Numerical Coupled Liouville Approach: Dependence of Polarizability on Field Intensity and the Size of Linear Molecular Aggregates

Masayoshi Nakano* and Kizashi Yamaguchi

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560, Japan

Received: January 5, 1998

The polarizabilities of linear molecular aggregates are calculated by using the numerical coupled Lioville approach (NCLA), which can describe the intermolecular interaction by using the propagation of retarded electric fields among the monomers. The polarizabilities for intermediate-size molecular aggregates under near-resonant intense external fields are found to exhibit abrupt changes such as the phase-transition behaviors as the field intensity increases. The polarizability at each molecule site is investigated by elucidating the variation in the amplitude and the phase of a polarization at each molecule site.

1. Introduction

Already over 30 years old, the size dependence of various properties for molecular aggregates has gotten much attention both experimentally and theoretically. In particular, the enhancement of linear and nonlinear optical responses,[1] superradiance,[2−5] and intrinsic optical bistability[6,7] have been widely investigated. These features originate in the collective characters of the aggregate wave functions. These phenomena are investigated by using a linear chain model of atoms with retarded dipole−dipole interactions.[2,7] Recently, Malyshev and Moreno performed analytical and numerical calculations of the large-size aggregate population by considering the optical retardation effects under rotating wave approximation (RWA) and some other simplifications.[7] They found that the intrinsic bistability behavior occurs in the population differences between the ground and the excited states of large-size linear molecular aggregates. In our previous papers,[8,9] we developed a numerically exact approach of quantum dynamics and applied this to the calculations of population differences between the ground and the excited states and (hyper)polarizabilities for dimer models. The population difference and the (hyper)polarizabilities of a dimer model with a large retarded intermolecular interaction were found to be abruptly changed at the intensity of the applied electric field. These features are considered to be ascribed to the feedback effects of the retarded fields, which are generated from induced dipoles and propagate over the dipoles. We also elucidated that the feature of variations in the population differences for field intensity is influenced by the size of molecular aggregates. In contrast to the case of the dimer model,[8] plural abrupt changes in averaged population differences appear for the intermediate-size ($n \geq 8$) molecular aggregates. The magnitudes of the amplitudes for the retarded field plus the external field at each molecule site were found to be different from each other, causing the different population differences at each molecule site. Namely, the intermolecular interaction described by the propagation of retarded fields is found to influence the coherence of excitation in linear molecular aggregates under intense electric fields.

Considering such effects of retarded fields, the polarizabilities of intermediate-size aggregates are expected to exhibit similar abrupt changes as external field intensity increases. In this paper, therefore, we investigate the dependence of a polarizability on external field intensity and on the size of the molecular aggregates. In the same manner as our previous works,[8,9] linear molecular aggregates composed of two-state monomers are considered in this study. We employ the numerical coupled Liouville approach (NCLA),[8] which can treat optical retarded effects, essentially contributing to molecular interactions in the wave zone[10] and optical bistability effects[6,7] for mesoscopic-size aggregates. First, the size dependence of the polarizability averaged over the linear aggregate is elucidated for several different-size aggregates ($n = 4$, 8, 12, 16, 20, and 24; n is the number of the monomers). Second, the polarizability at each molecule site is examined for different field intensities. The amplitude and the phase of the polarization at each molecule site are also investigated in order to elucidate the interference effect of the retarded field at each molecule site.

2. Numerical Coupled Liouville Approach

In the NCLA, we use a semiclassical approach, in which molecules are treated quantum mechanically, while fields are considered to be classical time-dependent fields. This semiclassical treatment is well-known to be acceptable for the case of intense external fields. The time evolution of a molecular system is described by the following density matrix equation:[8]

$$i\hbar \frac{\partial}{\partial t}\rho(t) = [H(t),\rho(t)] - i\Gamma\rho(t) \tag{1}$$

where $\rho(t)$ indicates the total molecular density matrix and the second term in the right-hand side of eq 1 represents relaxation and feeding processes in the Markoff approximation. The semiclassical Hamiltonian $H(t)$ is expressed by[10]

$$H = H_{\mathrm{mol}} + H_{\mathrm{int}} \tag{2}$$

where the Hamiltonian of the molecular part is

$$H_{\mathrm{mol}} = \sum_{\zeta}\left\{\frac{1}{2m}\sum_{\alpha}(\mathbf{p}_{\alpha}^{(\zeta)})^2 + V^{(\zeta)}\right\} \tag{3}$$

and the interaction part between semiclassical fields and molecules is

S1089-5639(98)00631-8 CCC: $15.00
Published on Web 08/05/1998

$$H_{\mathrm{int}} = -\sum_{\zeta} \boldsymbol{\mu}^{(\zeta)} \cdot \mathbf{E}(\mathbf{R}^{(\zeta)}) \tag{4}$$

