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Numerical Coupled Liouville Approach: Application to Nonperturbative Second Hyperpolarizability of a Molecular Aggregate

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In our previous paper (*Int. J. Quant. Chem.*, in press[1)]) we discussed a novel numerical calculation scheme for the dynamics of a quantum network for linear molecular aggregates under time-dependent electric fields. The population and polarizability spectra for dimer models were found to exhibit a change, like a phase-transition behavior, for applied field intensities. In the present work we apply this method to a calculation of nonperturbative second hyperpolarizability γ of a dimer model and investigate the dependence of γ on the field intensity.

Recently, much attention has been focused on the quantum dynamics of mesoscopic-size systems both experimentally and theoretically. In particular, attractive features of linear molecular aggregates, e.g., 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 characteristics of the aggregate wavefunctions. In a previous paper[1)] we proposed a novel numerically exact calculation scheme concerning the quantum dynamics of linear molecular aggregates by considering the retarded field induced by each monomer to the external fields. This method is referred to as the numerical coupled-Liouville approach (NCLA), which can be used to 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 requires fewer computational resources than does the conventional dynamics using dipole–dipole static coupling.

From the previous results for dimers,[1)] the population and polarization changes were found to exhibit a phase transition-like behavior with respect to the increasing field intensity. This feature is ascribed to feedback effects of the retarded fields on each dipole. In this paper, as the next step, the effects of a retarded field on the third-order one-photon resonant nonlinear optical phenomena are considered. The calculation method of the second hyperpolarizability γ-spectrum in the one-photon resonant region is presented by using the definition of nonperturbative hyperpolarizability proposed in the numerical Liouville approach (NLA).[7)]

First, we briefly explain a quantum-electrodynamical formalism for aggregate-external electric field-coupled systems. We performed a semiclassical approximation, i.e., the interaction terms between monomer and field were considered classically. Second, the nonperturbative γ-spectrum for a dimer model constructed from two-state monomer systems was calculated, and its dependence on the intermolecular distance and external field intensity was elucidated compared with the γ-spectrum of a monomer.

Methodology. **Semiclassical Hamiltonian.** In this section we briefly explain the semiclassical Hamiltonian. In a semiclassical approach, molecules are treated quantum mechanically, while fields are taken to be classical time-dependent fields; thus the field-part Hamiltonian disappears. This semiclassical treatment is found to be acceptable for the case of intense external fields. The semiclassical Hamiltonian is expressed by Eqs. 1, 2, and 3:[1)]

$$H = H_{\mathrm{mol}} + H_{\mathrm{int}}, \tag{1}$$

where the Hamiltonian of molecular part is

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

and the interaction part between the semiclassical fields and molecules is

$$H_{\mathrm{int}} = -\frac{1}{\varepsilon_0} \sum_{\zeta} \boldsymbol{\mu}(\zeta) \cdot \boldsymbol{d}^{\perp}(\boldsymbol{R}_{\zeta}). \tag{3}$$

Here, ζ indicates the molecule ζ. In Eq. 2, $\frac{1}{2m}\sum_{\alpha}\boldsymbol{p}_{\alpha}^{2}(\zeta)$ and $V(\zeta)$ represent the kinetic and intramolecular Coulomb potential parts of molecule ζ, respectively. In Eq. 3, $\boldsymbol{d}^{\perp}(\boldsymbol{R}_{\zeta})$ represents the classical external electric fields acting on molecule ζ plus the fields induced by the remaining molecules. We can recognize that Eq. 3 does not involve a Coulomb static potential for the intermolecular interaction, and only involves interactions between the dipole moment ($\boldsymbol{\mu}(\zeta)$) and the field ($\boldsymbol{d}^{\perp}(\boldsymbol{R}_{\zeta})$), which is fully retarded. This intermolecular interaction can be described by an exchange of transverse photons in quantum electrodynamics, while in the semiclassical approach this is described by the propagation of classical time-dependent fields.

