Optical Properties of a Push−Pull Polyene in Solution

Minhaeng Cho

Department of Chemistry, Korea University, Seoul 136-701, Korea

Received: June 3, 1997; In Final Form: October 20, 1997

The frequency shift and IR and Raman intensity changes of the characteristic vibrational mode of a push−pull polyene in polar solvent are described theoretically by using a simple two-state model. Depending on the electronic structure of the ground state in solution, the characteristic vibrational frequency can be either red-shifted or blue-shifted as the solvent polarity increases. The IR and Raman intensities are also found to be greatly influenced by the solvation. Finally, the solvation effects on the vibrational contributions to the molecular hyperpolarizabilities are briefly discussed.

I. Introduction

Nonlinear optical properties of push−pull polyenes have been studied extensively in the recent decade because of their possibilities for photonic and optoelectronic applications.[1−20] This type of polyenes consist of electron-donating and -accepting groups, and a conjugated linker. As has been shown recently, the strong electron−vibration coupling is an interesting intrinsic feature of this type of molecules. Also in connection with this aspect, it was found that there exists a strong IR-active vibrational mode associated with stretching motions of carbon atoms. Only this vibrational normal mode—so-called effective conjugation coordinate[21] or dimerization coordinate defined as the in-phase stretching of all C=C bonds and a simultaneous shrinking of all C−C single bonds of the chain—is strongly associated with the modulation of the ground-state dipole moment. This mode will be denoted as Q-mode. Besides the push−pull polyenes, the Schiff bases, charged polyenes, and peptide bond do have a common feature, that is to say, their IR intensities are unusually large.[22−29] Recently, these phenomena were theoretically investigated by Torii and Tasumi by using a simple two-state model for the electronic structures of these molecules and performing ab initio molecular orbital calculations.[30] They found that the electronic structure predicted by the two-state model, often called valence-bond charge-transfer model in ref 16, is strongly coupled to the vibrational motion, and discussed this effect by using the charge fluxes.

On the basis of the presence of highly mobile conjugated π-electrons strongly coupled with the particular nuclear displacement, Zerbi and co-workers[18] and Kim et al.[19] recently showed that the vibrational contributions to the molecular hyperpolarizabilities are quantitatively similar to the electronic ones. Therefore, it was suggested that the vibrational spectroscopies can be directly used to estimate the magnitudes of the hyperpolarizabilities.

In this paper we focus on how the solvation of a push−pull polyene modifies the vibrational characteristics, such as vibrational frequency and IR and Raman intensities. Here we closely follow theories presented by Chen, Lu, and Goddard III.[20] They showed that the solvation effect on the nonlinear optical properties of push−pull polyenes can be successfully explained by using the valence-bond charge-transfer (VB-CT) model in combination with the Marcus theory[31] for solvation of electron donor−acceptor system. Their empirical approaches to obtaining a few parameters needed were accurate enough to reproduce the experimental results obtained by Marder and co-workers.[32] With an emphasis on the self-consistent nature we calculate the magnitude of the solvation-induced vibrational frequency shift as well as vibrational intensity changes in IR and Raman. Furthermore, the vibrational contributions to the molecular hyperpolarizabilities are also discussed as a function of solvent polarity.

II. Vibrational Characteristics

It is assumed that the model Hamiltonian describing the push−pull polyene with the characteristic vibrational mode is given as

$$H = \begin{bmatrix} {}^{1}\!/_{2}k(Q - Q_{VB}^0)^2 & -t \\ -t & V_0 + {}^{1}\!/_{2}k(Q - Q_{CT}^0)^2 + \Delta E_{sol} \end{bmatrix} \quad (1)$$

