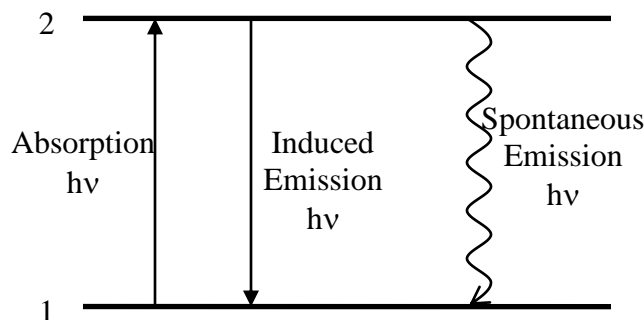




CH101

Classes 10-14; Physical Chemistry

**Spectroscopy:** Absorption and emission of radiation



Einstein A and B coefficients

Consider that the population of the ground state (1) =  $N_1$

Consider that the population of the upper state (2) =  $N_2$

When there is interaction between radiation and matter, the population in states (1) and (2) will change as a result of that.

Einstein considered the rate of change of population of the two states and equated the steady state rate of upward and downward transitions to be equal.

The rate of transition from the ground state to upper state per molecule (by absorption of radiation);  $w \propto \rho$ ; where  $\rho$  is the intensity (density) of radiation. The expression for  $\rho$  is given by Planck distribution.

$$\rho = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}$$

The rate per molecule is given as  $w = B\rho$ . B is the Einstein coefficient of absorption. However, if the population of the ground state  $N_1$  is then the total rate of transition;

$$W = N_1 B \rho$$

One should consider that the transition to the upper state is possible in the presence of radiation; thus is an induced process.

On the other hand the transition from the upper state to the ground state can be both induced by radiation and also can occur spontaneously.

One can then write the total rate for all the molecules as  $W' = N_2(B'\rho + A)$

Here A is the coefficient of spontaneous emission and B' is the coefficient of induced emission.

At thermal equilibrium the total rate of absorption is equal to the total rate of emission.

Thus  $N_1 B \rho = N_2 (B' \rho + A)$ ; We know from Boltzmann distribution function that

$$\frac{N_2}{N_1} = e^{-\Delta E / kT} = e^{-h\nu / kT}$$

$$\text{Or } \rho = \frac{A / B}{N_1 / N_2 - B' / B} = \frac{A / B}{e^{h\nu / kT} - B' / B} = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu / kT} - 1}$$

This is possible if

$$\frac{A}{B} = \frac{8\pi h \nu^3}{c^3} \text{ and } B' = B$$

$$\text{Thus } A = \frac{8\pi h \nu^3}{c^3} B$$

The probability of spontaneous emission goes up with frequency. This is in the UV region spontaneous emission is more dominant than induced emission.

On the other hand, spontaneous emission can be largely ignored at the relatively low frequencies of vibrational and rotational transitions. If intensities of these transitions can be discussed in terms of stimulated emission and absorption, then the net rate of absorption is given by

$$W_{\text{net}} = N B \rho - N' B' \rho = (N - N') B \rho$$

It is important to remember that induced emission is the same as stimulated emission.

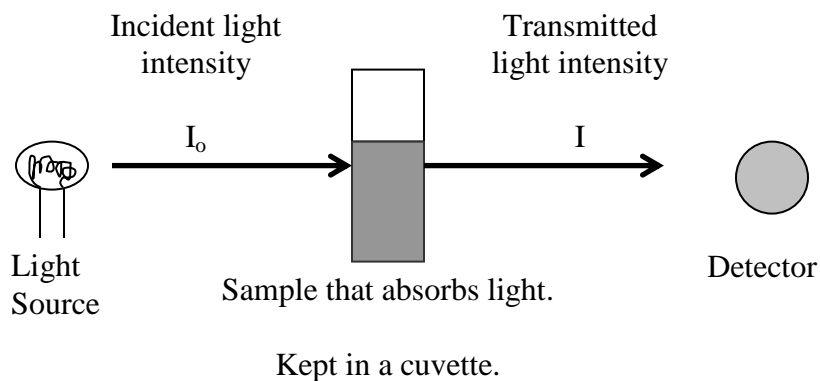
**Homework:**

The transition energy between two electronic states is  $20,000\text{ cm}^{-1}$ , the same for two vibrational states is  $2000\text{ cm}^{-1}$  and the same for two rotational energy is  $20\text{ cm}^{-1}$ . Calculate the population of the upper state, with respect to the ground state, for all the above transitions. Assume that at room temperature  $kT = 200\text{ cm}^{-1}$ .

