Lasers

PH 645/ OSE 645/ EE 613
Summer 2010 Section 1: T/Th 2:45- 4:45 PM
Engineering Building 240

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Chapter 5: Radiative Transitions and Emission Linewidth

- Molecular Energy Levels and Spectra
- Liquid Energy Levels and Their Radiation Properties
- Energy Levels in Solids – Dielectric Lasers
- Energy levels in Solids – Semiconductor Lasers – See notes from Kasap/Yariv

Chapter 5 Homework: 1, 4, 5, 6, 7, 12, 14, 15

All figures presented from this point on were taken directly from (unless otherwise cited): W.T. Silfvast, Laser Fundamentals 2nd ed., Cambridge University Press, 2004.
Atomic and Molecular Bonding

• Attractive forces between atoms form strong intramolecular bonds as a result of chemical interactions
  – Covalent: carbon-carbon
  – Ionic: sodium-chloride

• Intermolecular bonding:
  – Van der Walls
  – Ion-Dipole
  – Binding interactions between molecules – Hydrogen bonding
    • Twice as strong as dipole-dipole bonding
    • 2.5-3.5 Ang in length (covalent H- is <2 Ang)

\[ U_{\text{ionic}} = B e^{-\frac{R}{r}} - \frac{A Q_1 Q_2 e^2}{4\pi\varepsilon_0 r} \]

Types of Intramolecular bonding

- **Ion-Ion and Ion-Dipole Interactions**
  - Purely electrostatic

- **Van der Waals**
  - Dipole-Dipole interactions
  - Coulombic alignment of two or more permanent dipoles

- **Hydrogen Bonding**
  - Extremely strong dipole-dipole interactions
  - Occurs between two highly electronegative and small atoms like O and N and a shared H.
  - Highly directional and quite specific

- **Hydrophobic Interactions**
  - Bonding between nonpolar molecules in aqueous solvents
  - Alignment of nonpolar regions changes the shape of the molecule and provides more attachment for polar sections through hydrogen or other intramolecular bonding mechanisms.

- **Repulsive Forces**
  - Steric repulsion occurs when electron clouds overlap
  - Hydrophilic repulsion occurs in polar liquids with nonpolar elements in attempt to maximize hydrogen bonding
  - Repulsive entropic elasticity: repulsive forces due to compression of long chain macromolecules
  - Repulsive osmotic: from electrical double layers between two charged surfaces and steric alignment in macromolecules
Quantized Energy Levels vs. Separation Distance

- As two atoms are brought together, the resulting energy levels of the combined atoms become the energy levels of the molecule formed.
- The median dip in energy associated with the mean binding distance predicted by the Leonard Jones potential of each species provides the separation distance of between atoms in the molecule.
- A dissociation energy, $D_o$, must be applied to
Classification of Molecules

- Consider a molecule with N atoms
- Each atom has 3 degrees of freedom (DoF)
- The molecule therefore has 3N degrees of freedom
- 3 DoF involve translational directions of motion
- 3 DoF involve rotation of the entire molecule about the central axis
- The remaining 3N-6 involve different vibrational modes of each atom in the molecule
  - If molecule is linear, the value is 3N-5
- Simple molecules are categorized into 4 basic types
  - Linear
  - Spherical Top
    - too complex for further discussion
  - Symmetrical Top
  - Asymmetrical Top
    - too complex for further discussion
Rotational Molecular Energies of Linear Molecules

- Allowed rotational energies depend on the molecules and their atomic angular momentum
  \[ E_{\text{rot}}^J = \frac{J(J + 1)\hbar^2}{2I} = J(J + 1)Bhc \]
  \[ B = \frac{\hbar}{8\pi^2cI} \]

- The moment of inertia, \( I \), is the summation of the masses of each atom times the square of the distance between them:
  \[ I = \sum m_i r_i^2 \]

- If we define \( r \) as the center of gravity, then
  \[ r = \frac{\sum_i m_i r_i}{\sum_i m_i} \]

- For a 1-D molecule,
  \[ I = m_1 r_1^2 + m_2 r_2^2 \]

- Thus, the moment of inertia equals
  \[ I = \frac{m_1 m_2}{m_1 + m_2} (2r)^2 \]

- Allowing one to define the effective (reduced) mass of the molecule as:
  \[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

**Oxygen**  |  **Carbon**  |  **Oxygen**
Radiative Decay of Excited States from Isolated Atoms

• This reduction in energy generally occurs in two ways:
  – Inelastic scattering of atoms leading to momentum transfer and loss
  – Isolated atoms that do not scatter but instead radiate light from into the system in order to reduce their energy states from $E_u - E_1$

• For optical systems we are primarily concerned with radiative energy transfer which we define as *spontaneous emission*
Wavelengths Emitted by Changes in Rotational Energy