where the electronic energy gap between the two states in an isolated molecule is denoted as V_0, and t denotes the transfer integral and was estimated to be 1.184 eV.[20] The electronic structure of the ground state is thus assumed to be given as a linear combination of the two basis functions denoted as $|\phi_{VB}\rangle$ and $|\phi_{CT}\rangle$. As usual, we assume that the wave function of the VB state is orthogonal to that of the CT state, i.e., $\langle\phi_{VB}|\phi_{CT}\rangle = 0$. The vibrational force constant k was estimated to be 33.55 eV/Å^2.[20,33] The two equilibrium positions associated with the VB and CT states are denoted as Q_{VB}^0 and Q_{CT}^0, respectively, and they are given as $Q_{VB}^0 = -Q_{CT}^0 = -0.12$ Å, so that the maximum bond length alternation (BLA) is assumed to be 0.12 Å. Finally, the solvation energy difference between the VB and CT states is denoted as $\Delta E_{sol} \propto E_{CT}^{sol} - E_{VB}^{sol}$ in eq 1.

The electronic ground-state wave function is then given as $\psi_g = (1 - f)^{1/2}\phi_{VB} + f^{1/2}\phi_{CT}$ where the fraction (weighting factor) of the CT state in the ground state is represented by f. The CT
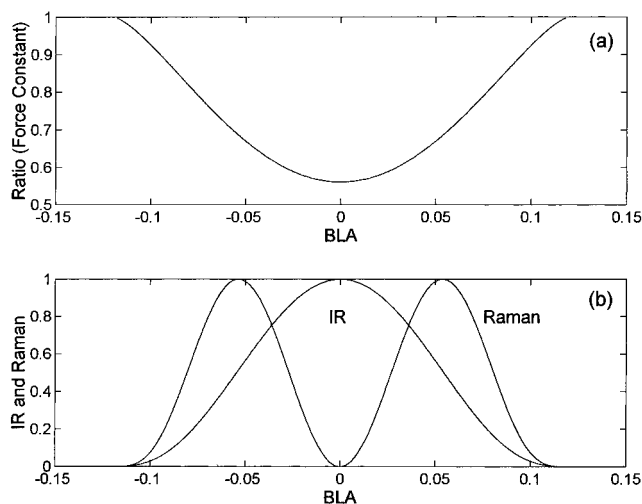
Figure 1. (a) Ratio, k_0/k, as a function of BLA. (b) Normalized IR and Raman intensities, $|(\partial M_{g,z}/\partial Q)_0|^2$ and $|(\partial \alpha_{zz}/\partial Q)_0|.^2$

character, f, which is a function of the vibrational coordinate as well as the solvent polarity, is

$$f(\epsilon) \equiv \frac{1}{2} - \frac{k\delta Q + \eta(\epsilon)}{2(\{k\delta Q + \eta(\epsilon)\}^2 + 4t^2)^{1/2}} \quad (2)$$

where

$$\delta \equiv Q^0_{VB} - Q^0_{CT}$$

$$\eta(\epsilon) \equiv V_0 + \Delta E_{sol} \quad (3)$$

The adiabatic potential energy surface of the ground state is

$$E_g(Q) = \frac{1}{2}[V_0 + \frac{1}{2}k(Q - Q^0_{VB})^2 + \frac{1}{2}k(Q - Q^0_{CT})^2 + \Delta E_{sol}] - \frac{1}{2}[\{k\delta Q + \eta(\epsilon)\}^2 + 4t^2]^{1/2} \quad (4)$$

Now the equilibrium vibrational coordinate in the ground state will be denoted as Q_0, and it is determined by putting the first derivative of $E_g(Q)$ with respect to Q equal to zero. In ref 16 it was shown that Q_0(BLA) is related to the CT character as $Q_0 = Q^0_{VB} - f(Q^0_{VB} - Q^0_{CT})$. It should be noted that the BLA, Q_0, is an implicit function of $\eta(\epsilon)$. Based on this model, the permanent dipole moment of the ground state is given as $M_g = f\mu_{CT}$, where μ_{CT} is the dipole moment of CT state, $\mu_{CT} = qeR_{DA}$. q and R_{DA} are the effective charge and distance between the donor and acceptor.

