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Dye Lasers

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DYE LASERS

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INTRODUCTION

In the past decade dye lasers have become indispensable tools of laser spectroscopy and have also found an ever increasing number of other scientific and technological applications. The basis of their success is their broad tunability as well as a number of other outstanding properties that are never found in this singular combination in any other class of lasers. This is caused by the fact that the active medium in dye lasers is in general a liquid solution of organic dyes and thus enter the powerful synthetic methods of organic chemistry to create an infinite variety of different molecules which can be tailor-made to meet the constantly increasing demands of new applications.

The present wavelength coverage of dye lasers is from about 300 nm to about 1500 nm and the prospects for a further extension towards longer and shorter wavelengths with newly synthesized dyes are good. The typical tuning range of a single dye is about 50 nm and can be extended in special cases to 130 nm.

The gain of dye lasers can be made extremely high, so that lasers with only a few microns of active length can be operated. In amplifiers one has actually achieved amplification factors of 10^8.

In this context it is important to mention the very large cross-sections of dye molecules in absorption as well as in emission, which are of the order of 10^{-16} cm^2. These together with the wide spectral bandwidth are the reason for the good mode-locking that is possible with dye lasers and which has resulted in the shortest laser pulses of only 30 fs that have been achieved recently.

Another important advantage of dye lasers is that the active medium is generally used in the liquid phase, even though operation of dye lasers with the active medium in the vapor phase or in solid solution is possible. This means that flow systems can be used to carry away excess heat and to cool the active medium as well as the reservoir to any wanted operating temperature even at high average powers. Recently more than a kW of average output power was obtained in a pulsed dye laser and there is no physical reason why it should not be possible to realize even much higher powers.

The high powers just mentioned could make dye lasers candidates for industrial applications, provided the efficiency is high enough. This unfortunately is a serious drawback of dye lasers at the present time, since the highest wall-plug efficiencies reported are those of flashlamp-pumped dye lasers with about 1.0%. There is good hope, however, that new dyes could raise this efficiency to over 5%, which could make dye lasers become competetive with CO_2 lasers in applications where the shorter wavelength of dye lasers is important.

Finally, one must also be aware of the fact that dyes as active medium are extremely cheap compared to crystals and glasses of solid-state lasers, even though the photo-degradation of dyes during laser operation makes a constant partial replacement of the dyes necessary. The problem of dye photo-degradation might, however, soon be solved at least in certain chemical classes of dyes on which synthetic work in this direction is in progress.

In the following section the general properties of dyes will be discussed in more detail, in particular chemical structure, light absorption and emission and pathways for radiationless deactivation of dyes. The second, third, and fourth section will discuss laser-pumped, flashlamp-pumped, and continuous-wave dye lasers, respectively. The next sections will explain tuning methods, dye laser amplifiers, and mode-locking of dye lasers. Finally some special types of dye lasers will be discussed.

1.

GENERAL PROPERTIES OF ORGANIC DYES

All organic dyes in the proper sense of the word, meaning compounds having a high absorption in the visible part of the spectrum, possess several conjugated double bonds. The basic mechanism for light absorption by compounds containing conjugated double bonds is the same, in whatever part of the spectrum these compounds have their longest wavelength absorption band, whether near-infrared, visible, or near ultraviolet. We thus use the term dye in the wider sense as encompassing all substances containing conjugated double bonds.

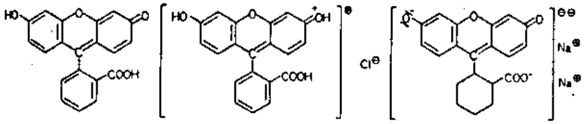
Organic compounds without double or triple bonds usually absorb at wavelengths below 160 nm, corresponding to a photon energy of 180 kcal/-mole. This energy is higher than the dissociation energy of most chemical bonds, therefore photochemical decomposition is likely to occur, so such compounds are not very suitable as the active medium in a laser.

If we have two conjugated double bonds, as in the molecule butadiene, $H_2C{=}CH{-}CH{=}CH_2$, the long-wavelength absorption band is at about 220 nm. Since the fluorescence, and hence the laser emission is always red-shifted, dye lasers can hardly be expected to operate below about 250 nm.

The long-wavelength limit of dye laser operation is determined by the chemical stability of the dye. A dye absorbing in the infrared has a low-lying excited singlet state and, even slightly lower than that, a metastable triplet state. The triplet state has two unpaired electrons and thus, chemically speaking, biradical character. There is good reason to assume that most of the dye molecules that reach this highly reactive state by thermal excitation will react with solvent molecules, dissolved oxygen, impurities, or other dye molecules to yield decomposition products. The decomposition would be of pseudo-first order with a reaction constant $k_1{=}A\exp(-E_a/RT)$, where A is the Arrhenius constant and has most often a value of about $10^{12}\,\mathrm{sec}^{-1}$ for reactions of this type (ranging from 10^{10} to 10^{14} sec^{-1}), E_a is the activation energy, R is the gas constant and T the absolute temperature. The half-life of such a dye in solution then is $t_{1/2}{=}\ln2/k_1$. Assuming as a minimum practical lifetime one day, the above relations yield an activation energy of 24 kcal/mole, corresponding to a wavelength of 1.2 µm. If $A{=}10^{10}$ sec^{-1}, this shifts the wavelength to 1.7 µm. Obviously there is little hope of ever preparing a dye absorbing beyond 1.7 µm that will be stable in solution at room temperature. Thus dye-laser operation at room temperature in the infrared will be restricted to wavelengths not extending far beyond 1.7 µm.

An important subdivision of dyes is into ionic and uncharged compounds. This feature mainly determines melting point, vapor pressure, and solubility in various solvents. An uncharged dye already mentioned is butadiene; other examples are aromatics: anthracene, pyrene, perylene, etc. Examples of neutral moelcules that are efficient laser dyes, like coumarins, stilbenes, or oxazones will be discussed later. They usually have low melting points, relatively high vapor pressures, and good solubility in unpolar solvents, like benzene, cyclohexane, chloroform, etc. Examples for cationic dyes include most of the cyanine dyes. These compounds are salts, consisting of the positively charged dye ion and some negatively charged counterion, like chloride, tetrafluoroborate, perchlorate, etc. They have high melting points, very low vapor pressure over the temperature region where they are stable, good solubility in more polar solvents like alcohols, and only slight solubility in less polar solvents. The same can be said of anionic dyes, which usually have some metal counter-ion.

Many dyes can exist as cationic, neutral and anionic molecules depending on the pH of the solution, e.g. fluorescein:



Neutral form
(alcoholic solution)

Cationic form
(hydrochloric acid solution)

Di-anionic form
sodium hydroxyde solution

It should be stressed here that dyes can be used as active media in the solid, liquid and vapor phase. It is clear from the above discussion that only uncharged dyes would work well in the vapor phase. Since most dyes form good single crystals, it might seem attractive to use them directly in this form. There are, however, two main obstacles to that: The extremely high values of the extinction coefficients in dyes, which prevents the pump light from exciting more than a surface layer a few microns thick; and the concentration quenching of fluorescence that usually sets in, whenever the dye molecules approach each other closer than about 10 nm.

Doping a suitable host crystal with a small fraction (one thousandth or less) of dye circumvents these difficulties. On the other hand, solid solutions of many different types can be used. For instance, one can dissolve a dye in the liquid monomer of a plastics material and then polymerize it; or one can dissolve it in an inorganic glass (e.g. boric acid glass) or an organic glass (e.g. sucrose glass) or some semirigid material like gelatine or polyvinylalcohol. One can also operate a dye laser at low temperatures in an organic solvent or solvent mixture like EPA, a mixture of 5 parts of ethylether, 5 parts isopentane, and 2 parts ethanol that forms a clear organic glass when cooled down to 77 K.

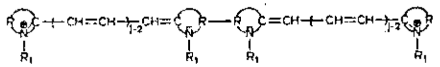
1.1 Light Absorption by Organic Dyes

Wavelengths and strength of light absorption of dyes can be calculated in good agreement with experimental data by the highly refined methods of quantum chemistry. The best physical insight, however, is provided by a highly simplified quantum-mechanical model, such as the free-electron gas model developed by KUHN(1). This model is based on the fact that dye molecules are essentially planar with all atoms of the conjugated chain lying in a common plane and linked by sigma-bonds. By comparison, the pi-electrons have a node in the plane of the nuclei and form a charge cloud above and below this plane along the conjugated chain. The centers of the upper and lower lobes of the pi-electron cloud are about one half bond-length distant from the molecular plane. Hence the electrostatic potential for any single pi-electron moving in the field of the rest of the molecule may be considered constant, provided all bond lengths and atoms are the same. Assume, that the conjugated chain which extends approximately one bond length to the left and right of the terminal atoms has length L. Then the energy E_n of the n-th eigenstate of this electron is given by $E_n = h^2n^2/8mL^2$, where h is PLANCK's constant, m is the mass of the electron, and n is the quantum number giving the number of antinodes of the eigenfunction along the chain. According to the Pauli principle each state can be occupied by two electrons. Thus, if we have N electrons, the lower 1/2N states are filled with two electrons each, while all higher states are empty (provided N is an even number; this is usually the case in stable molecules since only highly reactive radicals possess an unpaired electron). The absorption [illegible] (where λ is the wavelength of [illegible] radiation [illegible]

