Appl. Phys. B 48, 111–113 (1989)

Applied Physics B Photophysics and Laser Chemistry

Laser Emission from the Organic Free Radical 9-Julolidylthiyl in Solution

S. Ishizaka

Max-Planck-Institut für biophysikalische Chemie, Abteilung Laserphysik, Am Fassberg, D-3400 Göttingen, Fed. Rep. Germany

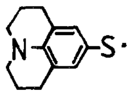
Received 7 Juni 1988/Accepted 6 October 1988

Abstract. Pulsed-laser emission in the near IR from the short-lived free radical 9-julolidylthiyl, which is generated photolytically in solution, has been observed. An apparent energy efficiency of 0.3% is achieved.

PACS: 33.00, 42.55M

Fluorescence from aromatic free radicals in solution is a rare phenomenon, because radicals have fast radiationless processes from electronically excited states, and because they are also essentially short-lived due to their chemical reactivity. Fluorescence from radicals in solution has been studied by laser-induced fluorescence spectroscopy [1–5]. We have pointed out that some organic free radicals should be considered for laser dyes and already reported laser emission from an organic free radical, p-aminophenylthiyl [6]. That was the first observation of laser emission from transient organic free radicals in solution.

In order to find other lasing organic radicals, we produced photolytically some sulfur radicals which are derivatives of p-aminophenylthiyl: p-dimethylaminophenylthiyl, p-diethylaminophenylthiyl and 9-julolidylthiyl. Fluorescence was observed from all three radicals in solution. However, laser emission was only observed from 9-julolidylthiyl



in several solvents. In this paper we report the lasing properties of 9-julolidylthiyl.

1. Experimental

Bis(julolidine) disulfide was synthesized as in [7]; it was repeatedly recrystallized from ethanol. All solvents were spectroscopic grade and used without further purification.

An experimental set-up for the radical laser, it is shown in the insert of Fig. 3, consisted of a 20 mm long silica cell with a magnetic stirrer, a silica cylindrical lens ($f = 150$) and two flat resonator mirrors. The output mirror consisted of a transparent glass plate, set at a separation of 80 mm from the other, totally reflecting aluminum mirror. A XeCl excimer laser (Lambda Physik EMG101E with pulse width of 8 ns) was used for pumping and operated at 1 Hz. The radical emission spectrum was measured with a 0.5 m monochromator (Spex 1702) and a photomultiplier (Hamamatsu R928). The signal was processed with a boxcar integrator (Lambda Physik LF300). The output energies of the XeCl and the radical lasers were measured with energymeters (Gentec ED-500 and Laser Precision Corp. RJP-735, respectively). Pulse shapes were measured with a PIN photodiode (rise time 200 ps) and a fast oscilloscope (Tektronix 7104 with plug-ins 7A29 and 7B15). For nanosecond transient spectroscopy, the XeCl excimer laser was utilized for pumping the sample and the dye laser (Lambda Physik FL2000) was used for monitoring the transmission of the sample. For measuring the time-decay, a He–Ne laser was used for the probe light source. All measurements were performed at room temperature.

2. Results and Discussion

Figure 1 shows the schematic energy diagram for 9-julolidylthiyl radical laser. The radical was produced

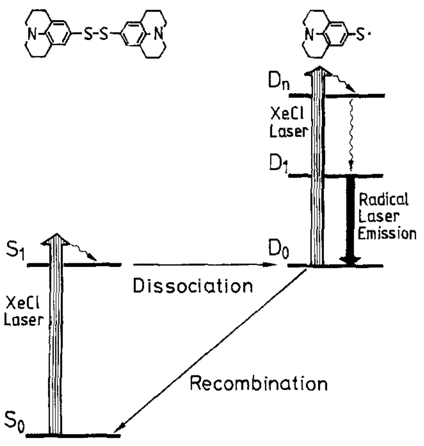


Fig. 1. Essential energy diagram for the 9-julolidylthiyl radical laser

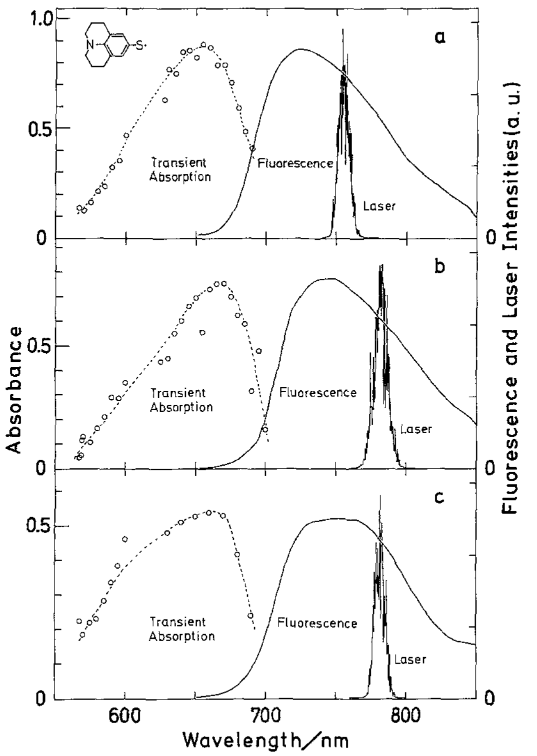


Fig. 2a–c. Spectra of the untuned laser emission, compared to the fluorescence spectra and the transient absorption spectra, in **a** diethyl ether, **b** THF, **c** 1,4-dioxane

