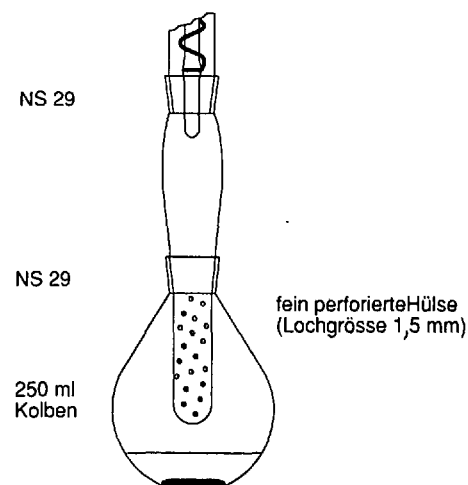


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Solid-State Tunable Lasers in the Visible, Based on Luminescent Photoresistant Heterocyclic Colorants

Renata Reisfeld* and Gunther Seybold**

Abstract. Tunable lasers in the visible can be designed by incorporating perylene dyes into composite glass-polymer materials. Criteria of photostability will be discussed, and possible uses of these lasers indicated.

Introduction

Tunable lasers can be induced to emit an almost monochromatic line selected in a fairly broad luminescence band. Since a decade, several transition-group ions (such as Ti(III) and Cr(III)) in crystals are known to emit in the IR, and the conditions for tunable lasing have been studied extensively. Such conditions have not been found in the visible.

The need for a *solid-state* tunable laser is obvious. Liquid dye lasers are found in all physical or chemical research laboratories and are now being used in such fields as selective destruction and photodynamic therapy (e.g. the recent technique of laser lithotripters) and *in situ* diagnostics of tissues. However, one of the important aspects of the relatively slow acceptance of laser technology in medicine is the cumbersome technique involving the flow of liquid dye, problems of maintenance such as changing of the spectral range of the laser emission (and sometimes the use of toxic organic solvents). In medicine as well as in

industry, there is a need for a completely reliable 'black box' with minimum maintenance and fast and easy change of wavelengths. Solid lasers have clear technical advantages over liquid dye lasers, such as compactness and absence of toxic solutions, qualities particularly appealing in clinical use.

The laser transitions in partly filled 3d or 4f shells are parity-forbidden, and frequently also spin-forbidden [1]. The tunability of transition-metal ions arises from the fact that the terminal laser levels in certain cases consist of a large number of vibronic excitations (resolved or appearing as a continuum) of the electronic ground-state. Although the stability of these systems is excellent, the low-absorption cross-sections require strong pumping illumination in order to achieve the laser threshold [1]. These high energy concentrations may also be responsible for excited-state absorption, the luminescent state absorbing some of the emitted photons to arrive at various higher excited states. The best known tunable lasers based on Cr(III) [2]

[3] and on Ti(III) [4] operate in the near IR part of the spectrum.

Organic dyes have usually cross-sections of absorption and emission several orders of magnitude higher than transition-group elements, and correspondingly lower threshold powers for laser action. Furthermore, laser emission of several selected dyes can be obtained, covering the entire VIS spectrum [5].

In this paper, we shall first summarize the principles of laser action of organic dyes and discuss the requirements for their stability, followed by a description of stable solid-state tunable lasers and a brief review of recent advances in medical treatment using lasers, and finally a sketch will be made of how to operate lasers in the entire VIS spectrum.

Principle of Operation of Lasers Based on Organic Dyes

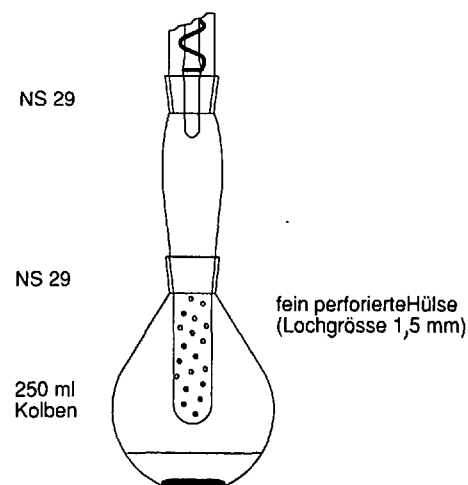
By absorbing light of appropriate frequency, a molecule is transferred from its electronic ground state (1S_0) to its first excited (1S_1) or highly lying excited singlet states (1S_n) (cf. Fig. 1). In the condensed phase, the molecule undergoes a fast radiationless deactivation within 10^{-13} s to the vibrational ground state of the first excited singlet state (1S_1). From this state, there exists at least three deactivation pathways, namely internal conversion (k_{IC}) - a radiationless process to the ground state (1S_0) -, fluorescence emission (k_F) into the ground