Usually, the intermolecular interactions are treated by including instantaneous electrostatic interactions, i.e., dipole–dipole coupling. However, only including these interactions cannot describe the optical retarded effects, which are essential for describing wave-zone intermolecular interactions. The purpose of this study is to develop a numerical nonperturbative method for treating the nonlinear optical responses of mesoscopic (intermediate)-size molecular aggregates interacting with intense external fields. Therefore, we use the semiclassical formulation (Eqs. 1, 2, and 3) in this study.

Density Matrix Formalism for One-Dimensional Molecular Aggregates under Intense Electric Fields. The time evolution of a molecular system is described by the following density matrix equation:[7,8]

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

where $\rho(t)$ indicates the total molecular density matrix and the second term on the right-hand side of Eq. 4 represents the relaxation processes in the Markoff approximation. As mentioned in the above section, 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

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

In this case, Eq. 4 can be reduced to each one-molecule density matrix equation,[5] 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 considered based on an electric field involving not only external fields, but also fields induced by the remaining 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 $r_{\zeta\zeta'} = |\boldsymbol{r}_{\zeta} - \boldsymbol{r}_{\zeta'}|$ and having an angle θ between the dipole and the longitudinal axis. This approximation is considered to be accepted in the case of an intermolecular distance larger than the size of the element molecule.

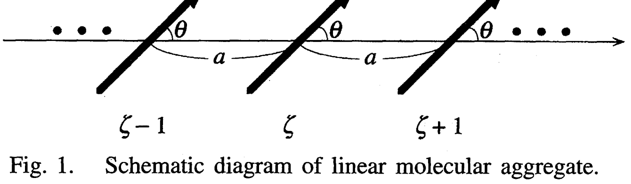

Fig. 1. Schematic diagram of linear molecular aggregate. The arrow represents the direction of the dipole of the one-molecular system aligned with the angle θ from the longitudinal axis. These molecules are separated each other by the distance a.

Suppose that an aggregate is composed of N identical molecules, and that each molecule is constructed by M states; the matrix representation of Eq. 7 is then expressed as

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

Here, E_{ij} ($\equiv E_i - E_j$) is the transition energy, and $\rho^{(\zeta)}(t)$ is the density matrix of molecule ζ. The interaction term ($H^{(\zeta)}_{\text{int}}(t)$) involves electric field $\boldsymbol{E}^{(\zeta)}$ acting on molecule ζ. $\boldsymbol{E}^{(\zeta)}$ is expressed as[5]

$$\boldsymbol{E}^{(\zeta)} = \boldsymbol{E}^{\text{ext}(\zeta)} + \sum_{\zeta'\neq\zeta}^{N} \boldsymbol{E}^{(\zeta\zeta')}, \tag{9}$$

where the first term is the external electric field ($\boldsymbol{E}^{\text{ext}(\zeta)}$) and the second term is the field induced by the rest of the aggregates at position ζ. The incident field is assumed to be a plane wave with frequency ω and wave vector $\boldsymbol{k}$ travelling perpendicular to the longitudinal axis, and the polarization vector is parallel to the dipole vector, so that the $\boldsymbol{E}^{\text{ext}(\zeta)} = \boldsymbol{E}^{\text{ext}}$ for arbitrary ζ. Since the field induced by molecule ζ' is regarded as being the classical field radiated by the a classical dipole, $\boldsymbol{E}^{(\zeta\zeta')}(t)$ is represented by[9]

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

where $t' = t - r_{\zeta'\zeta}/c$, $\boldsymbol{n} = \boldsymbol{\mu}/\mu$, and $\boldsymbol{r}_{\zeta'\zeta} = (\zeta' - \zeta)\boldsymbol{a}$. 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. In this study we consider the retardation effects in a numerically exact manner in order to treat arbitrary-size molecular aggregates. Suppose that an external field is produced by a continuous-wave laser,

$$\boldsymbol{E}^{\text{ext}}(t) = \boldsymbol{F}\cos\omega t = (\boldsymbol{F}/2)(e^{i\omega t} + e^{-i\omega t}). \tag{11}$$

