

Chemical Bonding and Off-Resonance Nonlinear Polarizabilities of Conjugated Organic Molecules

Guanhua Chen, Akira Takahashi and Shaul Mukamel

Center for Photoinduced Charge Transfer, Department of Chemistry, University of Rochester,

Rochester, New York 14627

(December 27, 1993)

Abstract

We employ the Pariser-Parr-Pople (PPP) Hamiltonian to calculate the three lowest polarizabilities (α , β and γ) of Octatetraene. By applying a strong static electric field, the molecule undergoes a significant structural change, which affects the optical polarizabilities. We find that these polarizabilities can be described using a small number of charge fluctuation modes. We further relate the magnitude and sign of these polarizabilities with some coarse features of the ground state reduced single electron density matrix, which in turn is directly related to the chemical bonding.

I. INTRODUCTION

Conjugated organic molecules are important optical materials because of their large off-resonance hypolarizabilities [1-6]. Marder and co-workers [3] employed a four orbitals model [3,4] and used a semi-empirical procedure (AM1) [3] to study the static hypolarizabilities of polyenes di-substituted with electron donor and acceptor. They related the magnitudes of β and γ with a structural property: the bond length alternation (BLA). Since polarizabilities are determined by the detailed electronic structures, a deeper understanding of the electronic origin of this correlation is warranted.

In this paper, we study the correlations between the static polarizabilities and the ground state reduced density matrix for conjugated polyenes. We employ the PPP Hamiltonian and use a Time Dependent Hartree Fock (TDHF) method [6] to calculate the static and dynamic polarizabilities α , β and γ . We identify which charge fluctuation modes are responsible for the off-resonance polarizabilities, and we further relate the polarizabilities to some coarse features of the ground state density matrix. Our analysis provides a direct relationship between the magnitudes and signs of the polarizabilities and the nature of chemical bonding in these systems.

*Proceedings of the SPIE OSA Conference
(1995)*

II. THEORY

A. Model

We use the PPP Hamiltonian for polyenes interacting with a strong static electric field and with an optical field. The total Hamiltonian is,

$$H = H_{PPP} + H_{dc} + H_{opt} \quad (1)$$

where H_{PPP} is PPP Hamiltonian. Its form and parameters can be found in [6,7].

We apply a static electric field along the z axis, which modifies the molecular structure. Within the dipole approximation, the second term in the total Hamiltonian is

$$H_{dc} = -E_0 P, \quad (2)$$

where P is the polarization operator along z axis,

$$P = e \sum_{n,\sigma} z_n \left(\frac{1}{2} - \rho_{nn}^\sigma \right). \quad (3)$$

ρ_{nm}^σ is the reduced density matrix operator, which is defined as,

$$\rho_{nm}^\sigma = c_{m,\sigma}^+ c_{n,\sigma}; \quad (4)$$

where $c_{n,\sigma}^+$ ($c_{n,\sigma}$) is σ -spin electron creation (annihilation) operator at the n 'th carbon atom.

The third term in H represents the interaction between the π electrons and the optical electric field $\mathcal{E}(t)$, which is assumed to be polarized along the chain axis z .

$$H_{opt} = -\mathcal{E}(t)P. \quad (5)$$

B. Time Dependent Hartree Fock

To calculate the polarizabilities, we adopt a similar approach to that developed by Takahashi and Mukamel [6].

First we solve for the Hartree Fock ground state with full geometry optimization in the absence of the optical field. From the ground state wavefunction we construct the reduced density matrix $\bar{\rho}$. $\bar{\rho}_{nm} = \sum_k a_{kn}^* a_{km}$, where k sums over occupied molecular orbitals, a_{kn} is the coefficient of n th site for the k th single electron molecular orbital.

