

Kiton red S dye: Photophysical, photostability, photothermal and narrow-band laser performances using different solvents

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Abstract. Many aspects of photophysical, photostability and laser properties of kiton red S dye remain unresolved, particularly for pumping with 578 nm radiation of CVL and 532 nm output of Nd:YAG lasers, and these are studied using different alcohol- and water-based binary solvents. Our results show that methanol is better suited for low and high-repetition-rate KRS dye lasers because of its superior laser efficiency, photostability as well as photothermal properties.

Keywords. Dye lasers; Kiton red S; photothermal.

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1. Introduction

High-average power narrow-band dye lasers, pumped by high-repetition-rate copper vapour lasers (CVL) or diode-pumped solid-state green lasers (DPSSGL), are used for many scientific and technological applications such as sensitive and selective detection of ultratrace concentration of elements and isotopes, remote monitoring of atmospheric pollutants, producing laser guide star, etc. To develop such dye lasers, in oscillator-amplifier configuration, important criteria for selecting the dyes and solvents are the low photochemical degradation yield of the dye molecule in the solvent environment as well as its high conversion efficiency. Photodegradation of the dye molecules results in a deterioration of the laser output, and the consequent generation of new products may absorb either at the laser or pump wavelengths and degrade the dye laser operation severely. Some commonly used laser dyes emitting in the red region are the xanthene class – rhodamine B (RhB), Kiton red S (KRS), Rhodamine 3B (Rh3B) and rhodamine 101 (Rh101). Quantum yields of fluorescence and laser efficiencies of these dyes generally decrease in

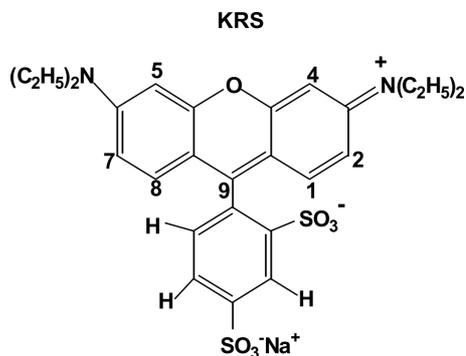


Figure 1. Molecular structure of the KRS dye.

the order Rh101 > KRS > RhB > Rh3B. Among these red dyes, KRS dye could be efficiently pumped by both the green (510 nm) and yellow radiations (578 nm) of high-repetition-rate [1] copper vapour lasers (CVL). Our earlier work [2] with the ethanol solution of KRS dye laser (DL) oscillator, excited by only the yellow component of CVL, produced tunable laser output in the wavelength range 590–635 nm, with flat peak response (efficiency $\sim 9\%$) in the region 600 nm to 620 nm. But, during the amplification of KRS dye laser oscillator output, near the oscillator peak wavelengths, with CVL (578 nm) pumped KRS dye amplifier, considerably smaller gain was observed when compared with other red dyes, such as Rh101. Also, deterioration of KRS dye laser efficiency was found at a faster rate, when compared with other xanthene dyes, which disrupted long-term operation of dye lasers.

Laser action on KRS dye was studied [3] using different pump sources, such as XeCl-excimer, nitrogen, CVL, CW-Ar⁺ lasers and flash lamp. But, studies on the performances of KRS dye lasers, excited by the second-harmonic output of Nd:YAG laser (532 nm) is limited. We have developed a narrow-band dye laser, pumped by commercially available Q-switched Nd:YAG laser, for studying the performances of KRS dye lasers using a few commonly used organic solvents such as ethanol (EtOH), methanol (MeOH), trifluoroethanol (TFE), n-propanol (n-PrOH), iso-propanol (iso-ProH) and binary solvents with water, to choose superior solvent for CVL-pumped KRS dye lasers.

2. Photophysical properties

The laser-grade dye (KRS) was procured from Radiant (Germany) and all solvents were spectroscopy grade, and used as-received. The molecular structure of KRS dye is shown in figure 1. Absorption and fluorescence (after 530 nm excitation) spectra were recorded with a UV/VIS spectrophotometer (JASCO, V-550) and on a (JASCO, FP-6500) spectrofluorimeter respectively, using various solvents. Quantum yield of fluorescence (Φ) was calculated by considering KRS in ethanol as the standard [4].

