

Photophysical and photochemical properties of electronically excited fluorescent dyes: a new type of time-resolved laser-scanning spectroscopy

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ABSTRACT. The capacity of a new type of time-resolved laser-scanning spectroscopy is discussed. Due to the developed modulation technique we obtain a high sensitivity in the absorption measurement as well as a very efficient suppression of the background absorption. The new technique has been used to investigate photophysical and photochemical properties of fluorescent dyes. All presented results are discussed in view of potential applications like dye laser and fluorescence labelling.

The possibility of intermolecular triplet state quenching by molecular oxygen and further agents is considered in detail. The quenching process is described in terms of diffusion controlled interaction. It is shown that under ambient conditions quenching agents can inhibit the quenching by molecular oxygen and therefore the generation of the chemically highly reactive singlet molecular oxygen. It can be expected that the obtained information can be used in order to increase the photostability not only of rhodamine dyes.

1. INTRODUCTION AND OVERVIEW

1.1. Experimental challenge. The precise quantitative detection of weakly absorbing transient states is still a challenge in the study of photochemical and photophysical processes. In order to explain the photophysical behaviour of a sample it is essential to get precise information about the population of each state as a function of time. So two kinds of information have to be supplied by the experiment. First of all, the states have to be identified, this can usually be accomplished by the *spectral dependence* of the signal. Secondly, the *time dependence* of the population has to be measured [1]. Both measurements have to provide highly precise data, because the signals suffer from strong interference of the ground state. Most of the applied experimental methods are not capable of providing this data simultaneously. This introduces difficulties, because the results of two different experiments have to be compared.

We present a new time-resolved laser-scanning spectrometer, that allows a precise detection of the absorption of transient states in the whole visible and NIR range of the spectrum. We can determine the spectral features of the transient states as well as the time dependence of the population of the transient states in the *same* experiment. Due to the developed modulation technique see (Chapter 2.1) we obtain a high sensitivity in the absorption measurement (In current experiments it could be shown that the sensitivity of our technique is sufficient to measure absorption at *single molecule level*.) and a very strong suppression of the background absorption simultaneously. An efficient suppression of the background is obtained even in the case of similar spectral distributions of ground state and transient

absorption. The time-resolution in the presented spectrometer is achieved by a working principle that can be compared to a motion picture camera. The picture at the end of the strip obviously shows the object at a distinct period later than the first picture. This technique has been used to investigate photophysical and photochemical properties of fluorescent dyes.

1.2. Fluorescent dyes. Xanthene derivatives especially rhodamine dyes, occupy an important position among different families of dyes, owing to a number of reasons related to their photochemical and photophysical properties. Because of their high fluorescence quantum yield rhodamine dyes have wide spread technological and scientific applications *e.g.*, single molecule detection [2, 3], fluorescence labelling [4], dye lasers [5, 6, 7], conversion and storage of solar energy [8] *etc.* These dyes are also applied in medicine *e.g.*, for the staining of damaged cells [9], as antitumor agent [10], and in photosensitized cell killing [11, 12]. For nearly all applications a high photostability is required. This goal can be approached by fast deactivation of the excited molecules to their ground state. Consequently the competition of photochemical processes will be suppressed and therefore their importance decrease. Owing to its metastable character the triplet state *T* is of particular interest for photochemical reactions.

1.3. The triplet state in dye lasers. In dye laser technology a short triplet state lifetime is of two fold importance. Besides an increased photostability a reduced triplet state lifetime leads to a decreased triplet-triplet absorption which can be decisive for laser efficiency [13, 14, 15, 16, 17, 18]. For a number of rhodamine dyes important molecular parameters for dye laser action were measured in our group by using the time resolved laser-scanning-microscopy technique [19, 20, 21]. In

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[22] a modification of the scanning-microscopy technique is applied for intracavity absorption measurements. A general overview will be given in [23].

1.4. Fluorescence reduction by population of the triplet state. In many applications mentioned above the dye molecules are often expected to emit maximum-intensity fluorescence. The primary requirement for this is a high fluorescence quantum yield. Beyond this, it must be considered that fluorescent molecules located in a meta-stable triplet state are not able to emit radiation. This represents a reduction of the intensity of the fluorescence, often underestimated in its importance. The size of this perturbation can be grasped by knowledge of the quantum yield for occupation of the triplet state and its lifetime. In [24] the time resolved laser-scanning-microscopy technique has been used to measure the solvent dependency of the triplet state properties of four medically and biologically relevant dyes [25, 26, 27, 28, 29, 30, 31, 32, 33].