We then write $\rho(t) = \bar{\rho} + \delta\rho(t)$ and solve the TDHF equation for $\delta\rho$ [6].

$$i\hbar\dot{\delta\rho} - [\bar{h}, \delta\rho] - [\delta h, \bar{\rho}] = [f, \bar{h}] + [f, \delta\rho] + [\delta h, \delta\rho], \quad (6)$$

where the zero order Fock operator \bar{h} is [6]

$$\bar{h}_{nm} = t_{nm} + 2\delta_{nm} \sum_l \gamma_{nl} \bar{\rho}_{ll} - \gamma_{nm} \bar{\rho}_{nm}. \quad (7)$$

Here t_{nm} and γ_{nm} are the electron transfer matrix element and the coulomb repulsion between sites n and m , respectively. f is the Fock operator corresponding to H_{opt} ,

$$f_{nm}(t) = \delta_{nm} e z_n \mathcal{E}(t), \quad (8)$$

and δh the change of the Fock operator due to the change of ρ ,

$$\delta h_{nm} = 2\delta_{nm} \sum_l \gamma_{nl} \delta \rho_{ll} - \gamma_{nm} \delta \rho_{nm}. \quad (9)$$

After solving the TDHF equation to the first, second and third order in $\mathcal{E}(t)$, we project the solution $\delta \rho(\omega)$ at each order onto the space spanned by the eigenvectors $\{\rho^\nu\}$ of the homogeneous TDHF equation,

$$\hbar \Omega_\nu - [\bar{h}, \rho^\nu] - [h^\nu, \rho] = 0, \quad (10)$$

where $h^\nu = 2\delta_{nm} \sum_l \gamma_{nl} \rho_{ll}^\nu - \gamma_{nm} \rho_{nm}^\nu$. We can then use the expression

$$\delta \rho(\omega) = \sum_\nu c_\nu(\omega) \rho^\nu. \quad (11)$$

The main difference between our current procedure and that of [6] is that we solve the full homogeneous TDHF equation for the eigenmodes while in [6] an approximate homogeneous equation which corresponds to the Random Phase Approximation (RPA) [6] was adopted.

III. RESULTS

All calculations were made for all trans Octatetraene which has eight carbon atoms [8]. This size is large enough to provide some essential features of large polyenes, yet relatively small for fast computer calculations.

A. Hartree Fock, Bond Length Alternation and the Reduced Density Matrix

We solve the static Hartree Fock equation with full geometry optimization. From the resulting structure, we evaluate the BLA, which is defined as the deviation of the actual bond length from the average bond length. From the resulting single electron wavefunctions we construct the reduced density matrix $\bar{\rho}_{nn}$.

We subject Octatetraene to static electric fields of different strengths, with the field E_0 varying from 0 to 0.4 V/Å. As the field amplitude increases, the structure is driven away from its native structure. Around $E_0 = 0.15$ V/Å the BLA reaches its minimum. At $E_0 = 0.2$ V/Å the single and double bond pattern is reversed, as shown in Fig 1. At $E_0 = 0.4$ V/Å, the two bonds at both ends are much longer than the other bonds. This indicates that they are decoupled from the rest of system. In panels a, b and c of Fig. 2 we plot the reduced density matrix $\bar{\rho}$ and the corresponding contours, for $E_0 = 0, 0.15$ and 0.30 V/Å. As the electric field is increased, an electron is transferred from site one to site eight. This is clearly illustrated by the changes of the diagonal elements. The off-diagonal elements of the reduced density matrix represent the chemical bond-order [9]. The nearest neighbor (n.n.) off-diagonal elements are much larger than the remaining of off-diagonal elements. This implies that π chemical bonds exist only between nearest neighbors. As the electric field increases, the double-single bond topology changes to delocalized π bond topology, and then to single-double bond topology. This is accompanied by the structure changes: large BLA to near zero BLA and to large reversed BLA. The density matrix illustrates the electronic structural change underlining the geometrical structural change.

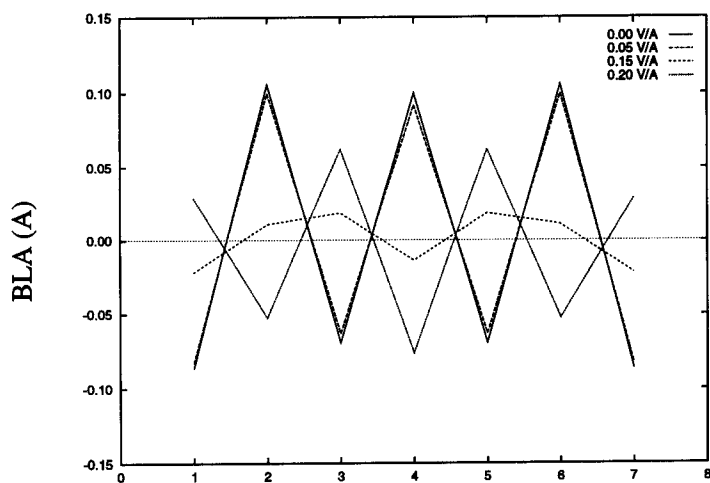


Fig. 1 Bond length alternation for Octatetraene in different static fields ($E_0 = 0.00, 0.05, 0.15$ and 0.20 V/A)

