Tunable Lasers. Organic Dye lasers

From a structural standpoint, organic dye molecules that contain carbon-carbon double bonds and, in particular, sequences of alternate single and double bonds, such structures are said to be conjugated structures.

Usually all dye molecules contain the hexagonal carbon ring structures (benzene rings) that characterize aromatic hydrocarbons.

Relatively loosely bound electrons associated with these benzene rings lead to the interesting energy level structures of organic dyes.

These electrons travel freely from nucleus to nucleus within the plane of the ring.

In the orbital motion in the ground state, there are an even number of electrons that can be grouped together in pairs. Each pair consists of one electron with the direction of its spin momentum vector pointing up and the other pointing down, so the overall spin moment is zero.
in a single emission. Above, we can observe these transitions.
in a simple model the fluorescence and absorption spectra should be mirror images.

Fig. 12.3. (a) Idealized absorption and fluorescence spectra of an aromatic organic dye. The vibrational structure is usually smeared out in solution.

Fig. 12.3. (cont.)
(b) Absorption and emission spectra of the organic dye Rhodamine 6G dissolved in ethanol.
Absorption of a photon from the pump:

\[ h \nu_{\text{pump}} + (\text{dye at } q_0 \text{ in } S_0) \rightarrow (\text{dye at } q_0 \text{ in } S_1) \]

Relaxation in the upper \( S_1 \) manifold:

\[ (\text{dye in } S_1 \text{ at } q_0) + (\text{solvent}) \xrightarrow{\text{very fast}} (\text{dye in } S_1 \text{ at } q_1) \]

Spontaneous or stimulated emission back to \( S_0 \)

\[ (\text{dye at } q_1 \text{ in } S_1) + (h \nu_{\text{laser}}) \xrightarrow{\text{stimulated emission}} (\text{dye at } q_1 \text{ in } S_0) \]

Relaxation in the lower \( S_0 \) manifold:

\[ (\text{dye at } q_1 \text{ in } S_0) + (\text{solvent}) \xrightarrow{\text{very fast}} (\text{dye at } q_0 \text{ in } S_0) \]

\textbf{Possible losses:}

- \( T_1 \rightarrow T_2 \) is at the same wavelength as \( S_1 \rightarrow S_0 \)
- \( S_1 \rightarrow S_2 \) absorption
- Regions of unpumped dye
<table>
<thead>
<tr>
<th>Dye</th>
<th>Structure</th>
<th>Solvent</th>
<th>Wavelength</th>
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<tbody>
<tr>
<td>Acridine red</td>
<td><img src="image" alt="Acridine red" /></td>
<td>EtOH</td>
<td>Red</td>
</tr>
<tr>
<td>Puronin B</td>
<td><img src="image" alt="Puronin B" /></td>
<td>MeOH, H₂O</td>
<td>Yellow</td>
</tr>
<tr>
<td>Rhodamine 6G</td>
<td><img src="image" alt="Rhodamine 6G" /></td>
<td>EtOH, MeOH, H₂O, DMSO, Polymethylmethacrylate</td>
<td>Yellow</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td><img src="image" alt="Rhodamine B" /></td>
<td>EtOH, MeOH, Polymethylmethacrylate</td>
<td>Red</td>
</tr>
<tr>
<td>Na-fluorescein</td>
<td><img src="image" alt="Na-fluorescein" /></td>
<td>EtOH, H₂O</td>
<td>Green</td>
</tr>
<tr>
<td>2,7-Dichlorofluorescein</td>
<td><img src="image" alt="2,7-Dichlorofluorescein" /></td>
<td>EtOH</td>
<td>Green</td>
</tr>
<tr>
<td>7-Hydroxycoumarin</td>
<td><img src="image" alt="7-Hydroxycoumarin" /></td>
<td>H₂O (pH ~ 9)</td>
<td>Blue</td>
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<tr>
<td>4-Methylumbelliferone</td>
<td><img src="image" alt="4-Methylumbelliferone" /></td>
<td>H₂O (pH ~ 9)</td>
<td>Blue</td>
</tr>
<tr>
<td>Esculin</td>
<td><img src="image" alt="Esculin" /></td>
<td>H₂O (pH ~ 9)</td>
<td>Blue</td>
</tr>
</tbody>
</table>