A. Vibrational Properties without Solvent. Before we take into account of the solvation-induced effects on various properties, it turns out to be useful to examine the BLA dependencies of vibrational force constant, and infrared and Raman intensities. From the Hamiltonian with $\Delta E_{sol} = 0$, one can obtain the energy of the ground state and find the vibrational force constant

$$k_0 = \frac{\partial^2 E_g(Q)}{\partial^2 Q}\Big|_{Q=Q_0} = k - \frac{2k^2\delta^2 t^2}{[(k\delta Q_0 + V_0)^2 + 4t^2]^{3/2}} \quad (5)$$

As can be seen in eq 5, the force constant differs from k when the electronic structure is neither VB nor CT state. In Figure 1a, we plot k_0/k with respect to BLA. It is noted that the force constant is minimum when the BLA equals zero. This is understandable since the force constant should be minimum when the bond order is minimum.

We next focus on the IR intensity of Q-mode, which is proportional to the square of $(\partial M_{g,z}/\partial Q)_0$:

$$\left(\frac{\partial M_{g,z}}{\partial Q}\right)_0 = \left(\frac{\partial f}{\partial Q}\right)_0 \mu_{CT} = -\frac{2t^2 k\delta\mu_{CT}}{[(k\delta Q_0 + V_0)^2 + 4t^2]^{3/2}} \quad (6)$$

In Figure 1b, the IR intensity is plotted with respect to BLA. As BLA approaches to zero, the relative IR intensity increases. This is because the resonance structure of molecules having BLA zero exhibits a large modulation of the dipole moment by the oscillating Q-mode. Second, the Raman intensity is proportional to the square of $(\partial \alpha_{zz}/\partial Q)_0$:

$$\left(\frac{\partial \alpha_{zz}}{\partial Q}\right)_0 = 2t^2\mu_{CT}^2\left[\frac{\partial}{\partial Q}\left(\frac{1}{\Delta(Q)^3}\right)\right]_0 = -\frac{6t^2\mu_{CT}^2(k\delta Q_0 + V_0)k\delta}{[(k\delta Q_0 + V_0)^2 + 4t^2]^{5/2}} \quad (7)$$

In Figure 1b, the Raman intensity is plotted with respect to BLA, and we find that the Raman intensity becomes maximum at $Q_0 \cong \pm 0.05$ Å.

Based on the theoretical results, eqs 5, 6, and 7, with Figure 1, it is possible to draw the following conclusions:[34]

(i) Case 1. BLA < 0: Type I. This is the case when the donor and acceptor strengths are relatively weak so that the ground state resembles VB state more than CT state. Then, as BLA increases, the vibrational frequency decreases (red shift), IR intensity increases, and Raman intensity increases or decreases depending on the precise BLA.

(ii) Case 2. BLA > 0: Type II. This is the case when the donor and acceptor strengths are sufficiently large so that the ground state resembles CT state. Then, as BLA increases, vibrational frequency increases (blue shift), IR intensity decreases, and Raman intensity increases or decreases depending on BLA.

B. Solvation Effects on Vibrational Properties. Now the solvation is taken into account in the model Hamiltonian. For the sake of simplicity, the solvation energy of the fictitious VB state is assumed to be negligibly small in comparison to that of the CT state containing fully separated charges. Although there exist various levels of theoretical methods of calculating solvation energy, we shall use the simplest method which was originally applied to the electron-transfer problem by Marcus.[31]

Based on VB-CT-S model,[20] the solvation energy difference was obtained as

$$\Delta E_{sol} = -\frac{e^2}{4\pi\epsilon_0}(1 - \epsilon^{-1})fq^2\left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{R_{DA}}\right) \quad (8)$$

where r_D, r_A, and R_{DA} denote the effective radii of the donor, acceptor, and the distance between the donor and acceptor, respectively. q is the effective charge developed in the donor and acceptor in the CT state. ϵ is the static dielectric constant of the solvent.