Here, ζ indicates the molecule ζ. In eq 3, $(1/2m)\sum_{\alpha}(\mathbf{p}_{\alpha}^{(\zeta)})^2$ and $V^{(\zeta)}$ represent the kinetic and the intramolecular Coulomb potential parts of the molecule ζ, respectively. In eq 4, the $\mathbf{E}(\mathbf{R}^{(\zeta)})$ represents the classical external electric fields acting on the molecule ζ plus the fields induced by the rest of the molecules. It is noted that eq 4 does not involve the Coulomb static potential for the intermolecular interaction and only involves the interactions between the dipole moment $\boldsymbol{\mu}^{(\zeta)}$ and the field $\mathbf{E}(\mathbf{R}^{(\zeta)})$, which is fully retarded. This intermolecular interaction can be described by the propagation of classical time-dependent fields.

The total Hamiltonian $H(t)$ is expressed by the sum of the one-molecule Hamiltonian $H^{(\zeta)}(t)$, as follows:

$$H(t) = \sum_{\zeta}^{n} H^{(\zeta)}(t) \tag{5}$$

where

$$\begin{aligned} H^{(\zeta)}(t) &= H_{\mathrm{mol}}^{(\zeta)}(t) + H_{\mathrm{int}}^{(\zeta)}(t) \\ &= \frac{1}{2m}\sum_{\alpha}(\mathbf{p}_{\alpha}^{(\zeta)})^2 + V^{(\zeta)} - \boldsymbol{\mu}^{(\zeta)} \cdot \mathbf{E}^{(\zeta)} \end{aligned} \tag{6}$$

In this case, eq 1 can be reduced to each one-molecule density matrix equation[8] expressed by

$$i\hbar \frac{\partial}{\partial t}\rho^{(\zeta)}(t) = [H^{(\zeta)}(t), \rho^{(\zeta)}(t)] - i\Gamma\rho^{(\zeta)}(t) \tag{7}$$

The intermolecular interaction is described by the electric field involving external fields and the fields induced by the rest of the molecular aggregates. In this study, we consider the linear molecular aggregate shown in Figure 1. Each molecule is assumed to be a dipole. The intermolecular distance is $r_{\zeta\zeta'} = |\mathbf{r}_{\zeta} - \mathbf{r}_{\zeta'}|$, and the angle between the dipole and the longitudinal axis is θ. This approximation is considered to be accepted in the case of an intermolecular distance larger than the size of the element molecule.[10]

Suppose that an aggregate is composed of n identical molecules and each molecule is constructed by m states; the matrix representation of eq 7 is expressed as

$$\begin{aligned} \dot{\rho}_{ij}^{(\zeta)}(t) = -i(1-\delta_{ij})E_{ij}\rho_{ij}^{(\zeta)}(t) - i\sum_{k}^{m}(H_{\mathrm{int}\,ik}^{(\zeta)}(t)\,\rho_{kj}^{(\zeta)}(t) - \\ \rho_{ik}^{(\zeta)}(t)\,H_{\mathrm{int}\,kj}^{(\zeta)}(t)) - (\Gamma\rho^{(\zeta)}(t))_{ij} \end{aligned} \tag{8}$$

Here, the E_{ij} ($\equiv E_i - E_j$) is the transition energy and $\rho^{(\zeta)}(t)$ is the density matrix of the molecule ζ. The interaction term $H_{\mathrm{int}}^{(\zeta)}(t)$ involves the electric field $\mathbf{E}^{(\zeta)}$ acting on the molecule ζ. This field $\mathbf{E}^{(\zeta)}$ is expressed as[7,8]

$$\mathbf{E}^{(\zeta)} = \mathbf{E}^{\mathrm{ext}(\zeta)} + \sum_{\zeta' \neq \zeta}^{n} \mathbf{E}^{(\zeta\zeta')} \tag{9}$$

where the first term is an external electric field $\mathbf{E}^{\mathrm{ext}(\zeta)}$ and the second term is the field induced by the rest of the molecules at the position ζ'. The incident field is assumed to be a linearly polarized plane wave with a frequency ω and a wave vector $\mathbf{k}$ travelling perpendicular to the longitudinal axis, and the polarization vector is parallel to the dipole vector, so that the

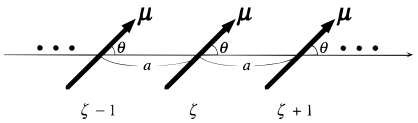

Figure 1. Schematic diagram of linear molecular aggregate. The arrow represents the direction of the dipole of the one-molecular system aligned with the angle θ from the longitudinal axis. These molecules are separated from each other by the distance a.

