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Quantum dynamics of exciton recurrence motion in dendritic molecular aggregates

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Abstract

The quantum master equation approach involving weak exciton–phonon coupling has been applied to the investigation of the exciton recurrence motion in molecular aggregate models with dendritic structures. Each monomer in the models is assumed to be a dipole unit (a two-state monomer) coupled with each other by the dipole–dipole interaction. Two types of the dendritic molecular aggregates, which have mutually different interactions through the branching points, are examined. A generation of one-exciton states by an electric field and its subsequent exciton dynamics with and without relaxation terms have been investigated. It is found that the configuration of each dipole unit significantly affects the coherent motions of the exciton population. We also suggest the possibility of controlling the coherent exciton motions by tuning the frequency of an external electric field.

Keywords: Quantum dynamics; Exciton; Recurrence motion; Molecular aggregates; Coherence; Quantum beat

1. Introduction

Energy transfer is one of the most fundamental processes in chemistry. Dendrimers with fractal dimensions are known to show the efficient excitation energy transfer from the external to the central regions [1–3]. Such molecules have ordered geometries and well-directed energy gradients between the peripheral and the core regions. It has also revealed that the relaxation effect is important for the directional energy migration, i.e. population relaxation [4,5]. Because the population relaxation also contributes to the phase relaxation, such energy migration is an incoherent process. Recently, coherent processes have attracted much attention in relation to developments of quantum molecular devices [6–8] by the use of spin and pseudo spins, such as exciton. For example, coherent superposition of the excited states generated by optical method causes a recurrence motion of the excitation between constituent units in molecular systems.

Hochstrasser and co-workers [9,10] have investigated the coherent excitation energy transfer between two-identical chromophores (2,2′-binaphthyl, BN) in solution, and have found a damped oscillation corresponding to exciton recurrence associated with the interaction energy ($\Delta = 41\,\mathrm{cm}^{-1}$) and the dephasing time (T_2') of 0.2 ps. Wynne and Hochstrasser [11] have presented a theoretical framework for the coherent energy transfer in solution and have applied it to the analysis of their experiments.

Yamazaki et al. have investigated the intramolecular energy transfer of various anthracene dimers, e.g. dianthrylbenzene (DAB) and dithiaanthracenophane (DTA) groups (Fig. 1), in solution [12–14]. The fluorescence anisotropy decay of these molecules displays the oscillatory behavior originated from the recurrence motion of an excitation between two anthracenes. This suggests that the intramolecular energy transfer proceeds coherently in these systems. Generally, it is very difficult to observe such oscillatory signals because of the rapid dephasing by solvent molecules and of the difficulty in detecting the fluorescence signals from a mate of the dimer selectively. Yamazaki et al. have concluded that the relatively rigid molecular structures of DAB and DTA are key factors in detecting the quantum

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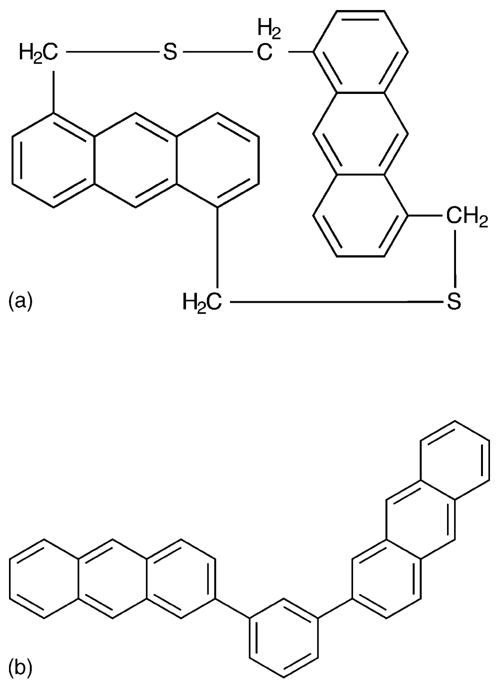

Fig. 1. Molecular structures of (a) DTA and (b) DAB.

beat of fluorescence anisotropy decay. They have pointed out that the longer dephasing time in DTA (1.0 ps) can be explained by the less flexible and more rigid conformation than that in BN (0.2 ps).