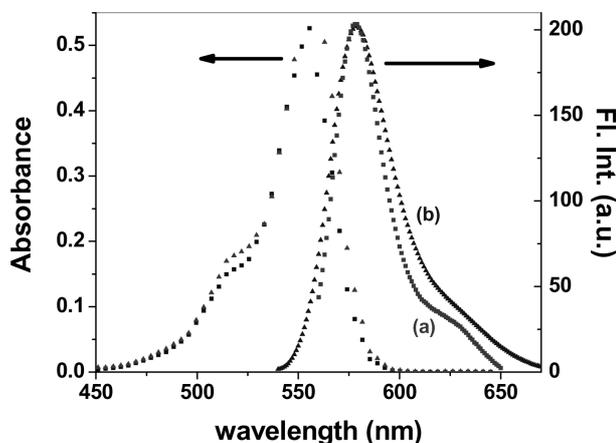


Figure 2. Absorption and fluorescence spectra of KRS dye in (a) EtOH, (b) TFE solvents.

The photophysical properties in diluted dye solutions ($<2 \times 10^{-6}$ M) were studied in 1-cm optical path length quartz cuvette. The absorption and fluorescence spectra of KRS dye in EtOH and TFE solvents are shown in figure 2. The time-resolved fluorescence measurements were carried out using a time-correlated single photon counting (TCSPC) set-up. Fluorescence decay curves were fitted as a single-exponential decay and the fluorescence lifetime (τ) was calculated from the slope. The rate constants for the radiative (k_r) and non-radiative (k_{nr}) decay of the respective dye solutions were calculated using $k_r = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$. Table 1 summarizes the photophysical properties of the KRS dye using different solvents. Trifluoroethanol solvent produced the highest fluorescence yield, followed by methanol, ethanol, iso-propanol, n-propanol in the decreasing order. To improve flow characteristics of solvents such as PrOH and TFE, photophysical properties of KRS dye were studied using the binary mixture of solvents with water. In our earlier work [5], we have observed highly efficient laser action with rhodamine 6G dye using water-based binary solvent consisting of 20% n-propanol. However, for KRS dye solutions, with increase in proportion of water in binary solvents, it was observed that absorption/emission spectra produced a large bathochromic shift, and a poor fluorescence yield. This is presumably due to water-solvated SO_3^- groups at pendant phenyl ring at 9-carbon atom of KRS molecule, which enhanced the non-radiative deactivation rate of the excited molecule through hydrogen bonding network. Thus, further laser studies on KRS dye were carried out using pure ethanol, methanol and TFE solvents.

3. Laser properties

Lasing properties of KRS dye, using EtOH, MeOH and TFE solvents, were studied in a narrow-band dye laser, transversely pumped by the second-harmonic (at 532 nm) output of a Q-switched pulsed (rep. rate = 10 Hz) Nd:YAG laser with pulse

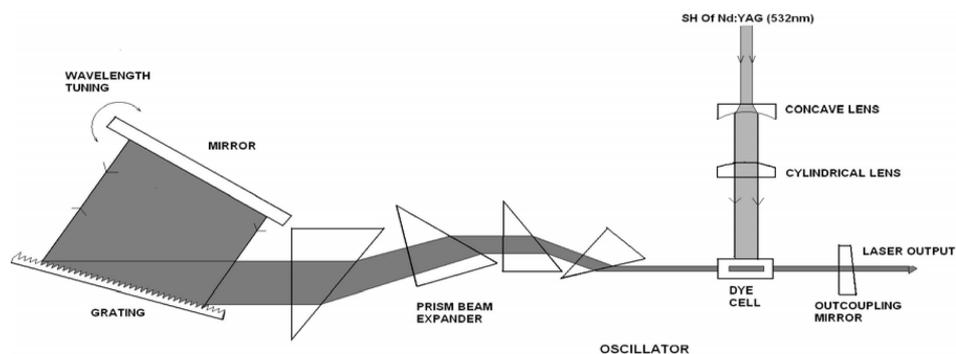


Figure 3. Schematic of the Nd:YAG pumped pulsed dye laser set-up for testing the dye solutions.

