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# Numerical coupled Liouville approach: dependence of population differences between excited and ground states on field intensity and size of molecular aggregates

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## Abstract

In our previous paper, we developed a novel numerical calculation method of quantum dynamics for linear molecular aggregates and investigated the population differences between excited and ground states for dimer models under intense external electric fields. The population and polarizability spectra for dimer models exhibited an abrupt change, like the phase-transition behavior for the applied field intensities. In this Letter we investigate dependences of the population differences on the applied field intensity and size of the molecular aggregates. Plural abrupt changes are found to appear for the intermediate-size aggregates. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In our previous paper [1], we found a unique feature of variations in population difference of the dimer model under intense near-resonant electric field. The population difference of the dimer model with substantial effects of retarded fields was found to be abruptly changed at an intensity of applied electric field. This feature is considered to be ascribed to feed back effects of retarded fields, which are generated from induced dipoles and propagate over the dipoles. Therefore, the feature of variations in population differences for the field intensity is expected to be influenced by the size of the molecular aggregates. The size dependence of various properties for molecular aggregates has received much attention both experimentally and theoretically. In particular, the enhancement of linear and nonlinear optical responses [2], superradiance [3] and intrinsic optical bistability [4,5], have been widely investigated. These features originate in the collective characters of the aggregate wavefunctions. In this Letter, we investigate the dependence of population difference between the excited and ground states on the size of molecular aggregates. We employ a numerical coupled Liouville approach (NCLA) [1], which can treat optical retarded effects essentially contributing to molecular interactions in the wave-zone [6] and optical bistability effects [4,5] for mesoscopic-size aggregates. This method also has the advantage of treating large size molecular aggregates with fewer computational resources compared to the conventional dynamics using dipole–dipole static coupling.

Linear molecular aggregates composed of two-state monomers are considered in this study. First, the size dependence of population differences averaged over the linear aggregate is elucidated for several different-size aggregates ( $n = 4, 8, 12, 16, 20$  and  $24$ ;  $n$  = number of monomers). Since the retarded fields are considered to cause different population differences at each molecular site, the population difference at each molecular site is investigated for different field intensities. Second, the feature of the intermolecular interaction at each molecular site is elucidated by investigating retarded field effects on each molecular site. A relation between the actual field and population difference at each molecular site is discussed.

## 2. Numerical coupled Liouville approach (NCLA)

### 2.1. Semiclassical hamiltonian

In the semiclassical approach, molecules are treated quantum mechanically, while fields are considered to be classical time-dependent fields. This semiclassical treatment is found to be acceptable for the case of intense external fields. The semiclassical hamiltonian is expressed by Eq. (1) [1]:

$$H = H_{\text{mol}} + H_{\text{int}}, \quad (1)$$

where the molecular part of the hamiltonian is

$$H_{\text{mol}} = \sum_{\varsigma} H_{\text{mol}}(\varsigma) = \sum_{\varsigma} \left\{ \frac{1}{2m} \sum_{\alpha} p_{\alpha}^2(\varsigma) + V(\varsigma) \right\} \quad (2)$$

and the interaction part between semiclassical fields and molecules is

$$H_{\text{int}} = - \sum_{\varsigma} \boldsymbol{\mu}(\varsigma) \cdot \mathbf{E}(\mathbf{R}_{\varsigma}). \quad (3)$$

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

The intermolecular interactions are usually treated by including instantaneous electrostatic interactions, i.e. dipole–dipole coupling. However, this treatment cannot describe the optical retarded effects, which are essential for describing wave-zone intermolecular interactions. As we focus on the size dependency of the population differences for intermediate-size aggregates, the intermolecular interaction is treated by using the semiclassical formulation (Eqs. (1)–(3)) in this study.