1.5. Triplet state quenching and singlet molecular oxygen production. Because of the low lying excited singlet state of the omnipresent molecular oxygen $^3\text{O}_2$ this molecule frequently operates as efficient intermolecular quencher for excited singlet and triplet states. Under ambient conditions in solution almost all dye triplets are quenched by molecular oxygen. As reaction product the chemically highly reactive $^1\text{O}_2$ can be formed [34, 35, 36, 37, 38, 39]. This molecular species may activate the photodecomposition of the dye molecules or can lead to a phototoxic action of the dye.

Several techniques have been used to detect $^1\text{O}_2$ in condensed phase like $^1\text{O}_2 \rightarrow ^3\text{O}_2$ NIR phosphorescence [40, 41, 42, 43, 44, 45, 46, 47, 48], time resolved thermal lens spectroscopy [41, 49, 50], and the analysis of $^1\text{O}_2$ specific reaction products [36, 44, 51, 52, 53, 54]. Quantum yields of $^1\text{O}_2$ production have been investigated for a large number of sensitizers. Values for $^1\text{O}_2$ production rates are reported [51, 50, 55, 56, 57] even for a couple of hydroxy xanthenes as fluoresceine, eosin and rose bengal which show a relatively high triplet quantum yield. Rhodamine dyes possess a very low triplet quantum yield (1% or less) [58]. Nevertheless the relation between the photostability of xanthene dyes and the presence of $^1\text{O}_2$ is frequently discussed [34, 50, 55, 59, 60, 61, 62, 63]. To our knowledge in [64] for the first time we have directly proved the formation of $^1\text{O}_2$ sensitized by rhodamine dyes.

1.6. Elementary photoreactions of rhodamine dyes in basic solvents. By applying the time-resolved laser-scanning-microscopy technique in [66] we show that rhodamine dyes which contain secondary amino-groups can be easily deprotonated being in their triplet state. The deprotonated triplet state undergoes a fast reaction leading to a comparatively long living state. The absorption spectrum of this new state is close to the ground state. We suppose the state to be the radical ion of the dye produced by electron transfer of the

deprotonated triplet state.

This fast reaction being coupled to the deprotonation equilibrium significantly decreases the lifetime of the triplet state. The ground state depletion shows biexponential recovery due to superposition of accelerated triplet decay and slow decay of the new state.

Until now proton phototransfer involving rhodamine dyes in the triplet state has hardly been studied. To our knowledge [66] is the first paper which reports that the deprotonated triplet state is an efficient source of a remarkably long living transient species. The results are of particular interest in view of the photostability of widely used rhodamine dyes. Under constant irradiation this long lifetime causes the build-up of a distinct concentration of probably radical ions that might be chemically reactive. Thus the presence of a base probably opens a pathway of irreversible photodecomposition of the dye.

2. MATERIALS AND METHODS

As mentioned above a high photostability can be approached by fast deactivation of the excited molecules to their ground state. This can be done through inter- or intramolecular processes. In [65] intramolecular quenching processes are investigated on the basis of electronically excited trichromophoric rhodamine molecules. In the following the efficiency of intermolecular quenching of excited rhodamine 6 G is investigated in detail. We present agents which *selectively* influence the fluorescence, the intersystem crossing rate or the triplet lifetime of rhodamine 6 G. The influence is described in terms of diffusion controlled interaction. Moreover even under ambient conditions the addition of *e.g.*, TEMPO in a sufficient high concentration can inhibit the quenching by molecular oxygen and therefore the generation of the chemically highly reactive singlet molecular oxygen. It can be expected that the obtained information can be used in order to increase the photostability not only of rhodamine dyes.

2.1. Experimental setup. Experimental details of the used time-resolved laser-scanning-microscopy technique have been described elsewhere [19, 24, 65, 66]. Briefly, the sample (see Figure 1) consists of a mixture of rhodamine 6 G and the quenching agent dissolved in deoxygenated ethylene glycol. The solution is pressed through a nozzle producing a fast flowing jet stream ($\ell = 100 \mu\text{m}$ thickness). (Instead of the jet a fast rotating dye cell can be used [24]. With this technique of course the solvent viscosity is not important. Moreover rotating discs of solid samples can also be used.) This jet is commonly known from cw dye lasers. A continuous excitation beam is focused by a lens ($f = 50 \text{ mm}$) onto the sample. The excitation (absorbed power typically 100 mW) produces a characteristic spatial distribution of transient states. The transmission of the sample is measured using a focused continuous probe beam (Instead of the used laser a Xe-arc lamp can also be applied as probe beam source [66].) ($< 10 \text{ mW}$). In order