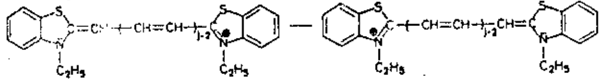
light) raises one electron from an unoccupied to an empty state. The longest wavelength absorption band then corresponds to a transition from the highest occupied to the lowest empty state with

$$\Delta E_{min} = \frac{h^2}{8mL^2}(N+1) \quad \text{or} \quad \lambda_{max} = \frac{8mc_0}{h}\,\frac{L^2}{N+1}.$$

This indicates that to a first approximation the position of the absorption band is determined only by the chain length and by the number of pi-electrons N. Good examples of this relation are the symmetrical cyanine dyes of the general formula



where j is the number of conjugated double bonds, R_1 a simple alkyl group like C_2H_5, and R indicates that the terminal nitrogen atoms are part of a larger group, as for example in the following dye (homologous series of thiacyanines):



The double headed arrow means that the two formulae are limiting structures of a resonance hybrid. The pi-electrons in the phenyl ring can be neglected in first approximation, or treated as a polarizable charge cloud, leading to an apparent enlargement of the chain length L. In the case of the last-mentioned dye, good agreement is found between calculated and experimental absorption wavelength, when the chain length L is assumed to extend 1.3 bond lengths (instead of 1.0 bond length as above) beyond the terminal atoms. The bond length in cyanines is 1.40 angstrom. The good agreement between the results of this simple calculation and the experimental data is shown by the following comparison:

Wavelength (in nm) of absorption maximum for thiacyanines

	Number of conjugated double bonds j=			
	2	3	4	5
Calculated	395	521	649	776
Experimental	422	556	652	760

Similarly good agreement can be found for all other homologous series of symmetrical cyanines, once the value of the end length extending over the terminal nitrogen atoms is found by comparison with the experimentally observed absorption wavelength for one member of the series.

A simple perturbation treatment allows to calculate the influence of such factors as hetero atoms in the conjugated chain, variable bond lengths as in polyenes, or branching of the pi-electron system as in many dyes, e.g. those of the xanthene class of laser dyes. The oscillator strength of the absorption bands can also be calculated easily by the free-electron model and yields good agreement with experimental data. For a more detailed description the reader is referred to (1).

A peculiarity of the spectra of organic dyes as opposed to atomic and ionic spectra is the width of the absorption bands, which usually covers several tens of nanometers. This is immediately comprehensible when one recalls that a typical dye molecule may possess fifty or more atoms, giving rise to about 150 normal vibrations of the molecular skeleton. These vibrations together with their overtones, densely cover the spectrum between a few wavenumbers and 3000 cm^{-1}. Many of these are closely coupled to the electronic transition. Furthermore, collisional and electrostatic perturbations, caused by their surrounding solvent molecules broaden the individual lines of such vibrational transitions. As a further complication, every vibrational sublevel of every electronic state, including the ground state, has superimposed on it a ladder of rotationally excited sublevels. These are extremely broadened because of the frequent collisions with solvent molecules which hinder the rotational movement so that there is a quasicontinuum of states superimposed on every electronic state. The population of theses levels in contact with thermalized solvent molecules is determined by a Boltzmann distribution. After an electronic transition, which leads to a non-equilibrium state (Franck-Condon state), the approach to thermal equilibrium is very fast in liquid solutions at room temperatures, usually taking less than a picosecond (2). Thus the absorption is practically continuous all over the absorption band. The same is true for the fluorescence emission corresponding to the transition from the electronically excited state to the ground state. This results in a fluorescence band which is a mirror image of the absorption band, displaced towards lower wavenumbers by reflection at the the wavenumber of the purely electronic transition (0-0 transition).

Recently it has become possible to obtain absorption and emission spectra of laser dyes at very low temperatures in the gas phase (3). These spectra exhibit a number of sharp lines as is to be expected from the above discussion of the influence of temperature and solvent.

The concentration dependence of dye spectra is most pronounced in solutions where the solvent consists of small highly polar molecules, notably water. Dispersion forces between the large dye molecules tend to bring the dye molecules together in a position with the planes of the molecules parallel, where the interaction energy usually is highest. This is counteracted by the repulsive Coulomb forces if the dye molecules are charged. In solvents of high dielectric constants this repulsion is lowered and the monomer-dimer equilibrium is far to the side of the dimer.

The spectral differences between monomer and dimer can easily be understood at least qualitatively (4). The degenerate energy levels of two monomers split into two levels of different energies if they come close enough to experience interaction energy and the concomitant formation of a dimer. Now two transitions are possible, and these in general possess different transition moments depending on the wave functions of the dimer. Most often the long-wavelength transition has a practically vanishing transition moment, so that only one absorption band of the dimer is observed, lying to the short-wavelength side of the monomer band. This has an important consequence for the fluorescence of such dimers. Since the upper level from which the fluorescence starts is always the lowest-lying excited electronic level, and since a small transition moment is coupled to a long lifetime of the excited state, these dimers would show a very slow decay of their fluorescence. This, however, makes them susceptible to competing quenching processes, which in liquid solutions are generally diffusion-controlled and hence very fast processes. Consequently, in most of the cases the fluorescence of the dimers is completely quenched and cannot be observed.

This is the reason why dimers constitute an absorptive loss for the pump radiation in dye lasers and must be avoided by all means. There are several ways in which this may be done. One is to use a less polar solvent, like alcohol or chloroform. There are very few dyes which show dimerization in alcohol at the highest concentrations and at low temperatures. Another possibility is to add a detergent to the aqueous dye solution, which then form micelles that contain one molecule each (5).

Acid-base equilibria have already been mentioned above for the case of fluorescein. Very often these equilibria are less obvious and several examples will be shown, when specific classes of laser dyes are discussed.

1.2 Light Emission by Organic Dyes

There are many processes by which an excited molecule can return directly or indirectly to the ground state. Some of these are schematically depicted in Fig. 1.

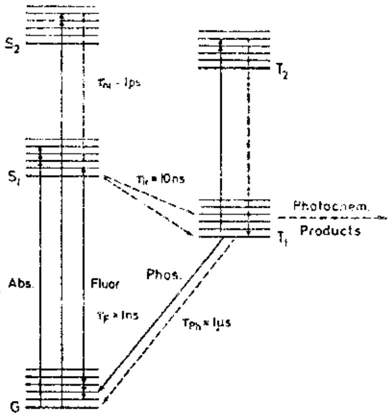


Fig 1. Energy level diagram of a typical dye molecule with radiative (solid lines) and non-radiative (broken lines) transitions

It is the relative importance of these which mainly determine how useful a dye will prove in dye lasers. The one process that is directly used in dye lasers is the radiative transition from the first excited singlet state S_1 to the ground stat G. If this emission, termed "fluorescence", occurs spontaneously, its radiative lifetime τ_{rf} is connected with the Einstein coefficient A and the oscillator strength f of the pertinent absorption band by

$$A \equiv 1/\tau_{rf} = (8\pi^2\mu^2 e_0^2/m_0 c_0)\tilde{\nu}^2 f,$$

where μ is the refractive index of the solution, e_0 is the charge and m_0 is the mass of the electron, c_0 is the velocity of light, and $\tilde{\nu}$ denotes the wavenumber of the center of the (narrow) absorption band. This relation is valid if the half-width of the emission band is small and its position is not shifted significantly from that of the absorption band. Since the f-values of the transitions are near unity in most dyes, the radiative lifetime τ_{rf} is typically of the order of a few nanoseconds. Generally, however, the fluorescence spectrum is broad and shows considerable Stokes shift. In this case the radiative lifetime can be computed with the Strickler-Berg relation (6):

$$\frac{1}{\tau_{rf}} = 2.88\times10^{-9}\mu^2 \frac{\int F(\tilde{\nu})d\tilde{\nu}}{\int \tilde{\nu}^{-3}F(\tilde{\nu})d\tilde{\nu}} \int_{\substack{\text{longest}\\ \text{wavelength}\\ \text{absorption band}}} \frac{\varepsilon(\tilde{\nu})d\tilde{\nu}}{\tilde{\nu}}$$

where $F(\tilde{\nu}) = dQ/d\tilde{\nu}$ is the fluorescence spectrum (in Quanta Q per wavenumber) and $\varepsilon(\tilde{\nu})$ is the molar decadic extinction coefficient.

The actually measured fluorescence lifetime τ_f is always shorter than the radiative lifetime because of the radiationless deactivation processes competing with deactivation by fluorescence. The ratio $\tau_f/\tau_{rf} = \phi_f$, the quantum yield of fluorescence. This is so, since the quantum yield of fluorescence is defined as the number of fluorescence quanta emitted divided by the number of quanta absorbed, and the rate of fluorescence quanta emitted is given by $1/\tau_{rf}$, while the rate of molecules deactivated (which in steady state equals the rate of absorption) is given by $1/\tau_f$.

The fluorescence lifetime can usually be measured with good accuracy and the absorption even more so. Thus it is generally easy to obtain reliable values of the quantum yield of fluorescence for a dye by this method. In contrast to this, the determination of absolute quantum yields by direct measurements of absorbed and emitted quanta is very difficult and usually the accuracies obtained are unsatisfactory (7). Easier than an absolute determination is the measurement of relative quantum yields by comparison to a standard solution of a dye with known quantum yield of fluorescence, which has a fluorescence emission in the same spectral region. Good laser dyes should have quantum yield as high as possible, i.e. near 100%, but recently laser emission has been obtained even with dyes having quantum yields as low as 0.1% (8).