In order to find the optimized f in solution, one can use the iteration procedure self-consistently. (1) First, calculate f of a given push−pull polyene without solvent. (2) Use the calculated f to evaluate ΔE_{sol} given in eq 8. (3) Inserting ΔE_{sol} into the model Hamiltonian gives a new f. (4) Iterate the steps (2) and (3) until the CT character f converges to the optimum f^*. This self-consistent approach was used in ref 20 to study the solvation-induced changes of molecular hyperpolarizabilities of 1,1-dicyano-6-(dibutylamine)hexatriene. Here we shall use the
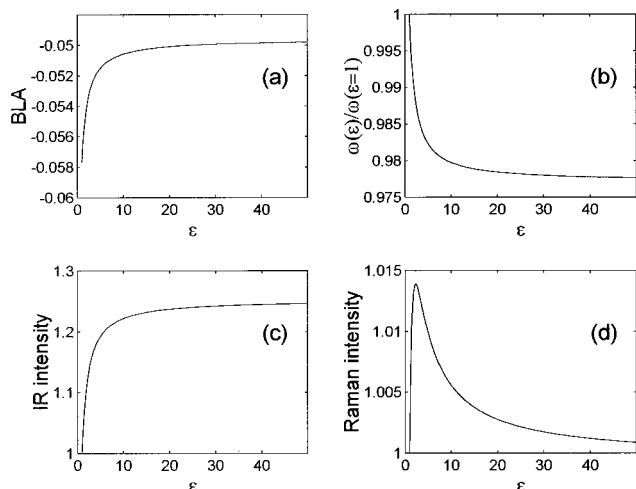
Optical Properties of a Push−Pull Polyene in Solution

J. Phys. Chem. A, Vol. 102, No. 4, 1998 **705**

Figure 2. Various properties are plotted for type I molecule, 1,1-dicyano-6-(dibutylamine)hexatriene. The parameters obtained in ref 20 are $V_0 = 0.833$ eV, $t = 1.184$ eV, $R_{DA} = 7.30$ Å; $k = 33.55$ eV/Å^2. (a) BLA vs ϵ. (b) $\omega(\epsilon)/\omega(\epsilon=1)$ vs ϵ. (c) IR intensity ratio, $|(\partial M_{g,z}(\epsilon)/\partial Q)_0|^2/|(\partial M_{g,z}(\epsilon=1)/\partial Q)_0|^2$ vs ϵ. (d) Raman intensity ratio, $|(\partial\alpha_{zz}(\epsilon)/\partial Q)_0|^2/|(\partial\alpha_{zz}(\epsilon=1)/\partial Q)_0|^2$, vs ϵ.

Figure 3. For type II molecule with the same parameters given in Figure 2 except for $V_0 = -0.833$ eV. (a) BLA vs ϵ. (b) $\omega(\epsilon)/\omega(\epsilon=1)$ vs ϵ. (c) IR intensity ratio, $|(\partial M_{g,z}(\epsilon)/\partial Q)_0|^2/|(\partial M_{g,z}(\epsilon=1)/\partial Q)_0|^2$, vs ϵ. (d) Raman intensity ratio, $|(\partial\alpha_{zz}(\epsilon)/\partial Q)_0|^2/|(\partial\alpha_{zz}(\epsilon=1)/\partial Q)_0|^2$ vs ϵ.

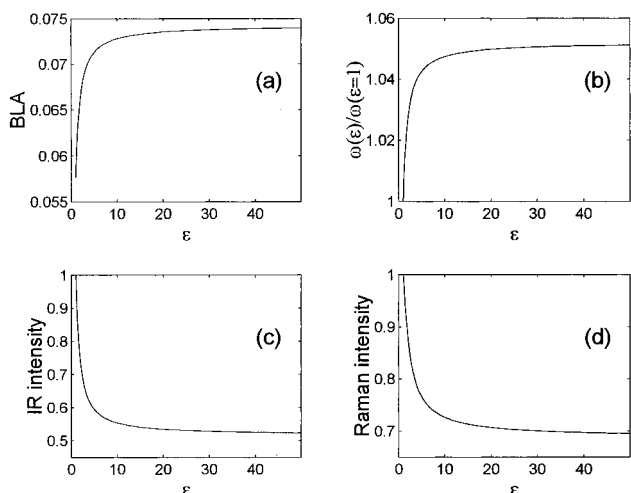same parameters to demonstrate that the vibrational frequency shift and intensity are greatly changed as the solvent polarity increases.

