

## Module 6 : Reaction Kinetics and Dynamics

### Lecture 31 : Lasers in Chemistry

#### Objectives

After studying this lecture you will be able to do the following

- Outline the principles of laser action.
- Rationalize the working of gas lasers, solid – state lasers, dye lasers and semiconductors lasers.
- Outline the techniques for generating Lasers of short pulses.
- Elaborate on the applications of lasers to chemistry.
- Highlight the advantages of laser spectroscopy.

Lasers have become powerful technological tools today to do precision science and engineering. From our point of view, the interest lies in understanding them precisely through “molecular science”, i.e., energy levels, transitions between them, populating the higher levels in a non-equilibrium distribution and finally getting “laser action” by stimulating the excitations “stored” in higher occupied levels to fall down to lower levels, with the accompanying laser light. The acronym laser expands as light amplification by stimulated emission of radiation. The principles involved in the action of a laser are outlined below. The first difference between normal emission and laser is that in a Laser, there is a stimulated emission. Most excited states are unstable and have a short life span. The excited states, on their own (spontaneously), decay to the ground or lower states. It is these spontaneous processes which are responsible for “equilibrium” or the Boltzmann distribution of energies. However, some excited states are metastable, i.e., they can exist for a sufficiently long time so that they can be populated a lot more than what is permitted by thermal equilibrium. This corresponds to a “population inversion”.

If the equilibrium population of states 3, 2 and 1 are, say  $10^3$ ,  $10^7$  and  $10^{15}$  a non–equilibrium or inverted population of these states is like  $10^3$ ,  $10^{14}$  and  $0.9 \times 10^{14}$ . In this example, the second state is very highly populated. In the three level laser depicted below the ground state G is excited to the state E by pumping the energy (absorbing radiation) into the system. If there is a metastable state M very near the level E, then considerable energy from E is transferred to M and M gets populated. M is said to be a laser state, because by stimulating M with a photon of frequency  $\nu_L$ , laser action can be accomplished.

Figure 31.1 Illustration of the principles involved in laser action a) A 3 – level Laser and b) A 4 – level Laser.

In a four level Laser, the steps upto the population of M are the same as in the case of a 3 level laser. If there is a level G' above the ground state G into which the state M can be stimulated to decay, then the “population inversion” is readily accomplished because the population of G' is initially zero! If the transition from G' to G are rapid, then the laser action with frequency  $\nu_2$  can be obtained on a nearly continuous basis.

The stimulated emission is illustrated below.

Figure 31.2 Laser action.

Before the stimulation photon is incident on the metastable state, there are five excited molecules. Once the stimulating photon induces another deexcitation and this process repeats until all other excited molecules are deexcited, and six photons come out of the system. It is like one person shouts “FIRE” and enters a room and all the persons in the room also shout fire and the entering person and all the persons in the room rush out of the room!

Lasers can be classified in many ways. One way is to consider the number of levels involved in them, such as 3 – level lasers, 4 level lasers and so on. Another way is to use the classification as gas – lasers, solid state lasers, tunable lasers and so on. We shall use the later classification.

### 31.2Laser Types

#### Gas Lasers

We begin with gas lasers. In gas lasers, usually there is a mixture of gases. One of the gas types is excited by an electric discharge. The excitation energy of one kind of atom or molecule is transferred to a closely lying level of another kind of atom/molecule in a collision. Once the metastable level of the second molecule is populated, laser action becomes possible. The He - Ne laser is a typical example. The ground  $1s^2$  state of He is excited to the  $1s^1 2s^1$  state, which transfers energy to Ne and the excited Ne atoms exhibit laser action at several wavelengths ranging from 633 nm to 3.4 m.

In the argon laser, the electric discharge produces several ions like  $\text{Ar}^+$  and  $\text{Ar}^{2+}$  in the excited states. These states are metastable states and exhibit laser action at wavelengths 514 nm (green) and 488 nm (blue). The krypton ion laser emits at 647 nm (red) and these Lasers are used in light shows as well as for generating radiation with high power.