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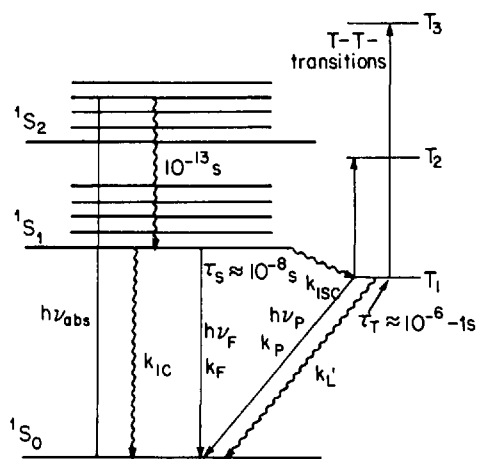


Fig. 1. Jablonski diagram

state, and finally an intersystem crossing process (k_{ISC}) to the triplet term system.

The triplet state is a long-lived metastable state during which various photochemical processes may occur. It is, therefore, important for the molecules designed for lasers that the singlet-triplet transfer be minimized or preferable absent.

Fluorescence emission should be the predominating process for laser dyes. The laser dyes should have fluorescence quantum yields near 1.

Stable Dyes which Can Be Used for Lasers

Perylimide dyes of the type exemplified in the Scheme are characterized by their extreme photostability and negligible singlet-triplet transfer [6]. They have also high quantum efficiency because of the absence of non-radiative relaxation. The perylene dyes are also characterized by limited solubility in conventional solvents due to the planar structure of the molecule which facilitates the formation of crystals with high lattice energies. These dyes have been applied for fluorescent solar concentrators made of poly(methyl methacrylate) [6] [7]. However, the acrylic system was not stable enough for application in lasers [8].

Scheme

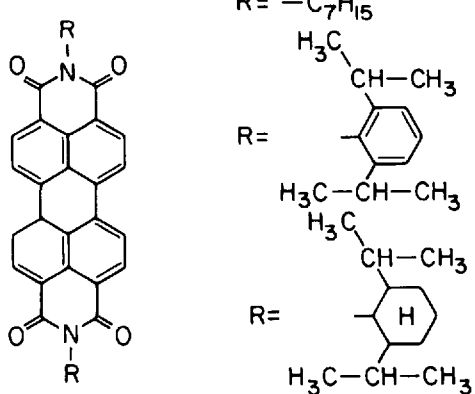


Table. Optical Characteristics of Perylene Dyes

Dye	$\lambda_{abs\ max}$ [nm]	$\lambda_{em\ max}$ [nm]	Molar extinc. coeff.	Quantum efficiency [%]
Yellow	474	508	48000	91
Orange	525	540	85000	100
Red	578	613	44000	96
Blue	610	685	63000	92

Polycyclic dyes derived from perylene have the spectroscopic properties given in the Table.

In recent years, it has been shown that a great number of organic dyes soluble in alcohol can be introduced at low temperature into inorganic glasses prepared by the sol-gel method [9].

The low-temperature process for preparing inorganic glasses by sol-gel synthesis consists of hydrolysis of alkoxy-silanes followed by polycondensation (Fig. 2). During this process, an organic dye can be introduced into the starting solution and finally incorporated in the monomeric form in the glass. For the perylimide dyes insoluble in the reaction precursors a slightly modified process has to be used [10].

Rhodamine 6G and coumarin dyes [9] [11] and sulforhodamine dyes [12] introduced into sol-gel glasses exhibited laser characteristics; however, because of the low photostability of the dyes the laser was photodecomposed shortly after excitation.

Photostable perylene dyes can be introduced into composite glasses in which the sol-gel method is also applied. The composite glasses are prepared by the method described in [13]. The perylene dye is dissolved in methyl methacrylate at a concentration of $ca. 10^{-3}$ M. The sol-gel bulks are then impregnated by immersion in the dyed solution of the monomer catalyzed by 2% benzoyl peroxide. After impregnation, the bulks are reimmersed in the solution of methyl methacrylate catalyzed by 0.5% of benzoyl peroxide in a sealed container for 4 d at 60°. The samples are then withdrawn, cleaned, and polished manually to a reasonable surface quality to obtain slabs with typical dimensions of $10 \times 2 \times 2$ mm.