## Experimental Spectroscopy:

A simplified experimental geometry for the spectroscopic measurement of absorption of light by substance kept in a solution.

Notice that in the diagram below in both  $I_0$  and  $I$ , it is assumed that monochromatic wavelength of light is present. In really one has to use a modified setup (like the use of a prism to achieve monochromatic light source).



It is known that  $-dI$  is proportional to the length of the cuvette, intensity of the incident radiation and the concentration of the sample in the solution that absorbs light.

Thus one can write:  $-dI = kcdl$

Here  $dl$  is the differential length of the cuvette,  $I$  is the intensity of the light and  $c$  is the concentration of the species.

When the concentration all over the cuvette is uniform then upon integration we get

$$\int_{I_0}^I \frac{dI}{I} = -kc \int_0^l dl \quad \text{Or} \quad \ln \frac{I_0}{I} = -kcl$$

One can then convert logarithmic base to ten. The equation then becomes

$\log_{10} \frac{I_0}{I} = \epsilon cl$ . This equation is known as Beer-Lambert law and the coefficient  $\epsilon$  is known as molar absorption coefficient.

Definitions:

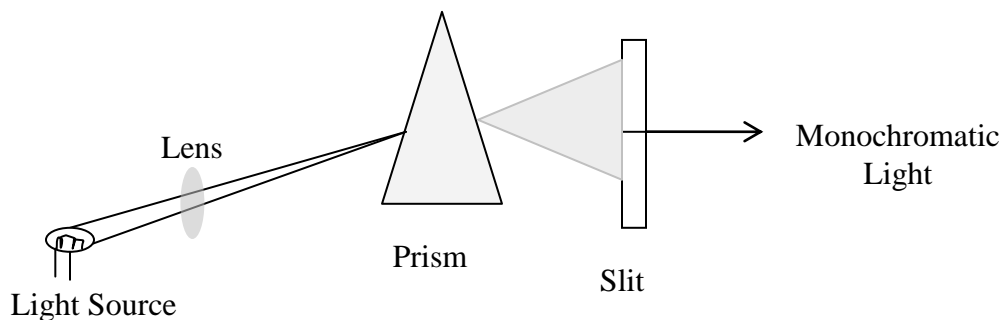
$$\text{Absorption: } A = \log_{10} \frac{I_0}{I} \quad \text{Transmittance: } T = \frac{I}{I_0}$$

$$\% \text{Transmittance} = \%T = \frac{I}{I_0} \times 100$$

The relationship between  $A$  and  $\%T$  is  $A = 2 - \log_{10}(\%T)$

## How does one generate monochromatic light from white light?

Use a prism or a grating to disperse and then use a slit to select the wavelength. A simplified geometric arrangement is shown below.



## Selection Rules and Transition Moments

Transition dipole moment:  $\mu_{fi} = \int \Psi_f^* \mu \Psi_i d\tau$ ; Here  $\mu$  is the electric dipole moment operator. Interaction of radiation will change the charge distribution of the molecule. For an effective transition the transition dipole moment must be non-zero.

The intensity of spectral transition is proportional to  $|\mu_{fi}|^2$ .

A detailed analysis would give,

$$B = \frac{|\mu_{fi}|^2}{6\epsilon_0 \hbar^2} ; \text{ For effective transition } \mu_{fi} \neq 0$$

There are specific selection rules for each kind of transition.

Electronic transition: Symmetry factor and Franck-Condon factor and angular momentum quantum number change:  $\Delta l = \pm 1$

Vibration transition; general:  $\Delta v = \pm 1$

Rotational Transition: for diatomic molecules:  $\Delta J = 0, \pm 1$

## Spectral Linewidths:

A number of effects contribute to the broadening of spectral line.

(a) **Doppler Broadening:** Doppler effect: Radiation is shifted in frequency when the source is moving towards or away from the observer.