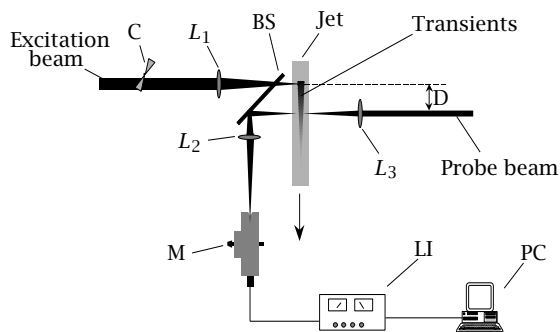


Figure 1. Laser-scanning microscope. Jet: the dye jet is produced by a combination of a pump module (model 591, Coherent Radiation) and a nozzle (taken from a dye laser CR 599, Coherent Radiation); Excitation and probe beam: Kr-ion laser (531 nm, model CR 3000K, Coherent Radiation) or Ar-ion laser (514 nm, model Innova 70, Coherent Radiation); C: chopper (model 220 A, HMS); M: monochromator (model H20, Jobin Yvon); LI: lock-in amplifier (model 5101, EG & G); L₁ and L₂: achromatic focusing lens ($f = 50$ mm); L₃: lens ($f = 100$ mm); PC: Computer; BS: beam splitter (5% reflection); D indicates the distance between excitation and detection.

to increase the signal to noise ratio the excitation beam is chopped and the detector current is recorded by a lock-in amplifier (see Figure 1). Due to the adjustable distance D between the foci of the probe and the excitation beam one can detect the distribution of transient states in the sample. Because of the motion of the sample the spatial evolution of the transmission can be transformed into the time domain. Consequently it is possible to identify individual states by analysing the temporal decrease of the transient absorption. The waist diameter $2a$ of the focused beams is $15 \mu\text{m}$. A typical jet velocity v_{jet} is 15 m/s . Thus a time resolution of $2a/v_{\text{jet}} = 1 \mu\text{s}$ can be obtained.

The jet technique restricts the number of useable solvents to those showing a sufficient high viscosity. Using these solvents a high uniformity of the jet velocity is observed. The jet velocity is given by the measured phase difference between the chopped excitation and the resulting change in probe beam transmission as function of D .

The absorption and fluorescence spectra of the used dye solution (see Figure 2) are measured by a spectrophotometer (model Lambda 19, Perkin Elmer) and a fluorimeter (model Fluorolog 2, Spex) respectively. The measured fluorescence data are corrected to the photon spectra by using a calibrated halogen lamp (Model 245C, Optronic Laboratories).

2.2. Chemicals. In the time-resolved experiments presented below the dye rhodamine 6G (Radiant Dyes) in ethylene glycol (Merck, puriss. p.a.) is used. The chemical structure of rhodamine 6G is shown in

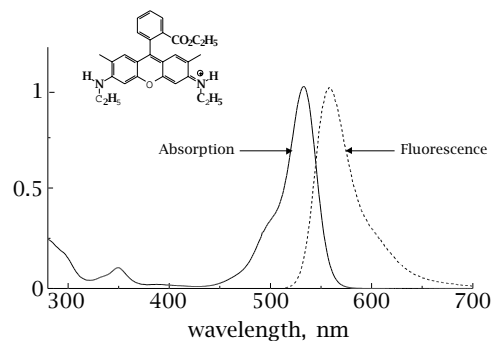


Figure 2. Normalised absorption and emission spectrum of rhodamine 6G in ethylene glycol. The molar decadic extinction coefficient at the wavelength of maximal absorbance is in the order of $10^5 \ell/(\text{mol} \cdot \text{cm})$.

Figure 2. The dye concentration (0.3 mM) is adjusted to an absorbance of 3 per mm at the maximum of the main absorption band. The dye was checked for purity by HPLC and did not contain a significant amount of impurities.

The agents used for intermolecular quenching are described in Table 1. The molecular oxygen concentration $[\text{O}_2]$ is adjusted by flushing (15 minutes) with the corresponding $\text{N}_2\text{-O}_2$ -gas mixture. The solubility of molecular oxygen in ethylene glycol is $k_{\text{Henry}} = 0.58 \times 10^{-3} \text{ mol}/(\ell \cdot \text{atm})$ [67]. Assuming an ideal behaviour of gaseous elements in acetonitrile and almost complete gas displacement, one gets for the $^3\text{O}_2$ concentration $[\text{O}_2]$ the values 0.58, 0.12 and < 0.01 mM for oxygen, air and nitrogen flushed solution respectively.

All measurements are carried out at a solvent temperature of 20°C .