The interaction term ($H^{(\zeta)}_{\text{int}ik}(t)$) is expressed using Eqs. 9 and 10 as

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

The relaxation term ($-(\Gamma\rho^{(\zeta)}(t))_{ij}$) in Eq. 8 can be considered as the following two types of mechanisms:[7,8]

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

and

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

Here, we assume that the damping parameters are identical for all 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 parameter is expressed as

$$\Gamma_{ij} = \frac{1}{2}(\Gamma_{ii} + \Gamma_{jj}) + \Gamma'_{ij} \tag{15}$$

and

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

where Γ'_{ij} is the pure dephasing factor. In this study, since we assume a closed system, 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 for treating aggregates with an arbitrary number of molecules with any M states. Equation 8 is solved in a numerically exact manner by using the sixth-order Runge–Kutta method. To perform this time-evolution, we must calculate the electric field ($E_{\zeta}(t)$) acting on molecule ζ at each time step. From Eq. 10, $E_{\zeta}(t)$ includes the polarizability ($p^{(\zeta')}(t')$) and its time-derivatives ($\dot{p}^{(\zeta')}(t')$ and $\ddot{p}^{(\zeta')}(t')$) for molecules at different positions ($\zeta'\neq\zeta$) in the past, $t'(=t-r_{\zeta\zeta'}/c)$. $p^{(\zeta')}(t')$ is calculated quantum mechanically by

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

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

$$\dot{p}^{(\zeta')}(t') = \frac{p^{(\zeta')}(t'+\Delta t) - p^{(\zeta')}(t'-\Delta t)}{2\Delta t} \tag{19}$$

and

$$\ddot{p}^{(\zeta')}(t') = \frac{p^{(\zeta')}(t'+\Delta t) - 2p^{(\zeta')}(t') + p^{(\zeta')}(t'-\Delta t)}{(\Delta t)^2}. \tag{20}$$

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

$$\rho_{ii}^{\mathrm{av}}(t) = \frac{\sum_{\zeta}^{N} \rho_{ii}^{(\zeta)}(t)}{N}. \tag{21}$$

It is noted that we have to store the past polarizabilities for each molecule ζ in order to calculate E_{ζ}, including any retarded effects.

The NCLA procedure is shown in Fig. 2. NCLA includes five steps. It is noted that the procedure has a feedback effect, i.e., the polarizabilities ($p^{(\zeta')}(t')$) for molecules ζ' at time t' are used to calculate the field ($E^{(\zeta)}(t)$) acting on molecule ζ at time t ($>t'$). This feedback effect is considered to cause various collective phenomena, e.g., intrinsic optical bistability for a large molecular aggregate.[4,5]

Nonperturbative Second Hyperpolarizability. We explain our calculation method for the nonperturbative second hyperpolarizability (γ).[7,8] The γ in the third-harmonic generation (THG) is considered as an example. The γ in other nonlinear optical phenomena can be calculated similarly.[8] The polarization ($p^{(\zeta)}(t)$) is transformed to $p^{(\zeta)}(\omega)$ in the frequency domain by using the following discrete Fourier transformation:

