EFFECT OF CONFIGURATIONAL AVERAGING ON OBSERVABLES

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Effect of the distribution of the structural parameters on the time evolution of the fluorescence intensity is discussed. The influence of this distribution in two limit regimes of the excitation energy transfer — coherent and incoherent one are compared. It is shown that in many cases the fluorescence intensity measurements do not enable to decide between the two regimes.

1 Introduction

The time resolved fluorescence is the usual method of investigating the excitation energy transfer in molecular systems. This method is often applied to biological systems (e.g. photosynthetic units [1]). In the analysis of experimental spectra not only the parameters of the excitation pulse, time and spectral resolution of the experimental apparatus and the size of the sample but also fluctuations of the distances and the orientations of the molecules must be taken into account. The influence of these fluctuations is studied on the set of molecular dimers. This model makes it possible to illustrate these effects in a transparent way.

2 Model

We consider two states for each molecule at the dimer — the ground state and the first excited state. Denoting $P_{\alpha i}$ the probability of finding the $\alpha$-th molecule at the $i$-th dimer in the excited state and by $k_{\alpha i}$ the fluorescence rate constant of this molecule, we can describe the intramolecular transfer from the first excited state to the ground state leading to the fluorescence by the well-known equation

$$\frac{dP_{\alpha i}}{dt} = -k_{\alpha i}P_{\alpha i}.$$  \hspace{1cm} (1)

Assuming that at most one single photon is absorbed at $t = 0$ by the $i$-th dimer, the probabilities $P_{\alpha i}$ fulfil the inequality

$$0 \leq P_{11}(t) + P_{22}(t) \leq 1.$$  \hspace{1cm} (2)

For the same initial condition we obtain for the total fluorescence intensity $I(t)$

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if the set of dimers [2]
\[ I(t) = \sum_{\alpha i} k_{\alpha i} P_{\alpha i}(t). \] (3)

Observing only the fluorescence of the first molecule of the dimers (e.g. by the distinct polarization of the fluorescence of the molecules forming the dimers) we get
\[ I_1(t) = \sum_{i} k_{1i} P_{1i}(t) \] (4)
(analogously for \( \alpha = 2 \)).

There are two limit regimes of the intermolecular excitation energy transfer — coherent and incoherent one [2–4]. To obtain the most simple results, we consider a system of the dimers consisting of identical molecules and neglect excitation energy transfer between the dimers. Assuming the initial excitation at \( t = 0 \) at the second molecule, i.e.,
\[ P_1(t = 0) = 0, \quad P_2(t = 0) = 1, \] (5)
we get in the coherent case
\[ P_1^{\text{coh}}(t) = \exp \left( -\frac{t}{\tau} \right) \sin^2 \left( \frac{Vt}{\hbar} \right), \] (6)
\[ P_2^{\text{coh}}(t) = \exp \left( -\frac{t}{\tau} \right) \cos^2 \left( \frac{Vt}{\hbar} \right), \] (7)
where \( \tau = 1/k \) (\( k_{\alpha i} = k \) for all \( \alpha \) and \( i \)) is the excited state life time and \( V \) is the interaction energy between the molecules of the dimer (see Fig. 1a). In the usual dipole–dipole approximation, \( V \sim R^{-3} \), where \( R \) is the intermolecular distance. In the incoherent case, another time evolution is obtained [4]:
\[ P_1^{\text{incoh}}(t) = \left[ 1 - \exp(-2Ft) \right] \frac{1}{2} \exp \left( -\frac{t}{\tau} \right), \] (8)
\[ P_2^{\text{incoh}}(t) = \left[ 1 + \exp(-2Ft) \right] \frac{1}{2} \exp \left( -\frac{t}{\tau} \right), \] (9)
where \( F \) denotes the Pauli Master Equation rate constant (see Fig. 2a). In the dipole–dipole approximation, \( F \sim R^{-6} \).

In more complicated systems, the probabilities are linear combinations of the terms similar to the expressions given above.

3 Fluorescence

In the case of the undistinguishable fluorescence of the molecules forming the dimer, we obtain for the total fluorescence intensity the same time evolution in the coherent and the incoherent regime
\[ I(t) = N \exp \left( -\frac{t}{\tau} \right), \] (10)

where \( N \) is the total number of excited dimers in the sample. We see that the total fluorescence intensity cannot be used if we want to observe effects in the coherent regime. Therefore, we study in the rest of this paper only the time evolution of the fluorescence from the first molecules (\( \alpha = 1 \)) described by intensity \( I_1(t) \).

Under real conditions there are fluctuations of the intermolecular distances and mutual orientation of the molecules forming the dimers. We assume that the dis-
Fig. 2. The total fluorescence intensity for the sample with very high number of the dimers. Case a) corresponds to the coherent regime while b) is for the incoherent one. The calculations were done for the set of the dimers containing two chlorophyll a molecules in the most favourable orientation of their transient dipole moments giving the largest value of $V$ and $F$, the average intermolecular distance $R = 12 \, \text{Å}$, the half-widths $\Delta V$ and $\Delta F$ of the Gaussian distributions correspond to the distribution of the intermolecular distances $1 \, \text{Å}$ and the initial conditions $P_1(t=0) = 0$, $P_2(t=0) = 1$.

The distribution function $p(V)$ of the interaction energy $V$ has the form

$$p(V) = \frac{1}{\Delta V \sqrt{\pi}} \exp \left( - \frac{(V - \bar{V})^2}{\Delta V^2} \right).$$  \hfill (11)

Fig. 3. The total fluorescence intensity for the randomly chosen one hundred dimers from the set of dimers with the same parameters as in Fig. 2. Cases a) and b) correspond to two different random choices.
For the distribution function of the rate constant $F$ we assume analogously

$$p(F) = \frac{2}{\Delta F \sqrt{\pi}} \exp \left(-\frac{(F - \bar{F})^2}{\Delta_F^2}\right).$$ (12)

It can be shown that for a sample with a very high number of the dimers the time evolution of the fluorescence intensity $I_1(t)$ equals

$$I_{1}^{\text{coh}}(t) = \frac{1}{2} \left\{ 1 - \exp \left[ -\left(\frac{\Delta v t}{\hbar}\right)^2 \right] \cos \left(\frac{\bar{F} t}{\hbar}\right) \right\} \exp \left(-\frac{t}{\tau}\right)$$ (13)

in the coherent case and

$$I_{1}^{\text{incoh}}(t) = \frac{1}{2} \left\{ 1 - \text{erfc} \left(\frac{-F + \Delta_F t}{\Delta_F}\right) \exp \left(-\frac{\bar{F} t + \Delta_F^2 t^2}{\Delta_F^2}\right) \right\}$$ (14)

in the incoherent one. Here, erfc(x) is the complementary error function. For longer times, the form of the time evolution of the fluorescence intensity is the same in the both limit regimes (see Fig. 2).

Two illustrative calculations are shown in Fig. 3. In both cases we randomly chose one hundred dimers from the set of dimers with the distribution function (11) and computed the fluorescence intensity. Its form is different not only from the above intensity (13) but also depends on the concrete dimers chosen.

4 Summary

In this paper, we discussed the effect of real experimental conditions in the biological samples on the measurements of the time resolved fluorescence intensity. We considered the coherent as well as incoherent regimes of the excitation energy transfer. We showed that, in spite of very different fluorescence from the single molecules, the fluorescence intensities of the samples are very similar in both transfer regimes even for very short times.

References


