# Charge and bonding redistribution in octatetraene driven by a strong laser field: Time-dependent Hartree–Fock simulation

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The time evolution of the reduced single electron density matrix for the  $\pi$  electrons in conjugated molecules in an intense laser field is calculated by numerically integrating the time-dependent Hartree–Fock equations for the Pariser–Parr–Pople model Hamiltonian. We study the field frequency and intensity dependence of the  $\pi$ -electron response, the charge fluctuations with respect to the ground state, and the molecular polarization in unsubstituted and acceptor–donor substituted octatetraene, where we also examine the interaction between a permanent electric dipole moment and the laser field. Our results demonstrate the origin of large nonperturbative changes in the  $\pi$ -electronic charges and bond orders (diagonal and off-diagonal density matrix elements, respectively) induced by a strong laser field. © 2003 American Institute of Physics. [DOI: 10.1063/1.1594721]

## I. INTRODUCTION

Recent developments in femtosecond laser techniques have made it possible to investigate various ultrafast processes in atoms, diatomic or polyatomic molecules, and in the condensed phase.<sup>1,2</sup> Multiphoton dissociation and ionization of molecules in strong laser fields are important processes which allow one to probe the control of electronic and nuclear dynamics by electric forces. The dissociation and ionization of small molecules such as H<sub>2</sub>, HCl, N<sub>2</sub>, O<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub> have been extensively studied, both theoretically and experimentally.<sup>3–13</sup> When the field intensity exceeds  $10^{14}$  W/cm<sup>2</sup>, the response cannot be described by a perturbative calculation in the field. In the low-frequency (electronically off-resonant) regime, such ionization phenomena can be understood qualitatively in terms of a quasistatic tunneling model based on the adiabatic response of a single active electron.<sup>14–16</sup>

Intense field dissociation and ionization processes in conjugated polyatomic molecules such as benzene, naphthalene, anthracene, hexatriene, decatetraene, and  $C_{60}$  have been reported recently.<sup>17–25</sup> In these molecules many-body effects strongly influence the electron dynamics, and electrons are emitted through nonadiabatic multielectron excitation processes.<sup>13,24,25</sup>

Exact numerical simulation of these processes can be carried out in small molecules such as  $H_2$  or HCl, where the number of active electrons is limited to one or two. Such calculations are not feasible in polyatomic molecules. Ivanov *et al.* have studied this multiexcitation process in polyatomic molecules with eight electrons using an approximate theory which includes the electron–electron Coulomb interaction, but neglects exchange.<sup>25</sup> The goal of the present paper is to study the nonperturbative electronic response of  $\pi$ -conjugated systems to strong external fields, including multielectron excitation induced by both Coulomb and the exchange interactions. We simulate the time evolution of charge and bond order of  $\pi$  electrons in octatetraene subjected to a strong femtosecond laser field by solving the time-dependent Hartree–Fock equation for the Pariser– Parr–Pople model Hamiltonian. Our study focuses on the elementary changes in electronic structure which are precursors to the field-induced ionization processes; these are not included in the present simulation.

#### **II. MODEL HAMILTONIAN AND THE TDHF SIMULATION**

We describe the many  $\pi$ -electrons system coupled to the radiative field by the model Hamiltonian

$$H = H_{\rm PPP} + H_{\rm ext}, \tag{2.1}$$

$$H_{\text{PPP}} = \sum_{n,m,\sigma} t_{m,n} \hat{\rho}_{nm}^{\sigma} + \frac{1}{2} \sum_{n} K(x_n - x)^2 + \sum_{n} U \hat{\rho}_{nn}^{\alpha} \hat{\rho}_{nn}^{\beta} + \frac{1}{2} \sum_{n,m,\sigma\sigma'}^{n\neq m} \gamma_{nm} \hat{\rho}_{nn}^{\sigma} \hat{\rho}_{mm}^{\sigma'}, \qquad (2.2)$$

$$H_{\text{ext}} = -E(t)\hat{P}, \qquad (2.3)$$

$$\hat{\rho}_{nm}^{\sigma} = a_{m\sigma}^{\dagger} a_{n\sigma}. \tag{2.4}$$

 $H_{\rm PPP}$  is the Pariser–Parr–Pople Hamiltonian for  $\pi$  electrons which, with a proper choice of parameters, has been demonstrated to successfully describe many optical properties of conjugated molecules and polymers.<sup>26,27</sup> These include linear