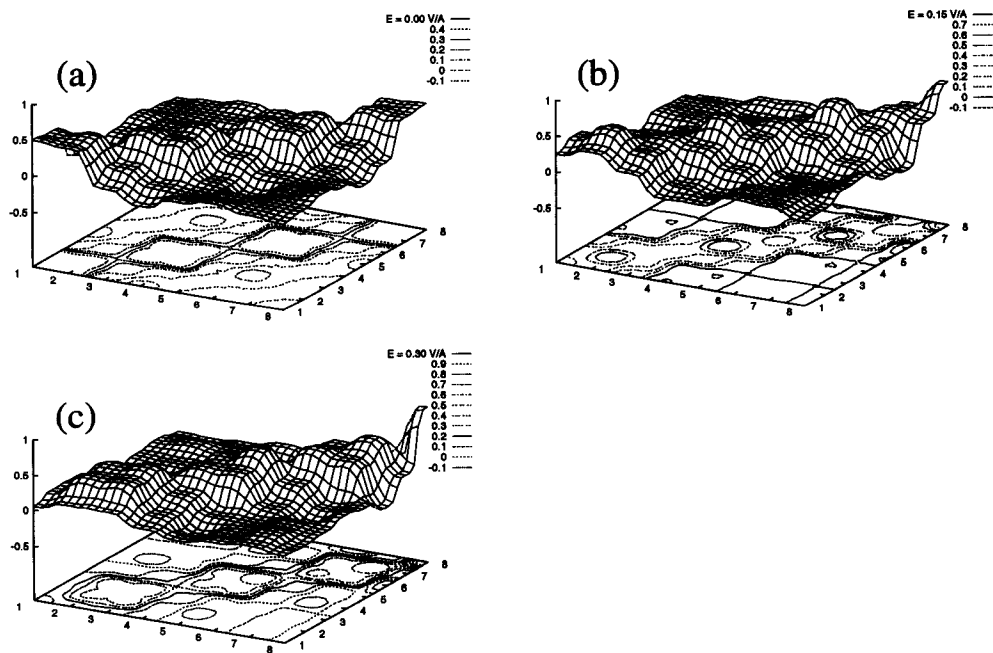


Fig. 2 Reduced density matrix $\bar{\rho}$ for Octatetraene subject to static external fields. The numbers in the x and y axis are the site numbers of carbon atoms (1 \rightarrow 8). There are 64 discrete points for $\bar{\rho}$. The surfaces and contours are obtained by interpolation. (a) $E_0 = 0.00$ V/A; (b) $E_0 = 0.15$ V/A; (c) $E_0 = 0.30$ V/A.

B. Time Dependent Hartree Fock Solution

In Fig. 3 we plot the polarizabilities α , β (second harmonic generation) and γ (third harmonic generation) against the external static field E_0 . In all calculations the frequency of the optical wave was taken $\omega = 0.02$ eV. Around $E_0 = 0.15$ V/A where BLA reaches its minimum, α , β and γ all exhibit rich features. α has its maximum value, the magnitude of β is approximately zero, and γ is negative and its magnitude reaches maximum. At $E_0 \approx 0.10$ and 0.18 V/A, β reaches its maxima. At the same time, the corresponding reduced density matrix indicates a transition in the nature of chemical bonding: localized bonding to delocalized bonding. This is illustrated in Fig. 4

