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 laser 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 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] and on Ti(III) [3] 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 [4].

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.

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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 (λ = 1.06 μm) and 1 mm for the Ar⁺ laser (λ₁ = 488 and λ₂ = 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].

Abnormal spectroscopic aspects in terms of absorption properties play a part in photothermal and photoablativ 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].

Although a photographic 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 endothelial 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 state to the S₂ 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 (λ = 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 outweighing in the VIS range could be produced in a fiber format 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 Bauer 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 composite glass so that there are no losses due to reflection and scattering as in conventional systems.

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