Lasers—An Introduction

William F. Coleman

University of New Mexico, Albuquerque, NM 87131

The thrust of this symposium on "Lasers in Chemistry" is directed toward the application of lasers and laser-based techniques to the solution of chemical problems. This initial paper is intended to provide the reader with the background necessary to understand the laser aspects of the experiments which follow. The paper is divided into four major sections: (1) the lasing process, (2) properties of laser light of interest to chemists; (3) modifying the laser output, and (4) a survey of laser types. The coverage is by no means intended to be comprehensive but, rather, seeks by example to illustrate various aspects of lasers which make them of such tremendous value to chemists. The author has recently published a paper dealing with a course on "Lasers in Chemistry" which included an extensive annotated bibliography (1). Frequent reference will be made to that bibliography.

The Lasing Process

The acronym LASER stands for Light Amplification by the Stimulated Emission of Radiation. In order to understand the basic principles of laser action, it is necessary to establish why the process of stimulated emission can give rise to light amplification. The framework for the amplification of the electromagnetic radiation by stimulated emission was developed by Einstein in 1917 (2). The basis for laser action lies in the processes of absorption and emission of radiation. Figure 1 illustrates the three different absorption/emission processes which must be considered for a two-level system. In Figure 1a, a system in its ground state interacts with a resonant photon, absorbs the photon, and is raised to the excited state. Neglecting, for the time being, nonradiative pathways for relaxation, there are two radiative paths by which the system can relax back to the ground state. Figure 1b illustrates the process of spontaneous emission where, in the overly simplistic two-level scheme illustrated here, the system returns to the ground state by emission of a resonant photon. This process of spontaneous emission, more commonly characterized as fluorescence or phosphorescence depending upon the absence or presence of a spin change in the transition, does not result in the amplification of radiation. In addition, the radiation is emitted through a wide region of solid angle and possesses none of the directional properties characteristic of laser radiation. Figure 1c illustrates the process of stimulated emission. A system in an excited state, where the excited state is produced by a wide variety of techniques including absorption of light, electron bombardment, etc., interacts with a resonant photon. In a simplified picture, the interaction can be said to produce two resonant photons, which are in phase with one another, resulting in the systems return to the ground state. In this simple framework, it is clear that stimulated emission can result in the amplification of photons. It can also be seen that some of the unique coherent properties of laser light are a direct consequence of the coherent nature of the stimulated emission process. It is clear then that, if amplification is to occur, conditions must be found to insure that the process of simulated emission dominates the emission processes.

Figure 2 illustrates the Einstein coefficients for absorption and emission in a two-level system where the number of particles in levels one and two are given by N_1 and N_2 with degeneracies g_1 and g_2 . The photon flux, or density of radiation at a given frequency, is represented by $\rho(\nu)$. The kinetics of



Figure 1. Absorption and emission processes in a two-level system. (a) absorption; (b) spontaneous emission; (c) stimulated emission.



Figure 2. Einstein coefficients in a two-level system.

this two-level system are discussed in a variety of texts in physical chemistry and spectroscopy. Of paramount importance to us is the fact that the ratio of the rate for spontaneous emission (A_{21}) to that for stimulated emission $(B_{21}\rho(\nu))$ is given by:

$$\frac{A_{21}}{B_{21}\rho(\nu)} = e^{h\nu/kT} - 1$$

For a light source whose temperature is 10^3 K the rates of spontaneous and simulated emission are equal when the frequency is 1.44×10^{13} Hz ($\sim 20\mu$). At a wavelength of 5000 Å, the ratio of spontaneous to stimulated emission is approximately $10^{12.5}$. Clearly, increasing the temperature of this system will not help. As long as the system remains at thermal equilibrium $N_1 > N_2$ and, neglecting degeneracy effects, stimulated absorption will be the dominant interaction with the photon field. In order to force stimulated emission to dominate in this system, a population inversion $(N_2 > N_1)$ is needed. The population inversion represents a non-equilibrium situation. The frequently used analogy to a negative temperature, from the Boltzmann Distribution, is false since the Boltzmann Distribution applies only to systems at thermal equilibrium.

Consider the situation shown in Figure 3. Radiation with an intensity at the front of the cell of I(0) is then moderated by absorption and or emission throughout the path length being investigated. It can be shown that dI(z)/dz is proportional to $(N_1 - N_2)$.

