Lasers in Chemistry

<u>L</u>ight <u>A</u>mplification by <u>S</u>timulated <u>E</u>mission of <u>R</u>adiation

I. Requirements for a laser

II. Two state, three state, and four state systems.

III. Survey of tunable lasers.

IV. Applications

Requirements for a laser

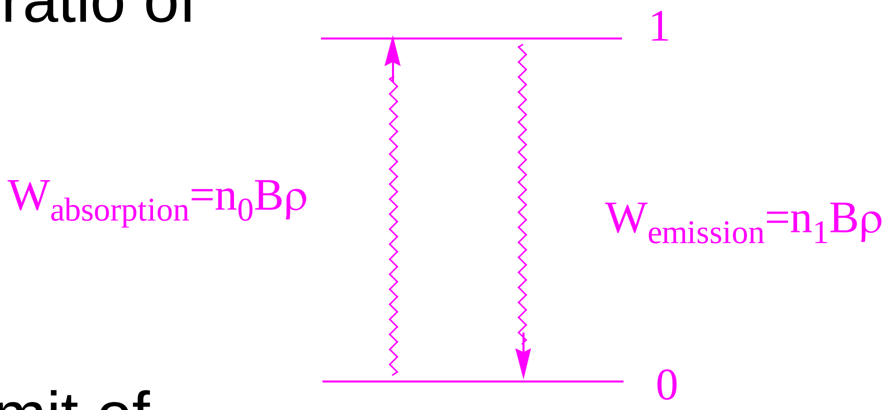
- Gain (population inversion)
- Laser cavity (reflecting mirrors)
- Output coupler (semi-reflective mirror)
- Standing waves can be obtained for $n\lambda=2L$
- The bandwidth in the laser cavity can be modulated using birefringent filters, etalons, or grating/prism combinations.

Gain can only be achieved with a population inversion

- Gain represents the increase in photons emitted from the sample compared to a Boltzmann distribution.
- The Boltzmann distribution will never allow for more population in an excited state than in the ground state.
- Gain represents a non-Boltzmann distribution induced by optical or electrical pumping.

Two Level System in Spectroscopy

- For states 0 and 1 the Einstein B coefficients are equal
- High fluence limit results in a ratio of populations determined by microscopic reversibility
- At equilibrium $W_{absorption} = W_{emission}$
- Since Br is the same, in the limit of large r we have that $n_1 = n_0$, and there is no population inversion (i.e. $n_1 < n_0$).

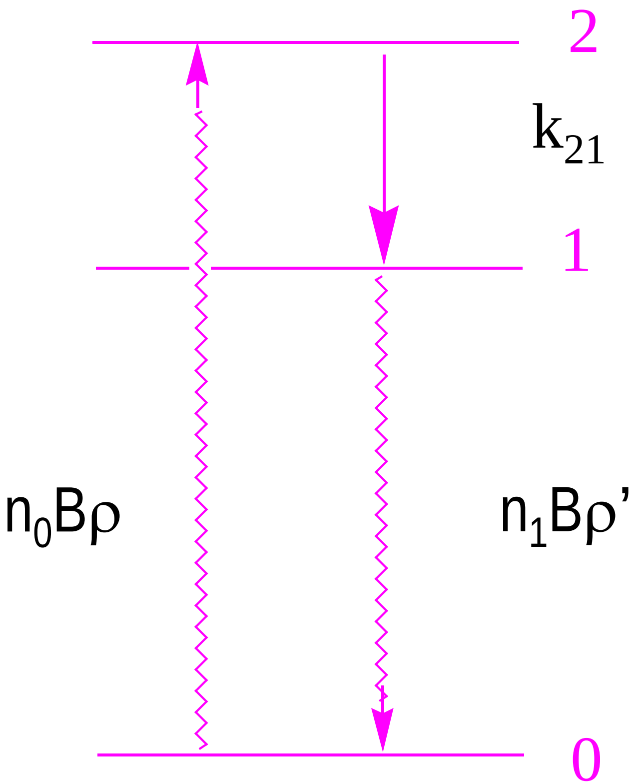


A Three Level System: Laser

- Optical or electrical pumping is used.
- Pump to intermediate state that decays into long-lived emissive state.
- Ground state population must be overcome to make a population inversion in the emissive state.
- Example: the ruby laser, $Cr{:}Al_20_3$ in which Cr d-d transitions give a population inversion in a state that emits at 594 nm.