• Compute the first excited rotational energy \((J=1)\) of the H\(_2\) molecule, the ground \((J=0)\) and the radiation wavelength associated with the transition

• Assume a separation radius, \(r = 0.0535\) nm = \(\text{b}\)

\[
M = 2M_H = 2 \times 1.67 \times 10^{-27} \text{ kg} \\
I = Mb^2 = (3.34 \times 10^{-27} \text{ kg})(0.0535 \text{ nm})^2 = 9.56 \times 10^{-48} \text{ kg-m}^2 \\
B = \frac{h}{8\pi^2 cl} = \frac{6.62 \times 10^{-34} \text{ J-s}}{8\pi^2 (3 \times 10^8 \text{ m/s})(9.56 \times 10^{-48} \text{ kg-m}^2)} \\
= 2.92 \times 10^3 \text{ J-s}^2/\text{kg-m}^3.
\]

\[
E_{rot}^J = \frac{J(J+1)\hbar^2}{2I} = J(J+1)Bhc \\
= J(J+1)(2.92 \times 10^3 \text{ J-s}^2/\text{kg-m}^3)(6.62 \times 10^{-34} \text{ J-s})(3 \times 10^8 \text{ m/s}) \\
= J(J+1)(5.80 \times 10^{-22} \text{ J}^2/\text{kg-m}^2) = J(J+1)(5.80 \times 10^{-22} \text{ J}).
\]

\[
E_{rot}^1 = 1(1+1)(5.80 \times 10^{-22} \text{ J}) = 1.16 \times 10^{-21} \text{ J} = 7.25 \times 10^{-3} \text{ eV}
\]

\[
\lambda_{10} = \frac{hc}{E_{rot}^1 - E_{rot}^0} = \frac{(6.62 \times 10^{-34} \text{ J-s})(3 \times 10^8 \text{ m/s})}{1.16 \times 10^{-21} \text{ J}} \\
= 1.71 \times 10^{-4} \text{ m} = 171 \mu\text{m},
\]
Example: First 5 Rotational Energy Levels of a Diatomic molecule

- The separation ratio of different atomic states increases as:

\[
\frac{(J + 1)(J + 2)Bhc}{J(J + 1)Bhc} = \frac{J + 2}{J}
\]

\[
\Delta J = 0, \pm 1
\]
Rotational Molecular Energies of Symmetric Top Molecules

- Allowed rotational energies depend on the molecules and their atomic angular momentum

\[ E_{\text{rot}} = J(J + 1)Bhc + K^2(C - B)hc \]

- \( K \) has values of 1, 2, 3, …
- \( J = K, K + 1, K + 2, \text{ etc.} \)

- \( I_c \) is the rotation about the symmetry axis and \( I_b \) is the rotation about the perpendicular axis:

\[ B = \frac{h}{8\pi^2 c I_b}, \quad C = \frac{h}{8\pi^2 c I_c} \]

- Selection rules involving rotational levels

\[ \Delta J = 0, \pm 1, \quad \Delta K = \pm 1 \]

- Where \( J \) and \( K \) are quantum numbers and must be separated between neighboring states by +/- 1
Rotational – Vibrational Transitions

• J selection rule for Rotational - Vibrational Transitions

\[ \Delta J = 0, \pm 1, \quad \Delta J = J_u - J_l \]

\[ \Delta J = -1 \quad \text{P branch} \]
\[ \Delta J = 0 \quad \text{Q branch} \]
\[ \Delta J = +1 \quad \text{R branch} \]

• In most diatomic molecules, Q branch transitions are not allowed
• In tri-atomic molecules, the selection rules, \( \Delta v = \pm 1 \) is not always relevant, b/c transitions can occur from one vibration mode to another
  – Example: \( \text{CO}_2 \)

\[ v_1 = 0, \; v_2 = 0, \; v_3 = 1 \quad (0, 0, 1) \]
\[ v_1 = 0, \; v_2 = 2, \; v_3 = 0 \quad (0, 2, 0) \]

Allowed b/c \( J=1 \) to \( J=2 \)

Oxygen – Carbon – Oxygen

\( J=1 \)  \( \rightarrow \)  \( J=2 \)
Rotational – Vibrational Transitions

**Figure 5-5** Energy-level diagram, showing two specific vibrational levels within a single vibrational mode of a molecule along with the rotational sublevels, as well as the presence of the P- and R-branch transitions and absence of Q-branch transitions.

\[ \Delta J = 0, \pm 1, \quad \Delta J = J_u - J_l \]

- \( \Delta J = -1 \) P branch
- \( \Delta J = 0 \) Q branch
- \( \Delta J = +1 \) R branch
Energy level Diagram of Vibrational Energies of a 10.6 um CO$_2$ laser

- Assume the laser has an operating temperature of 500 K
- Assume (correctly) that CO2 is a linear triatomic molecule with three normal modes of vibration

![Diagram of CO$_2$ molecule with normal modes]

For CO$_2$, the normal mode frequencies are:

- $v_1 \approx 4.16 \times 10^{13}$ s$^{-1}$, symmetric stretch mode ($v_1$).
- $v_2 \approx 2.00 \times 10^{13}$ s$^{-1}$, bending mode ($v_2$).
- $v_3 \approx 7.05 \times 10^{13}$ s$^{-1}$, asymmetric stretch mode ($v_3$).

