

# Lasers, Laser Spectroscopy, and Photochemistry

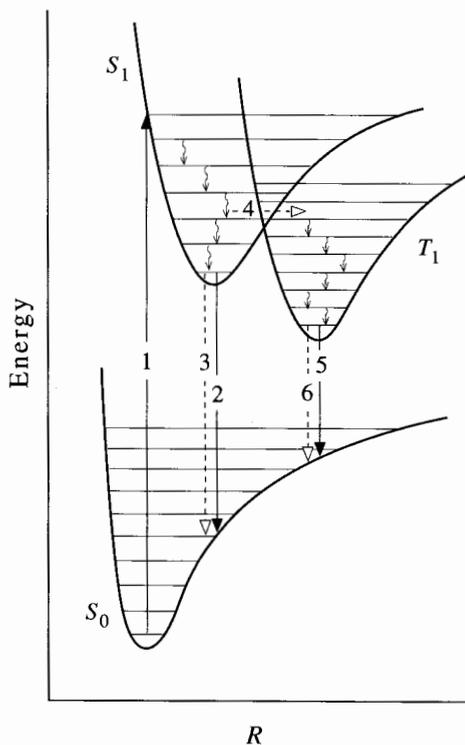
The word *laser* is an acronym for *light amplification by stimulated emission of radiation*. Lasers are used in a variety of devices and applications such as supermarket scanners, optical disk storage drives, compact disc players, ophthalmic and angioplastic surgery, and military targeting. Lasers have also revolutionized research in physical chemistry. Their impact on the field of spectroscopy and light-initiated reactions, or *photochemistry*, has been tremendous. Using lasers, chemists can measure the spectra and photochemical dynamics of molecules with high spectral or time resolution. Furthermore, the techniques are so sensitive that a single molecule can be studied. Every chemist today should know how lasers work and understand the unique properties of the light they generate.

To understand how a laser works, we first must learn about the various pathways by which an electronically excited atom or molecule can decay back to its ground state. The generation of laser light depends on the rates at which these excited atoms or molecules decay back to their ground states. Therefore, we will discuss a rate-equation model developed by Einstein that describes the dynamics of spectroscopic transitions between atomic energy levels. We will see that before we can even consider building a laser, we must understand transitions between more than two atomic energy levels. We will then discuss the general principles of laser design and describe some of the lasers used in research chemistry laboratories. In particular, we will illustrate the specifics of how a laser works by examining the helium-neon laser in detail. Using the laser spectroscopy of iodine chloride,  $\text{ICl}(\text{g})$ , as an example, we will see that spectral features can be resolved by lasers that cannot be observed using conventional lamp-based spectrometers. We will then examine a photochemical reaction, the light-induced dissociation, or *photodissociation*, of  $\text{ICN}(\text{g})$ . We will learn that the time required for the I–CN bond to break after absorption to a dissociative electronic state can be measured using lasers with outputs of femtosecond ( $10^{-15}$  s) light pulses.

## 15-1. Electronically Excited Molecules Can Relax by a Number of Processes

A molecule will not remain in an excited state indefinitely. After an excitation to an excited electronic state, a molecule invariably will relax back to its electronic ground state. Although we will consider a diatomic molecule to illustrate the mechanisms by which an electronically excited molecule can relax back to its ground state, our discussion also applies to polyatomic molecules. We will assume that the ground electronic state of the diatomic molecule is a singlet state, which we denote by  $S_0$ . Figure 15.1 shows a plot of the potential energy curves for the ground electronic state and the first excited singlet state,  $S_1$ , and the first excited triplet state,  $T_1$ . (Recall from Section 9-16 that the energy of the triplet state is less than that of the singlet state.) So that the various processes can be viewed easily, we assume that the equilibrium bond length in these three electronic states increases in the order  $R_e(S_0) < R_e(S_1) < R_e(T_1)$ . The vibrational levels of the ground and electronically excited states are indicated by the horizontal solid lines. The spacing between rotational levels is small compared with that between vibrational levels, so there are discrete rotational levels (not indicated in the figure) that lie between the indicated vibrational levels.

Absorption to  $S_1$  produces a molecule that is in an excited vibrational (and possibly rotational) state, and from our study of the Franck-Condon principle in Section 13-7,



**FIGURE 15.1**

A schematic illustration of the absorption and the subsequent radiative and nonradiative decay pathways for an electronically excited diatomic molecule: 1, absorption from  $S_0$  to  $S_1$ ; 2, fluorescence (a radiative transition from  $S_1$  to  $S_0$ ); 3, internal conversion (a nonradiative transition from  $S_1$  to  $S_0$ ); 4, intersystem crossing (a nonradiative transition from  $S_1$  to  $T_1$ ); 5, phosphorescence (a radiative transition from  $T_1$  to  $S_0$ ); and 6, intersystem crossing (a nonradiative transition from  $T_1$  to  $S_0$ ). The wavy arrows between adjacent vibrational states illustrate the nonradiative process of vibrational relaxation.

we know that electronic transitions are depicted by vertical lines in a diagram such as in Figure 15.1. An excited-state molecule can relax by many different mechanisms. Transitions between energy levels that involve either the absorption or the emission of radiation are called *radiative transitions*. Transitions between energy levels that occur without the absorption or emission of radiation are called *nonradiative transitions*.

The various types of arrows in Figure 15.1 indicate the types of relaxation processes that can occur between the different energy levels shown. Solid arrows are used to depict radiative transitions, wavy arrows to indicate nonradiative transitions within a single electronic state, and dashed lines with an unfilled arrow tip to indicate nonradiative transitions between two electronic states. In the absence of collisions, an excited molecule can undergo only processes that conserve energy, and therefore the return to the ground state must involve the emission of a photon. Collisions between an excited molecule and other molecules in the sample, however, can result in an exchange of energy that removes some of the excess vibrational energy. This process is called *vibrational relaxation*. Because of vibrational relaxation, an excited molecule quickly relaxes to the lowest vibrational state of  $S_1$ . Once the molecule reaches the lowest vibrational state of  $S_1$ , it can relax to the ground state  $S_0$  by either emitting a photon (a radiative process) or by exchanging energy in a collision such that it makes a nonradiative transition from the excited electronic state to one of the rotational-vibrational energy levels of the ground electronic state of the molecule. The radiative decay process involves a transition between states of the same spin multiplicity and is called *fluorescence*. The nonradiative decay process also involves the transition between states of the same spin multiplicity and is called *internal conversion*.