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4722

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spectra, nonlinear optical response, photoluminescence, and electroluminescence.<sup>28</sup> A simplified Hamiltonian neglects the Coulomb interaction U [known as the Su, Schriefler, and Heeger (SSH) model] has also been used to predict the structural changes induced upon photoexcitation, including the formation of elementary excitations such as polarons and solitons. Here,  $a_{m\sigma}^{\dagger}(a_{m\sigma})$  is the creation (annihilation) operator of a  $\pi$  electron with spin  $\sigma$  ( $\equiv \alpha, \beta$ ) at the *m*th carbon atom.

The first term in Eq. (2.2) gives the one-electron interaction energy, and  $t_{m,n}$  is the hopping parameter. Its diagonal element,  $t_{m,m}$  represents the Coulomb integral at the *m*th carbon atom

$$t_{m,m} = \varepsilon_m - \sum_n \gamma_{mn} , \qquad (2.5)$$

where  $\varepsilon_m$  is the electron energy of the *m*th site and  $\gamma_{mn}$ , which represents the repulsion between *m*th and *n*th sites, is assumed to be the Ohno form

$$\gamma_{mn} = \frac{U}{\sqrt{1 + (r_{mn}/a_0)^2}},$$
(2.6)

where  $r_{mn}$  is the distance between the two atoms and  $a_0$  is a unit cell length,  $U \equiv U_0 / \epsilon_d$  is the on-site repulsive Hubbard energy.  $\epsilon_d$  is the static dielectric constant and  $U_0$  is the unscreened on-site repulsion.  $t_{m,n}$  with  $(m \neq n)$  denotes the resonance transfer integral of  $\pi$  electrons. We restrict  $t_{m,n}$  to a nearest-neighbor form

$$t_{mn} = \begin{cases} \beta - \beta' \Delta z_m, & \text{for } n = m+1\\ 0, & \text{otherwise,} \end{cases}$$
(2.7)

where  $\beta$  denotes the mean transfer integral between nearestneighbor sites,  $\beta'$  is the electron-phonon coupling constant, and  $\Delta z_m$  is the bond length deviation from the average.

The second term in Eq. (2.2) denotes the elastic energy between carbon sites representing the  $\sigma$  bonds, and K is its harmonic force constant.  $x_n$  is the *n*th bond length along the chain axis *z*, and *x* is the equilibrium bond length. The third and fourth terms in Eq. (2.2) represent electron–electron Coulomb interaction.

 $H_{\text{ext}}$  is the interaction Hamiltonian between the  $\pi$  electrons and the external electric field [E(t)] polarized along the chain z axis.  $\hat{P}$  is the molecular polarization operator, which in the dipole approximation reads

$$\hat{P} = -e \sum_{n\sigma} z(n) \hat{\rho}^{\sigma}_{nn}, \qquad (2.8)$$

where z(n) is the z coordinate of the *n*th carbon atom.

The one-electron density matrix element is defined as  $\rho_{nm}^{\sigma}(t) \equiv \langle \Psi(t) | \hat{\rho}_{nm}^{\sigma} | \Psi(t) \rangle$ , where  $| \Psi(t) \rangle$  is the total manyelectron wave function. We have simulated the time evolution of the density matrix by starting with the Heisenberg equation of motion

$$i\hbar\dot{\rho}_{nm}^{\sigma}(t) = \langle \Psi(t) | [\rho_{nm}^{\sigma}, H] | \Psi(t) \rangle$$

$$= \sum_{i} (t_{ni}\rho_{im}^{\sigma}(t) - t_{im}\rho_{ni}^{\sigma}(t)) + U(\langle \hat{\rho}_{nn}^{-\sigma}\hat{\rho}_{nm}^{\sigma} \rangle)$$

$$- \langle \hat{\rho}_{mm}^{-\sigma}\hat{\rho}_{nm}^{\sigma} \rangle) + \frac{1}{2} \sum_{i,\sigma'}^{i\neq n} \gamma_{ni}(\langle \hat{\rho}_{ii}^{\sigma'}\hat{\rho}_{nm}^{\sigma} \rangle)$$

$$+ \langle \hat{\rho}_{nm}^{\sigma}\hat{\rho}_{ii}^{\sigma'} \rangle) - \frac{1}{2} \sum_{i,\sigma'} \gamma_{mi}(\langle \hat{\rho}_{ii}^{\sigma'}\hat{\rho}_{nm}^{\sigma} \rangle)$$