Molecular structure, laser wavelength, and solvents for some laser dyes.
Performance of various dyes when pumped with an argon-ion or Krypton-ion laser.
Pulsed Laser Excitation

Fig. 12.4. Simple arrangements for (a) side-pumping and (b) end-pumping of simple pulsed dye lasers. In each case the dye solution is contained in an optical cuvette with wedged, antireflection coated (AR) faces. In (a) the laser beam is focused with a cylindrical lens (CL) to a line image in the cuvette. In (b) the pump laser is focused with a spherical lens (L). \( M_1 \) and \( M_2 \) are the dye laser cavity mirrors.
Fig. 12.5. Schematic diagram of a high energy pulsed dye laser using a coaxial flashlamp. The liquid filter absorbs short wavelength ultraviolet that can photodissociate dye molecules.

\[ Q \cdot \theta_e = Q_m + Q_c \cdot 0.2 \quad \theta_e = \frac{Q_0 - Q_m}{2} \beta = \theta \]

Fig. 12.6. A pulsed dye laser design that uses a reflective diffraction grating for wavelength tuning and an intracavity etalon for line-narrowing. This is referred to as a Hansch-type dye laser.[123]

\[ m = \sin \theta \]

Condition for ultrastability

Fig. 12.7. Littman-type pulsed dye laser[123,126] that uses a grazing incidence grating for simultaneous tuning and line-narrowing.
Hänsch-type dye laser with transverse pumping and beam expander. The wavelength is tuned by turning the grating. Light with a different wavelength $\lambda_D + \Delta \lambda$ is diffracted out of the resonator.

Possible resonator designs for longitudinal pumping of dye lasers.
Short dye-laser cavity with grazing incidence grating. Wavelength tuning is accomplished by turning the end mirror, which may also be replaced by a Littrow grating.

Littman laser with grazing incidence grating and Littrow grating using longitudinal pumping.
Excimer-laser pumped dye laser with oscillator and two amplifier stages. This design suppresses effectively the ASE (Lambda-Physik FL 3002)
CW Dye Laser Operation

Fig. 12.8. Schematic of a CW dye laser design incorporating an astigmatically compensated laser cavity and an intracavity flowing dye jet at Brewster's angle.

Fig. 12.9. Typical tuning curves of various dyes pumped by argon and krypton ion laser lines. The dyes and pump wavelengths are as follows: S1 (Stilbene 1, Ar+ 351–364 nm); S3 (Stilbene 3, Ar+ 351–364 nm); C102 (Coumarin 102, Kr+ 407–423 nm); C7 (Coumarin 7, Ar+ 476 nm); C6 (Coumarin 6, Ar+ 488 nm); R110 (Rhodamine 110; Ar+ 458–514 nm); R6G (Rhodamine 6G, Ar+ 458–514 nm); DCM (Ar+ 458–514 nm); PYR1 (Pyridenel1, Ar+ 458–514 nm); LD700 (Kr+ 647 and 676 nm); OX750 (Oxazine, 750 Kr+ 647 and 676 nm); STY (Styryl 9 Ar+ 458–514 nm); HITC (HITC-P Kr+ 647 and 676 nm); IR140 (Kr+ 752 and 799 nm) (Tuning curves courtesy of Spectra-Physics, Inc.).
Three possible standing-wave resonator configurations used for CW dye lasers: (a) collinear pumping geometry, (b) folded astigmatically compensated resonator of the Kogelnik type [5.135] with a Brewster prism for separation of pump beam and dye-laser beam, and (c) the pump beam is focussed by an extra pump mirror into the dye jet and is tilted against the resonator axis.
Calculation of Threshold. Pump Power in Dye Lasers

- Losses - possible build-up of triplet state molecules in the T1 state.

- \( \Delta I_p = \sigma_p N \)
  - \( \sigma_p \) - absorb. cross section at the pump wavelength.
  - \( N \) - ground state dye concentration.