2.3. Theory and results. The analysis of the signals recorded by the laser-scanning microscope is carried out on the basis of the Jablonski energy state diagram [68] which is usually accepted for characterisation of organic dyes. Owing to the short lifetime of higher excited states only the first excited singlet S_1 and the lowest triplet state T is populated noticeably. The excitation beam generates a characteristic population of the excited states S_1 and T, which can be detected by the probe beam. In order to measure the transient amount of the total transmission the intensity of the probe beam I^i , having transient states populated (excitation beam on) is compared with the intensity I , having no transient states populated (excitation beam off). Owing to the polarisation and orientation of excitation and probe beam the orientation of the dye molecules in ground state and excited states can be anisotropic [58]. In order to consider the effect of anisotropy the transmission of the probe beam is measured for parallel and perpendicular polarisation of excitation and probe beam which is indicated by $i = \parallel$ and \perp . The change of the transmitted intensity

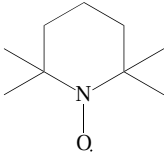

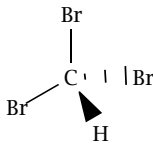
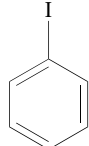
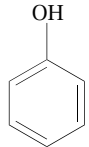
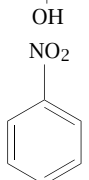
$$\frac{\Delta I^i}{I} = \frac{I_1^i - I}{I} \quad (1)$$

is recorded. Positive values indicate an increased

Table 1. Intermolecular quenching of rhodamine 6 G in ethylene glycol (deoxygenated) and different agents.

¹⁾ For preparation of the N₂-O₂-gas mixture nitrogen (Messer-Grießheim) of the purity 99.99% is used.

²⁾ A gas-chromatographic analysis indicates the following impurities: 1.5% benzene; 0.8% benzophenone; 0.4% fluorene; 6% dimeric COT.

Structure	Name	Purity	Maximum applied concentration, mM	$k_Q^T 10^{-8}$ l/(mol s)	$k_Q^S 10^{-8}$ l/(mol s)
O ₂	oxygen	Messer-Grießheim ¹⁾ 99.99%	0.58	16	17
	TEMPO	Aldrich 98%	6	1.18	0.71
	COT	Radiant Dyes ²⁾	6	0.94	0
	bromoform	Merck-Schuchardt z.S. > 99%	350	0	0.14
	iodobenzene	EGA-Chemie 99%	18	0	0.96
	hydroquinone	laboratory quality 4 times recrystallized	6	0	0
	nitrobenzene	Fluka puriss. p.a. > 99.5%	6	0	0

transmission of the excited sample compared to the sample with just a ground-state population. From measured functions $\Delta I^i/I$ the signal $\Delta I/I$ which would be obtained if the probe molecules were oriented isotropically can be calculated by [58]

$$\frac{\Delta I}{I} = \frac{1}{3} \left(\frac{\Delta I^{\parallel}}{I} + 2 \frac{\Delta I^{\perp}}{I} \right) \quad (2)$$

Equation (2) is valid for $\Delta I/I \ll 1$. This relation is fulfilled in all experiments. Typical measured signals are shown in Figure 3.

The wavelength of the probe beam is tuned to the main ground state absorption band of rhodamine 6 G. The ground-state depletion causes an increase of the

transmitted beam intensity. With respect to the high extinction coefficient of the ground state the absorption of the transient states at this wavelength can usually be neglected [19] and the transmission change can be approximated as

$$\frac{\Delta I}{I} = 10^{\ell \cdot \epsilon_0 \cdot [c_1(D) + c_T(D)]} - 1 \quad (3)$$

For $D = 0$ (complete overlap between excitation and probe beam) the dye solution is bleached by the population of the S₁ and T state. Because of the short lifetime of the S₁ state (< 10 ns) the ground state depletion for $D > 30 \mu\text{m}$ (no overlap between excitation and probe beam) is determined exclusively by the population of

Table 2. Experimental details for the measurement shown in Figure 3. In all cases is $a = 8 \mu\text{m}$.

$[\text{O}_2]$, mM	v_{jet} , m/s	$k_{\text{ST}}/10^6$, s^{-1}	τ_{T} , μs	$c_1(d=0)/\text{c},\%$	$c_{\text{T}}(d=0)/\text{c},\%$	$M/10^{-3}$
< 0.01	12	0.75	100	2.77	1.17	5.6
0.12	22	0.81	4.97	3.02	0.71	58.8
0.23	22	1.03	2.38	3.07	0.85	113
0.35	22	1.26	1.67	2.90	0.94	155
0.46	22	1.29	1.27	2.93	0.98	204
0.58	22	1.35	1.08	2.95	1.02	237

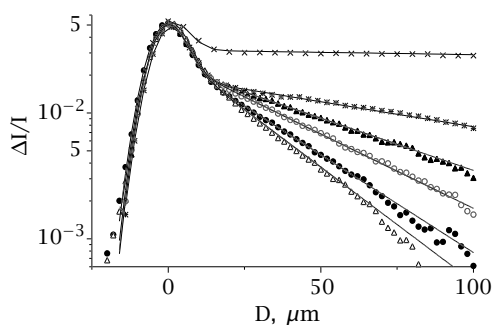


Figure 3. Typically obtained transmission change $\Delta I/I$ with oxygen as quenching agent. Excitation and probe beam wavelength 514 nm. Power of the excitation and probe beam 120 mW and 5 mW. Dye concentration $c = 0.3 \text{ mM}$. \times : $[\text{O}_2] < 0.01 \text{ mM}$, $*$: $[\text{O}_2] = 0.12 \text{ mM}$, \blacktriangle : $[\text{O}_2] = 0.23 \text{ mM}$, \circ : $[\text{O}_2] = 0.35 \text{ mM}$, \bullet : $[\text{O}_2] = 0.46 \text{ mM}$ and \triangle : $[\text{O}_2] = 0.58 \text{ mM}$. The solid lines are fitted to equation (3) with data given in Table 2.