The radiative transition from T_1 to G is termed "phosphorescence". In principle, one should be able to estimate the radiative lifetime τ_{rp} of the phosphorescence on the basis of the G to T_1 absorption. Since this very weak forbidden transition is normally completely obscured by absorption due to impurities, the phoshorescence radiative lifetime can be obtained from the directly measured quantum yield of phosphorescence ϕ_p and the observed phosphorescence lifetime τ_p, as in the case of fluorescence: $\tau_{rp} = \tau_p/\phi_p$. As expected for spin-forbidden transitions, it is extremely long, ranging from milliseconds to many seconds. Consequently, even relatively slow quenching processes can lead to radiationless deactivation in liquid solution. Hence the observed quantum yield is generally very low in liquid solution, becoming appreciable only at low temperatures, e.g. at 77 K in solid solutions. Usually no measurable phosphorescence can be observed in liquid solutions. Here τ_p, which is identical with the triplet lifetime τ_t, is often determined by flash spectroscopy from the vanishing of the triplet-triplet absorption bands. Assuming the radiative lifetime at elevated temperatures is the same as at low temperatures, the quantum yield of phosphorescence at elevated temperatures can be obtained.

From the foregoing discussion of light emission by dye molecules one might come to the conclusion that there are two possible ways, at least in principle, of using an organic dye solution as the active medium in a laser: One might utilize either the fluorescence or the phosphorescence emission. At first sight the long lifetime of the triplet state makes phosphorescence look more attractive. On the other hand, due to the strongly forbidden transition a very high concentration of dye is required to obtain an amplification factor large enough to overcome the inevitable cavity losses in a laser. In fact, for many dyes this concentration would be higher than the solubility of the dye in any solvent. A further unfavorable property of these systems is that there will almost certainly be losses due to the triplet-triplet absorption. These absorption bands are generally very broad and diffuse and the probability that they overlap the phosphorescence band and thus attenuate the phosphorescence emission by reabsorption is high. Because of these difficulties no laser using the phosphorescence of a dye has yet been reported. The possibility can not be excluded, however, that further study of phosphorescence and triplet-triplet absorption in molecules of different types of chemical constitution might eventually lead to a laser operating, for example, at the temperature of liquid nitrogen. On the other hand, the probability for this seems low at present and these systems will not be considered here. For a more detailed discussion of phosphorescent systems the reader is referred to the literature(9).

1.3 Radiationless Deactivation of Organic Dyes

Radiationless deactivation of excited states of dye molecules is of utmost importance in dye lasers. In most cases they constitute loss mechanisms in dye lasers but can in some cases be helpful, as will be shown later. Only the more important of these processes will be discussed here (10).

The radiationless decay from some excited singlet state directly to the ground state is termed "internal conversion". The rate of this relaxation pathway can vary by many orders of magnitude depending on the molecular structure and the solvent. There are several processes that are known to enhance the rate of internal conversion (11). A famous example is the comparison of the molecular structure of the two dyes phenolphthalein and fluorescein. The latter contains an oxygen bridge between the two phenyl rings that carry the phenol groups. In this way the molecule becomes very rigid, while in phenolphthalein the two phenyl rings can rotate and thus dissipate energy. Consequently, phenolphthalein is non-fluorescent in alkaline solution while fluorescein has a quantum yield of fluorescence of 90%. Similarly the mobility of the diethylamino groups in rhodamine B is responsible for the temperature dpendent quantum yield: only a few percent in boiling alcohol, 40% at room temperature, increasing to nearly 100%, when the temperature is lowered or a highly viscous solvent like glycerol is used, that can dampen the out-of-plane torsional movement of the diethylamino group setting in in the excited state. If these groups are rigidized, as in the dye rhodamine 110, the quantum yield is found to be virtually 100%, independent of temperature (12). One must not conclude, however, that a rigid molecular structure will always lead to a high quantum yield of fluorescence or that a non-rigid molecule always has a low quantum yield, since other dissipative mechanisms, to be discussed below, might have a stronger influence in this respect.

Another effective mechanism for internal conversion consists in the coupling of the electronic transition to normal modes of vibrations involving hydrogen atoms in end-positions. If this coupling is strong, a high probability exists that the molecule makes an adiabatic transition from the lowest vibronic level of the first excited state S_1 to highlying vibronic levels of the ground state G. This process has an increasing probability with increasing vibronic energy, since then the change in vibrational quantum number is minimized. Because of the small mass of the hydrogen atom, vibrations involving hydrogen atoms have the highest energy and are thus very likely to contribute to this process. This is corroborated by the fact that deuteration in the end-positions usually increases the fluorescence quantum yield. Furthermore, this effect is more pronounced in infrared laser dyes, since here the electronic energy is low and consequently the change in vibronic quantum number is smaller.

Whenever a dye is excited into S_2 or a higher state internal conversion goes via S_1. Since the time for internal conversion between higher excited states and S_1 is of the order of 1 ps, and thus very short compared to the fluorescence lifetime, the quantum yield of fluorescence is generally independent of the excitation wavelength. For a long time the aromatic molecule azulene was the only known exception to this rule, with its fluorescence emitted as a transition from S_2 to G, while emission from S_1 to G is extremely weak. Only recently weak fluorescence from S_2 could be detected in several other molecules with strong laser excitation (13).

The radiationless transition from S_1 to the lowest triplet level T_1 is termed "intersystem crossing". It is extremely important that the intersystem crossing rate be as low as possible to make a good laser dye. As mentioned above, the triplet state is metastable, so that high concentrations of dye molecules can accumulate in the triplet state during a pump cycle and attenuate or even quench the laser radiation by triplet-triplet absorption. The ratio of the intersystem crossing rate to the total deactivation rate is defined as the triplet yield of a dye. DREXHAGE (14) has empirically found a rule that allows a semiquantitave correlation between molecular structure and intersystem crossing rate or triplet yield.

DREXHAGE's loop rule states that in a dye where the pi-electrons of the chromophore can make a loop when oscillating between the end groups, the triplet yield will be higher than in a related compound where this loop is blocked. It may be said that the circulating electrons create an orbital magnetic moment which couples with the spin of the electrons. This increased spin-orbit coupling then enhances the rate of intersystem crossing, thus giving rise to a higher triplet yield. This loop rule has proven very useful in the design of new laser dyes. It predicts e.g. low triplet yields in the rhodamines compared to the acridines, which differ only by the substitution of the oxygen atom in the xanthene structure by a nitrogen atom. Experimentally a triplet yield of 1% was found in rhodamine 6G (15) and 10% in acridine orange (16). Similarly well confirmed predictions were made for many other dyes.

Spin-orbit coupling can also be enhanced and thus intersystem crossing rate increased by the introduction of heavy atoms into the molecular structure. This heavy-atom effect is clearly demonstrated in the dye eosin, which is a tetrabromo-substituted fluorescein. While the triplet

yield of fluorescein in alkaline solution is only 3%, it is as high as 76% in eosin (16). In the dye erythrosin, where the four bromine atoms of eosin are replaced by four iodine atoms, the triplet yield is even higher. Obviously, it is advisable to avoid heavy-atom substituents in the synthesis of new laser dyes.

The intersystem rate is also enhanced by an external heavy-atom effect, which can be studied when the dye is dissolved in organic solvents containing heavy atoms, like iodomethane or iodobenzene. This effect has been exploited by DREXHAGE in an ingeniously simple method for the determination of relative triplet yields. He found that the mentioned solvents increase the value of the intersystem rate in first approximation by a constant factor independent on its magnitude. Hence in the case of a dye in which the triplet yield is small compared to the quantum yield of fluorescence, the enhancement of the intersystem crossing rate by, say a factor of 1000 will not change the fluorescence efficiency appreciably. However, in a dye where the triplet yield and the quantum yield of fluorescence are comparable, the same enhancement of the intersystem crossing rate will cause a reduction of the quantum yield of fluorescence by three orders of magnitude. Thus, for an approximate determination of triplet yield, one simply adds an equal amount of iodomethane to the ethanolic dye solution and observes the concomitant reduction in fluorescence intensity.

Another intermolecular pathway of deactivation is created by charge transfer interactions. It has long been known (17) that the fluorescence of dyes is quenched by certain anions. The strength of the quenching action is decreasing in the order: iodide, thiocyanate, bromide, chloride, perchlorate, suggesting a charge transfer (redox-reaction) in the excited state of the dye. Since many dyes are cations that must have of necessity a negatively charged counter-ion, this means that it is preferable to use the perchlorate ion for this purpose, whenever possible. This is most important, when a less polar solvent is used, where the dye-counterion pair is not fully dissociated, whereas in a polar solvent the counter-ions in dilute solution are usually so far away from the excited dye molecule that it cannot reach the dye molecule by diffusion during the lifetime of the excited state. There are many other molecules in addition to the anions mentioned above, that can quench the fluorescence by a charge transfer in the excited state of the dye molecule.

The effect of dimerization on fluorescence quenching has been discussed above. A more detailed account of this effect can be found in (18).

Reactions in the excited state can result in new pathways of radiative as well as radiationless deactivation. The more important of these reactions are the formation of excited complexes, so-called "exciplexes", protolytic reactions in the excited state, and a great variety of photoreactions, that lead to a photodecomposition of the dye molecule.

Exciplexes usually have a low quantum efficiency. In the few cases where fluorescence efficiency is high one can expect good lasing efficiencies, since the lower laser level is unstable and thus an inversion easily obtained (19).