Clearly, in a two-level system, the system is transparent when $N_2 = N_1$. At this point, the system is said to be saturated, analogous to the saturation observed in NMR spectroscopy. For this reason, two-level systems are not commonly considered for the design of lasers. Figure 4 shows a variety of different pumping schemes which can lead to effective lasing action. Figure 4a, a three-level scheme, is representative of the scheme used in the ruby laser. The system is pumped from E_1 to E_3 and then undergoes a rapid non-radiative relaxation to E_2 . Laser action then is on the transition $E_2 \rightarrow E_1$. This system would require a tremendous amount of pumping power since level 1 is the terminus of the lasing transition. This requires that the population inversion be $N_2/N_1 > 1$. In addition, this level scheme can saturate rather rapidly unless the non-radiative process $E_3 \dashrightarrow E_2$ is very fast so that $N_1 > N_3$ even though $N_2 > N_1$. A simpler three-level lasing scheme is shown in Figure 4b. In this scheme, the lasing transition occurs from level E_3 to level E_2 . Thus, the necessary population inversion $(N_3/N_2 > 1)$ is easy to establish and maintain since the



Figure 3. Intensity of radiation as a function of distance as it passes through an absorbing/emitting medium.



Figure 4. Multilevel lasing schemes. (a) and (b) are three-level systems and (c) and (d) are four-level systems.

population in E_2 is essentially zero prior to the start of the experiment. The only way in which the lasing action could be easily shut down would be if the $E_2 \dashrightarrow E_1$ process were slow and eventually destroyed the population inversion. Figure 4c illustrates a further modification of 4b in which the lasing occurs between two levels $(E_3 \rightarrow E_2)$ which are not involved in the pump process. Figure 4d shows a more realistic representation of this type of lasing scheme. In a variety of diatomic molecules, notably diatomic interhalogens such as IF, excitation takes place from the lowest vibrational level of the ground electronic state, in a vertical transition, to a high vibrational level in the excited electronic state. This excitation is then followed by rapid vibrational deactivation in the excited electronic state and lasing is observed as a vertical transition from the lowest vibrational level of the excited electronic state to high vibrational levels of the ground electronic state. This is followed by very rapid vibrational deactivation within the ground state vibrational manifold.

The transition from the lasing diagrams such as those shown in Figure 4 to a functional laser is largely a problem in applied physics and engineering. This paper will make no attempt to discuss the various optical and mechanical features of a functioning laser. Figure 5 is a schematic representation of a variety of types of lasing systems. The active medium is ex-



Figure 5. A generalized laser cavity. M_1 is chosen so that its reflectivity is as close to 100% as possible at the wavelength(s) of interest. The reflectivity of the output coupler (M_2) depends on the gain of the particular laser system.



(d)

cited by some means not shown in the figure, and the active medium together with the back reflector (M_1) and the output coupler (M_2) form the laser cavity. Although many lasing systems do not require such a cavity, it is illustrative of a very common laser design. The stimulated emission is amplified by many passes through the laser cavity. This multipass feature is made possible by the fact that M_2 allows only a small fraction of the laser light to leave the cavity on any given round trip.

There are several terms used in discussing and describing laser systems which are relevant to this paper. The gain of a system is the amount of amplification, usually per round trip through the cavity, for a given population inversion. The threshold of the system is the gain needed to overcome the optical losses in the cavity, from the mirror surfaces, losses from drawing power from the system, etc. The critical relationship between the two parameters is that a system will not lase unless its gain exceeds its threshold. Gain is a time-dependent phenomenon and a system with gain > threshold gain will cease lasing, if the gain drops below threshold at any time.

The cavity shown in Figure 5 is similar to a Fabry-Perot interferometer which is discussed in a variety of texts on instrumental analysis. The resonance condition for maintaining standing waves in such a cavity is $\nu = mc/2d$ where m is some integer, c is the speed of light, and d is the cavity length. Figure 6 shows the superposition of a spectral line, such as the emission one would obtain from a lasing material, and the cavity resonance conditions. The cavity resonant modes (the longitudinal or axial modes of the cavity) are separated by a spacing of c/2d. Whether or not all of the modes which are permitted by the cavity are actually seen in lasing depend on which modes have a gain sufficiently high to exceed the threshold. Although the conversion is not completely straightforward, it is clear that modes occurring in regions of the spectral line which have very low intensity probably will have correspondingly low gains and may be unlikely to be seen in lasing. The interested reader is referred to the discussion of gain saturation in the references of reference (1). Laser radiation also exhibits a set of modes known as transverse modes symbolized by TEM_{nm} . These modes represent the spatial distribution of the laser output in a plane parallel to the output coupler (M_2) in Figure 5. Figure 7 shows several TEM modes for specific values of *nm*. One final term relating to laser cavities is the Q of the cavity. This term has been



Figure 6. Superposition of laser cavity modes on the spectral line giving rise to laser action.



