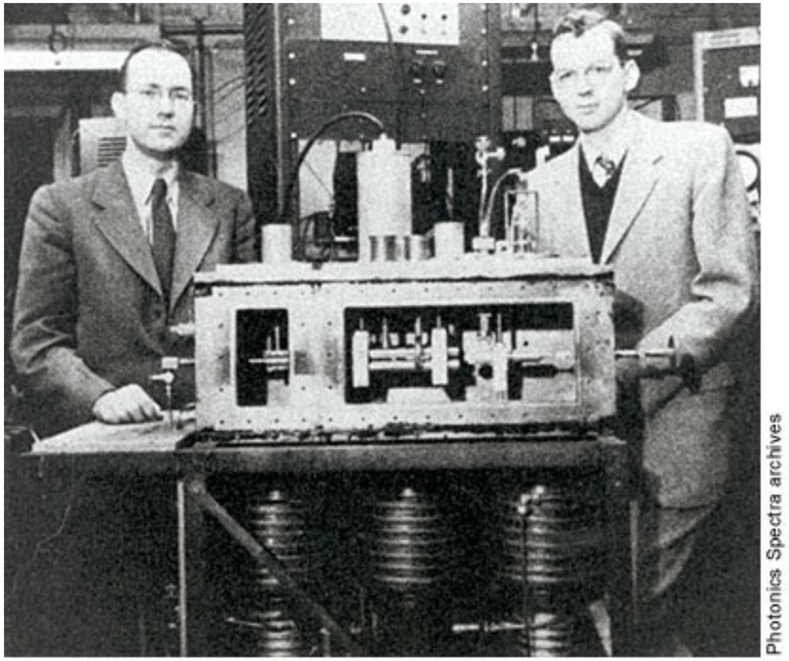
Lasers in chemistry

Key properties:

- Directionality of laser beam (low angular divergency): nearly diffraction limited, $\theta_B = 2.44\frac{\lambda}{D}$
- High power density (W/cm^2 or J/cm^2) in the beam or in the focal point because of low divergency;
- Narrow spectral linewidth (all photons are almost of the same wavelength)
- High spectral brightness (number of photons within a small spectral interval $\Delta\lambda$): for a laser pointer the spectral brightness corresponds to radiation of a blackbody with 6'000-10'000 K.
- Coherence up to meters
- Wavelength can be changes continuously or from line to line (tunable);
- Pulses can be as short as a few fs: these pulses are of extremely high intensity ($W=E/\tau$).

Milestones of lasers



Charles Townes (left) and James P. Gordon

1954: Townes demonstrates the first ammonia maser at Columbia University.

Simultaneously, a maser was demonstrated by Basov and Prokhorov at Physical Institute in Moscow.

λ= 1 cm, P= 10^{-9} W (nW).

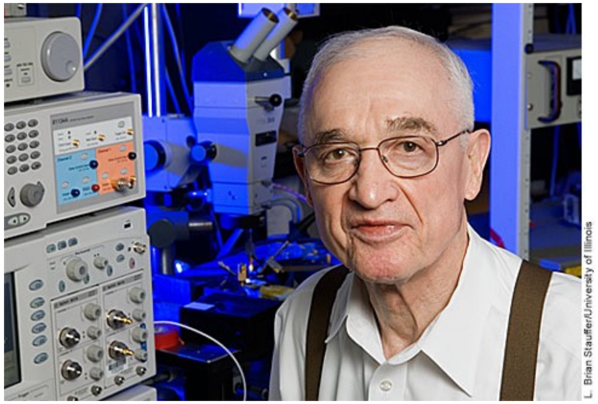
Milestones of lasers

May 16, 1960: Theodore H. Maiman, a physicist at Hughes Research Laboratories in Malibu, Calif., constructs the first visible (red, λ=694 nm) laser using synthetic ruby.

June 1962: Bell Labs reports the first pulsed yttrium aluminum garnet (YAG) laser. λ=1064 nm, near IR.

1963: ideas to build semiconductor lasers from heterostructure devices. The work leads to Kroemer and Alferov winning the 2000 Nobel Prize in physics.

Milestones of lasers



October 1962: Nick Holonyak invented a"visible red" GaAsP (gallium arsenide phosphide laser diode, (red LEDs used in CDs, DVD players).

1964: Townes, Basov and Prokhorov are awarded the Nobel prize.

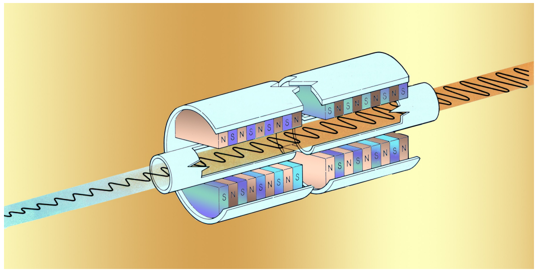
1964: The first cw carbon-dioxide (CO_2) laser. λ=10 μm, IR, watts of power.

1965: the first chemical laser: HCl, λ=3.7 μm, IR. watts of power.

1966: The dye laser is discovered by Peter P. Sorokin.
1967: tunable dye laser.

1970: Nikolai Basov, V. A. Danilychev, and Yu. M. Popov develop the excimer laser at Physical Institute in Moscow. λ=350 nm, UV, μJ of power (J energy currently).

Milestones of lasers

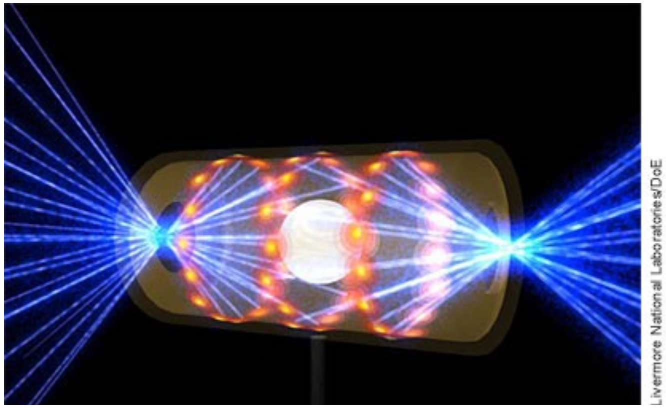


1976: John Madey and his group at Stanford University demonstrate the first free-electron laser (FEL).

1996: The first pulsed atom laser, which uses matter instead of light

2010: ultrashort laser pulse (single cycle of light), 4.3 fs.

