

Excited State Processes and Application to Lasers

The technology of the laser (Light Amplified by Stimulated Emission of Radiation) was developed in the early 1960s. The technology is based on an understanding of excited state processes. We have thus far considered absorption and emission, without detailed consideration of the evolution of the excited state. The Einstein coefficients tell us that there are two fundamental emission processes in the excited state, spontaneous and stimulated emission. However, there is vibrational relaxation and there are other competing processes that can cause non-radiative decay from the excited state. In this chapter we consider excited state dynamics and how it relates to the use of stimulated emission as a technology.

1.0 Excited state processes

The fate of excited states can be divided into the processes that take place within the initially prepared excited state and transitions from that state. Within the initial excited state, a molecule can relax to a new equilibrium position of the nuclei. That position is different from the nuclear equilibrium position both in terms of the bonds and the salvation shell around the molecule. Vibrational relaxation (shown in Figure 1) leads to a new equilibrium distribution of the vibrational energy in the excited state. Likewise, following fluorescence or other processes that take the system back to the ground state, there will be vibrational relaxation in the ground state manifold. We refer to a manifold as collection of vibrational levels in a potential energy surface.

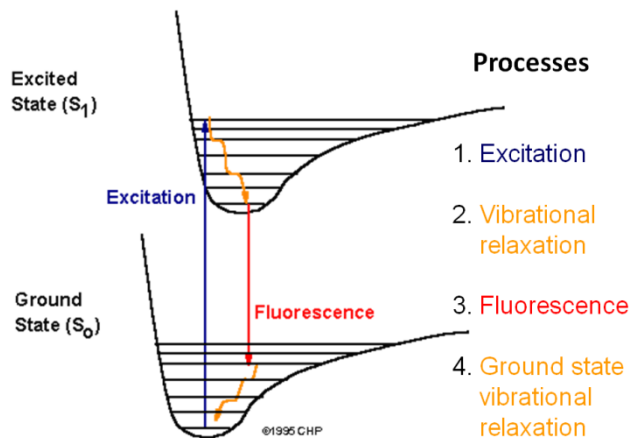


Figure 1 Relaxation processes within an excited state or the ground state.

Relaxation between states is usually represented using a Jablonski diagram, such as that shown in Figure 2. The ground state S_0 refers to a singlet. Not all ground states are singlets, but this is a common situation. The first singlet excited state is S_1 . The triplet state is T_1 . The non-radiative processes shown include internal conversion (IC) and intersystem crossing (ISC), which represent conversion of the S_1 state to the singlet ground state and triplet states, respectively. Both of these processes compete with fluorescence and reduce the fluorescence quantum yield. Internal conversion involves coupling of the excited state to the ground state by means of the Born-Oppenheimer breakdown operator,

$$H = \frac{\partial}{\partial Q}$$

This operator represents a part of the Hamiltonian neglected when the Born-Oppenheimer approximation is made Section 6.6. This term can couple states perturbatively. Coupling of the S_1 state to T_1 involves the spin-orbit coupling operator. The relaxation of the triplet state to the ground state can be non-radiative, i.e. yet another ISC process, or radiative. A radiative $T_1 \rightarrow S_0$ process is called phosphorescence. Since triplet-singlet processes are formally forbidden the lifetime of the triplet state is typically quite long compared to the singlet state.

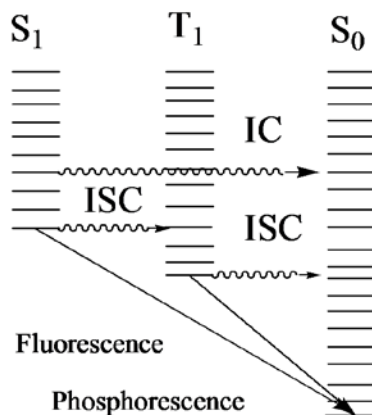


Figure 2 Example Jablonski diagram shown the processes of internal conversion (IC), intersystem crossing (ISC), $S_1 \rightarrow S_0$ fluorescence and $T_1 \rightarrow S_0$ phosphorescence.

Stimulated emission is only practical from a singlet state. The ideal laser material has a large absorption, and therefore stimulated emission, coefficient. However, spontaneous emission can compete with the stimulated emission. In practice organic laser dyes are fluorophores as well.