**Source:** emitting a radiation frequency of  $\nu$  and moving with a speed of  $s$  with respect to the observer.

$$\nu_{receding} = \nu \left( \frac{1-s/c}{1+s/c} \right)^{1/2} \text{ and } \nu_{approaching} = \nu \left( \frac{1+s/c}{1-s/c} \right)^{1/2}$$

For non-relativistic speed i.e.,  $s \ll c$ , the expressions reduce to

$$\nu_{receding} \approx \frac{\nu}{1+s/c} \text{ and } \nu_{approaching} \approx \frac{\nu}{1-s/c}$$

Now, following Boltzmann distribution, one can write that the intensity of a spectral transition at temperature  $T$  can be written as,

$$I(\nu_{obs}) \propto e^{-ms^2/2kT} \propto e^{-mc^2(\nu_{obs}-\nu)^2/2\nu^2kT}$$

Thus the full width at the half maximum can be calculated to be

$$\delta\nu_{obs} = \frac{2\nu}{c} \left( \frac{2kT \ln 2}{m} \right)^{1/2}$$

(b) Lifetime broadening

Quantum mechanical energy states and their lifetimes give (uncertainty principle)

$$\delta E \approx \frac{\hbar}{\tau}; \text{ here } \tau \text{ is the lifetime of the state (say excited state).}$$

$$\text{Hence linewidth, } hc\delta\nu \approx \frac{\hbar}{\tau} \text{ or } \delta\nu \approx \frac{1}{2\pi\tau} \approx \frac{5.3 \text{ cm}^{-1}}{\tau / \text{ps}}$$

(c) Collisional linewidth is proportional to the pressure of the gas

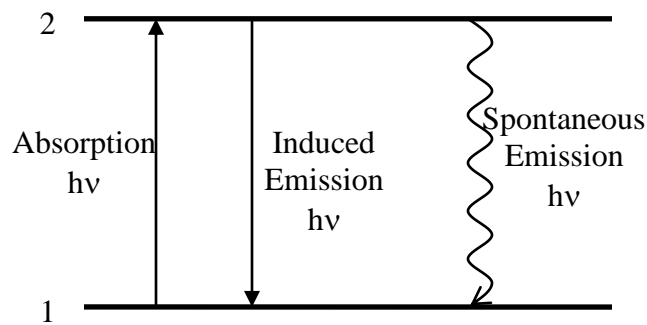
$$\delta E_{col} \approx \frac{\hbar}{\tau_{col}}; \text{ where } \tau_{col} = \frac{1}{z} = \frac{1}{\text{collisional frequency}}$$

### A simple picture of laser action

A laser action is possible when in an atomic, molecular or crystalline system there are more population in the upper state than in the ground state. However, as you remember from your class before in a two level system one can never achieve more population in the upper state than the ground state as the transition probability (rate) is dependent on population difference between the two states.

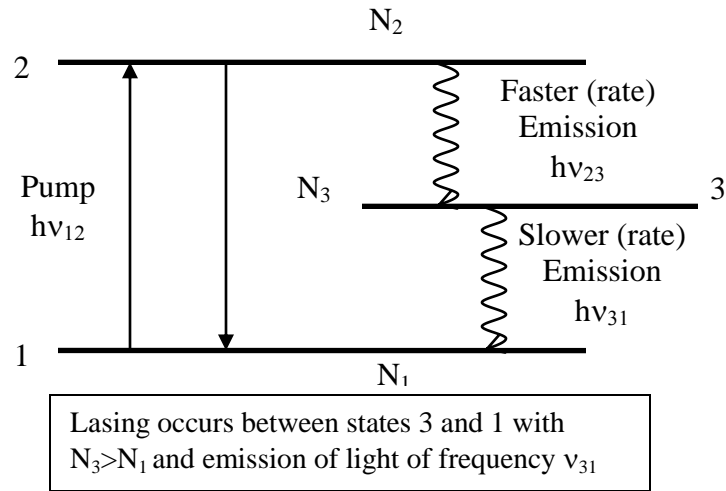
$$\text{The net population change rate} = W_{12} - W_{21} = B\rho N_1 - B\rho N_2 - AN_2$$

The maximum population in the upper state that one can attend is half the total population i.e. when the upper state has the same population as the ground state.



In a two level system the inversion of population is not possible by simple absorption and emission of light.