Depending of the sign of BLA, we separately considered two types, type I and type II as mentioned above, that are also associated with the cases of $V_0 > 0$ and $V_0 < 0$, respectively. For example, 1,1-dicyano-6-(dibutylamine)hexatriene belongs to type I. In this case, the ground-state equilibrium coordinate Q_0, which is the bond length alternation (BLA), is negative (note that $Q_{VB}^0 = -0.12$ Å), and in Figure 2a we plot Q_0 as a function of the solvent dielectric constant, ϵ. As the solvent polarity increases, the BLA increases. This can be understood by noting that the CT-state is preferentially stabilized by the polar solvent. In case of the type II molecules, the BLA also increases as solvent polarity increases (see Figure 3a). Here the same parameters except that $V_0 = -0.833$ eV are used to demonstrate the general patterns. Note that the first hyperpolarizabilities of type I molecules are usually positive, whereas those of type II molecules are negative. Therefore, it is now possible to predict the sign of the first hyperpolarizability by

measuring IR spectra of a given push−pull polyene in various polar solvents. Although not shown, the BLA coordinate is almost linearly proportional to $(1 - \epsilon^{-1})$ so that it is suggested that one could plot various vibrational properties, such as vibrational frequency, and IR and Raman intensities, as a function of $(1 - \epsilon^{-1})$ instead.

We now consider the force constant of the characteristic vibrational mode, which is found to be

$$k(\epsilon) = \frac{\partial^2 E_g(Q)}{\partial Q^2}\Big|_{Q=Q_0} = k - \Delta k(\epsilon) \qquad (9)$$

where the solvation-induced shift of the force constant, $\Delta k(\epsilon)$, is

$$\Delta k(\epsilon) \equiv \frac{2k^2\delta^2 t^2}{[(k\delta Q_0 + \eta(\epsilon))^2 + 4t^2]^{3/2}} \qquad (10)$$

The characteristic vibrational frequency is therefore shifted, when the push−pull polyene is solvated, as

$$\frac{\omega(\epsilon)}{\omega(\epsilon=1)} = \left[\frac{k - \Delta k(\epsilon)}{k - \Delta k(\epsilon=1)}\right]^{1/2} \qquad (11)$$

Here $\omega(\epsilon=1)$ is the vibrational frequency of an isolated molecule and it was assumed that the reduced mass does not depend on the solvent polarity. As can be seen in eq 10, it is observed that $\Delta k(\epsilon)$ is always greater than zero, so that the force constant in solution is always smaller than the estimated value $k = 33.55$ eV/Å^2. However, whether the frequency shows a red shift or a blue shift by the solvation is critically dependent on whether the target molecule belongs to type I or type II. In Figure 2b, the ratio $\omega(\epsilon)/\omega(\epsilon=1)$ is plotted for 1,1-dicyano-6-(dibutylamine)hexatriene as a representative example for type I. In this case, the vibrational frequency is red-shifted. In order to estimate the magnitude of the frequency shift, assume that the vibrational frequency, $\omega(\epsilon=1)$, is about 1600 cm^{-1}.[21] Then the frequency shift is approximately 35 cm^{-1} when the dielectric constant increases from 1 to 50. Next we calculate $\omega(\epsilon)/\omega(\epsilon=1)$ for a type II molecule and plot them in Figure 3b. In contrast, the frequency is blue-shifted by about 80 cm^{-1}. These tendencies can be understood as follows. As mentioned above, when the BLA equals zero, the vibrational force constant is minimum for a given push−pull polyene. Therefore, the solvation of type I molecule stabilizes the CT state and makes the BLA increase toward zero. Consequently, the vibrational frequency is red-shifted. The opposite effect on type II molecules by solvation should occur.