by symmetric photodissociation of bis(julolidine) disulfide with a XeCl excimer laser pulse. The produced radicals may absorb a photon in the same laser pulse and are electronically promoted to their higher excited state (D_n). Then, these radicals relax to their first excited state (D_1). Fluorescence from the radical was observed around 750 nm and the spectra are shown in Fig. 2. The fluorescence intensity from the radical increases in proportion to the square of the XeCl laser intensity. This quadratic dependence indicates that radicals, when they are photolytically generated, are in their electronic ground state (D_0). Transient absorption spectra of the radical, which were recorded at 1 ns after the excitation, are also shown in Fig. 2. The transient absorption spectrum of the radical corresponds to its fluorescence spectrum. From the absorption decay at 632.8 nm, the radical disappears with a second-order kinetics. The main reaction is recombination which regenerates the parent compound. The ratio (k_r/ε) of the rate constant (k_r) for recombination and the extinction coefficient (ε) at 632.8 nm was obtained to be $1.4 \times 10^4\,\mathrm{cm\,s^{-1}}$ in diethyl ether, $1.1 \times 10^4\,\mathrm{cm\,s^{-1}}$ in tetrahydrofuran (THF) and $1.5 \times 10^4\,\mathrm{cm\,s^{-1}}$ in 1,4-dioxane.

The following solvents were used: ethanol, chloroform, benzene, 1,4-dioxane, cyclohexane, THF, diethyl ether, dimethyl sulfoxide, and mixed solvents of diethyl ether and cyclohexane. Laser emission was observed in mixed solvents of diethyl ether and cyclohexane, diethyl ether, 1,4-dioxane and THF solutions with a concentration of bis(julolidine) disulfide of (3–5) $\times 10^{-3}\,\mathrm{mol\,l^{-1}}$. Figure 2 shows the laser emission for diethyl ether, THF and 1,4-dioxane solutions. The dependence of the radical laser energy as a function of the XeCl laser energy is shown in Fig. 3. The threshold of laser emission is just below 30 mJ. This value is six times higher than that of p-aminophenylthiyl. A maximum overall efficiency of 0.3% was achieved. Note that this value includes the photolytic generation of the radical from the parent compound. For diethyl ether, the maximum extinction coefficient of the radical is assumed to be the same as that of

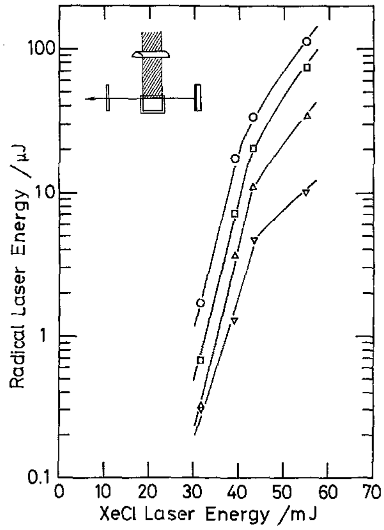


Fig. 3. Dependence of the radical laser energy on the XeCl laser energy, in (○) diethyl ether, (□) THF, (△) mixed solution of cyclohexane and diethyl ether with volume ratio of 1 : 1, and (▽) 4 : 1

Table 1. Peak wavelengths, output energies, efficiencies and pulse widths of the 9-julolidylthiyl radical laser[a]

Solvent	Wavelength [nm]	Output energy [μJ]	Efficiency [%]	Pulse width [ns]
Cyclohexane: Diethyl ether (4:1)	730	10	0.02	2.6
Cyclohexane: Diethyl ether (1:1)	740	35	0.06	3.3
Diethyl ether	754	160	0.30	3.1
1,4-Dioxane	781	5	0.01	1.6
THF	782	75	0.14	1.2

[a] Pumped by a XeCl laser using 55 mJ/pulse

p-aminophenylthiyl (1×10^4 $\mathrm{mol^{-1}\,l\,cm^{-1}}$ [8]). A maximum absorbance of 0.9 was obtained when the parent concentration was 1.0×10^{-4} $\mathrm{mol\,l^{-1}}$, the pumping intensity was 28 $\mathrm{mJ\,cm^{-2}}$ and the excited length was 1 cm. The radical concentration of 9×10^{-5} $\mathrm{mol\,l^{-1}}$ was produced. One should recall that one parent molecule makes two radicals. Therefore, at least 45% of the parent molecules was photodissociated. At the laser threshold, the concentration of the parent compound and the pumping intensity were both 30 times higher than those of the transient absorption measurement. We roughly speculate that at least 45% of the parent molecules could be photodissociated at the laser threshold.

Laser wavelengths, maximum output energies and pulse widths are summarized in Table 1. The emission cross section of 0.3 Å^2 at 654 nm in diethyl ether was estimated from the corresponding value of the quantum distribution over wavenumber (normalized to one, Fig. 2a) and the radiative lifetime of the radical [9, 10]. The radiative lifetime of 60 ns in diethyl ether was calculated by use of the Strickler-Berg formula [11], if the extinction coefficient of the radical was assumed to be 1×10^4 $\mathrm{mol^{-1}\,l\,cm^{-1}}$. The pulse width of the radical laser was quite sensitive to the XeCl laser energy: 3.1 ns at 55 mJ, 1.2 ns at 43 mJ and 0.7 ns at 39 mJ were observed in diethyl ether. This pulse shortening can be explained as follows. This radical laser process needs essentially two photons, the density of the upper laser level (D_1) increases in proportion to the square of the XeCl laser energy. Therefore, the pulse width of the laser is strongly affected by the pumping energy.

By comparison, the laser wavelength is 100 nm longer than that of p-aminophenylthiyl in the same solvent, while the output energy is one order of magnitude lower.

Acknowledgements. The author is indebted to Prof. F. P. Schäfer for valuable discussions. A research fellowship from Alexander von Humboldt-Foundation is gratefully acknowledged.

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