- If all the pump radiation of intensity \( I_p \) is absorbed by the dye solution of thickness \( d \), the pumping rate

\[ \frac{dN}{dt} + N_2 = R - \frac{N_2}{\tau_p} - k_{sp} N_2 \]
Pulsed Operation
For RG

\[ \lambda_r = 5.66 \times 10^{-3} \text{ mm} \]

\[ \Delta Y = 60 \text{ mm} = 5.4 \times 10^{-3} \text{ m} \]

\[ I_{\rho} = \frac{2 \pi^2 \times 0.01 \times 5.4 \times 10^{-3} \times 6.2 \times 10^{-3} (5.66 \times 10^{-3})}{(5.80 \times 10^{-5})^2 \times 10^{-2}} = 20 \text{ KW/cm}^2 \]

if the width of the beam is 1 mm

\[ P = 2 \text{ KW} \]

for \( t_p = 10 \text{ ns} \)

\[ E_{\text{in}} = 2.0 \mu \text{J} \]
CW Operation

- We can no longer neglect the distort. loss ch. that results from transfer of mol. to triplet state.

- for triplet state

\[ \frac{dN_T}{dt} = N_0 K_{st} - \frac{N_T}{T_T} \]

- The S→T transfer rate can be estimated from the fluorescence quantum efficiency \( \phi \) by assuming that any molecule that does not fluoresce to the ground state crosses to \( T \).

\[ \phi = \frac{1}{T_T + K_{st}} \quad \Rightarrow \quad K_{st} = \frac{1}{T_T} (1 - \phi) \]

- in equilibrium \( \frac{dN_T}{dt} = 0 \) \( \Rightarrow \) \( N_T = N_0 K_{st} T_T \)

- the threshold gain is

\[ \gamma_T(\lambda) = \lambda(\lambda) - \frac{1}{2c} c \mu R_1(\lambda) R_2(\lambda) \]

- the distributed loss comes from \( S_0 \to S_1 \) and \( T_1 \to T_2 \)

\[ \lambda(\lambda) = N_0 \sigma_{a,1}(\lambda) + N_T \sigma_{T,1}(\lambda) \]

\( \sigma_{a,1}(\lambda), \sigma_{T,1}(\lambda) \) - abs. cross-sections for absorb. at the laser wavelength, \( \lambda \) from the ground state and from \( T_1 \), respectively.
if we write \( J^*(\lambda) = N_2 \sigma_2(\lambda) \)
where \( \sigma_2 \) is the stimulated emission cross-section, then

\[
N_2 \sigma_2(\lambda) = N_0 \sigma_2(\lambda) + N_T \sigma_T(\lambda) - \frac{1}{2e} \ln R_1(\lambda) R_2(\lambda)
\]

where \( N \) is the total dye concentration \( N \) must satisfy

\[
N = N_0 + N_2 + N_T
\]

\[
N_T = N_2 K_{ST} T_T
\]

\[
\Rightarrow N_2 \sigma_2(\lambda) = \left[ N - N_2 - N_2 K_{ST} T_T \right] \sigma_2(\lambda) + N_2 K_{ST} T_T \sigma_T(\lambda) - \frac{1}{2e} \ln R_1(\lambda) R_2(\lambda)
\]

\[
N_2 \left[ \sigma_2(\lambda) + \sigma_T(\lambda) - K_{ST} T_T (\sigma_T(\lambda) - \sigma_2(\lambda)) \right] = N \sigma_2(\lambda) - \frac{1}{2e} \ln R_1(\lambda) R_2(\lambda)
\]

\[
\Rightarrow N_2(\lambda) = \frac{N \sigma_2(\lambda) - \frac{1}{2e} \ln R_1(\lambda) R_2(\lambda)}{\sigma_2(\lambda) + \sigma_T(\lambda) - K_{ST} T_T (\sigma_T(\lambda) - \sigma_2(\lambda))}
\]

for ideal dye \( \sigma_T(\lambda) = 0 \) \( K_{ST} T_T = 0 \)

\[
\Rightarrow N_2(\lambda) = \frac{- \frac{1}{2e} \ln R_1(\lambda) R_2(\lambda)}{\sigma_2(\lambda)} = \frac{\frac{1}{2e} \ln R_1(\lambda) R_2(\lambda)}{\sigma_2(\lambda)}
\]

\[
\frac{2 \pi^2 T_T T_2 v}{\lambda^2 e}
\]