Notice that some of the vibrational and rotational states of the  $S_1$  electronic state overlap the vibrational and rotational states of the  $T_1$  electronic state in Figure 15.1. When such an overlap occurs, the molecule may undergo a nonradiative transition between states of different spin multiplicity, a process called *intersystem crossing*. Because intersystem crossing requires a change in the spin of an electron, it is usually a slower process than internal conversion. If intersystem crossing produces a molecule in the  $T_1$  state with an excess of vibrational energy, then vibrational relaxation can occur in the  $T_1$  state until the molecule reaches the  $v = 0$  level of this state. Once the molecule reaches the lowest vibrational level in the  $T_1$  state, it can relax to the ground electronic state by either emitting a photon (a radiative process) or by exchanging energy in a collision such that it makes a nonradiative transition from the excited electronic state to one of the rotational-vibrational energy levels of the ground electronic state. The radiative decay process involves a transition between states of different spin multiplicity ( $T_1 \rightarrow S_0$ ) and is called *phosphorescence*. The nonradiative decay process also involves a transition between states of different spin multiplicity and is therefore another example of intersystem crossing. Because phosphorescence requires a change in the spin of an electron, it is usually a slower process than fluorescence. Because the  $T_1$  state in Figure 15.1 is lower in energy than the  $S_1$  state, phosphorescence occurs at a lower energy than fluorescence. Figure 15.1 and Table 15.1 summarize the various relaxation processes we have described.

Consider the absorption and fluorescence spectra of a diatomic molecule when  $R_e(S_0) = R_e(S_1)$ . In this case, the minimum of the potential curve for the  $S_1$  state

TABLE 15.1

Typical time scales of the various processes by which a molecule in an excited electronic state can relax.

Process	Transition	Change in spin multiplicity	Time scale
Fluorescence	Radiative $S_1 \rightarrow S_0$	0	$10^{-9}$ s
Internal conversion	Collisional $S_1 \rightarrow S_0$	0	$10^{-7}$ – $10^{-12}$ s
Vibrational relaxation	Collisional		$10^{-14}$ s
Intersystem crossing	$S_1 \rightarrow T_1$	1	$10^{-12}$ – $10^{-6}$ s
Phosphorescence	$T_1 \rightarrow S_0$	1	$10^{-7}$ – $10^{-5}$ s
Intersystem crossing	$T_1 \rightarrow S_0$	1	$10^{-8}$ – $10^{-3}$ s

shown in Figure 15.1 would sit directly above that of the  $S_0$  ground state. Figure 15.2 shows a plot of both the absorption and the fluorescence spectra in this case. The energy levels that give rise to the observed transitions are indicated above the spectra. The vibrational quantum numbers for the ground electronic state and excited electronic states are denoted by  $v''$  and  $v'$ , respectively. The absorption spectrum consists of a series of lines reflecting the transitions from the  $v'' = 0$  level of the ground electronic state to the  $v' = 0, 1, 2, 3, \dots$  levels of the excited electronic state. The data in Table 15.1 show that vibrational relaxation occurs more rapidly than electronic relaxation. Therefore, we can reasonably assume that the excited molecule relaxes to the lowest vibrational state of the  $S_1$  electronic state before any fluorescence occurs. The fluorescence spectrum will then consist of a series of lines reflecting the transitions from the  $v' = 0$  level of the excited electronic state to the  $v'' = 0, 1, 2, \dots$  levels of the ground electronic

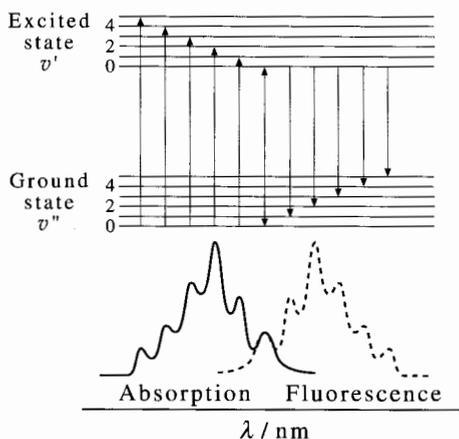


FIGURE 15.2

An illustration of fluorescence transitions of a diatomic molecule. Both the absorption and fluorescence spectra have peaks corresponding to a transition between  $v'' = 0$  and  $v' = 0$ . The spacing between lines in the absorption spectrum is determined by the energy gap between vibrational states in the excited electronic state. The spacing between lines in the fluorescence spectrum is determined by the energy gap between vibrational states in the ground electronic state.

state. Note that both the absorption and fluorescence spectra will contain a transition between the  $v'' = 0$  and  $v' = 0$  levels, which is called the 0,0-transition. The remaining absorption bands occur at higher energy than the 0,0-transition, and the remaining fluorescence bands occur at lower energy than the 0,0-transition. The spacing between the lines in the absorption spectrum depends on the energy gaps between the vibrational levels of the excited electronic state. The spacing between the lines in the fluorescence spectrum depends on the energy gaps between the vibrational levels of the ground electronic state. If the vibrational frequencies of the ground electronic state and the excited electronic state are the same, the absorption and fluorescence spectra appear to be mirror images of one another, as shown in Figure 15.2. The relative intensities of the absorption and fluorescence lines can be determined using the Franck-Condon principle (see Section 13-7).

## 15-2. The Dynamics of Spectroscopic Transitions Between the Electronic States of Atoms Can Be Modeled by Rate Equations

To understand how lasers work, we need to learn about the rate at which atoms and molecules undergo radiative transitions. To illustrate the concepts of radiative decay, we will focus our discussion on atoms, so that we need consider only electronic states. Molecules can be treated in a similar way, but the mathematical equations become more complicated because of the need to include transitions among the various vibrational and rotational levels in addition to electronic levels. Actually, many lasers are based on the radiative properties of atomic transitions. A phenomenological approach that describes the rates of the various transitions between electronic states was proposed by Einstein at the beginning of this century. Einstein's approach is based on a few simple assumptions that account for how atoms absorb and emit photons. (His assumptions can be justified using time-dependent quantum mechanics.) The elegance of Einstein's approach is that no quantum mechanics is required except that the energy levels of the atom are assumed to be quantized.