### 2.2. Density matrix formalism

The time evolution of a molecular system is described by the following density matrix equation [7,8]:

$$i\hbar \frac{\partial}{\partial t} \rho(t) = [H(t), \rho(t)] - i\Gamma\rho(t), \quad (4)$$

where  $\rho(t)$  indicates the total molecular density matrix and the second term on the right-hand side of Eq. (4)

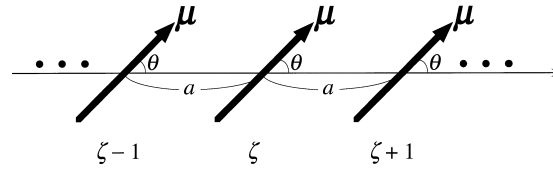


Fig. 1. Schematic diagram of a linear molecular aggregate. The arrow represents the direction of the dipole of the one-molecular system aligned with an angle  $\theta$  from the longitudinal axis. These molecules are separated from each other by the distance  $a$ .

represents the relaxation processes in the Markoff approximation. As mentioned in Section 2.1, the total hamiltonian  $H(t)$  is expressed by the sum of the single molecule hamiltonians  $H^{(s)}(t)$ , as follows:

$$H(t) = \sum_s^N H^{(s)}(t), \quad (5)$$

where

$$H^{(s)}(t) = H_{\text{mol}}^{(s)}(t) + H_{\text{int}}^{(s)}(t) = \frac{1}{2m} \sum_{\alpha} p_{\alpha}^{(s)2} + V^{(s)} - \mu^{(s)} \cdot \mathbf{E}^{(s)}. \quad (6)$$

In this case, Eq. (4) can be reduced to each single-molecule density matrix equation [5] expressed by

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

The intermolecular interaction is considered by the electric field involving, not only external fields, but also the fields induced by the rest of the molecular aggregates. In this study, we consider the linear molecular aggregate shown in Fig. 1. Each molecule is assumed to be a dipole, separated by a distance  $r_{ss'} = |\mathbf{r}_s - \mathbf{r}_{s'}|$  and with an angle  $\theta$  between the dipole and the longitudinal axis. This approximation is considered to be accepted in the case with an intermolecular distance larger than the size of the element molecule.

Supposed that an aggregate is composed of identical  $N$  molecules and each molecule is constructed by  $M$  states, the matrix representation of Eq. (7) is expressed as

$$\dot{\rho}_{ij}^{(s)}(t) = -i(1 - \delta_{ij})E_{ij}\rho_{ij}^{(s)}(t) - i \sum_k^M \left( H_{\text{int}ik}^{(s)}(t)\rho_{kj}^{(s)}(t) - \rho_{ik}^{(s)}(t)H_{\text{int}kj}^{(s)}(t) \right) - (\Gamma\rho^{(s)}(t))_{ij}. \quad (8)$$

Here,  $E_{ij} (= E_i - E_j)$  is the transition energy and  $\rho^{(s)}(t)$  is the density matrix of the molecule  $s$ . The interaction term  $H_{\text{int}}^{(s)}(t)$  involves the electric field  $\mathbf{E}^{(s)}$  acting on molecule  $s$ . This field  $\mathbf{E}^{(s)}$  is expressed as [5]

$$\mathbf{E}^{(s)} = \mathbf{E}^{\text{ext}(s)} + \sum_{s' \neq s}^N \mathbf{E}^{(ss')}, \quad (9)$$

where the first term is the external electric field  $\mathbf{E}^{\text{ext}(s)}$  and the second term is the field induced at the position  $s$  by the rest of the aggregates. It is noted that electron exchange between molecules is ignored. The incident field is assumed to be a plane wave with frequency  $\omega$  and wave vector  $\mathbf{k}$ , travelling perpendicular to the longitudinal axis and the polarization vector is parallel to the dipole vector, so that the  $\mathbf{E}^{\text{ext}(s)} = \mathbf{E}^{\text{ext}}$  for arbitrary  $s$ . The field induced by molecule  $s'$  is regarded as the classical field radiated by a classical dipole, so that the  $\mathbf{E}^{(ss')}(t)$  is represented by [9]

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

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

$$\mathbf{E}^{\text{ext}}(t) = \mathbf{F} \cos \omega t = \frac{\mathbf{F}}{2} (\mathbf{e}^{i\omega t} + \mathbf{e}^{-i\omega t}), \quad (11)$$

the interaction term  $H_{\text{int } ik}^{(s)}(t)$  is expressed using Eqs. (9) and (10) as

$$\begin{aligned} H_{\text{int } ik}^{(s)}(t) &= -\boldsymbol{\mu}_{ik} \cdot \mathbf{E}^{(s)}(t) = -\boldsymbol{\mu}_{ik} \cdot \mathbf{E}^{\text{ext}}(t) - \sum_{s' \neq s}^N \boldsymbol{\mu}_{ik} \cdot \mathbf{E}^{(s's)}(t) \\ &= -\boldsymbol{\mu}_{ik} \left( F \cos \omega t + \sum_{s' \neq s}^N \left[ f_1(t') (r_{s's} \cos \theta)^2 - f_2(t') \right] \right) \equiv -\boldsymbol{\mu}_{ik} E_s(t). \end{aligned} \quad (12)$$

The relaxation term  $-(\Gamma \rho^{(s)}(t))_{ij}$  in Eq. (8) is considered in the Markoff approximation. Details are explained in our previous papers [7,8].

