# MODELING OF CONCENTRATION QUENCHING IN TWO-DIMENSIONAL SYSTEMS

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### **INTRODUCTION**

- Concentration quenching occurs when fluorescence quantum yield decreases upon increasing concentration of fluorophores in solution.
- The origin of concentration quenching is not fully understood to this day.
- It has been observed in chlorophyll solutions [1].
- Interestingly, at similar fluorophore concentrations the fluorescence is usually significantly quenched in artificial systems compared to unquenched in vivo systems.
- In this work, concentration quenching was simulated using approach similar to ref. [2].
- Real life equivalent of our two-dimensional model could be an especially thin film or membrane.
- Quenching was achieved by introducing infinitely deep traps: excitation, after reaching one, could not escape.

### RESULTS

Mean excitation lifetime values were obtained by summing up those elements of  $\vec{P}$  that describe fluorescing molecules (not traps) at each point in time and calculating the integral of the resulting curve. Results were averaged over different molecule distributions.



#### THEORY

Molecules, each 1 nm in diameter, were scattered in a 10000 nm<sup>2</sup> area using a uniform distribution. Different concentrations were obtained by changing the number of molecules (N).

Traps were formed when two or more molecules were closer to each other than a certain distance  $(R_{trap})$ .



Molecule distribution example (*N* = 200)

Time dependence of the total excitation probability  $\vec{P}$  (a vector of excitation probabilities for every molecule) was calculated by solving a differential equation:

#### 100 200 300 900 1000 Number of molecules in 10000 nm<sup>2</sup> area

Dependence of mean excitation lifetime on different molecular

#### **COMPARISON WITH EXPERIMENT**

concentrations and relative amount of traps ( $\tau = 5 \text{ ns}$ ,  $R_{F} = 10 \text{ nm}$ )

In order to fit the experimental data of measurements of chlorophylls in monolayers [3] the model was slightly modified; parameter  $\kappa_{ij}$  was introduced to describe the orientation of transition dipole moment of each molecule and the elements of  $\widehat{K}$  are now calculated using this formula:

$$K_{ij} = \frac{1}{\tau} \frac{\kappa_{ij}^2}{\left\langle \kappa_{ij}^2 \right\rangle_{\text{or}}} \left( \frac{R_{\text{F}}}{R_{ij}} \right)^6$$

Parameter  $\tau$  was now set as a fixed parameter, equal to the maximum excitation lifetime ( $\tau_0 = 5.5$ ns) divided by fluorescence quantum yield (QY = 0.33).

Optimization was done by calculating the minimum average square difference between experimental data and calculated results using the model. Parameters  $R_{trap}$  and  $R_{F}$  were changed during the optimization process to find their optimal values.





 $\widehat{K}$  is a matrix of energy transfer rates between molecules:

 $K_{ij} = \frac{1}{\tau} \left( \frac{R_{\rm F}}{R_{ii}} \right)^6.$ 

#### **CONCLUSIONS**

- As expected, we can observe that in larger concentrations quenching is more rapid (bigger  $R_{trap}$  values correspond to higher concentrations of traps).
- The final model describes experimental data sufficiently well.
- Best results were achieved with parameter values  $R_{trap} = 3.15$  nm and  $R_{\rm F} = 5.21 \, \rm nm.$
- It is not possible to fit the experimental data without including the orientations of transition dipole moments.

Fitting of experimental data ( $R_{trap} = 3.15 \text{ nm}$ ,  $R_F = 5.21 \text{ nm}$ )

#### References

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- [3] M. L. Agrawal, J.-P. Chauvet, L.K. Patterson, The Journal of Physical Chemistry 89 (14), 2979-2982 (1985).