energy (~ 6.9 mJ) of 5–7 ns duration. The dye laser was set up in a grazing-incidence-grating prism pre-expander [6] configuration. In this configuration, the grating is used as a disperser, as well as, an expander. The beam expansion of the grating is given by $\cos \phi / \cos \theta$, where θ and ϕ respectively, the angles of incidence and diffraction, are determined by grating equation, $a(\sin \theta + \sin \phi) = m\lambda$, where a and m are the groove spacing and the order of diffraction, respectively. To keep the cavity loss low and linewidth of the dye laser narrow, the grating was used in the first-order diffraction, as well as, higher angle of incidence. Intracavity prism pre-expander was used so that the grating could be used at an angle of incidence ($\theta \sim 81^\circ$). The schematic of the dye laser set-up is shown in figure 3.

Oscillator cavity has 32 cm length and dye laser output was derived from a 4% reflectivity wedge flat output coupler. A 6-cm long dielectric-coated tuning mirror with high reflectivity (flatness of $\lambda/10$ at 600 nm) was used to obtain the narrow linewidth (~ 0.13 cm $^{-1}$) dye laser. The green pump beam was expanded by a plano-concave ($f = -50$ cm) lens and line focussed by a cylindrical lens ($f = 15$ cm) onto a flow-through dye cell (18 mm gain length, Lambda Physik made). The image of the pump beam formed on the dye cell has a spot size of 0.5×20 mm 2 and cross-sectional area of 0.5×0.5 mm 2 so that the dye laser output was nearly circular. The flow speed of the dye solution through the dye cell was measured by a photothermal deflection spectroscopy technique, and was found to be ~ 1 m/s with ethanol solvent. This was found adequate to clear the excited hot zone in dye cell before the next pump pulse arrived (100 ms intrapulse time). The dye laser was built mainly out of kinematically designed S.S. optical mounts and assembled on a stainless steel base plate for good thermal and mechanical stabilities. The concentration of solutions of KRS dye in ethanol, methanol and trifluoroethanol was taken for similar gain depth of pump (o.d. ~ 0.8 at 532 nm for 1 mm cell) to compare the dye laser efficiencies. The tuning curve of each dye solutions was obtained by scanning the wavelength of the dye laser through the gain profile of the dye and measuring the average pump and dye laser power with the same power meter (Ophir make). Figure 4 shows narrow-band laser performances of KRS dye using different solvents. Both the TFE- and MeOH solvent-based KRS dye lasers gave slightly higher efficiency (1–2%), and a little red-shifted (2–4 nm) peak in comparison to those of ethanol

Kiton red S dye

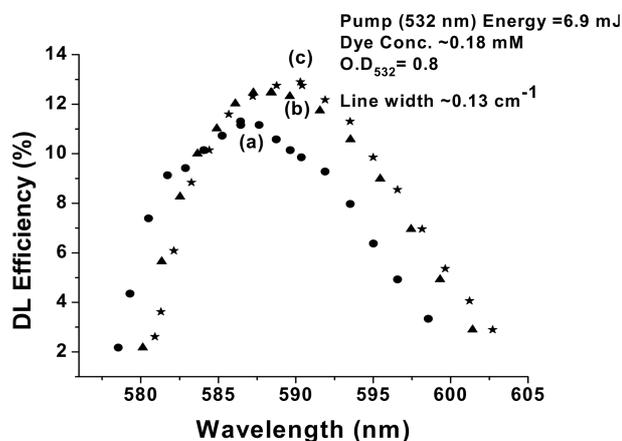


Figure 4. Narrow-band laser performances of KRS dye solutions using (a) EtOH, (b) MeOH and (c) TFE solvents.

solvent (refer table 2). But, TFE solution of KRS in dye amplifier for boosting signal from dye laser oscillator at peak wavelengths, pumped by the yellow component (578 nm) of CVL, produced non-linear amplification of the pump beam (578 nm) itself and, thus, offered poor amplifier efficiency. This was understood as large-emission cross-section of KRS dye solution at the pump wavelength of CVL (578 nm).