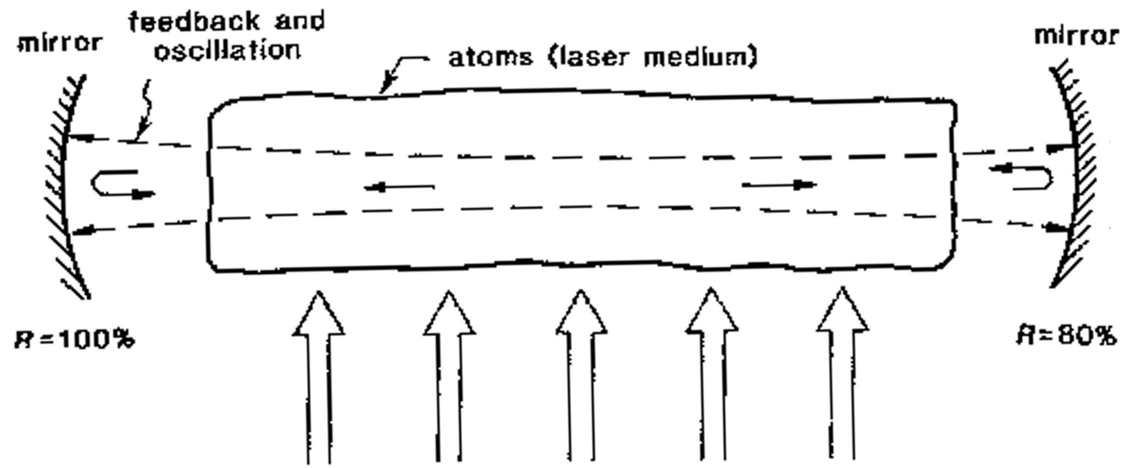
2010: historic level of laser energy — more than 1 MJ in 5 ns pulse (nuclear fusion) (PP= 500x USA consumption) .



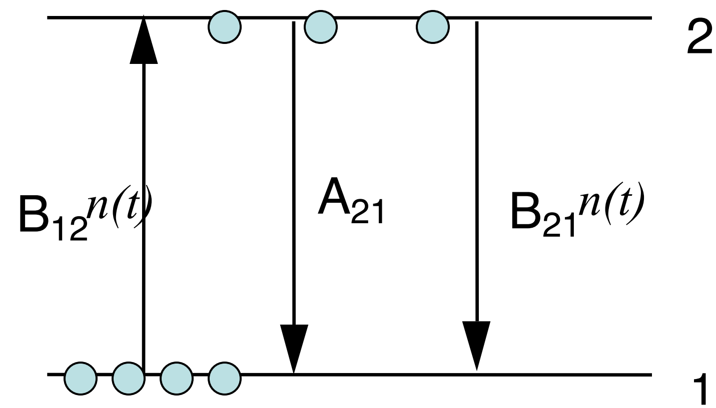
Fundamentals of lasers

Light
Amplification by
Stimulated
Emission
Radiation

- Pump source,
- Laser medium,
- Resonator,
- Output coupler.



Light Amplification Conditions



No thermal equilibrium!

$\boldsymbol{n}$(t) - photon density of the ν_{12} frequency;

Spontaneous emmision:

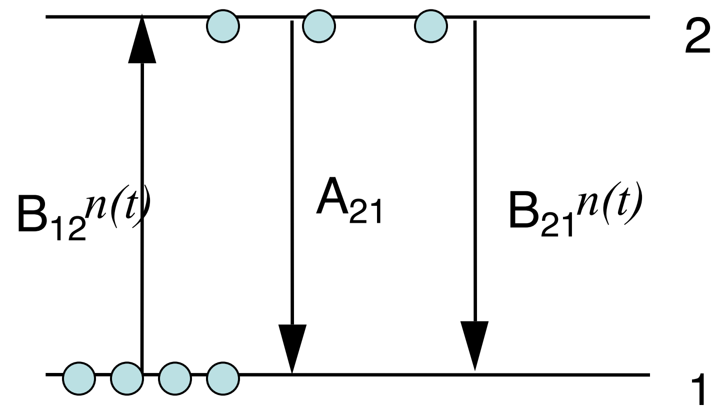
$$\left.\frac{dN_2(t)}{dt}\right|_{\text{spontaneous}} = -\left.\frac{dN_1(t)}{dt}\right|_{\text{spontaneous}} = -A_{21}N_2(t)$$

Stimulated emmision:

$$\left.\frac{dN_2(t)}{dt}\right|_{\text{stimulated downward}} = -B_{21}\, N_2(t)\, n(t)$$

<u>*Stimulated absorption:*</u>

$$\left.\frac{dN_2(t)}{dt}\right|_{\text{stimulated upward}} = B_{12}\, N_1(t)n(t)$$



<u>*The total rate equation:*</u>

$$\left.\frac{dN_2(t)}{dt}\right|_{\text{total}} = \left.\frac{dN_2(t)}{dt}\right|_{\text{stimulated downward}} + \left.\frac{dN_2(t)}{dt}\right|_{\text{stimulated upward}} + \left.\frac{dN_2(t)}{dt}\right|_{\text{spontaneous}}$$

$$\left.\frac{dN_2(t)}{dt}\right|_{\text{total}} = n(t)[B_{12}N_1(t) - B_{21}N_2(t)] - A_{21}N_2(t)$$

Energy conservation: $$\frac{dn(t)}{dt} = -\frac{dN_2}{dt}$$

Change of photon density: $$\frac{dn(t)}{dt} \cong -n(t)[B_{12}N_1(t) - B_{21}N_2(t)]$$

Principle of detailed equilibrium: $$B_{12}g_1 = B_{21}g_2$$

$$\frac{dn}{dt} = n(t)B_{12}g_1\left(\frac{N_2}{g_2} - \frac{N_1}{g_1}\right).$$

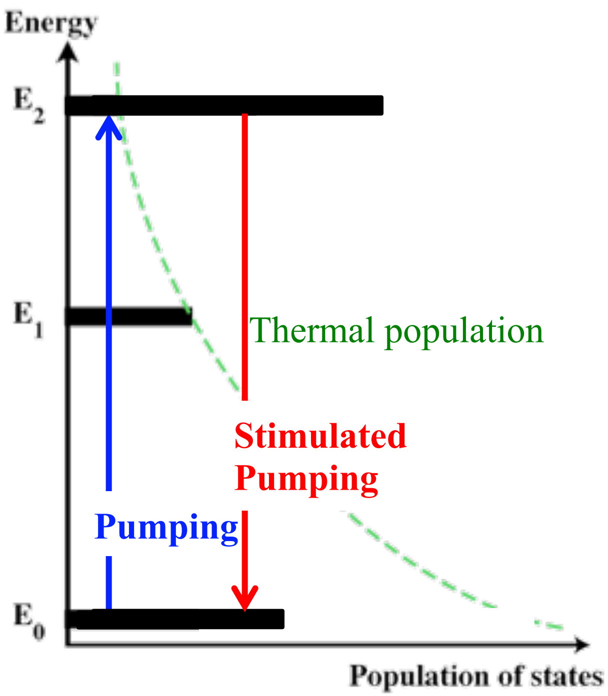
A) $\left(\frac{N_2}{g_2} - \frac{N_1}{g_1}\right) < 0$ ⇒ Absorption