Consider the interaction of light with a sample of  $N_{\text{total}}$  identical atoms. We will assume for simplicity that each atom has only two electronic levels, a ground level (with energy  $E_1$ ) and an excited level (with energy  $E_2$ ). Furthermore, we will assume that each level is nondegenerate and therefore, each level represents a single state of the system. The number of atoms in each state is designated by  $N_1$  and  $N_2$ , respectively (see Figure 15.3). Because there are only two possible states that the atom can occupy,

$$N_2 = 4 \quad \text{---} \text{○○○○} \text{---} \quad E_2$$

$$N_1 = 8 \quad \text{---} \text{○○○○○○○○} \text{---} \quad E_1$$

**FIGURE 15.3**

A schematic representation of a two-level energy diagram. Both levels are nondegenerate and therefore each one indicates a single state of the system. The circles represent the number of atoms in each state, eight in the ground state and four in the excited state.

$N_{\text{total}} = N_1 + N_2$ . We will learn in Chapters 17 and 18 that the average energy of an atom or a molecule depends upon the kelvin temperature,  $T$ , and is of the order of  $k_B T$ , where  $k_B$  is the Boltzmann constant. Consequently, for atoms in which  $E_2 - E_1$  is much greater than the thermal energy  $k_B T$ , the atoms do not have sufficient (thermal) energy to make a transition from state 1 to 2. Therefore, essentially all the atoms in the sample will be in the ground state, so  $N_1 = N_{\text{total}}$ . If we expose the sample to electromagnetic radiation of frequency  $\nu_{12}$ , where  $h\nu_{12} = E_2 - E_1$ , some of the atoms will absorb light and make a transition from state 1 to state 2, (Figure 15.4).

The energy density of the light is described by two related quantities. The *radiant energy density*,  $\rho$ , is defined as the radiant energy per unit volume and has units of  $\text{J} \cdot \text{m}^{-3}$ . The *spectral radiant energy density*,  $\rho_\nu$ , is a measure of the radiant energy density per unit frequency,  $\rho_\nu = d\rho/d\nu$ , and has units of  $\text{J} \cdot \text{m}^{-3} \cdot \text{s}$ . Because the transition between states 1 and 2 occurs only if light at  $\nu = \nu_{12}$  is provided, we will be interested in the spectral radiant energy density at  $\nu_{12}$ ,  $\rho_\nu(\nu_{12})$ , of the incident light source.

Einstein proposed that the rate of excitation from the ground electronic state to the excited electronic state is proportional to  $\rho_\nu(\nu_{12})$  and to  $N_1$ , the number of molecules present in the ground state at time  $t$ . The rate of excitation from the ground electronic state to the excited electronic states is given by  $-dN_1(t)/dt$ , where the negative sign indicates that  $N_1(t)$  decreases with increasing time. Because  $-dN_1(t)/dt$  is proportional to both  $\rho_\nu(\nu_{12})$  and  $N_1(t)$ , we can write

$$\text{rate} = -\frac{dN_1(t)}{dt} \propto \rho_\nu(\nu_{12})N_1(t)$$

or

$$\text{rate} = -\frac{dN_1(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) \quad (15.1)$$

where  $B_{12}$  is a proportionality constant called an *Einstein coefficient*. The “12” subscript of the  $B$  coefficient refers to the order of the states involved for the particular transition being discussed ( $1 \rightarrow 2$ ). In the absence of any decay mechanism, the rate of growth of the excited-state population must be the negative of the rate of depletion of the

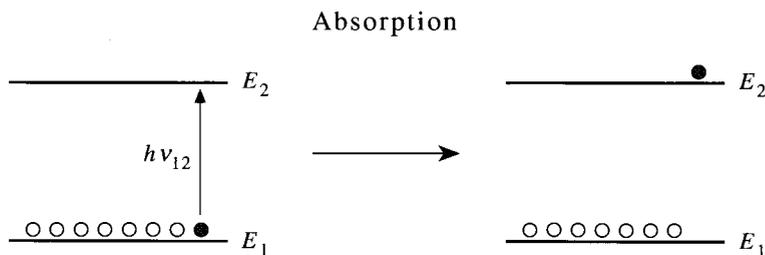


FIGURE 15.4

An illustration of the absorption process. Light of energy  $h\nu_{12} = E_2 - E_1$  can be absorbed by an atom, which causes the atom to make a transition from the ground state to an electronically excited state.

ground-state population,  $-dN_1(t)/dt = dN_2(t)/dt$ , because  $N_1(t) + N_2(t) = N_{\text{total}} = \text{constant}$ . Therefore,

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) \quad (\text{absorption only}) \quad (15.2)$$

Note that  $N_1(t)$  decreases and  $N_2(t)$  increases with increasing time.

### EXAMPLE 15-1

The output of a light source is usually given by a measure of its intensity. The intensity  $I$  is defined as the radiant energy per time that passes through a cross-sectional area perpendicular to the direction of propagation of the light. Show that

$$I = \rho c$$

where  $\rho$  is the radiant energy density and  $c$  is the speed of light.

SOLUTION: Consider a light beam of radiant energy  $dQ$  that passes through a cross-sectional area  $dA$  during a time period  $dt$ . The intensity is then defined as

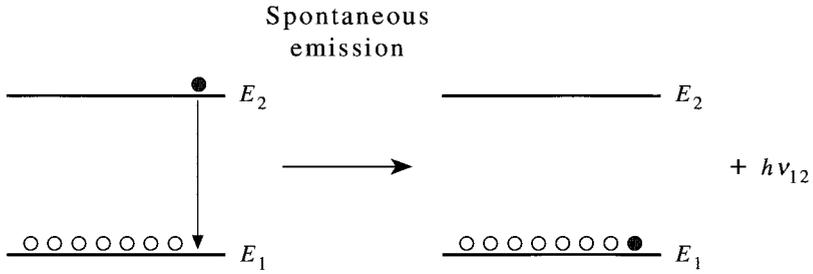
$$I = \frac{dQ}{dt dA} \quad (1)$$

and has units of  $\text{J} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$ . During the time  $dt$ , the light beam travels a distance  $cdt$ . Therefore,  $dQ$ , the radiant energy that has passed through the cross-sectional area  $dA$  in the time  $dt$  is now contained in the volume  $cdAdt$ . The radiant energy density is then

$$\rho = \frac{dQ}{cdAdt} \quad (2)$$

Solving Equation 1 for  $dQ$  and substituting the result into Equation 2 gives us  $I = \rho c$ . Note that we can also define a spectral intensity  $I_\nu(\nu) = dI/d\nu$ , which has units of  $\text{J} \cdot \text{m}^{-2}$ . Because  $I = \rho c$ , we see that the spectral intensity is related to the spectral radiant energy density by  $I_\nu(\nu) = \rho_\nu(\nu)c$ , where  $\rho_\nu(\nu) = d\rho/d\nu$ .