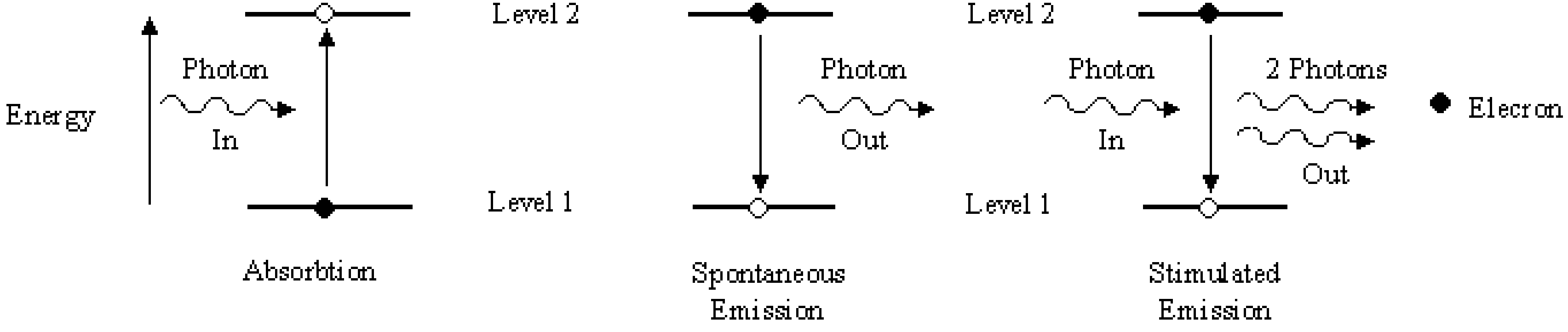
A three-level system provides a route to a population inversion

- We can simplify the rate equations by assuming that
- If $k_{21}n_2 >> n_1B\rho$ then a population build-up in n_1 can lead to an population inversion $n_1 >> n_0$.
- Still has disadvantage that population in n_0 is dominating at equilibrium.



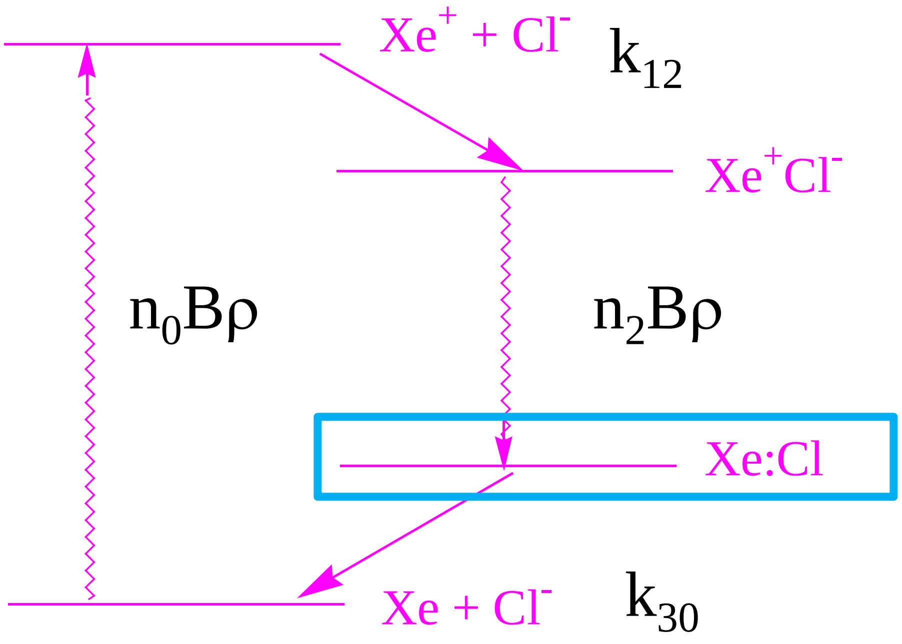
Basic physical justification

The figure shows why a population inversion is needed. It you want to get more photons out than you put in you need many molecules in the excited state to start a cascade of output photons.