- Thus it has three separate quantum numbers, $v_1, v_2, v_3$.

$$E_{total}(v_1, v_2, v_3) = h v_1 (v_1 + \frac{1}{2}) + h v_2 (v_2 + \frac{1}{2}) + h v_3 (v_3 + \frac{1}{2})$$

$$E_1 = v_1 h v_1 = 1 \cdot (4.14 \times 10^{-15} \text{ eV-s})(4.16 \times 10^{13} \text{ s}^{-1}) = 0.172 \text{ eV.}$$

$$E_2 = v_2 h v_2 = 0.083 \text{ eV} \quad \text{for } v_2 = 1, \ v_1 = 0, \ v_3 = 0;$$

$$E_3 = v_3 h v_3 = 0.292 \text{ eV} \quad \text{for } v_3 = 1, \ v_1 = 0, \ v_2 = 0.$$
Energy level Diagram of Vibrational Energies of a 10.6 um CO₂ laser

- Thus the ground state of the CO₂ molecule is:

\[ E(0, 0, 0) = \frac{1}{2}(h\nu_1 + h\nu_2 + h\nu_3) \]

- Each vibrational level has a superimposed set of rotational levels solved using \( B = 39/m \)

\[ E_{\text{tot}} = J = J(J + 1)Bhc \]

\[ = J(J + 1)(39 \text{ m}^{-1})(4.14 \times 10^{-15} \text{ eV-s})(3 \times 10^8 \text{ m/s}) \]

\[ = J(J + 1)(4.84 \times 10^{-5}) \text{ eV.} \]

- Thus the rotational levels are spaced at roughly 3 orders of magnitude smaller than the vibrational energies.

- Using selection rules: \( \Delta J = 0, \pm 1 \)

- And noting that CO₂ is a linear triatomic molecule that does not demonstrate a Q branch, then radiative emission occurs between:

  \((0,0,1) \rightarrow (1,0,0)\)

  \((0,0,1) \rightarrow (0,2,0)\)
Energy level Diagram of Vibrational Energies of a 10.6 um CO\textsubscript{2} laser

- Other common transitions occur between 
  \((0,0,1) \rightarrow (0,2,0)\) P(20) and R(20) transitions
- The P symbol indicates a \(\Delta J = -1\) transition requiring the transition to occur from the \(J=19\) of the \((1,0,0)\) state to the \(J = 20\) of the \((0,0,1)\) state
- The R(20) transition requires the \(\Delta J = +1\) transition from the \(J=21\) of the \((0,0,1)\) state to the \(J = 20\) of the \((1,0,0)\) state
- For reasons of symmetry, alternate lines of the P and R states are missing and not shown in the figure
Energy level Diagram of Vibrational Energies of a 10.6 um CO₂ laser

- The Doppler line width of these transitions is obtained using the equations from chapter 4 and mass numbers provided in the appendix of your text

\[
\Delta \nu_D = (7.16 \times 10^{-7}) \nu_0 \sqrt{\frac{T}{M_N}} = (7.16 \times 10^{-7}) \frac{3 \times 10^8 \text{ m/s}}{10.6 \times 10^{-6} \text{ m}} \sqrt{\frac{500K}{44}}
\]

\[
= 6.83 \times 10^7 \text{ Hz},
\]

- The corresponding energy associated with the Doppler shift is

\[
\Delta E = h \Delta \nu = 2.83 \times 10^{-7} \text{ eV}
\]

- Because the separation between the 10.6 um and the 9.4 um line is large, compared to the Doppler broadening, one will observe 2 distinct laser lines.

- Pressure broadening of CO₂ lasers begins to affect emission line widths at 50 Torr

- Above 8 atm, pressure broadening becomes so large that emission lines smear to create a continuous spectrum between 9.4 and 10.6 um.