While the above examples use electronic excitations the  $\text{N}_2$  -  $\text{CO}_2$  laser uses vibrational excitations of  $\text{N}_2$  molecules that are collisionally transferred to the excited vibrational levels of  $\text{CO}_2$  which then undergo laser transitions. Several vibrational levels of  $\text{CO}_2$  are involved and these lasers are in the IR frequency range.

Fig 31.3 Argon Laser.

Fig 31.4 The  $\text{N}_2$  - $\text{CO}_2$  laser.

### Solid State lasers.

In a solid state laser, the material that participates in laser action is a solid (single crystal) or a glass. Ruby laser (Figure 31.5) consist of  $\text{Al}_2\text{O}_3$  (alumina) doped with  $\text{Cr}^{3+}$  ions.

The ground state of  $\text{Cr}^{3+}$  is represented as  $^4\text{A}_2$ . The left superscript is  $2S + 1$  where  $S$  is the total spin of the system. There are three unpaired electrons in  $\text{Cr}^{3+}$  contributing to  $S = 3 \times 1/2 = 3/2$ . The right subscript indicates the value of the total angular momentum quantum number which is  $J = L + S$ , where  $L$  = total orbital angular momentum quantum number. The values of  $J$  vary from  $L + S$  to  $L - S$ . The Roman letter represents the value of  $L$  ( $S$  corresponds  $L = 0$ ,  $P$  corresponds to  $L = 1$  and so on) or the symmetry of the ground state. This ground state can be excited by a pump to one of the several excited states  $^4\text{F}_1$  or  $^4\text{F}_2$ . The exciting radiation need not be monochromatic as there are several excited states. These excited states quickly decay to a metastable  $^2\text{E}$  state. The  $^2\text{E}$  state gets populated in a short time span and can be stimulated to decay to the ground  $^4\text{A}_2$  state by a stimulating photon of 694.3 nm wavelength. The energy level diagram is shown in Figure 31.5.

Figure 31.5 The energy level diagram for a ruby laser

Since this ground state  $^4\text{A}_2$  is always significantly populated due to laser action, it is difficult to maintain a population inversion and the laser has to be switched on and off intermittently. This is called a pulsed laser as against a continuous laser.

### Tunable Lasers.

The lasers that we have considered so far operate at fixed or discrete frequencies. To obtain tunable lasers (wherein the laser frequency can be adjusted to be any value in a given range), we need a broad range of frequencies wherein the laser can be made to operate. The solvent broadening of the vibrational spectrum of dye molecules is used to accomplish this. Due to solvation of dye molecules, the fluorescence band is red shifted (shifted to higher wavelengths) relative to the absorption band. The range of frequencies where laser action is possible is shown in Fig 31.6

## Figure 31.6 Wavelength region for laser action in a dye laser.

In the laser cavity of a dye laser, a diffraction grating is placed. By changing the angle of the grating relative to the pump radiation, shifts in laser wavelengths are achieved. To avoid heating, the dye solution is made to flow through the cavity continuously. An example of a dye is Rhodamine 6G in methanol.

In addition to the above three types of lasers, other modes of laser action have been developed. Band gaps of semiconductors and the metastable vibrationally excited states of molecules formed during chemical reactions are two examples in this group. Let us now consider some chemical applications of lasers.

### 31.3 Chemical Applications of Lasers.

The principle advantages of laser light over ordinary light is that it is monochromatic (very narrow range of wavelengths in the laser beam), it is coherent (all photons in the same phase), it has high power and it can be collimated over long path lengths. A laser can be pulsed, i.e., short bursts of laser light can be generated for durations of pico seconds and femtoseconds and this feature has enabled chemists to probe processes at very very short time scales. The high power and minute focusing has made lasers a powerful tool in surgery as well as physiotherapy. Applications of lasers in spectroscopy and chemical reaction dynamics are wide spread (we have already considered some aspects earlier). We will first consider a practical application in isotope separation.