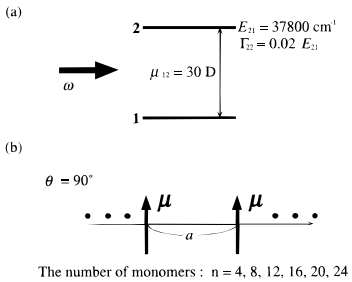

Figure 2. Two-state model (constructed from ground (1) and excited (2) states) for one-molecule system (a). The transition moment is $\mu_{12} = 30$ D, the transition energy is $E_{21} = 37\,800$ cm^{-1}, and the damping factor is $\Gamma_{22} = fE_{21}(f=0.02)$. The aggregate (b) with $\theta = 90°$ is considered. The intermolecular distance (a) is fixed to 25 au. Six sizes of aggregates ($n = 4$, 8, 12, 16, 20, 24; $n =$ the number of monomers) are considered.

$\mathbf{E}^{\mathrm{ext}(\zeta)} = \mathbf{E}^{\mathrm{ext}}$ for an arbitrary ζ. In this study, we focus on the case where the polarizations of monomers are parallel to their dipole vectors though the polarizations of monomers can be generally elliptically polarized. The field induced by the molecule ζ is regarded as the classical field radiated by a classical dipole, so that the $\mathbf{E}^{(\zeta\zeta')}(t)$ is represented by[11]

$$\begin{aligned} \mathbf{E}^{(\zeta\zeta')}(t) &= \left[\frac{3p^{(\zeta')}(t')}{r_{\zeta'\zeta}^{\,5}} + \frac{3\dot{p}^{(\zeta')}(t')}{cr_{\zeta'\zeta}^{\,4}} + \frac{\ddot{p}^{(\zeta')}(t')}{c^2 r_{\zeta'\zeta}^{\,3}}\right](\mathbf{n}\cdot\mathbf{r}_{\zeta'\zeta})\mathbf{r}_{\zeta'\zeta} - \\ &\qquad \left[\frac{p^{(\zeta')}(t')}{r_{\zeta'\zeta}^{\,3}} + \frac{\dot{p}^{(\zeta')}(t')}{cr_{\zeta'\zeta}^{\,2}} + \frac{\ddot{p}^{(\zeta')}(t')}{c^2 r_{\zeta'\zeta}}\right]\mathbf{n} \\ &\equiv f_1(t')(\mathbf{n}\cdot\mathbf{r}_{\zeta'\zeta})\mathbf{r}_{\zeta'\zeta} - f_2(t')\mathbf{n} \end{aligned} \tag{10}$$

where $t' = t - r_{\zeta'\zeta}/c$, $\mathbf{n} = \boldsymbol{\mu}/\mu$, and $\mathbf{r}_{\zeta'\zeta} = (\zeta' - \zeta)\mathbf{a}$. The polarization $p^{(\zeta')}(t')$ and its time derivatives, $\dot{p}^{(\zeta')}(t')$ and $\ddot{p}^{(\zeta')}(t')$, are calculated quantum mechanically. These quantities are shown to be fully retarded. Suppose that an external field is a continuous laser wave

$$\mathbf{E}^{\mathrm{ext}}(t) = \mathbf{F}\cos\omega t = \epsilon(\omega)(\mathrm{e}^{i\omega t} + \mathrm{e}^{-i\omega t}) \tag{11}$$

The interaction term $H_{\mathrm{int}\,ik}^{(\zeta)}(t)$ is expressed, using eqs 9 and 10, as

$$\begin{aligned} \mathbf{H}_{\mathrm{int}\,ik}^{(\zeta)}(t) &= -\boldsymbol{\mu}_{ik}\cdot\mathbf{E}^{(\zeta)}(t) \\ &= -\boldsymbol{\mu}_{ik}\cdot\mathbf{E}^{\mathrm{ext}}(t) - \sum_{\zeta'\neq\zeta}^{n}\mu_{ik}\cdot\mathbf{E}^{(\zeta'\zeta)}(t) \\ &= -\mu_{ik}(F\cos\omega t + \sum_{\zeta'\neq\zeta}^{n}[f_1(t')(r_{\zeta'\zeta}\cos\theta)^2 - f_2(t')]) \\ &= -\mu_{ik}E^{(\zeta)}(t) \end{aligned} \tag{12}$$