the T state. Therefore the lifetime τ_{T} of the triplet state can be obtained by analysing the signal in this region. The values of ℓ and ε_0 are given from conventional absorption measurement. From the recorded signal the functions $c_1(D)$ and $c_{\text{T}}(D)$ can be calculated by using equation (3). These concentrations are to be interpreted as an average over the probe beam area for isotropic orientation of the molecules in ground and excited states. By comparison of the obtained concentrations the rate constant k_{ST} for intersystem crossing can be calculated by [58]

$$k_{\text{ST}} = \frac{c_{\text{T}}(0)}{c_1(0) \cdot \tau_{\text{T}} \cdot M}. \quad (4)$$

Owing to the jet motion and diameter of the excitation focus the dye molecules require a certain time to cross the region of excitation. This time is in the same order as the triplet lifetime. This fact is taken into account by introducing the factor M which is given by [58]

$$M = \frac{2}{3} \cdot \left(1 + \frac{\gamma^2}{2 \cdot (\gamma^2 + \omega^2)} - \frac{\omega^5}{\pi \cdot \gamma \cdot (\gamma^2 + \omega^2)^2} \right) \times \exp\left(-\frac{\pi \cdot \gamma}{\omega}\right) \cdot \sinh\left(\frac{\pi \cdot \gamma}{\omega}\right) \quad (5)$$

with $\gamma = 1/(v_{\text{jet}} \cdot \tau_{\text{T}})$ and $\omega = \sqrt{\pi}/a$.

For a more detailed discussion of data analysis and the spectroscopic potential of the time-resolved laser-scanning-microscopy technique see [19, 58, 65].

2.4. Intermolecular quenching of the triplet state of rhodamine 6 G. The transient absorption of a mixture of rhodamine 6 G and the agents shown in Table 1 in deoxygenated ethylene glycol is measured. These measurements are repeated for different concentrations of the agents. As exemplary shown in Figure 3 the addition of the agent leads to a change in the recorded signal. A shortening of the triplet lifetime as well as a change in the rate constant for intersystem crossing is observed. By addition of all agents shown in Table 1, the influence of the agent can be quantified by the theory of diffusion controlled interaction [69] as

$$\frac{1}{\tau_{\text{T}}} = \frac{1}{\tau_{\text{T}}^0} + k_{\text{Q}}^{\text{T}} \cdot [\text{Q}] \quad (6)$$

and

$$k_{\text{ST}} = k_{\text{ST}}^0 + k_{\text{Q}}^{\text{S}} \cdot [\text{Q}] \quad (7)$$

where

$[\text{Q}]$ concentration of the added agent,

k_{ST}^0 and τ_{T}^0 the rate constant of intersystem crossing and the triplet lifetime of rhodamine 6 G without the addition of the agent,

k_{Q}^{S} and k_{Q}^{T} quenching constants defined in equation (7) and (6).

In the coordinate system shown in Figure 4 equation (6) and (7) represents linear functions. The measured data are in good agreement with the theoretical prediction and the quenching constants can be obtained by a linear fit. In Table 1 the obtained quenching constants are given. In order to demonstrate the low triplet quantum yield Φ_{T} of rhodamine 6 G in Figure 4a the second ordinate is given.

2.5. Discussion

Oxygen. It is well known that molecular oxygen $^3\text{O}_2$ efficiently quenches triplet states. This is also measured for rhodamine 6 G triplets. Its high efficiency is apparently caused by the relatively small size of the oxygen molecule, which provides a high diffusion mobility. Beside its particular diffusion properties, molecular oxygen possesses a low lying excited singlet niveau [70] which allows triplet-triplet energy transfer from the rhodamine. Owing to its paramagnetic character [69]