A four-level system produces superior results for laser design

- A four level system provides ease of creation of an inversion since state 3 is essentially unpopulated at equilibrium.



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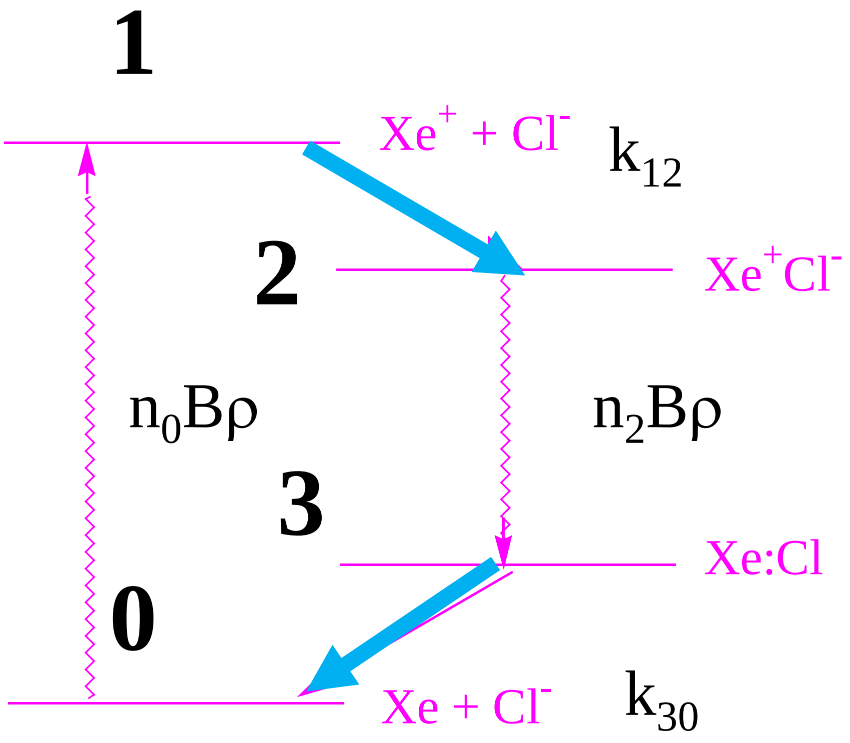
- In order for this scheme to work the rate
- **Rate from 1 to 2 is rapid**
- **Rate from 3 to 0 is rapid.**