The relaxation and feeding term $-(\Gamma\rho^{(\zeta)}(t))_{ij}$ in eq 8 is considered in the Markoff approximation. It can be considered

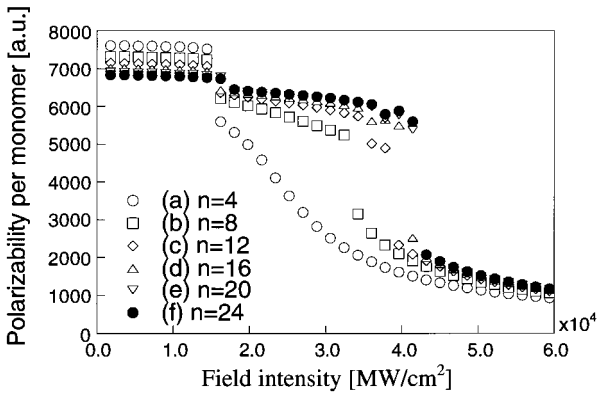

Figure 3. Variations in polarizability α per monomer for the linear aggregates with $\theta = 90°$ and $a = 25$ au as a function of the intensity of the external electric field. The frequency of the field is 37 787 cm^{-1} as compared to the resonant value of 37 800 cm^{-1}. Results are shown at six sizes of aggregates: (a) $n = 4$, (b) $n = 8$, (c) $n = 12$, (d) $n = 16$, (e) $n = 20$, and (f) $n = 24$.

as the following two types of mechanisms:[12,13]

$$-(\Gamma\rho^{(\zeta)}(t))_{ii} = -\Gamma_{ii}\rho_{ii}^{(\zeta)}(t) + \sum_{j\neq i}^{m}\gamma_{ji}\rho_{jj}^{(\zeta)}(t) \tag{13}$$

$$-(\Gamma\rho^{(\zeta)}(t))_{ij} = -\Gamma_{ij}\rho_{ij}^{(\zeta)}(t) \tag{14}$$

The damping parameters are assumed to be identical for all the molecules. Equations 13 and 14 describe the population and coherent damping mechanisms, respectively. The γ_{ij} ($\neq\gamma_{ji}$) represents a feeding parameter. The off-diagonal damping parameters

$$\Gamma_{ij} = {}^1/_2(\Gamma_{ii} + \Gamma_{jj}) + \Gamma_{ij}' \tag{15}$$

$$\Gamma_{ij} = \Gamma_{ji} \tag{16}$$

where Γ_{ij}' is the pure dephasing factor. In this study, we assume a closed system, and then the factor γ_{ij} is related to the decay rate as

$$\Gamma_{ii} = \sum_{l\neq i}^{m}\gamma_{il} \tag{17}$$

We perform a numerically exact calculation treating the aggregates with an arbitrary number of molecules with any m states. The eq 8 is solved in a numerically exact manner by using the sixth-order Runge−Kutta method. To perform this time evolution, we have to calculate the electric field $E^{(\zeta)}(t)$ acting on the molecule ζ at each time step. From eq 10, the $E^{(\zeta)}(t)$ includes the polarization $p^{(\zeta')}(t')$ and its time derivatives, $\dot{p}^{(\zeta')}(t')$ and $\ddot{p}^{(\zeta')}(t')$, for the molecules at the different position ($\zeta'\neq\zeta$) at the past time t' ($=t - r_{\zeta\zeta'}/c$). The $p^{(\zeta')}(t')$ is calculated quantum mechanically by

$$p^{(\zeta')}(t') = \sum_{i,j}^{m}\mu_{ij}\rho_{ji}^{(\zeta')}(t') \tag{18}$$

and the $\dot{p}^{(\zeta')}(t')$ and $\ddot{p}^{(\zeta')}(t')$ are calculated by using the numerical differentiation formulas.[8]

The NCLA includes five steps. It is noted that the procedure has a feedback effect; i.e., polarizabilities $p^{(\zeta')}(t')$ for molecules ζ' at the time t' are used to calculate the field $E^{(\zeta)}(t')$ acting on the molecule ζ at the time t ($>t'$). This feedback effect is considered to cause various collective phenomena, e.g., intrinsic optical bistability.[6,7]

