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Nomenclature, Symbols, Units and their Usage in Spectrochemical Analysis—XV

LASER-BASED MOLECULAR SPECTROSCOPY FOR CHEMICAL ANALYSIS: LASER FUNDAMENTALS

(IUPAC Recommendations 1995)

Prepared for publication by

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CONTENTS

Nomenclature, symbols, units and their usage in spectrochemical analysis—XV. Laser-based molecular spectroscopy for chemical analysis—laser fundamentals (IUPAC Recommendations 1995)

SYNOPSIS

This report is 15th in a series on Spectrochemical Methods of Analysis issued by IUPAC Commission V.4. It is concerned with the fundamental properties of lasers as used in analytical molecular spectroscopy in the optical wavelength region. The present report has five main sections: Introduction to lasers, Types of lasers, Laser propagation, Laser dynamics, and Exploitation of laser properties.

1 INTRODUCTION

A series of documents dealing with nomenclature, symbols and units used in spectrochemical analysis is issued by IUPAC.

Part I [Pure Appl. Chem., 30, 653-679 (1972)] is concerned mainly with general recommendations in the field of emission spectrochemical analysis.

Part II [Pure Appl. Chem., 45, 99-103 (1976)] gives some basic rules on data interpretation.

Part III [Pure Appl. Chem. 45, 105-123 (1976),] deals extensively with the nomenclature of analytical flame (atomic emission and absorption) spectroscopy and associated procedures.

Part IV [Pure Appl. Chem. 52, 2541-2552 (1980)] concerns X-ray emission (and fluorescence) spectroscopy.

Part V [Pure Appl. Chem. 57, 1453-1490 (1985)] deals with the classification and description of radiation sources.

Part VI [Pure Appl. Chem. 56, 231-345 (1984)] covers molecular luminescence spectroscopy.

Part VII [Pure Appl. Chem. 60, 1449-1460 (1988)] is concerned with molecular absorption spectroscopy (UV/VIS).

Part VIII [Pure Appl. Chem. 63, 735-746 (1991)] deals with a new nomenclature system for X-ray spectroscopy.

Part IX [Pure Appl. Chem. 67, 1725-1744 (1995)] covers fundamental aspects of spectral dispersion and isolation of radiation.

Part X [Pure Appl. Chem. 60, 1461-1472 (1988)] deals with sample preparation for analytical atomic spectroscopy and other related techniques.

Part XI [Pure Appl. Chem. 67, 1745-1760 (1995)] deals with the detection of radiation.

Part XII [Pure Appl. Chem. 64, 253-259, 1992] deals with terms related to electrothermal atomization.

Part XIII [Pure Appl. Chem. 64, 261-264, 1992] deals with terms related to chemical vapour generation.

A document on laser-based atomic spectroscopy is in the approval process.

This document, Part XV, deals with the fundamental properties of lasers used in laser-based molecular spectroscopy for chemical analysis. It complements parts I, V, VI, VII, IX, and XI, and lays the ground work for Parts XVI (Luminescence), XVII (Absorption), XVIII (Raman Scattering Processes), and XIX (Photothermal Detection) of the series.

Basic aspects of lasers, types of lasers, principles of laser propagation, and details of the dynamical properties of lasers are covered, as used in molecular spectroscopy for chemical analysis. The spectral region considered ranges from 100 nm to 1 mm.

2 INTRODUCTION TO LASERS

2.1 Definition of a laser

The word *laser* [see Part III 3.1.3.3, Part V 1, and Part VII 3.1] is an acronym taken from the phrase *l*ight *a*mplification by *s*timulated *e*mission of *r*adiation. The essential elements of a laser are: (a) an *active medium* [V 6.1]; (b) a *pumping process* to produce a *population inversion* [V 6.1]; and (c) suitable

geometry of *optical feedback elements*. The active medium consists of a *host material* (gas, liquid, or solid) containing an *active species* (see Sect. 3 below).

2.2 Energy levels and transitions [see Note[1]]

Every atom, molecule, or ion has its own characteristic set of *quantum energy levels*. These species can be excited to higher quantum energy levels and can decay through *radiative* and *nonradiative decay* processes. Radiative decay can occur by means of (i) *spontaneous emission* and (ii) stimulated emission [V 2.3.5].

Spontaneous emission, stimulated emission and absorption are quantified by *Einstein transition probabilities*. For a species with lower energy level i of energy E_i and upper energy level j of energy E_j, the rate of spontaneous emission, independent of the presence of radiation, is given by

$$dN_j / dt = - A_{ij} N_j$$

where N_j is the population in j, and A_{ij} is the Einstein transition probability for spontaneous emission for that transition. The *radiative lifetime* t_{rad} of the upper level is the reciprocal of A_{ij} (if no more than one transition from the upper level is possible). In the presence of electromagnetic radiation, *stimulated transitions* can be induced. A transition from a lower energy level to a higher one is called absorption [V 2.3.5], while stimulated emission occurs when the transition is from a higher energy level to a lower one. The rates of these transitions are:

$$dN_j/dt = - \sum_i \rho_{\tilde{\nu}}(\tilde{\nu}_{ij}) B_{ij} N_j \qquad \text{for stimulated emission}$$

$$dN_i/dt = - \sum_j \rho_{\tilde{\nu}}(\tilde{\nu}_{ij}) B_{ji} N_i \qquad \text{for absorption}$$

where $\rho_{\tilde{\nu}}(\tilde{\nu}_{ij})$ is the spectral radiant energy density in unit wavenumber interval at wavenumber $\tilde{\nu}_{ij}$ and B_{ji} and B_{ij} are the Einstein transition probabilities (in terms of wavenumbers) for stimulated transitions. The Einstein transition probabilities are proportional to each other:

$$A_{ji} = (8\pi h c_0 \tilde{\nu}_0^3) B_{ji}$$

$$B_{ij} = B_{ji} (g_j/g_i)$$

where h is Planck's constant, c_0 is the speed of light in vacuum, $\tilde{\nu}_0$ is the wavenumber at the center of the transition, and g_i and g_j are degeneracy factors.

