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Theoretical Study on Near-Resonant Third-Order Nonlinear Optical Properties (γ) of Dendritic Molecular Aggregates: Intermolecular-Interaction and Relaxation Effects on γ

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Second hyperplarizability (γ) of dendritic molecular aggregate (D25) is calculated using a coupled-dipole model in the Markoff approximation. At the near resonant region, intermolecular-interaction and relaxation effects on γ are found to remarkably change the γ value.

Keywords: hyperpolarizability; dendrimer; exciton; aggregate; near-resonance; Markoff approximation; dipole-dipole interaction

INTRODUCTION

Recently, supramolecules called dendrimers, which have highly branched fractal architectures, have attracted much attention because of their light harvesting ability: they absorb light at their periphery and transfer the photon energy from the periphery to the core efficiently. It is reported that there are two primary origins of this behavior. One is their structural specificity: π-electron conjugation between each generation is decoupled since each generation is linked with each other at the meta-branching point (phenyl rings).[1,2] The other is the fact that the relaxation occurs among the exciton states.[3-5] Although the light-harvesting ability of dendrimers is actively studied, there have been few reports on other

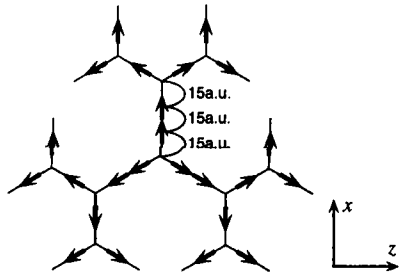

FIGURE I Structure of dendritic molecular aggregate D25. The transition energy and transition moment of a monomer are assumed to be 38000 cm^{-1} and 5.0D, respectively. The intermolecular distance is assumed to be 15a.u.

properties such as nonlinear opticalproperty. Therefore, we investigate the microscopic third-order nonlinear optical (NLO) property, i.e., second hyperpolarizability (γ), of a dendritic aggregate, which mimics the fractal structure and the light- harvesting behavior of a dendrimer. In our previous papers,[6,7] although the features of γ of dendritic molecular aggregates in the off-resonant region were discussed from the viewpoint of the intermolecular-interaction and the relaxation effects, these effects were found to be negligibly small. In contrast, in the near-resonant region, these effects are expected to be observed remarkably. We therefore consider the near-resonant region to elucidate a structure-property relation of γ for dendritic systems.

CALCULATION METHOD AND AGGREGATE STRUCTURES

A model aggregate (Fig.1) is composed of two-state dipole units coupled by the dipole-dipole interaction. We firstly construct Hamiltonian for this aggregates:

$$H_{agg} = \sum_{k=1}^{N}\sum_{i_k}^{2} E_{i_k}^{k} a_{i_k}^{+} a_{i_k} + \sum_{k<l}^{N}\sum_{\substack{i_k,i_l \\ i_k,i_l}}^{2} \mu_{i_k i_k'}^{k} \mu_{i_l i_l'}^{l} \left[\frac{\cos(\theta_k - \theta_l) - 3\cos\theta_k \cos\theta_l}{4\pi\varepsilon_0 R_{kl}^{3}}\right] a_{i_k}^{+} a_{i_k'} a_{i_l}^{+} a_{i_l'} \qquad (1)$$

where $a_{i_k}^{+}$ and a_{i_k} are creation and anihilation operators for aggregates basis. The basis of this aggregate using the basis of monomer k ($|\varphi_{i_k}^{k}\rangle$) is $|\{i_k\}\rangle (\equiv |\varphi_{i_1}^{1}\varphi_{i_2}^{2}\cdots\varphi_{i_N}^{N}\rangle = |\varphi_{i_1}^{1}\rangle|\varphi_{i_2}^{2}\rangle\cdots|\varphi_{i_N}^{N}\rangle)$, where N is the number of monomers. By diagonalizing this Hamiltonian matrix, we firstly obtain eigenvalues $\{E_l^{agg}\}$, and eigenstates $\{|\varphi_l^{agg}\rangle\}$. Next, using numerical Liouville approach (NLA),[8] which gives numerically exact solutions of Liouville equation:

$$i\hbar\frac{\partial}{\partial t}\rho(t)=[H(t),\rho(t)]-i\Gamma\rho(t)\,, \qquad (2)$$

we calculate polarization $p(t)$. Here $i\Gamma\rho(t)$ is a relaxation term in the Markoff approximation. Using the external field amplitude $\varepsilon(\omega)$ and the Fourier transformed polarization $p(3\omega)$, γ is calculated by the following equation:

$$\gamma(-3\omega;\omega;\omega;\omega)=\frac{p(3\omega)}{27\varepsilon^3(\omega)}. \qquad (3)$$

In this study, we focus on a dendritic molecular aggregate D25 (Fig.1). Two-exciton model is adopted since two exciton states are at least necessary for describing the virtual excitation processes of γ.[8] We consider three types of aggregates (A, B and C): (A) involves both intermolecular-interaction and relaxation terms, (B) involves only intermolecular-interaction, and (C) doesn't involve neither intermolecular-interaction nor relaxation term. The relaxation effect can be elucidated by the comparison of (A) with (B), and the intermolecular-interaction effect is elucidated by the comparison of (B) with (C). The frequency of electric fields is taken to be 37950 cm^{-1}, which is close to the highest exciton state which has the largest transition moment.

RESULTS AND DISCUSSION

The γ value of each aggregate is given in Table1. It is clear that there are pronounced differences in the values of γ among these aggregates. The effects of intermolecular-interaction and relaxation are given in Table2. It is found that the effect of intermolecular-interaction decreases γ, while the relaxation effect allowed exciton states except for the highest allowed exciton state, the γ value becomes negative in sign. For the systems without relaxation (B and C), the γ values tend to diverge at the resonance point. In contrast, including the relaxation

TABLE 1 γ values [a.u.] of three types of dendritic aggregates. (A) involves both intermolecular-interaction and relaxation terms, (B) involves only the intermolecular-interaction term, and (C) doesn't involve neither interaction nor relaxation term.

Aggregate type	(A)	(B)	(C)
γ	-3.7771×10^{4}	-8.3994×10^{7}	4.7781×10^{9}

TABLE 2 Effects of intermolecular-interaction and relaxation on γ [a.u].

	Intermolecular-interaction	Relaxation
Contribution	-4.8621×10^{9}	8.3956×10^{7}

term, system (C) exhibits a broad spectrum of γ, so that in the near resonant region, system (A) exhibit much smaller $|\gamma|$ than systems (B) and (C).

SUMMARY

In this study, we investigated the characteristics of γ for the dendritic molecular aggregate D25. Both relaxation and intermolecular-interaction effects are shown to dramatically change the near-resonant γ values. These remarkable effects are predicted to be unique for dendritic aggregates with a fractal structure since such fractal-dimensional system possesses a multi-step allowed exciton state. For example, the relaxation effects in one- and two-dimensional systems are predicted to exhibit moderate changes of γ since such systems possess almost only one allowed exciton state. The present results suggest the existence of a novel relation between architecture and NLO property for the fractal-dimensional system. The investigation of NLO properties for other dendritic aggregates and dendrimers are now in progress in our laboratory.

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