Figure 7. Several transverse (TEM_{nm}) laser modes and the corresponding values of n and m.

borrowed from microwave technology and is given by the expression

$$Q = 2\pi \times \frac{\text{the energy stored}}{\text{the energy discharged}} \text{ per cycle}$$

In general, lasers have very high Q's and the modes which lase are the modes which have high Q's.

Unique Properties of Laser Light

Part of the purpose of this symposium is to illustrate some of the many areas of chemistry which have made use of lasers and laser techniques. It is appropriate at this point to examine those aspects of laser light which are unique and which make it so attractive for use in the study of a variety of chemical, physical, and biological problems. Although one could list a variety of such properties, I have chosen to discuss only five. They include: directional properties, frequency purity, power (or energy), pulse durations, and tunability.

The directional properties of lasers are among their more obvious characteristics. The very low beam diversion displayed by lasers is the most graphic demonstration that indeed laser light possesses properties which are different from those exhibited by a normal light source. The directional properties have a number of advantages in designing and carrying out experiments. The laser beam is easily manipulated around an experimental set up. This enables one to study samples in relatively inaccessible locations.

The frequency purity of the laser enables one to deposit an extremely precisely known amount of energy into an atomic or molecular system. This is essential, for example, in laser-induced isotope separation processes where the object is to excite the molecule containing one isotope of a particular element while leaving molecules containing a second isotope of the same element unexcited. It is routine to have visible lasers whose wavelength is known to the nearest 0.01 Å and infrared diode lasers with a resolution of 10^{-5} cm⁻¹.

There are a number of ways to express the output power of a particular laser. For the continuous wave (CW) lasers, which have a relatively constant output, the power is generally given in watts. Pulsed lasers (*vide infra*) present a different problem. There are three common ways to characterize the output of a pulsed laser: the energy per pulse, the peak power, or the average power. As an example of the interconversion among these three concepts, consider a pulsed laser which lases at 500 nm in five nanosecond pulses at a rate of 50 pulses/s with an energy of 100 mJ/pulse. The peak power in such a laser would be

$$\frac{0.1 \text{ J}}{5 \times 10^{-9} \text{s}} = 20 \times 10^6 \text{ W}$$

This number is, of course, somewhat deceiving because the power is 20 MW for an extremely short time and then the system is off for a very long time relative to the pulse duration. The average power is obtained in the following manner

$$0.1 \text{ J/pulse} \times 50 \text{ pulses/s} = 5 \text{ J/s} = 5 \text{ W}$$

It is also frequently of interest to compute the number of photons that are being emitted by the laser either per second or per pulse. The number of photons/sec is given by the formula

$$\frac{(\text{average power mW})(\text{wavelength in nm})}{1.987} \times 10^{1}$$

while the number of photons in a particular pulse is given by the formula

$$\frac{(\text{energy/pulse in mJ})(\text{wavelength in nm})}{1.987} \times 10^{10}$$

The very high powers, energies, and photon fluxes obtained from laser systems enable extremely small amounts of materials to be examined both from an analytical point of view and also for the study of physical and chemical phenomena involving small collections of atoms and molecules. In addition, the high powers make it possible to cause and observe atomic and molecular phenomena that are impossible using the very low photon fluxes generated by conventional light sources.

In many lasing systems, either due to properties of the lasing medium itself or to the design of the laser system, the gain exceeds the threshold gain only a short period of time. This results in a burst of laser light being emitted by the system which then shuts down. If an additional pulse of light is desired, energy must be provided to the laser to bring the gain back above threshold. Such pulse laser systems are extremely attractive to chemists because of their short pulse times and high pulse energies. Well-characterized pulses of 10⁻⁶-10⁻¹³ s are available. For some of the very short pulses, it is necessary to modify the output of the laser slightly using some of the techniques to be discussed later. These very short pulses offer several major advantages over the use of CW lasers. First of all, they make possible the study of very fast chemical and physical processes, including a number of biologically important chemical reactions such as various steps in the vision process. Secondly, the sample being investigated does not suffer the long-term heating effects experienced with CW lasers. Thus, using a high-powered pulsed laser system, it is possible to deliver an extremely large number of photons to the system in a very short time.