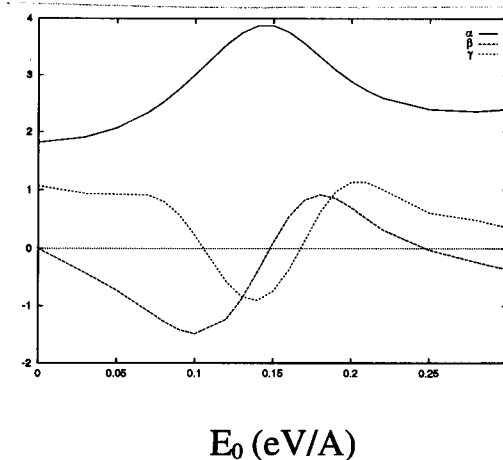


Fig. 3 Polarizabilities α , β and γ . The optical frequency $\omega = 0.02$ eV. The horizontal axis corresponds to E_0 (in the units of V/A). $E_0 = 0 \rightarrow 0.3$ V/A. The solid line is for α , the dashed for β and the dotted for γ .

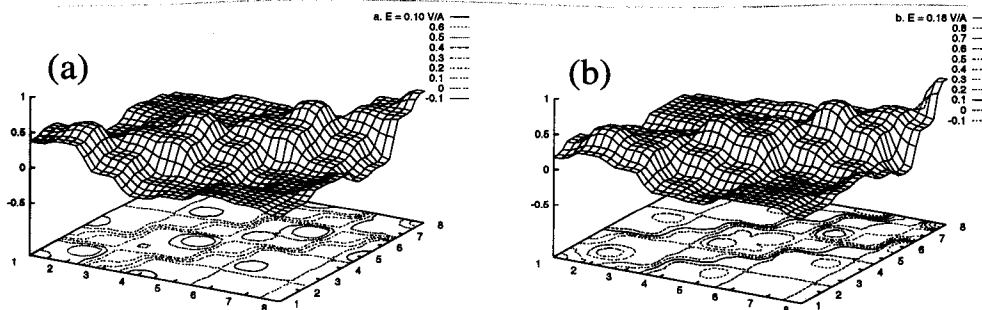


Fig. 4 Ground state reduced density matrix for Octatetraene at the static fields which maximize $|\beta|$. These fields correspond to an intermediate bonding between the localized π bonding and the delocalized bonding (a) $E_0 = 0.10$ and (b) 0.18 V/A.

To illustrate the different role of chemical bonding and geometry (bond lengths), we used the optimized geometries for different electric fields, $E_0 = 0$ to 0.3 V/A. We then removed the external field and calculated α , β and γ while keeping the geometry fixed. Because of the inversion symmetry, $\beta = 0$. In this case α and γ (Fig. 5a) do not change much with geometry. In Fig. 5b we plot the ground state reduced density matrix for a structure corresponding to $E_0 = 0.15$ V/A. The density matrix is now very similar to that of Fig. 2a. This is true for every case between $E_0 = 0$ to 0.3 V/A. This explains why α and γ do not change much for various structures, see Fig. 5a.

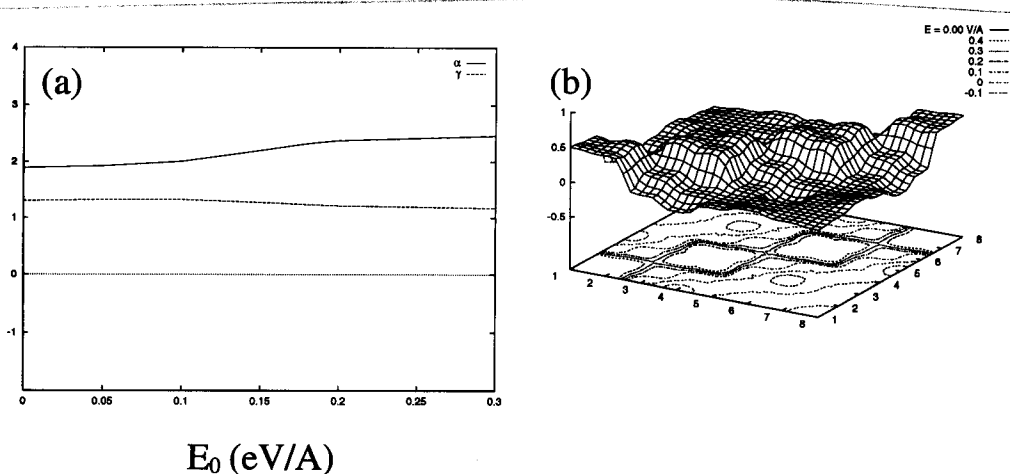


Fig. 5 (a) Polarizabilities for $E_0 = 0$ but with geometry fixed at the optimized value with an electric field which varies from $0 \rightarrow 0.3$ V/A, as given by the horizontal axis. Solid line- α ; dashed line- γ ; $\beta = 0$. (b) Reduced density matrix $\bar{\rho}$ for $E_0 = 0.00$ V/A, while the structure is fixed at the optimized geometry for $E_0 = 0.15$ V/A.