2.3 Laser amplification

Optical radiation that passes through a collection of absorbing species is absorbed or attenuated with distance z. The transmitted *radiant power* $\Phi(z)$ [V 6] of the radiation (of moderate power) is given by the Lambert-Beer Law:

$$\Phi(z) = \Phi_0 \exp[-\alpha(\tilde{\nu})z]$$

where $\alpha(\tilde{\nu})$ is the *napierian absorption coefficient* . The absorption coefficient is proportional to the *population difference* ($N_i g_i - N_j g_j$) between the two levels involved in the transition. If the population difference, through some pumping process, can be made to change sign (i.e. $N_j > N_i g_i/g_j$) creating a population inversion, the same equations apply except that now the transmitted radiant power will increase with distance leading to laser *gain*. When $N_j = N_i g_i/g_j$ (effectively zero population difference) *saturation* occurs. (see Sec. 5)

2.4 Pumping processes

Many laser pumping processes have been demonstrated. Examples are *gaseous discharge pumping* using direct current (dc) or radio frequency sources including *glow discharges*, hollow cathodes, arc discharges, and *pulsed axial* and *transverse discharges* (involving both *direct electron excitation* and *two-stage*

[1] Some of these terms are defined in Quantities, Units and Symbols in Physical Chemistry, (Blackwell, Oxford, 1993), Sec. 2.6, 2.7

collisional pumping); *optical pumping* using flashlamps, arc lamps (pulsed or dc), tungsten lamps, semiconductor LEDs, other lasers, and even direct sunlight; *chemical reaction pumping* where the chemical reaction produces the population inversion;*direct current injection* into semiconductor injection lasers; pumping by means of supersonic expansion of gases creating *gas-dynamic lasers*; *plasma pumping* in hot dense plasmas created by plasma pinches, focused high-power laser pulses, or electrical pulses; and accerated electrons as used in the *free-electron laser.*

With only two energy levels population inversion cannot be achieved because the absorption and stimulated emission rate constants are the same. Pumping for population inversion requires at least three energy levels (see Fig. 1). In *three-level lasers*, the species initially in the *lower level* must be pumped to the *upper pumping level* from where it relaxes into the *upper laser*

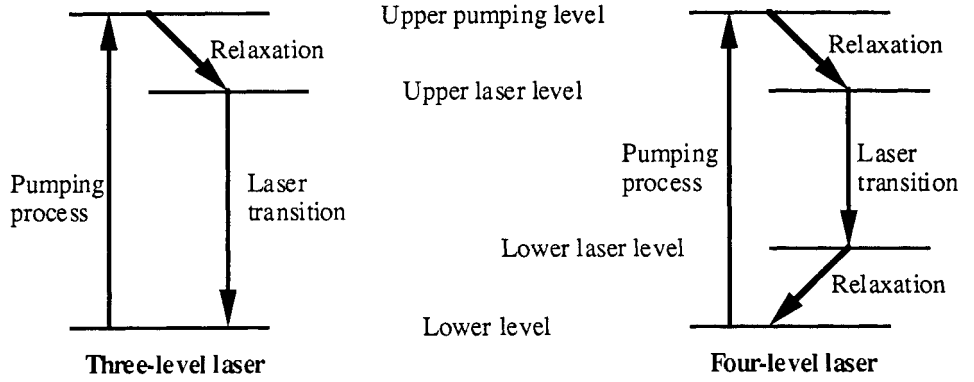

Figure 1. Schematic representations of three and four-level lasers

level before any inversion is obtained. Greater efficiency can usually be obtained in *four-level lasers* wherein pumping occurs between the lower level and the upper pumping level, with fast nonradiative relaxation into the upper laser level. Fast relaxation processes also connect the *lower laser level* with the lower level.

2.5 Laser cavity modes

A *laser cavity* is formed when the optical feedback elements are *end mirrors*. A complete pass of the optical radiation through the cavity, returning to the original location and direction, is known as a *round trip*. When the round-trip laser gain is equal to the round-trip *cavity losses* the laser has reached the *threshold condition*. Once the threshold condition is exceeded, the circulating radiation builds exponentially in intensity until the steady-state condition is reached (see Sec.5.1).

The round-trip path length of a linear resonator must be a half integral number of laser wavelengths. This restriction results in a set of *axial modes* with discrete and equally spaced *axial-mode frequencies* $\nu_{ax} = nc/2L$ (see Fig. 2).

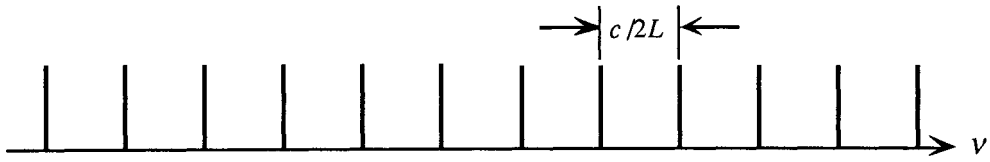

Figure 2. Axial mode frequencies ν_{ax} of a linear cavity

The variation of the optical field perpendicular to the direction of propagation of the radiation in the laser cavity determines the *transverse mode properties* (see Fig. 3 and also Sec. 4). The finite diameters of the active medium and the end mirrors produce a discrete set of *transverse eigenmodes*, or distinct amplitude and phase patterns for the circulating beam, which reproduce themselves after each round trip. The diffraction losses are generally very small in *stable laser cavities*, in which a paraxial ray continues to

remain close to the optic axis, even after many reflections. End mirror configurations designed to more completely utilize laser media of larger diameter are used in *unstable laser cavities*, although in these a ray initially paraxial in the cavity diverges from the axis upon multiple reflections.

