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INVITED REVIEW

FLUORESCENCE DEPOLARIZATION IN DIFFERENT MOLECULAR SYSTEMS

HACKJIN KIM[1] and TAI JONG KANG[2]
[1]Department of Chemistry, College of Natural Sciences, Chungnam National University
Taejon, 305-764, Korea
[2]Department of Chemistry, College of Natural Sciences, Taegu University
Kyungsan, 713-714, Korea

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Abstract—General features of the fluorescence depolarization are briefly reviewed. Molecular rotations and electronic excitation transports are considered to account for the fluorescence depolarization. Various molecular systems studied by the fluorescence depolarization are described. The Förster theory which forms a basis for the energy transfer is revisited. Several theoretical treatments for the fluorescence depolarization in liquid and solid phases such as classical hydrodynamics, probability distribution function, Green's function formalism, molecular dynamics simulation and Monte Carlo methods are introduced.

INTRODUCTION

The electronic excitation of most organic molecules occurs through the absorption of uv or visible light. The electronic excitation then relaxes into different forms of energy or migrates to other molecules. Often the electronic excitation is accompanied by photochemical reactions. Mechanisms involved in the relaxation of the electronic energy are generally divided into two processes - radiative and nonradiative.[1-3] Radiative processes are classified as flourescence and phosphorescence depending on the spin states of the involved electronic states. As the spin state is conserved in one-photon absorption process, the molecules reside in the excited singlet state since the ground state of most molecules is singlet. There is a corresponding triplet state of lower energy for each excited singlet state and the transition probability for a singlet-singlet transition is much larger than a singlet-triplet transition. There exist associated vibrational states in each electronic state and the transition probabilities to the vibrational states of the excited electronic state are determined by Franck-Condon factors. In condensed media, excess vibrational energy of excited states is transferred to the surroundings in a few picoseconds or less. Therefore, the fluorescence originates from the ground vibrational state of an upper electronic state. All other processes by which an initially excited molecule loses the electronic energy are referred to nonradiative energy transfer. No general theories applicable to all physical circumstances have been developed and various theoretical models have been suggested for individual systems. In fluid medium, the energy transfer is closely related to the molecular motions. Meanwhile the electronic states of molecular crystals are delocalized and the energy transfer takes place through interactions of excitons and lattice vibrations.

Since many processes of photoscience are initiated with the electronic excitation, the electronic dynamics has long been an important topic.[3] Steady state and time resolved fluorescence depolarization have been measured to study the electronic dynamics in various ordered and disordered systems.[4] When a molecular system is irradiated with a polarized light, only molecules whose transition dipole moments lie parallel to the direction of the light polarization are excited and the subsequent fluorescence yields the same polarization as the initial excitation light. However, if the excited molecules undergo reorientational motions before they fluoresces or the excitation energy is transferred to nearby molecules of different orientations, the degree of polarization decreases. Any processes which disturb initial orientations of the excited molecules will result in the fluorescence depolarization (FD). The FD study provides information on molecular motions and intermolecular interactions. With the development of pulse lasers, measurements of FD are easily performed in the psec or fsec time scale nowadays.

Depolarization of fluorescence is usually ex-pressed in terms of florescence anisotropy, r(t) defined as

$$r(t) = \frac{I_h(t) - I_v(t)}{I_h(t) + 2I_v(t)} \qquad (1)$$

where $I_h(t)$ and $I_v(t)$ are the fluorescence intensities whose polarizations are parallel and perpendicular to the excitation polarization, respectively. The decay of FD shows complicated time dependence if

the time constants for molecular motions and energy transfer are comparable to the fluorescence lifetime. The steady state FD, $r(\tau)$ which is an average of the time-dependent anisotropy by the impulse response for the total fluorecence intensity, is given by

$$r(\tau) = \tau^{-1} \int r(t) \exp(t/\tau)\, dt \qquad (2)$$

where τ is the average time available for depolarization.