2.0 Lasers

The laser phenomenon involves a stimulated emission of light that results in gain. One input photon can stimulate emission of a second photon, which initiates a chain reaction. However, in order for such a chain reaction to take place the system must be poised so that there is a great deal of excess energy in the excited state. It must be pumped in some way and it must be able to store the energy. We have already shown in the section on the Einstein coefficients that the maximum excited state population is $\frac{1}{2}$ in a two-level system. We shown this again in a slightly different way below and compare a two-level system with a three level system and qualitatively with a four-level system to show progressively greater efficiency in generating the population inversion. Aside from this gain medium, the lasing process must take place in a cavity that can store the energy. The condition for this is that the round trip distance in the laser cavity ($2L$) must be equal to an integral number of wavelengths ($N\lambda$). If this condition is not satisfied the laser light interferes with itself. The laser must have a partially reflective mirror (output coupler) to permit a small fraction of the energy to escape and be used. Thus, the essential features of a laser are that it must have:

1. a gain medium
2. a laser cavity (reflecting mirrors)

3. an output coupler (semi-reflective mirror)
4. standing waves, which can be obtained for $(N\lambda/2=L)$
5. birefringent filters, etalons, or gratings to modulate the frequency bandwidth

2.1 The gain medium

Although laser light is perhaps the purest form of light, it is not of a single, pure frequency. All lasers produce light over some natural bandwidth or range of frequencies. A laser's bandwidth of operation is determined primarily by the gain medium that the laser is constructed from, and the range of frequencies that a laser may operate over is known as the *gain bandwidth*. For example, a HeNe gas laser has a gain bandwidth of 1.5 GHz. Ti:sapphire has a bandwidth of about 128 THz. We will consider some of the most widely used gain media below, once we have understood the combined basic phenomena needed. The gain bandwidth will permit certain standing waves to be amplified as shown in Figure 3.

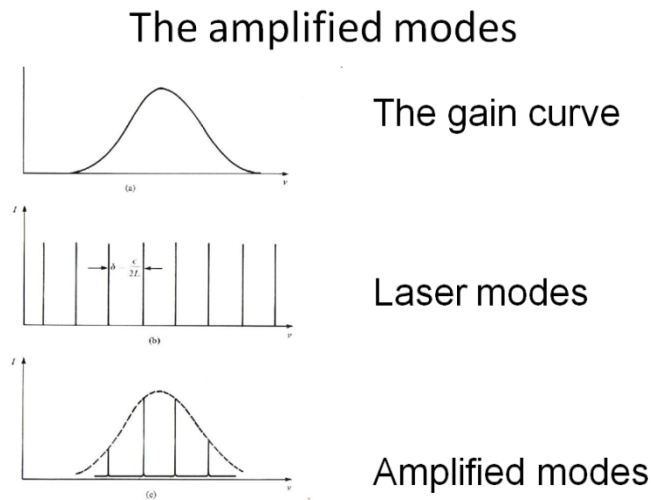


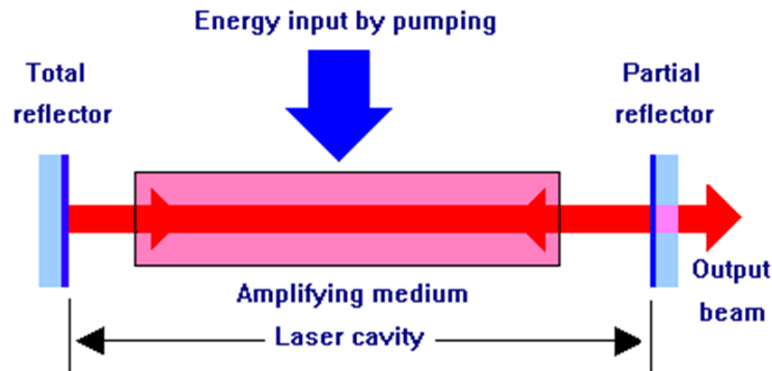
Figure 3 The gain curve is the frequency dependence of the gain medium. The laser modes are those modes that are permitted in laser cavity of length $L (=N\lambda/2)$. The amplified modes is the combination of the gain curve and the allowed laser modes.

Depending on the width of the gain curve hundreds or thousands of laser modes will be allowed in a given laser medium and cavity combination.

2.2 The laser cavity

The gain of a lasing medium can be enhanced by placing it between a pair mirrors to increase the effective length and restrict the allowed spatial and spectral modes of operation, greatly improving coherence and reducing pumping power requirements. This optical configuration is similar to the Fabry-Perot cavity, and is the most common laser interferometer. The basic laser cavity is shown in Figure 4. The gain medium is externally excited by light or voltage to generate excited states that can be stimulated. As light passes back and forth through the gain medium it builds up to an intense beam.

The laser cavity



The partial reflector is usually called the output coupler.

Figure 4. The laser cavity is shown with an amplifying medium (gain medium) and two mirrors. The total reflector is 100% reflecting and the partial reflector permits a small amount of the laser light to escape from the cavity.

