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Vaclav Kapsa and Lubomir Skála

REMARKS ON EFFECT OF EXPERIMENTAL RESOLUTION ON OBSERVABLES

Summary

Effect of the experimental resolution, form of the excitation pulse, size of the sample, configurational averaging and temperature on the experimental observables is discussed. It is shown that the original information carried by the observables may be destroyed by these effects. A few examples of such a loss of information are given.

1. Introduction

There is an important tool for studying molecular aggregates — optical spectroscopy. The high resolution luminescence spectroscopy is used for studying many different systems — from crystals to solutions, clusters and molecular aggregates. We have devoted considerable amount of time to study the excitation energy transfer in the photosynthetic units which can be described as molecular aggregates of the chlorophyll (Chl) and polypeptides molecules [1]. There are few different theories of the excitation energy transfer among the Chl molecules with different prediction of the time evolution of the fluorescence intensity. We have shown [1] that taking into consideration real experimental conditions the time evolution of the resulting fluorescence intensities can be almost identical for these theories.

Our approach is general and can be used for many other systems, particularly for samples containing many small aggregates or clusters.

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distance in the photosynthetic apparatus of green plants and bacteria) leads to the relative change of the intermolecular rate constants by 20–60 % for the incoherent transport and by 10–30 % for the coherent one. It is obvious that such changes can influence the resulting form of the observables very significantly.

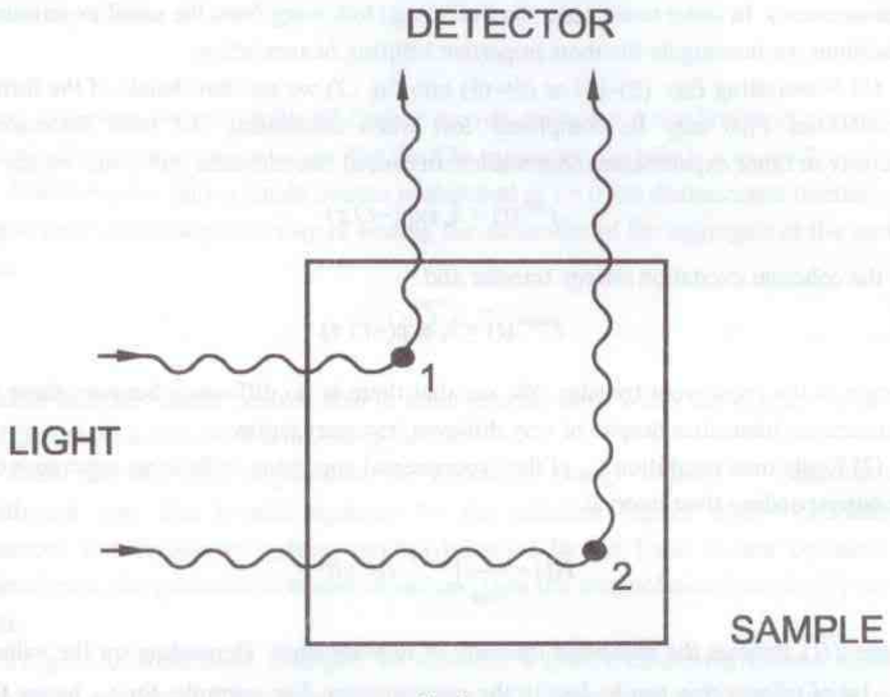

Fig. 1.
Different optical paths for different aggregates (dots).

In order to illustrate the effect of the configurational averaging we show in Fig. 2 the probability of finding the excitation at one of the molecules in the aggregate consisting of two chlorophyll a (Chl a) molecules for the cases without and with the Gaussian distribution of the Chl a – Chl a distance R (a mixed statistical ensemble). It is obvious that the resulting averaged probabilities in the coherent regime may be very different from the original probabilities $P_i(t)$. This averaging influences most significantly the characteristic quantum beats which may disappear for $t > 0.1$ ps. In the incoherent case, this effect is less significant. It can be shown that the configurational averaging of $P_i(t)$ for aggregates with N molecules can be reduced to a sum of functions similar to those shown in Fig. 2. Therefore, this conclusion has general validity.

(6) Theoretical calculations are performed usually for the temperature $T = 0$ K. Experiments are carried out at temperatures T > 0 K, often at the room temperature. The vibrations of the system can change the geometry of the aggregates. Therefore, the effect of temperature can be similar to the configurational averaging.