The laser action of orange perylimide (cf. the Table) was tested by frequency-doubled Nd-YAG. The laser threshold is less than 60 mJ and slope efficiency so far obtained is 7.4%.

A significant increase of the efficiency is expected with large size samples.

The dye characteristics as a laser material were obtained by pumping transversely with a frequency doubled pulsed Nd-YAG laser [14]. The 532-nm pump beam was focused onto the dye sol-gel glass surface by a combination of spherical and cylindrical lenses to form a line of dimensions 5×0.2 mm. Lasing was obtained in a cavity of either a combination of a 100% reflecting metallic black mirror and around 30% reflecting output coupler, or a combination of a grating of 2400 grooves/mm at Littrow configuration as the back reflector, and an 8% reflecting window as the output coupler.

Absorption and fluorescence emission spectra of the sample under continuous illumination are presented in Fig. 3. The spectra exhibit the expected Stokes shift (~ 20 nm for the 0-0 transition) and mirror image between absorption and fluorescence, with a pronounced structure reflect-

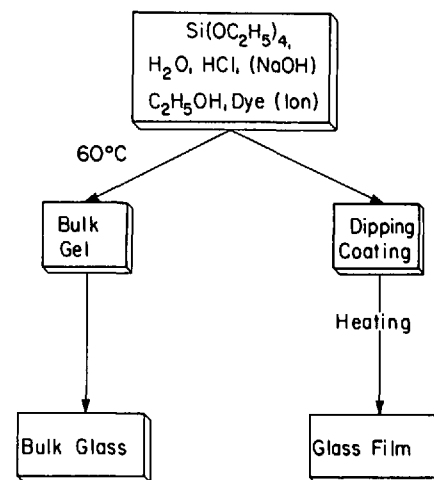


Fig. 2. Scheme of preparation of sol-gel bulks and films

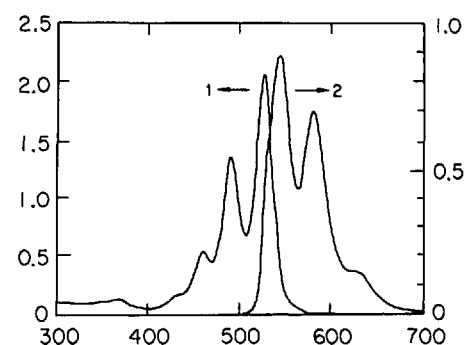


Fig. 3. Absorption and emission spectra of perylene dye BASF-241 in a composite material. Ordinate left, optical density (1). Ordinate right, relative intensity of fluorescence (2). Abscissa, wavelength in nm.

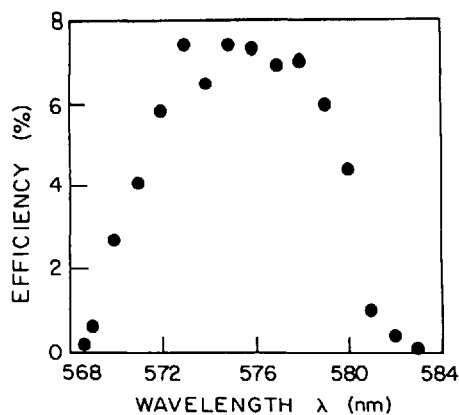


Fig. 4. BASF 241 laser efficiency vs. wavelength for a 532-nm pump wavelength of energy of 2 mJ/pulse

ing the coupling of the electronic transition with the bending modes of the perylene skeleton at ~ 1300 cm^{-1} . The three prominent fluorescence peaks are centered at ~ 540 , ~ 580 , and ~ 630 nm.

The laser efficiency spectrum in the cavity configuration which consisted of the grating and the 8% reflecting output coupler is given in Fig. 4.

Laser Applications in Medicine

Laser applications in medicine constitute a rapidly growing field. Lasers are well known in surgery as effective cutting tools,

and surgeons find them especially useful when dealing with hypervascularized tissue because of the coagulating properties of the radiation. The penetration depth of laser light into tissue is largely determined by the absorption properties of water, hemoglobin, and the skin pigment melanin. The resulting effective surgical penetration in the tissue is about 0.1 mm for the CO₂ lasers ($\lambda = 1.06 \mu\text{m}$) and 1 mm for the Ar⁺ laser ($\lambda_1 = 488$ and $\lambda_2 = 515$ nm) [15].