The ground-state dipole moment derivative with respect to the characteristic vibrational coordinate is given as, when the solvation is taken into account

$$\left(\frac{\partial M_{g,z}}{\partial Q}\right)_0 = -(\Delta k(\epsilon)/k)\frac{\mu_{CT}}{\delta} \qquad (12)$$

where $\Delta k(\epsilon)$ was defined in eq 10. In the case of the type I molecule, the IR intensity increases as the solvent dielectric constant increases, whereas the opposite result should be observed for type II molecules (see Figure 2c in comparison with Figure 3c). Note that the intensity change is, in this case, about 20−50% so that this tendency should be easily observed in experiment. These patterns can also be understood by noting

that the absolute magnitude of $(\partial M_{g,z}/\partial Q)_0$ is maximum when the BLA equals to zero (see Figure 1b). As the solvent polarity increases for the type I molecule, the BLA increases from negative to zero so that the IR intensity increases. On the other hand, the opposite applies to the type II molecules.

Finally, we consider the solvation effect on the Raman intensity, which is proportional to the square of

$$\left(\frac{\partial \alpha_{zz}}{\partial Q}\right)_0 = -\frac{6t^2 \mu_{CT}^2 (k\delta Q_0 + \eta(\epsilon))k\delta}{(\{k\delta Q + \eta(\epsilon)\}^2 + 4t^2)^{5/2}} \quad (13)$$

In Figures 2d and 3d, the Raman intensities of type I and II molecules are plotted. These can also be understood by carefully examining the BLA dependence of Raman intensity plotted in Figure 1b and by noting the increment of BLA by the solvation.

It should be mentioned that the results, eqs 7 and 13, are qualified in the case when the *zz* component of the polarizability derivative is dominant over other components. Although most of the push−pull polyenes belong to this case, if other components contribute significantly to the polarizability derivative, they should be properly taken into account.

III. Solvation Effects on Vibrational Contributions to Molecular Hyperpolarizabilities

As recently discussed by Zerbi and co-workers[18] and by Kim et al.,[19] the electronic (first) hyperpolarizability, β^e, was found to be quantitatively similar to the vibrational correspondence, denoted as β^v, measured experimentally. Furthermore, the vibrational second hyperpolarizability was also shown to be in quantitative agreement with the electronic one, when a two-state approximation is invoked.[19]

A. Solvation Effect on Vibrational First Hyperpolarizability: β^v. The vibrational contributions to the molecular first hyperpolarizability, β^v, within the harmonic approximation, is given as[18,34,35]

$$\beta_{zzz}^v = \frac{1}{2!4\pi^2 c^2} \sum_k \left(\frac{1}{\nu_k^2}\right)\left(\frac{\partial M_{g,z}}{\partial Q_k}\right)_0 \left(\frac{\partial \alpha_{zz}}{\partial Q_k}\right)_0 \quad (14)$$

where the harmonic vibrational frequency of the *k*th mode is denoted as ν_k. β_{zzz}^v can be calculated by measuring the IR and Raman spectra and extracting the information on $(\partial M_{g,z}/\partial Q_k)_0$ and $(\partial \alpha_{zz}/\partial Q_k)_0$ from them. Here we use the results obtained above, eqs 12 and 13, to study the solvation effect on β_{zzz}^v. As usual, it is assumed that there is only one vibrational mode relevant in the summation of eq 14.

Inserting eqs 12 and 13 into 14 gives

$$\beta_{zzz}^v = \beta_{zzz}^e \bar{\beta} \quad (15)$$

where the electronic contribution, β_{zzz}^e, and the additional factor are given as

$$\beta_{zzz}^e = \frac{3t^2 \mu_{CT}^3 (k\delta Q_0 + \eta(\epsilon))}{(\{k\delta Q_0 + \eta(\epsilon)\}^2 + 4t^2)^{5/2}}$$

$$\bar{\beta}(\epsilon) \equiv \frac{6t^2 k\delta^2}{(\{k\delta Q_0 + \eta(\epsilon)\}^2 + 4t^2)^{3/2}} \quad (16)$$

The relationship between β_{zzz}^e and β_{zzz}^v, eq 15, for an isolated

push−pull polyene was obtained in ref 19. Here it is generalized to the case in solution.