$$+ \langle \hat{\rho}_{nm}^{\sigma}\hat{\rho}_{ii}^{\sigma'} \rangle) + e[z(n) - z(m)]E(t)\rho_{nm}^{\sigma}(t), \qquad (2.9)$$

where  $\langle \cdots \rangle \equiv \langle \Psi(t) | \cdots | \Psi(t) \rangle$  denotes the expectation value, with respect to the time-dependent wave function. Closed equations of motion are obtained using the time-dependent Hartree–Fock (TDHF) approximation, which assumes that  $|\Psi(t)\rangle$  can be represented by a single Slater determinant at all times. The TDHF approximation describes quantum fluctuations around the Hartree–Fock ground state, partially taking some electron correlation effects into account. This results in the following factorization of the expectation value of two-electron operators

$$\langle \hat{\rho}_{nm}^{\sigma} \hat{\rho}_{ij}^{\sigma'} \rangle = \rho_{nm}^{\sigma}(t) \rho_{ij}^{\sigma'}(t) - \delta_{\sigma\sigma'} \rho_{im}^{\sigma}(t) \rho_{nj}^{\sigma}(t) + \delta_{\sigma\sigma'} \delta_{nj} \rho_{im}^{\sigma}(t).$$
 (2.10)

Substituting Eq. (2.10) into Eq. (2.9), we obtain a closed, nonlinear self-consistent equation of motion for the one-electron density matrix

$$i\hbar\dot{\rho}^{\sigma}(t) = [h^{\sigma}(t) + f(t), \rho^{\sigma}(t)], \qquad (2.11)$$

where  $h^{\sigma}(t)$  and f(t) are  $N \times N$  (N is the basis set size) matrices defined by

$$h_{nm}^{\sigma}(t) = t_{nm} + \delta_{n,m} \sum_{\ell,\sigma'} \gamma_{n\ell} \rho_{\ell\ell}^{\sigma'}(t) - \gamma_{nm} \rho_{nm}^{\sigma}(t), \quad (2.12)$$

and

$$f_{nm}(t) = \delta_{n,m} e z(n) E(t).$$
(2.13)

The TDHF approach has been widely used for computing the optical response of conjugated molecules by solving the equations perturbatively in the field.<sup>28</sup> In this study we will avoid the expansion; instead, the time evolution of  $\rho_{nm}^{\sigma}(t)$  is computed by numerically solving Eq. (2.11) using the fourth-order Runge–Kutta technique.<sup>29</sup> In this method, we introduce the discrete time series  $\{t_0, t_1, t_2, ..., t_s, ..., t_f\}$ , and  $\rho_{nm}^{\sigma}(t_{s+1})$  is given from the previous  $\rho^{\sigma}(t_s)$  as follows:

$$\rho_{nm}^{\sigma}(t_{s+1}) = \rho_{nm}^{\sigma}(t_s) + \frac{1}{6}\Delta t (k_{nm}^{\sigma(1)} + 2k_{nm}^{\sigma(2)} + 2k_{nm}^{\sigma(3)} + k_{nm}^{\sigma(4)}), \qquad (2.14)$$

where

$$\begin{aligned} k_{nm}^{\sigma(1)} &= -\frac{i}{\hbar} F_{nm}^{\sigma}(\rho(t_s), t_s), \\ k_{nm}^{\sigma(2)} &= -\frac{i}{\hbar} F_{nm}^{\sigma} \bigg( \rho(t_s) + \frac{1}{2} \Delta t k^{(1)}, t_s + \frac{1}{2} \Delta t \bigg), \end{aligned}$$

$$k_{nm}^{\sigma(3)} = -\frac{i}{\hbar} F_{nm}^{\sigma} \left( \rho(t_s) + \frac{1}{2} \Delta t k^{(2)}, t_s + \frac{1}{2} \Delta t \right), \qquad (2.15)$$
$$k_{nm}^{\sigma(4)} = -\frac{i}{\hbar} F_{nm}^{\sigma} (\rho(t_s) + \Delta t k^{(3)}, t_s + \Delta t),$$

and

$$F_{nm}^{\sigma}(\rho(t),t) \equiv i\hbar \dot{\rho}_{nm}^{\sigma}(t), \qquad (2.16)$$

$$\Delta t \equiv t_{s+1} - t_s \,. \tag{2.17}$$

The time evolution of the density matrix is computed by recursive calculations. The initial values of  $\rho_{nm}^{\sigma}(t)$  [= $\rho_{nm}^{\sigma}(t_0)$ ] are determined by the ground-state charge distribution (no external field) given by the Hartree–Fock solution of  $H_{\text{PPP}}$  with geometry optimization. We verified that this method gives stable solutions even for very intense fields ( $\geq 10^{15}$  W/cm<sup>2</sup>).