Table I. The eigenvalues Ω_ν (in eV) and their degeneracies (Deg) of the homogeneous Time Dependent Hartree Fock equation for $E_0 = 0.0$ V/A.

#	Ω_ν	Deg	#	Ω_ν	Deg	#	Ω_ν	Deg	#	Ω_ν	Deg
1	0	4	7	4.034	1	13	7.604	1	19	10.745	1
2	1.047	2	8	4.603	2	14	7.979	1	20	10.988	1
3	1.630	2	9	5.739	1	15	8.166	1	21	11.290	1
4	1.925	2	10	6.064	1	16	9.131	1	22	12.847	1
5	2.677	2	11	6.932	1	17	9.452	1	23	13.025	1
6	3.555	2	12	7.301	1	18	9.964	1			

In Table I we present the eigenvalues of the homogeneous TDHF equation and their degeneracy. To study the origin of the induced polarization, we projected the solutions of the inhomogeneous TDHF equation onto the space spanned by the eigenvectors $\{\rho^\nu\}$ of the homogeneous TDHF, and obtained $c_\nu(\omega)$ of Eq.(11). We denote the polarizability corresponding to mode ν as p_ν ($p_\nu \equiv \sum_n z_n \rho_{nn}^\nu$). In Fig. 6 we plot the contribution of mode ν to the polarizabilities $W_\nu \equiv c_\nu(\omega) p_\nu / \mathcal{E}$ vs. the mode frequency Ω_ν at each order (1st, 2nd and 3rd). Obviously, only a few modes make a noticeable contributions to the polarizabilities. In Table II we list the frequencies of the first absorption peaks. As the field increases, the frequency decreases first and then increases. These values are identical to the frequencies of the eigenmodes which make the dominant contributions to α .

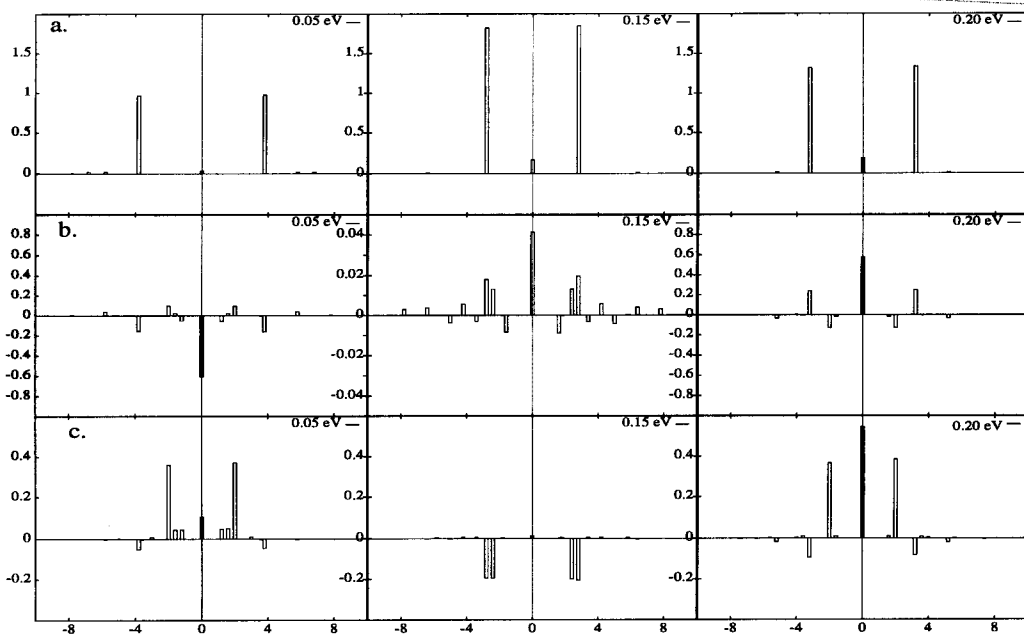


Fig. 6 W_ν (in a.u.). Contributions of eigenmodes of the homogeneous TDHF to polarizabilities for three cases: $E_0 = 0.05, 0.15$ and 0.20 V/A. The horizontal axis represents eigenfrequencies Ω_ν (in eV). (a) α ; (b) β ; (c) γ . Note that in (b) the vertical scale for $E_0 = 0.15$ V/A is very small. The sum of all contributions in each case is equal to the polarizability of that order.

