# Laser pulse induced multiple exciton kinetics in molecular ring structures

Xiao Hou, Luxia Wang *

Department of Physics, University of Science and Technology Beijing, 100083 Beijing, China

## ARTICLE INFO

## ABSTRACT

Multiple excitons can be formed upon strong optical excitation of molecular aggregates and complexes. Based on a theoretical approach on exciton–exciton annihilation dynamics in supramolecular systems (May et al., 2014), exciton interaction kinetics in ring aggregates of two-level molecules are investigated. Excited by the sub-picosecond laser pulse, multiple excitons keep stable in the molecular ring shaped as a regular polygon. If the symmetry is destroyed by changing the dipole of a single molecule, the excitation of different molecules becomes not identical, and the changed dipole–dipole interaction initiates subsequent energy redistribution. Depending on the molecular distance and the dipole configuration, the kinetics undergo different types of processes, but all get stable within some hundreds of femtoseconds. The study of exciton kinetics will be helpful for further investigations of the efficiency of optical devices based on molecular aggregates.

## 1. Introduction

There is an ongoing interest in optical properties of molecular aggregates [1,2]. Upon strong optical excitation, multiple excitons can be produced. Multiple exciton interactions and subsequent transformations have distinct effects on the optical response of molecular aggregates. There are some attractive photonic phenomena related to exciton kinetics in molecular complexes. For example, mobile excitons can be hosted in aggregates of chromophores [3] and the energy can be transferred along them via exciton diffusion [4]. The photoluminescence and optical absorption of five rhodamine dyes can be measured in the solid state. Due to the molecular exciton coupling, all solid-state rhodamine dyes strongly absorb light in the UV and visible region, but emit only in red and near infrared [5].

Exciton–exciton interactions and the corresponding experimental phenomena also stimulate theoretical interests. There are some theoretical models built to simulate exciton kinetics in molecular aggregates. For instance, a time-dependent variational method is used in Refs. [6,7] to calculate the time evolution of the photoexcited state of a molecular chain [8]. The Pauli master equation is used to describe the evolution of the populations of localized exciton states in linear Frenkel exciton systems [9]. The pulse optimization technique is applied to describe Frenkel excitons, and the dynamics of two-exciton states in linear aggregates are initiated with an ultrafast and properly shaped laser pulse [10]. While these studies use rather simple models, a more detailed description of excitation energy transfer is given, for example, in [11]. It includes an atomistic resolution of vibrational dynamics as it can be achieved in the mixed quantum–classical description.

Less interest so far found the investigation of multiple excitons formed due to a more intensive optical excitation. In order to study such a situation we use the approach of Ref. [12] and apply it to a molecular ring aggregate [13] with several molecules (cf. Fig. 1). In the next section, we introduce a model of the molecular ring system, and describe the system dynamics with the equations of motion for density matrix. The results and the corresponding discussions are offered in Section 3. Finally, some concluding remarks are given in Section 4.

## 2. Model and method

To investigate the exciton interaction in molecular aggregates, we design a simple model for a molecular ring aggregate forming a regular polygon, with all molecules having the same properties. To distinguish them for the later investigations, we count them by $m = 1, 2, 3 \ldots$ in an anticlockwise manner (cf. Fig. 1). In general, upon the presence of a strong laser pulse, electrons can be excited to the first or to higher excited states of all the molecules simultaneously. In this paper, we ignore the process of exciton–exciton annihilation, and only consider the molecules with two energy
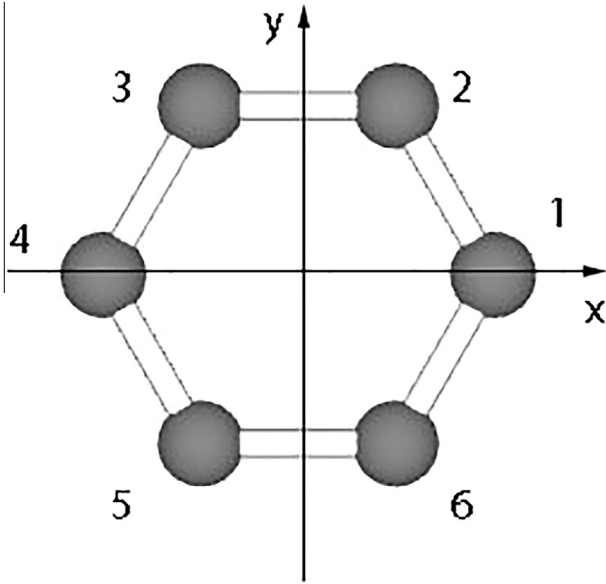
**Fig. 1.** A molecular ring with 6 molecules forming a regular hexagon (the center of it fixes the origin of the used Cartesian coordinate system).