# **III. APPLICATION TO OCTATETRAENE**

We applied our method to octatetraene, using the following parameters:  $\varepsilon_n = 0$ ,  $a_0 = 1.2935 A$ ,  $U_0 = 11.13 \text{ eV}$ ,  $\epsilon_d = 1.5$ ,  $\beta = -2.4 \text{ eV}$ ,  $\beta' = -5.6 \text{ eV A}^{-1}$ ,  $K = 80 \text{ eV A}^{-2}$ , and x = 1.512 A.<sup>27</sup> These parameters reproduce the experimental energy gap for octatetraene (4 eV) and its chemical structure, i.e., the 0.09 Å bond length alternation.

The external electric field E(t) is assumed to have a Gaussian envelope

$$E(t) = E \frac{1}{\sqrt{2\pi\delta}} \exp\left[-\frac{(t-t_p)^2}{2\delta^2}\right] [\exp(-i\Omega t) + \exp(i\Omega t)], \qquad (3.1)$$

where the amplitude *E* and carrier frequency  $\Omega$  are the important parameters which determine the electronic response. The present study focuses on the charge and the bonding redistribution induced by a strong laser field, which are precursors to the ionization process. To avoid the ionization channel we used intensities in the range  $10^{13}$  and  $10^{15}$  W/cm<sup>2</sup> and kept the field frequencies  $\Omega$  lower than 5000 cm<sup>-1</sup>. Typical ionization experiments use lower intensities and frequencies.

#### A. Dependence on field frequency

We first consider the dependence of the  $\pi$ -electron response on field frequency  $\Omega$ . In Fig. 1, we show the field amplitude E(t) for various values of  $\Omega$ . In all cases we assumed pulse duration  $\delta = 10$  fs and the center of the pulse at  $t_p = 50$  fs. The time evolution of  $\rho^{\sigma}(t)$  is calculated between 0 and 100 fs.

In Fig. 2, we display the diagonal density matrix elements  $\rho_{ii}(t)$  at each carbon site as a function of time for  $\Omega$  = 1668 and 3336 cm<sup>-1</sup>. The field intensity ( $I \equiv \epsilon_0 c E^2/2$ ) is fixed as  $3.3 \times 10^{14}$  W/cm<sup>2</sup>, where  $\epsilon_0$  is the vacuum permittivity and *c* is the speed of light in vacuum. Intensity of 1  $\times 10^{14}$  W/cm<sup>2</sup> corresponds to electric field strength of 2.75 V/A. Figure 1 and Fig. 2 show that  $\rho_{ii}(t)$  follows the profile of E(t) adiabatically. The sign of the change in  $\rho_{ii}(t)$  alternates between odd and even sites, implying that the  $\pi$  electric field strength of 2.75 the speed of the change in  $\rho_{ii}(t)$  and the speed of the ch



FIG. 1. Field envelope E(t) for various values of  $\Omega$ . The pulse duration  $\delta = 10$  fs and the center of the pulse  $t_n = 50$  fs.

trons move in the inverse direction of the electric field and oscillate between nearest-neighbor sites following the field. As a result of this vibration, a charge density wave (CDW)like charge fluctuation is instantaneously induced by the pulse. In the CDW state, charge transfer occurs between nearest-neighbor carbon atoms and the excitation appears as a charge density wave on the carbon sites. The density matrix  $\rho_{ii}(t)$  is depicted in Fig. 3 at 0, 50, and 100 fs for  $\Omega$ =1668 cm<sup>-1</sup> and  $I=3.3\times10^{14}$  W/cm<sup>2</sup>. At this intensity there is no appreciable change in the off-diagonal part of the density matrix, and the electronic structure (bond alternation) remains almost unchanged during the laser pulse. The offdiagonal density matrix elements are relevant to bond order, which is connected to the bond length. In a bond order wave (BOW)-like state, the off-diagonal density matrix elements are modulated periodically, resulting in a similar modulation of the bond length.