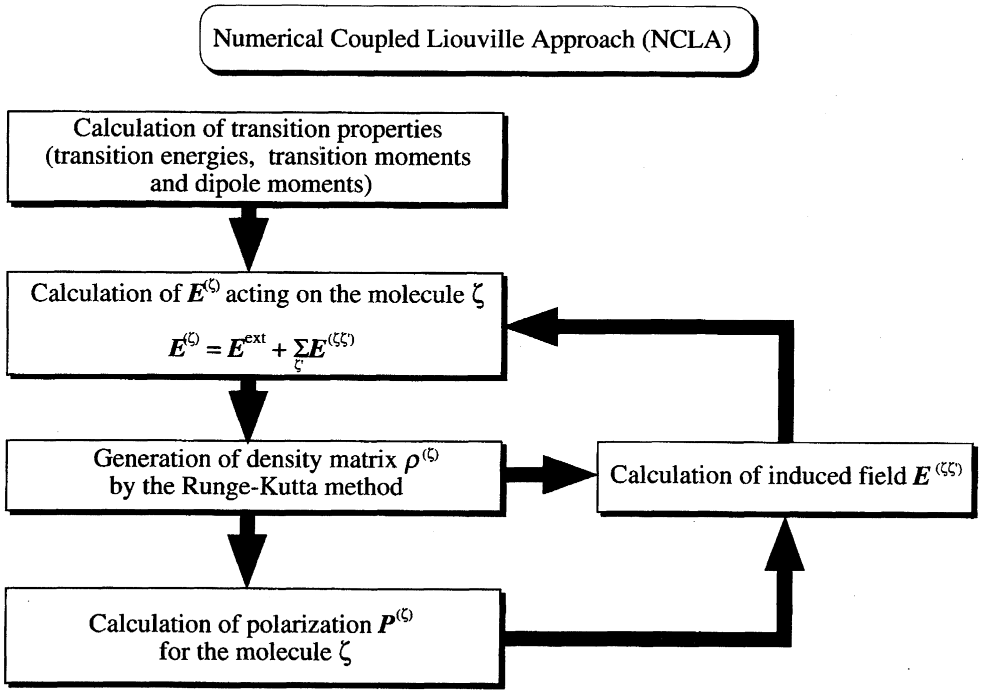

Fig. 2. Schematic diagram describing the process of the numerical coupled Liouville approach (NCLA).

$$p^{(\zeta)}(\omega_j)=\frac{1}{n}\sum_{k=0}^{n-1}p^{(\zeta)}(t_k)\exp\left[i\left(\frac{2\pi}{n}jk\right)\right] \tag{22}$$

$$(j=0,1,\cdots,n-1;\quad k=0,1,\cdots,n-1).$$

Here, the used number of time-series data is n, the kth discrete time is $t_k=(L/n)k$, and the jth discrete frequency is $\omega_j=(2\pi/L)j$, where the minimum t value (t_0) is 0 and the maximum t value (t_{n-1}) is L. Using the external field amplitude $\varepsilon(\omega)(=F/6)$ and the polarization $p^{(\zeta)}(\omega)$, the nonperturbative second hyperpolarizability $\gamma(-3\omega;\ \omega,\omega,\omega)$ for a molecular aggregate is calculated by

$$\gamma(-3\omega;\ \omega,\omega,\omega)=\frac{\sum_{\zeta=1}^{N}p^{(\zeta)}(3\omega)}{27\varepsilon^3(\omega)}. \tag{23}$$

For weak fields, this quantity coincides with the conventional perturbative, $\gamma(-3\omega;\ \omega,\omega,\omega)$. In contrast, for intense external fields, this quantity can exhibit various intensity-dependent phenomena, such as spectral broadening, as well as a displacement and the appearance of a new resonance peak.[10]

Variations in γ of the Dimer Model for Intermolecular Distances and Field Intensities. We consider the γ of an artificial dimer model comprising the two-state, one-molecule systems shown in Fig. 3. It is well-known that the feature 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 more clearly elucidate the intermolecular distance dependences of γ for the dimer model, we use the value of 30D as the transition moment, though this is unrealistically large. For more realistical cases, the features obtained in this study would be observed by enhancing the field intensity. The damping factor (Γ_{22}) is determined by an energy-dependent relation, $\Gamma_{22}=fE_{21}$ ($f=0.02$).[11] The external single-mode laser has a frequency (37787 cm^{-1}), compared to the resonant frequency (37800 cm^{-1}) for the two-state one-molecule model. The division number of the one optical cycle of the external field is 1000, and γ is calculated by using the Fourier transformation of polarization for 100 optical cycles after a non-stationary time evolution (400 cycles). As an example, we consider the case of an angle of 90° between the dipole for each molecule and the longitudinal axis. This corresponds to the case of the H aggregate.[2]