The above discussion accounts for only the absorption process. Atoms do not remain in excited states indefinitely, however. After a brief time, an atom emits energy and returns to the ground electronic state. Einstein's treatment proposes two pathways by which atoms relax back to the ground electronic state: *spontaneous emission* and *stimulated emission*. Spontaneous emission accounts for the process by which atoms spontaneously emit a photon of energy  $h\nu_{12} = E_2 - E_1$  at some time after excitation (Figure 15.5). The rate at which spontaneous emission occurs can be described by  $-dN_2(t)/dt$ , where the negative sign indicates that  $N_2(t)$  decreases with increasing time. We assume that the rate of spontaneous emission is simply proportional to the number of atoms in the excited state,  $N_2(t)$ , at time  $t$ . The proportionality constant



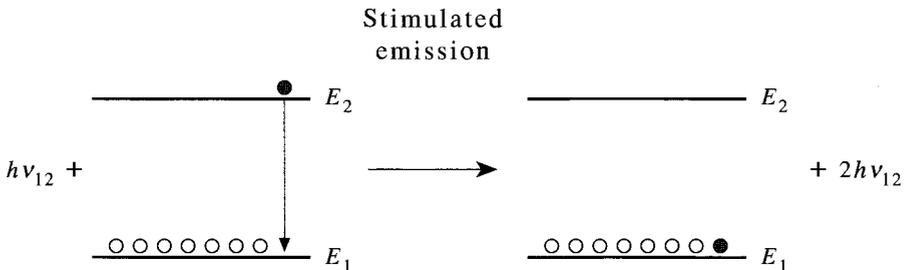
**FIGURE 15.5**

The spontaneous-emission process. Light of energy  $h\nu_{12} = E_2 - E_1$  is emitted by an excited atom when the atom makes a transition from the electronically excited state to the ground state.

relating the rate of excited state decay,  $-dN_2(t)/dt$ , to the population of that level,  $N_2(t)$ , is given by another Einstein coefficient,  $A_{21}$ :

$$-\frac{dN_2(t)}{dt} = A_{21}N_2(t) \quad (\text{spontaneous emission only}) \quad (15.3)$$

In addition to spontaneous emission, Einstein proposed that the exposure of an atom in an excited electronic state to electromagnetic radiation of energy  $h\nu_{12} = E_2 - E_1$  could stimulate the emission of a photon and thereby regenerate the ground-state atom (Figure 15.6). As for spontaneous emission, the rate of stimulated emission also depends on the number of excited molecules. Unlike spontaneous emission, however, the rate of stimulated emission is proportional to the spectral radiant energy density,  $\rho_\nu(\nu_{12})$ , in addition to  $N_2(t)$ , the number of atoms in state 2 at time  $t$ . The proportionality constant relating the rate of stimulated emission,  $-dN_2(t)/dt$ , to  $\rho_\nu(\nu_{12})$  and  $N_2(t)$ , is given by a third Einstein coefficient,  $B_{21}$ . The order of the subscript of  $B$  is 21, indicating that



**FIGURE 15.6**

The stimulated-emission process. Incident light of energy  $h\nu_{12} = E_2 - E_1$  stimulates an atom in an excited electronic state to emit a photon of energy  $h\nu_{12}$  and thereby causes the atom to make a transition from the excited electronic state to the ground electronic state.

the transition takes place from the excited state (level 2) to the ground state ( $2 \rightarrow 1$ ). The rate of decay of  $N_2(t)$  as a result of stimulated emission is given by

$$-\frac{dN_2(t)}{dt} = B_{21}\rho_\nu(\nu_{12})N_2(t) \quad (\text{stimulated emission only}) \quad (15.4)$$

Notice that the stimulated-emission process amplifies light intensity; one photon at frequency  $\nu_{12}$  stimulates an atom to emit another, thus generating a second photon at frequency  $\nu_{12}$ . In a large sample of atoms, this process can occur many times, resulting in a substantial amplification of an incident light beam at frequency  $\nu_{12}$ . Lasers are devices that exploit the amplification of light through stimulated emission (recall that the word, laser, stands for *light amplification by stimulated emission of radiation*).

Upon exposure to light, a sample of atoms simultaneously undergoes all three processes, absorption, spontaneous emission, and stimulated emission. Thus, the rate of change in the population of either the ground electronic state or the excited electronic state must be the sum of the rates of these three individual processes, Equations 15.2, 15.3, and 15.4:

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B_{12}\rho_\nu(\nu_{12})N_1(t) - A_{21}N_2(t) - B_{21}\rho_\nu(\nu_{12})N_2(t) \quad (15.5)$$

### EXAMPLE 15-2

What are the units of the Einstein  $A$  and  $B$  coefficients?

SOLUTION: We can use Equations 15.3 and 15.4 to determine the units of the Einstein  $A$  and  $B$  coefficients. First, consider Equation 15.3:

$$-\frac{dN_2(t)}{dt} = A_{21}N_2(t)$$

Solving this equation for  $A_{21}$  gives us

$$A_{21} = -\left(\frac{1}{N_2(t)}\right)\left(\frac{dN_2(t)}{dt}\right)$$

The units of  $1/N_2(t)$  and  $dN_2(t)/dt$  are  $\text{number}^{-1}$  and  $\text{number}\cdot\text{s}^{-1}$ , respectively, and so the units of  $A_{21}$  are  $\text{s}^{-1}$ .

Now consider Equation 15.4:

$$-\frac{dN_2(t)}{dt} = B_{21}\rho_\nu(\nu_{12})N_2(t)$$

Solving this equation for  $B_{21}$  gives us

$$B_{21} = -\left(\frac{1}{\rho_\nu(\nu_{12})N_2(t)}\right)\left(\frac{dN_2(t)}{dt}\right)$$

The units of the spectral radiant energy density of the electromagnetic radiation,  $\rho_\nu(\nu_{12})$ , are  $\text{J}\cdot\text{m}^{-3}\cdot\text{s}$ . Thus, the units of  $B_{21}$  are

$$(\text{J}^{-1}\cdot\text{m}^3\cdot\text{s}^{-1}\cdot\text{number}^{-1})(\text{number}\cdot\text{s}^{-1}) = \text{J}^{-1}\cdot\text{m}^3\cdot\text{s}^{-2} = \text{kg}^{-1}\cdot\text{m}$$

A comparison of Equations 15.2 and 15.4 shows that  $B_{12}$  and  $B_{21}$  have identical units.