The electronic dynamics of any fluorescent molecules can be studied through FD and even the dynamics of nonfluorescent molecules can be investigated by attaching a fluorescent probe to the molecule of interest or by simply mixing together. In this review, various molecular systems studied via FD are introduced and the experimental aspects of FD are also briefly described. Förster theory which has been the basis for many theoretical models are summarized in the fourth section and several theoretical methods related with FD are discusssed in following sections.

MOLECULAR SYSTEMS STUDIED BY FLUORESCENCE DEPOLARIZATION

Molecular motions related to intermolecular interactions in liquid have been studied by using many spectroscopic techniques.[5] Time-resolved spectroscopy with ultrashort pulse lasers has provided detailed information on the molecular motions. Fluorescence experiments usually investigate the molecular motions in the excited electronic state, but the absorption based measurements such as optical Kerr effect and absorption dichroism give information on the rotational motions in the ground electronic state. FD method has been one of the most efficient and sensitive techniques to probe molecular rotations in liquid and has been applied to many organic molecules in a variety of solvents. Organic dye molecules such as rhodamines are an example of the FD study, and rotational diffusion time constants in the excited electronic state have been determined very accurately in pure and mixed solvents.[6-8] Simple models of classical rotors have been employed to interprete FD results. Radiationless decays and conversion of intra- and intermolecular electronic state have been also studied *via* FD.

Although polymers and liquid crystalline materials have been extensively studied for practical purposes, their microscopic properties relevant to motions of long molecular chains are not well known. FD of fluorophores included in polymeric media provides knowledge about the molecular motions and the excitation transfer in the inhomogeneous systems. Wide distributions of molecular weights request statistical methods, and intermolecular radial distribution function and radius of gyration are investigated through the FD measurements. Naphthyl group of a long fluorescence lifetime often serves as a probe in the FD studies.[9-11]

FD techniques are effective in the study of biological systems such as the internal dynamics of protein, restricted motions in membrane, torsional motion in DNA, etc. Those studies are important for understanding the relationships among the structure, the dynamics and the function of proteins. Molecules attached to the membrane undergo restricted motions like wobbling rather than free rotation. Polarization decay is related to the fluctuation of molecular reorientation. A fluorescent probe such as 1,6-diphenyl-1,3,5-hexatriene (DPH) was used for the dynamics study of hydrocarbon region of lipid bilayers.[12,13] The motion of DPH molecule which reflects the motion of lipid chain was interpreted as wobbling and tumbling motions. A considerable fluctuation of the chains exists but still retains the overall reorientational arrangement.[14] FD is also helpful for the study of local motions of the DNA helical chain. DNA is a relatively stiff chain molecule because of the double strand conformation, by which the local dynamics is affected. Time-dependent anisotropy of DNA has been evaluated by several models such as the elastic model[15], spring-bead model[16] and helical worm-like chain-model.[17,18] The different anisotropy decays are assigned to different types of local motions such as twisting and bending. These motions are important in understanding protein functions and site recognition.

Molecular crystals show important characteristics of an ordered system. Electronic states of molecular crystals are delocalized to form exciton band structure and clearly reveal quantum behaviors. In the crystalline phase, resticted molecular motions appear as delocalized phonons and affect the dynamics of the electronic state. Because of the strong anisotropy of the lattice structure, the FD has not been applied for the dynamics of molecular crystals. However, the electronic dynamics in molecular crystals give important ideas on the excitation transport in condensed media. Aromatic crystals such as naphthalene, anthracene and some mixed crystals have been extensively studied.[19,20]

The electronic processes of optically excited semiconductors have been studied by time-resolved luminescence spectroscopy where the radiative recombination of electrons and holes is probed.[21] The redistribution of electrons and holes in GaAs is observed to occur within 100 fs after excitation. Excited carriers produced by polarized light can possess preferred orientation. This orientational effect is lost in the subsequent relaxation processes -

mainly scattering with phonons, impurities and other carriers. The study of luminescence depolarization offers an insight into the relaxation mechanisms.