We perform a numerically exact calculation treating the aggregates with an arbitrary number of molecules with any  $M$  states. 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  $E_s(t)$  acting on the molecule  $s$  at each time-step. From Eq. (10),  $E_s(t)$  includes the polarizability  $p^{(s')}(t')$  and its time-derivatives,  $\dot{p}^{(s')}(t')$  and  $\ddot{p}^{(s')}(t')$ , for the molecules at a different position ( $s' \neq s$ ) at the previous time  $t' (= t - r_{s's}/c)$ . The  $p^{(s')}(t')$  is calculated quantum mechanically by

$$p^{(s')}(t') = \sum_{i,j}^M \mu_{ij} \rho_{ji}^{(s')}(t') \quad (13)$$

and the  $\dot{p}^{(s')}(t')$  and  $\ddot{p}^{(s')}(t')$  are calculated by using the numerical differentiation formulae:

$$\dot{p}^{(s')}(t') = \frac{p^{(s')}(t' + \Delta t) - p^{(s')}(t' - \Delta t)}{2\Delta t} \quad (14)$$

and

$$\ddot{p}^{(s')}(t') = \frac{p^{(s')}(t' + \Delta t) - 2p^{(s')}(t') + p^{(s')}(t' - \Delta t)}{(\Delta t)^2}. \quad (15)$$

Here,  $\Delta t$  is a minimum interval of time determined by  $\Delta t = T/L$ , where  $T$  is the period of the external field and  $L$  is the division number of the period. The population averaged over the molecular aggregate is presented by

$$\rho_{ii}^{\text{av}}(t) = \frac{\sum_i^N \rho_{ii}^{(s)}(t)}{N}. \quad (16)$$

It is noted that we have to store the past polarizabilities for each molecule  $s$  in order to calculate the  $E_s$  including retarded effects.

The NCLA includes the five steps. It is noted that the procedure has a feed back effect, i.e. polarizabilities  $p^{(s')}(t')$  for molecules  $s'$  at the time  $t'$  are used to calculate the field  $E^{(s)}(t)$  acting on the molecule  $s$  at the time  $t(>t')$ . This feed back effect is considered to cause various collective phenomena, e.g. intrinsic optical bistability [4].

### 3. Population differences of linear molecular aggregates under intense electric field

Fig. 2 shows a linear molecular aggregate model composed of two-state one-molecule systems. It is well known that the features of the molecule-field interaction in the near- and on-resonant cases is sufficiently described by using a two-state model which is resonant with the external field. In order to elucidate the intermolecular distance dependences of population differences for the dimer model more, we use a value of 30 D as the transition moment, though this is unrealistically large. For more realistic cases, the features obtained in this study would be observed by enhancing the field intensity. In this study, we consider the case of an angle of  $90^\circ$  between the dipole for each molecule and the longitudinal axis and the intermolecular distance is fixed to 25 au. In this case, an abrupt change in the population difference for a dimer model is predicted as the field intensity increases [1]. This aggregate corresponds to the case of the *H* aggregate [2]. Six sizes of molecular aggregates,  $n = 4, 8, 12, 16, 20$  and  $24$  ( $n$  = number of monomers), are considered. The damping factor  $\Gamma_{22}$  is determined by an energy-dependent relation:  $\Gamma_{22} = fE_{21}$  ( $f = 0.02$ ) [10]. The external single-mode laser has a frequency ( $37787 \text{ cm}^{-1}$ ) as compared to the resonant frequency ( $37800 \text{ cm}^{-1}$ ) for the two-state one-molecule model. The division number of the one optical cycle of the external field is 1000 and the averaged population differences ( $\Delta\rho = \rho_{22}^{\text{av}} - \rho_{11}^{\text{av}}$ ) between the ground (1) and excited (2) states are calculated by using 100 optical cycles after initial non-stationary time-evolution (400 cycles).