Protolytic reactions in the excited state occur in quite a number of laser dyes, since these dyes become more acidic or more basic upon excitation; they thus may pick up a proton from the solvent or lose one to it, depending on its pH (20). A good example of this behaviour is found in the class of coumarin dyes. While in these dyes the new species formed in the excited state is often as highly fluorescent as the mother molecule, only in a different wavelength region, this effect can be used advantageously in dye lasers. Often, however, the new species exhibits a high rate of radiationless deactivation and thus is detrimental to laser action. In contrast to this, one might occasionally find dyes that are normally nonfluorescent and only become fluorescent in the new species formed in a protolytic reaction in the excited state.

Photodegradation of laser dyes is a major problem in dye lasers and has been studied by many authors (21), although only few papers have investigated the underlying chemical processes in detail (22). Usually it is not so much the diminishing concentration that abates laser action, but rather the reabsorption of laser radiation by the photoproducts. Since most photoreactions will start from the triplet state of the dye molecule because of its long lifetime, a reduction of triplet lifetime can alleviate this problem to some extent. This is particularly true for the new laser dyes with intramolecular energy transfer that will be discussed later.

Radiationless energy transfer, intermolecular as well as intramolecular, is another pathway for radiationless deactivation of excited dye molecules. The conditions for radiationless energy transfer are given by the FÖRSTER-DEXTER theory (23). Efficient singlet-singlet energy transfer from S_1 of a dye molecule (the donor) to S_1 of some other molecule (the acceptor) will always occur, if there is a good spectral overlap of the fluorescence band of the donor and the absorption band of the acceptor, provided the intermolecular distance is not greater than a characteristic distance R_0, that can be computed from theory and spectroscopic data and often is of the order of 50 angstrom. For triplet-triplet energy transfer this characteristic distance is only a few angstrom.

If singlet-singlet energy transfer is from the excited dye to a nonfluorescent molecule, it constitutes a loss mechanism for laser action. If, on the other hand energy is transferred to some other highly fluorescent laser dye, it only brings about a spectral shift of the laser emission, that is often advantageous.

Triplet-triplet energy transfer is used to great extent in dye laser operation to reduce the triplet lifetime of laser dyes by the addition of so-called triplet quenchers. An effective triplet quencher is molecular oxygen, that is usually dissolved in any dye solution in equilibrium with laboratory air at an approximately 10^{-3} molar concentration. A disadvantage of molecular oxygen as triplet quencher is the fact that in the process highly reactive singlet oxygen is created that can readily attack many dye molecules and thus enhance the photodecomposition rate. Another disadvantage is the fact that molecular oxygen enhances the intersystem crossing rate, too, so that more triplets are created. The relative magnitude of this effect determines whether the net effect of molecular oxygen on dye laser action is positive or negative. With rhodamine 6G, for example, dye laser efficiency is greatly improved by oxygen, while with brilliantsulphaflavin dye laser emission is extinguished even with minor traces of oxygen. Other well-known triplet quenchers are unsaturated hydrocarbons with low-lying triplets. The most often used of these is cyclooctatetraene (generally abbreviated COT). It has the disadvantage of being also quite reactive, in particular prone to polymerization in the absence of specially added stabilizers. The concentrations of these triplet quenchers needed for effective operation is quite high, due to the small characteristic distance R_0, which aggravates the above-mentioned adverse effects on dye laser action. If, on the other hand, intramolecular triplet-triplet energy transfer is used, as is done in the new laser dyes to be discussed below, each dye has its individual triplet quencher chemically linked to it, which means a much reduced bulk concentration.

[illegible] A Survey of Laser Dyes

[illegible] the [illegible] known laser dyes belonging to the [illegible] classes of compounds [illegible] the reader is referred to the excellent review [illegible] (1978) [illegible]. Here only newer developments and [illegible] of special interest will be discussed.

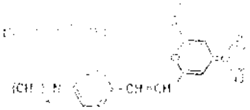
The dye p-terphenyl has for a long time been known as an efficient laser dye that yielded the shortest wavelengths (down to 340 nm) of dye laser emission. Recently, a considerable number of substituted p-terphenyls have been investigated (24) and the dye 2,2''-dimethylterphenyl was found to emit down to 318 nm and, at the temperature of liquid nitrogen, even down to 311 nm, the shortest wavelength obtained in dye laser operation up to now (25).

Many scintillator dyes, developed three decades ago for nuclear physics, are efficient laser dyes, in particular for laser pumping. Since these dyes in general are uncharged, neutral molecules of low molecular weight, they have a relatively high vapor pressure, so that dye laser operation in the vapor phase becomes possible. The scintillator dye POPOP was the first dye to exhibit the laser emission in the vapor phase (26). Later a number of other dyes were found to give vapor phase dye laser action, in particular the class of indolines, that extended vapor phase dye laser action from the ultraviolet and blue of the scintillator dyes into the green spectral region (27).

Another new class of dyes that may prove to be especially useful for cw-dye laser operation in the near ultraviolet are the polyphenyls. The shortest wavelength obtained until now is 362 nm with the dye polyphenyl 1 with pumping by the ultraviolet argon-ion laser lines (28).

Chemically closely related to the oxazines are the oxazones, which are noteworthy for two reasons. In contrast to the ionic oxazine dyes, the oxazones are uncharged, neutral molecules with a high dipole moment in the ground state, which changes drastically upon excitation of the molecule. This results in a strong solvatochromic effect, which practically means that a dye laser operated with these dyes can be tuned continuously by a change of solvent or solvent mixture. In addition the oxazones exhibit a much greater photochemical stability than the most-often used xanthene dyes (29).

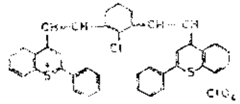
A very efficient laser dye for operation around 700 nm, that has recently become available is generally known by the abbreviation DCM. Its chemical formula shows it to be an uncharged merocyanine:



This dye has an outstanding tuning range, (605 to 725 nm), because of its broad fluorescence band, and an efficiency and photochemical stability that is at least as high as rhodamine 6G (30).

Most infrared laser dyes belong to the large class of cyanine dyes (consisting of more than 20000 compounds). Most of these dyes operate best in the solvent dimethylsulfoxide (DMSO), which has a remarkably low solubility for molecular oxygen and a high solvating capability for cations. The performance data of some good infrared laser dyes of this type are given in (31).

Remarkable progress in photochemical stability was recorded for a rigidized heptamethine dye of the following formula:



This dye has a tuning range from 1.15 µm to 1.28 µm and has a photochemical stability that is at least 10^5 times higher than that of the thiacyanines used in this spectral region before (32).

The new dye LD 700 belonging to the xanthenes has the carboxyphenyl group of the rhodamines replaced by a CF_3-group and thus extends the tuning range of this dye class up to 805 nm (33).

The last two examples clearly show that planned chemical synthesis in the classical way is still able to make considerable progress in designing better laser dyes with remarkable improvments in various dye properties. On the other hand there is no doubt that there is an asymptotic limit for this procedure. To overcome these limitations a new approach is needed, similar to the procedure of nature, where in the many crucial points of evolution new molecules made up from smaller functional subunits provided new functional capabilities. It was pointed out some years ago that chemical linking of several properly chosen chromophores would provide a means to reach higher efficiency in flashlamp-pumped dye lasers and that triplet quenchers, also linked chemically to a laser dye would result in a much reduced triplet loss in a laser utilizing this dye (34).

Recently the first few laser dyes designed according to this new principle have been synthesized and their laser characteristics studied. The dye p-terphenyl was linked to the dye dimethyl-POPOP by a CH_2-group and resulted in a bifluorophoric dye that has a 30% higher absorption for the pump light of a xenon flashlamp and an accordingly increased higher efficiency (34). A much more dramatic increase in efficiency was achieved by the introduction of stilbene as a triplet quencher for the dye dimethyl-POPOP that was again linked by a CH_2-group. It was found that the laser energy per pulse was 110 times that of dimethyl-POPOP when pumped with the same electrical energy of 50 joule per pulse in a small coaxial-flashlamp-pumped dye laser (35). Following the decay of the triplet-triplet absorption after short-pulse excitation by a XeCl-laser it was shown that this dramatic efficiency improvement was indeed caused by a thousandfold reduction in the triplet lifetime of the dimethyl-POPOP-moiety through energy-transfer from the dimethylPOPOP-moiety to the stilbene-moiety (36). Further work along the lines indicated here only briefly will certainly increase the efficiency and photochemical stability very considerably.

Finally the interested reader is referred to the informational material of laser dye manufacturers, which gives tuning ranges and efficiency data for a great number of dye and solvent combinations (37) and to a recent publication that gives information on the relative photochemical stability and the concomitant operational cost for a number of dyes for cw-dye laser operation (38).

2.

LASER-PUMPED PULSED DYE LASERS

The main complication in dye lasers is the existence of triplet states. The intersystem crossing rate is high enough in most dyes to reduce the quantum yield of fluorescence to values substantially below unity. As indicated above, this has the two-fold consequence of, firstly, reducing the population in the first excited singlet state and hence the amplification factor and, secondly, enhancing the triplet-triplet absorption losses by increasing the population density of the lowest triplet state.