The advantages outlined above are somewhat diminished if they are available, in a given laser, at only a single wavelength. Most lasing systems actually lase from several discrete transitions. In some cases, however, commercial lasers of a particular type may be designed to allow the selection of only a single line. This is frequently the case of small helium-neon lasers which operate at 632.8 nm. Other lasers, for example the argon ion gas lasers, have a number of lines on which they can be operated. Gas lasers based on molecules such as CO2 can be tuned to lase on various of the rotational lines of the vibrational transitions in CO₂. Continuous tunability over a very wide wavelength range is obtained by using dye lasers (vide infra). The use of dye lasers coupled with several of the methods for modifying the laser output which will be discussed later in this paper makes it possible to continually tune, with all of the other advantages mentioned previously, from the near ultraviolet region well into the near infrared. In addition, there are tunable infrared lasers.

Modifying the Laser Output

A number of techniques have been devised to modify the laser output. Depending upon the particular application, an investigator may wish to change the frequency dependence of his or her laser output, its temporal dependence, or its power (energy). These tasks may be accomplished either intracavity or extracavity. Only a few of these techniques will be mentioned here. The interested reader is referred to the references in reference (1).

1) Intracavity Line Selection. In a laser in which a number of transitions exceed threshold, individual line selection is most easily accomplished by the insertion of a grating, prism, filter, or other wavelength selection device into the laser cavity.

2) Single Mode Operation. There are several ways to achieve single mode operation, two of which are outlined here. One may design the cavity such that c/2L is greater than the transition line width. In such a case, only one cavity mode will be contained within the line width, and the laser will operate single mode. This is rarely a practical approach to the problem. Alternatively, the use of an intercavity etalon allows one to select a single mode from the laser transition line. An etalon is a piece of glass with two highly polished parallel surfaces which possesses broad, widely spaced resonances. The total Q of the laser now includes contributions both from the cavity and the etalon and the superposition produces a total Q which may allow only a single mode to lase.



Figure 8. Schematic diagram of a *Q*-switched laser. The *Q* of the cavity is a very strong function of θ , rising rapidly as θ approaches zero.

3) Time Dependence. There are a large number of techniques available for modifying the time dependence of the laser pulse, and we will consider only one in this papernamely the technique of Q switching. We understand the relationship of the Q of the system to the lasing phenomenon so the process of Q switching, which is diagrammed in Figure 8, follows directly. One begins with a very high loss cavity (low Q) and starts to build up a population inversion. A large inversion can be achieved without the onset of lasing in this very high loss cavity. The cavity Q is rapidly increased (the threshold is decreased) by the rotation of the mirror. When the two mirrors are properly aligned, the Q of the cavity will rise very rapidly and then fall again as the rotation of the mirror continues and moves out of alignment with the cavity. Thus, the output will be obtained in a very short spike during the time that the Q is at a high value. Another technique, that of mode locking, produces a series of very short pulses from the laser output.

4) Extending the Laser Range. Non-linear optical phenomena offer us the possibility of extending the laser range. A non-linear optical phenomenon is, in general, one in which light of one frequency is converted to a different frequency. There are a number of different non-linear techniques in use and we will concentrate on one, multiple harmonic generation. In multiple harmonic generation, light passes through an appropriate non-linear crystal and is converted, with a particular conversion efficiency, to light whose frequency is some integral multiple of the incident frequency (the wavelength is an integral divisor of the incident wavelength). Two frequently used non-linear crystals for visible multiple harmonic generation are ammonium dihydrogen phosphate (ADP) and lithium niobate. Under the appropriate conditions, the conversion can be quite high. For example, in a neodynium-YAG laser operating at 10 pulses/s in 20-ns pulses, the energy of the TEM_{00} mode at 1064 nm (the fundamental frequency) may be on the order of 350 mJ. This particular system can be frequency multiplied to produce 125 mJ at 532 nm, 45 mJ at 355 nm and 25 mJ at 266 nm. The obvious application of multiple harmonic generation is to take the output of a dye laser and frequency-multiply it. This provides the best currently available source for tunable ultraviolet radiation.

Survey of Laser Types

Since the first working ruby laser was constructed in 1960, several thousand molecules have shown the ability to lase. It is obviously impossible to discuss many different lasing systems in a survey of this type. For the purposes of this symposium, I have divided laser types into five categories. In each category, I will discuss one or more lasers of that type which are important in current chemical research.

Solid State Lasers

The first laser, based on the lowest lying spin forbidden transition in Cr^{3+} in Al_2O_3 , was of this type. A variety of problems with the ruby laser make it relatively infrequently used today. The most commonly used solid state laser is the Nd/YAG laser (YAG is yttrium aluminum garnet). Since solid state species frequently have broad absorption bands, it is possible to pump this laser using optical techniques, such as a flashlamp. The laser is based on a four-level scheme (see Fig. 4) and, hence, requires relatively low pumping power. The laser produces short, high-powered pulses and makes an extremely good dye laser pump when frequency-multiplied.