First, we consider the field intensity dependence of  $\Delta\rho = \rho_{22}^{\text{av}} - \rho_{11}^{\text{av}}$ . As is well known, for a two-state system, the population of the excited state is in proportion to the external field intensity in the case of a weak field, while for the intense external field, the dependence of the population of the excited state on the external field intensity becomes nonlinear and exhibits a saturation behavior of the excitation. As a result, the maximum population of the excited state for a two-state system becomes 0.5 (the population difference  $\Delta\rho$  is 0). As shown in Fig. 3, however, the aggregate (a)  $n = 4$  has an abrupt change around the intensity of  $1.5 \times 10^4 \text{ MW/cm}^2$ , while the aggregate (b)  $n = 8$  has an additional abrupt change around the intensity of  $3.5 \times 10^4 \text{ MW/cm}^2$ . Further, the aggregate (c)  $n = 12$  has one more abrupt change around the intensity of  $4.0 \times 10^4 \text{ MW/cm}^2$ . The magnitudes of abrupt changes of  $\Delta\rho$  are found to be reduced, except for the last abrupt changes around  $4.0 \times 10^4 \text{ MW/cm}^2$ , as the size of the aggregate increases. Therefore the abrupt changes become unclear as the aggregate grows large.

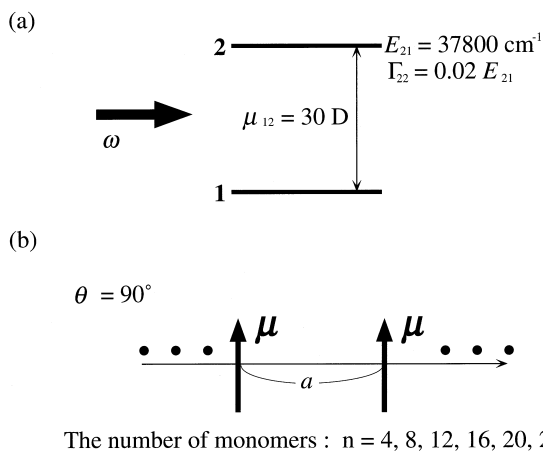


Fig. 2. Two-state model (constructed from ground (1) and the excited (2) states) for a one-molecule system (a). The transition moment is  $\mu_{12} = 30 \text{ D}$ , the transition energy is  $E_{21} = 37800 \text{ cm}^{-1}$  and the damping factor is  $\Gamma_{22} = fE_{21}$  ( $f = 0.02$ ). The aggregate (b) with  $\theta = 90^\circ$  is considered. The intermolecular distance ( $a$ ) is fixed at 25 au. Six sizes of aggregate ( $n = 4, 8, 12, 16, 20, 24$ ;  $n$  = number of monomers) are considered.

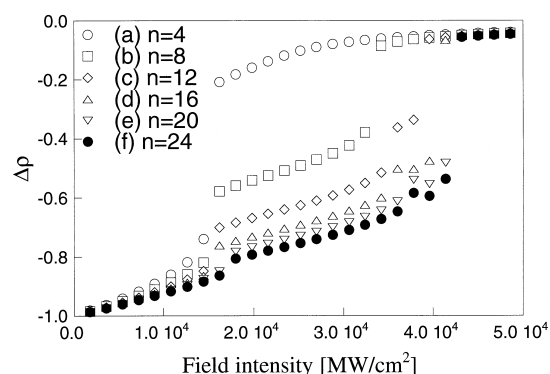


Fig. 3. Variations in averaged population differences  $\Delta\rho$  for the linear aggregates with  $\theta = 90^\circ$  and  $a = 25$  au as a function of the intensity of the external electric field. The frequency of the field is  $37787\text{ cm}^{-1}$  as compared to the resonant value of  $37800\text{ cm}^{-1}$ . Results are shown at six sizes of aggregate: (a)  $n = 4$ , (b)  $n = 8$ , (c)  $n = 12$ , (d)  $n = 16$ , (e)  $n = 20$  and (f)  $n = 24$ .