3. Nonperturbative Polarizability

In this section, we apply the calculation method of a nonperturbative polarizability[12,13] to the NCLA. The polarization $p^{(\zeta)}(t)$ is transformed to the $p^{(\zeta)}(\omega)$ in the frequency domain using the discrete Fourier transformation. Using the external field amplitude $\epsilon(\omega)$ and the polarization ($p^{(\zeta)}(\omega)$, the nonper-

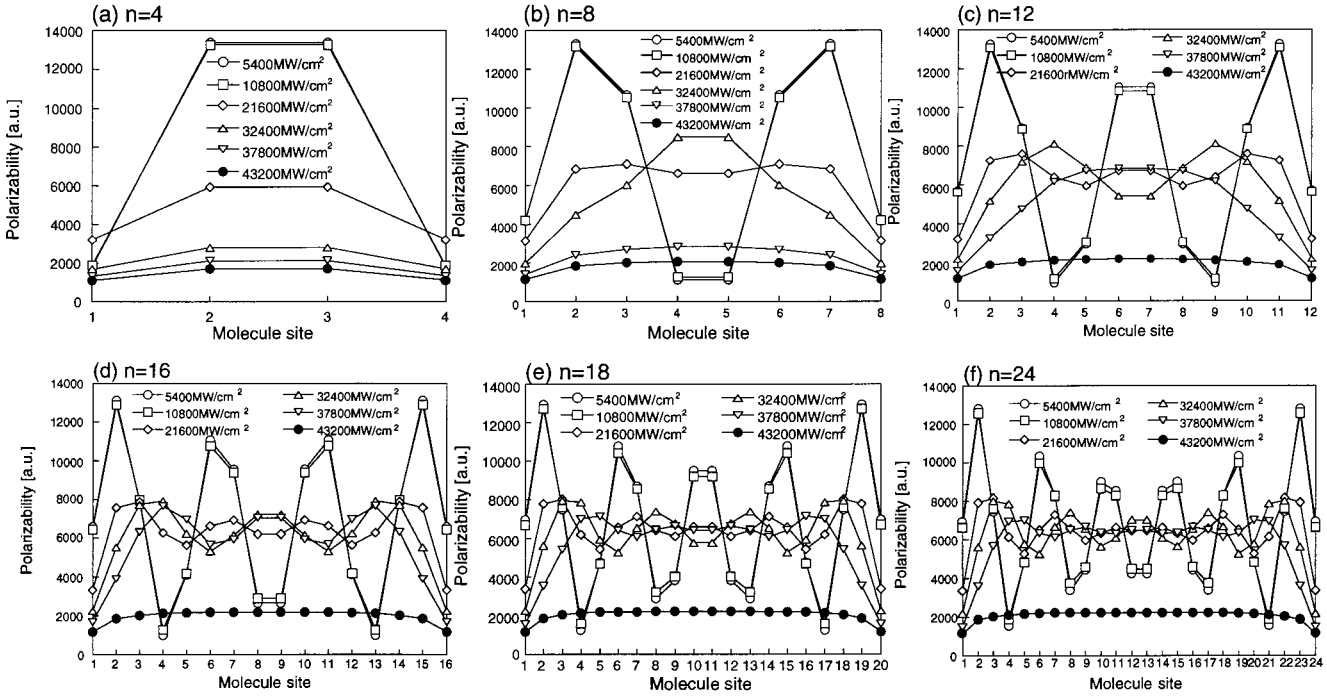

Figure 4. Polarizability $\alpha^{(\zeta)}$ at each molecule site ζ for the linear aggregates under six types of external electric fields (5400, 10 800, 21 600, 32 400, 37 800, and 43 200 MW/cm^2). The frequencies of the fields are 37 787 cm^{-1} as compared to the resonant value of 37 800 cm^{-1}. Results are shown at six sizes of aggregates: (a) $n = 4$, (b) $n = 8$, (c) $n = 12$, (d) $n = 16$, (e) $n = 20$, and (f) $n = 24$.

turbative polarizability at the molecule site ζ is calculated by

$$\alpha^{(\zeta)}(\omega) = p^{(\zeta)}(\omega)/\epsilon(\omega) \tag{19}$$

The nonperturbative polarizability for a molecular aggregate is calculated by

$$\alpha(\omega) = \sum_{\zeta=1}^{n} \alpha^{(\zeta)}(\omega) = \frac{\sum_{\zeta=1}^{n} p^{(\zeta)}(\omega)}{\epsilon(\omega)} \tag{20}$$