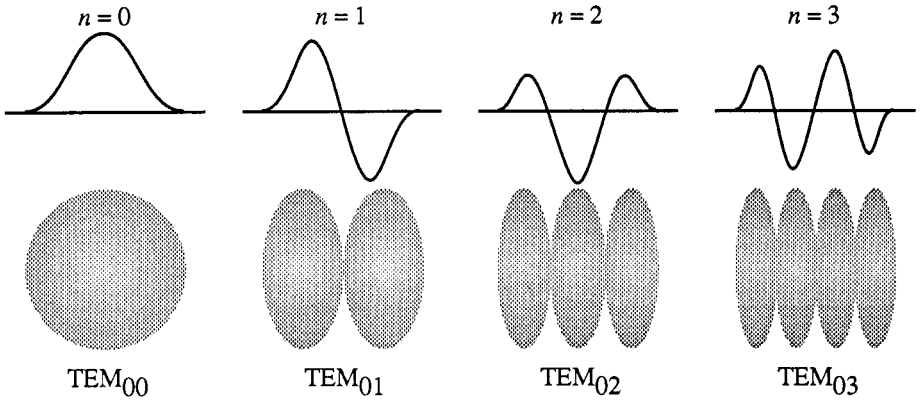

Figure 3. Some transverse eigenmodes of a laser cavity

2.6 Laser beam properties

The output beam from a laser is fundamentally different from the radiation emitted by any other source of electromagnetic radiation. The output of lasers exhibits *spatial* and *temporal coherence*. Spatial coherence implies a small variation in coherence across the wavefronts in the direction transverse to the propagation direction. Temporal, or longitudinal, coherence refers to the correlation between the wave at one spatial position at two different times. Some of these properties are imparted by the cavity. In an actual laser many axial and transverse modes are possible. A small number of these can be selected using wavelength selective elements in the cavity. *Spectral purity* [IX 7.1] is determined primarily by the *transition linewidth* Γ of the active medium, as well as by the *instrument function* [IX 7.1] of the laser cavity. The instrument function can be affected by mechanical vibrations, thermal expansion, and other effects.

2.6.1 Laser temporal properties

There are *pulsed lasers* and *continuous wave lasers* (see also 5.1). The output of a laser can be described by the *average power*, Φ_{ave}, or energy per time. For a pulsed laser, a more complete description includes *pulse duration* t_p, *pulse repetition rate* f_p, and *pulse energy* E_p. The *pulse duration* t_p [V 6.1] is determined by the pumping pulse duration, relaxation processes, and/or modulation of the laser resonator. The *peak power* Φ_{pk} [V 6.1] is the maximum power achieved during a pulse. The relationships between these parameters depends on the *pulse shape*.

2.6.2 Laser wavelength properties

Laser cavity stability limits the ultimate *frequency bandwidth* $\Delta\omega$ (or *wavenumber bandwidth* $\Delta\tilde{\nu}$) of a laser. Some lasers are made *wavelength tunable* by introducing *wavelength selective elements* into the cavity. Examples of such devices are prisms, gratings, Fabry-Perot etalons, *birefringent filters*, dielectric filters, and *electro-optic filters*. The *wavelength tuning range* is also determined by the gain characteristics of the active medium. Some lasers can achieve population inversion for more than one transition, leading to *multiwavelength lasers*.

2.6.3 Laser polarization properties

The optical properties of the laser resonator can produce various polarizations of the laser beam. The state of the polarization of a light wave can be characterized using *Stokes parameters*. In general, a light wave has *elliptical polarization*. The Stokes parameters s_1, s_2, and s_3 are related to the Stokes intensity parameter s_0, the orientation angle of the ellipse (with respect to laboratory coordinates), ψ, and the eccentricity of the ellipse, χ, as follows:

$$s_1 = s_0 \cos 2\chi \cos 2\psi$$
$$s_2 = s_0 \cos 2\chi \sin 2\psi$$
$$s_3 = s_0 \sin 2\chi$$

The state of polarization can be changed using, e.g. *birefringence*.

The output beam of a laser is the sum of many light waves, so that the polarization of the entire beam is the sum of the polarizations of the individual waves. We may regard the beam to be the sum of the *completely polarized* part and a small *completely unpolarized* part. The total power of the beam is Φ_{tot} and the total power of the polarized part of the beam is Φ_{pol}. The *degree of polarization* $P = \Phi_{pol} / \Phi_{tot}$ and varies from $0 \leq P \leq 1$, where $P = 1$ for completely polarized and $P = 0$ for completely unpolarized (also called *natural light*). For most lasers P is close to 1. In many applications, the orientation of the polarization of a laser beam with respect to an optical surface is important. The laser beam power can be decomposed into a part with its electronic vector oriented parallel to the plane of incidence (*parallel polarized power*), $\Phi_{//}$ and a part perpendicular [see Note[2]] (*perpendicular polarized power*), $\Phi_{\perp}$.