Species that have the same molecular structure but differ only in their isotopic composition are called isotopomers. Because of their differing mass, their vibrational energy levels are different. If a mixture of two isotopomers is ionized directly, both members get ionized and it is difficult to separate either one of them by deflecting them by electromagnetic fields. However, if we first excite one of the two species selectively by a tunable laser and then ionize the excited state of this isotopomer, the ions of this isotopomer can easily be separated from the other unionized isotopomer by electric fields. Thus, the separation is done in two steps by two laser beams. The example of the separation of  $^{235}\text{U}$  from  $^{238}\text{U}$  is shown in Figure 31.7. The separation of  $^{32}\text{SF}_6$  and  $^{34}\text{SF}_6$  by selective vibrational excitation of one of them by IR laser photons and then dissociating this with another UV photon is shown in Figure 31.8.

Fig 31.7 Separation of isotopomers  $^{235}\text{U}$  from  $^{238}\text{U}$ . Fig 31.8 Separation of isotopomers  $^{32}\text{SF}_6$  and  $^{34}\text{SF}_6$ .

### 31.4 Spectroscopic Applications:

In Raman spectroscopy, in addition to the incident beam of frequency  $\nu_i$ , the scattered beam contains frequencies  $\nu_i \pm n \nu_M$  where  $n$  = integer and  $\nu_M$  is the molecular excitation energy. The monochromaticity of laser light allows for easy identification of these closely spaced frequencies. Since the laser beam can be collimated over long paths, the above spread in frequencies can even be detected in the direction of the incident beam itself, which is not possible in Raman spectroscopy with ordinary light.

One of the major problems in spectroscopy is the noise of the detector and the interference caused by the background radiation. When these interferences are more than a few percent of the intensity of the absorbing light it is difficult to distinguish between signals and noise. Since the laser beams have high intensity, the laser light is particularly useful in measuring the intensities of the scattered light. This is a major advantage in Raman spectroscopy which studies frequencies of scattered radiation.

The high power of the laser beam also allows one to precisely locate the absorption maxima, which could be rather broad when laser light is not used. Another area of spectroscopy that has grown with lasers is multiphoton spectroscopy. Normal selection rules use only the linear terms in the electric field in transitions allowed by the transition dipole moment. The linear term in the transition in the dipole moment is  $\propto E$  (where  $\propto$  = polarizability and  $E$  is the electric field).

When the light intensity is very high, the non-linear terms like  $\beta E^2$  begin to contribute. The electric field is expressed as  $E_0 \cos(\omega t)$ . The square of the electric field contains terms such as  $\cos(2\omega t)$  (recall that  $\cos^2 \omega t = 1/2 (1 + \cos 2\omega t)$ ) and thus two photons of frequency  $\omega$  can cause a transition with frequency  $2\omega$  in a molecule (under intense laser radiation). This is called multiphoton spectroscopy. Transitions that are disallowed in ordinary spectroscopy become accessible in multiphoton spectroscopy.

We know that reaction rates can be increased by increasing the temperature. But increasing the temperature increases the energies of not only the relevant molecules, but all molecules. For example, the reaction  $\text{BCl}_3 + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5 - \text{BCl}_2 + \text{HCl}$  occurs with significant rates only above  $600^\circ\text{C}$  and in the presence of a catalyst. But with a laser light of  $10.6 \mu\text{m}$  of a  $\text{CO}_2$  laser, the reaction occurs at room temperature without a catalyst. The reason for this is that with the laser light, one is able to excite the relevant vibrations/excitations selectively! Thus, if low cost laser beams are available, a lot of reactions can be carried out with state selectivity and many compounds which are unstable at high temperatures can be made at room temperature.

#### Some Technical details about Lasers.

For the laser to give out an intense light beam, the collection of photons have to be stimulated in a region or cavity containing the material or medium that is lasing. Usually this cavity is a region between two mirrors which reflect the photons from one side to the other. For accumulating photons in the cavity, the wavelength  $\lambda$  of the photon must be related to the cavity length ( $L$ ) by

$$n * (\lambda/2) = L \quad (31. )$$

Where  $n$  is an integer. For wavelengths not following eq. (31.1), there is destructive interference. The “standing waves” in the cavity are called cavity modes and the modes (photons of given frequency) that contribute to laser action are called resonant modes.