MEASUREMENTS OF FLUORESCENCE POLARIZATION DECAY

Fluorescence decay can be measured by various techniques such as time-correlated single photon counting, streak camera, fluorescence upconversion, and phase shift technique.[4,5] Each technique has both advantages and disadvantages. All of these methods except the phase shift technique use short pulses of polarized light and the emission is detected at the parallel and perpendicular direction to the excitation polarization. Measured fluorescence decay is deconvoluted from the instrument response function to give true decay functions. In general, one or more exponential functions are assumed for true decay functions when carrying out the convolution. Total fluorescence intensity and anisotropy are two quantities of interest. The total fluorescence intensity is a sum of the parallel and twice of the perpendicular component. The total fluorescence decay function should be determined prior to estimation of the anisotropy. The total intensity is proportional to the concentration of molecules in the excited state and its time decay is determined by collecting separately the parallel and the perpendicular component. Alternatively, it can be obtained by adopting a *magic angle* collection scheme where the excitation and detection polarization make a magic angle, 54.7°. The magic angle method is convenient because only one decay curve is involved and routinely used for the lifetime measurements. Due to the anisotropic nature of the excitation light, molecular distribution of the photo-selected ensemble is different from the bulk. The magic angle is an angle where the polarization dependence is removed and the measured fluorescence intensity is directly proportional to the total intensity. In a system where only a single process is responsible for FD, the anisotropy decay is fit to a single exponential function, but in most cases the dynamics shows non-single-exponential behavior, which reflects the complicated relaxation processes.

FÖRSTER THEORY

As discussed in the previous sections, molecucular motions and excitation transfer are the main mechanisms for FD in liquid. In solid where molecular reorientation is restricted, excitation transfer accounts for most part of FD. Förster theory is the first successful theory about the excitation transport in solution.[22] Förster theory will be briefly discussed here.

Förster established the electronic energy transfer theory in terms of dipole-dipole interaction and later multipole interactions and exchange mechanism were considered by Dexter.[23] Förster theory has been the basis for explanation of intermolecular energy transfer and applied to various situations with some modifications. Förster's expression for the energy transfer rate between a donor, D and an acceptor, A seperated by distance R is given by

$$k_{DA} = \frac{3}{2}\kappa^2 \left(\frac{1}{\tau_D}\right)\left(\frac{R_0}{R}\right)^6 \qquad (3)$$

where κ is related to the relative orientation of the transition dipole moments of a donor and an acceptor molecule and τ_D is the fluorescence lifetime. The energy transfer rate constant is proportional to the sixth power of the seperation distance. The orientation factor, κ is given by

$$\kappa = e_D \cdot e_A - 3(e_D \cdot e_R)(e_A \cdot e_R) \qquad (4)$$

where e_D is a unit vector for transition moment of a donor and e_A is a unit vector for an acceptor and e_R is a unit vector connecting two vectors e_D and e_A. The factor κ can be expressed in terms of angles of these unit vectors. The Förster radius R_o is a parameter representing the degree of donor-acceptor interaction. It is defined as a mean distance where the rate constant for energy transfer is equal to the radiative rate constant of a donor in the absence of an acceptor molecule. The Förster radius is expressed explicitly in the following equation.

$$R_0 = \frac{9000\ \ln(10)\kappa^2\phi_D}{128\pi^5 n^4 N} \int F_D(\nu)\varepsilon_A(\nu)\, d\nu \qquad (5)$$

Thus, the Förster radius depends on the fluorescence quantum yield of a donor ϕ_D, the fluorescence spectrum of a donor $F_D(\nu)$, and the molar absorption coefficient of an acceptor $\varepsilon_A(\nu)$. The refractive index of the solvent n and Avogadro number N are also included in the expression. The integration indicates that the Förster radius is related with the spectral overlap of the fluorescence of a donor and the absorption of an acceptor.