2.7 Generation of other frequencies

The frequency of the laser output can be changed using *nonlinear optical methods*. Such techniques as *second harmonic generation*, *sum* and *difference frequency generation*, *third harmonic generation*, *stimulated Raman scattering*, and *parametric oscillation* are common. Very short pulses (less than a few ps), when focussed into a medium, e.g. water, can produce an ultrafast *supercontinuum* covering a range of ~ 10 000 cm^{-1}.

3 TYPES OF LASERS

3.1 Gas Lasers

In *gas lasers*, the active medium is a gas containing a laser active species. These lasers are typically composed of a *plasma discharge tube* containing a gas that can be excited with an electric discharge (see 2.5). The discharge tube may be provided with *Brewster-angle end windows* and external end mirrors (see Fig. 4), or the end mirrors may be sealed directly to the tube. For dc discharge pumping, the output of this type of laser is usually continuous wave. Alternatively, the laser can be excited using a pulsed transverse or axial electric discharge, resulting in a pulsed output.

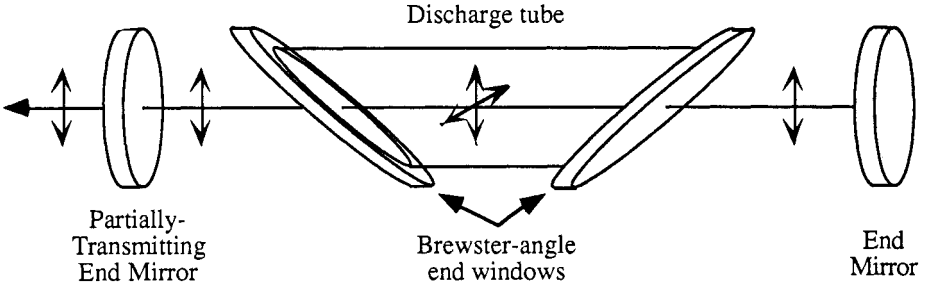

Figure 4. Schematic representation of a gas laser cavity. Double-headed arrows indicate electric field polarization directions, and show the beam polarization produced using Brewster-angle end windows on the discharge tube.

3.1.1 Atomic lasers

An example of continuous wave *atomic lasers* is the helium-neon (HeNe) laser. The copper vapour laser is an example of the pulsed type.

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[2] A beam with its electric vector oriented parallel or perpendicular to the plane of incidence is often called "p" or "s" polarized, respectively.

Other atomic lasers are pumped using *energy transfer* from other atoms or molecules. One type of iodine laser operates by electronic energy transfer from $^1\Delta_g$ O_2 molecules created by chemical reactions or by electric discharge.

3.1.2 Ion lasers

Ion lasers operate in a way similar to atomic lasers, except that the active species is an ion formed in the electric discharge. Most practically important lasers of this type have continuous wave (cw) output. Examples are the argon ion, krypton ion and helium-cadmium (HeCd) lasers.

3.1.3 Molecular lasers

Molecular lasers make use of electronic, vibrational, or rotational energy levels in molecules. The molecules can be excited by an electric discharge, as in the case of the N_2 or CO_2 laser, by chemical reactions, as in the HF or DF chemical lasers, or by another laser, as in the CH_3F far IR laser. Molecular lasers can be pulsed or cw.

3.1.4 Excimer lasers

In an *excimer laser*, an electric discharge pulse in a mixture of gases creates excited atoms that bind with other atoms in the mixture. The bond formed is only stable in the excited state, so that the molecule dissociates after emission. Because there is no population in the lower level, the population inversion is guaranteed. *Rare gas/halogen lasers* such as ArF and XeCl are common examples and have short pulse output.

3.2 Solid state lasers

The active medium of *solid state lasers* is composed of a solid material containing a laser active species.

3.2.1 Glass lasers

When the active medium is a glass host that supports the active species, the lasers are called *glass lasers*. The neodynium-doped phosphate glass laser is one example. These lasers can be pulsed or cw and are usually pumped using external light sources.

3.2.2 Crystal lasers

A large number of solid state lasers have an active medium composed of ionic species supported in a crystalline host. The first laser used a ruby crystal in which chromium ions as the active medium are supported in an aluminum oxide (sapphire) crystal. One of the most common *crystal lasers* involves neodynium atoms in a yttrium aluminum garnet host crystal (the YAG:Nd laser). These lasers can be operated using both pulsed and continuous-wave pumping schemes, and have pulsed or cw output. Several materials, usually with transition metal dopants, allow wavelength tunability, such as the titanium-doped sapphire laser. Concerted energy transfer processes between different ions in a crystal can lead to laser action at a shorter wavelength than that of the pump source in an *up-conversion laser*, such as the thulium-doped yttrium lithium fluoride (YLF:Tm) laser. In the infrared, *colour-center lasers* such as KCl:Li or LiF are very useful tunable sources.

3.2.3 Diode lasers

In *diode lasers* [see Note[3]] the laser-active medium is the *p-n junction* between p-type and n-type semiconductor host materials. The resonant cavity is formed by cleaving the semiconductor crystal at the junction ends (see Fig. 5). These cleaved ends can function as end mirrors because the large refractive index change at the semiconductor-air surface results in a large reflectivity.

[3] The term diode laser is preferred over the sometimes-used term semiconductor laser. Although semiconductor lasers without a p-n junction do exist, they have found little analytical usage.