- Radiative Transition probabilities for CO₂ are also low:

- 10.6 \mu m (0, 0, 1) \rightarrow (1, 0, 0) \quad A_{ul} = 0.35/s
- 9.4-\mu m (0, 0, 1) \rightarrow (0, 2, 0) \quad A_{ul} = 0.2/s
- 4.3 \mu m (1, 0, 0) \rightarrow (0, 0, 0) \quad A_{ul} = 200-210/s
Emission Linewidth for Molecular Transitions

- As noted in Chapter 4, the line width radiated in an atomic transition is determined by summing the homogenous and inhomogeneous line broadening of the atom.
- If the quantum broadening terms (homogenous) overlap due to similar atomic transitions that occur in each atom of the molecule for rotation and vibration, then the broadening will be much greater.
- Again this can be explained by the smearing effect observed in CO2 laser emissions operating at higher atmospheric pressures.
Probabilities of Rotational and Vibrational Transitions

- Note that it is the relative arrangement of various atoms in a molecule with respect to one another that defines the rotational-vibrational states.
- Simple molecules are have well defined spatial arrangements due to allowable movements of their individual bonds.
- More complex molecules will have bond arrangements that would lend to fold over on top of other portions of the molecule if it were not for dipole repulsion.
- Solutions for atomic placement in a molecule are completed by solving the Schrödinger equation using measured values for the mean binding distance (and for very large molecules adding an extra potential terms for dipole and/or H-bond interactions that might occur).
- Solutions for molecules of more than 5 atoms can become extremely complex unless additional symmetry considerations come into play.
- For simple molecules, the QM equation below for electric dipole interactions provides typical decay rates for rotational –vibrational \(10^{-1}\) to \(10^3\) s\(^{-1}\) range of

\[ M_{ul} = \langle er \rangle = \int \psi_u^* e \mathbf{r} \psi_l dV \]

- Pure rotational translations are even slower.
Electronic Energy Levels in Molecules

- Energy levels in molecules are labeled similarly to that of atomic levels except that one uses capital Greek letters.
- For angular momentum:
  \[ \Lambda: 0, 1, 2, 3, \]
  \[ \text{electronic state: } \Sigma, \Pi, \Delta, \Phi \]
- Where the quantum number \( J = \Lambda, \Lambda+1, \Lambda+2, \ldots \)
- The spin determines the multiplicity of the state and is given by \( 2S+1 \)
- The spin describes the sub-levels of a given \( J \) value.
- Singlet states are \( S = 0 \)  \( ^1\Sigma, ^1\Pi, ^1\Delta, \ldots \)
- Doublet states are \( S = \frac{1}{2} \) \( ^2\Sigma, ^2\Pi, ^2\Delta, \ldots \)
- As before multiplicity of degenerate sublevels is always odd if the number of electrons is even and vice versa.
- Excited states (\( n = 1, 2, 3, \ldots \)) are labeled as \( X, A, B, C \ldots \) where \( X \) is the ground state, and \( A, B, C \) are the first second and third excited states.
- Finally, the parity of the system is denoted in the subscript. \( g \) for even parity, \( u \) for odd parity.
- Thus a molecular excitation might be written as
  \[ X^2 \Sigma_u \rightarrow A^2 \Pi_g \]
Electronic Transitions and Associated Selection Rules for Molecules

- Electronic energy levels are superimposed upon the various possible sublevels for each molecule.
- This is because no matter what state the molecule is in, it is still vibrating and rotating due to its individual component solutions.
- Thus the following selection rules apply for electronic transitions:
  \[ \Delta \Lambda = 0, \pm 1 \]
  \[ \Delta S = 0 \]

- Simply put, electronic transitions between states within a molecule can only be achieved by changes in the rotational-vibrational angular momentum of the individual bound states. Thus only changes in J terms provide allowable energy transitions.
- Shifts in orbital angular momentum in molecules are observed using absorption and emission based molecular spectroscopy which provides a measure of the individual state transitions as well as the distances between bound atoms within the molecules. These values are then used to aid in the solution of the Schrödinger equations to predict various allowed states.
Electronic Transitions and Associated Selection Rules for N$_2$

- Nitrogen is one of the most heavily studied molecules
  - Its very abundant
  - Complex enough to require complex solutions
  - Simple enough to solve
  - Does not contain H-bonding issues
  - Easily observed spectroscopically
The Frank-Condon Principle

- All electronic transitions either upward or downward on the molecular energy diagram take place **vertically**
- It is assumed that electronic transitions take place so rapidly that the atoms do not have time to separate from each other in time
- This rule places clear restrictions on which energy levels and sublevels can interact
- It also requires that excited electron states produced via lower electron states have end points of their orbital in same radial location as the lower state it originated in
- The idea stems from the fact that atoms spend most of their vibrational time at the edges of the potential well and thus will radiate from that location
Example: Excimer Energy Levels