Assume a light flux density which rises slowly to a level P (quanta sec^{-1} cm^{-2}), a molecular absorption cross-section σ (cm^2), a quantum yield ϕ_T of triplet formation, a triplet lifetime τ_T, population density of the triplet and ground state of n_T and n_0 (cm^{-3}), respectively, and, neglecting the small population of the excited singlet state, a total dye molecule concentration of $n = n_0 + n_T$. A steady state is reached when the rate of triplet formation equals the rate of deactivation:

$$P\sigma n_0 \phi_T = n_T/\tau_T . \qquad (2.1)$$

Thus the fraction of molecules in the triplet state is given by

$$n_T/n = P\sigma\phi_T\tau_T/(1 + P\sigma\phi_T\tau_T) . \qquad (2.2)$$

Assuming some typical values for a dye, $\sigma = 10^{-16}$ cm^2, $\phi_T = 0.1$ (corresponding to a quantum yield of fluorescence of at most 0.9), and $\tau_T = 10^{-4}$ sec, the power to maintain half of the molecules in the triplet state is $P_{1/2} = 10^{21}$ quanta sec^{-1} cm^{-2}, or an irradiation of only 1/2 kW cm^{-2} in the absorption band of the dye. This is much less than the threshold pump power calculated below. Hence a slowly rising pump light pulse would transfer most of the molecules to the triplet state and deplete the ground state correspondingly. On the other hand, the population of the triplet state can be held arbitrarily small, if the light flux density rises fast enough, i.e. if it reaches threshold in a time that is small compared to the reciprocal of the intersystem crossing rate. For a typical value of the intersystem crossing rate of 10^7 sec^{-1}, the risetime should be less than 100 ns. This is easily achieved with Q-switched solid state lasers, nitrogen lasers, or excimer lasers. In such a laser-pumped pulsed dye laser one may neglect all triplet effects in a first approximation.

2.1 Oscillation Condition

It is easy then to write down the oscillation condition for a dye laser. In its simplest form a dye laser consists of a cuvette of length L (cm) with a dye solution of concentration n (cm^{-3}) and two parallel end windows carrying a reflective layer each of reflectivity R for the laser resonator. With n_1 molecules/cm^3 excited to the first singlet state, the laser will start oscillating at a wavenumber $\tilde{\nu}$, if the overall gain is equal to or greater than one:

$$\exp[-\sigma_a(\tilde{\nu})n_0 L] R \exp[+\sigma_f(\tilde{\nu})n_1 L] \geq 1 . \qquad (2.3)$$

Here $\sigma_a(\tilde{\nu})$ and $\sigma_f(\tilde{\nu})$ are the cross-sections for absorption and stimulated fluorescence at $\tilde{\nu}$, respectively, and n_0 is the population of the ground state. The first exponential term gives the attenuation due to reabsorption of the fluorescence by the long-wavelength tail of the absorption band. The cross-section for stimulated fluorescence is related to the Einstein coefficient B

$$\sigma_f(\tilde{\nu}) = g(\tilde{\nu}) B h\tilde{\nu}/c_0 \qquad \int\limits_{\text{fluorescence band}} g(\tilde{\nu})d\tilde{\nu} = 1 . \qquad (2.4)$$

Substituting the Einstein coefficient A for spontaneous emission according to

$$B = \frac{1}{8\pi\tilde{\nu}^2} A \frac{1}{h\tilde{\nu}} \tag{2.5}$$

and realizing that $g(\tilde{\nu})A\phi_f = Q(\tilde{\nu})$, the number of fluorescence quanta per wave number intervall, one obtains

$$\sigma_f(\tilde{\nu}) = \frac{1}{8\pi c_0 \tilde{\nu}^2} \cdot \frac{Q(\tilde{\nu})}{\phi_f}. \tag{2.6}$$

Since the fluorescence band usually is a mirror image of the absorption band, the maximum values of the cross-sections in absorption and emission are found to be equal:

$$\sigma_{f,\max} = \sigma_{a,\max}. \tag{2.7}$$

Taking the logarithm of (2.3) and rearranging it leads to a form of the oscillation condition which makes it easier to discuss the influence of the various parameters:

$$\frac{S/n + \sigma_a(\tilde{\nu})}{\sigma_f(\tilde{\nu}) + \sigma_a(\tilde{\nu})} \leq \gamma(\tilde{\nu}). \tag{2.8}$$

where $S = (1/L)\ln(1/R)$ and $\gamma(\tilde{\nu}) = n_1/n$.

The constant S on the left-hand side of (2.8) only contains parameters of the resonator, i.e. the active length L, and the reflectivity R of the mirrors. Other types of losses, like scattering, diffraction, etc., may be accounted for by an effective reflectivity R_{eff}. The value of $\gamma(\tilde{\nu})$ is the minimum fraction of the molecules that must be raised to the first excited singlet state to reach the threshold of oscillation. One may then calculate the function $\gamma(\tilde{\nu})$ from the absorption and fluorescence spectra for any concentration n of the dye and value S of the cavity. In this way one finds the frquency for the minimum of this function. This frequency can also be obtained by differentiating (2.8) and setting the differential quotient $d\gamma(\tilde{\nu})/d\tilde{\nu} = 0$. This yields

$$\frac{\sigma_a'(\tilde{\nu})}{\sigma_f'(\tilde{\nu}) + \sigma_a'(\tilde{\nu})} (\sigma_f(\tilde{\nu}) + \sigma_a(\tilde{\nu})) = S/n \tag{2.9}$$

(prime means differentiation with respect to $\tilde{\nu}$) from which the start-oscillation frequency can be obtained. If one plots the laser wavelength (i.e. the wavelength at which the minimum of $\gamma(\tilde{\nu})$ occurs) versus the concentration with S a fixed parameter or versus the active length L of the cuvette with the concentration of the dye as a parameter, one immediately realizes the wide tuning range of a dye laser that can be induced by changing the dye concentration or the length or the Q of the resonator. It also demonstrates the high

gain, which permits the use of extremely small active lengths of only a few µm.

The absorbed power density W necessary to maintain a fraction γ of the molecular concentration in the excited singlet state is

$$W = \gamma n h c_0 \tilde{\nu}_p / \tau_f, \tag{2.10}$$

and the power flux P, assuming the incident radiation is completely absorbed in the dye sample,

$$P = W/n\sigma = \gamma h c_0 \tilde{\nu}_p / \tau_f \sigma \tag{2.11}$$

where $\tilde{\nu}_p$ is the wave number of the absorbed pump radiation. If the radiation is not completely absorbed, the relation between the incident power W_{in} and the absorbed power is $W = W_{in}(1 - \exp(-\sigma_p n_0 L))$. Since in most cases n nearly equals n_0, this reduces for optically thin samples to $W = W_{in}\sigma_p nL$. The threshold incident power flux P_{in} then is

$$P_{in} = (\gamma h c_0 \tilde{\nu}_p)/(\tau_f \sigma_p) \tag{2.12}$$

In the above derivation of the oscillation condition and concentration dependence of the laser wavelength, broad-band reflectors have been assumed. The extension to the case of wavelength-selective reflectors and/or dispersive elements in the cavity is straight-forward and will not be treated here.

2.2 Practical Pumping Arrangements

There are two distinctly different methods of pumping, namely transverse and longitudinal pumping. In transverse pumping, the pump-laser radiation impinges on the dye cuvette in a direction normal to the axis of dye laser emission. In the simplest case a cylindrical lens focusses the pump-laser beam into a simple rectangular spectrophotometer type of cuvette so that the focal line lies directly behind and parallel to the entrance window. If the focal line is normal to the exit windows of the dye laser beam, dye laser emission can easily be achieved with the Fresnel reflection from the windows providing the feedback. This is, indeed, the easiest arrangement for a quick test of the lasing capabilities of a dye. In most cases, however, an external laser resonator with dispersive elements for tuning the dye laser radiation will be used and then this feedback is unwanted and can be removed very simply by tilting the cuvette a few degrees. For higher pulse repetition rates the solution must at least be stirred with a small magnetic stirrer, and, at higher pump-pulse energies, a more or less elaborate flow system is usually employed to avoid laser beam degradation due to the heat-induced schlieren in the solution.

The laser beam diameter can be manipulated to some extent in this arrangement by the judicious choice of the dye concentration, that determines the penetration depth, and the focal length of the cylindrical lens, that determines the height of the pumped region. A distinct disadvantage of this simple pumping arrangement is the spatial non-uniformity of the inversion caused by the pumping from one side only. A recent publication shows a way around this (39). The dye cell shown schematically in Fig. 2 is a bore in a prism that is placed in such a geometrical position that a collimated pump-laser beam entering the hypothenuse face of the prism is divided into four equal parts that impinge on the bore as indicated in the figure so that the solution is uniformly irradiated over its surface.

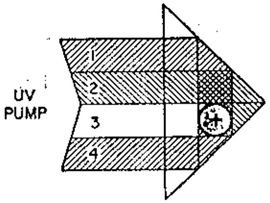


Fig. 2 BETHUNE-cell

The gain in transversely pumped dye solutions can reach very high values. This makes transverse pumping especially suitable for oscillators and small-signal preamplifiers where a large beam cross-section is not normally needed. For end-stages of an amplifier chain, however, one has to use large cross-sections because of the low saturation intensities of dyes, lying usually in the region of MW/cm^2. These large cross-sections cannot be pumped transversely because of the low penetration depth of the pump radiation for reasonably high dye concentrations. The concentrations cannot be made too low, if a useful gain is to be obtained. Thus longitudinal pumping is generally used in these cases. Cuvettes for longitudinal pumping are normally provided with Brewster windows. This has the additional advantage of a higher angle of incidence for the shorter-wavelength pump radiation so that a perfect spatial overlap of pump and dye laser beams inside the cuvette is possible, while they are seperated outside the cuvette. If windows normal or inclined a few degrees to the dye laser axis are used, one has either to sacrifice complete spatial overlap of pump and dye laser beam inside the dye cuvette or use beamsplitters for combining pump and dye laser beams, which apart from the added complexity usually introduces unwanted losses.