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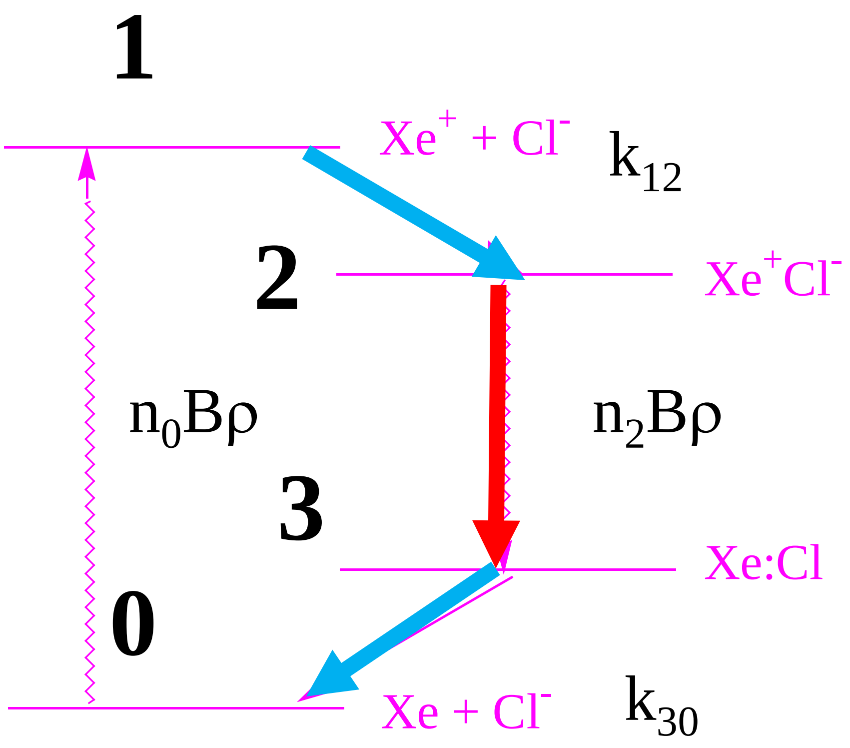
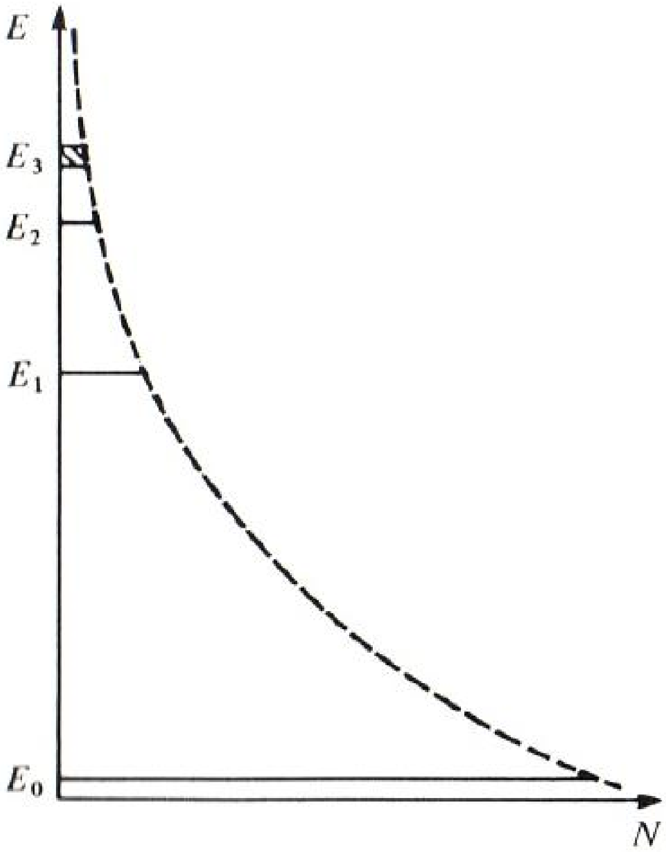
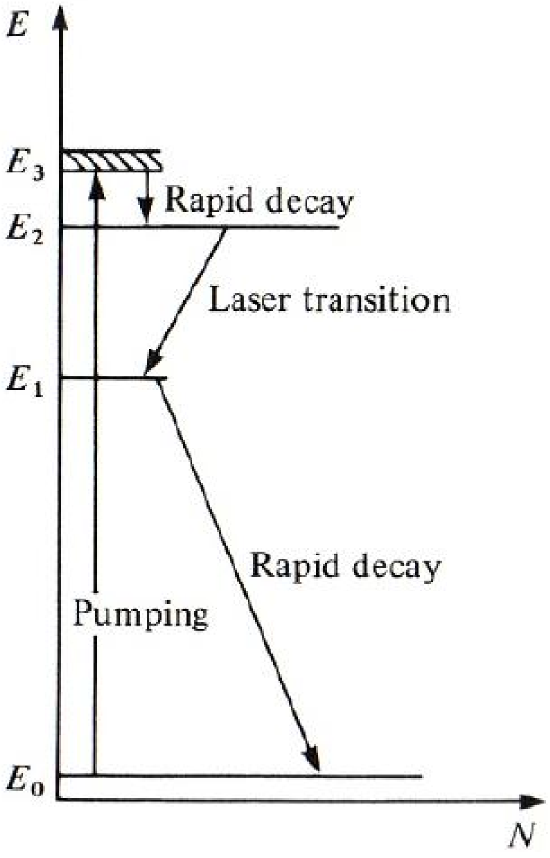
- A four level system provides ease of creation of an inversion since state 3 is essentially unpopulated at equilibrium.
- In order for this scheme to work the rate
- **Rate from 1 to 2 is rapid**
- **Rate from 3 to 0 is rapid.**
- The population inversion is set up between 2 and 3.