Gas Lasers

In general, gas lasers produce narrower lines than those obtained from solid state systems. Since no broad absorption bands exist in the gases, it is more convenient to use electrical methods for achieving the population inversion. There are four basic types of gas lasers:

- a) neutral atom lasers such as He/Ne or I lasers
- b) ion lasers such as Ar⁺ or metal vapors
- c) molecular lasers such as CO_2 or N_2
- d) excimer lasers

In the iodine atom laser, a molecule containing an iodine is photodissociated to produce excited state $({}^{2}P_{1/2})$ iodine atoms. Many organic molecules when photodissociated produce as much as 90% of the iodine atoms in this excited state. The lasing is then observed on the transition ${}^{2}P_{1/2} \rightarrow {}^{2}P_{3/2}$ (lasing is at 1.315 μ m)

The Ar⁺ laser normally operates on 14–15 lines and is a CW laser. Up to 20 W of power are easily obtained for all lines in the system.

Molecular lasers such as CO_2 or N_2 lase from either excited electronic or vibrational states. They frequently contain a large number of lines due to the rotational and/or vibrational structure of the particular lasing transition.

Excimer lasers are based on molecules such as ArF which possess no bound ground states. A mixture of Ar, F_2 , and He is subjected to a discharge which creates ArF molecules in bound excited states. Thus, a population inversion is easily obtained as there is no corresponding ground state. Such excimer lasers lase in the ultraviolet region of the spectrum and provide high power short pulses at high repetition rates. For example, argon fluoride lases at 193 nm. The excimer lasers are, in general, tunable over very small ranges but can be tuned to discrete lines in the vacuum ultraviolet using a Raman shifting technique. XeCl lasers are rapidly beginning to compete with Nd/YAG lasers as pump lasers for dye laser systems.

Dye Lasers

It has been mentioned previously that dye lasers offer the ultimate in tunability. The active medium in a dye laser is, usually, a solution of a fluorescent organic molecule. Solvents which are used include ethanol, toluene, DMF, and water. By pumping the dye with an appropriate optical source, either another laser or a flashlamp, and placing the dye sample in a tunable optical cavity, it is possible to tune the dye laser over much of the fluorescence spectrum of the dye. With proper choice of dyes, it is possible to observe lasing from less than 300 to greater than 1000 nm with all the other laser advantages which have been discussed previously. Tuning over this range would require a number of dyes as each individual dye offers the potential of being tuned over approximately 40–50 nm. Dyes are frequently frequency-doubled or tripled to extend further the tuning range.

Chemical Lasers

All of the lasers considered to this point derive their initial excitation to produce the population inversion from some external source such as optical pumping or electrical pumping. The general idea behind the chemical laser is that an excergic chemical reaction produces product molecules in excited states with population inversion, and lasing then occurs on these particular transitions. The best known example of such a process is that of the hydrogen fluoride laser. It has been pointed out that this is not a true chemical laser as one step in the production of hydrogen fluoride involves electrical discharge through the reactants to generate hydrogen atoms and fluorine atoms. For our purpose, we will examine only the final population distribution and avoid the semantic dispute. If one considers the reaction $F + H_2 \rightarrow HF + F$, the product HF molecules are populated in vibrational levels with quantum number $v \leq 3$. The table below shows the relative populations of the various v levels following this reaction.

V	n(v)
3	5
2	10
1	2
0	1

Assuming that the lasing will take place on a $\Delta v = 1$ transition, population inversions exist between v = 2 and v = 1 and between v = 1 and v = 0. A large number of other systems are being examined currently as possible chemical lasers.

Semiconductor Lasers

In these devices, the population inversion is established between the conduction and valence bands. When the lasers are operated at low temperatures (less than or equal to $10-20^{\circ}$ K), extremely narrow linewidths, on the order of 10^{-6} cm⁻¹, may be obtained. The lasers are tunable over a range of approximately 20-50 cm⁻¹.

Summary

This paper has attempted to outline some of the salient features of lasers that make them such unique and valuable tools for the study of fundamental atomic and molecular processes. In many cases, these are the same features that make lasers so attractive for a variety of applications outside of the areas of chemistry, physics, and biology, such as medicine, metallurgy (in processes such as welding and heat treating), communications, precision measuring, etc. If there is a single unifying theme to this introductory presentation, it is that the laser is basically a spectroscopic device and that most of its properties and operations can be understood using fundamental spectroscopic principles. Perhaps a second theme, common to the remainder of the symposium, is that the laser is indeed a tool to be used just like an infrared spectrometer, a gas chromatograph, or an NMR spectrometer.

Literature Cited

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