Three dimensional diffusion of singlet oxygen in lipid suspensions using Monte Carlo Simulations

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Introduction

- The lifetime of singlet oxygen depends on the environments in which singlet oxygen stays. In diminutive structures like bilayers of lipids the singlet oxygen can escape and diffuse in the surroundings. In that case the lifetime of singlet oxygen depends on different conditions like environment, diffusion length of singlet oxygen and location of activation of singlet oxygen.
- To get informations about the behavior of singlet oxygen in diminutive structures Monte Carlo Simulations were done.

Experimental Setup

- Singlet oxygen is directly detected by time resolved measurement of its luminescence at 1270 nm in near-backward direction with respect to the excitation beam using an infrared sensitive photomultiplier.

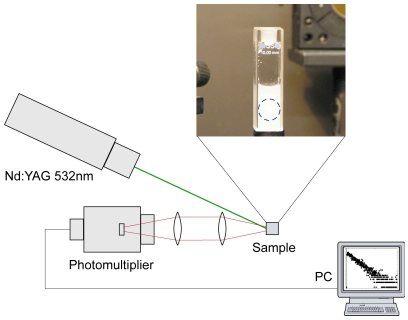
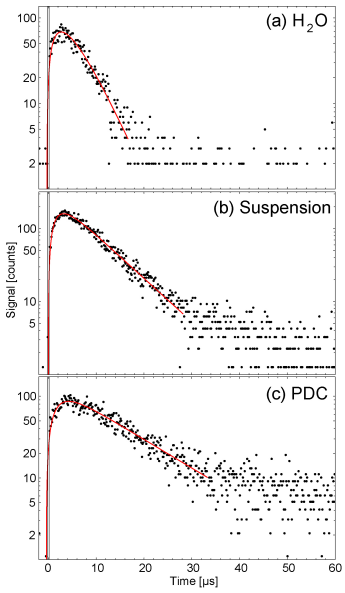


Figure 1. Experimental Setup. The photosensitizer and lipid are dissolved, filled in a cuvette and irradiated by the laser (532 nm) at a given spot size (blue ring)

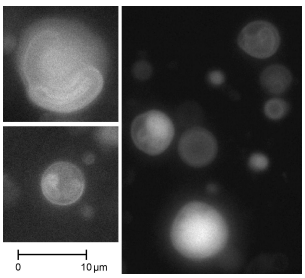
Experimental Results

- Luminescence of singlet oxygen at 1270 nm generated by (a) 50 µg/ml Photofrin in H_2O, 50 µM ATMPn in (b) suspension of 15 mg/ml phosphatidylcholine in H_2O and (c) pure phosphatidylcholine versus time.
- The lifetime (decay time of luminescence) of singlet oxygen in H_2O was appointed to (a) 3.5 ± 0.5 µs and in (c) pure phosphatidylcholine to 16 ± 2 µs.
- When adding ATMPn in aqueous suspensions of phosphatidylcholine, ATMPn is not water soluble, it can be assumed that the sensitizer is restricted to the lipid droplets. Nevertheless the lifetime of singlet oxygen is between H_2O and pure phosphatidylcholine at 10 ± 2 µs



Microscopy

- The fluorescence of 50 µM ATMPn in suspension of 15 mg/ml phosphatidylcholine in H_2O was researed.
- ATMPn is only located in lipid areas. The image of fluorescence shows vehicles like Micelles containing lipid bilayers surrounded by water.



Simulations

- A cubical system which contains one lipid droplet in an aqueous environment and water inside was simulated (Fig. 2). The concentration of phosphatidylcholine in H_2O was 15 mg/ml.
- Singlet oxygen was generated exclusively in lipid and was able to diffuse in the surrounded water.
- The shell diameter must be in the range of the diffusion length of singlet oxygen to get a intermediate life time of singlet oxygen between water and lipid.
- The three dimensional diffusion of singlet oxygen was executed by random walks during time steps (Fig 3). After each time step the singlet oxygen can decays with a mathematical probability depending on the relaxation rate of singlet oxygen in the environment in which the singlet oxygen stays.

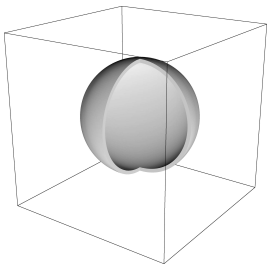


Figure 2. Model for simulations. A shell of lipid in water.

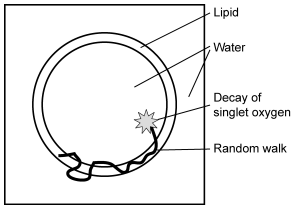
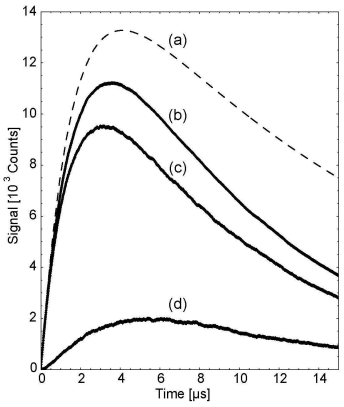


Figure 3. Random walk of singlet oxygen

Result of Simulations

- The simulation displays the amount of singlet oxygen molecules in water (d) and in lipid (c) and the sum (b) of both per time step. The Line (a) describes the theoretical curve for singlet oxygen in lipid without diffusion.
- The theoretical signal (a) has a rise and decay time (lifetime of singlet oxygen) of 1.6 µs and 16 µs, respectively, which is confirm to the experimental data of pure lipid. In contrast the curve of simulation of singlet oxygen molecules in lipid (c) yields a rise time of 1.5 µs and a decay time of 8.4 µs. The diffusion seems to be a mechanism of deactivation which generates a higher rise and decay rate or a lower rise and decay time in comparison to the theoretical curve (a).



- The sum (b) of singlet oxygen in water and in lipid is equivalent to the experimental measurement of ATMPn in aqueous suspensions of phosphatidylcholine
- The shape of the calculated luminescence of the singlet oxygen in water (d) is given by diffusion.

Summary

- It is possible to describe the three dimension diffusion of singlet oxygen in lipid suspensions by using Monte Carlo Simulations.
- The model of one lipid shell droplet surrounded by water yields results which are in good agreement to the experimental results.
- **OUTLOOK:** It should be possible to simulate the diffusion of singlet oxygen in more complex structures like cells.

References

J. Baier, M. Maier, R. Engl, M. Landthaler and W. Bäumler, **Time-Resolved Investigations of Singlet Oxygen Luminescence in Water, in Phosphatidylcholine, and Aqueous Suspension of Phosphatidylcholine or HT29 Cells**, J. Phys. Chem. B 109 (2005) 3041