Comparison of thermal and pumped population

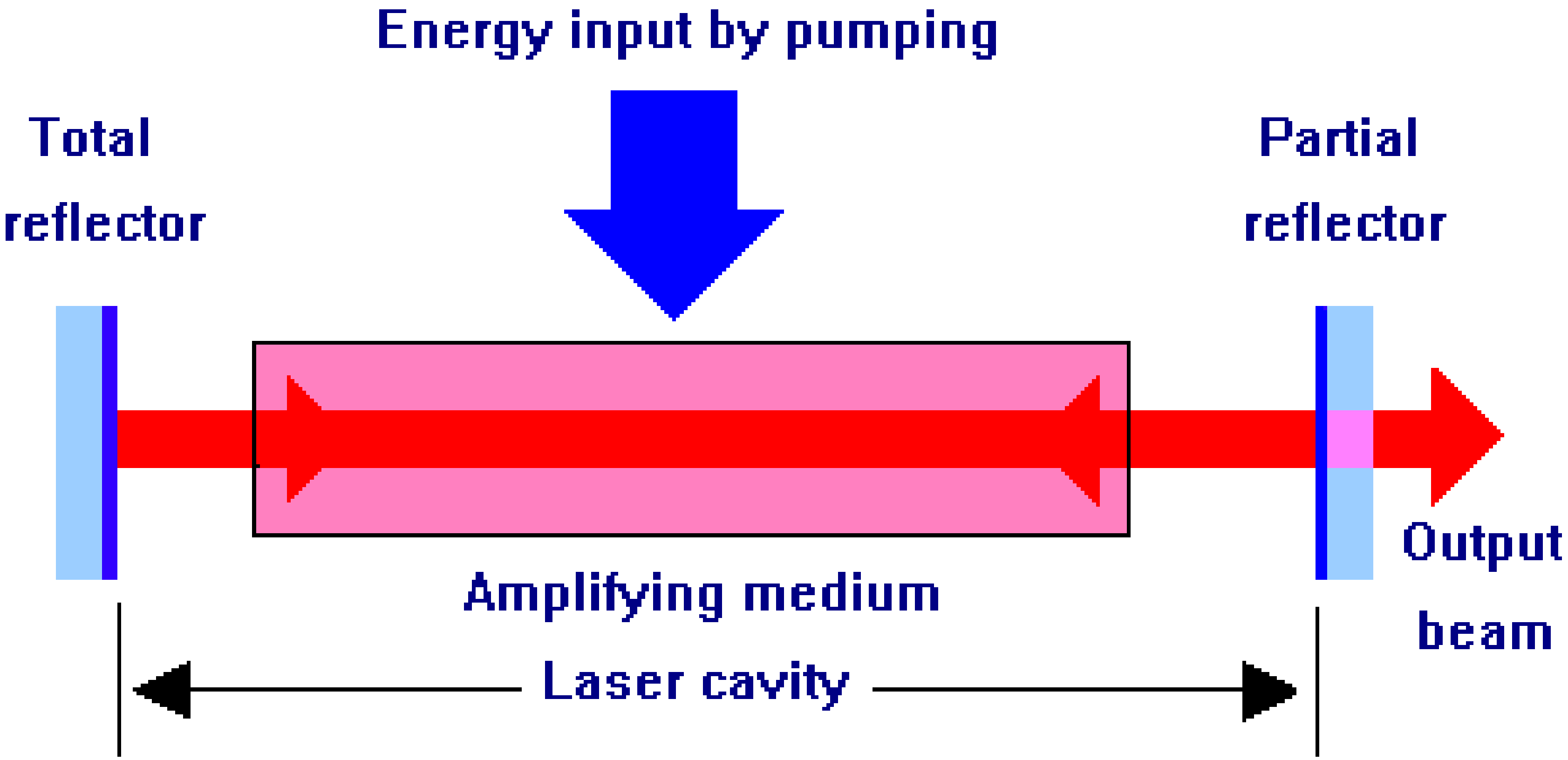


Thermal



Pumped

The laser cavity



The partial reflector is usually called the output coupler.

The gain bandwidth

Although laser light is perhaps the purest form of light, it is not of a single, pure frequency. All lasers produce light over some natural bandwidth or range of frequencies. A laser's bandwidth of operation is determined primarily by the gain medium that the laser is constructed from, and the range of frequencies that a laser may operate over is known as the *gain bandwidth*. For example, a HeNe gas laser has a gain bandwidth of1.5 GHz Ti:sapphire has a bandwidth of about 128 THz

Exercise: convert these to wavenumbers!