2.3 Longitudinal modes

These standing waves form a discrete set of frequencies, known as the longitudinal modes of the cavity. These modes are the only frequencies of light which are self-regenerating and allowed to oscillate by the resonant cavity; all other frequencies of light are suppressed by destructive interference. For a simple plane-mirror cavity, the allowed modes are those for which the separation distance of the mirrors L is an exact multiple of half the wavelength of the light λ , such that $L = N\lambda/2$, when N is an integer known as the mode order.

In practice, the separation distance of the mirrors L is usually much greater than the wavelength of light λ , so the relevant values of N are large (around 10^5 to 10^6). Of more interest is the frequency separation between any two adjacent modes N and $N+1$; this is given (for an empty linear resonator of length L) by $\Delta\nu$:

$$\Delta\nu = \frac{c}{2L}$$

where c is the speed of light ($\approx 3 \times 10^8 \text{ m} \cdot \text{s}^{-1}$).

2.4 Output modes

Figure 3 shows the combination of the gain bandwidth and longitudinal modes. This leads to a discrete set of wavelengths that are output from the laser within the bandwidth.

3.0 The population inversion

Gain represents the increase in photons emitted from the sample compared to a Boltzmann distribution. The Boltzmann distribution will never allow for more population in an excited state than in the ground state. Therefore, gain represents a non-Boltzmann distribution induced by optical or electrical pumping. Figure 5 shows why a population inversion is needed. If you want to get more photons out than you put in you need many molecules in the excited state to start a cascade of output photons. In Figure 5A the idea of a single photon excited more than one output photon requires that there be more population on the upper level (Level 2). As shown below, it is not possible to generate the required population inversion in a two level system. Figure 5B shows a three-level system, which is one method to generate a population inversion. First the transition of $0 \rightarrow 2$ generates population in 2, which rapidly relaxes to state 1. The population in state 1 builds up and surpasses the population in state 0. The amount of stimulated emission is still limited in a three level system because the population of state 0 can never be zero. Since it would be advantageous to have the largest population difference possible, the four-level system shown in Figure 5C is a common type of system used in laser design.

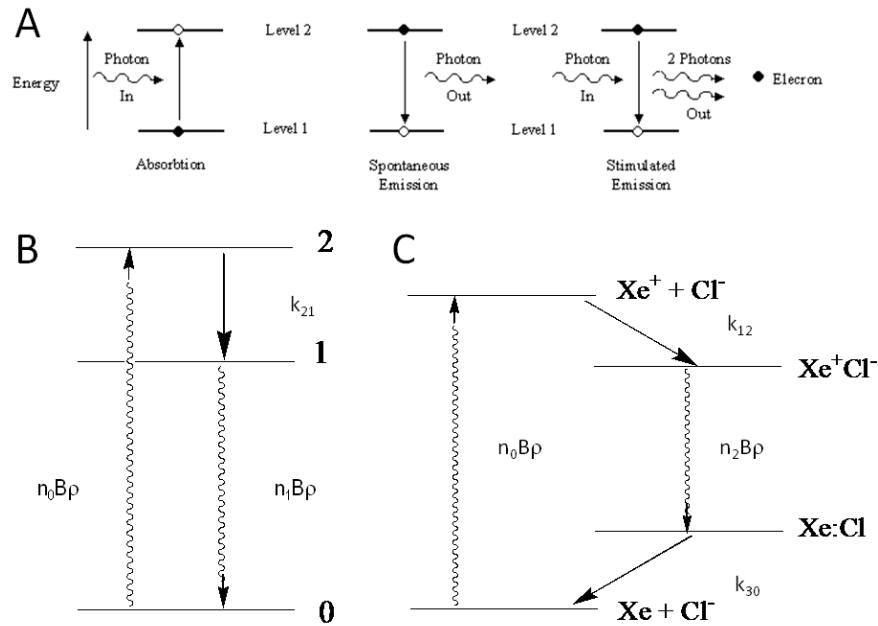


Figure 5 A. Illustration of the stimulated emission effect to create an amplification. B. Depiction of the three-level system used to generate a population inversion in state 1. C. Depiction of a four-level system, which leads to a population inversion an upper state that emits to a vacant state.