The dependence of γ on the applied field intensities are investigated for the dimer model. Figure 4 shows the results at seven intermolecular distances: (a) infinite, (b) 80 a.u., (c) 60 a.u., (d) 50 a.u., (e) 40 a.u., (f) 30 a.u., and (g) 25 a.u. The result of case (a) is obtained by using noninteracting dimer model. As shown in Fig. 4, the γ values for cases (a)—(e) are found to increase with a decrease in the intermolecular distance in the low field-intensity region (around 5.0×10^3 MW cm^{-2}), while those for cases (f) and (g) are found to be reduced in the same region. However, the γ values for cases (f) and (g) show abrupt increases at 5.0×10^3 and 1.3×10^4 MW cm^{-2}, respectively. Similar to the abrupt population differences observed in our previous paper,[1] the γ value is found to exhibit an abrupt change around the same intermolecular distance.

These abrupt changes in γ at the high intensity of the field are considered to originate in the retarded intermolecular interaction. A feedback effect involved in the induced field ($E^{(\zeta\zeta')}$) describing the intermolecular interaction seems to be related to changes in the resonance frequency and the γ-spectral shape, which cause the abrupt increase behaviors. In order to elucidate these effects, we next consider the γ-spectra of the dimers for various field intensities and intermolecular distances.

Dependences of γ-Spectrum for Dimer Model on Intermolecular Distances and Field Intensities. In this section we consider the dependences of the γ-spectrum for the dimer model shown in Fig. 3 on the intermolecular distances and the field intensities. The real-part spectra of γ for the dimer model are shown in Fig. 5. The results are

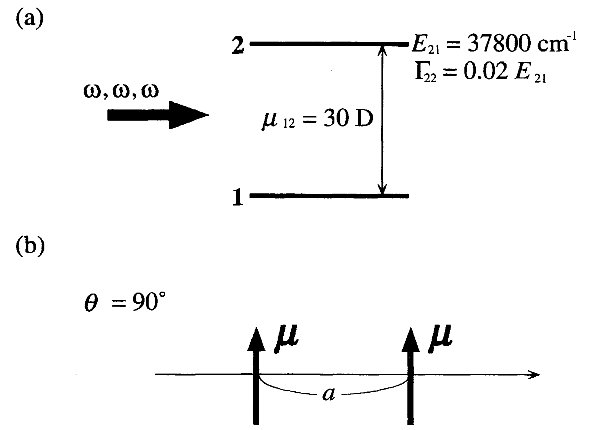

Fig. 3. Two-state model (constructed from ground (**1**) and the excited (**2**) states) for one-molecule system (a). The dimer (b) with θ=90° is considered. The transition moment is μ_{12}=30 D, the transition energy is E_{21}=37800 cm^{-1}, and the damping factor is $\Gamma_{22}=fE_{21}$ ($f=0.02$).

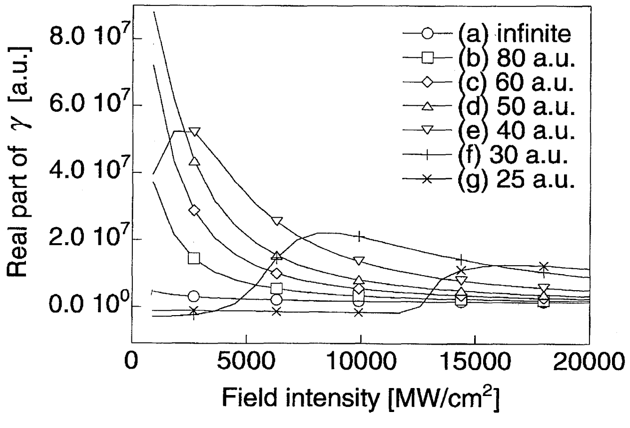

Fig. 4. Variations in second hyperpolarizability γ for the dimer model with θ = 90° as a function of the intensity of the external electric field. The frequency of the field is 37787 cm^{-1} as compared to the resonant value of 37800 cm^{-1}. Results are shown at seven intermolecular distances: (a) infinite, (b) 80 a.u., (c) 60 a.u., (d) 50 a.u., (e) 40 a.u., (f) 30 a.u., and (g) 25 a.u.