Longitudinal modes

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

Longitudinal modes

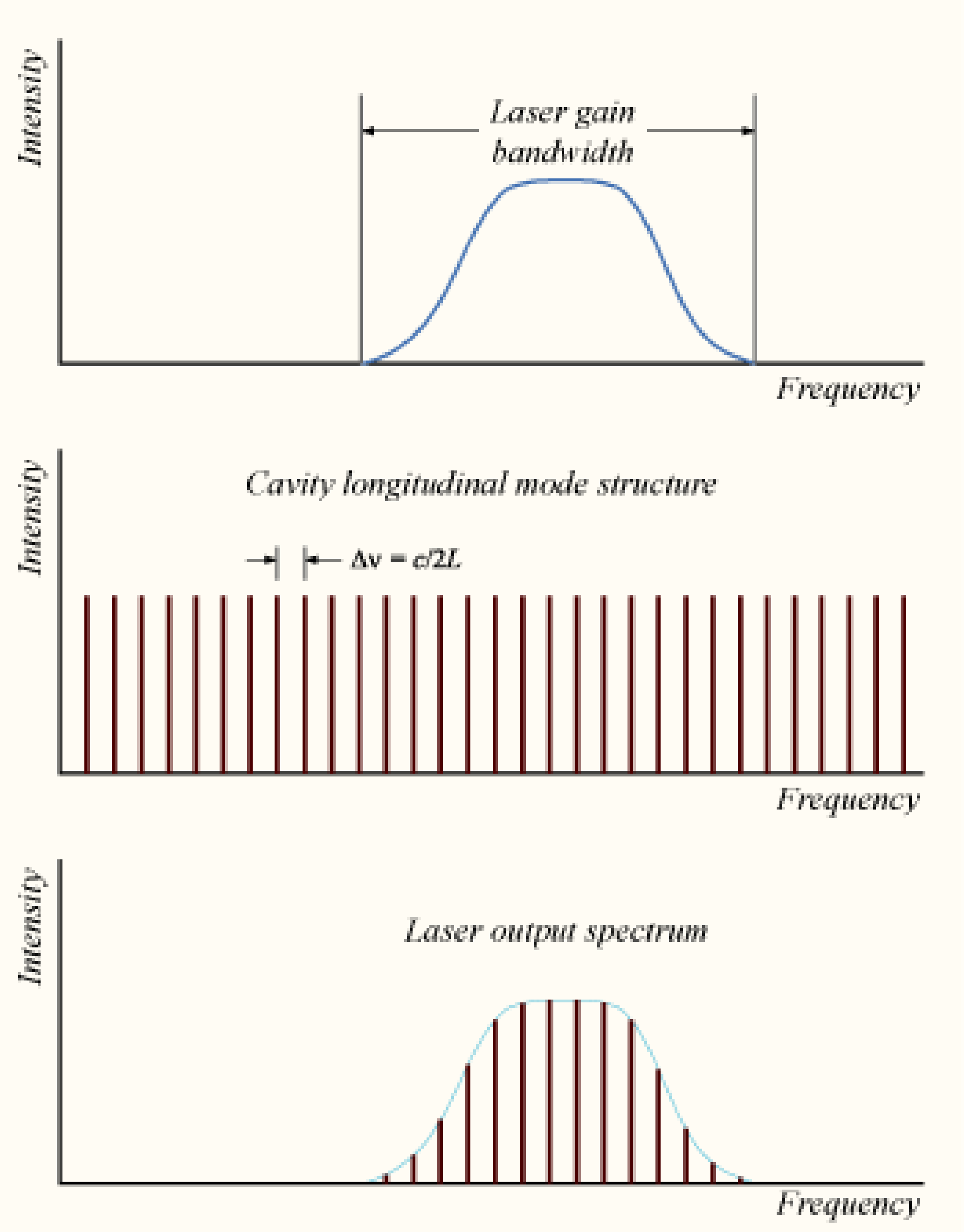
In practice, the separation distance of the mirrors *L* is usually much greater than the wavelength of light λ, so the relevant values of *N* are large (around 10^5 to 10^6). Of more interest is the frequency separation between any two adjacent modes *N* and *N*+1; this is given (for an empty linear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

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

where *c* is the speed of light ($\approx 3\times10^8$ m·s^{-1}).