- **Excimer** molecules are diatomic and triatomic molecules formed by quantum excitation that lead to laser output and subsequent molecular dissociation.
- Excimer molecules have stable excited states but repulsive or loosely attractive ground states.
- Thus the molecules are formed by thermal or light absorption of a gas mixture.
- The excited state has a fast radiative decay rate relative to its collision decay rate that tends to dissociate the molecular state and provide optical light.
  - $A_{ul} = 1-5 \text{ ns}$ typically
- Common excimers are XeCl, KrF, ArF, XeF, HgBr, Xe$_2$, Ar$_2$, F$_2$.
Liquid Energy levels And Their Radiation Properties
Structure of Dye Molecules

• Organic dyes are complex molecules belonging to one of the following classes:
  – Polymethene dyes: 700 – 1500 nm
  – Xanthene dyes: 500 – 700 nm
  – Couramin dyes: 400 – 500 nm
  – Scintillator dyes: 320 – 400 nm
• When used as laser media, they are dissolved in a solvent such as water, alcohol or ethylene glycol
• Typical molar concentration of dye in solvent is 0.01%, yielding physical isolation that reduces the probability of collisional losses
• Typically have strong absorption bands at shorter wavelengths than the emission band
• The efficiency of the optical absorption allows for pumping to be performed by flash lamps or other lasers
• Pumping concentrations generally relate to the geometry of the system holding the liquid to provide enough absorption and emission without excess broadening due to elastic collisions
Structure of Dye Molecules

- The radiating portion of an organic dye is known as the chromophor and is defined by the covalent bond structure and allowable molecular motions of the molecule.
- The energy levels of the chromophor are very similar to those described for any other laser system.
- The molecular structure of a laser dye is such that it shields the chromophor from the solvent medium to reduce elastic scattering and generate a radiative decay.
- We define the quantum yield of the laser material as the ratio of radiating molecules to those involved in nonradiative decay processes.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Structure</th>
<th>Solvent</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acridine red</td>
<td><img src="image" alt="Acridine red structure" /></td>
<td>EtOH</td>
<td>Red 600 - 630 nm</td>
</tr>
<tr>
<td>Rhodamine 6G</td>
<td><img src="image" alt="Rhodamine 6G structure" /></td>
<td>EtOH, MeOH, H₂O, DMSO</td>
<td>Yellow 570 - 610 nm</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td><img src="image" alt="Rhodamine B structure" /></td>
<td>EtOH, MeOH, Polymethylmethacrylate</td>
<td>Red 606 - 635 nm</td>
</tr>
<tr>
<td>Na-fluorescein</td>
<td><img src="image" alt="Na-fluorescein structure" /></td>
<td>EtOH, H₂O</td>
<td>Green 530 - 560 nm</td>
</tr>
<tr>
<td>7-Hydroxycoumarin</td>
<td><img src="image" alt="7-Hydroxycoumarin structure" /></td>
<td>H₂O (pH 9)</td>
<td>Blue 450 - 470 nm</td>
</tr>
</tbody>
</table>
Energy Levels of Dye Molecules

- Both singlet (S) and triplet (T) manifolds exist in an organic dye.
- In the singlet state system, the spin of the electron is antiparallel to the spin of the remaining molecule.
- For triplet states, the spins are parallel.
- As before, the probability for an S or T transition is much more likely than a ST transition.
- In most atoms, the singlet states are lower than the triplet states, yielding a much higher probability density.
- Thus most laser action occurs in the singlet state.
- In dyes, absorption from the triplet ground state to excited triplet states lead to problems with quantum yield.
- Vibrational modes separating energy states within specific S and T states are typically 0.1 – 0.15 eV yielding 8 – 10 um transitions with very short decay times (i.e. large ΔE spreads).
Excitation and Emission of Dye Molecules

- Note that broad band excitation from the $S_0$ ground state to the $S_1$ excited state populates all of the vibrational modes of the excited state.
- Vibrational levels are observed to decay with very fast time constants ($10^{-12}$ - $10^{-13}$ s) to the lowest $S_1$ exited state.
- Radiative transitions times for $S_1 \rightarrow S_0$ are typically $1-5 \times 10^{-9}$ s.
- Thus one should expect radiative states from the lowest $S_1$ to some $S_0$ value with an energy spread between that and all lower $S_0$ values in the molecule.
- As a reminder, the Frank-Condon principle restricts the range of possible radiative decay states from the lowest $S_1$ based on radial displacement of the $S_1$ and $S_0$ states in the molecule. Thus the spread must be dependent on extremely rapid vibrational decay rates within the $S_0$ state.
Detrimental Triplet States of Dye Molecules

• Dye molecules that exist in triplet states are only weakly coupled to singlet states by weak radiative or collisional processes.

• As presented because, T1 lies below S1, there is some probability of decay from S1 to T1 and then from T1 to S0. However, the time constant associated with these transitions is on the order of 10 - 100 us.