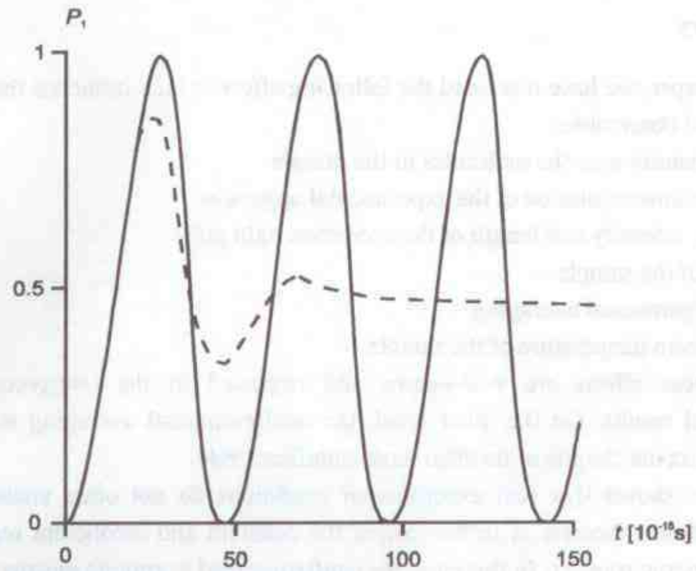

Fig. 2a.

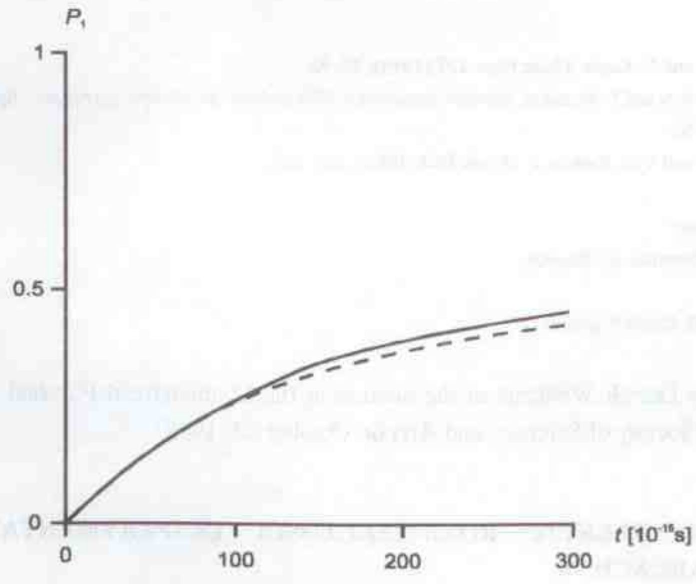

Fig. 2b.

The illustration of the effect of the configurational averaging on the probabilities $P_i(t)$. The calculations were done for the aggregate containing two chlorophyll molecules in the most favourable orientation of their transient dipole moments giving the largest value of V and F, $R = 35$ Å. The initial excitation is assumed at the second Chl molecule ($P_1(t = 0) = 0$, $P_2(t = 0) = 1$). Case (a) corresponds to the solution of the Schrödinger Equation (coherent case) while (b) follows from the Pauli Master Equation (incoherent case). The full lines are the probabilities $P_i(t)$ with no configurational averaging. The dashed lines show $P_i(t)$ for an ensemble of aggregates with Gaussian distribution of the intermolecular distance R. The average distance is $R = 35$ Å, the half-width of the Gaussian distribution being 3 Å.

4. Summary

In this paper, we have discussed the following effects which influence the form of the experimental observables

- summation over the molecules in the sample
- finite time resolution of the experimental apparatus
- form, intensity and length of the excitation light pulse
- size of the sample
- configurational averaging
- non-zero temperature of the sample.

Most of these effects are well-known and respected in the interpretation of the experimental results. On the other hand, the configurational averaging is not usually taken into account despite of its often most significant role.

We have shown that real experimental conditions do not often enable to decide between different theories as in the case of the coherent and incoherent regimes of the excitation energy transfer. In this case, the configurational averaging destroys most of the information from the early stages of the transfer.

References

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Charles University
Faculty of Mathematics and Physics
Ke Karlovu 3
121 16 Prague 2, Czech Republic

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UWAGI O EFEKCIE ROZDZIELCZOŚCI EKSPERYMENTALNEJ NA OBSERWABLACH

S t r e s z c z e n i e

Rozdzielczość eksperymentalna, kształt wzbudzonego impulsu, rozmiar próbki, temperatura, przede wszystkim zaś uśrednienie po konfiguracjach są to czynniki, które wpływają na wyniki pomiarów obserwabli doświadczalnych. W pracy wykazano, że oryginalna informacja zawarta w pomiarze uśrednionych wartości dla obserwabli może być zniekształcona i zagubiona ze względu na występowanie omawianych czynników. Przytoczono kilka przykładów strat informacji.