THEORETICAL MODELS RELATED TO FLUORESCECNE DEPOLARIZATON

Rotational diffusion in solution

If the excited molecule remains stationary for the period of fluorescence, the fluorescence decays exponentially. The decay of the polarized fluorescence is affected when the molecules rotate in a time scale similar to the fluorescence lifetime. FD due to the

rotational motion is expressed with the rotational diffusion coefficient, which depends on temperature, viscosity, and molecular structure.

Einstein-Smoluchowski equation shows that the rotational diffusion coefficient, D is equal to $d^2/2\tau$ for a spherical molecule where d is the intermolecular distance and τ is the rotational reorientation time. The relation between the diffusion coefficient and the solvent viscosity η is given by Stokes-Einstein equation.[24,25] The rotational reorientation time is then related to the viscosity and the molecular shape via the Debye-Stoke-Einstein equation.

$$\tau = \frac{V\eta f}{kTS} + \tau_0 \qquad (6)$$

where V is the volume of a molecule and S is the correction factor for a non-spherical molecule. From the FD measurements in various solvents of different viscosities, the rotational reorientation time at zero viscosity, τ_0 is obtained. The frictional coefficient f, depends on both the molecular shape and the solute-solvent interaction.

The frictional coefficient becomes one for the stick boundary condition where solvent molecules stick to a solute molecule and rotate together. Meanwhile in the slip boundary condition where the surrounding solvent molecules have no effects on the rotation of solute molecules, the frictional coefficient depending on the molecular shape is less than one.

Probability distribution function and Wigner rotation matrices

Probability evolution function is useful in dealing with the effect of rotational motion on the fluorescence anisotropy. As shown in Fig. 1, the fluorescent molecule is placed at the origin of the coordinate system. The sample is excited by a z-polarized light propagating along the x axis. Parallel and perpendicular components of polarized emission are measured in the y axis. Two angles (θ,ϕ) are required to specify the orientation of the transition dipole of the molecule with respect to the space fixed axes. Tao's derivation[26] of time-dependent fluorescence depolarization is reproduced below. For the sake of simplicity, only the overall rotational motions are considered here. Similar results were derived for the emission anisotropy of a cylindrical probe in liquid crystals by Szabo.[27,28]

Time dependence of flourescence anisotropy can be determined through the probability $W(\theta,\phi,t)$ that the dipole moment vector is oriented (θ,ϕ) at time t. Time evolution of $W(\theta,\phi,t)$ is given by the Green's function as

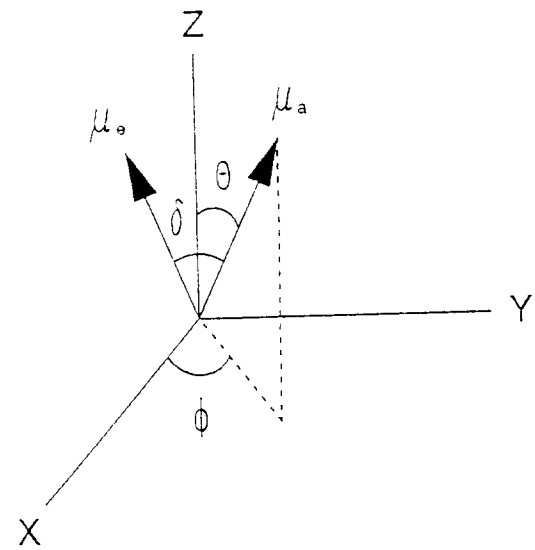

Figure 1. Schematics of the transition dipole orientation in the fluorescence depolarization. A fluorophore is placed at the origin of the coordinate system. The absorption dipole μ_a and the emission dipole μ_e make an angle of δ. Two angles (θ,ϕ) specify the orientation of the transition dipole with respect to the space fixed axes.