### Figure 31.9 A Laser Cavity.

Only the resonant modes get amplified in the cavity. The modes parallel to the axis of the cavity get amplified and have a very narrow range of wavelengths  $\Delta\lambda$ . The coherence length  $l_c$  is the range of wavelengths contained in the laser beam and is given by

$$l_c = \lambda^2 / (2 \Delta\lambda) \quad (31.2)$$

For a strictly monochromatic beam,  $l_c$  is infinite but in practice, they can be from a few centimeters (for He-Ne laser,  $\Delta\lambda \approx 2$  pm and  $l_c = 10$  cm) to a few meters.

For ordinary light bulbs, the coherence length is very small,  $\sim 500$  nm.

Often lasers are made to operate in pulses whenever it is not possible to maintain the high population of the excited states and when it is necessary to cool the medium by discarding the heat generated in the medium during laser action. The Laser output power  $P$  is given by the amount of energy released during a pulse.

$$P = \text{energy released} / \text{pulse duration} \quad (31.3)$$

For a ns pulse, if the energy released is 1 MJ, the power is 1 MW (megawatt).

A standard method of generating pulses is accomplished by Q - switching. The principle involved here is to make the cavity absorb the pump energy causing population inversion when the cavity is not resonant (so that during the time of absorption, there is no laser action) and after the pump energy has caused sufficient population inversion, initiate laser action.

One way to achieve this is to insert a 'saturable dye' in the laser cavity. A saturable dye is a compound which can absorb a range of photons and once its excitations have been saturated it can not absorb any more photons and this makes the cavity transparent and the resonant modes (which were blocked before saturation) become active and laser action is accomplished by opening the switch

Figure 31.10 Non resonant and resonant cavities in Q - switching. Pulses of 2 to 20 ns can be obtained by this method.

### Laser pulses for time resolved spectroscopy

To study fast processes such as collision induced decays of excited molecules, isomerization of excited molecules, photoexcitation of rhodopsin molecules of the retina in the eye and several other ultrafast processes, we need good time resolution which can be obtained by generating ultrashort laser pulses. Time resolution in the femtosecond ( $1\text{fs} = 10^{-15}\text{ s}$ ) has been achieved now. In this section we outline some features involved in getting these ultrashort pulses. If  $\Delta t$  is the duration of the light pulse, the spectral resolution  $\Delta \nu$  is given by  $1 / \Delta t$ . The duration of the pump pulse is dependent on the electric discharge which could be of the order of nanoseconds.

The intensity vs time of the laser pulse (referred to as the time profile) is determined by the relaxation times ( $\tau$ ) of the upper and lower levels ( $\tau_u$  and  $\tau_L$ ). If these times are short compared to the rise time of the pump pulse, then a smooth time profile of the laser pulse  $P_L(t)$  is obtained. The intensity of  $P_L(t)$  depends on the inverted population difference  $\Delta N(t)$  of the upper and lower states. The pump and laser time profiles of gas lasers and solid state lasers are shown below

Figure 31.11 Figure showing the growth of the pump pulse, the laser pulse and the inverted population difference  $\Delta N(t)$ . Laser time profile" is large when  $\Delta N(t)$  is large. a) gas lasers, b)  $\text{N}_2$  laser and c) solid state lasers.

If the values of  $\tau_u$  and  $\tau_L$  are large, the induced emission does not deplete the upper level. These can be combined with amplification of induced light emission to get the spikes shown in Fig 31.11 (c)

To obtain a powerful laser pulse instead of irregular sequence of spikes, the technique of Q switching is used. In Q - switching, the cavity losses are kept high till some time so that the population inversion can build up. If by opening a switch the losses are suddenly lowered, a giant laser pulse can be made to emanate from the laser cavity. The intensity profiles are shown in Fig 31.12.



Figure 31.12 Q - switching. a) Intensity profiles of  $P_p(t)$ ,  $P_L(t)$  and  $\Delta N(t)$ , b) Nonresonant cavity and c) Resonant cavity.