FIG. 2. Diagonal part of the density matrix  $\rho_{ii}(t)$  at each site as a function of time for  $\Omega = 1668$  and 3336 cm<sup>-1</sup>. The intensity of the field is  $I = 3.3 \times 10^{14}$  W/cm<sup>2</sup>.



FIG. 3. Two-dimensional plots of the density matrix  $\rho_{ij}(t)$  at the times of 0, 50, and 100 fs for  $\Omega = 1668 \text{ cm}^{-1}$  and  $I = 3.3 \times 10^{14} \text{ W/cm}^2$ .

In order to examine the overall response to the external field, we have calculated the variance of the charge fluctuation with respect to the ground state

$$\Delta \rho(t) \equiv \sqrt{\sum_{i=1}^{8} (\rho_{ii}(t) - \rho_{ii}(0))^2}.$$
(3.2)

 $\Delta \rho(t)$  provides a global measure for the changes in the molecular charge distribution induced by the strong laser field. Figure 4 depicts  $\Delta \rho(t)$  for various values of  $\Omega$ . In comparison with Fig. 1, we note that the charge fluctuation  $\Delta \rho(t)$ remains finite even when E(t)=0. This means that as  $\Omega$  is increased the electrons can no longer follow E(t) adiabatically. This nonadiabaticity becomes noticeable for frequencies above  $\Omega = 3000$  cm<sup>-1</sup>.



FIG. 4. Dispersion of the charge fluctuation with respect to the ground state  $\Delta \rho(t)$  as a function of time for various values of  $\Omega$ .  $I=3.3\times10^{14}$  W/cm<sup>2</sup>.



FIG. 5. Molecular polarization  $M_p(t)$  for various values of  $\Omega$  as a function of time.  $I=3.3\times10^{14}$  W/cm<sup>2</sup>.

We have also computed another characteristic global property of the molecule; the time-dependent molecular polarization

$$M_{p}(t) \equiv \operatorname{Tr}\{-er\rho\}. \tag{3.3}$$

The  $\Omega$  dependence of  $M_p(t)$ , which has the same direction as E(t), is depicted in Fig. 5. The time profile of  $M_p(t)$  follows E(t) adiabatically.

We conclude from these results that when  $\Omega$  is less than 7000 cm<sup>-1</sup>, even when the laser field is as intense as  $I = 3.3 \times 10^{14}$  W/cm<sup>2</sup>, the molecular polarization follows the field adiabatically. In contrast, the charges fluctuate nonadiabatically during the excitation. This can be rationalized as follows: The charge fluctuation is directly related to microscopic motion of the electrons. However, the molecular polarization which is a highly physical quantity, can respond to the external field almost adiabatically.

## B. Dependence on field intensity

We have examined the dependence of the response on the field intensity I for  $\Omega = 1334$  cm<sup>-1</sup>. In Fig. 6 we display the diagonal part of the density matrix at each site as a function of time for  $I = 4.7 \times 10^{14}$  and  $3.0 \times 10^{15}$  W/cm<sup>2</sup>. We note that as I approaches the  $10^{15}$  W/cm<sup>2</sup> threshold, the density matrices of the inner second to seventh sites can no longer follow the external field, and the time dependence of the corresponding density matrix elements saturates as I is increased. This leads to the CDW charge order at the inner sites whose amplitude is almost independent on field intensity. In contrast, the end (first and eighth) sites are primarily responsible for a field-induced charge transition. The dependence on field intensity is shown in Fig. 6. In Fig. 7 we depict the time-dependent off-diagonal part of the density matrix for  $I = 3.0 \times 10^{15}$  W/cm<sup>2</sup> and  $\Omega = 1334$  cm<sup>-1</sup> at 0, 40, 50, 60, and 100 fs. The CDW-like charge fluctuation appears at 50 fs and the BOW electronic structure disappears, as is seen from the off-diagonal part of the density matrix,  $\rho_{i,i+1}$  (50 fs). Thus, the  $\pi$ -electronic structure changes from BOW to CDW type as a result of the interaction with the



FIG. 6. Diagonal part of the density matrix  $\rho_{ii}(t)$  at each site as a function of time for  $I = 4.7 \times 10^{14}$  and  $3.0 \times 10^{15}$  W/cm<sup>2</sup>.  $\Omega = 1334$  cm<sup>-1</sup>.