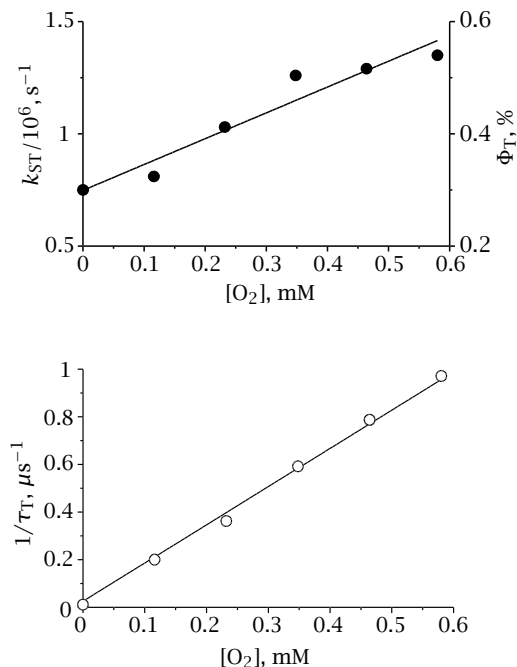


Figure 4. Rate constant for intersystem crossing and triplet lifetime of rhodamine 6G as function of the concentration of dissolved oxygen. The corresponding measurement is shown in Figure 3. The symbols indicate the measured values. The solid line is obtained by a linear fit to equation (7) and (6). The quenching constants are given in Table 1.

the presence of molecular oxygen stimulates the rhodamine molecule to an increased probability of intersystem crossing.

TEMPO. This agent also quenches the rhodamine triplet. In comparison to oxygen the quenching constant of TEMPO is considerably lower. This is not unexpected in view of its molecular dimension. As well as oxygen the paramagnetic TEMPO increases the rate constant of intersystem crossing.

COT. COT is often described as triplet quencher [71]. Nevertheless the quenching efficiency, if there is any, is discussed controversially. By the presence of COT in [72, 73] an increased intersystem crossing rate of rhodamine 6G is published. Whereas in [74, 75] COT is presented as agent which decreases the intersystem crossing rate of rhodamine 6G. The quenching constants measured in our experiment (Table 1) show the triplet state quenching efficiency of COT unambiguously. In contrast the intersystem crossing rate of rhodamine 6G is not affected by the presence of COT.

Bromoforn and iodobenzene. These agents does not influence the triplet lifetime of rhodamine 6G. The intersystem crossing rate of rhodamine 6G is increased. Owing to the presence of the heavy atoms this result is expected.

Hydroquinone and nitrobenzene. The addition of these agents neither influence the triplet lifetime nor the intersystem crossing rate of rhodamine 6G. It should be mentioned that addition of hydroquinone as well as nitrobenzene quenches the rhodamine fluorescence.

A more complete presentation of the experiments will be given in [76].

3. CONCLUSIONS

The introduced time-resolved laser-scanning-microscopy technique is very useful to investigate photophysical and photochemical properties of fluorescent dyes. Despite of its low quantum yield (1%) for triplet state population even for rhodamine dyes the population of the triplet state has still important consequences. An efficient triplet quenching can lead to improvements in widespread dye applications like dye laser, fluorescence labelling and lead to an increased photostability. It is shown that under ambient conditions quenching agents can inhibit the quenching by molecular oxygen and therefore the generation of the chemically highly reactive singlet molecular oxygen. It can be expected that the obtained information can be used in order to increase the photostability not only of rhodamine dyes.

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REFERENCES

- [1] V. Brückner, K.-H. Feller, and U.-W. Grummt, *Applications of Time-Resolved Optical Spectroscopy*, Elsevier, Amsterdam, 1990.
- [2] R. Rigler, J. Widengren, and Ü Mets, *Fluorescence spectroscopy* (Wolfbeis, ed.), Springer-Verlag, 1992, p. 13.
- [3] R. A. Keller, W. P. Ambrose, P. M. Goodwin, J. H. Jett, J. C. Martin, and M. Wu, *Appl. Spectroscopy* 7 (1996), 12A.
- [4] D. L. Taylor, A. S. Waggoner, R. F. Murphy, F. Lanni, and R. R. Birge (eds.), *Applications of Fluorescence in the Biomedical Sciences*, Alan R. Liss Inc., New York, 1986.
- [5] K. H. Drexhage, *Dye Lasers* (F. P. Schäfer, ed.), Springer-Verlag, Berlin, Heidelberg.
- [6] O. G. Peterson, *Methods of Experimental Physics* (C. I. Tang, ed.), Academic Press Inc., New York, 1979.
- [7] F. J. Duarte and L. W. Hillmann (eds.), *Dye Laser Principles*, Academic Press Inc., New York, 1990.
- [8] M. D. Archer and M. I. C. Ferreira, *Photochemical Conversion and Storage of Solar Energy* (J. S. Connolly, ed.), Academic Press, New York, 1982, p. 201.
- [9] J. Chodosh, R. D. Dix, R. C. Howell, W. G. Stroop, and S. C. G. Tseng, *Invest. Ophthalm. and Vis. Sci.* 35 (1994), 1046.
- [10] P. Morlière, R. Santus, M. Bazin, E. Kohen, V. Carillet, F. Bon, J. Rainasse, and L. Dubertret, *Photochem. Photobiol.* 52 (1990), 703.
- [11] R. C. Richmond and O'Hara, *Photochem. Photobiol.* 57 (1993), 291.