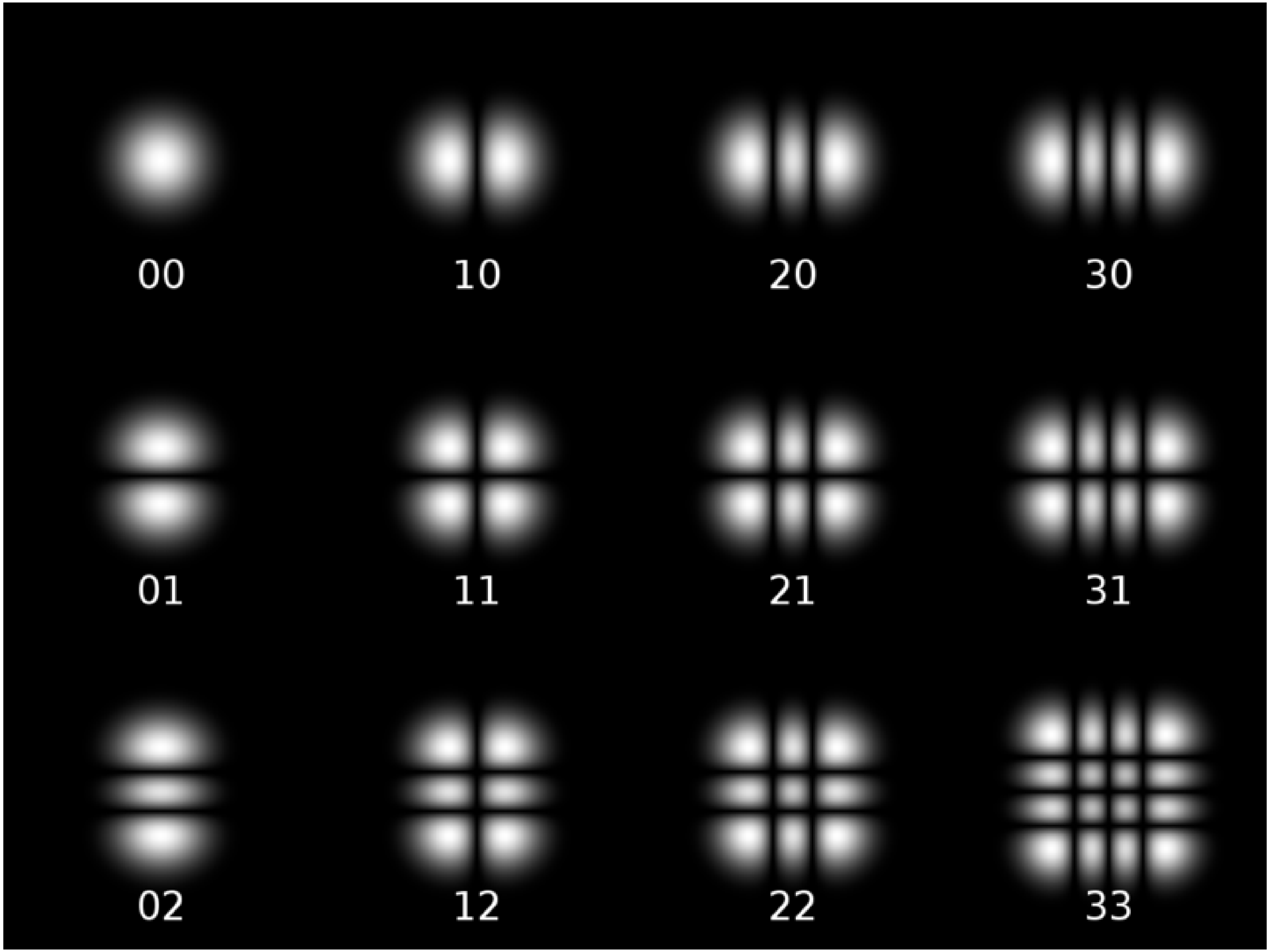
Output modes

The figure on the right shows the combination of the gain bandwidth and longitudinal modes. This leads to a discrete set of wavelengths that are output from the laser within the bandwidth.