• Also of note is that the wavelength region over which absorption occurs from T1 to T2 is the same as that of the emission region from S1 to S0.

• Thus the triplet state absorption can cancel the laser gain generated by the singlet transition.

• It is for this reason that continuous wave (cw) laser operation is desirable in liquid flows of dye across the excited region such to prevent “burn out” by singlet state emitters pumping triplet states.
Rhodamine-B (RhB) Example

- Rhodamine-B in ethyl Alcohol
- Emission spectrum: 525 to 625 nm with peak at 656 nm
- The emission originates from the bottom of the S1 state
- However a $\Delta \lambda$ spread is due to fast decay rates within the S0 state so:

$$\Delta E = h\Delta \nu = \frac{hc}{\lambda^2} \Delta \lambda$$

$$|\Delta \nu| = \frac{c}{\lambda^2} |\Delta \lambda|$$

RhB, $\lambda \approx 565$ nm

$$\Delta \lambda = 625 \text{ nm} - 525 \text{ nm} = 100 \text{ nm}$$

$$\Delta E = \frac{hc}{\lambda^2} \Delta \lambda = \frac{(6.63 \times 10^{-34} \text{ J-s})(3 \times 10^8 \text{ m/s})}{(5.65 \times 10^{-7} \text{ m})^2} (100 \times 10^{-9} \text{ m})$$

$$= 6.23 \times 10^{-20} \text{ J} = 0.389 \text{ eV}$$
Energy Levels in Solid Dielectric Laser Materials
Structure of Dye Molecules

- Dielectric solids generally consist of some ionic species grown or doped into a host material such as \( \text{Cr}^{3+} \) in Alumina (\( \text{Al}_2\text{O}_3 \)) or \( \text{Nd}^{3+} \) in yttrium aluminum garnet (YAG).
- Dopant molar concentrations typically vary from 0.1 to 10 percent.
- This the system is similar to a liquid dye suspension in a frozen matrix.
- The isolation of ions prevents nonradiative decay between.
- Materials are typically grown for a very specific set of properties:
  - Long upper laser level lifetime (\( 10^{-6} - 10^{-3} \) s)
  - Specific emission linewidths
  - High structural and device density
- These systems are engineered for particular applications, whereas atomic, and molecular gas lasers are used in their native form.
Host materials

• Host materials are optically transparent with uniform refractive index over the laser frequency band
  – Poor optical properties lead to undesired absorption, scattering, and irregular beam output
• They typically have good thermal and mechanical properties to handle the loads required
  – Poor mechanical and thermal properties lead to deformation or fracture of the host under high pulse repetition or long term steady state pumping

• Host fall into two categories: crystalline and glasses
• Crystal hosts
  – have higher thermal conductivity and provide narrower linewidths but are often size constrained
  – provide highly regular arrays of uniform electronic structure yielding homogeneous line broadening
• Glass Hosts
  – provide irregular structural units that are randomly oriented, yielding inhomogeneous line broadening.
  – grown cheaply over very large size scales while maintaining very good optical quality
Dopant Ions

• The trick to long excited state lifetimes is a set of inner shells states where the electron wave function is confined over a small spatial extent, thereby providing a significant amount of shielding from the host materials

• Shielding of the dopant from the host prevents phonon affects

• Thus good dopants are rare-earth ions, transition metal ions and actinide ions
  – Rare earths
    • have a number of sharp transitions from radiating 4f states (for Nd3+ a very narrow emission occurs between two (4f)$^3$ states with the same parity, but shielding provides state mixing with 3-d electron orbitals of opposite parity)
    • Found in tri valent (+3) form
    • Some are successfully used in +2 form
  – Transition metal ions such as Cr$^3+$, Ti$^3+$, Ni$^2+$, and Co$^2+$ successfully shield their d states
  – Actinides use 5f state electrons, but most successfully cations are from radioactive materials and are therefore not used

• Narrow emission linewidths are used
• Broadband emission linewidths are used for tunable systems
Dopant Ions