10x more laser focused 
\( p_{min} = 25 \text{ MW/cm}^2 \)
Spectral gain profiles of different laser dyes, illustrated by the output power of pulsed lasers (a) and CW dye lasers (b) (Lambda-Physik and Spectra-Physics information sheets).

(a) Schematic energy level scheme and pumping cycle in dye molecules, and (b) absorption and fluorescence spectrum of rhodamine 6G solved in ethanol.
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<tr>
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<tbody>
<tr>
<td>Excimer laser</td>
<td>370÷985</td>
<td>10÷200</td>
<td>$\leq 10^7$</td>
<td>$\leq 300$</td>
<td>20÷200</td>
<td>0.1÷10</td>
</tr>
<tr>
<td>N₂ laser</td>
<td>370÷1020</td>
<td>1÷10</td>
<td>$&lt;10^5$</td>
<td>$&lt;1$</td>
<td>$&lt;10^3$</td>
<td>0.01÷0.1</td>
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<tr>
<td>Flash lamp</td>
<td>300÷800</td>
<td>300÷$10^4$</td>
<td>$10^2÷10^4$</td>
<td>$&lt;5000$</td>
<td>1÷100</td>
<td>0.1÷200</td>
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<td>Ar⁺ laser</td>
<td>400÷1100</td>
<td>CW</td>
<td>CW</td>
<td>-</td>
<td>CW</td>
<td>0.1÷5</td>
</tr>
<tr>
<td>Kr⁺ laser</td>
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<td></td>
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<tr>
<td>Nd:YAG laser</td>
<td>400÷920</td>
<td>10÷20</td>
<td>$10^5÷10^7$</td>
<td>10÷100</td>
<td>10÷30</td>
<td>0.1÷1</td>
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<tr>
<td>Copper vapor laser</td>
<td>530÷890</td>
<td>30÷50</td>
<td>$\approx 10^4÷10^5$</td>
<td>$\approx 1$</td>
<td>$\approx 10^4$</td>
<td>$\leq 10$</td>
</tr>
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Inorganic Liquid Dye

Table 12.1. Some liquid lasers.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Solvent</th>
<th>Laser wavelength (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$^{3+}$</td>
<td>SeOCl$_2$–SnCl$_4$</td>
<td>1.056, 1.33</td>
</tr>
<tr>
<td></td>
<td>POCl$_3$–SnCl$_4$</td>
<td>1.052–1.06</td>
</tr>
<tr>
<td>Eu$^{3+}$ (in a complex with phosphorous ions and benzoylacetone)</td>
<td>POCl$_3$–ZrCl$_4$</td>
<td>1.056</td>
</tr>
<tr>
<td>Eu$^{3+}$ (in a complex with dimethyl ammonium ions and trifluoroacetyleacetone)</td>
<td>Ethanol</td>
<td>0.6129</td>
</tr>
<tr>
<td>Eu$^{2+}$</td>
<td>Acetonitrile</td>
<td>0.6119</td>
</tr>
<tr>
<td>Tb$^{3+}$ (in a complex with phosphorous ions and thenoyltrifluoroacetone)</td>
<td>Polymethylmethacrylate (plexiglas)</td>
<td>0.545</td>
</tr>
</tbody>
</table>

Fig. 12.12. Fluorescence spectra of Nd$^{3+}$ ions in:
(a) SeOCl$_2$ solvent;
(b) POCl$_3$ solvent; (c) glass.
3. A 5-W argon laser operating at 514.5 nm is used as a pumping beam for Rhodamine 6G dye laser. The dye gain medium consists of a rapidly flowing dye jet stream of thickness 0.5 mm. The dye concentration is of sufficient density such that 100% of the pump beam is absorbed in the dye. What spot size (diameter) would the pump laser need in order to produce a single pass exponential gain of 1 ($\sigma_{NL}=1$)? Assume the upper laser level lifetime of the dye is $\tau_2=5$ ns, $A_{21}=1/\tau_2$ and every pump photon that is absorbed is converted to an upper laser level species within the lifetime of that level. Assume that the lower laser level population is negligible since it rapidly decays ($\tau_1=0$) to the bottom of the singlet ground state.