Two level systems

For states 0 and 1 the Einstein B coefficients are equal. High fluence limit results in a ratio of populations determined by microscopic reversibility. At equilibrium

$$W_{\text{absorption}} = W_{\text{emission}}$$

which leads intuitively to the conclusion that the excited state population cannot exceed the ground state population. This can be seen from the rate equations for a two level system with transition rate constant B (Einstein coefficient $B_{21} = B_{12}$) and energy density ρ .

$$\frac{\partial n_0}{\partial t} = -n_0 B \rho + n_1 B \rho = (n_1 - n_0) B \rho$$

$$\frac{\partial n_1}{\partial t} = -n_1 B \rho + n_0 B \rho = (n_0 - n_1) B \rho$$

The trial solution is

$$n_0 = A e^{-\lambda t}$$

This system of equations can be solved using the secular determinant

$$\det \begin{vmatrix} -B\rho - \lambda & B\rho \\ B\rho & -B\rho - \lambda \end{vmatrix} = 0$$

$$\lambda = 2B\rho$$

$$n_1 = n_0(1 - e^{-2B\rho t})$$

This significance of this equation is that n_1 is zero at $t = 0$. If a light source with energy density ρ is used to illuminate the sample the population of the excited state, n_1 , will increase. However, even if the intensity is infinite (i.e. $e^{-2B\rho t} = 0$) the population n_1 can at most be equal to n_0 , but never greater. A population inversion is impossible.

Three level systems

Optical or electrical pumping is often used in a three level system. The pumping process populates an intermediate state that decays into long-lived emissive state (i.e. the lasing state). However, the ground state population must still be sufficiently depleted to make a population inversion in the emissive state. This can be done at high pumping rates, but it is difficult. The ruby laser is an example of the three level system. $\text{Cr:Al}_2\text{O}_3$ is the gain medium in which Cr d-d transitions give a population inversion in a state that emits at 694 nm.

$$\frac{\partial n_0}{\partial t} = -n_0 B \rho + n_1 B \rho$$

$$\frac{\partial n_1}{\partial t} = -n_1 B \rho + k_{21} n_2$$

$$\frac{\partial n_2}{\partial t} = -n_0 B \rho - k_{21} n_2$$

This scheme is simplified since it assumes that the Einstein coefficient for states 1 and 2 are the same with respect to 0. We use the same trial solution to obtain

$$\det \begin{vmatrix} -B\rho - \lambda & B\rho & 0 \\ 0 & -B\rho - \lambda & k_{21} \\ B\rho & 0 & -k_{21} - \lambda \end{vmatrix} = 0$$

$$(B\rho + \lambda)^2(k_{21} + \lambda) - B^2\rho^2 k_{21} = 0$$

$$(\lambda^2 + 2\lambda B\rho + B^2\rho^2)(k_{21} + \lambda) - B^2\rho^2 k_{21} = 0$$

$$(\lambda^3 + 2\lambda^2 B\rho + \lambda B^2\rho^2 + \lambda^2 k_{21} + 2\lambda B\rho k_{21} + B^2\rho^2 k_{21}) - B^2\rho^2 k_{21} = 0$$

$$\lambda^2 + (2B\rho + k_{21})\lambda + B^2\rho^2 + 2B\rho k_{21} = 0$$

$$\lambda = 0$$

$$\lambda_{\pm} = \frac{(2B\rho + k_{21}) \pm \sqrt{(2B\rho + k_{21})^2 - 4(B^2\rho^2 + 2B\rho k_{21})}}{2}$$

$$\lambda = \frac{(2B\rho + k_{21}) \pm \sqrt{k_{21}^2 - 4B\rho k_{21}}}{2}$$

We can simplify the rate equations by assuming that if $k_{21}n_2 \gg n_1 B \rho$ then a population build-up in n_1 can lead to a population inversion $n_1 \gg n_0$. Still has disadvantage that population in n_0 is dominating at equilibrium.

4.0 Laser technology implementation

Lasers can be divided into continuous wave and pulsed lasers. Atomic lasers include the ion lasers (Ar⁺ and Kr⁺), HeNe and HeCd lasers and metal vapor lasers (Cu and Au). Molecular lasers include CO₂, N₂ and Excimer. All of these laser types are pumped to an excited state electrically. The dye lasers consist of fluorescent dyes that can be pumped into a liquid jet

excited by another laser to produce new laser wavelengths. Solid state lasers include neodymium lasers, Nd:YAG and Nd:YLF, transition metal lasers, ruby and alexandrite, and the workhorse of modern laser technology, Ti:sapphire (titanium sapphire).

4.1 Argon ion and Krypton ion lasers

The principle of operation of the noble gas ions laser involves creation of high energy ions in an electric discharge. The ions have specific electronic transitions that give rise to lasing at specified wavelengths. The gain bandwidth is typically very narrow in these lasers. This is positive aspect of these lasers since it means that reasonably narrow pulses in the frequency domain can be obtained without the need for optical elements to filter the laser pulse (e.g. birefringent filters used in Ti:sapphire and other broad band gain media). Ar^+ ion lines are observed at 275, 363, 457, 476, 488, 501 and 514.5 nm. Kr^+ ion lines are observed at 406, 413 and 752 nm. Gas phase lasers of this type are continuous wave (cw) and are non-tunable. They provide a useful narrow bandwidth source for pumping cw dye lasers.