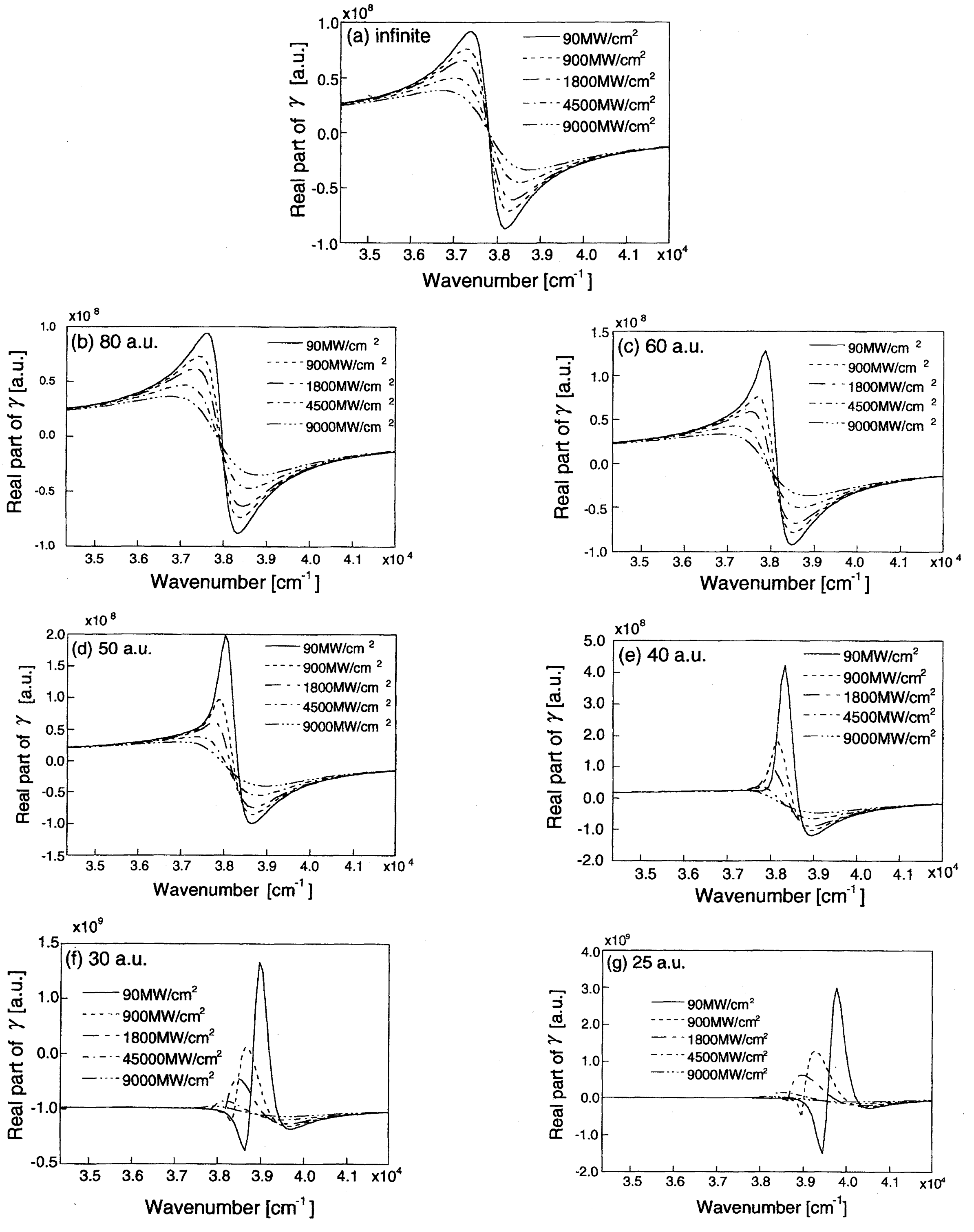

Fig. 5. Real part of spectra of second hyperpolarizability γ for the dimer model (θ=90°, See Fig. 3(b)). Results are shown at seven intermolecular distances: (a) infinite, (b) 80 a.u., (c) 60 a.u., (d) 50 a.u., (e) 40 a.u., (f) 30 a.u., and (g) 25 a.u. The frequencies of these fields are the same value, 37787 cm^{-1}, as compared to the resonant value of 37800 cm^{-1}.