- [12] M. W. Ferguson, P. C. Beaumont, S. E. Jones, S. Navaratnam, and B. J. Parsons, *Phys. Chem. Chem. Phys.* **1** (1999), 261.
- [13] F. C. Strome, Jr. and S. A. Tuccio, *IEEE J. Quant. Electr. QE* **9** (1973), 230.
- [14] O. G. Peterson, *Methods of Experimental Physics* (C. L. Tang, ed.), Academic Press, New York, 1979, p. 251.
- [15] C. Jensen, *High-Power Dye Lasers* (F. J. Durte, ed.), Springer, New York, 1991, p. 45.
- [16] P. N. Everitt, *High-Power Dye Lasers* (F. J. Durte, ed.), Springer, New York, 1991, p. 183.
- [17] L. Hollberg, *Dye Laser Principles* (F. J. Durate and L. W. Hillmann, eds.), Academic Press, Inc., Boston, 1990, p. 185.
- [18] E. Thiel, *Eigenschaften angeregter Rhodamin-Farbstoffe und deren Wirkung im Farbstofflaser*, Shaker, Aachen, 1996, p. 99.
- [19] E. Thiel, *Eigenschaften angeregter Rhodamin-Farbstoffe und deren Wirkung im Farbstofflaser*, Shaker, Aachen, 1996, p. 23.
- [20] R. Menzel, Ph.D. thesis, University of Siegen, 1998.
- [21] R. Menzel, R. Bornemann, and E. Thiel, *Phys. Chem. Chem. Phys.*, in print.
- [22] E. Thiel, *Opt. Commun.* **160** (1999), 162.
- [23] E. Thiel, *Ullmann's Encyclopedia of Industrial Chemistry*, accepted for publication in Sixth Edition.
- [24] Ma. Heupel and E. Thiel, *J. Fluoresc.* **7** (1997), 371.
- [25] S. A. Soper and E. B. Shera, *Anal. Chem.* **63** (1991), 432.
- [26] D. A. Cremers and R. A. Keller, *Applied Optics* **20** (1981), 3838.
- [27] N. J. Dovichi and J. C. Martin, *Anal. Chem.* **56** (1984), 348.
- [28] J. Widengren, *Fluorescence Correlation Spectroscopy-Photophysical Aspects and Application*, Stockholm, 1996.
- [29] S. A. Soper, L. M. Davies, and E. B. Shera, *J. Opt. Soc. Am. B* **9** (1992), 1761.
- [30] D. C. Nguyen and R. A. Keller, *J. Opt. Soc. Am. B* **4** (1987), 138.
- [31] M. Sauer, K. T. Han, R. Müller, A. Schulz, R. Tadday, S. Seeger, J. Wolfrum, J. Arden-Jacob, G. Deltau, N. J. Marx, and K. H. Drexhage, *Journal of Fluorescence* **3** (1993), 131.
- [32] M. Sauer, K. T. Han, R. Müller, S. Nord, A. Schulz, S. Seeger, J. Wolfrum, J. Arden-Jacob, G. Deltau, N. J. Marx, C. Zander, and K. H. Drexhage, *Journal of Fluorescence* **5** (1995), 247.
- [33] J. Arden-Jacob, Ph.D. thesis, University of Siegen, 1993.
- [34] G. Jones, II, *Dye Laser Principles* (F. J. Duarte and L. W. Hillmann, eds.), Academic Press, Inc., Boston, 1990, p. 302.
- [35] H. G. O. Becker, *Einführung in die Photochemie*, p. 381, Deutscher Verlag der Wissenschaften, Berlin, 1991.
- [36] N. J. Turro, *Modern Molecular Photochemistry*, p. 579, Benjamin Publishing, Menlo Park, California, 1978.
- [37] H. H. Wasserman and R. W. Murray, *Singlet Oxygen*, *Organic Chemistry* 40 (H. H. Wasserman, ed.), Academic Press, New York, 1979.
- [38] A. P. Schaap (ed.), *Singlet Molecular Oxygen*, *Benchmark Papers in Organic Chemistry* 5, Dowden, Hutchinson & Ross, Stroudsburg, 1976.
- [39] B. Ranby and J. F. Rabek, *Singlet Oxygen*, John Wiley & Sons, Chichester, 1978.
- [40] A. A. Karasnovsky, Jr., *Photochem. Photobiol.* **29** (1987), 29.
- [41] R. W. Redmond and S. E. Braslavsky, *Chem. Phys. Letters* **148** (1988), 523.
- [42] E. Oliveros, P. Suardi-Murasecco, T. Aminian-Saghafi, A. M. Braun, and H.-J. Hansen, *Helv. Chim. Ac.* **74** (1991), 79.
- [43] A. U. Kahn and M. Kasha, *Proc. Natl. Acad. Sci. USA* **91** (1994), 12356.
- [44] D. R. Kearns, *Chem. Rev.* **71** (1971), 395.
- [45] J. R. Hurst, J. D. McDonald, and G. B. Schuster, *J. Am. Chem. Soc.* **104** (1982), 2065.
- [46] R. Schmidt, *J. Phys. Chem.* **100** (1996), 8049.
- [47] A. N. Macpherson, T. G. Truscott, and P. H. Turner, *J. Chem. Soc. Faraday Trans.* **90** (1994), 1065.
- [48] M. Mir, L. M. G. Jansen, F. Wilkinson, J. L. Bourdelande, and J. Marquet, *J. Photochem. Photobiol. A* **63** (1998), 63.
- [49] J. Georges, *Spectrochim Acta Rev.* **15** (1993), 39.
- [50] R. Brennetot and J. Georges, *Chem. Phys. Letters* **289** (1998), 19.
- [51] E. Gandin, Y. Lion, and A. Van de Vorst, *Photochem. Photobiol.* **37** (1983), 271.
- [52] H. Rosenand and S. J. Klebanoff, *J. Biol. Chem.* **252** (1977), 4803.
- [53] B. Stevens and B. E. Algar, *J. Phys. Chem.* **72** (1968), 3794.
- [54] B. Stevens and B. E. Algar, *Chem. Phys. Letters* **1** (1967), 58.
- [55] M. I. Gutiérrez and N. A. Garcia, *Dyes and Pigments* **38** (1998), 195.
- [56] R. A. Kenley, N. A. Kirshen, and T. Mill, *Macromolecules* **13** (1980), 808.
- [57] G. P. Gurinovich, O. M. Petsol'd, and I. M. Byteva, *Biofizika* **19** (1974), 249.
- [58] R. Menzel and E. Thiel, *Chem. Phys. Letters* **291** (1998), 237.
- [59] P. Meallier, M. Moullet, S. Guittonneau, F. Chabaud, P. Chevrou, and C. Niemann, *Dyes and Pigments* **2** (1998), 161.
- [60] P. Qu, J. Zhao, T. Shen, and H. Hidaka, *J. Mol. Catal. A: Chem.* **129** (1998), 257.
- [61] D. C. Neckers and O. M. Valdes-Aguilera, *Advances in Photochemistry* (D. Volman, G. S. Hammond, and D. C. Neckers, eds.), vol. 18, John Wiles & Sons, 1993, p. 315.
- [62] P. Meallier, A. Desmartin, F. Chabaud, P. Chevrou, and C. Nieman, *Bull. Soc. Chim. Fr* **131** (1994), 949.
- [63] M. D. Rahn, T. A. King, A. A. Gorman, and I. Hamblett, *Appl. Opt.* **36** (1997), 5862.