In order to explore the cause of the plural abrupt changes, the population difference at each molecular site is investigated. Fig. 4 shows the population differences ( $\Delta\rho_i$ ) at each molecular site  $i$ , for six intensities of external fields: 5400, 10800, 21600, 32400, 37800 and 43200  $\text{MW}/\text{cm}^2$ . For aggregate (a)  $n = 4$  under an external field with an intensity of 5400  $\text{MW}/\text{cm}^2$ , the population differences at central sites ( $i = 2$  and 3) are found to be larger than those at both ends. The population differences at each site for aggregate (a)  $n = 4$  are shown to change abruptly between 10800 and 21600  $\text{MW}/\text{cm}^2$ . This feature corresponds to the abrupt change in averaged population difference at around  $1.5 \times 10^4\text{ MW}/\text{cm}^2$ . From the results of other sizes of aggregates, the population differences at 5400  $\text{MW}/\text{cm}^2$  are found to be varied repeatedly for the unit of four site

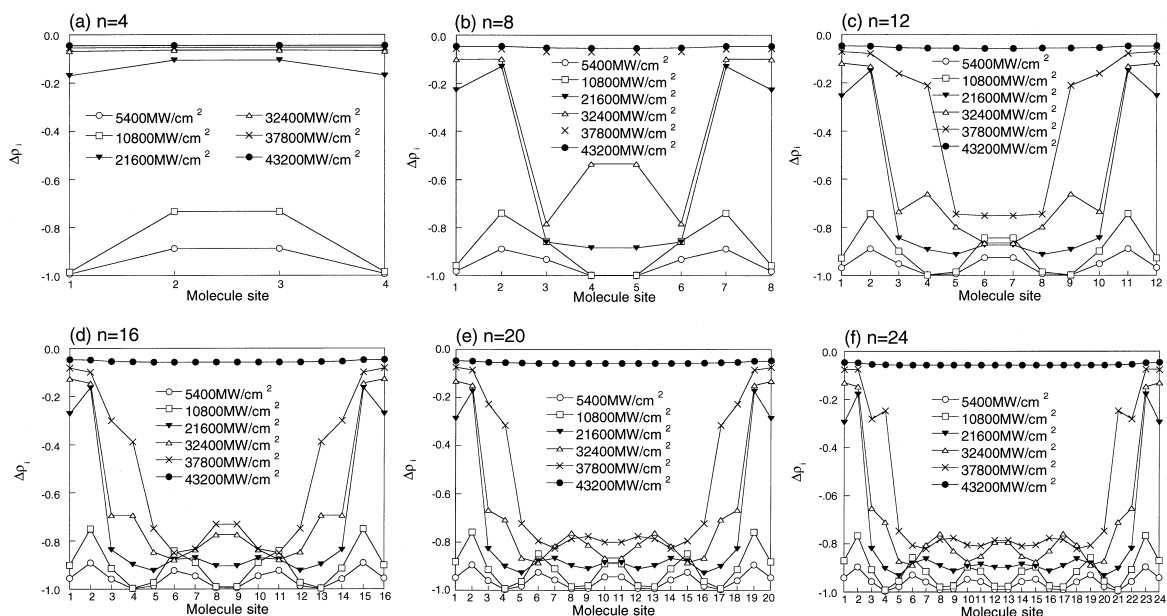


Fig. 4. Population difference  $\Delta\rho_i$  at each molecular site  $i$  for the linear aggregates under six types of external electric fields (5400, 10800, 21600, 32400, 37800 and 43200  $\text{MW}/\text{cm}^2$ ). The frequencies of the fields are  $37787\text{ cm}^{-1}$  as compared to the resonant value of  $37800\text{ cm}^{-1}$ . Results are shown at six sizes of aggregate: (a)  $n = 4$ , (b)  $n = 8$ , (c)  $n = 12$ , (d)  $n = 16$ , (e)  $n = 20$  and (f)  $n = 24$ .

molecules. The first abrupt change in  $\Delta\rho$  corresponds to the abrupt changes in population differences at both-ends, two molecular sites (1, 2,  $n-1$  and  $n$ ). The second abrupt change in  $\Delta\rho$  corresponds to the abrupt changes of population differences at the next internal two sites (3, 4,  $n-3$  and  $n-2$ ). This feature seems to be related to the interference of retarded fields. In Section 4, we elucidate the external electric field plus retarded fields acting on each molecular site for the aggregate (b)  $n = 8$ .