Previously, we have performed theoretical investigations of energy migration in dendrimers on the basis of the quantum master equation [15,16]. As a continuation of previous work, we here focus on the coherent process, such as recurrence motion of excitons in dendritic systems using two types of molecular aggregate structures. One is an aggregate modeled after the real extended phenylacetylene dendrimers [1–3] (see Fig. 2b), while the other one is a different aggregate model with significant interactions between neighboring monomers through the branching points (see Fig. 2c). Such difference in modeling is expected to cause variations in the energetics and also the coherent dynamics of exciton population. A possibility of controlling the coherent exciton motions by tuning the frequency of an external field is also examined. Implications of the computational results are discussed in relation to importance of aggregate structures for less decoherence rule.

2. Methods

2.1. Model Hamiltonians

We consider molecular aggregate systems composed of two-state monomers $\{i\}$ with the excitation energy $\{E_i\}$ and the dipole moment $\{\mu_i\}$ ($i = 1, 2, \ldots, N$; N is the number of monomers). Interactions between i- and j-th monomers are assumed to be represented by the dipole–dipole interaction J_{ij}. This approximation is considered to be valid when the intermolecular distance R is larger than the size of a monomer. The

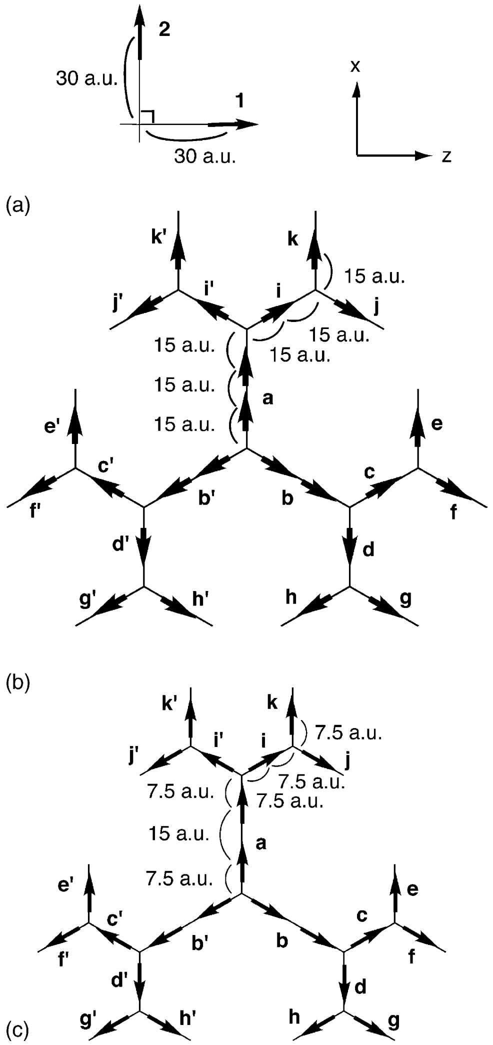

Fig. 2. Structures and labeling of the models used in this paper: (a) dimer model, (b) dendritic model I and (c) dendritic model II. Each two-state monomer dipole unit is represented by an arrow. For the dendritic models I and II, the angle between neighboring linear legs at all branching points is assumed to be 120°.

Hamiltonian for the aggregate system is expressed by

$$H_\mathrm{S} = \sum_{i}^{N} E_i |i\rangle\langle i| + \frac{1}{2}\sum_{i \neq j}^{N} J_{ij} |i\rangle\langle j|, \tag{1}$$

where

$$J_{ij} = \frac{1}{4\pi\varepsilon_0 R_{ij}^3}\mu_i\mu_j\{\cos(\theta_{i_j} - \theta_{j_i}) - 3\cos\theta_{i_j}\cos\theta_{j_i}\}. \tag{2}$$

Here, $|i\rangle$ is the aggregate basis, which means that the i-th monomer is excited, and R_{ij} is the intermolecular distance between i- and j-th monomers. $\theta_{i_j}(\theta_{j_i})$ is the angle between the dipole moment of i(j)-th monomer and the vector drawn from i-th monomer to j-th monomer.

In the one-exciton approximation, aggregate system is described in the eigenstates $\{|\psi_k\rangle\}$ with energies $\{\omega_k\}$. We obtain $|\psi_k\rangle$ and ω_k by solving the following eigenvalue equation

$$H_\mathrm{S}|\psi_k\rangle = \omega_k|\psi_k\rangle, \tag{3}$$