

Lasers in Chemical Analysis

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Section One

Lasers and Laser Optics

Chapter 1

Laser Fundamentals

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1. Introduction

For the purpose of the following discussion a laser will be considered to have three subunits—an optical amplifier, an excited state pump, and an optical resonator. The optical amplifier is the collection of atoms, ions, or molecules that have a non-Boltzmann distribution of energy among some set of quantum states. This population inversion, as it is called, has the unique property of amplifying certain frequencies of light via the stimulated emission of radiation. The excited state pump is the device or mechanism used to generate and maintain the population inversion. The exact approach used to accomplish this task depends upon the details of the energy levels and the matrix in which the atom, ion, or molecule is found. The resonator is used to convert the amplifier into an optical oscillator. Although this final step may seem to involve only passive components, the resultant laser radiation has many properties that owe primarily to the resonator design. Thus, a complete description of operating principles must include treatment of all three laser subunits.

2. The Optical Amplifier

2.1. Thermal Energy Distribution

A generalized two-level system is shown in Fig. 1, where E_1 and E_2 are the energies of states 1 and 2, and N_1 and N_2 are the number of such systems per cubic meter in that energy state. These levels can represent the energy of any atomic or molecular property that is quantized. At thermal equilibrium and in the absence of a radiation field the relative population of these levels is given by the Boltzmann distribution,

$$N_2/N_1 = (g_2/g_1) \exp(-\Delta E/kT) \quad (1)$$

where g_1 and g_2 are the degeneracies of each level, ΔE is the energy difference between the levels, T is the absolute temperature, and k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$). From this expression it can be seen that large values of ΔE and low temperatures both favor systems almost entirely in E_1 . This is qualitatively shown in Table I where the

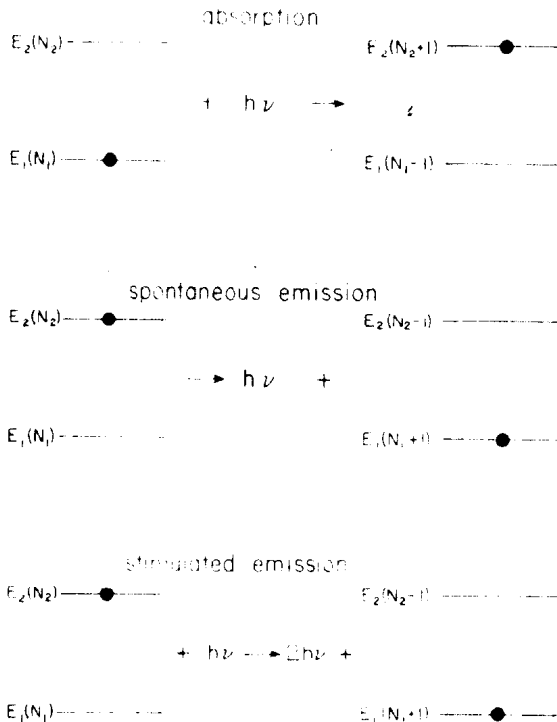


FIG. 1. Generalized energy level diagrams showing the three basic processes involving the absorption or emission of radiation. The term $h\nu$ represents a photon with a frequency satisfying Planck's Law.

Table 1
Relative Populations (N_2/N_1) in a Two-Level System Using the Boltzmann Factor and Assuming That $g_1 = g_2$

Region	λ	Hz	ΔE , J	Collisions ^a
Radiowave	5 m	6×10^7	4×10^{-26}	1–10
Microwave	5 mm	6×10^{10}	4×10^{-23}	10^3 – 10^2
Infrared	5 μm	6×10^{13}	4×10^{-20}	10^3 – 10^6
Visible	500 nm	6×10^{14}	4×10^{-19}	10^6 – 10^8
N_2/N_1				
	4° K	77° K	298° K	1000° K
Radiowave	0.9993	1	1	1
Microwave	0.48	0.96	0.99	1
Infrared	0	4.5×10^{-17}	6.0×10^{-5}	0.06
Visible	0	0	5.7×10^{-43}	2.5×10^{-13}

^aAverage number of collisions required to convert the quantized energy into thermally equilibrated translational motion.

N_2/N_1 ratio has been computed for typical energy separations corresponding to various regions of the electromagnetic spectrum over a wide range of temperatures. For a visible transition, very high temperatures are required to populate a significant percentage of the high levels, whereas for a microwave or radiofrequency transition very low temperatures are required to significantly reduce the population of the high levels. When $N_2 \sim 0$, E_1 is called the ground state and E_2 is called the excited state. Thus, any atom or molecule that exists in E_2 will have a strong thermodynamic driving force to return to E_1 . For the sake of simplicity these are the only systems that will be utilized in the following discussion.

2.2. Absorption of Radiation

Electromagnetic radiation can be absorbed when it interacts with the ground state of a system. The result of this interaction is the loss of a photon and the simultaneous generation of the system in its excited state. This is shown diagrammatically in Fig. 1.