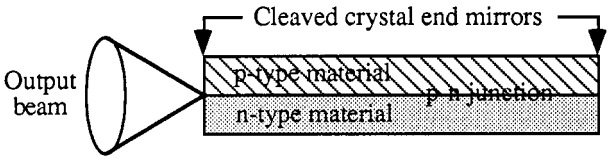

Figure 5. Schematic representation of a diode laser

The laser emission is restricted to the region in the immediate vicinity of the junction which results in a large and asymmetric output beam divergence angle (see Sec. 4.1 and Fig. 6). The broad emission bandwidth near the *band gap energy* [XI] between the valence and conduction bands enables laser action over a large wavelength range. The wavelength can be varied within this range using *temperature tuning* (temperature varies the cavity length and Fermi energy). The short cavity leads to a large difference between axial mode frequencies (see Sec. 2.5), allowing single-mode operation under certain current and temperature conditions in *single-mode diode lasers*. Because of the direct conversion of electrical current into light energy, diode lasers are very efficient. The wavelength of the output beam can be modulated using *drive current modulation* and can be stabilized and/or tuned using external cavities.

3.3 Liquid lasers

A liquid solution is the active medium in *liquid lasers* .

3.3.1 Organic Dye lasers

Organic dyes in solvents are the active medium in *organic dye lasers*. These lasers are of the four-level type. The laser transition is usually between the lowest vibrational states of the upper laser level and the upper vibrational states of the lower laser level. *Vibrational relaxation* processes ensure rapid depopulation of the lower laser level, sustaining the population inversion. The emission covers a broad wavelength range allowing broad tunability and exhibits a large *Stokes shift* to smaller wavenumbers from the pump wavelength. Laser design and pulse length restrictions may occur because of *intersystem crossing* into *triplet levels* [VI] that absorb the laser output wavelength, thermal effects, achievable dye concentrations, and paramagnetic interactions with dissolved oxygen.

3.3.2 Liquid excimer lasers

Excimer species in liquids have also been used as laser-active medium. An example of the *liquid excimer laser* is the KrF in liquid Kr laser.

3.3.3 Liquid ion lasers

Rare-earth ions in solution have been used as laser-active medium in *liquid ion lasers*. These lasers were the first liquid lasers, and have used Eu^{3+}, Nd^{3+} and other rare-earth ions to produce output in the visible and IR spectral range.

4 LASER PROPAGATION

4.1 Wave optics and Gaussian beams

The *lowest order tranverse mode* beam (TEM_{00}) (see Fig. 3) can be characterized by a *beam waist* w_0 and a planar (*radius of curvature* $R = \infty$) wavefront at the waist. All the important parameters of this beam can be related to w_0 and to the wavelength λ (see Fig. 6).

The *Rayleigh range* $z_R = \pi w_0^2/\lambda$ marks the approximate dividing line between *near field* (or Fresnel) and *far field* (or Fraunhofer) regions for a beam propagating in the z direction from a waist. The spherical radius of curvature of this beam wavefront varies with distance along the beam axis as $R(z) = z + z_R^2/z$. The wavefront is planar at the waist, gradually becomes curved, with maximum curvature at z_R, and then becomes less curved with further propagation. In the far field the beam spreads to a radius $w(z) = \lambda z / \pi w_0$. Focusing a TEM_{00} beam produces the reverse of this process, giving an effective beam radius at the

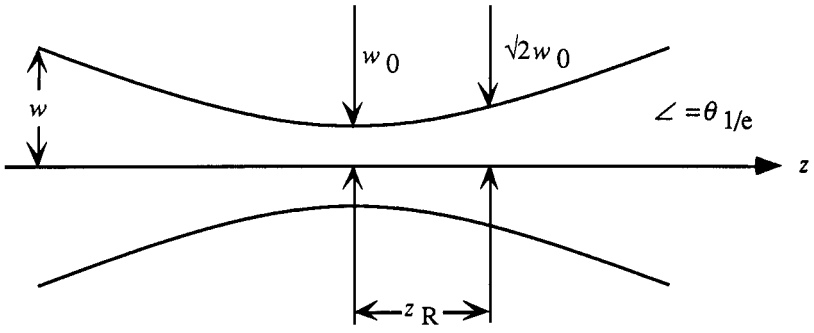

Figure 6. Parameters of a lowest order tranverse mode beam near a beam waist. See text for explanation of symbols.

focus of $w_0 = f\lambda/\pi w$ where f is the *focal length* of the lens. The *depth of focus* b is twice the Rayleigh range ($b = 2\ z_R$) and is the distance over which the beam exhibits *collimation*. The *divergence angle* $2\theta_{1/e}$ of the beam propagating from a waist is given by $2\theta_{1/e} = 2\lambda/\pi w_0$. Lasers with small exit beam waists (e.g. diode lasers) have large divergence angles (see Sec. 3.2.3).

The *radial intensity* I_r along a line passing radially through the axis of a TEM_{00} beam has a Gaussian profile at all axial positions, i.e. $I_r \propto \exp(-r^2/w^2)$ (see Fig. 7).

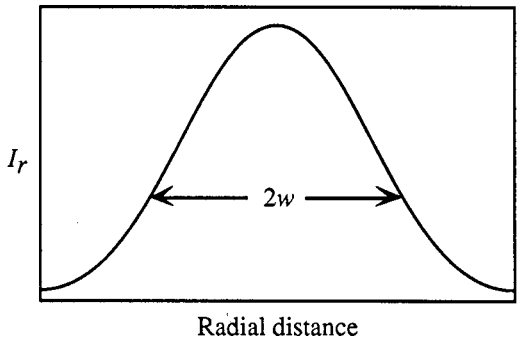

Figure 7. Radial intensity of a TEM_{00} beam

5 LASER DYNAMICS

5.1 Laser cavity equations

The *exponential growth* of the radiation intensity I(t) inside a laser cavity has the general form

$$I(t) = I_0 \exp[(\gamma_m - \gamma_c)t].$$

where γ_m and γ_c are the *cavity growth* and *decay rates*, respectively, given by

$$\gamma_m = 2\alpha_m L_m / t_{rt} \quad \text{and} \quad \gamma_c = [2\alpha_0 L + \ln(1/R_{tot})]/t_{rt}.$$