$$W(\theta,\phi,t) = \int d\phi_0 \int \sin\theta_0 \, d\theta_0 \, W(\theta_0,\phi_0) \, G(\theta_0,\phi_0|\theta,\phi,t) \qquad (7)$$

where $W(\theta_0,\phi_0)$ is the initial distribution of the orientation of the dipole moment. For generality, it is assumed that the absorption dipole and the emission dipole are not parallel and make an angle of δ with respect to each other. In this case, a new coordinate system for the emission dipole whose z axis coincides with the direction of the absorption dipole, is obtained by a coordinate transformation. Then the initial distribution of the emission dipole oriented along this axis is found to be

$$W(\theta_0,\phi_0) = \frac{3}{4\pi}\cos^2\theta_0 \, P_2(\cos\delta) + \frac{3}{4\pi}\frac{\sin^2\delta}{2} \qquad (8)$$

where $P_2(\cos\delta)$ is the second order Legendre polynominal.

The Green's function is expanded in terms of the spherical harmonics.

$$G(\theta_0,\phi_0|\theta,\phi,t) = \sum\sum c_{l,m}(t) \; Y^*_{l,m}(\theta_0,\phi_0) Y_{l,m}(\theta,\phi) \qquad (9)$$

where $c_{l,m}(t)$'s are the expansion coefficients. It can be shown from the normalization and the boundary

condition that $c_{0,0}(t) = 1$ and $c_{l,m}(0) = 1$ for all l,m. By substituting Eqs. (8) and (9) into Eq. (7), evolution of the probability distribution function is obtained.

$$W(\theta,\phi,t)=\frac{1}{4\pi}[1+2\,c_{2,0}(t)P_2(\cos\theta)]\,P_2(\cos\delta) + \frac{3}{4\pi}\frac{\sin^2\delta}{2} \tag{10}$$

From the definition of $W(\theta,\phi,t)$, it is clear that

$$I_h(t)=\int\int d\phi\ \sin\theta\ d\theta\ i_h(\theta,\phi,t)\ W(\theta,\phi,t) \tag{11a}$$

$$I_v(t)=\int\int d\phi\ \sin\theta\ d\theta\ i_v(\theta,\phi,t)\ W(\theta,\phi,t) \tag{11b}$$

where $i_h(\theta,\phi,t)$ and $i_v(\theta,\phi,t)$ are contributions to the total intensities from individual transition dipoles with a particular orientation (θ,ϕ) and proportional to $\mu^2\cos^2\theta$ and $\mu^2\sin^2\theta\cos^2\theta$, respectively. From the above relations and Eq. (1), the fluorescence anisotropy decay is derived.

$$r(t)=\frac{2}{5}c_{2,0}(t)P_2(\cos\delta) \tag{12}$$

The coefficient $c_{2,0}(t)$ is expressed by the ensemble average of the correlation function.

$$c_{2,0}(t)=<P_2[\mu(0)\cdot\mu(t)]> = \frac{1}{4\pi}\int\int \sin\theta d\theta d\phi \int\int \sin\theta_0 d\theta_0 d\phi_0 P_2[\mu(0)\cdot\mu(t)] \times W(\theta_0,\phi_0)G(\theta_0,\phi_0|\theta,\phi,t) \tag{13}$$

the excitation transport is to set up the master equation. In the system of N molecules randomly distributed with the number density ρ in a volume Ω, each configuration of the system, denoted by R, is specified by the locations of the molecules, $(r_1,r_2,\cdots\cdots r_N)$. The probability that an excitation is found on the jth molecule in the configuration R at time t, $p_j'(R,t)$ satisfies the master equation

$$\frac{dp_j'(R,t)}{dt} = -\frac{p_j'(R,t)}{\tau} + \sum w_{jk}\,[p_k'(R,t)-p_j'(R,t)] \tag{14}$$

where τ is the measure of the excitation lifetime and w_{jk} is the transfer rate between molecules j and k. The rate w_{jj} is defined to be zero. The substitution $p_j(R,t)=p_j'(R,t)\exp(t/\tau)$ removes the decay term in the master equation and the introduction of the matrix expression for the transfer rate, W gives

$$\frac{dp(R,t)}{dt} = W\cdot p(R,t) \tag{15}$$

In some other literatures,[27,28] this correlation function is conveniently treated in terms of Wigner rotation matrices. When the absorption and emission dipole are parallel ($\delta=0$), the anisotropy represented by Eq. (12) reduces to $(2/5)c_{2,0}(t)$. The magic angle where the rotational effect is completely removed is also calculated from Eq. (12).

