

Influence of the excitation light intensity on the rate of fluorescence quenching reactions

Gonzalo Angulo¹, Jadwiga Milkiewicz¹, Daniel Kattnig², Michał Nejbauer¹, Yuriy Stepanenko¹, Jan Szczepanek¹, Czesław Radzewicz^{1,3}, Paweł Wnuk^{1,3-5}, and Günter Grampp⁶

¹*Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland*

²*Physical and Theoretical Chemistry Laboratory, University of Oxford, Oxford OX1 3QZ, UK*

³*Institute of Experimental Physics, University of Warsaw, 02-093 Warsaw, Poland*

⁴*Max-Planck-Institut für Quantenoptik, 85748 Garching, Germany*

⁵*Fakultät für Physik, Ludwig-Maximilians-Universität München, 85748 Garching, Germany*

⁶*Institute of Phys. and Theor. Chemistry, Graz University of Technology, 8010 Graz, Austria*

E-mail: gangulo@ichf.edu.pl

Chemical reactions in solution develop at rates that depend on a number of factors: temperature, pressure, electric and magnetic fields, driving force and solvent characteristics such as the refractive index, the dielectric constant and the viscosity. However, for photoinduced reactions it has never been explored experimentally if the rate of the bimolecular reactions depends itself on the intensity of the triggering light. The present work attempts to elucidate this question.

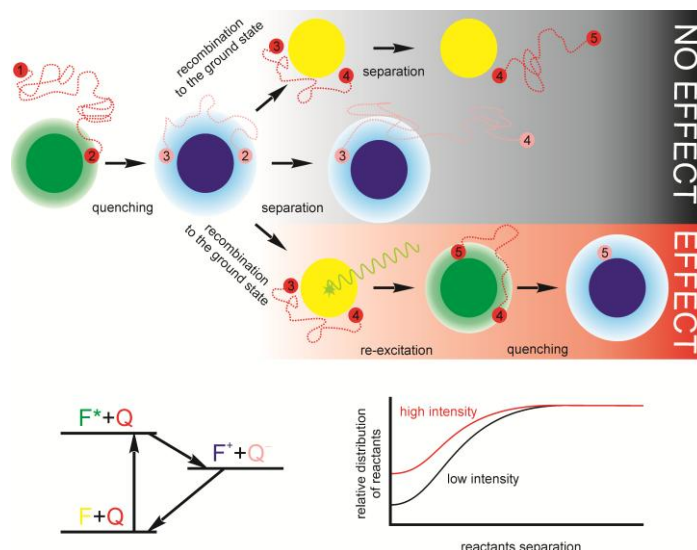


Figure 1. The effect of multiple excitation events on the same pair of reactants is illustrated sequentially from left to right with three different possibilities: upper part no effect is observed on increasing the excitation intensity of after a second pulse because either there is no absorption of a second photon before the reactants separate, or because there is no recombination back to the ground state. In the lower part of the panel an effect is observed because the recombination is fast enough and a second photon is absorbed. In the lower panel a simplified reaction scheme is shown, and the fluorophore-quencher pair distribution function changes under CW excitation on increasing the light intensity.

More precisely, the effect of multiple light excitation events on bimolecular photo-induced electron transfer reactions in liquid solution is studied experimentally. It is found that the decay of fluorescence can be up to 25% faster if a second photon is absorbed after a first cycle of quenching and recombination. A theoretical model is presented which ascribes this effect to the enrichment of the concentration of quenchers in the immediate vicinity of fluorophores that have been previously excited. In figure 1 a simplified picture of the effect and the model is presented. Despite its simplicity, the model delivers a qualitative agreement with the observed experimental trends. The original theory by Burshtein and Igoshin was created for continuous light excitation though.^[1] A qualitative extrapolation from the here presented pulse experiments to the continuous excitation conditions lead us to conclude that in the latter the order of magnitude of the increase of the quenching efficiency upon increasing the light intensity of excitation, must also be on the order of tens of percent. These results mean that indeed the rate constant for photo-induced bimolecular reactions depends also on the intensity of the excitation light.^[2]

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