Gaussian beam optics

Transverse resonator modes

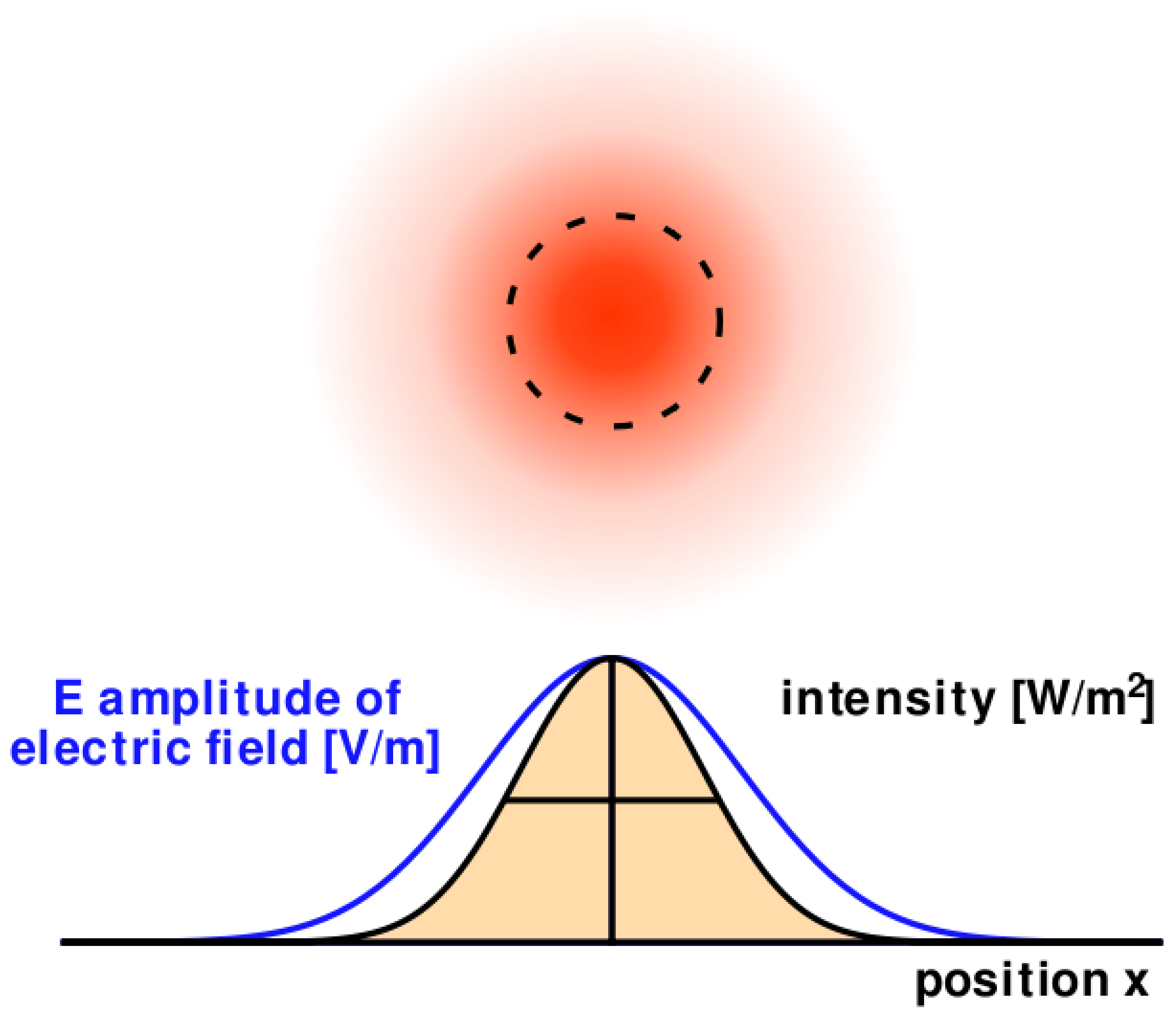


Introduction to the Gaussian beam

A Gaussian beam has a transverse electric field and intensity distribution that are well represented by a Gaussian function. This is observed when the laser operates using the fundamental transverse mode (TEM_{00} mode) of the optical resonator.

When refracted by a diffraction-limited lens, a Gaussian beam is transformed into another Gaussian beam (characterized by a different set of parameters). This optical model is a convenient model used in laser optics.

Intensity profile of TEM_{00}



The concept of a beam waist