3.
FLASHLAMP-PUMPED DYE LASERS

In the case of flashlamp-pumped dye lasers, triplet effects become important because of the long risetime or duration of the pump light pulse. Several authors have treated the kinetics of dye laser emission by a set of coupled rate equations including terms to acount for triplet-triplet absorption losses. Since the triplet losses are time-dependent, they affect the efficiency as well as the emission wavelength of the dye laser. The results apply only to the specific light pulse form considered. It is therefore worthwhile to have an expression connecting population densities in the ground, lowest excited singlet, and triplet states with the laser wavelength and cavity parameters.

The following simple modification of the oscillation condition discussed for the case of laser-pumped dye lasers takes into account triplet-triplet absorption losses, characterized by an absorption cross-section σ_T. Let $\alpha = n_0/n$ be normalized ground state population density, and $\beta = n_T/n$ the normalized triplet population density. Then the oscillation condition, its derivative with respect to wave number, and the balance of population densities give the following three equations for α, β, γ (prime denotes differentiation with respect to wave number):

$$-\sigma_s\alpha - \sigma_T\beta + \sigma_f\gamma = S/n\,, \qquad (3.1a)$$

$$-\sigma_s'\alpha - \sigma_T'\beta + \sigma_f'\gamma = 0\,, \qquad (3.1b)$$

$$\alpha + \beta + \gamma = 1\,. \qquad (3.1c)$$

From these equations and the observed laser wavelength, the population densities in the ground, excited singlet, and triplet state can be obtained.

The ratio β/γ, obtained from the above relations, and the time t_0 to reach threshold can be used for an estimate of the intersystem crossing rate k_{ST}, if one assumes that t_0 is small compared to the triplet lifetime and that the pump-light intensity is rising linearly. Then we have $d\gamma/dt$ = constant and $d\beta/dt = k_{ST}\beta$, which yields after integration $\beta/\gamma = k_{ST}t_0/2$. On the other hand, the observed t_0 can give an upper limit for σ_T at the laser wavelength for known k_{ST}, since laser emission can only be achieved for $\gamma\sigma_f > \beta\sigma_T$, yielding $\sigma_T < 2\sigma_f/t_0k_{ST}$ (40).

For pulses that are long compared [illegible] time or for continuous operation a steady state must be reached. Then the triplet production rate [illegible] k_{ST} [illegible] equals the deactivation rate [illegible] τ_T, so that the ratio [illegible] $k_{ST}\tau_T$. Setting this ratio equal to that obtained above from the observed laser wavelength, an estimate of τ_T can be obtained.

To obviate the need for a rapidly rising pump light intensity and to achieve cw operation, one must reduce the triplet population density to a sufficiently low level by reducing the triplet lifetime using either external or intramolecular triplet quenching as discussed before.

3.[illegible] Practical Pumping Arrangements

Flashlamp-pumped dye laser heads consist in principle of the dye cuvette, the flashlamp, and a pump light reflector or diffuser. The latter serves to concentrate the pump light emitted from the extended, uncollimated, broad-band source, the flashlamp, onto the absorbing dye solution in the cuvette. The reflector can be of the imaging type, e.g. an elliptical cylinder whose focal lines determine the position of the linear lamp and cuvette, or it can be of the close-coupling type, which is especially advisable where there are several flashlamps surrounding the cuvette. Instead of a specular reflector, a diffusely reflecting layer of $BaSO_4$ or compressed teflon powder behind a glass tube surrounding flashlamp and cuvette is often used.

The design of the pump cavity is thus similar to that of solid-state lasers, except that for dye lasers it is even more important to prevent non-uniform heating of the dye solution in order to avoid thermal schlieren. Furthermore, it is advisable to use some means of filtering out photochemically active short wavelengths which might decompose the dye molecules. At low pulse repetition rates it is often sufficient to use an absorbing glass tube for the cuvette. At higher pulse repetition rates it is advisable to use a double-walled cuvette with a temperature-controlled flowing filter solution and/or a filter solution surrounding the flashlamp(s).

For maximum utilization of the pumplight the length of the cuvette will generally be about the same as that of the flashlamp. This in turn makes a flow system almost mandatory, because in a long cuvette even a small thermal gradient can severely degrade the resonator characteristics. The dye flow through the cuvette may be longitudinal or transverse. In either case the flow velocity should be high enough to be in the turbulent regime. This rapidly mixes the liquid and hence reduces thermal gradients due to non-uniform pump light absorption in the cuvette. The materials of O-rings, tubing, circulating pump, and the reservoir must be carefully chosen to be compatible with the solvents used. Even clear plastic tubing can give off absorbing or quenching plasticizer and filler material.

A great variety of flashlamps have been used in dye lasers. The simplest possibility is the use of commercial xenon flashlamps. The risetime of linear and helical flashlamps can be reduced and the output power increased by the introduction of a high-voltage, high-current switch in the discharge circuit. Spark-gaps, thyratrons and thyristors have been used for this purpose (41). An increase in lifetime by at least a factor of ten is possible, if some preionization method is used. One can either apply a constantly flowing simmer current upon which the main discharge is superimposed (42) or use a low-energy preionization discharge about a µs before the main discharge (43).

Another type of flashlamp with a very fast risetime is a low inductance coaxial lamp in which a cylindrical plasma sheet surrounds the cuvette. With this lamp, too, a spark gap or simlar switching means is used in series with the lamp, so that a voltage much higher than the self-firing voltage of the lamp can be used to insure rapid plasma build-up. At the same time the pressure can be adjusted so that the plasma fills the lamp uniformly (44). Risetimes below 100 ns can be achieved with this type of lamp and not too high pulse energies. Coaxial flashlamps are now also available commercially.

This configuration is also amenable to up-scaling, and this has been done by russian workers (45), who obtained dye laser pulses of up to 150 joule output energy.

The average power available in flashlamp-pumped dye lasers has constantly increased over the years. Recently a highly reliable laser with an average power of over 100 W using rhodamine 6G and broad-band operation was reported, that can operate for at least 10^5 shots without interruption for lamp replacement at a 50 Hz pulse repetition rate (46). Very recently average powers of over 1kW were reported for short term operation of several seconds only.

Wall-plug efficiencies of flashlamp-pumped dye lasers at present are typically between 0.6 to 0.8% (47).

4.

CONTINUOUS-WAVE DYE LASERS

From many experimental threshold data of flashlamp-pumped dye lasers one can conclude that for continuous operation of these lasers one would need arc lamps of at least 5 kW electrical input power, which would have to be accomodated into the same pump cavities. No such lamps are available at present. Consequently as of yet no incoherently pumped cw-dye lasers do exist. On the other hand it is easy to focus the beam of an argon-ion laser of only a few watt output power into a spot of about 10 µm diameter and thus reach a power density that is higher than the threshold values that can be calculated from the oscillation conditions given above. One immedeately sees, however, that thermal problems are much more serious here and that flow velocities of several meters per second are needed to remove the heat developed in the focal spot sufficiently fast to prevent thermal degradation of the resonator properties.

In the first cw-dye lasers (48) sapphire windows were used for the dye flow cells, but even these were often quickly damaged by particulate matter adhering to the windows in the pumped region. This problem was solved by the introduction of the free-jet technology (49). A jet of dye solution using a sufficiently viscous solvent like ethylene glycol ejected from a nozzle several mm wide and 100 µm to 1mm high exhibits excellent optical properties as long as laminar flow is maintained. This limits the heat load that can be removed by the jet and thus the output of the dye laser in this configuration usually is limited to a few watts. The introduction of solvents of higher heat capacity, e.g. aqueous solutions of polyvinylalcohol, improved the output capability to tens of watts (50).

The main trick of cw-dye laser operation is the achievement of perfect mode matching of the dye laser mode and the pump mode. For this reason simple plane-plane resonators cannot be used and confocal resonators are commonly employed. The wavelength-selective resonators for this application will be discussed in the next section. While the spectral bandwidth of pulsed dye lasers can at best be narrowed down to the Fourier limit determined by the pulse duration, cw-dye lasers are free from this limitation. Consequently, frequency stabilization and mode selection techniques have been refined to a high degree of perfection. In fact, the spectral resolution in the Mhz to kHz region now obtainable with cw-dye lasers, have made them indispensable tools of high resolution spectroscopy that are now also commercially available in many different versions.

5.

WAVELWENGTH-SELECTIVE RESONATORS FOR DYE LASERS

A coarse selection of the dye-laser emission wavelength is possible by judicious choice of the dye, the solvent, and the resonator Q and length, as described above. Fine tuning and simultaneous attainment of small linewidths can only be achieved by using a wavelength-selective resonator.

Up to now the following four classes of wavelength-selective resonators have been employed:

1) resonators including devices for spatial wavelength separation,
2) resonators including devices for interferometric wavelength discrimination,
3) resonators including devices with rotational dispersion,
4) resonators with wavelength-selective distributed feedback.

The literature abounds with the various implementations of these four classes and combinations thereof. For lack of space only a few typical and generally useful examples will be discussed here.