1) $g(\nu, \nu) = \frac{2}{\pi A\nu} \frac{2}{1 + \left(\frac{2(\nu - \nu_0)}{\Delta \nu}\right)^2} = \frac{2}{\pi A\nu} = \frac{2}{5.4 \times 10^{-13}} = 117 \times 10^{-5}$

2) $\sigma = \frac{C^2 A_{21}}{8\pi \gamma^2} g(\nu, \nu) = \frac{\alpha^2 A_{21}}{8\pi \left(\frac{8 \times 10^{-3}}{5.8 \times 10^{-3}}\right)^2} = \frac{1.17 \times 10^{-4}}{3.3 \times 10^{-10} m^2} = 3.3 \times 10^{-6} cm^2$

3) $f(\nu) = \frac{\Delta N_0}{(1 + \frac{I\nu}{f(\nu)})}$

$I_S = \frac{8\pi h\nu^3}{C^2 \sigma} g(\nu, \nu) = \frac{8\pi \cdot 6.62 \times 10^{-34} \cdot \frac{3}{\nu^2}}{\frac{8\pi \cdot 6.62 \times 10^{-34} \cdot \frac{3}{\nu^2}}{1 \times 117 \times 10^{-14} (5.8 \times 10^{-3})^3} = \frac{1}{1 \times 117 \times 10^{-14} (5.8 \times 10^{-3})^3} = 1.6 \times 10^{-5} \text{ m}^2$

$\Phi = A_{21} \tau_2 \left[1 + (1 - A_{21} \tau_2) \frac{\nu_0}{\nu}\right] = A_{21} \tau_2 = \frac{1}{\tau_2} \cdot \tau_2 = 1$

4) $\frac{dN_2}{dt} = R_2 - \frac{N_2}{\tau_2} \Rightarrow \Delta N_2 = N_2^0 = R_2 \tau_2 = \frac{I\nu}{h\nu} \tau_2 = \frac{5.5 \times 10^{-9}}{6.62 \times 10^{-34} \cdot 3 \times 10^8} = \frac{1.3 \times 10^{-14}}{A} \text{ m}^{-3}$

5) $f(\nu) = \sigma N = \frac{\sigma_{NL} I_0}{L} = \frac{1}{0.5 \times 10^{-3}} = 2000 \text{ m}^{-1}$

6) find $I_0$ or $I_0 / f(\nu)$
Optimal transmitted intensity from the laser can be obtained by replacing $T$ by $T_{\text{opt}}$ in equation for the output intensity at each mirror (5.55). It will result in:

$$I_{\text{max}} = \left( \frac{T_{\text{opt}}^2}{2} \right) I_s$$

- Absorption losses
  - $\alpha = 0.02$; 2%
  - $T_{\text{opt}} = 0.2$; 20%

$$I_{\text{max}} = \left( \frac{0.2^2}{2 \times 0.02} \right) I_s = I_s = 1.6 \times 10^9 \text{ W/m}^2$$

$$\frac{I_{\text{max}}}{I_s} = 5 \Rightarrow I_{\text{max}} = 5 I_s$$

$$\Rightarrow \frac{I_{\text{r}}}{I_s} \leq 5$$

2) $J(V) = \frac{\Delta N^o}{(1 + \frac{I_{\text{r}}}{I_s})}$

$$2000 = \frac{1.3 \times 10^{14} \times 3.3 \times 10^{-20}}{1 + 5} = \Rightarrow A = 3.5 \times 10^{-10} \text{ m}^2$$

$$d = \sqrt{\frac{4A}{n}} = 2.1 \times 10^{-6} \text{ m} = 21 \mu\text{m}$$