FIG. 7. The density matrix  $\rho_{ij}(t)$  at the times 0, 40, 50, 60, and 100 fs for  $\Omega = 1334 \text{ cm}^{-1}$  and  $I = 3.0 \times 10^{15} \text{ W/cm}^2$ .



FIG. 8. The degree of the BOW electronic structure  $\rho_{\text{BOND}}(t)$  as a function of time for various values of *I*.  $\Omega = 1334 \text{ cm}^{-1}$ .

intense laser field. The ground electronic structure is strongly modified by the field and a new dynamical electronic order is created for the electron–field coupled system.

To further examine the variation of the bond order induced by the laser field, we have introduced the following measure of BOW:

$$\rho_{\text{BOND}}(t) = \sum_{i=1}^{6} (\rho_{i,i+1}(t) - \rho_{i+1,i+2}(t))^2.$$
(3.4)

When  $\rho_{\text{BOND}}(t)$  vanishes, the BOW disappears as well. The time evolution of  $\rho_{\text{BOND}}(t)$  is depicted in Fig. 8 for various values of *I*. When *I* is less than  $\sim 10^{13}$  W/cm<sup>2</sup>, the BOW order is hardly affected by the field. As *I* approaches  $\sim 10^{15}$  W/cm<sup>2</sup> the ground-state electronic structure is strongly affected by the field and the bond order alternation disappears during the pulse.

We next examine the intensity dependence of the dynamical charge fluctuation. In Fig. 9 we depict  $\Delta \rho(t)$  for various values of *I* and  $\Omega = 1334$  cm<sup>-1</sup>. The time evolution of the charge fluctuation closely follows the external field. In



FIG. 9. Dispersion of the charge fluctuation with respect to the ground state  $\Delta \rho(t)$  as a function of time for various values of *I*.  $\Omega = 1334$  cm<sup>-1</sup>.



FIG. 10. Integrated charge fluctuation  $\Delta \rho(t)$  as a function of  $\sqrt{I}$ .  $\Omega = 1334 \text{ cm}^{-1}$ .

order to illustrate the net effect of the field on the charge fluctuation, we looked at the total charge fluctuation during the pulse,  $\Delta \rho(t)$  integrated over time, as a function of  $\sqrt{I}$  is displayed in Fig. 10. Since  $I \sim E^2$ , we see that the total charge fluctuation is proportional to the electric field amplitude *E* in the intensity region below  $1 \times 10^{15}$  W/cm<sup>2</sup>. At higher intensities, however, the charge fluctuation deviates from this linear relation, and eventually saturates. This is because CDW-like charge order is created in intense fields and the charge is not mobile in the inner atoms of the molecule. The charge fluctuation is restricted by this fieldinduced electronic structure as *I* is increased.

The time-dependent molecular polarization  $M_p(t)$  is shown in Fig. 11 for various values of I.  $M_p(t)$  is induced in the direction of the field and follows its time profile. The maximum values of  $M_p(t)$ , i.e.,  $M_p(50 \text{ fs})$ , are displayed versus  $\sqrt{I}$  in Fig. 12. The intensity region below 1  $\times 10^{14}$  W/cm<sup>2</sup>,  $M_p(50 \text{ fs})$ , is proportional to the electric field amplitude E, and the dependence becomes increasingly



FIG. 12. Maximum values of  $M_p(t)$ , that is  $M_p(50 \text{ fs})$ , as a function of  $\sqrt{l}$ .  $\Omega = 1334 \text{ cm}^{-1}$ .

nonlinear at higher intensities. This nonlinearity originates from end effects; as discussed in Fig. 6, when the field intensity approaches  $\sim 10^{15}$  W/cm<sup>2</sup>, charge transfer between atoms 1 and 8 becomes larger than among the other atoms. A nonlinear molecular polarization is induced by the enhancement of end-to-end charge transfer when the field intensity exceeds that value.