In the first class, using spatial wavelength separation, usually gratings or prisms are employed. In the first implementation of a wavelength-selective resonator one of broadband dielectric mirrors of the resonator was replaced by a plane optical grating in Littrow mounting. The spectral resolution obtainable with this simple arrangement is mainly determined by the beam divergence of the laser. The passive spectral width is

$$\Delta\lambda_\alpha = \frac{2d\cos\alpha}{m}\Delta\alpha . \qquad (5.1)$$

where γ is the wavelength, d the grating constant, m the diffraction order, α the angle of incidence, and $\Delta\alpha$ the beam divergence angle. If the laser has a diffraction-limited beam divergence, the passive bandwidth is

$$\Delta\lambda_D = 2.44\, d\lambda\cos\alpha/mD . \qquad (5.2)$$

where D is the inner diameter of the cuvette. If beam-expanding optics are used inside the resonator to decrease the beam-divergence angle by the magnification ratio, the passive bandwidth is reduced by the same amount. The active spectral bandwidth is smaller than the passive bandwidth depending on the available gain, sometimes by factors of up to 100. Nevertheless, passive bandwidths are given here since these give an upper limit for the spectral bandwidth.

While high-quality gratings can have efficiencies of up to 95% at the blaze wavelength, most gratings have lower efficiencies, 65% being a realistic values. Thus, the insertion loss due to a grating is substantial and makes resonators containing gratings in general unsuitable for lasers with relatively low gain, in particular cw-dye lasers. Another disadvantage of gratings is the reflecting metal-film coating which may be damaged by high power and energy pulses. This problem can be circumvented to some extent by the introduction of intra-cavity beam-expanding optics which at the same time improves the spectral resolution as explained above. This is especially true for laser-pumped pulsed lasers in the transverse pumping configuration where the beam cross-section is generally very small.

Another arrangement using a grating without the need for intra-cavity beam expansion is the grazing incidence configuration. Of the many variants of this configuration that have been published, only one is shown in Fig. 3 (51). In this configuration the grating itself acts as a beam expander of high magnification. Later it was shown that it is more efficient to use a two-prism beam expander in series with a grating in grazing incidence (52). These arrangement can be made very compact and are thus especially well suited for pumping with short-pulse nitrogen lasers, where the cavity round-trip time of the dye laser must be short enough for the spectrally dispersed feedback to reach the dye cell in a state of high inversion.

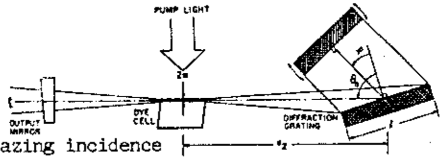


Fig. 3 Use of a grating in grazing incidence

If prisms are used as dispersive elements in a wavelength-selective resonator, a single prism has too low an angular dispersion to be able to reduce the bandwidth of the laser significantly. For this reason multiple prism arrangements are often used. Working near the Brewster angle, where $d\alpha/d\mu = 2$, (μ is the refractive index of the prism material), the angular dispersion of a prism is

$$d\alpha/d\lambda = 2d\mu/d\lambda. \quad (5.3)$$

Using z prisms in autocollimation with a laser of beam divergence $\Delta\alpha$, the passive spectral width is

$$\Delta\lambda_{*} = \frac{\Delta\alpha}{4z\,d\mu/d\lambda}. \quad (5.4)$$

and in the diffraction-limited case

$$\Delta\lambda_D = \frac{1.22\lambda/D}{4z\,d\mu/d\lambda}. \quad (5.5)$$

Evaluating these equations e.g. for the case of 60°-prisms of Schott-glass SF 10 for which $\mu_D = 1.72802$ and $d\mu/d\lambda = 1.35\times10^{-4}$, one sees that a 6-prism arrangement in autocollimation has a smaller passive bandwidth than a grating with 1200 lines/mm in autocollimation. The total insertion loss of 6 prisms is quite low since the prisms are used near the Brewster angle.

Prisms are especially well suited as dispersive elements in ring laser resonators. Fig 4 shows a design using four 90° constant-deviation prisms that are simultaneously counter-rotated for wavelength tuning. With prisms made from SF 10 the spectral range covered reached from 430 nm to beyond 700 nm and the spectral width was 0.8 nm at 600 nm and decreased towards shorter wavelength (53). A noteworthy advantage of these multiprism ring lasers is that they obviate the need for mirrors with broadband dielectric reflective coatings. Another advantage is the ease with which travelling wave operation can be achieved, which avoids spatial hole-burning effects. Output can e.g. be obtained from an intra-cavity beam splitting cube.

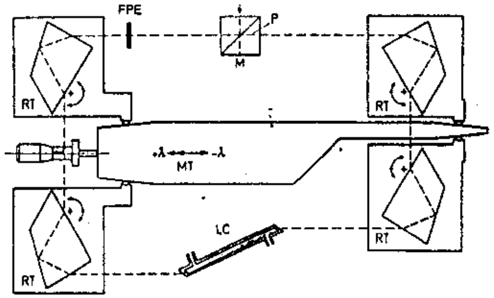


Fig. 4 Ring laser with four 90° constant- deviation prisms. RT rotating prism tables, MT movable table, LC laser cuvette, P beam splitter.

The interferometric method most often used for tuning dye lasers is the insertion of one or more Fabry-Perot etalons or interference filters into the laser resonator. The wavelength λ of maximum transmission in k-th order for a Fabry-Perot of thickness d, refractive index μ, and with an angle α between its normal and the optical axis, is given by $k\lambda = 2\mu d\cos\alpha'$. Here α' is the refracted angle inside the etalon. Thus for air the angular dispersion is $d\lambda/d\alpha = \lambda\tan\alpha$. Hence the spectral bandwidth for beam divergence Δα is

$$\Delta\lambda_a = \lambda\Delta\alpha\tan\alpha. \tag{5.6}$$

The wavelength shift $\Delta\lambda_s$ for turning the Fabry-Perot from a position normal to the optical axis ($\alpha = 0$, corresponding to a wavelength λ_0) through an angle α is $\Delta\lambda_s = (1-\cos\alpha)\lambda_0$. (5.7)

The free spectral range $\Delta\lambda_F$ between adjacent orders is $\Delta\lambda_F = \lambda/k$.

The spectral width near λ_0 is determined by the reflection coefficient R of the Fabry-Perot mirrors, $\delta\lambda = \Delta\lambda_F/F$, (5.8)

where $F = \pi\sqrt{R/(1-R)}$ $F = \frac{\pi\sqrt{R}}{1-R}$ (5.9)

is the so-called finesse factor.

From these relations it is easy to determine the required properties of the laser and the Fabry-Perot for narrow band emission and wide tunability. The attainable minimum bandwidth is determined by the minimum angle which avoids reflections from the first mirror of the Fabry-Perot back into the cuvette. If q is the ratio of the diameter of the cuvette to the distance between the Fabry-Perot and the nearest cuvette window, the minimum bandwidth is $\Delta\lambda_{a\,\min} = \lambda\Delta\alpha\tan\frac{1}{2}q$. (5.10)

As the angle is increased to tune over the free spectral range, the bandwidth increases according to (5.6). Thus, a large tuning range is possible only at the expense of a relatively large increase in bandwidth. In addition to an increasing bandwidth, the use of a Fabry-Perot at high angles also introduces serious walk-off losses, which become the more serious the larger the ratio of etalon thickness to beam diameter and the higher the angle. In order to realize a specified narrow bandwidth, one would have to reduce the tuning range and/or the beam divergence of the laser. Wavelength selection and simultaneous spectral narrowing down to less than 1 pm were achieved in this way in laser-pumped and flashlamp-pumped dye lasers (54).

Nowadays Fabry-Perot etalons are generally used in conjunction with gratings to achieve a wide tuning range together with a constant narrow bandwidth. Microprocessors or microcomputers are usually employed to steer the motors that turn the axis of the Fabry-Perot etalons and the grating while tuning in order to keep the wavelength of both devices in synchronism. As soon as the limit of the tuning range of one of the etalons is reached, it is switched to the next order.

If the bandwidth is narrowed down so much by one or more Fabry-Perots that only one longitudinal mode is oscillating the resonator length determines the laser wavelength. Accordingly, again length actuators and turning motors of the Fabry-Perots must be kept in synchronism by computers when tuning. This is especially true with cw-dye lasers with wavelength stabilization.

Pressure tuning of Fabry-Perot etalons is often applied for scanning over a limited wavelength range because of the simplicity of this method in pulsed lasers as well as in cw-dye lasers (55).