Green's function for excitation transport

In the previous section, it is explicitly assumed that the FD is caused only by the rotational motions. In a rigid medium, however, the excitation tranport is more important in FD. The excitation transport has been treated in two limiting cases. When the concentration of a system is high and the fluorophores are uniformly distributed, the excitation transport can be seen as a random walk on a perioidic lattice and consequently the transport is diffusive. In a dilute solution, a molecule is considered to interact with only one neighbor and the transport is reduced to a two-body problem. The excitation transport can be described by the master equation, and Haan and Zwanzig obtained a Green's function formalism for the generalized diffusion equation.[29]

Based on the Förster mechanism and Haan and Zwanzig's earlier work, Gochanour et al. developed a model which can be applicable to both low and high density regime.[30] The first step in the study of where $W_{jk}=w_{jk}-\delta_{jk}\sum w_{jk}$, and p(R,t) is a vector with components $(p_1(R,t), p_2(R,t),\cdots\cdots,p_N(R,t))$.
The formal solution of the master equation is given by

$$p(R,t)=\exp(tW)\cdot p(R,0) \tag{16}$$

From the solution, the average density of excitation is obtained.

$$P(r,t)=<\sum\delta(r_j-r)\ p_j(R,t)> \tag{17}$$

The ensemble average density of excitation given by Eq. (17) can be written in terms of a Green's function

$$P(r,t)=\int dr'\ G(r,r',t)\ P(r',0) \tag{18}$$

where $G(r,r',t) = \rho^{-1} < \sum\sum \delta(r_j-r)\ \delta(r_k-r)\ [\exp(tW)]_{jk} >$. To calculate the average excitation dennsity, density expansion and diagrammatic expansion of the Green's function are empolyed. The density expansion method gives accurate results for the low density limit, while the diagrammatic expansion method is applicable to the high as well as the low density regime.

Mixing of rotation and electronic state dynamics

The previously introduced formulations assume that only rotational motions are responsible for depolarization and the probe molecule has a single excited state. If the probe diffuses isotropically, the anisotropy decay is simply correlated with the rotational diffusion constant. This idealized situation is very rare and more complicated ones are encountered. For example, there are a variety of complications such as anisotropic rotation, restricted motion, relaxation of the initially excited state, excitation transfer, presence of energetically accessible nearby states and interconversion between the states, etc. If the timescales of molecular rotations and electronic state dynamics are comparable, the analysis of fluorescence depolarization data is not simple. In this case, the fluorescence anisotropy decay is affected not only by rotational motions but also by state-to-state dynamics. It is reported for the tryptophan molecule in water that vibronic coupling and vibrational relaxation also affect the anisotropy decay. It is not easy to include all of these effects. In addition, the state dependent rotational dynamics is generally required. A theory of fluorescence depolarization which takes into account both electronic state dynamics and molecular reorientaion is presented by several groups.[31,32] Cross et al. have considered the coupling of level kinetics and rotational diffusion. The anisotropic absorption of the two-level system and the four-level photoisomerization process are examined with this model.[28,31,32] More general formalism including both electronic state dynamics and rotational dynamics was derived by Szabo.[28] The following equation is the result of his derivation.

$$r(t)=\frac{2}{5}\frac{<k_F(t)\rho(\omega)P_2[\mu_e(t)\cdot\mu_a(0)]>}{<k_F(t)\rho(\omega)>} \tag{19}$$

Here k_F and $\rho(\omega)$ are the radiative rate constant and the line shape function, respectively.