With time varying coefficients (important in mode locking - see 5.5) the growth equation is:

$$dI(t)/dt = [\gamma_m(t) - \gamma_c(t)]\ I(t)$$

and α_m is the *gain coefficient* of the active medium, α_0 is the *cavity scattering loss coefficient*, L is the overall cavity length, L_m is the length of the active medium, R_{tot} is the product of the reflectivity of the cavity mirrors, and t_{rt} is the *cavity round-trip time*. The laser output is then determined by the net loss per length, the net gain per length, and the axial mode frequencies, as in Fig. 8. The net loss per length is determined by the reflectivities of the mirrors and the reflectivities and scattering of other optical elements including cell windows. For low-gain lasers, mirror reflectivities are typically > 99%; higher-gain lasers may have an *output coupler* with fairly low reflectivity (< 50%). The effective number of laser cavity modes lying within the laser transition linewidth can be very large for ordinary laser cavities with high mirror reflectivities, with values typically of the order of 10^2 to 10^5. Fluctuations among the intensities of these individual modes leads to *mode noise*. Although there is a large number of possible cavity modes in a typical laser, it is possible to restrict *laser action* to a single preferred cavity mode as in *single-mode lasers*.

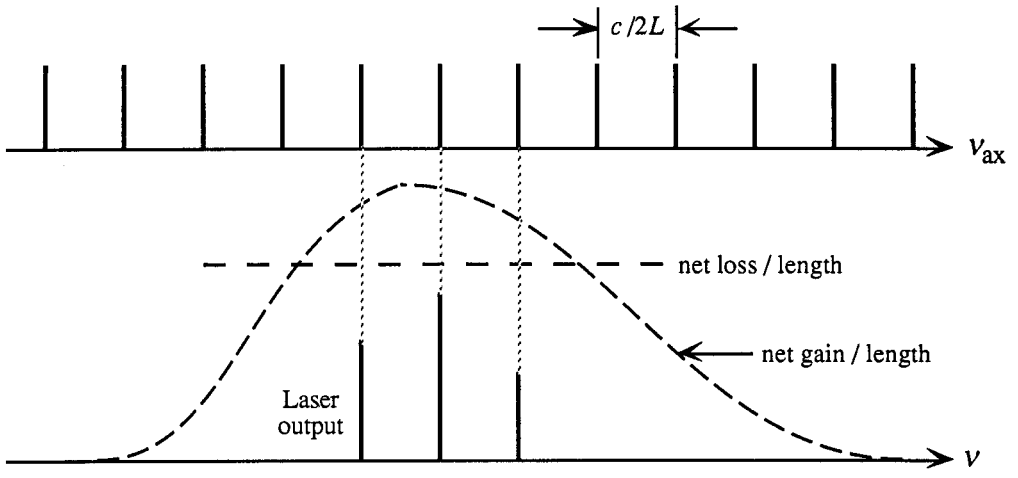

Figure 8. Laser output frequencies are determined by axial mode frequencies. Laser output only occurs for frequencies where the net gain/length is greater than the net loss/length.

The intensity in a laser cavity builds up exponentially with time, starting from an *initial noise intensity* I_0 until the *circulating intensity* I_{circ} reaches the *steady-state intensity* I_{ss} when the laser gain saturates (i.e. the cavity growth and decay rates are equal). Above the steady-state intensity, the ratio of laser output intensity to the *pump intensity* I_p is the *slope efficiency* (see Fig. 9).

The *oscillation buildup time* t_b (time to reach the steady-state intensity) can be approximated using the *normalized inversion ratio* $r_{inv} = \delta_{m0} / \delta_c$, where δ_{m0} is the *initial unsaturated gain coefficient* and δ_c is the *cold-cavity loss coefficient*. The ratio of the steady-state intensity to initial noise intensity may range from 10^8 to 10^{12}, implying that the oscillation buildup time may vary from 10 to 30 *cavity decay times*, $t_{cd} = 1/\gamma_c$. The parameters t_b and t_{cd} are important in *intracavity absorption* spectrochemical methods. The high sensitivity of these methods also depends on the large effective absorption path length resulting from the many passes of the radiation through the absorbing species within the cavity.

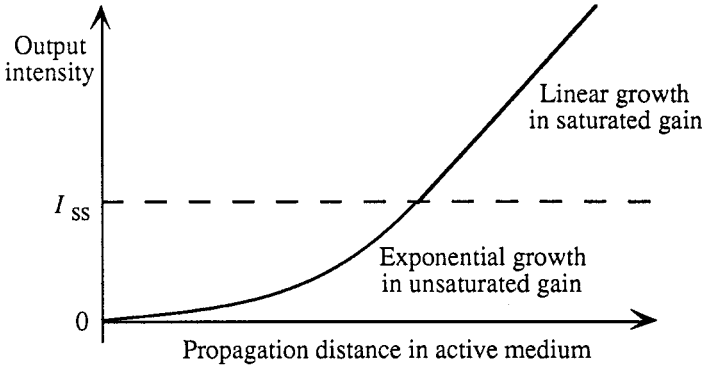

Figure 9. Growth of the output intensity in a laser.

The cavity growth or decay rates can be time varying because of saturation of the gain coefficient or because of deliberate modulation of the cavity losses or cavity output coupling with time. The total radiant energy inside the laser cavity can be expressed by defining a *number of photons n(t)* in a *standing-wave cavity* of length L (or a *ring cavity* of *perimeter length* L) and cross-sectional area A as:

$$n(t) = 2AI_{circ}(t)L / h\tilde{\nu}c = 2V_cI_{circ}(t)/h\tilde{\nu}c$$

where $V_c = AL$ is the *cavity mode volume*.