B) $\left(\frac{N_2}{g_2} - \frac{N_1}{g_1}\right) > 0$ ⇒ **Amplification !!!**

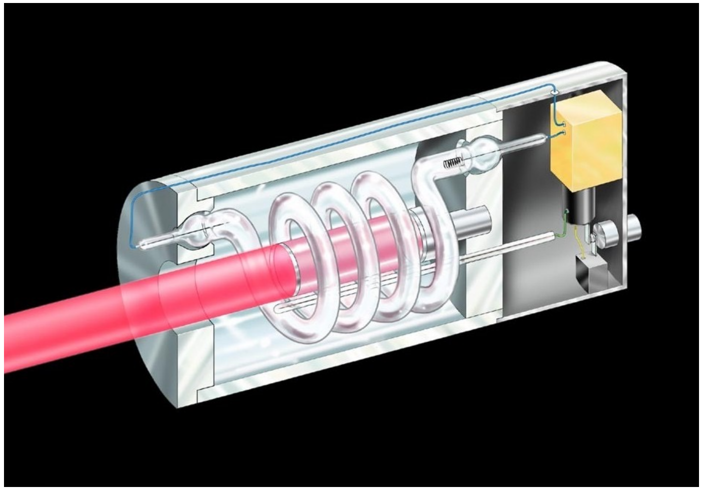
(Population inversion)

How to create inversion population?

Three-level system:

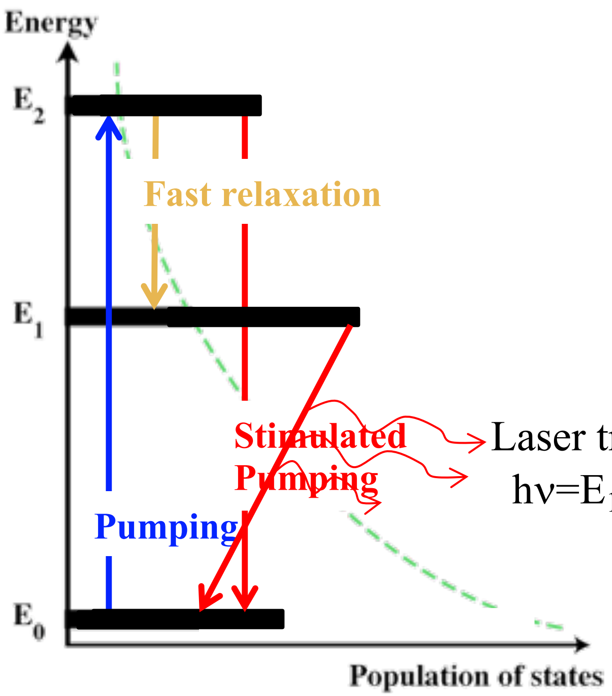


The first visible laser, ruby



How to create inversion population?

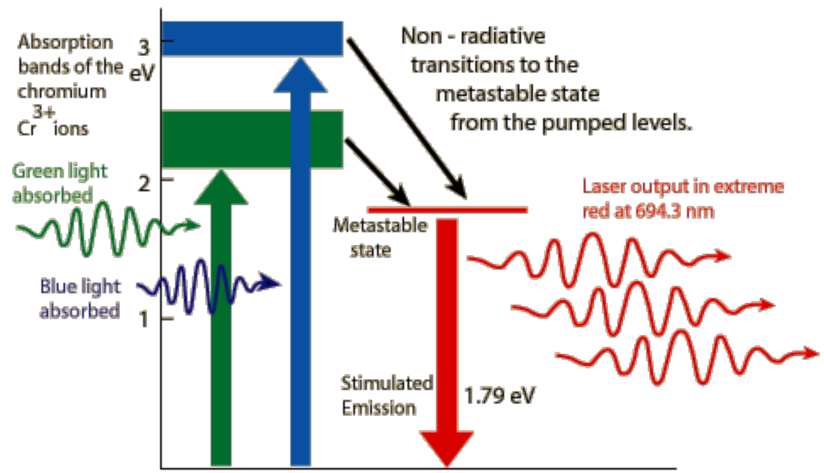
Three-level system:



Laser transition:

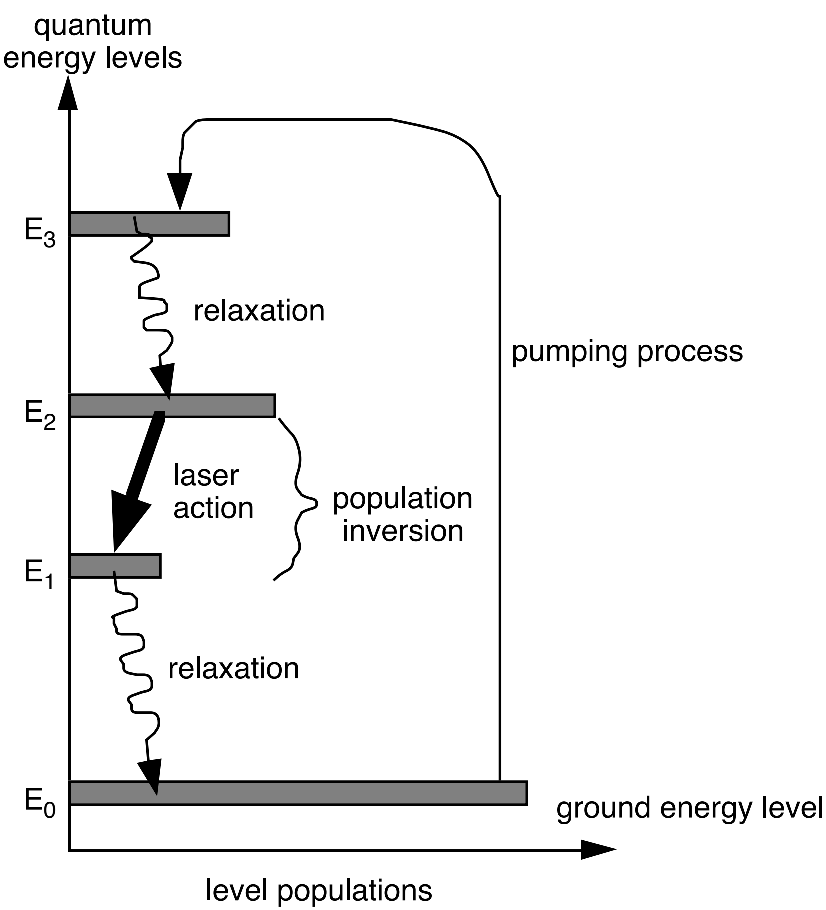
$h\nu = E_1 - E_0$

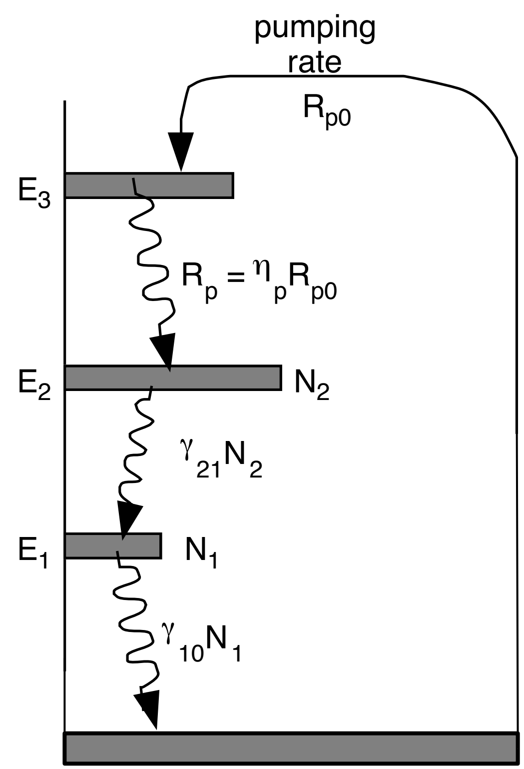
The first visible laser, ruby



How to create inversion population?