For weak fields, this quantity coincides with the conventional perturbative polarizability. In contrast, for intense external fields, this quantity can exhibit various intensity dependent nonlinear optical phenomena.[12,13]

4. Polarizability of Linear Molecular Aggregates under Intense Electric Field

A model of linear molecular aggregate composed of two-state one-molecule systems are shown in Figure 2. In this study, we consider a case of a 90° angle between each dipole and the longitudinal axis, and the intermolecular distance is fixed to 25 au. This aggregate corresponds to the case of the *H* aggregate.[1] In this case, abrupt changes in the population difference for intermediate-size aggregate models are predicted as field intensity increases.[5,6] Six sizes of molecular aggregates, n = 4, 8, 12, 16, 20, and 24 (n = the number of monomers), are considered. The damping factor Γ_{22} is determined by an energy-dependent relation: $\Gamma_{22} = fE_{21}(f=0.02)$.[14] The external single-mode laser has a frequency (37 787 cm^{-1}) as compared to the resonant frequency (37 800 cm^{-1}) for the two-state one-molecule model. The division number of the one optical cycle of the external field used in the numerical calculation is 1000, and the polarizability is calculated by using 100 optical cycles after an initial nonstationary time evolution (400 cycles).

First, the field intensity dependence of the polarizability α per monomer is considered. Under the present condition (θ = 90° and a = 25 au), the population difference between the excited and the ground states was found to exhibit abrupt changes.[8,9] Therefore, the polarizability is expected to have similar abrupt changes. As shown in Figure 3, the aggregate (a) n = 4 has an abrupt change in the polarizability per monomer around the intensity of 1.5×10^4 MW/cm^2, while the aggregate (b) n = 8 has an additional abrupt change in the polarizability per monomer around the intensity of 3.5×10^4 MW/cm^2. These field intensities coincide with those at which the population differences exhibit abrupt changes.[9] Further, the aggregate (c) n = 12 seems to have one more abrupt change around the intensity of 4.0×10^4 MW/cm^2. Similarly to the case of population differences, the magnitude of abrupt changes in the polarizability per monomer is found to be reduced except for the last abrupt changes around 4.0×10^4 MW/cm^2 as the size of the aggregate increases. Therefore the abrupt changes become unclear as the aggregate grows large.

Second, we examine the feature of the polarizability $\alpha^{(\zeta)}$ at each molecule site ζ. Figure 4 shows the results for six intensity of external fields: 5400, 10 800, 21 600, 32 400, 37 800, and 43 200 MW/cm^2. For the aggregate (a) n = 4 under the external field with the intensity of 5400 MW/cm^2, the $\alpha^{(\zeta)}$ at central sites (ζ = 2 and 3) are shown to be larger than those at both ends. The $\alpha^{(\zeta)}$ at each molecule site for the aggregate (a) n = 4 are shown to change abruptly between 10 800 and at 21 600 MW/cm^2. This feature corresponds to the abrupt change in the polarizability α per monomer around 1.5×10^4 MW/cm^2. From