4. Photothermal properties

Comparative investigations on the thermo-optic characteristics of KRS dye solutions based on MeOH, EtOH and TFE solvents in a dye cell that is transversely excited by the second harmonic (532 nm) of a Nd:YAG laser, was carried out using a photothermal deflection technique, described elsewhere [5]. It consisted of a circulated dye solution through a dye cell, which was transversely excited by the pump laser and probed by a focussed red He-Ne laser ($\lambda = 632.8$ nm), as shown in figure 5. He-Ne laser was sent along the longer dimension of the dye cell, grazing the liquid dye-cell interface at the pump window. The probe beam was always kept just above (upstream) the pump beam incidence position at the dye cell by a known vertical separation (typically 0.5–2 mm). As the excited hot zone was carried upstream by the circulating dye solution, the accompanying temperature gradients and, thus, refractive index gradient produced in the hot zone due to attenuation of pump beam in dye solution caused transient deflection of the probe beam. The deflection was detected by monitoring the intensity of the probe beam by a PIN photodiode (PD) and recorded using an oscilloscope. The intense light due to the amplified spontaneous emission (ASE) from the excited region was separated from the probe signal using a grating. For similar pump energy, flow rate and probe alignment condition, as well as, comparable attenuation depth of the pump beam in KRS dye solutions comprising of MeOH, EtOH and TFE solvents gave charac-

Table 1. Photophysical properties of KRS dye in different solvents.

Solvent	λ_{\max}^a (nm)	λ_{\max}^e (nm)	Φ_f	τ (ns)	k_r ($\times 10^8$) s $^{-1}$	k_{nr} ($\times 10^8$) s $^{-1}$
EtOH	554	575	0.80	3.2	2.5	0.62
MeOH	555	576	0.86	3.11	2.76	0.45
TFE	557	578	0.90	3.50	2.74	0.11
TFE : H ₂ O 75 : 25	558	579	0.73	2.86	2.55	0.94
TFE : H ₂ O 50 : 50	559	580	0.66	2.58	2.55	1.31
n-PrOH	554	575	0.74	2.96	2.5	0.87
n-PrOH : H ₂ O 25 : 75	565	588	0.46	2.10	2.19	2.57
n-ProH : H ₂ O 50 : 50	562	585	0.43	1.97	2.18	2.89
Iso-ProH	553	573	0.79	3.12	2.53	0.67
Iso-ProH : H ₂ O 25 : 75	564	586	0.34	1.64	2.07	0.4
Iso-ProH : H ₂ O 50 : 50	561	584	0.47	2.12	2.21	2.5

λ_{\max}^a = absorption maximum, λ_{\max}^e = emission maximum, Φ_f = quantum yield of fluorescence, k_r = radiative rate and k_{nr} = non-radiative rate.

Table 2. Photodegradation rate (Q_P) and photothermal properties of KRS dye solutions.

Solvent	Tuning range (nm)	Lasing max. (nm)	% DL efficiency	Q_P ($\times 10^{-6}$)	PTD signal (V)	PTD width (μ s)
MeOH	580–601	588	12.5	6.1	4.0	400
EtOH	578–598	586	11.2	22.9	4.63	625
TFE	581–602	590	12.8	14.2	4.06	450

teristic pulses depending on the thermo-optic properties of the respective solvents. A typical photothermal deflection (PTD) signals in EtOH and TFE solvents are shown in figure 6 and average data are listed in table 2. Our results show that thermo-optic properties of MeOH and TFE are much better than that of EtOH solvent and, therefore, better suited for high-repetition rate KRS dye lasers.