Multilevel systems:

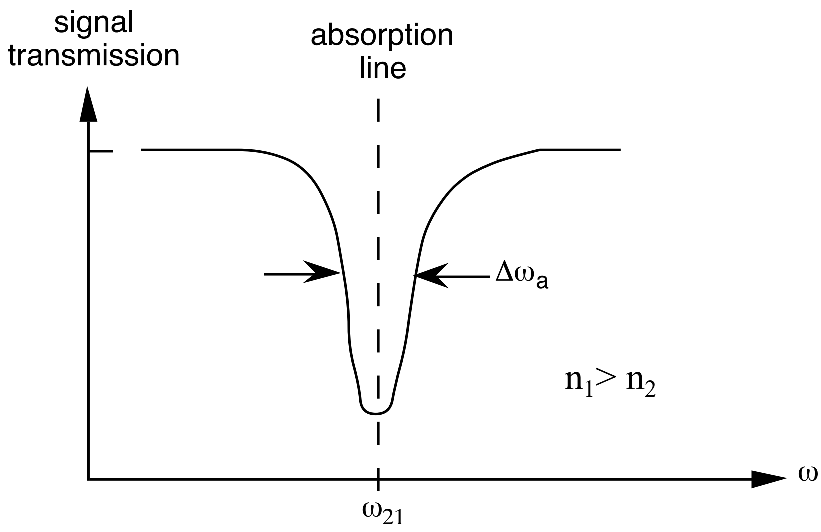




Light absorption:

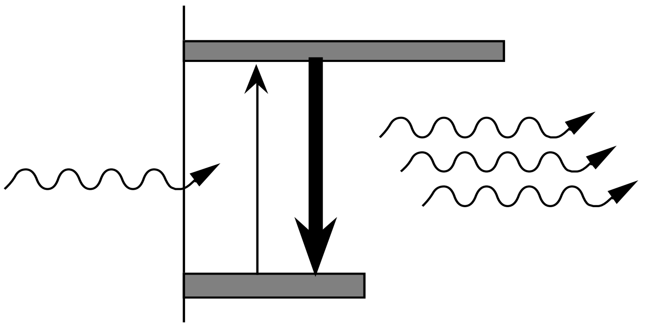
$$I(z) = |E(z)|^2 = |E_0|^2 e^{-2\alpha(\omega)z} = I_0 e^{-2\alpha(\omega)z}$$

$$\alpha(\omega) = \frac{\lambda^2}{4\pi} \frac{\gamma_{rad}}{\Delta\omega_a} \frac{n_1 - n_2}{1 + \left[\frac{2(\omega - \omega_{21})}{\Delta\omega_a}\right]^2}$$



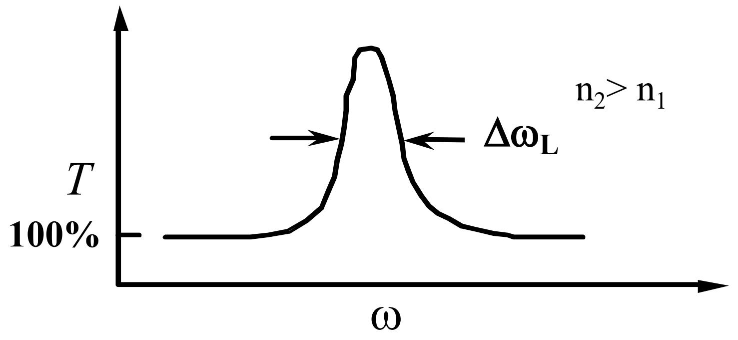
Light amplification (n₂ > n₁):

$$I(z) = |E(z)|^2 = I_0 e^{+2\alpha(\omega)_L z}$$



Laser gain profile:

$$\alpha(\omega)_L = \frac{\lambda^2}{4\pi} \frac{\gamma_{rad}}{\Delta\omega_a} \frac{n_2 - n_1}{1 + \left[\frac{2(\omega - \omega_{21})}{\Delta\omega_a}\right]^2}$$



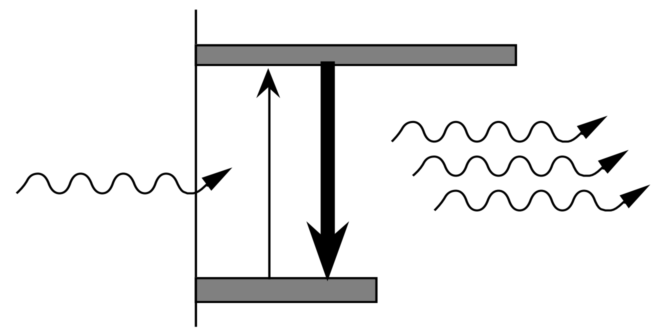
• *Laser generates what it may absorb*

- Amplification varies within the gain profile
- Amplification can be reduced by losses,

such that there is no amplification even for inversion population.

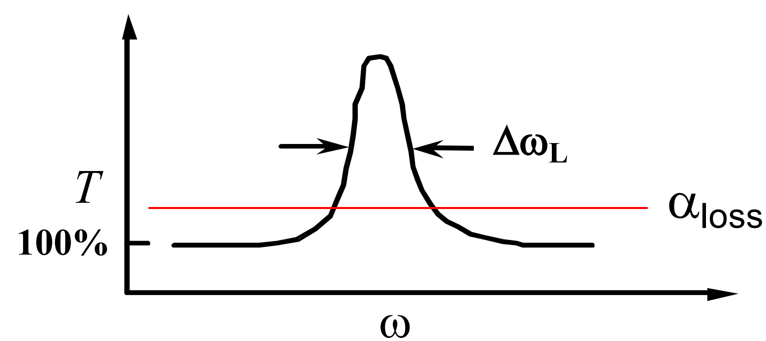
Light amplification:

$$I(z) = |E(z)|^2 = I_0\, e^{+2\alpha(\omega)_L z}$$



Laser gain profile:

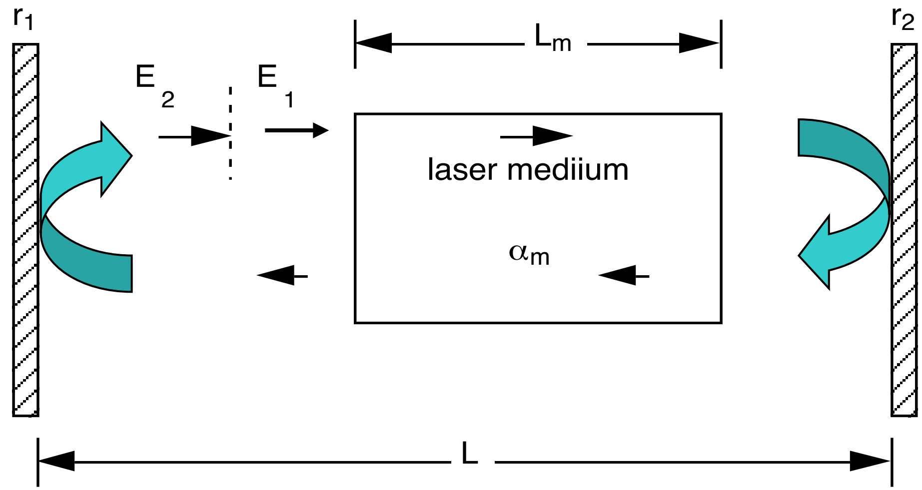
$$\alpha(\omega)_L = \frac{\lambda^2}{4\pi}\,\frac{\gamma_{rad}}{\Delta\omega_a}\,\frac{n_2 - n_1}{1 + \left[\frac{2(\omega - \omega_{21})}{\Delta\omega_a}\right]^2} - \alpha_{loss}$$



Laser medium in resonator

$$E_1 = E_0 e^{i(\omega t + \varphi_0)}$$

$$E_2 = r_1 r_2 E_0 e^{2\alpha_m L_m + i(\omega t + \varphi_0 - 2\omega L/c)}$$



Steady state conditions:

$$\frac{E_2}{E_1} = r_1 r_2\, e^{2\alpha_m L_m - 2i\omega L/c} = 1$$

a) *Round trip amplitude conditions:*

$Re(E_1/E_2)=1,$

b) *Round trip phase conditions:*

$Im(E_1/E_2)=1,$

Threshold inversion population

Round trip amplitude conditions:

$$r_1 r_2 e^{2\alpha_{ss} L_m} = 1$$

$$\ln(r_1 r_2 e^{2\alpha_{ss} L_m}) = \ln 1$$

$$\ln(r_1 r_2) + \ln(e^{2\alpha_{ss} L_m}) = 0$$

$$\ln(r_1 r_2) = -2\alpha_{ss} L_m$$

$$r_1 = \sqrt{R_1}, \quad r_2 = \sqrt{R_2}$$

$$\ln(r_1 r_2) = \ln(\sqrt{R_1 R_2}) = \frac{1}{2}\ln(R_1 R_2) = -\frac{1}{2}\ln(\frac{1}{R_1 R_2})$$

$$2\alpha_{ss} L_m = \frac{1}{2}\ln(\frac{1}{R_1 R_2})$$

$$\alpha_{ss} L_m = \frac{1}{4}\ln(\frac{1}{R_1 R_2});$$

Threshold inversion population

Round trip amplitude conditions:

$$r_1 r_2 \, e^{2\alpha_{ss} L_m} = 1$$

$$\alpha_{ss} L_m = \frac{1}{4} \ln\left(\frac{1}{R_1 R_2}\right)$$

At the maximum of laser gain (homogeneous broadening):

$$\alpha(\omega_{21}) = \frac{\lambda^2}{4\pi} \frac{\gamma_{rad}(n_2 - n_1)}{\Delta\omega_a}$$

$$\alpha(\omega_{21}) \geq \alpha_{ss}$$

$$(n_2 - n_1) \geq \frac{\pi \, \Delta\omega_a}{\lambda^2 \, \gamma_{rad} \, L_m} \ln\left(\frac{1}{R_1 R_2}\right)$$

To make the threshold lower:

- *High reflectivity,*
- *Narrow linewidth,*
- *Longer medium,*
- *Longer wavelength*

Round trip phase conditions:

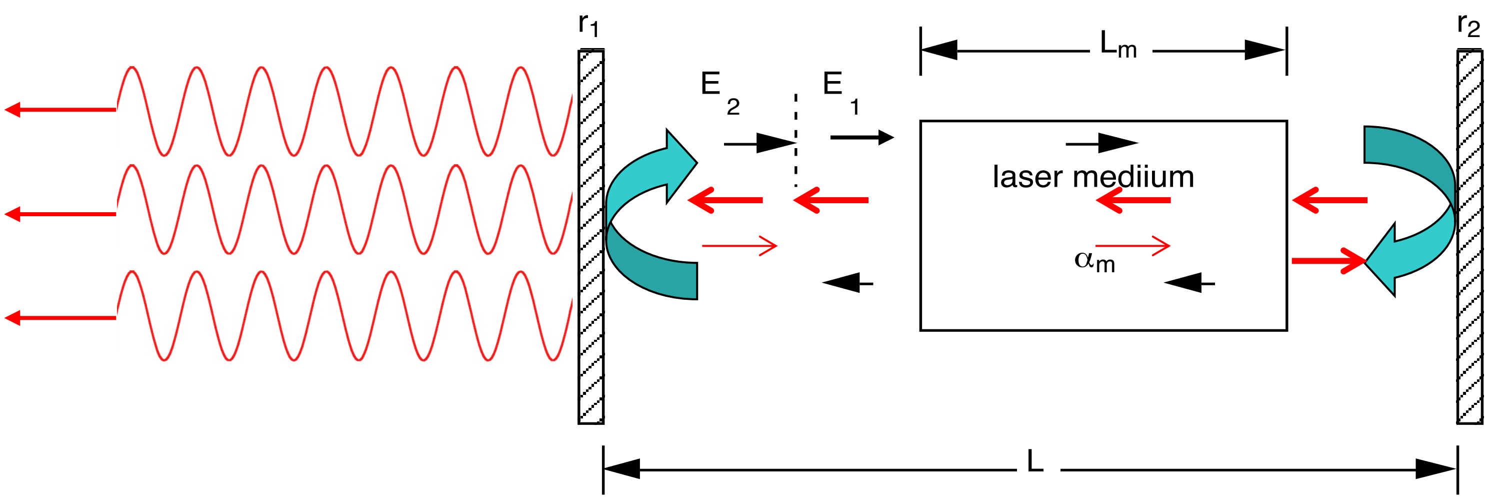
$$\frac{E_2}{E_1} = r_1 r_2\, e^{2\alpha_m L_m - 2i\omega L/c} = 1$$

$$\mathrm{Im}(r_1 r_2\, e^{2\alpha_m L_m - 2i\omega L/c}) = \cos(\frac{2\omega L}{c}) = 1$$

$$\lambda = \frac{2\pi \cdot c}{\omega}$$

$$\frac{2\omega L}{c} = q\,2\pi \quad \Rightarrow \quad \omega = \omega_q = q\,2\pi\left(\frac{c}{2L}\right);$$

$$q\lambda_q = 2L$$



Round trip phase conditions:

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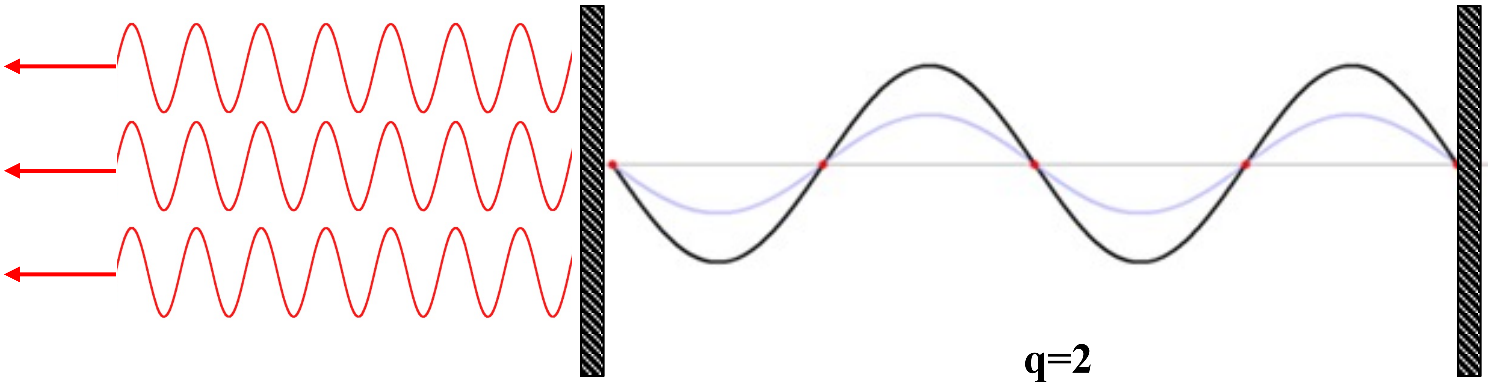

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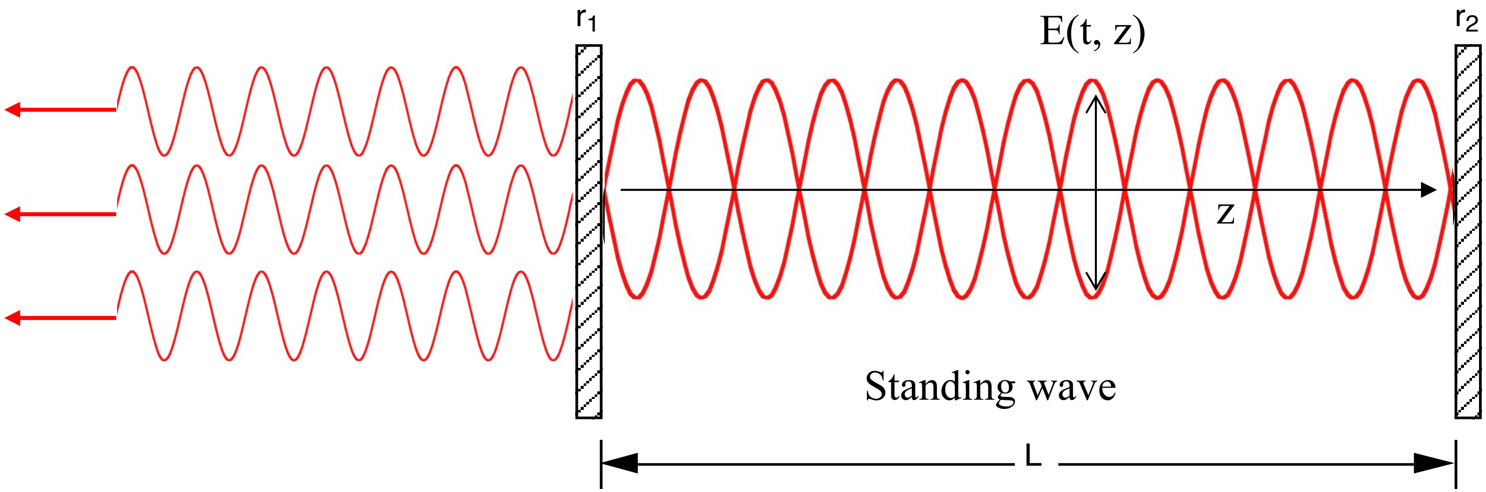

Round trip phase conditions:

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$$\frac{2\omega L}{c} = q\,2\pi \;\Rightarrow\; \omega = \omega_q = q\,2\pi\left(\frac{c}{2L}\right);$$

$$q\lambda_q = 2L$$

Expressed in wavenumber: $q = 2L\tilde{\nu}_{ax}$

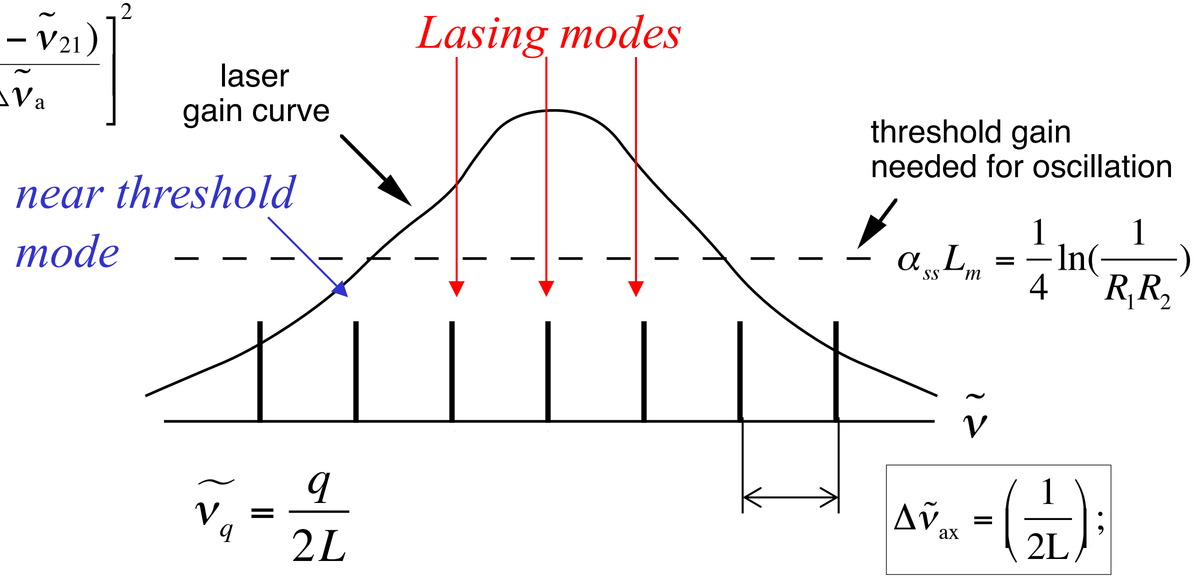
$$\Rightarrow\; \partial q = 2L \cdot \partial\tilde{\nu}_{ax}$$