Table II. Variation of the absorption peak frequency Ω in the static electronic field.

E_0 (V/A)	0.00	0.05	0.10	0.15	0.18	0.20	0.30
Ω (eV)	4.03	3.77	3.18	2.86	3.05	3.27	3.66

IV. DISCUSSION

A. Contributions to the static α , β and γ

There are a few important points to note from the above calculations. First, only a few homogeneous TDHF eigenvectors have noticeable contribution to off-resonance polarizabilities. The mode which dominates the absorption peak always makes a large contribution to the off-resonance α , β and γ .

B. Off-Resonant Polarizabilities and Chemical Bonding

We showed that for conjugated organic molecules the off-resonance polarizabilities have some simple relations with the reduced density matrix $\bar{\rho}$. These relations can be explained by the nature of chemical bonding in these systems. When π orbitals become delocalized along the molecule, α reaches its maximum, β is zero, and γ is negative and reaches its minimum; as the π orbitals change their nature from delocalized to localized and back, the magnitude of β reaches its maxima, as shown in Figs. 3 and 4.

To explain these observations, Marder and co-workers [3] used a four orbital model and discussed them in terms of the sum-over-states formula. Therefore they invoked the properties of excited states (energies and dipole moments). We will explain these observations using the nature of the ground state of these systems.

First, we will illustrate why $\beta = 0$ when π electrons are delocalized. In the static limit, the ground state energy can be expanded as

$$E_g(\mathcal{E}) = E_g(0) - \frac{1}{2}\alpha\mathcal{E}^2 - \frac{1}{3}\beta\mathcal{E}^3 - \frac{1}{4}\gamma\mathcal{E}^4 + O(\mathcal{E}^5) \quad (12)$$

If β is not equal to zero when π electrons are completely delocalized, say $\beta > 0$, structures corresponding to $\mathcal{E} > 0$ are more favorable energetically than those corresponding to $\mathcal{E} < 0$. However, for delocalized π orbitals, it is energetically equivalent to form double/single bonds pairs on either side. Therefore, β is expected to be or close to zero when π orbitals are delocalized.

We next explain why α is at its maximum and γ at its minimum when π electrons are delocalized. To that end, we need to utilize the following relations, $\alpha = dP/d\mathcal{E}$, $\beta = d\alpha(\mathcal{E})/d\mathcal{E}$, and $\gamma = d^2\alpha(\mathcal{E})/d\mathcal{E}^2$. When $\beta = 0$, we conclude that α is at its maximum. The fact that α reaches its maximum when π orbitals are delocalized is physically intuitive. Since α is at its maximum, using the above relations we see that γ must be negative. Using a symmetry argument, we again know that $\delta = d\gamma/d\mathcal{E} = 0$ when π electrons delocalize along the chain, and we further conclude that γ is then at one of its minima.

Away from the delocalized π orbital case, β reaches its maximum and minimum, which means that the change of α with respect to E_0 is the largest. We correlate this with the transition of chemical bonding, see Fig. 4, and conclude that at the transition points, where the localized π electrons become delocalized, the magnitude of β reaches its maxima.

Finally, we would like to point out that all our arguments use only the ground state chemical bonding information. This suggests that for these systems the ground state reduced density matrix contains all the necessary information for predicting the trends of the off-resonant polarizabilities.

V. CONCLUSIONS

We analyzed the physics behind the structure relations of off-resonance polarizabilities for conjugated organic molecules [3] from a novel point of view. We investigated the correlation between the ground state reduced density matrix and the polarization. We are able to characterize the off-resonant polarizabilities in terms of the nature of chemical bonding in these systems. When π electrons are delocalized, we expect that: (1) the polarizability should be maximized; (2) because of the symmetry, β is close to zero; (3) γ should be negative and its magnitude reaches one of maxima. To reach these conclusions, we only utilize the nature of chemical bonding in the ground state.