- [64] F. Stracke, Ma. Heupel, and E. Thiel, *J. Photochem. Photobiol. A: Chemistry* **5320** (1999), 1.
- [65] R. Menzel and E. Thiel, *J. Phys. Chem. A* **102** (1998), 10916.
- [66] St. Becker, I. Gregor, and E. Thiel, *Chem. Phys. Letters* **283** (1998), 350.
- [67] S. L. Murov, I. Carmichael, and G. L. Hug, *Handbook of Photochemistry*, p. 289, Marcel Dekker, New York, 1993.
- [68] S. P. McGlynn, T. Azumi, and Kinoshita (eds.), *Molecular Spectroscopy of the Triplet State*, p. 2, Prentice-Hall International, Inc., London, 1969.
- [69] M. Klessinger and J. Michl, *Lichtabsorption und Photochemie Organischer Moleküle*, Verlag Chemie, Weinheim, 1989.
- [70] S. L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973.
- [71] G. Jones, II and F. J. Duarte, *Dye Laser Principles* (L. W. Hillmann, ed.), Academic Press, Inc., New York, 1990, p. 287.
- [72] B. Zietek, P. Targowski, A. Baczynski, and J. Bissinger, *SPIE Laser Technology II*, **859** (1987), 25.
- [73] B. Zietek, P. Targowski, J. Bissinger, and A. Baczynski, *Acta Physica Polonica A* **76** (1989), 735.
- [74] A. N. Rubinov and M. M. Asimov, *J. Lumin* **15** (1977), 429.
- [75] M. M. Asimov, V. N. Gavrilenko, and A. N. Rubinov, *Opt. Spectrosc.* **54** (1983), 263.
- [76] St. Becker, I. Gregor, Ma. Heupel, and E. Thiel, in preparation for *Chem. Phys. Letters*.



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