The three Einstein coefficients ( $B_{12}$ ,  $B_{21}$ , and  $A_{21}$ ) turn out to be related to each other. We can see this relation by considering the limit at which the two energy states are in thermal equilibrium, in which case  $N_1$  and  $N_2$  no longer vary with time,

$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = 0 \quad (15.6)$$

and  $\rho_\nu(\nu_{12})$  is the equilibrium spectral radiant energy density, which we can assume comes from a thermal blackbody radiation source. Recall that this quantity is given by Planck's blackbody distribution law (Equation 1.2),

$$\rho_\nu(\nu_{12}) = \frac{8\pi h}{c^3} \frac{\nu_{12}^3}{e^{h\nu_{12}/k_B T} - 1} \quad (15.7)$$

Now if we let  $dN_1/dt = 0$  in Equation 15.5 and solve for  $\rho_\nu(\nu_{12})$ , we obtain

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{(N_1/N_2)B_{12} - B_{21}} \quad (15.8)$$

We will learn in Chapter 17 that for a system in equilibrium at a temperature  $T$ , the number of atoms or molecules in the state  $j$  with energy  $E_j$  is given by

$$N_j = c e^{-E_j/k_B T} \quad (15.9)$$

where  $c$  is a proportionality constant. Using Equation 15.9 for states 1 and 2 gives us that

$$\frac{N_2}{N_1} = e^{-(E_2-E_1)/k_B T} = e^{-h\nu_{12}/k_B T} \quad (15.10)$$

at equilibrium. If we use Equation 15.10 in Equation 15.8, we obtain

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{B_{12}e^{h\nu_{12}/k_B T} - B_{21}} \quad (15.11)$$

Equations 15.7 and 15.11 are equivalent only if (Problem 15-4)

$$B_{12} = B_{21} \quad (15.12)$$

and

$$A_{21} = \frac{8h\pi\nu_{12}^3}{c^3} B_{21} \quad (15.13)$$

Note that we had to include the stimulated-emission process to have consistency between the Einstein theory and Planck's blackbody radiation law.

### 15-3. A Two-Level System Cannot Achieve a Population Inversion

Lasers are designed to amplify light by the stimulated emission of radiation. For this amplification to occur, a photon that passes through the sample of atoms must have a greater probability of stimulating emission from an electronically excited atom than of being absorbed by an atom in its ground state. This condition requires that the rate of stimulated emission be greater than the rate of absorption, or that (see Equations 15.2 and 15.4)

$$B_{21}\rho_\nu(\nu_{12})N_2 > B_{12}\rho_\nu(\nu_{12})N_1 \quad (15.14)$$

Because  $B_{21} = B_{12}$  (Equation 15.12), stimulated emission is more probable than absorption only when  $N_2 > N_1$ , or when the population of the excited state is greater than that of the lower state. Such a situation is called *population inversion*. According to Equation 15.10,  $N_2$  must be less than  $N_1$  because  $h\nu_{12}/k_B T$  is a positive quantity. Consequently, a population inversion, for which  $N_2 > N_1$ , is a nonequilibrium situation. Thus, before we can expect light amplification, a population inversion between the upper and lower levels must be generated. Let's see if a population inversion can be achieved for the two-level system discussed in Section 15-2.

The rate equation for a nondegenerate two-level system is given by Equation 15.5:

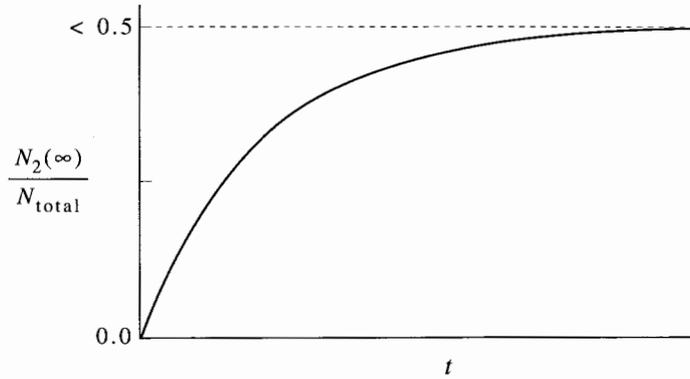
$$-\frac{dN_1(t)}{dt} = \frac{dN_2(t)}{dt} = B\rho_\nu(\nu_{12})\{N_1(t) - N_2(t)\} - AN_2(t) \quad (15.15)$$

where we have dropped the indices for the Einstein coefficients because  $B_{12} = B_{21}$  and the spontaneous emission process,  $A$ , occurs only from state 2 to state 1 in a two-level system. If we assume that all the atoms are in the ground state at time  $t = 0$  so that  $N_1 = N_{\text{total}}$  and  $N_2 = 0$ , Equation 15.15 gives us (Problem 15-5):

$$N_2(t) = \frac{B\rho_\nu(\nu_{12})N_{\text{total}}}{A + 2B\rho_\nu(\nu_{12})} \{1 - e^{-[A + 2B\rho_\nu(\nu_{12})]t}\} \quad (15.16)$$

Figure 15.7 shows a plot of  $N_2/N_{\text{total}}$  as a function of time. The value of the excited-state population reaches a steady state as  $t \rightarrow \infty$ . If we let  $t \rightarrow \infty$  in Equation 15.16, we find that

$$\frac{N_2(t \rightarrow \infty)}{N_{\text{total}}} = \frac{B\rho_\nu(\nu_{12})}{A + 2B\rho_\nu(\nu_{12})} \quad (15.17)$$



**FIGURE 15.7**

The ratio of the number of atoms in electronically excited states to the total number of atoms,  $N_2/N_{\text{total}}$ , is plotted as a function of time for a two-level system. The number of atoms in the excited state is always less than that in the ground state in a two-level system. Therefore, a two-level system can never achieve a population inversion.

Because  $A > 0$ , Equation 15.17 says that for all time  $t$ ,

$$\frac{N_2}{N_{\text{total}}} = \frac{N_2}{N_1 + N_2} < \frac{1}{2} \quad (15.18)$$

Equation 15.18 reveals that the number of atoms in the excited state can never exceed the number of atoms in the ground state (Problem 15–8). Thus, a population inversion cannot occur in a two-level system.