The *net emission rate* is proportional to the number of cavity photons plus one, where the one comes from the spontaneous emission. This additional photon can be viewed as an incoherent or noise-like driving term which excites the cavity mode in a random or noise-like fashion, acting as a *fundamental quantum noise source*. It is responsible for the *ultimate noise figure* of laser amplifiers and also for the quantum noise fluctuations in phase and amplitude that are present in even the most perfectly stabilized laser

oscillators or frequency standards. This noise obeys Poisson statistics and is similar to flicker noise [XI 4.3].

In very high gain laser media, very high-gain amplification of the internal spontaneous emission can result in *amplified spontaneous emission* (ASE). *Parasitic oscillation* can occur in cavities formed from stray or unwanted reflections.

5.2 Laser spiking and mode competition

In many high-gain lasers, the gain does not saturate immediately with increasing laser intensity, but only after a time delay necessary for the circulating laser intensity to reduce the excess population inversion (caused by large pumping intensities). The laser power in this situation may exhibit a strong transient overshoot, followed by quasiperiodic *relaxation oscillation*. *Laser spiking* occurs in laser systems in which the recovery time of the excited state population inversion is substantially longer than the laser cavity decay time.

Laser action in one laser mode will generally reduce the gain available for another mode. Laser *mode competition* then occurs by means of frequency-locking or frequency-pulling effects caused by scattering or by intracavity modulators, by means of *self saturation* of the gain of a laser mode due to its own intensity, or by means of *cross saturation* of the gain. Cross saturation is due to spatial overlap of each mode with the active medium and with other modes as well as to *lineshape factors* that include how far each of the wavelengths is off the resonance line center.

5.3 Laser Q-switching

Laser *Q-switching* [V 6.2.3] is produced by allowing a laser pumping process to build up a large population inversion inside a laser cavity, while not allowing laser action by removing the cavity feedback or greatly increasing the cavity losses. Then, after a large inversion has been developed, the cavity feedback is restored by switching the cavity *quality factor Q* [V 6.2.3] to a larger value (or, by reducing the cavity losses) allowing all the *accumulated population inversion* to be extracted from the active medium in a single short laser pulse. Lasers can be Q-switched using *rotating mirrors* or *prisms*, *electro-optic* (Pockels cell or Kerr cell) *modulators*, *magneto-optical shutters* [V 6.2.3], *acousto-optic modulators*, and *saturable absorber* dyes.

5.4 Laser cavity dumping

Laser *cavity dumping* is accomplished by allowing a large circulating intensity to develop using no output coupling. After a large circulating intensity is achieved, it can all then be switched out of the cavity using electro-optic or acousto-optic modulators as *cavity dumpers*. These are used mostly in low gain lasers where many cavity round trips are necessary to achieve a large I_{circ}, whereas in high gain lasers, few passes are necessary and Q switching is more appropriate.

5.5 Laser mode locking

Laser mode locking can provide ultrashort light pulses and other forms of periodically modulated laser power. Methods include *active* and *passive mode locking*.

5.5.1 Active mode locking

The electric field pattern inside a laser cavity periodically repeats with a period given by $2L/c$ for a cavity of length L, which is the inverse of the axial mode frequency. Modulating the cavity losses using, for example, an electro-optic or acousto-optic device at a *modulation frequency* ν_m that exactly matches the round-trip frequency of the cavity (or one of its harmonics) results in active mode locking. Viewed in the time domain, the modulator causes the radiation in the laser cavity to become a short pulse that passes through the modulator on each round trip just at the instant when the modulator transmission is at its maximum. In the frequency domain, the oscillating axial modes of frequency ν_{ax} acquire *modulation sidebands* of frequencies $\nu_{ax} \pm n\,\nu_m$ as a result of the modulation. The sidebands fall on top of other axial cavity modes, leading to mode-coupling of each axial mode to one or more of its neighboring modes, locking them in phase. Using either an *amplitude modulator* or a *phase* (or *frequency*) *modulator* leads to AM *mode locking* or FM *mode locking*, respectively. Use of a phase modulator can also lead to *frequency swept* operation.

5.5.2 Passive mode locking

A saturable absorber has optical absorptivity that is constant at low intensities but decreases and finally saturates with increasing laser intensity. Placing a saturable absorber inside a laser cavity can result in passive mode locking. With constant laser pumping the radiation intensity increases as described in 5.1.

When the increasing radiation intensity saturates the loss in the saturable absorber, preferential growth of an *initial noise spike* results in production of a very short pulse in the cavity.

5.5.3 Synchronous mode locking

By pumping a second laser with pulses from a mode locked laser, *synchronous mode locking* can be achieved. The excitation pulses modulate the laser amplification in the second laser. When the round-trip path length of the second laser is an integral or sub-integral multiple of that of the mode-locked excitation laser, very short pulses are produced. Synchronous mode locking has been used to produce sub-picosecond tunable-wavelength pulses from dye lasers and solid state lasers.

5.6 Laser injection locking

Coupling of one laser into another laser can result in *injection locking*. Given an injected frequency within a narrow locking range around the independent frequency of the second (usually larger) laser, the injected signal can capture or lock the subsequent oscillation behavior and define the laser frequency of the larger laser. If the injected intensity is weak (i.e. comparable to the spontaneous emission intensity) or present for only a short time, it can still establish the initial conditions from which the oscillation will build up, a process referred to as *injection seeding*.