B. Solvation Effect on Vibrational Second Hyperpolarizability: γ^v. The vibrational contribution to the second hyperpolarizability is[18,34,35]

$$\gamma_{zzzz}^v = \frac{1}{3!4\pi^2 c^2} \sum_k \left(\frac{1}{\nu_k^2}\right)\left\{4\left(\frac{\partial M_{g,z}}{\partial Q_k}\right)_0\left(\frac{\partial \beta_{zzz}}{\partial Q_k}\right)_0 + 3\left(\frac{\partial \alpha_{zz}}{\partial Q_k}\right)_0^2\right\} \quad (17)$$

Note that the second term in the summation is associated with the Raman intensity only, Herzberg−Teller terms, whereas the first term contains both the IR (derivatives of M_g) and hyper-Raman terms (derivatives of β). In order to complete the calculation of γ_{zzzz}^v experimentally, one should measure IR, Raman, and hyper-Raman spectra.

We find that γ_{zzzz}^v is related to γ_{zzzz}^e as

$$\gamma_{zzzz}^v = \gamma_{zzzz}^e \bar{\gamma}\left\{1 + \frac{9(k\delta Q_0 + \eta(\epsilon))^2}{8((k\delta Q_0 + \eta(\epsilon))^2 - t^2)}\right\} \quad (18)$$

where the electronic contribution, γ_{zzzz}^e, and the factor $\bar{\gamma}$ are defined as

$$\gamma_{zzzz}^e = \frac{4t^4 \mu_{CT}^4 [(k\delta Q_0 + \eta(\epsilon))^2 - t^2]}{(\{k\delta Q_0 + \eta(\epsilon)\}^2 + 4t^2)^{7/2}}$$

$$\bar{\gamma} \equiv \frac{4t^2 k\delta^2}{(\{k\delta Q_0 + \eta(\epsilon)\}^2 + 4t^2)^{3/2}} \quad (19)$$

Therefore, the magnitudes of the molecular hyperpolarizabilities can be approximately estimated from the vibrational spectroscopic measurements, by using eqs 15 and 18. Although not shown in this paper, based on the numerical calculations of β_{zzz}^v and γ_{zzzz}^v as functions of solvent polarity, we find that the general trends with respect to the solvent polarity are identical to β_{zzz}^e and γ_{zzzz}^e of a push−pull polyene in solution.[20]

IV. Summary and a Few Concluding Remarks

In this paper, a theoretical description of solvation effects on the vibrational frequency shift and intensity changes in IR and Raman was presented by using a simple two-state model. It was found that the vibrational frequency should be red(blue)-shifted for type I(II) molecules. The IR and Raman intensities are strongly influenced by the solvation. Therefore, by combining IR and Raman experiments, it is possible to obtain detailed information on the electronic structure of a given push−pull polyene in solution, which in turn can be used in understanding the optical nonlinearities in solution. Furthermore, it was discussed that the vibrational contributions to the molecular hyperpolarizabilities are strongly affected by the solvation. Recently, Zuliani et al.[36] carried out experimental measurements of the first hyperpolarizabilities of several push−pull polyenes in various polar solvents. A detailed comparison to these experimental data will be presented elsewhere together with quantum chemistry calculations.

References and Notes

(1) Prasad, P. N.; William, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymer*; John & Wiley: New York, 1991.

Optical Properties of a Push−Pull Polyene in Solution

J. Phys. Chem. A, Vol. 102, No. 4, 1998 **707**

(2) Chemla, D. S.; Zyss, J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic: New York, 1987.

(3) Marder, S. R.; Perry, J. W.; Schaeffer, W. P. *Science* **1989**, *245*, 626.

(4) Samuel, I. D. W.; Ledoux, I.; Dhenaut, C.; Zyss, J.; Fox, H. H.; Schrock, R. R.; Silbey, R. J. *Science* **1994**, *265*, 1070.

(5) Mukamel, S.; Takahashi, A.; Wang, H. X.; Chen, G. *Phys. Rev. Lett.* **1992**, *69*, 65.

(6) Spano, F. C.; Soos, Z. G. *J. Chem. Phys.* **1993**, *99*, 9265.

(7) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155.