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Element</th>
<th>Laser ion</th>
<th>Outer electronic configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>Lanthanum (La)</td>
<td>Ce³⁺</td>
<td>5d6s²</td>
</tr>
<tr>
<td>58</td>
<td>Cerium (Ce)</td>
<td>Ce³⁺</td>
<td>4f5d6s²</td>
</tr>
<tr>
<td>59</td>
<td>Praseodymium (Pr)</td>
<td>Pr³⁺</td>
<td>4f³ 6s²</td>
</tr>
<tr>
<td>60</td>
<td>Neodymium (Nd)</td>
<td>Nd³⁺</td>
<td>4f⁴ 6s²</td>
</tr>
<tr>
<td>61</td>
<td>Promethium (Pm)</td>
<td></td>
<td>4f⁵ 6s²</td>
</tr>
<tr>
<td>62</td>
<td>Samarium (Sm)</td>
<td>Sm²⁺</td>
<td>4f⁶ 6s²</td>
</tr>
<tr>
<td>63</td>
<td>Europium (Eu)</td>
<td>Eu³⁺</td>
<td>4f⁷ 6s²</td>
</tr>
<tr>
<td>64</td>
<td>Gadolinium (Gd)</td>
<td>Gd³⁺</td>
<td>4f⁷ 5d6s²</td>
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<tr>
<td>65</td>
<td>Terbium (Tb)</td>
<td></td>
<td>4f⁹ 6s²</td>
</tr>
<tr>
<td>66</td>
<td>Dysprosium (Dy)</td>
<td>Dy²⁺</td>
<td>4f¹⁰ 6s²</td>
</tr>
<tr>
<td>67</td>
<td>Holmium (Ho)</td>
<td>Ho³⁺</td>
<td>4f¹¹ 6s²</td>
</tr>
<tr>
<td>68</td>
<td>Erbium (Er)</td>
<td>Er³⁺</td>
<td>4f¹² 6s²</td>
</tr>
<tr>
<td>69</td>
<td>Thulium (Tm)</td>
<td>Tm³⁺</td>
<td>4f¹³ 6s²</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tm²⁺</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>Ytterbium (Yb)</td>
<td>Yb³⁺</td>
<td>4f¹⁴ 6s²</td>
</tr>
<tr>
<td>71</td>
<td>Lutetium (Lu)</td>
<td></td>
<td>5d6s²</td>
</tr>
</tbody>
</table>
# Dopant Ions

## Transition Metal Dopant Ions

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Element</th>
<th>Laser ion</th>
<th>Outer electronic configuration</th>
<th>Neutral atom</th>
<th>Laser ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Scandium (Sc)</td>
<td>Ti$^{3+}$</td>
<td>3d4s$^2$</td>
<td></td>
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</tr>
<tr>
<td>22</td>
<td>Titanium (Ti)</td>
<td></td>
<td>3d$^2$4s$^2$</td>
<td></td>
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<tr>
<td>23</td>
<td>Vanadium (V)</td>
<td>Cr$^{3+}$</td>
<td>3d$^3$4s$^2$</td>
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</tr>
<tr>
<td>24</td>
<td>Chromium (Cr)</td>
<td></td>
<td>3d$^5$4s</td>
<td>3d$^3$</td>
<td>4F$_{3/2}$</td>
</tr>
<tr>
<td>25</td>
<td>Manganese (Mn)</td>
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<td>3d$^5$4s$^2$</td>
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<tr>
<td>26</td>
<td>Iron (Fe)</td>
<td></td>
<td>3d$^6$4s$^2$</td>
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<tr>
<td>27</td>
<td>Cobalt (Co)</td>
<td>Co$^{2+}$</td>
<td>3d$^7$4s$^2$</td>
<td>3d$^7$</td>
<td>4F$_{9/2}$</td>
</tr>
<tr>
<td>28</td>
<td>Nickel (Ni)</td>
<td>Ni$^{2+}$</td>
<td>3d$^8$4s$^2$</td>
<td>3d$^8$</td>
<td>3F$_4$</td>
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<tr>
<td>29</td>
<td>Copper (Cu)</td>
<td></td>
<td>3d$^9$4s$^2$</td>
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<td></td>
</tr>
<tr>
<td>30</td>
<td>Zinc (Zn)</td>
<td></td>
<td>3d$^{10}$4s$^2$</td>
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</tr>
</tbody>
</table>
Ruby Lasers

- First laser ever made
- 1% Cr$^{3+}$ in Alumina (Al$_2$O$_3$)
- Among the reasons for trying this laser first, was the multiple means by which to pump the laser state
- Thus a broad range of energies provided by a flash lamp can be “concentrated” into one radiative excitation state
- Output is 694.3 nm (red)
Nedodymium Lasers

- 1.0 – 1.5% Nd in YAG for crystals
- Crystal size: 1cm diameter and 10 cm long
- Can be doped to high concentrations in glass
- Glass has lower conductivity and therefore a lower pulse rate
- Emission bands are much broader than crystal bands
- Additions of sensitizer ions improves upper state lifetimes

1.2 × 10^{11} Hz (Δλ = 0.45 nm)
upper level lifetime is 230 μs

1.06-μm Laser transition

Excitation (pumping)

Nonradiative decay

Ground state

Nonradiative decay

Pumping bands

Nd:YAG

11,502 cm^{-1}

Nd:Glass

11,390 cm^{-1}

4.8–7.5 × 10^{12} Hz
(18–28 nm)
lifetime is approximately 300 μs
Ytterbium YAG Lasers