Marder and co-workers [3] recently emphasised the structural relation of off-resonance hypolarizabilities. This is useful for the design of optical materials. We are interested in explaining the electronic origin of this structure-hypolarizability relation. Geometry and electronic structure are closely related. In Sec.III B we removed the external field E_0 and fixed the optimized structures. The calculated off-resonant α , β and γ are then very different from those with E_0 on. The relation between the nature of chemical bonds and off-resonance polarizability is the fundamental reason behind the structure/polarizability relationship [3].

Acknowledgments The authors would like to thank Dr. S. R. Marder for stimulating discussions. The support of the Air Force office of scientific research, the National Science Foundation, and the Center for Photoinduced Charge Transfer is gratefully acknowledged.

REFERENCES

- [1] *Nonlinear Optical Effects in Organic Polymers*, Edited by J. Mrssier, F. Kajzar, P. N. Prasad and D. R. Ulrich, NATO Advanced Study Institute, Ser. E. Vol. 162 (Kluwer Academic, Dordrecht, 1989); *Nonlinear Optical Properties of Organic Molecules and Crystals*, Edited by D. S. Chemla and J. Zyss, (Academic, New York, 1987); *Nonlinear Optical Properties of Polymers*, Edited by A. J. Heeger, J. Orenstein and D. R. Ulrich, Vol. 109 (MRS Publication, Pittsburg, 1988).
- [2] B. I. Greene, J. Orenstein and S. Schmitt-Rink, *Science* 247 (1990) 679; D. Yaron and R. Silbey, *Phys. Rev. B* 16, 776 (1992); W. E. Torruellas, D. Neher, R. Zanoni, G. I. Stegeman, and F. Kajzar, *Chem. Phys. Lett.* 175, 11 (1990).
- [3] S. R. Marder, D. N. Beratan, L. T. Cheng. *Science* 252, 103 (1991); S. R. Marder, C. B. Gorman, B. G. Tiemann, and L. T. Cheng, *Proc. SPIE* 1775,19 (1993); S. M. Risser, D. N. Beratan and S. R. Marder, *J. Am. Chem. Soc.* 115, 7719 (1993).
- [4] M. Stahelin, D. M. Burland, and J. E. Rice, *Chem. Phys. Lett.*, 191 (1992) 245.
- [5] S. Mukamel and H. X. Wang, *Phys. Rev. Lett.* 69, 65 (1992); H. X. Wang and S. Mukamel, *J. Chem. Phys.* 97, 8019 (1992); M. Hartmann, A. Takahashi and S. Mukamel, submitted to *J. Chem. Phys.*
- [6] A. Takahashi and S. Mukamel, *J. Chem. Phys.*, in press (1994).
- [7] H. Fukutome, *J. Mol. Str. (Theochem)* 188, 337 (1989).
- [8] W. J. Buma, B. E. Kohler and T. A. Shaler, *J. Chem. Phys.* 96, 399 (1992)
- [9] C. A. Coulson, *Proc. Roy. Soc. London* A169, 413 (1939).

TABLES

TABLE I. The eigenvalues Ω_ν (in eV) and their degeneracies (Deg) of the homogeneous Time Dependent Hartree Fock equation for $E_0 = 0.0$ V/Å.

#	Ω_ν	Deg	#	Ω_ν	Deg	#	Ω_ν	Deg	#	Ω_ν	Deg
1	0	4	7	4.034	1	13	7.604	1	19	10.745	1
2	1.047	2	8	4.603	2	14	7.979	1	20	10.988	1
3	1.630	2	9	5.739	1	15	8.166	1	21	11.290	1
4	1.925	2	10	6.064	1	16	9.131	1	22	12.847	1
5	2.677	2	11	6.932	1	17	9.452	1	23	13.025	1
6	3.555	2	12	7.301	1	18	9.964	1			

TABLE II. Variation of the absorption peak frequency Ω in the static electronic field.

E_0 (V/Å)	0.00	0.05	0.10	0.15	0.18	0.20	0.30
Ω (eV)	4.03	3.77	3.18	2.86	3.05	3.27	3.66