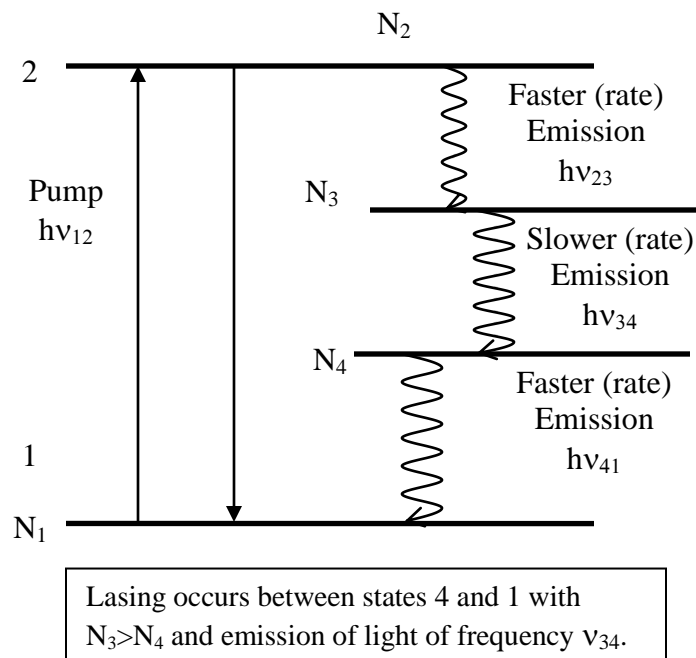
**Now consider a three level system.**



Now, it is possible to use a pump system (incident light) which would increase the population of state 3 via state 2. After sometime, as the emission rate from state 3 to state 1 is slow there would be an increase in population in state 3 in comparison to state 1. This is called population inversion.

Once the population inversion is achieved, one can use a light source to induce simultaneous (rapid) transition from state 3 to state 1 (just like giving a kick) and there would be intense, coherent emission from state 3 to state 1 with frequency  $\nu_{23}$ . Remember that  $\nu_{23}$  is different from  $\nu_{12}$  or  $\nu_{23}$ .