**EXAMPLE 15–3**

Consider a two-level system. An incident light beam of energy  $h\nu_{12} = E_2 - E_1$  is turned on for a while and then turned off. Describe how the system relaxes to equilibrium once the incident light source is turned off.

**SOLUTION:** Once the light source is turned off, the only pathway by which an excited atom can return to its ground state is by spontaneous emission. Because  $\rho_{\nu}(v_{12}) = 0$ , the rate equation (Equation 15.5) simplifies to

$$\frac{dN_2(t)}{dt} = -AN_2(t)$$

This equation can be integrated to give

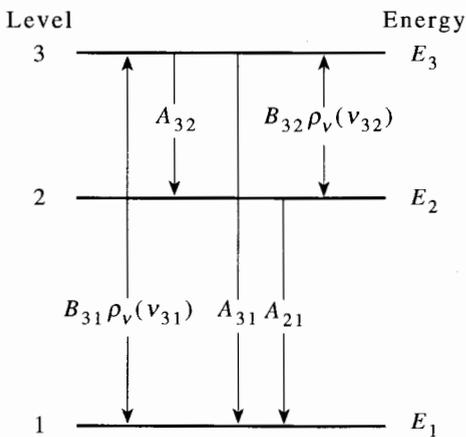
$$N_2(t) = N_2(0)e^{-At}$$

The reciprocal of  $A$  is denoted by  $\tau_R$  and is called the *fluorescence lifetime* or *radiative lifetime*.

## 15-4. Population Inversion Can Be Achieved in a Three-Level System

The ideas presented in Section 15-3 can be generalized to multilevel systems, and we will demonstrate here that a population inversion can be achieved in a three-level system. A schematic diagram of a three-level system is shown in Figure 15.8. Each level is once again assumed to be nondegenerate and therefore represents a single state of the system. In this figure, the ground state is labeled as 1 and has an energy  $E_1$ . We have drawn two excited states, labeled 2 and 3, which have energies  $E_2$  and  $E_3$ , respectively. We will show that under certain conditions, a population inversion can be achieved between the two excited states (in other words, that  $N_3 > N_2$ ). Once prepared, such a system provides a medium for the amplification of light of energy  $h\nu_{32} = E_3 - E_2$  and is said to be able to lase.

Many rate processes are labeled in Figure 15.8. The double-headed arrows indicate that both absorption and stimulated emission occur between the two states. A single  $B$  coefficient is used for absorption and stimulated emission between a set of two states because we know that  $B_{ij} = B_{ji}$ . Initially, all atoms are in the ground state, so that  $N_1(0) = N_{\text{total}}$ . We consider the case in which this three-level system is exposed to an incident light beam of spectral radiant energy density,  $\rho_\nu(\nu_{31})$  (where  $h\nu_{31} = E_3 - E_1$ ), which excites atoms from level 1 to level 3. A light beam such as this one that is used to create excited-state populations is referred to as a *pump source*. The pump source is assumed to have no spectral radiant energy density at  $h\nu_{12} = E_2 - E_1$ , and as a result no atoms are excited to state 2. Once an atom populates state 3, it can decay by stimulated emission back to state 1 (induced by the pump source) or by spontaneous emission to either state 2 or state 1. The rates of spontaneous emission to state 2 and state 1 can be different; thus, we must include subscripts on the  $A$  coefficients to indicate explicitly the two states involved in the transition. An atom that relaxes from state 3 to state 2 can in turn relax back to the ground state by spontaneous emission. If light of frequency  $\nu_{32}$  ( $h\nu_{32} = E_3 - E_2$ ) is available, both absorption and stimulated emission can occur between states 3 and 2. Light of this energy is inevitably



**FIGURE 15.8**

A three-level energy diagram. Pump light of frequency given by  $h\nu_{13} = E_3 - E_1$  excites an atom from the ground state (state 1) to state 3. Once populated, this excited state can relax by spontaneous emission to states 2 or 1 or by stimulated emission back to the ground state. Those excited-state atoms that relax by spontaneous emission to state 2 will also undergo spontaneous emission to state 1. If light of energy  $h\nu_{32} = E_3 - E_2$  is incident on the system, absorption and stimulated emission can occur between the excited states 3 and 2.

available because it is generated by the spontaneous-emission process between these two levels.

For a three-level system, the sum of the populations of the individual energy levels is equal to the total number of atoms:

$$N_{\text{total}} = N_1(t) + N_2(t) + N_3(t) \quad (15.19)$$

The processes indicated in Figure 15.8 give rise to rate equations for each of the three energy levels (Problem 15–11). Because each level is nondegenerate, these rate equations apply to the populations of states 1, 2, and 3. When the system achieves equilibrium, the population of each level will remain constant, so  $dN_1(t)/dt = 0$ ,  $dN_2(t)/dt = 0$ , and  $dN_3(t)/dt = 0$ . Although the three rate equations can be written and solved exactly to generate expressions for the time-dependent and equilibrium values of  $N_1$ ,  $N_2$ , and  $N_3$ , we can learn an important result by considering only the rate equation for state 2. The population of state 2,  $N_2$ , is a balance between spontaneous emission from state 3 to state 2 ( $A_{32}N_3$ ), spontaneous emission from state 2 to state 1 ( $A_{21}N_2$ ), stimulated emission from state 3 to state 2 [ $\rho_\nu(\nu_{32})B_{32}N_3$ ], and absorption from state 2 to state 3 [ $\rho_\nu(\nu_{32})B_{32}N_2$ ] (Figure 15.8). When equilibrium is achieved,  $dN_2/dt = 0$  and

$$\frac{dN_2(t)}{dt} = 0 = A_{32}N_3 - A_{21}N_2 + \rho_\nu(\nu_{32})B_{32}N_3 - \rho_\nu(\nu_{32})B_{32}N_2 \quad (15.20)$$

Equation 15.20 can be rearranged to become

$$N_3[A_{32} + B_{32}\rho_\nu(\nu_{32})] = N_2[A_{21} + B_{32}\rho_\nu(\nu_{32})] \quad (15.21)$$