There are two factors that control the extent to which this process can occur. The first is the quantum condition that the photon have the correct frequency. This frequency is determined by Planck's Law

$$\Delta E = h\nu \quad (2)$$

where h is Planck's constant (6.62×10^{-34} Js). No other frequency can promote the transition of the system from E_1 to E_2 (unless of course, one insists on including two photon processes). The second factor that controls the extent of absorption is kinetic in nature. That is, the probability of contact between the photon and the system, and the probability that the interaction will produce the excited state. This can actually be written in a second-order kinetic form as

$$dW_{1,2}/dt = B_{1,2}P(v)N_1 \quad (3a)$$

or

$$dP(v)/dt = -B_{1,2}P(v)N_1 \quad (3b)$$

where the derivative is either the transition rate or the rate of photon absorption, $W_{1,2}$ is the $E_1 \rightarrow E_2$ transition density in m^{-3} , $P(v)$ is the photon density in m^{-3} , and $B_{1,2}$ is the Einstein coefficient of absorption. $B_{1,2}$ is proportional to the quantum mechanical probability of the $E_1 \rightarrow E_2$ transition occurring and has the units of m^3s^{-1} .

Using the relationship that $dx/dt = c$ and by noting that $B_{1,2}/c$ has units of m^2 , Eq. (3b) can be rearranged into a form utilizing an absorption cross-section, $\sigma_{1,2}$. The result is

$$dP(v)/P(v) = -\sigma_{1,2}N_1dx \quad (4)$$

If it is now assumed that $N_1 \gg P(v)$, Eq. (4) can be integrated to yield

$$\ln [P(v,x)/P(v,0)] = -\sigma_{1,2}N_1x \quad (5)$$

or in exponential form

$$P(v,x)/P(v,0) = \exp(-\sigma_{1,2}N_1x) \quad (6)$$

Equation (5) can be rewritten in the more familiar Beer's Law form by converting photon density into photon flux density, I ,

$$I(m^{-2}s^{-1}) = P(m^{-3})/c(ms^{-1}) \quad (7)$$

cross-section into decadic molar absorptivity, ϵ ,

$$\epsilon(Lmol^{-1}cm^{-1}) = \sigma_{1,2}(m^2) \times 10^4(cm^2m^{-2}) \times 6.02 \times 10^{23}(mol^{-1}) / 2.303 \times 10^3(cm^3L^{-1}) \quad (8)$$

converting to base ten logarithms, and using molarity and centimeters.

2.3. Spontaneous Emission of Radiation

When the ratio N_2/N_1 is larger than the value predicted by the Boltzmann distribution, there is a thermodynamic drive for all excited systems to return to the ground state. In the absence of a radiation field

there are two general sets of reactions by which this can be achieved. The first set involves no photons and these are thus called dark reactions. For most molecules this is the dominant mode by which energy is lost, and can be achieved by distributing the energy among other sets of levels or by the transfer of the energy to the matrix via collisions. The net result is usually an increase in the translational temperature of the system.

The second method of returning to the ground state in the absence of a radiation field is by an optical transition. This process is shown diagrammatically in Fig. 1. The result of this spontaneous occurrence is the production of a photon with a frequency satisfying Planck's Law and the generation of the system in its ground state. Ignoring dark reactions this process can be written in kinetic form as

$$dW_{2,1}/dt = A_{2,1} N_2 \quad (9a)$$

or

$$dP(\nu)/dt = A_{2,1} N_2 \quad (9b)$$

where the derivative is either the $E_2 \rightarrow E_1$ transition rate or the rate of photon emission, and $A_{2,1}$ is the Einstein coefficient of spontaneous emission. $A_{2,1}$ is proportional to the probability of the $E_1 \leftarrow E_2$ transition occurring and has the units of s^{-1} .

Since every emitted photon equals a decrease in N_2 by one, Eq. (9) can also be written as

$$dN_2/dt = -A_{2,1} N_2 \quad (10)$$

which can be rearranged and integrated to yield

$$\ln [N_2(t)/N_2(0)] = -A_{2,1} t \quad (11)$$

or in exponential form

$$N_2(t) = N_2(0) \exp[-A_{2,1} t] \quad (12)$$

From this last expression it is possible to see that $A_{2,1}$ must be equal to the reciprocal of τ_2^0 , the intrinsic lifetime of the excited state.

The inclusion of both first- and second-order dark reactions will modify Eq. (10) to the following form

$$dN_2/dt = -(A_{2,1} + d_{2,1} + d_q N_Q) N_2 \quad (13)$$

where $d_{2,1}$ is the rate constant for the spontaneous dark path; d_q is the constant for the induced, or quenching, dark path; and N_Q is the number of excited state quenchers per cubic meter. For the case where $N_Q > N_2$, Eq. (13) can be rewritten as

$$dN_2/dt = -(A_{2,1} + D_{2,1}) N_2 \quad (14)$$