## IV. ACCEPTOR-DONOR SUBSTITUTED OCTATETRAENE

In this section we consider the optical response of acceptor-donor substituted octatetraene,<sup>30</sup> shown in Fig. 13. The substitutions are modeled by modifying the on-site energies,  $\varepsilon_1$  and  $\varepsilon_8$ . The donor (acceptor) is substituted at the first (eighth) site; its on-site energy is increased (decreased) with respect to the on-site energy of the carbon sites. We assume  $\varepsilon_1 = -\varepsilon_8$  and use the energy difference ( $\Delta \varepsilon = \varepsilon_1 - \varepsilon_8 \ge 0$ ) as a characteristic strength parameter of the acceptor-donor substitution. We use the following parameters:  $\Omega = 1334 \text{ cm}^{-1}$  and  $I = 3.3 \times 10^{14} \text{ W/cm}^2$ . When  $\Omega$ 



FIG. 11. Molecular polarization  $M_p(t)$  for various values of I as a function of time.  $\Omega = 1334$  cm<sup>-1</sup>.



FIG. 13. On-site energies of a simple model for an acceptor-donor substituted octatetraene. This effect is included in the changes in the on-site energies,  $\varepsilon_1$  (acceptor) and  $\varepsilon_8$  (donor).



FIG. 14. Diagonal elements of the density matrix  $\rho_{ii}(t)$  of the acceptordonor substituted octatetraene as a function of the site number at characteristic times for the typical cases of  $\Delta \varepsilon = 8 \text{ eV}$  for (a) E(t) and (b) -E(t).  $\Omega = 1334 \text{ cm}^{-1}$  and  $I = 3.3 \times 10^{14} \text{ W/cm}^2$ .

=1334 cm<sup>-1</sup>, the field E(t) has a maximum intensity at 50 fs and it points in the direction from the first to the eighth atom, as seen in Fig. 1.

The time evolution of the diagonal part of the density matrix  $\rho_{ii}(t)$  is shown as a function of site number for  $\Delta \varepsilon$ =8 eV for E(t) and the reverse field -E(t) in Figs. 14(a) and 14(b), respectively. For  $\Delta \varepsilon = 8 \text{ eV}$ , the substituted octatetraene has the permanent ground-state electric dipole moment in the negative z direction. From Fig. 14(a) we see that the external field around 50 fs weakens the permanent electric dipole moment due to the electronic transition from the negatively charged (even) sites to the positive (odd) sites. On the other hand, Fig. 14(b) shows that the reverse external field -E(t) enhances the permanent dipole by inducing electron transfer from the positively charged sites to the negative sites. In general, the external field induces an additional dipole moment in the molecule parallel to the field. Therefore, the CDW-like charge order weakens around 50 fs for E(t), and becomes stronger for -E(t), as shown in the thick lines in Figs. 14(a) and 14(b), respectively. Snapshots of the off-diagonal density matrix elements,  $\rho_{ii}(t)$  are shown at times 0, 50, and 100 fs for E(t) in Fig. 15(a) and in Fig. 15(b) for -E(t). For E(t), the amplitude of CDW-like charge order decreases around 50 fs and the BOW remains almost unchanged even at 50 fs. In contrast, when the field is reversed there are fewer changes in the CDW order during the laser irradiation, and the BOW order is hardly noticeable at 50 fs. This is the anticipated dynamical  $\pi$ -electron re(a) E(t) case  $\frac{1}{1-\frac{1}{$ 



FIG. 15. Time evolution of the off-diagonal elements of the density matrix  $\rho_{ij}(t)$  at times of 0, 50, and 100 fs for  $\Delta \varepsilon = 8 \text{ eV}$  for the cases of (a) E(t) and (b) -E(t).  $\Omega = 1334 \text{ cm}^{-1}$  and  $I = 3.3 \times 10^{14} \text{ W/cm}^2$ .

sponse when the permanent electric dipole moment is opposite or parallel to the external field, respectively.

 $\Delta \rho(t)$  is depicted for various values of  $\Delta \varepsilon$  for E(t) and -E(t) in Figs. 16(a) and 16(b), respectively. The charge fluctuation from the polarized ground state of the substituted



FIG. 16. Dispersion of the charge fluctuation with respect to the ground state  $\Delta \rho(t)$  as a function of time for various values of  $\Delta \varepsilon$  for the cases of (a) E(t) and (b) -E(t).  $\Omega = 1334$  cm<sup>-1</sup> and  $I = 3.3 \times 10^{14}$  W/cm<sup>2</sup>.