One way to keep the cavity non - resonant is to mount one of the mirrors on a spinning motor shaft. Only when the mirror is parallel to the resonator axis, high Q - value (quality of laser pulse) is attained . Another way to impair the resonance characteristics when the pump pulse is active is to include a saturable dye in the medium. When most of the dye molecules become excited by the pump pulse, it gets saturated with energy and can not absorb any more and it becomes transparent allowing the cavity to become resonant. Nanosecond pulses can be obtained by Q - switching.

To obtain pico second pulses, the method of mode locking or mode coupling is used. In the laser cavity, there are several resonating modes whose frequency differences are in multiples of  $c / 2L$  where  $L$  is the length of the cavity and  $c$  is the velocity of light. If the phase difference between these modes is random they can not interfere constructively. If however, the phase differences can be locked, we can get several sharp peaks of pico second duration. Mode locking can be achieved by periodically varying the Q factor of the cavity at the frequency  $c / 2L$  or by using a saturable dye. If the cavity length is 30 cms, the modes are separated by 2 ns. If 2000 modes can contribute, the pulse width will be 2 ps!

Femtosecond pulses can be obtained by using techniques such as colliding pulse mode locking, Kerr lens mode locking and by using chirped laser mirrors and fiber lasers.

The use of these Lasers to study ultrafast relaxation processes is referred to as the pump probe technique. The pump laser pulse excites a molecule from the state  $|10\rangle$  to state  $|11\rangle$ . The intensity of state  $|11\rangle$  decays as shown in Fig 31.13 (c). The population of  $|11\rangle$ ,  $N_1(t)$  is probed by a second Laser pulse called the probe pulse. The time delay between the two pulses,  $\tau$  is limited by the pulse width of the two pulses.

Figure 31.13 a) Pump and probe pulses, b) States  $|10\rangle$ ,  $|11\rangle$  and  $|12\rangle$  and their populations  $N_0$ ,  $N_1$  and  $N_2$  and fluorescences of the excited states  $|11\rangle$  and  $|2\rangle$ , c) Population decay of  $N$

This method is useful for studying collisional relaxation in liquids, electronic relaxations and well as in real time observations of molecular vibration.

### Problems

- 31.1) Find out how a laser pointer works. What are the precautions you should take while using lasers in general?
- 31.2) Draw the energy level diagram of the four level argon ion laser.
- 31.3) The neodymium Laser has two unstable excited states which quickly decay to a  $^4F$  metastable state. Laser action occurs between this state to the  $^4I$  stage at wavelength  $1.06 \mu\text{m}$ . The state  $^4I$  decays thermally to the ground state. Draw the energy level diagram for this laser.
- 31.4) Find out from literature/websites examples of dye lasers (tunable) and the range of frequencies wherein they can be used. If you need to excite the carbonyl group at  $1700 \text{ cm}^{-1}$ , which laser will you use?
- 31.5) If the coherence length for a sodium lamp is  $500\text{nm}$  and the wavelength of light is in the range of  $6000 \text{ \AA}$ , what is the spread in wavelengths,  $\Delta\lambda$ ?
- 31.6) Calculate the power output of a laser in which  $1\text{J}$  pulse can be given out in  $5 \text{ ns}$ .

### Recap

In this Lecture you have learnt the following

#### Summary

In this lecture, you have been introduced to lasers. The principles of laser action and the working of gas lasers, solid state lasers and dye lasers was outlined. The laser could also be classified in terms of the number of levels involved in laser action. Chemical applications of lasers such as isotope separation and spectroscopic applications were described. The attainment of state selectivity through laser pulses was illustrated for the reaction between  $\text{C}_6\text{H}_6$  and  $\text{BCl}_3$ . A few technical details about lasers were outlined in the later part of the lecture. The methods used for obtaining pulses of very short duration were also elaborated. For more details, you need to consult detailed technical books in the subject. (see references cited at the end of the module. The use of the pump-probe technique to study ultrafast relaxation processes was illustrated towards the later part of the lecture.