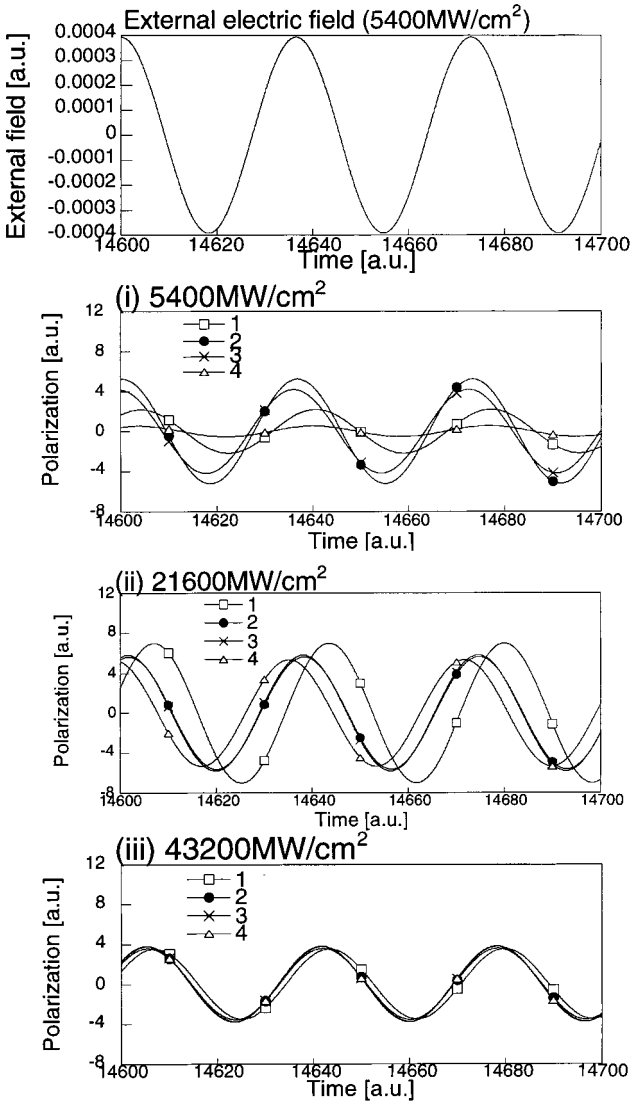

Figure 5. External electric field $E(t)$ with the intensity of 5400 MW/cm^2 and polarization $p^{(\zeta)}(t)$ at each molecule site (1−4) for linear aggregate (b) n = 8. The frequency of the external field is 37 787 cm^{-1} as compared to the resonant value of 37 800 cm^{-1}. Results are shown at three intensities of the external fields: (i) 5400, (ii) 21 600, and (iii) 43 200 MW/cm^2.

the results of other sizes of aggregates, the feature of variations in $\alpha^{(\zeta)}$((a) n = 4) over four molecule sites (ζ = 1−4) under the external field with the intensity of 5400 MW/cm^2 is shown to be nearly repeated. For the aggregate (b) n = 8, the first abrupt change in $\alpha^{(\zeta)}$ corresponds to the abrupt decrease in $\alpha^{(\zeta)}$ at sites 2, 3, 6, and 7 and to the abrupt increase in $\alpha^{(\zeta)}$ at the middle sites 4 and 5. After the first abrupt change, the $\alpha^{(\zeta)}$ values from sites 2−7 become similar to each other and then $\alpha^{(\zeta)}$ at both-sides sites 2, 3, 6, and 7 become small. In the second abrupt changes in α, the $\alpha^{(\zeta)}$ values from sites 2−7 decrease abruptly. For larger-size aggregates, a similar qualitative feature of changes in $\alpha^{(\zeta)}$ is observed. The abrupt changes in α after the first abrupt changes (except for the last abrupt change) are found to correspond to the decreases in $\alpha^{(\zeta)}$ in both-end regions. However, the magnitude of the changes in $\alpha^{(\zeta)}$ are found to be smaller than those of the first and the last abrupt changes. This feature makes the abrupt changes in the α unclear except for the case of the first and the last abrupt changes in the α. These differences in $\alpha^{(\zeta)}$ and their intensity dependences are related to the interference of retarded fields. In the next section,

therefore, the polarization $p^{(\zeta)}(t)$ at each molecule site ζ is elucidated for the aggregate (b) $n = 8$.

5. External Electric Field and Polarization at Each Molecule Site of Linear Molecular Aggregate ($n = 8$)

Figure 5 shows an external electric field $E(t)$ with the intensity of 5400 MW/cm^2 and the polarizations $p^{(\zeta)}(t)$ at the molecule sites (1−4) for the aggregate (b) $n = 8$ under three types of external fields: (i) 5400, (ii) 21 600, and (iii) 43 200 MW/cm^2. Since each molecule is exposed by different retarded fields induced by the rest of the molecules, the quantum interference occurs and then the polarization at each molecule site changes. Therefore, the polarizability $\alpha^{(\zeta)}$ at each molecule site becomes different. For case i, the amplitudes of $p^{(\zeta)}(t)$ at the molecule sites 2 and 3 are shown to be similar to each other and to be larger than those at the molecule sites 1 and 4. In addition, the phases of $p^{(\zeta)}(t)$ at the molecule sites 2 and 3 are found to be nearly equal to the phase of the external electric fields, while those at the molecule sites 1 and 4 are found to be different from the phase of the external electric field. These features correspond to the characteristics of the distribution of $\alpha^{(\zeta)}$ at 5400 MW/cm^2, where the $\alpha^{(\zeta)}$ values at sites 2, 3, 6, and 7 are shown to be larger than those at sites 1, 4, 5, and 8. It is shown from case ii that the amplitude of $p^{(\zeta)}(t)$ at molecule site 1 is larger than $p^{(\zeta)}(t)$ at sites 2−4. However, the phases of $p^{(\zeta)}(t)$ at sites 2−4 are found to be close to the phase of the external electric field, while the phase of $p^{(\zeta)}(t)$ at molecule site 1 is considerebly different from that of the external electric field. This feature supports the distribution of $\alpha^{(\zeta)}$ at 21 600 MW/cm^2. For case iii, all $p^{(\zeta)}(t)$ values at sites 1−4 are shown to possess almost the same phases and amplitudes, which are shown to be considerably smaller than the magnitude of $p^{(\zeta)}(t)$ in case ii. These differences in the magnitude and phase in $p^{(\zeta)}(t)$ at each molecule site are apparently considered to be evidence of the interference effects among the retarded fields.