octatetraene decreases at virtually all times compared with unsubstituted octatetraene ( $\Delta \varepsilon = 0$ ), indicating that the  $\pi$ electrons in substituted conjugated polymers are stabilized against the external field perturbation. This effect becomes even more pronounced as  $\Delta \varepsilon$  is increased. The maximum values of  $\Delta \rho(t)$  at 28, 39, 50, 61, and 72 fs are plotted in Fig. 17 versus  $\Delta \varepsilon$ . The solid lines represent E(t) and the dotted lines represent -E(t). At 50 fs, the permanent electric dipole moment is in the opposite (parallel) direction to



FIG. 17. Maximum values of the charge fluctuation  $\Delta \rho(t)$  at the times 28, 39, 50, 61, and 72 fs as a function of  $\Delta \varepsilon$ . The solid lines are for E(t) and the dotted lines represent -E(t).  $\Omega = 1334 \text{ cm}^{-1}$  and  $I = 3.3 \times 10^{14} \text{ W/cm}^2$ .



FIG. 18. Molecular polarization  $M_p(t)$  for various values of  $\Delta \varepsilon$  as a function of time. The solid lines are for E(t) and the dotted lines represent -E(t).  $\Omega = 1334 \text{ cm}^{-1}$  and  $I = 3.3 \times 10^{14} \text{ W/cm}^2$ .

the external field E(t) [-E(t)]. The 50 fs curve is asymmetric being larger when the field is E(t). Since the charges tend to be redistributed so that the permanent dipole becomes parallel to the external field, the charge fluctuation when the molecular permanent dipole is antiparallel to the external field is larger than in the parallel case.

Finally, the time evolution of the molecular polarization is shown in Fig. 18 for various values of  $\Delta \varepsilon$ . The solid lines represent E(t) and the dotted lines represent -E(t). There is no noticeable difference between unsubstituted and substituted octatetraenes; the  $\pi$ -electron response to the field is independent of the permanent dipole moment.

## **V. CONCLUSIONS**

We have calculated the time evolution of the  $\pi$ -electrons density matrix in unsubstituted and acceptor-donor substituted octatetraenes driven by an off-resonant strong laser field, using the PPP model Hamiltonian.

By investigating the field frequency and intensity dependence of the response in octatetraene, we found that even when E(t) vanishes, the field-induced charge fluctuation from the ground state remains finite and does not follow E(t)adiabatically. This nonadiabatic response becomes more pronounced as  $\Omega$  exceeds ~ 3000 cm<sup>-1</sup>. The total charge fluctuation is proportional to the electric field amplitude E in the intensity region below  $I=1\times10^{15}$  W/cm<sup>2</sup> and saturates at higher intensities. The molecular polarization is proportional to E in the intensity region below  $1\times10^{14}$  W/cm<sup>2</sup>. This dependence becomes gradually nonlinear as I is increased.

We have examined the interaction between the permanent electric dipole moment and the external field in acceptor-donor substituted octatetraene. In general, due to the external electric force, the charges are redistributed so as to make the permanent dipole parallel to the field. Therefore, when a molecule with a permanent dipole interacts with the antiparallel external field, the charge fluctuation is larger than the parallel case. In contrast, the field-induced molecular po-

larization is almost independent of the energy difference between the on-site energies of accepter-donor sites.

In the present work we focused on the charge redistribution induced by an intense field, and ionization processes were excluded. Simulations of the intense field ionization processes using the time evolution of the density matrix on the basis of the TDHF equations of motion will be carried out in the future. Let us make a few comments on the relevance of the present study to the ionization mechanism. When free-electron states and ionization channels are included, the localized molecular electronic states with energies near the free-electron continuum level couple to the continuum, and form a wave packet that spreads beyond the molecular region. In this case, when an intense field is applied, the adiabatic potential energy surface of localized electrons is tilted in the direction of field. This induces the charge redistribution, and the localized electrons subsequently escape to the free-electron continuum, similar to electrons moving across a potential barrier. This type of ionization process in polyatomic molecules has been investigated theoretically by Ivanov et al. on the basis of the nonadiabatic tunnel ionization and nonadaibatic multielectron dynamics using a smooth, one-dimensional particle-in-a-box potential model.<sup>25</sup> That theory was based on the electronic density, that is the diagonal element of the density matrix. In general, the off-diagonal elements carry a wealth of information on the electronic structure. Analyzing their role in intense field ionization processes will be the subject of a future study.

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