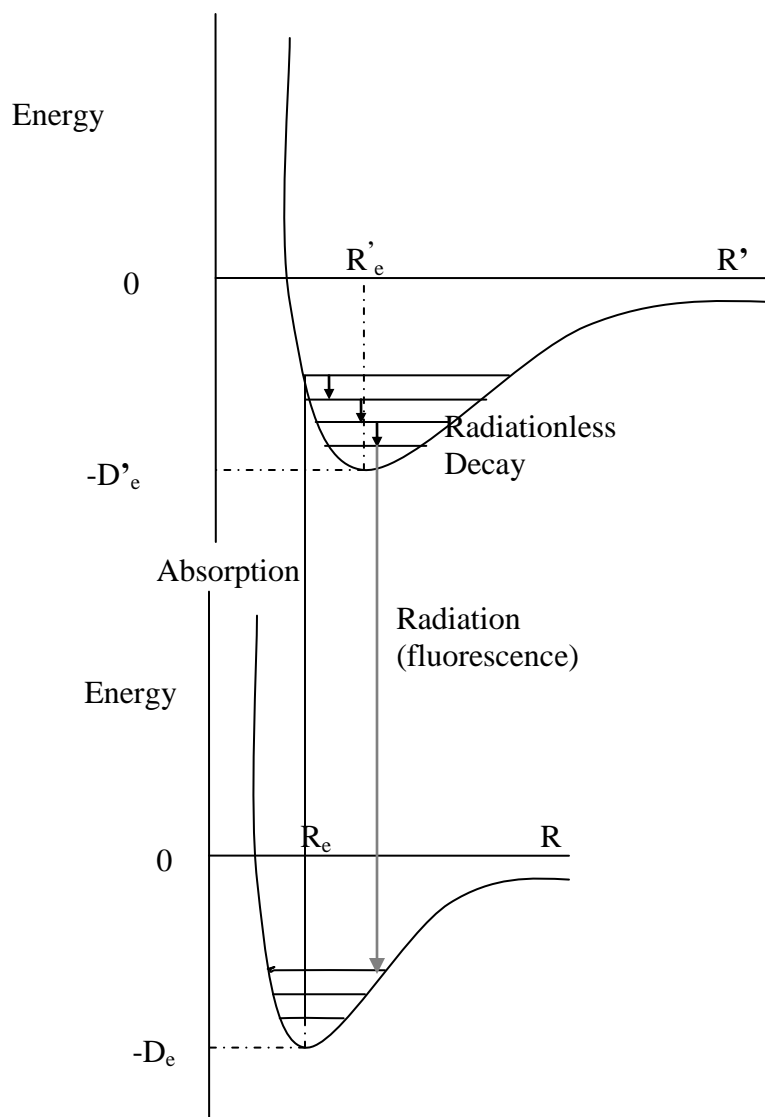
**Now, consider a four-level system.**



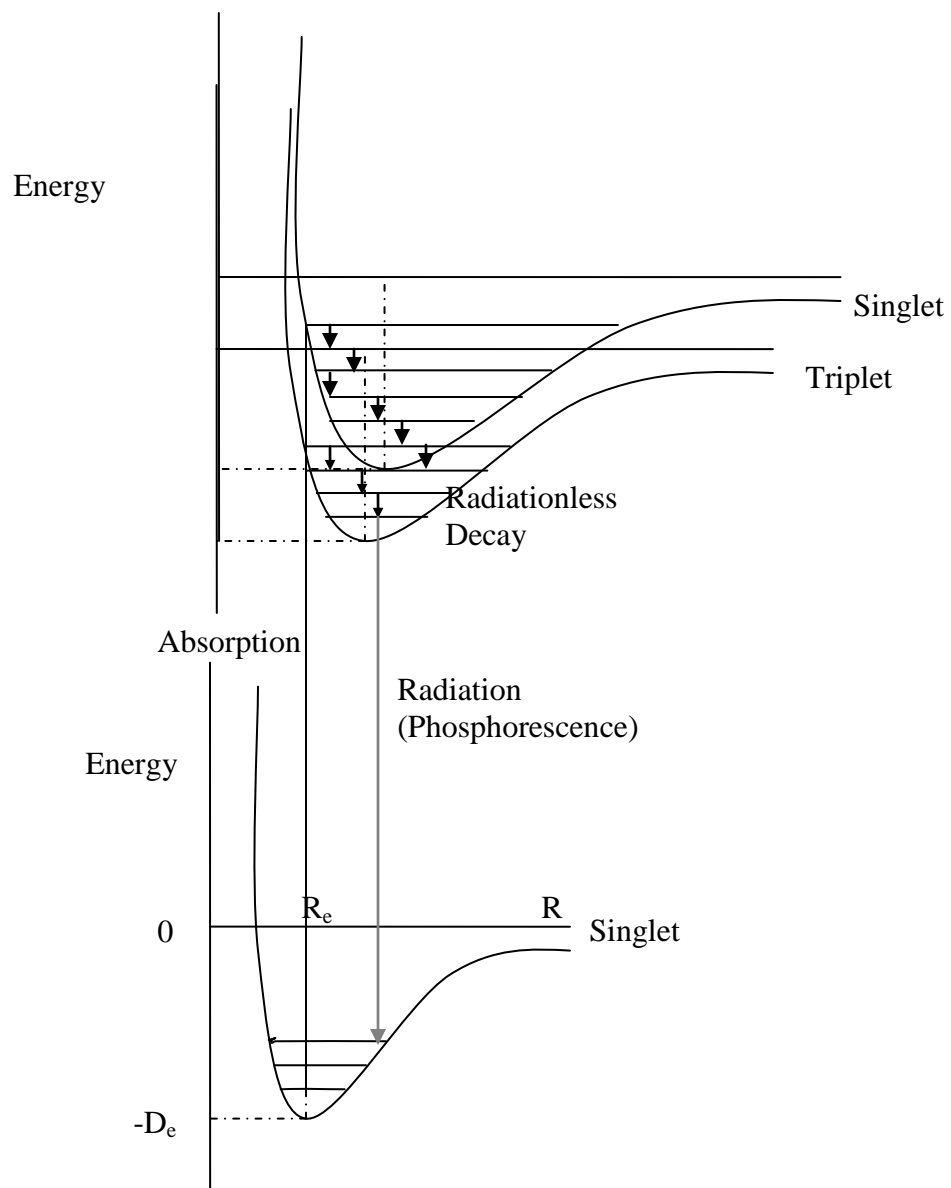


## The fate of electronically excited states

### Fluorescence



## Phosphorescence



## Fluorescence versus Phosphorescence (Intensity vs time)