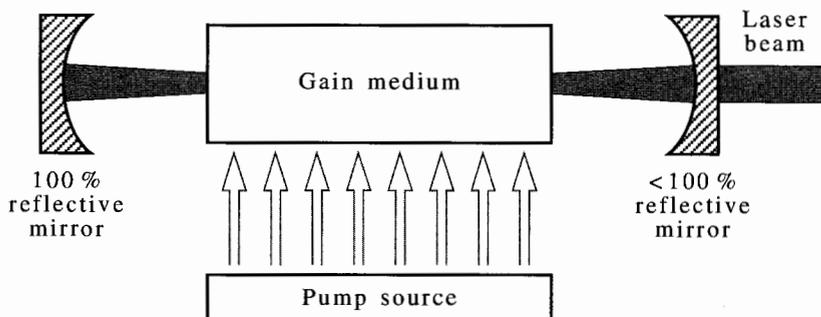
or

$$\frac{N_3}{N_2} = \frac{A_{21} + B_{32}\rho_\nu(\nu_{32})}{A_{32} + B_{32}\rho_\nu(\nu_{32})} \quad (15.22)$$

Notice that  $N_3$  can be larger than  $N_2$  if  $A_{21} > A_{32}$ . Therefore, a population inversion is possible between states 3 and 2 when the atoms excited to state 3 decay relatively slowly to state 2 and those in state 2 decay rapidly back to the ground state. If this is the case, a population of state 3 can be built up, and a system of atoms that satisfies this condition may lase. Such a system is called a *gain medium*.

### 15–5. What is Inside a Laser?

Lasers are composed of three essential elements (Figure 15.9): (1) a gain medium that amplifies light at the desired wavelength, (2) a pumping source that excites the gain medium, and (3) mirrors that direct the light beam back and forth through the gain medium. We will discuss each of these components in turn.



**FIGURE 15.9**

A diagram of the insides of a laser. The gain medium is placed between two mirrors; the arrangement of these components is called the laser cavity. A pump source excites the atoms, molecules, or ions that constitute the gain medium. The radiation that is emitted by the excited-state atoms is directed back and forth through the gain medium using the mirrors. One of the mirrors has a reflectivity that is less than 100%, which allows light to escape the cavity. This output light is the laser beam.

*Gain medium:*

The gain medium of a laser can be a solid-state material, a liquid solution, or a gas mixture. Since the report of the first laser in 1960, many different media have been used. In the following paragraphs, we discuss only a few of the materials currently used as laser gain media.

The first laser used a solid ruby rod as a lasing medium. Ruby is a crystal of corundum,  $\text{Al}_2\text{O}_3$ , in which some of the  $\text{Al}^{3+}$  ions are replaced by impurity  $\text{Cr}^{3+}$  ions. The impurity  $\text{Cr}^{3+}$  ions are the source of the laser light because the photophysical properties of the electronic energy levels of  $\text{Cr}^{3+}$  in the  $\text{Al}_2\text{O}_3$  host crystal are suitable for achieving a population inversion. Naturally occurring ruby is unsuitable as a laser gain medium because of its strains and crystal defects, so ruby lasers use synthetic rods grown from molten mixtures of  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ . A typical chromium doping level is about 0.05% by mass. There are many solid-state gain media, like ruby, in which the active ion ( $\text{Cr}^{3+}$  for ruby) is embedded in a host material ( $\text{Al}_2\text{O}_3$  for ruby). Examples of different solid-state gain media are given in Table 15.2 along with the wavelength of the laser light produced. Many commercially available lasers use  $\text{Nd}^{3+}$  as the gain medium. Note from the information given in Table 15.2 for various  $\text{Nd}^{3+}$  lasers that the host material can affect the wavelength of the laser light produced. Laser output can be a continuous light beam or a short burst of light. We see in Table 15.2 that solid-state lasers can produce both continuous and pulsed laser output.

**EXAMPLE 15-4**

A  $\text{Nd}^{3+}$ :YAG (YAG stands for yttrium-aluminum garnet) laser produces pulses at a repetition rate of 1 kHz. If each pulse is 150 ps in duration and has a radiant energy of

$1.25 \times 10^{-3}$  J, calculate  $P$ , the radiant power of each laser pulse, and  $\langle P \rangle$ , the average radiant power of the laser. Also, calculate the number of photons in a single pulse.

SOLUTION: Radiant power is a measure of radiant energy per unit time and has units of watts ( $1 \text{ W} = 1 \text{ J}\cdot\text{s}^{-1}$ ). Therefore the radiant power  $P$  of an individual laser pulse from the described laser is

$$P = \frac{1.25 \times 10^{-3} \text{ J}}{150 \times 10^{-12} \text{ s}} = 8.3 \times 10^6 \text{ W} = 8.3 \text{ MW}$$

The average radiant power of the laser is a measure of the total power emitted per second by the laser, or

$$\langle P \rangle = (1000 \text{ pulses}\cdot\text{s}^{-1})(1.25 \times 10^{-3} \text{ J}\cdot\text{pulse}^{-1}) = 1.25 \text{ W}$$

A  $\text{Nd}^{3+}$ :YAG laser produces light at  $\lambda = 1064.1 \text{ nm}$  (Table 15.2). The radiant energy of a 1064.1-nm photon,  $Q_p$ , is

$$\begin{aligned} Q_p = h\nu &= \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{1064.1 \times 10^{-9} \text{ m}} \\ &= 1.867 \times 10^{-19} \text{ J} \end{aligned}$$

The pulse radiant energy,  $Q$ , is given by  $Q = nQ_p$ , where  $n$  is the number of photons in the laser pulse. Therefore, the number of 1064.1-nm photons in a  $1.25 \times 10^{-3}$  J laser pulse is

$$n = \frac{Q}{Q_p} = \frac{1.25 \times 10^{-3} \text{ J}}{1.867 \times 10^{-19} \text{ J}} = 6.70 \times 10^{15}$$

Examples of different gas-phase gain media and the wavelengths produced by the lasers that use them are listed in Table 15.3. The active element in a gas-phase laser can be a noble-gas atom (e.g., the He-Ne laser, see Section 15-6), a positive ion (e.g.,  $\text{Ar}^+$  laser,  $\text{K}^+$  laser), a metal atom (e.g., He-Cd laser, Cu vapor laser), a neutral molecule (e.g.,  $\text{N}_2$  laser,  $\text{CO}_2$  laser), or an unstable complex created by the pumping process (e.g.,

**TABLE 15.2**

The gain medium (active ion and host) and laser wavelength of various solid-state lasers.