#### 4. External electric field and actual fields acting on each molecular site of the linear molecular aggregate ( $n = 8$ )

Since each molecule is exposed to different retarded fields, induced by the rest of the molecules, the quantum interference is caused and then the magnitude of the intermolecular interaction becomes different at the different position of each molecule. This effect is considered to cause the different changes in population differences at different molecular sites. In Fig. 5, we plot the external electric field and actual fields acting on the molecular sites (1, 2, 3 and 4) for aggregate (b)  $n = 8$  under three types of external fields: (i) 5400, (ii) 21600 and (iii) 43200 MW/cm<sup>2</sup>. It is seen for all cases (i)–(iii) that the amplitude of the actual field acting on each molecular

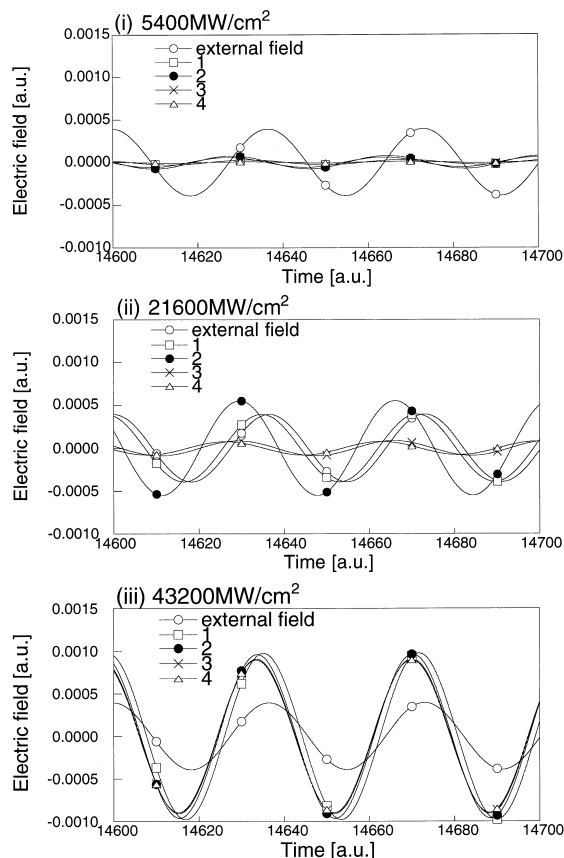


Fig. 5. External electric field and actual fields acting on each molecular site (1, 2, 3 and 4) for linear aggregate (b)  $n = 8$ . The frequency of the external field is  $37787\text{ cm}^{-1}$  as compared to the resonant value of  $37800\text{ cm}^{-1}$ . Results are shown at three intensities of the external fields: (i) 5400, (ii) 21600 and (iii) 43200 MW/cm<sup>2</sup>.



site changes remarkably, compared with that of the external field. For case (i), the amplitude of the actual field on each molecular site is shown to be smaller than that of the external electric field. It is shown from case (ii) that the amplitudes of fields acting on sites 3 and 4 are smaller than the amplitude of the external field, while those of the fields on sites 1 and 2 are equal to and larger than that of the external field, respectively. For case (iii), all actual fields acting on sites 1–4 possess almost the same phase and amplitudes, which are considerably larger than that of external field. In each case, the relative magnitudes of the population differences at each molecular site are found to be reflected in those of the amplitudes of the actual fields. This implies that the interference among retarded fields causes the enhancement and reduction of the external field amplitudes acting on each molecular site and then varies the population difference at the different molecular site.

## 5. Concluding remarks

In this Letter, we applied the NCLA to the investigation of the dependence of population differences  $\Delta\rho$  on the size of linear molecular aggregates. In contrast to the case of the dimer model [1], plural abrupt changes in averaged population differences appear for the intermediate-size ( $n \geq 8$ ) molecular aggregates. The increase in the number of such abrupt changes are found to be caused by the phased abrupt changes in population differences at each molecular site. This change is also found to start from both-ends sites. This regular spatial change in population difference is considered to be ascribed to the interference of the retarded fields. Actually, the magnitude of the amplitude for the retarded field plus external field at each molecular site is shown to be reflected in the population difference at each molecular site. As a result, the intermolecular interaction described by the propagation of the retarded fields influences the coherence of excitation in linear molecular aggregates under intense electric field. Predicted from these spatially regular changes in the population differences of  $4n$ -site aggregates under intense electric field, different population changes are expected to appear in different types of aggregates, e.g.  $3n$ -site aggregates. The analysis of these systems is now in progress in our laboratory.

## Acknowledgements

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