**Table 1**
Used parameters (for explanation see text).

| | |
|---|---|
| $N_{mol}$ | $6 \ldots 25$ |
| $d_{mol}$ | 8 D |
| $E_{mol}$ | 2.6 eV |
| $\hbar\kappa_{mol}$ | 3 meV |
| $\hbar k_m$ | 0.0001 meV |
| $r$ | $1.2 \ldots 2.7$ nm |
| $\tau_p$ | 20 fs |
| $t_p$ | 30 fs |
| $E_0$ | $5 \times 10^7$ V/m |

levels (an inclusion of annihilation process is shifted to the future). For molecule $m$, its ground-state is $|\varphi_{mg}\rangle$, which has the energy $E_{mg}$ set equal to zero in the following. Then, the first excited state $|\varphi_{me}\rangle$ is characterized by the energy $E_m$. We denote the overall Hamiltonian as

$$H(t) = H_{exc} + H_{field}(t). \tag{1}$$

The first part $H_{exc}$ is the Frenkel-exciton Hamiltonian which takes the form

$$H_{exc} = \sum_m E_m B_m^+ B_m + \sum_{m,n} J_{mn} B_m^+ B_n. \tag{2}$$

The transition operator $B_m^+ = |\varphi_{me}\rangle\langle\varphi_{mg}|$ initiates the motion of the $m$th molecule from its ground-state to its first excited state. The energy transfer (excitonic) coupling has been denoted by $J_{mn}$. Using the dipole–dipole approximation it reads

$$J_{mn} = \frac{1}{|\boldsymbol{R}_{mn}|^3}\left((\mathbf{d}_m \cdot \mathbf{d}_n^*) - 3(\mathbf{d}_m \cdot \mathbf{n})(\mathbf{n} \cdot \mathbf{d}_n^*)\right), \tag{3}$$

where $\boldsymbol{R}_{mn}$ is the vector connecting the center of mass between the different molecules $m$ and $n$. $\mathbf{n}$ labels the respective unit vector $\boldsymbol{R}_{mn}/|\boldsymbol{R}_{mn}|$, and $\mathbf{d}_m = d_m\mathbf{e}_m$ is the molecular transition dipole moment, with its unit vector $\mathbf{e}_m$.

The coupling to the radiation field $H_{field}$ is

$$H_{field}(t) = -\boldsymbol{E}(t) \cdot \sum_m \mathbf{d}_m B_m^+ + \text{H.c.}, \tag{4}$$

with the electric field-strength

$$\boldsymbol{E}(t) = \mathbf{n}_E E(t) e^{-i\omega_0 t} + \text{c.c.} \tag{5}$$

We introduce $\mathbf{n}_E$ as the unit vector of field polarization. $\omega_0$ is the carrier frequency and $E(t)$ is the field envelope. The latter has a Gaussian shape $E(t) = E_0 \exp\left(-2.8(t - t_p)^2/\tau_p^2\right)$ and $\tau_p$ is introduced as the pulse duration, $E_0$ as the amplitude, and $t_p$ as the time fixing the pulse center (concrete numbers for all parameters can be found in Table 1).