- Good for high power applications with narrow bands
- Absorption band however is narrow (18 nm) preventing flashlamp pumping
- InGaAs provides sufficient intensity within the absorption band to pump the laser
- $2F_{5/2} \rightarrow 2F_{7/2}$ with a 1.03 um emission
- Similar to that of dye lasers, fast relaxations bring the excited state to its minimum value which then radiates to the upper level of the ground state that also relaxes to within 0.077 eV of its ground state.
- The low level $S_0$ state is readily populated at room temperature, requiring the laser to be cooled to increase gain.
Erbium Lasers

- Not as efficient but has popular emission wavelengths: \(1.54 \mu m\) and \(2.9 \mu m\)
- 1.54 um is the optical communications band established by the IEEE
- 2.9 um is absorbed by water providing medical doctors with the ability to cut tissue
Broadband tunable Lasers

- Alexandrite, Ti Safire, and lithium strontium fluoride, and lithium strontium aluminum fluoride
- Emission bandwidth is 100 – 400 nm in all of these lasers
- These are the only laser materials besides organic dye lasers with large bandwidths
- In fact, these materials have wider bandwidths than current organic dyes due to coupling between vibrational and electronic states called **vibronic transition**

- **Alexandrite laser:** \( \text{Cr}^{3+} \) in \( \text{BeAl}_2\text{O}_4 \)
- 0.4% \( \text{Cr}^{3+} \) Doped in \( \text{BeAl}_2\text{O}_4 \)
- Optically and mechanically similar to ruby laser
- Chemical stability, hardness and thermal conductivity greater than Nd:YAG

pumping wavelength band ranges from 380 to 630 nm
peaks at 410 nm and 590 nm

\[ \Delta \lambda = 120 \text{ nm} \quad 700 \text{ to } 818 \text{ nm} \]
radiative lifetime of 260 \( \mu \text{s} \).
Ti: Sapphire Lasers

Ti:Al$_2$O$_3$ crystal

($\Delta \lambda = 400$ nm) 660 to 1,180 nm
Peak near 800 nm

Pump band from 400 nm to 600 nm

Short upper level lifetime of 3.2 us prevents flashlamp pumping

Usually pumped with Argon, frequency doubled Nd:YAG lasers, and blue-green diode lasers
Chromium LiSAF and LiCaF Lasers

Cr:LiSrAlF (or LiSAF for short)
Cr:LiCaF (LiCaF)

Pumped lifetime of 67 us for LiSAF and 190 us for LiSAF allows for sufficient flashlamp pumping

Absorption band of LISAF is 300 – 700 nm allowing the crystal to be pumped with semiconductor (Δλ = 250 nm)

Linewidth is narrower for LISAF than Ti sapphire

(Δλ = 250 nm)
The wavelength band is 800 – 1050 nm

LiSAF operates between 700 and 900 nm

Most crystals are chemically stable with good mechanical strength but not as good as sapphire. Crystals are slightly sensitive to water so not to be used in high humidity conditions
### Solid-state Dielectric Laser Characteristics

<table>
<thead>
<tr>
<th>Species</th>
<th>Laser wavelength (nm)</th>
<th>Upper-level lifetime (μs)</th>
<th>Emission linewidth (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr:Al₂O₃ (ruby)</td>
<td>694.3</td>
<td>3,000</td>
<td>3.3 × 10¹¹</td>
</tr>
<tr>
<td>Nd:YAG</td>
<td>1,064.1</td>
<td>230</td>
<td>1.2 × 10¹¹</td>
</tr>
<tr>
<td>Nd:glass</td>
<td>1,054–1,062</td>
<td>≈300</td>
<td>7.5 × 10¹²</td>
</tr>
<tr>
<td>Nd:YLF</td>
<td>1,047 &amp; 1,053</td>
<td>480</td>
<td>2 × 10¹¹</td>
</tr>
<tr>
<td>Nd:YVO₄</td>
<td>1,064</td>
<td>90</td>
<td>2.1 × 10¹¹</td>
</tr>
<tr>
<td>Yb:YAG</td>
<td>1,030</td>
<td>960</td>
<td>1.7 × 10¹²</td>
</tr>
<tr>
<td>Cr:BeAl₂O₃ (alexandrite)</td>
<td>700–800</td>
<td>260</td>
<td>≈5 × 10¹³</td>
</tr>
<tr>
<td>Ti:Al₂O₃</td>
<td>660–1,180</td>
<td>3</td>
<td>≈1.5 × 10¹⁴</td>
</tr>
<tr>
<td>Cr:LiSAF</td>
<td>800–1,050</td>
<td>67</td>
<td>≈9 × 10¹³</td>
</tr>
</tbody>
</table>