The alternative mechanism suggested is absorption of light in homogeneously distributed chromophores. Thermal relaxation of these chromophores causes superheating of water, and microexplosions result in ablation. No plasma emission can be detected. IR light is absorbed in the water, and the rapid vaporization of the water results in tissue ablation. The tissue is removed cell layer by cell layer, resulting in well-defined incisions with smooth tissue surface cuts; the surrounding tissue is not affected to any large extent. This ablative tissue interaction is useful in vascular surgery [15].

Although spectroscopic aspects in terms of absorption properties play a part in photothermal and photoablative treatment, they are much more important in the fields of photodynamic therapy and tissue diagnostics using laser-induced fluorescence (LIF). Laser interaction with tissue is reviewed in [16–18].

Another interesting medical application of a laser-produced plasma is to induce stone fracturing in biliary and urinary calculi (gallstones and kidney stones). By forming plasma at the surface of the stone submerged in a liquid, a shock wave with extremely high local pressures can be produced that will induce fracturing of the stone into small fragments (laser lithotripsy). For this application, a flashlamp dye laser is suitable, because hundreds of millijoules per pulse can be readily transmitted through a thin fiber. For the long pulses typical for these lasers (1 μs), no damage is induced in the fiber. For a Q-switched Nd-YAG pulse with a typical length of 10 ns, pulse energies well below 100 mJ must be chosen to avoid breakdown at the fiber surface. Again, the laser-produced plasma can be spectrally analyzed and differences in stone composition detected.

For some time, tumor-seeking agents such as hematoporphyrin derivative (HPD) have been used in combination with laser radiation to localize and treat malignant tumors. Recent progress in this field is described in the literature. In this technique, HPD is intravenously injected at a low concentration into the biological system, where the agent spreads and is subsequently cleared out of the body through natural processes. However, for reasons that remain partly unknown, the HPD molecules are selectively retained in the malignant tumor cells and in the endothelium cells in the tumor vascular system.

The excited HPD molecules can, alternatively, transfer their acquired energy to oxygen molecules in the tissue. This transfer is mediated by the long-lived triplet HPD state to which radiationless transitions occur. Triplet HPD molecules transfer their energy to oxygen molecules that are promoted from their ground X³ Σ_g^- state to the ¹A_g state. Singlet molecular oxygen is known to be a strong cytotoxic agent that violently oxidizes the surrounding (tumor) tissue. The laser-induced chemical process, which is referred to as HPD-PDT (hematoporphyrin derivative photodynamic therapy), is normally performed with laser light at 630 nm, where the HPD molecule has a minor absorption peak, and where the tissue has a much better light transmission than at shorter wavelengths. Although very small light doses are needed to induce observable fluorescence, efficient therapeutic action requires much more light, and normally a dye laser pumped by an Ar⁺ laser or a gold vapor laser ($\lambda = 628$ nm) is employed. Encouraging results have been obtained in clinical trials using HPD-PDT.

Because of the limited light penetration in tissue, only thin superficial lesions can be treated by direct surface irradiation. Deeper penetration could be obtained, if the laser fiber be implanted in the tumor mass through the lumen of a syringe needle.

Because of the reasons outlined in this paragraph, a glass laser emitting in the VIS range could be produced in a fiber form and introduced deep into the tissue needing to be tested and treated. As an excitation source for such a laser, it would be most reasonable to use either directly as a diode laser source or alternatively a Nd laser pumped by a diode laser whereby a second harmonic generation could be achieved.

Diode Lasers

The latest advances in pumped technology are diode lasers [19] which, with careful design of the pump optics and pumping, can provide slope efficiencies close to the theoretical limit. Diode lasers pumped solid lasers are efficient, compact solid-state sources for laser emission.

Second harmonic generation providing 530-nm radiation was reported recently by Fan *et al.* and Baer who demonstrated efficient internal second-harmonic generation with the nonlinear crystal lithium niobate in a diode laser-pumped Nd-YLF laser. The harmonic conversion efficiency can be further increased by generating high circulating powers in an external cavity which can be resonant at either the second-harmonic or at the fundamental wavelength [19].

Since, as described above, the tunable dye laser glasses are formed at room temperature, the diode-pumped lasers can be introduced as an integral part of the com-

posite glass so that there are no losses due to reflection and scattering as in conventional systems.

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