In order to describe photoinduced excitation energy transfer in the molecular aggregates we utilize the density operator $\widehat{\rho}(t)$. It is used in the following to define the expectation value of an arbitrary

operator $\widehat{O}$ as $O(t) = \langle\widehat{O}\rangle = \text{tr}\{\widehat{\rho}(t)\widehat{O}\}$. The operator itself will be understood as a combination of the $B_m^+$ and $B_n$. Accordingly, the kinetic equations needed for the subsequent investigations can be derived by considering the quantum master equation

$$\frac{\partial}{\partial t}\widehat{\rho}(t) = -\frac{i}{\hbar}[H(t), \widehat{\rho}(t)]_- - \mathcal{D}\widehat{\rho}(t), \tag{6}$$

where the dissipative part is written as

$$\mathcal{D}\widehat{\rho}(t) = \sum_m \frac{k_m}{2}\left([B_m^+ B_m, \widehat{\rho}(t)]_+ - 2B_m\widehat{\rho}(t)B_m^+\right). \tag{7}$$

$k_m$ denotes the decay rate of molecule $m$ from it's first excited state to it's ground state.

With the described density operator theory at hand, one can easily formulate the equation of motion for the expectation value of an arbitrary operator $\widehat{O}$:

$$\frac{\partial}{\partial t}\langle\widehat{O}\rangle = \text{tr}\left\{\frac{\partial}{\partial t}\widehat{\rho}(t)\widehat{O}\right\} = \frac{i}{\hbar}\langle[H(t), \widehat{O}]_-\rangle - \langle\widetilde{\mathcal{D}}\widehat{O}\rangle \tag{8}$$

with

$$\widetilde{\mathcal{D}}\widehat{O} = \sum_m \frac{k_m}{2}\left([B_m^+ B_m, \widehat{O}]_+ - 2B_m^+\widehat{O}B_m\right). \tag{9}$$

Accordingly, equations of motion for different choices of $\widehat{O}$ take the form

$$\begin{aligned}
\frac{\partial}{\partial t}\langle B_m^+\rangle =& \frac{i}{\hbar}E_m\langle B_m^+\rangle + \frac{i}{\hbar}\sum_k J_{km}\langle B_k^+(1 - 2B_m^+ B_m)\rangle \\
&- \frac{i}{\hbar}\boldsymbol{E}(t) \cdot \mathbf{d}_m^*\langle(1 - 2B_m^+ B_m)\rangle - \frac{k_m}{2}\langle B_m^+\rangle,
\end{aligned} \tag{10}$$

$$\begin{aligned}
\frac{\partial}{\partial t}\langle B_m^+ B_m\rangle =& \frac{i}{\hbar}\sum_k \left(J_{km}\langle B_k^+ B_m\rangle - J_{mk}\langle B_m^+ B_k\rangle\right) \\
&- \frac{i}{\hbar}\boldsymbol{E}(t) \cdot \mathbf{d}_m^*\langle B_m\rangle + \frac{i}{\hbar}\boldsymbol{E}(t) \cdot \mathbf{d}_m\langle B_m^+\rangle - k_m\langle B_m^+ B_m\rangle,
\end{aligned} \tag{11}$$

$$\begin{aligned}
\frac{\partial}{\partial t}\langle B_m^+ B_n\rangle =& \frac{i}{\hbar}(E_m - E_n)\langle B_m^+ B_n\rangle + \frac{i}{\hbar}\sum_k J_{km}\langle(1 - 2B_m^+ B_m)B_k^+ B_n\rangle \\
&- \frac{i}{\hbar}\sum_k J_{nk}\langle B_m^+ B_k(1 - 2B_n^+ B_n)\rangle \\
&- \frac{i}{\hbar}\boldsymbol{E}(t) \cdot \mathbf{d}_m^*\langle(1 - 2B_m^+ B_m)B_n\rangle \\
&+ \frac{i}{\hbar}\boldsymbol{E}(t) \cdot \mathbf{d}_n\langle B_m^+(1 - 2B_n^+ B_n)\rangle - \frac{k_m + k_n}{2}\langle B_m^+ B_n\rangle.
\end{aligned} \tag{12}$$

These equations are not closed but coupled to those for expectation values of three or four transition operators. However, a decoupling is achieved if the term $1 - 2B_l^+ B_l$ ($l = m, n$) whenever it appears is replaced by it's expectation value $1 - 2\langle B_l^+ B_l\rangle$. We introduce

$$\beta_m = \langle B_m^+\rangle, \tag{13}$$