shown at seven intermolecular distances: (a) infinite, (b) 80 a.u., (c) 60 a.u., (d) 50 a.u., (e) 40 a.u., (f) 30 a.u., and (g) 25 a.u. We employ five types of intensities for external electric fields (90, 900, 1800, 4500, and 9000 MW cm^{-2}). All of the fields have the same frequency (37787 cm^{-1}) compared to the resonant frequency (37800 cm^{-1}) for the one-molecular two-state system.

Similar to the α-spectra observed in our previous paper,[1] the resonance frequency (37800 cm^{-1} for the one-molecule) at the same field intensity is found to be shifted to a higher-frequency region as the intermolecular distance is reduced. This feature corresponds to the phenomenon observed in the

H (θ=90°) aggregate. Such a phenomenon is usually analyzed by using the dipole–dipole coupling.[2)] Namely, the sign of the dipole–dipole interaction is determined by angle θ among the parallel dipoles and the longitudinal axis, and the intermolecular distance affects the shift of the transition energy. For θ=90° (H-aggregate), the transition energy is known to become larger than that in the case without dipole–dipole coupling. It is also noted that the spectral peak in the frequency region below the resonance frequency is enhanced as the intermolecular distance is reduced. This feature supports the increase in the γ values for the cases (a)—(e) (shown in Fig. 4) with a decrease in the intermolecular distances in the low field-intensity region.

The intensity of the field is shown to change both the resonance frequency and the spectral line shape around the resonance region. The resonance frequency is found to be shifted to a lower-frequency region as the field intensity increases. For cases (f) and (g) with intermolecular distances less than 40 a.u., original resonance peaks are found to be shifted to a higher-frequency region, e.g., in the case of (g), 4.0×10^4 cm^{-1} at 90 MW cm^{-2}. Further, a new sharp resonance peak with a negative γ value appears above the original resonance frequency (37800 cm^{-1}). This new resonance peak is also found to be shifted to a lower-frequency region as the field intensity increases. The pass of the resonance frequency over the incident-field frequency (37787 cm^{-1}) along with an increase in the field intensity enhances the γ abruptly. This feature causes abrupt changes in the γ values for cases (f) and (g) around 5.0×10^3 and 1.3×10^4 MW cm^{-2}, respectively (See Fig. 4).

Concluding Remarks

In this paper we developed a novel numerically exact calculation method of the second hyperpolarizability spectrum for a linear aggregate including M-state molecules. This method has the advantage of treating the optical retarded effects, which lead to molecular interactions in the wave zone, and cause phase-transition like phenomena of population differences and hyperpolarizabilities for increasing the field intensity. As an example, we investigated the γ-spectrum for a two-state dimer with 90° between the molecular dipole and the longitudinal axis under intense electric fields with near resonance frequency for the one-molecule system. Similar to the results for the population differences and α-spectra for dimer models,[1)] the γ values showed abrupt changes at high-field intensity for the dimer system at small intermolecular distances. This phenomenon was found to be related to a shift of the resonance frequency and a change in the shape of the γ-spectrum in the resonance region. Although the changes were similar to those in the α-spectra, the changes in the γ-spectra are more complicated. For example, a new resonance peak is found to appear in the case of small intermolecular distances. These changes in the γ-spectrum are caused by intermolecular interactions and an increase in the field intensity. The behaviors in the hyperpolarizability spectra for intermediate-size aggregates under intense electric fields are expected to be interesting, judging from the results of the dimer model. Considering the features of this method, i.e., a numerically exact treatment of optical retardation effects, the present calculation approach is expected to provide reliable features for such phase transition-like behaviors of larger systems under various time-dependent intense external fields, though there are not any experiments concerning the present results.

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