There are several methods that make use of the rotation of polarization for wavelength selection (56), but the only one that has gained importance is the birefringent filter. In the simplest implementation it consists of a single quartz plate cut parallel to the optical axis of the crystal, which has a retardation of several half-wavelengths at the center of the tuning range, and which is introduced into the resonator at an angle α between the optical axis of the crystal and that of the resonator. The resonator must, of course, contain enough Brewster windows, so that linearly polarized laser radiation is emitted. In this case there are transmission maxima for retardations at half multiple wavelengths,

$$k\lambda/2 = \Delta\mu x_0\cos\alpha. \tag{5.10}$$

Here k is the order number, Δμ the birefringence, and x_0 the crystal thickness, both for normal incidence. Thus, the wavelength spread for a beam divergence Δα is

$$\Delta\lambda = -\lambda\tan\alpha\,\Delta\alpha = -\lambda\frac{\cos\alpha\sin\alpha}{\mu^2-\sin^2\alpha}\Delta\alpha. \tag{5.11}$$

This expression is very small near $\alpha \doteq 0$. Now, however, the bandwidth is not determined by the beam divergence of the laser, as in the methods discussed above, but rather by the transmission T of the birefringent filter. $T = \cos^2(\pi\Delta\mu d/\lambda)$. (5.12)

If a reduction of, say, 10% brings the laser below threshold, one would expect an active bandwidth of $\Delta\lambda_a = \frac{1}{6}\lambda^2/\Delta\mu d$. (5.13)

This bandwidth can be reduced further by the introduction of one or more additional quartz plates of greater thickness, as in Lyot or similar birefringent filters. Using KDP crystals of suitable orientation instead of one or more of the quartz plates, one can vary the transmission wavelength by applying a voltage (57). For further details on birefringent filters the reader is referred to the many papers dealing with this subject (58). Birefringent filters have now become the standard tuning elements of cw-dye lasers because of the ease with which they allow to achieve single longitudinal mode operation over a large tuning range. Wavelength selection by distributed feedback will be treated in section 8.

6.

DYE LASER AMPLIFIERS

The fluorescence decay time of dyes is only a few nanoseconds. This means that a dye-laser amplifier cannot store energy any longer, in contrast to solid-state laser amplifiers with their storage time µs to ms. Consequently ns pulses cannot be amplified to higher output powers than what could have been obtained in an equally high pumped oscillator. Nevertheless they are very useful to amplify the output from a low-power oscillator, that can much more easily be controlled as to spectral bandwidth and mode structure, to moderately high powers.

The usefulness of dye laser amplifiers is somewhat limited by amplified spontaneous fluorescence, which is an unavoidable background noise pedestal upon which the amplified signal sits. From basic quantum-mechanical principles it has been derived that this noise in the output of the amplifier corresponds to an input of at least one photon per mode, or to an input of blackbody-radiation of more than 20000 K. Hence only light from coherent sources strong compared to this noise will constitute useful input signals for such an amplifier.

Amplified spontaneous emission (abbreviated ASE) limits also the maximum single-pass gain of individual amplifier stages. If an amplifier stage is pumped too high, ASE will saturate both ends of the amplifier and thus deplete the inversion that was intended for signal amplification. This problem has been studied theoretically and experimentally (59), and it has been shown that in a specific example increasing the pump intensity by a factor of 100 raises the inversion available for signal amplification only by 40%. Usually amplification factors of not higher than 1000 have been obtained without an unduly high content of ASE. Sectioning the

amplifier into several stages separated by spatial, spectral, and intensity filters, however, much higher overall amplification factors are possible. An oscillator-amplifier system for ns pulses with three stages of amplification resulting in 55 mJ output energy at 220mJ pump energy is described in (60). Most commercial dye laser systems pumped by excimer lasers or frequency-multiplied Nd-YAG lasers now contain one or more amplifier stages. For details the reader is referred to the informational material of the manufacturers.

Very high peak powers can be obtained by the amplification of pulses with a pulse duration that is short compared to the fluorescence decay time. Several recent publications describe amplifiers that amplify the weak pulses of a mode-locked cw-dye laser into the GW range (61). In these systems it is especially important to suppress the ASE background which has a similar energy content because of its long duration as the ps signal. This is usually done by two or three cuvettes or free jets of saturable absorber solution, e.g. malachite green as absorber for amplifiers with rhodamine 6G as active medium. Small signal transmission is made so low (e.g. 10^{-7}) by chosing a sufficiently high absorber concentration that only the signal can saturate the absorption, giving a 50 to 70% transmission of the peak signal intensity. This also helps to compensate signal pulse broadening by saturation of the amplifier. In this way sub-ps pulses can be amplified without pulse-form degradation.

Several years ago a number of papers described regenrative dye laser amplifiers, which can be described as broadband oscillators with injection of the signal into their resonator (62). Now interest in these systems has subsided as travelling wave amplifiers have matured to give similar amplification factors without the difficulty of wild oscillations.

An interesting application of dye laser amplifiers is as image amplifier. Single pass gains as high as 30 dB and with diffraction-limited resolution have been obtained (63)

7.

MODE-LOCKING OF DYE LASERS

Dye lasers are the only source of ultrashort wavelength-tunable pulses down to fs pulse duration, working on a continuous, highly repetitive basis. They are capable of producing such pulses, since the frequency bandwidth required is still much less than that of a typical dye fluorescence band.

Mode-locking of dye lasers follows the same general ideas employed for mode-locking of solid-state dye lasers. At a suitable position in the resonator either a loss or a gain modulator is placed. Active mode-locking using electrically driven loss modulators only leads to pulses of 100 to 200 ps duration and has practically been abandoned. The only two methods that are presently being applied are passive mode-locking with organic dye solutions as saturable absorbers and gain modulation using the method that now is generally referred to as synchronous pumping.

The first passive mode-locking of a flashlamp-pumped rhodamine 6G laser used the absorber dye 3.3'-diethyloxadicarbocyanine iodide, now generally abbreviated DODCI (64). This dye is still the one that has given the shortest pulse widths. A very recent report (65) achieved pulse widths of 90 fs using this dye in a cw-dye ring laser. By a nonlinear optical method these pulses could be shortened down to 30 fs, which means the shortest optical pulse ever observed (66).

It is remarkable that the excited-state lifetime or ground-state recovery time of the saturable absorber does not determine the pulse width, which becomes immediately clear if one notices that this time in DODCI is about 1ns. Evidently, it is the interplay of saturation of the absorption and the saturation of amplification, that is important. While the saturable absorber steepens the front edge of the pulse, the trailing wing of the pulse is suppressed by the saturation of the amplification in the active medium. Not all possible pulse shapes experience this pulse sharpening mechanisms, pulses with a step-like front or Gaussian-shaped pulses are best suited for this mechanism (67). The two oppositely travelling waves in a ring laser colliding in the saturable absorber seem to enhance this effect, perhaps influenced by the grating induced by the standing wave thus created in a way that is not yet completely understood.

While passive mode-locking in pulsed dye lasers has been used in a fairly broad spectral region (68) and in cw-dye lasers only in a very restricted range due to the lack of known saturable absorbers, the method of synchronous pumping can be used in the whole spectral range of dye laser operation as long as suitable pump sources are available. Here the gain of the active medium is modulated by pumping the dye with a mode-locked pulse of an argon-ion or krypton-ion laser of typically about 100 ps pulse width. If the round-trip time of the dye laser resonator and the period of the pump-pulse occurrence are exactly matched (usually this must be done with an accuracy of at least 1μm), saturation of the dye sets in after a few round-trips and sharpens the pulse down to sub-ps pulse widths, provided all parameters are optimized (69).

8.

SPECIAL FORMS OF DYE LASERS AND OUTLOOK

Vapor-phase dye lasers have the (as of yet unfulfilled) promise of giving shorter wavelength laser emission than in solution, since most dyes show hypsochromic spectral shifts when going to the vapor phase. At the same time, however, photochemical stability is impaired because of a lack of stabilizing collisions with solvent molecules. Russian workers have successfully circumvented this difficulty by using high pressure (up to 30 bar) buffer gases like pentane or ether (70) and a flow sytem for the vapor (71). The molecular prerequisites for a good laser dye for use in the vapor phase have been discussed above.

The most severe drawback of solid-state dye lasers is the relatively bad photochemical stability of dyes imbedded in plastics material. As soon as better dyes are available they might become of high interest because of their intrinsic simplicity and cheapness (72). Also dyes embedded in crystals are no solution because of the softness and low optical damage threshold of the suitable crystals (73).

Distributed-feedback dye lasers, once more of a laboratory curiosity (74), have recently come into prominence because of their potential for generating tunable ps pulses in an astonishingly simple way. In these lasers two coherent pump beams impinge on a dye cuvette creating a fringe pattern in the surface layer of the dye. In the maxima the dye is pumped strongly, creating a phased array of excited dye layers that create gain-modulated distributed feedback without the need of an external resonator. The laser wavelength of such a device is determined by the fringe spacing and the refractive index of the solution by a simple Bragg condition. Tuning is possible in various ways: changing the index of refraction by pressurizing or changing the composition or temperature of the solvent, and changing the angle of incidence of the two pump beams. BOR was the first to notice the capability of a distributed-feedback dye laser pumped by short pulses of a nitrogen laser to generate single ps pulses (75). This comes about because of a self-Q-switching or cavity-dumping action that is best understood looking at the set of coupled rate equations describing laser action in these devices. For lack of space the reader is referred to the papers of BOR and coworkers (76).

Looking back at the one and a half decades of dye laser development, one notices that over 1000 papers have been published on dye laser development and many more on applications of dye lasers. Still the potential for further development seems tremendous. This starts with the active medium itself, where the carefully planned design of new laser dyes has just begun to show very promising results with higher efficiency, better photochemical stability and greater wavelength coverage. The extremely large spectral bandwidths available in dyes promise still shorter pulses, possibly down to 1 fs. With higher pump-pulse energies of excimer lasers becoming available one can expect further increase of peak power of ultrashort pulses, possibly into the terawatt region. Increasing efficiency of flashlamp-pumped dye lasers will bring the average power of these lasers into the multi-kilowatt region and might make them eligible for specialized industrial applications. These few examples may suffice to indicate that there is a bright future ahead for dye lasers.

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