If the nonradiative decay rates are assumed to be independent of orientation, the state dynamics and the rotational dynamics are uncoupled and the anisotropy decay is given by

$$r(t)=\frac{2}{5}\frac{\sum_{ij}k_F^j\rho_j(\omega)p(jt\,|\,i0)<P_2[\mu_e^j(t)\cdot\mu_a^i(0)]>p_0(i,\omega)}{\sum_{ij}k_F^j\rho_j(\omega)p(jt\,|\,i0)p_0(i,\omega)} \tag{20}$$

where $p(jt\,|\,i0)$ is the probability that the system evolves from state i at t = 0 to state j at time t, and $p_0(i,0)$ is the probability that the system is prepared in state i by excitation. This expression contains orientational correlation functions which involve the absorption dipole of one state and the emission dipole of another state (when $i \neq j$).

Molecular dynamics simulation and Monte Carlo method

Analytical methods for FD based on the quantum mechanical picture have limited appliations to the dynamics of macromolecules like proteins. Molecular dynamics (MD) and Monte Carlo (MC) simulation methods have been developed for the complex systems. The MD techniques, which correspond to solving the classical equations of motion for a set of particles under a given potential, are used to study internal motions of proteins.[33] Protein fluorescence is attributed to amino acid residues like tryptophan and tyrosine. The FD measurements are employed to investigate internal dynamics of proteins[34,35] and the decay is compared with the MD simulation results.[36-38] The direction of transition dipole moment determined by the polarized absorption and the reorientation is traced by the MD simulation. As the integration time interval in the MD simulation is usually 1 fsec or less, the nanosecond range dynamics is poorly simulated. Therefore, only the fsec or psec FD results can be properly compared with the simulation results.

Another method for the FD is MC simulation.[39-41] While the MD techniques simulate the atomic trajectories, the MC methods are applied to examine the evolution of the excitation probability. In a given system configuration, the probabilities for the excitation transport of the initially excited fluorophore to others can be determined by the Förster equation. In the MC simulation, random numbers are generated to determine two kind of information - the newly excited fluorophore and the elapsed time before the excitation leaves the fluorophore. The simulation results are comparable to the analytical methods based on the Green's function of many-body (two-body or three-body) problem for the excitation transfer.

Excitation transport in molecular crystal

The FD experiments for molecular crystals are very rare because of the inherent anisotropy of the crystal lattice. However, the excitation transport in the molecular crystals is worth mentioning. The electronic states of molecular crystals are quite different from isolated molecules. The molecules in the lattice of the translational symmetry feel periodic potentials and the electronic excited states form a band structure called the exciton.[3] As the band structure of the electronic state reveals the spatial dependence, the excitation transfer rate is not a

simple function of the intermolecular distance as is given by the Forster equation. The exciton dynamics is treated separately from the electronic dynamics in solutions or glasses because of the coherence of the exciton. In order to understand the exciton transport, quantum behaviors of the exciton such as amplitudes of the excitation probability, phase relations and interference should be considered. Because of high concentration of the fluorophore, the electronic transport in molecular crystals becomes a many-body problem. The diffusion equations utilizing random walk are often applied for the system represented by a site dependent wavefunction. The coherence of the exciton is usually perturbed in real crystals. Coupling with the lattice vibrations modifies the exciton coherence and the impurities of the crystals reduce the wave charactor of the exciton. Therefore, incoherent aspects of the excitation transport treated in the models of the previous sections should be included in the exciton dynamics of the molecular crystals.[42]

SUMMARY

The FD experiments have been used to understand the dynamics of the electronic states and related molecular motions. Rotations in the liquid phase have been extensively studied and knowledge about various solute-solvent interactions has been accumulated. Molecular motions of macromolecules such as polymers, proteins and membranes have been investigated with FD techniques.

Förster equation has been served as a basis for the electronic excitation transfer. Classical hydrodynamics is used for the molecular reorientation in solution. For the excitation transport in various molecular systems, Green's function formalism is frequently utilized. In addition to the analytical methods, the MD and MC simulation have been applied for the FD of complex systems. Experimental and theoretical studies of FD will enhance the microscopic understanding of the electronic dynamics.

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