Active ion	Host	Wavelength/nm	Output <sup>a</sup>	Duration
$\text{Cr}^{3+}$	$\text{Al}_2\text{O}_3$	694.3	Pulsed	10 ps
$\text{Nd}^{3+}$	$\text{Y}_3\text{Al}_5\text{O}_{15}$ (YAG)	1064.1	Both	10–150 ps
$\text{Nd}^{3+}$	$\text{Y}_3\text{Li}_x\text{F}_y$ (YLF)	1054.3	Both	10–100 ps
$\text{Nd}^{3+}$	Glass	1059	Pulsed	1 ps
$\text{Ti}^{3+}$	$\text{Al}_2\text{O}_3$ (sapphire)	780	Both	10 fs–5 ps

<sup>a</sup> The term “both” refers to both continuous and pulsed outputs.

**TABLE 15.3**

The gain medium and laser wavelength of various gas-phase lasers.

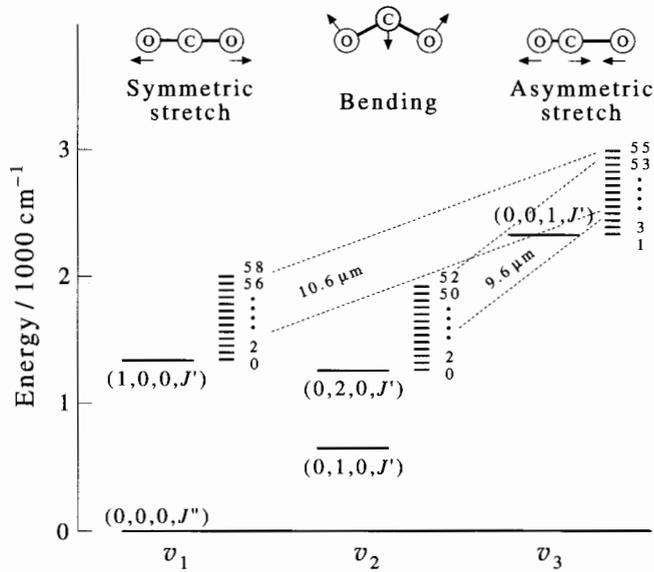
Gain medium	Wavelength/nm	Output	Pulse duration
He(g), Ne(g)	3391, 1152, 632, 544	Continuous	Continuous
N <sub>2</sub> (g)	337	Pulsed	1 ns
Ar <sup>+</sup> (g)	488, 515	Continuous	Continuous
K <sup>+</sup> (g)	647	Continuous	Continuous
CO <sub>2</sub> (g), He(g), N <sub>2</sub> (g)	Line tunable around 10 000	Pulsed	≥ 100 ns
Cu(g)	510	Pulsed	30 ns
He(g), Cd(g)	441, 325	Continuous	Continuous

XeCl<sup>\*</sup>). The wavelength data given in Table 15.3 reveal that gas-phase lasers produce light in the ultraviolet, visible, and infrared regions of the spectrum. Some of these lasers are capable of generating light at several different frequencies. For example, the CO<sub>2</sub> laser involves population inversion (and therefore lasing) between different rotational-vibrational levels of the electronic ground state. Laser light can be generated in small, discrete frequency steps dictated by the energy separation of the rotational levels of CO<sub>2</sub>. Figure 15.10 shows the frequencies of laser light that can be generated from a population inversion between the first excited asymmetric stretch and both the first excited symmetric stretch and the second excited state of the bending mode of CO<sub>2</sub>(g).

Because the energy of laser light must correspond to an energy difference between two quantized stationary states of the gain medium, the laser light must be monochromatic (single color). The electric field of a monochromatic light source can be expressed as  $E = A \cos(\omega t + \phi)$ , where  $A$  is the amplitude,  $\omega$  is the angular frequency of the light ( $\omega = 2\pi\nu$ ), and  $\phi$  is the phase angle, which serves to reference the field to some fixed point in time. The phases of light waves from a lamp vary randomly ( $0 \leq \phi \leq 2\pi$ ). In contrast, the stimulated-emission process requires that the phases of the incident light wave and stimulated light wave have the same phase. Thus, the light waves emitted from a laser are all in phase. This property of laser light is called *coherence*. Many modern spectroscopic techniques take advantage of the coherence of laser light. We will not discuss these techniques in this text, but you should be aware of this unique property of laser light.

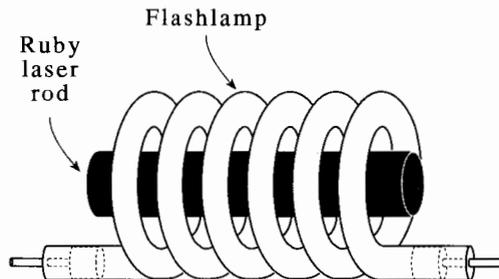
#### *Pumping sources:*

There are two common approaches for pumping the gain medium: optical excitation and electrical excitation. In optical excitation, a high-intensity light source is used to excite the gain medium. Devices that use continuous lamps, flashlamps, and lasers as pumping sources are commercially available. Figure 15.11 shows the optical pumping arrangement used for the first ruby laser (a solid-state gain medium of Cr<sup>3+</sup> doped into Al<sub>2</sub>O<sub>3</sub>). The ruby rod was surrounded by a high-intensity helical flashlamp.



**FIGURE 15.10**

The energies of several of the low vibrational-rotational states of CO<sub>2</sub> ( $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $J$ ). Laser light is generated by stimulating the emission between a pair of quantum states. The approximate wavelengths for the transitions between the  $(0,0,1,J')$  upper state and the  $(1,0,0,J')$  and  $(0,2,0,J')$  lower states are indicated. The exact wavelength depends upon the rotational quantum numbers of the upper and lower states. Because the rotational states have discrete energies, the CO<sub>2</sub> laser is not continuously tunable.



**FIGURE 15.11**

The arrangement for optically pumping a ruby rod, the gain medium of a ruby laser. The ruby rod is placed inside a helical flashlamp. The flashlamp emits a short burst of high-intensity light. This light excites the Cr<sup>3+</sup> atoms in the ruby rod, a process that creates a population inversion between two electronic states of the Cr<sup>3+</sup> atoms.

It is interesting to consider how efficiently lasers convert the energy of the pumping source into laser light. The energy of the pumping source places an upper limit on the energy output of a laser. Because of the discrete energy levels of the gain medium, a large fraction of the pump light is generally not absorbed by the gain medium. Thus,