5. Photodegradation properties

The photodegradation rate of KRS dye solutions, using EtOH, MeOH and TFE solvents, were determined experimentally, as described in our earlier work [5]. A known quantity of dye solution (2 ml) in a quartz dye laser cell was exposed to ~ 14.5 mJ pulse energy of a 10 Hz Nd:YAG laser at 532 nm. The concentration

Kiton red S dye

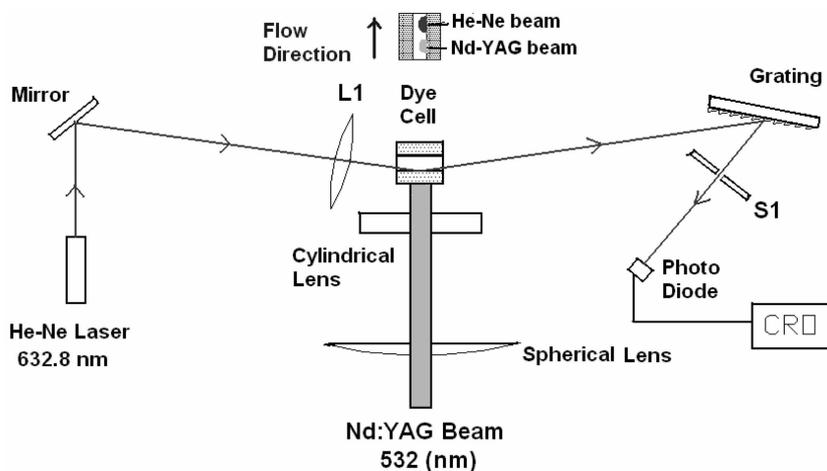


Figure 5. Photothermal deflection set-up for studying photothermal properties of dye solvents.

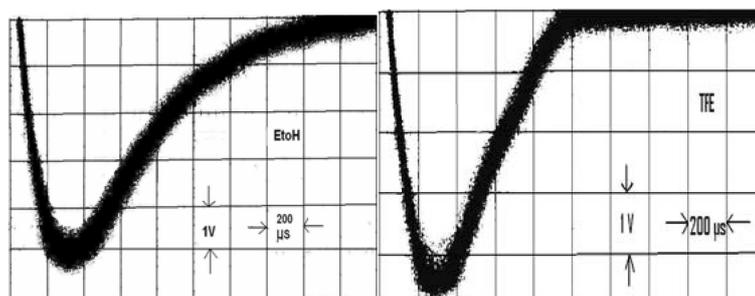


Figure 6. Photothermal deflection signals of KRS dye in (a) EtOH and (b) TFE solvents.

of the dye solutions was chosen such that the pump beam was totally absorbed during the exposure period of ~ 5 h. The number of photodegraded dye molecules in exposed volume of the dye solutions was quantitatively estimated from the measured absorbance, before, and after exposure of pump beam, at peak ($\lambda_{\text{max}}^{\text{a}}$) and other wavelengths within the absorption band using an absorption spectrophotometer. The quantum yield of the photodegradation (Q_{P}) of KRS dye solution was calculated by taking the ratio of the number of dye molecules degraded and total number of photons absorbed in the dye solution and was found to be lowest in MeOH solvent, among these three solvents (refer table 2).

6. Conclusion

In addition to generating photophysical properties of KRS dye using different solvents, the results showed that both the TFE- and methanol-based KRS dye lasers

gave slightly higher efficiency (1–2%) and a little red-shifted peak (2–4 nm) when compared with those of ethanol solvent. Further, the thermo-optic property of methanol and TFE were much better than the ethanol solvent and therefore better suited for high-repetition rate KRS dye lasers. The quantum yield of photodegradation (Q_P) of KRS dye solution was observed to be the lowest in methanol solvent, about four times less than in ethanol.

References

- [1] R S Hargrove and T Kan, *IEEE J. Quant. Electron* **QE-16**, 1108 (1980)
- [2] A K Ray *et al*, *Appl. Opt.* **41**, 1704 (2002)
- [3] U Brackmann, *Lamda Physik* (1986)
- [4] P C Beaumont, D G Johnson and B J Parsons, *J. Chem. Soc. Faraday Trans.* **94**, 195 (1998)
- [5] A K Ray, S Sinha, S Kundu, S Kumar and K Dasgupta, *Appl. Phys.* **B87**, 489 (2007)
- [6] K Dasgupta, Ph.D. Thesis (University of Mumbai, 1989)