(8) Levine, B. F.; Bethea, C. G. *Appl. Phys. Lett.* **1974**, *24*, 445.

(9) Clays, K.; Persoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980.

(10) Song, N. W.; Kang, T.-I.; Jeoung, S. C.; Jeon, S.-J.; Cho, B. R.; Kim, D. *Chem. Phys. Lett.* **1996**, *261*, 307.

(11) Cho, M. *J. Chem. Phys.* **1997**, *106*, 7550.

(12) Meyers, F.; Marder, S. R.; Pierce, B. M.; Bredas, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 10703.

(13) Joffre, M.; Yaron, D.; Silbey, R. J.; Zyss, J. *J. Chem. Phys.* **1992**, *97*, 5607.

(14) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Bredas, J. L.; Pierce, B. M. *Science* **1994**, *265*, 632.

(15) Gorman, C. B.; Marder, S. R. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 11297.

(16) Lu, D.; Chen, G.; Perry, J. W.; Goddard III, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 10679.

(17) Chen, G.; Mukamel, S. *J. Chem. Phys.* **1995**, *103*, 9355.

(18) Castiglioni, C.; Del Zoppo, M.; Zerbi, G. *Phys. Rev.* **1996**, *B53*, 13319.

(19) Kim, H.-S.; Cho, M.; Jeon, S.-J. *J. Chem. Phys.*, in press.

(20) Chen, G.; Lu, D.; Goddard III, W. A. *J. Chem. Phys.* **1994**, *101*, 5860.

(21) Castiglioni, C.; Del Zoppo, M.; Zerbi, G. *J. Raman Spectrosc.* **1993**, *24*, 485.

(22) Fincher, Jr., C. R.; Ozaki, M.; Heeger, A. J.; MacDiarmid, A. G. *Phys. Rev.* **1979**, *B19*, 4140.

(23) Harada, I.; Furukawa, Y.; Tasumi, M.; Shirakawa, H.; Ikeda, S. *J. Chem. Phys.* **1980**, *73*, 4746.

(24) Piaggio, P.; Dellepiane, D.; Piseri, L.; Tubino, R.; Taliani, C. *Solid State Commun.* **1984**, *50*, 947.

(25) Lussier, L. S.; Sandorfy, C.; Le-Thanh, L.; Vocelle, D. *J. Phys. Chem.* **1987**, *91*, 2282.

(26) Masuda, S.; Torii, H.; Tasumi, M. *J. Phys. Chem.* **1996**, *100*, 15335.

(27) Yamabe, T.; Akagi, K.; Tanabe, Y.; Fukui, K.; Shirakawa, H. *J. Phys. Chem.* **1982**, *86*, 2359.

(28) Boudreaux, D. S.; Chance, R. R.; Bredas, J. L.; Silbey, R. J. *Phys. Rev.* **1983**, *B28*, 6927.

(29) Zerbi, G.; Castiglioni, C.; Sala, S.; Gussoni, M. *Synth. Met.* **1987**, *17*, 293.

(30) Torii, H.; Tasumi, M. *J. Phys. Chem.* **1997**, B*101*, 466.

(31) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 996.

(32) Marder, S. R., Perry, J. W.; Bourhill, G.; Gorman, C. B.; Tiemann, B. G. *Science* **1993**, *261*, 186.

(33) Rappe, A. K.; Goddard III, W. A. *J. Phys. Chem.* **1991**, *95*, 2260.

(34) A preliminary numerical study of the AM1-level semiempirical and ab initio calculations on vibrational frequency shift and IR intensity change with respect to BLA confirms the theoretical predictions presented in this paper. More detailed calculations in comparison with experiments will be presented elsewhere.

(35) Flytzanis, C. *Phys. Rev.* **1972**, *B6*, 1264. Bishop, D. M. *Rev. Mod. Phys.* **1990**, *62*, 343.

(36) Zuliani, P.; Del Zoppo, M.; Castiglioni, C.; Zerbi, G.; Marder, S. R.; Perry, J. W. *J. Chem. Phys.* **1995**, *103*, 9935.