6. Concluding Remarks

In this paper, we applied the NCLA to the investigation of the intensity dependence of the polarizability α of linear molecular aggregates. Like the case of population differences,[8,9] plural abrupt changes in the α appear for the intermediate-size ($n \geq 8$) molecular aggregates. The increase in the number of such abrupt changes is found to be related to the phased abrupt changes in polarizability $\alpha^{(\zeta)}$ at each molecule site. The regular change in $\alpha^{(\zeta)}$ at each molecule site is considered to be ascribed to the interference of the retarded fields. The magnitude of an amplitude and a phase for the polarization $p^{(\zeta)}(t)$ at each molecule site is found to be reflected in $\alpha^{(\zeta)}$ at each molecule site. These changes in $p^{(\zeta)}(t)$ are considered to be caused by the interference among the retarded and external fields. The interference among retarded fields at each molecule site in linear molecular aggregates under an intense electric field is found to be an important factor for determining the response properties for molecular aggregates as well as the population differences between the excited and the ground states.

In some molecular aggregates, nonradiative incoherent energy transfers among the monomers may be singificant. In the present model, although the energy transfer can be treated by considering the retarded dipole−dipole interaction, the vibrational relaxation effects and high-order interactions, e.g., dipole−quadruple and quadruple−quadruple interactions, are not considred. Therefore, to clearly measure the present behavior for a long time period by experiments, such nonradiative incoherent processes will have to be suppressed by controlling the molecular size, the intermolecular interactions, the configuration of molecules, and an external temperature.

Acknowledgment. This work was supported by a grant from the Ministry of Education, Science and Culture of Japan (Scientific Research on Priority Areas, Grant No. 09241218 and No. 10149101) and a grant from INAMORI FOUNDATION.

References and Notes

(1) Spano, F. C.; Knoester, J. *Adv. Magn. Opt. Res.* **1994**, *18*, 117.
(2) Stroud, C. R.; Eberly, J. H.; Lama, W. L.; Mandel, L. *Phys. Rev. A* **1972**, *5*, 1094.
(3) Freedhoff, H.; Kranendonk, J. V. *Can. J. Phys.* **1967**, *45*, 1833.
(4) Zaitsev, A. I.; Malyshev, V.; Trifonov, E. D. *Sov. Phys. JETP* **1983**, *57*, 275.
(5) Avetisyan, Yu. A.; Zaitsev, A. I.; Malyshev, V. *Opt. Spectrosc. (USSR)* **1985**, *59*, 582.
(6) Bowden, C. M.; Sung, C. C. *Phys. Rev. A* **1979**, *19*, 2392.
(7) Malyshev, V.; Moreno, P. *Phys. Rev. A* **1996**, *53*, 416.
(8) Nakano, M.; Yamaguchi, K. *Int. J. Quantum Chem.*, in press.
(9) Nakano, M.; Yamaguchi, K. *Chem. Phys. Lett.* **1998**, *288*, 25.
(10) Craig, D. P.; Thirunamachandran, T. *Molecular Quantum Electrodynamics*; Academic: New York, 1984.
(11) Born, M.; Wolf, E. *Principles of Optics*; Pergamon: Oxford, U.K., 1980.
(12) Nakano, M.; Yamaguchi, K. *Phys. Rev. A* **1994**, *50*, 2989.
(13) Nakano, M.; Yamaguchi, K.; Matuzaki, Y.; Tanaka, K.; Yamabe, T. *J. Chem. Phys.* **1995**, *102*, 2986.
(14) Shuai, Z.; Brédas, J. L. *Phys. Rev. B* **1991**, *44*, 5962.