6 EXPLOITATION OF LASER PROPERTIES IN CHEMICAL ANALYSIS

6.1 Use of wavelength tunability

Tunability of lasers has been exploited in *excitation/fluorescence spectroscopy*, photochemistry, high resolution spectroscopy, etc. Combining tunable excitation with dispersed or synchronous fluorescence detection leads both to high sensitivity and to enhanced *selectivity*.

6.2 Use of collimation - remote techniques

The relationship between beam waist and Rayleigh range (see Sec. 4.1) implies that a beam with a large waist can remain collimated over considerable distances. *Remote detection* schemes using intense laser sources and backscatter of laser radiation make use of this principle and are common for atmospheric chemistry studies.

6.3 Use of diffraction-limited focusing - microscopic techniques

Spatial coherence allows focusing close to the diffraction limit, making microscopic analyses such as *laser microprobes* possible. Very high intensities are then also possible, which are exploited in *laser fusion devices*, as well as for studies of highly ionized matter and X-ray lasers.

6.4 Use of the near-field

Excitation sources with spatial resolution better than the diffraction limit (i.e. on the atomic scale) have been produced using very small point sources such as extruded and clad fibers or hollow scanning-tunneling microscope tips. This *near-field scanning optical microscopy* utilizes the near-field beam close to the exit of the point source where the size of the aperture still defines the spatial resolution.

6.5 Optical fiber transmission

Optical fibers made from transparent materials such as plastic or glass can be used to transmit laser light over long distances. Most fibers scramble the spatial mode properties of the laser because they are not *single-mode waveguides*. Others, called *single-mode fibers*, can also be *polarization preserving* by use of *strain birefringence*. The diffraction-limited focusing properties of lasers are used to efficiently couple light into the optical fibers and standard optical elements or *graded index* (GRIN) *lenses* are used to couple light out of the fibers.

6.6 Use of time resolution

Lasers can be made to provide pulses of duration from just a few optical cycles up to continuous wave. The shortest pulses are used in studies of fundamental chemical reaction dynamics and solid state material behavior, where the processes occur in the femtosecond time range. Time resolution on somewhat longer time scales is used in optical fiber communications using the technique of *time delay reflectometry*, and in an analog of radar known as *LIDAR*, for *light detection and ranging*.

6.7 Use of phase resolution

Phase sensitive detection for enhanced signal to noise, coherent detection methods such as *optical heterodyning*, and control of the time evolution of molecular wavefunctions are all made possible by

careful control of the phases of lasers. Recent advances include production of optical analogs of NMR pulse sequences using controlled phases in sequences of optical pulses, leading to the possibility of using *phase-controlled pulse sequences* to control paths of chemical reactions.

6.8 Use of polarization

The high degree of polarization of lasers is commonly used for Q-switching, cavity dumping, and mode locking. In addition, this property can be used to perform sensitive *ellipsometry* and linear and circular dichroism measurements.

6.9 Use of high intensity

The high intensity of laser sources has led to the development of many new spectrochemical methods. Levels forbidden for single photon transitions can sometimes be excited using *multiphoton excitation* methods. New photoionization methods using lasers as ionization sources have been developed such as *resonantly-enhanced multi-photon ionization*. Surface analysis can be done using *surface harmonic generation* or *surface-enhanced Raman scattering*. Methods using non-linear optical processes such as coherent anti-Stokes Raman scattering and stimulated emission pumping have been developed.

7 INDEX OF TERMS

Table XV.1: Table of symbols, definitions and units

Term	Symbol	Definition	SI unit
Average power	Φ_{ave}		J s^{-1}
Axial mode frequencies	ν_{ax}		s^{-1}
Beam waist	w_0	$w_0 = f\lambda / \pi w$	m
Cavity decay rate	γ_c	$\gamma_c = [2\alpha_0 L + \ln(1/R_{tot})]/t_{rt}$	s^{-1}
Cavity decay time	t_{cd}	$t_{cd} = 1/\gamma_c$	s
Cavity growth rate	γ_m	$\gamma_m = 2\alpha_m L_m / t_{rt}$	s^{-1}
Cavity length	L		m
Cavity mode volume	V_c	$V_c = LA$	m^3
Cavity round trip time	t_{rt}		s
Circulating intensity	I_{circ}		J s^{-1} m^{-2}
Depth of focus	b	$b = 2z_R$	m
Degree of polarization	P	$P = \Phi_{pol} / \Phi_{tot}$	
Divergence angle	$2\theta_{1/e}$	$2\theta_{1/e} = 2\lambda / \pi w_0$	rad
Frequency bandwidth	$\Delta\omega$		s^{-1}
Gain coefficient	α_m		
Modulation frequency	ν_m		s^{-1}
Number of photons	$n(t)$	$n(t) = 2V_c I_{circ}(t)/h\tilde{\nu}c$	
Peak power	Φ_{pk}		J s^{-1}
Population difference	$N_i g_i - N_j g_j$		m^{-3}
Pulse duration	t_p		s
Pulse energy	E_p		J
Pulse repetition rate	f_p		s^{-1}
Pumping rate	R_p		s^{-1}
Pump intensity	I_p		J s^{-1} m^{-2}
Radial intensity (Gaussian)	I_r	$I_r \propto \exp(-r^2/w^2)$	J s^{-1} m^{-2}
Radius of curvature	R		m
Rayleigh range	z_R	$z_R = \pi w_0^2/\lambda$	m
Steady-state intensity	I_{ss}		J s^{-1} m^{-2}
Wavenumber bandwidth	$\Delta\tilde{\nu}$		m^{-1}