When expressed in wavenumber units, the allowed laser modes are equidistant:

$$\Delta\tilde{\nu}_{ax} = \left(\frac{1}{2L}\right);$$

Frequency (mode) structure of laser radiation

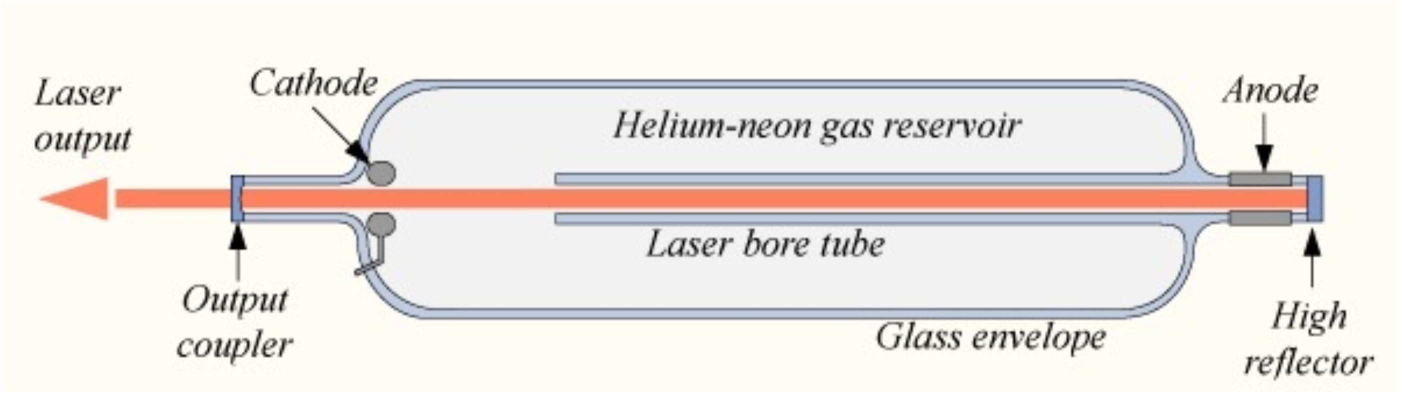
$$\alpha(\tilde{\nu})_L = A\,\frac{\lambda^2}{\Delta\tilde{\nu}_a}\,\frac{n_2 - n_1}{1 + \left[\dfrac{2(\tilde{\nu} - \tilde{\nu}_{21})}{\Delta\tilde{\nu}_a}\right]^2}$$



- *Linewidth of each mode,*
- *Number of modes*

Examples of Lasers

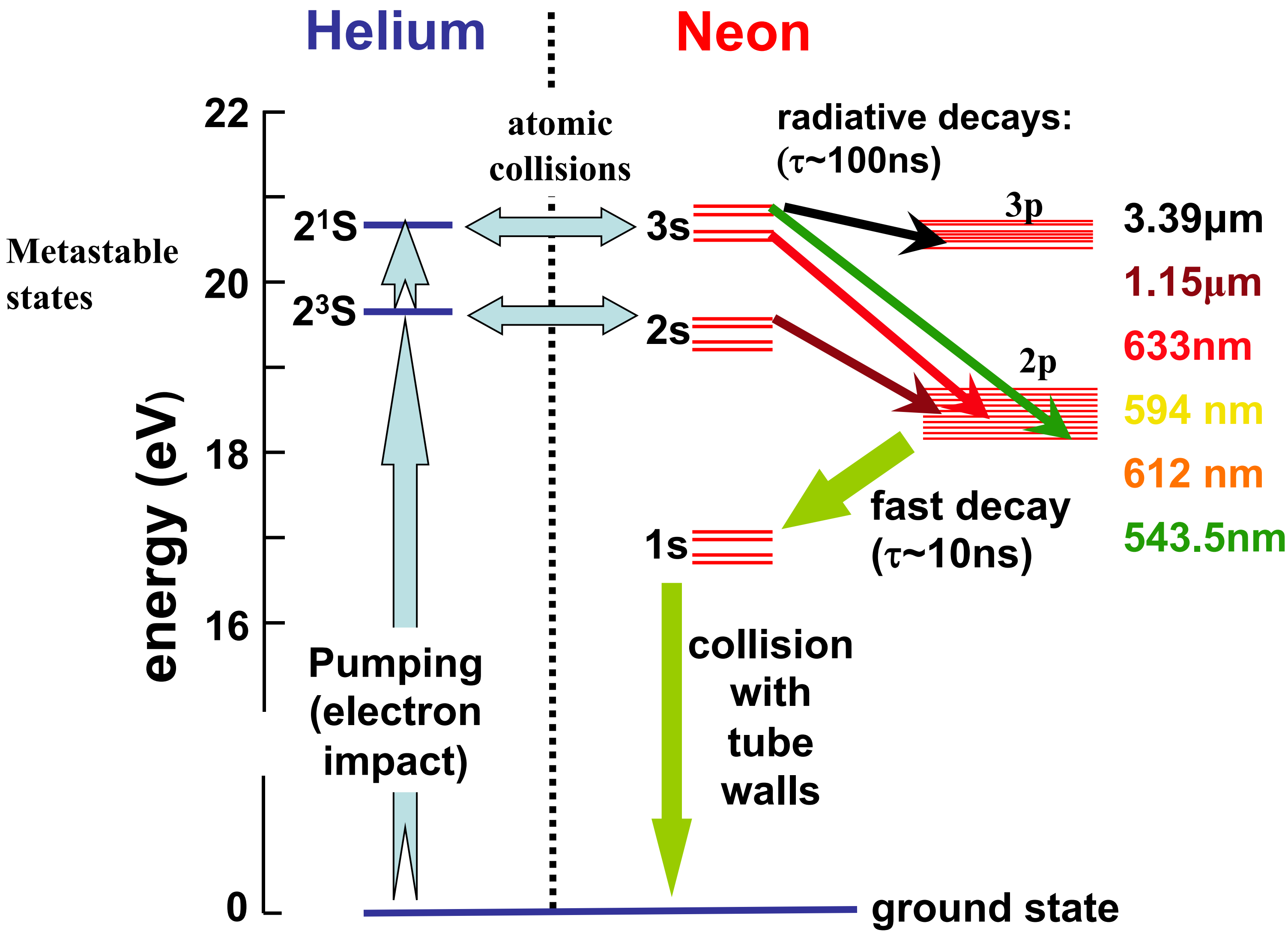
cw-lasers pumped by electrical discharge:



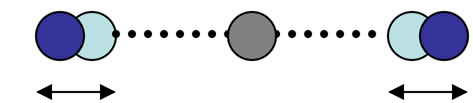
1. He-Ne laser:

Wavelengths: 543 nm, 632.8 nm, 1.15 μm, 3.39 μm

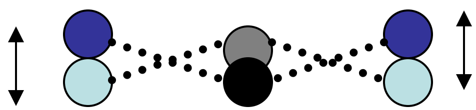
HeNe laser energy levels:



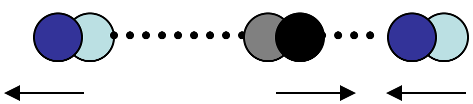
Energy diagram of CO_2 excitation



ν_1, sym stretch
1351.2 cm^{-1}

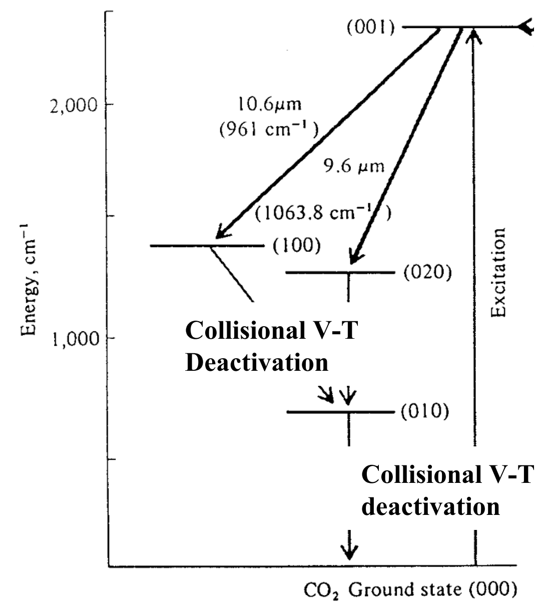


ν_2, bending
672.2 cm^{-1}



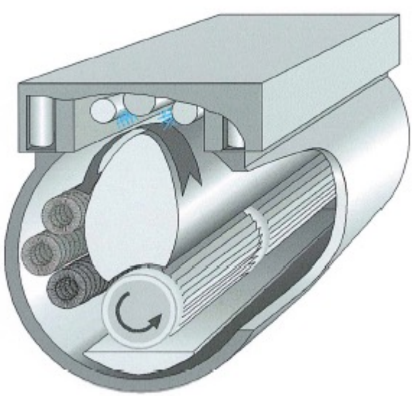
ν_3, asym stretch
2396.4 cm^{-1}

CARBON DIOXIDE LASER



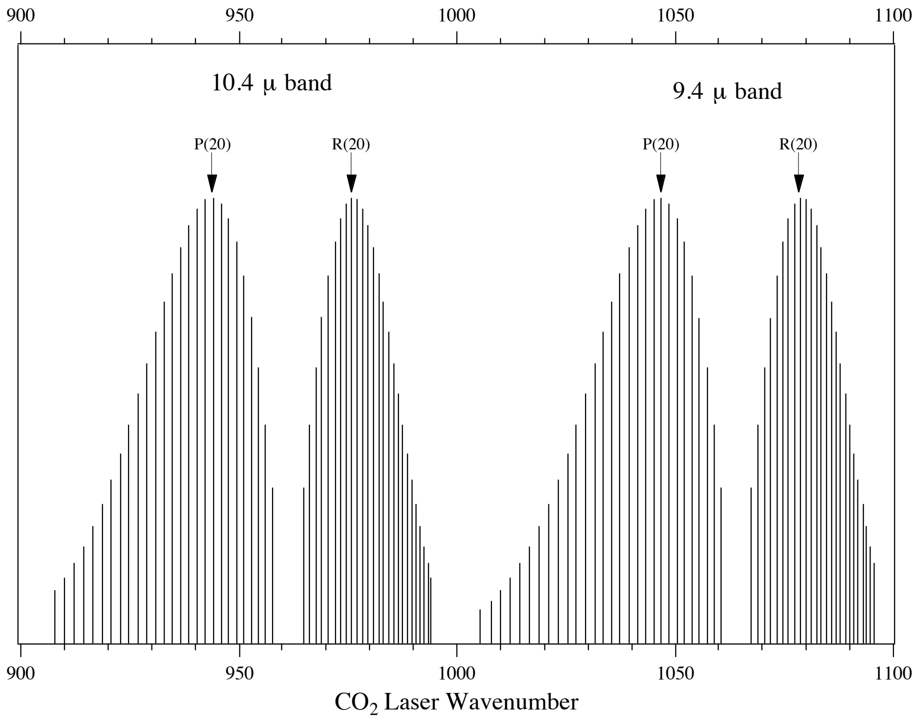
(a)

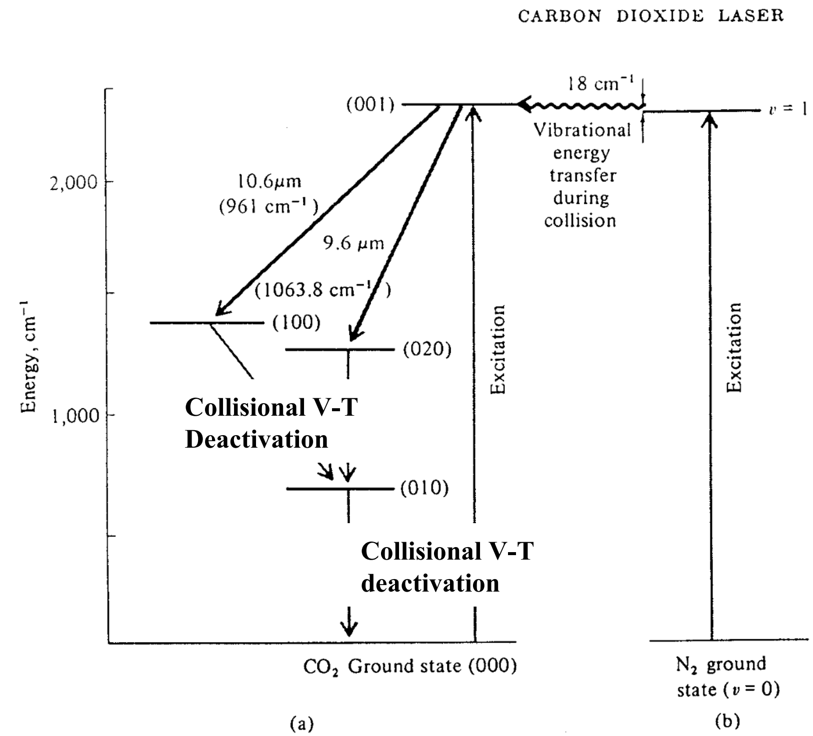
(a) Some of the low-lying vibrational levels of the carbon dioxide (CO_2) molecule, including the upper and lower levels for the 10.6-μm



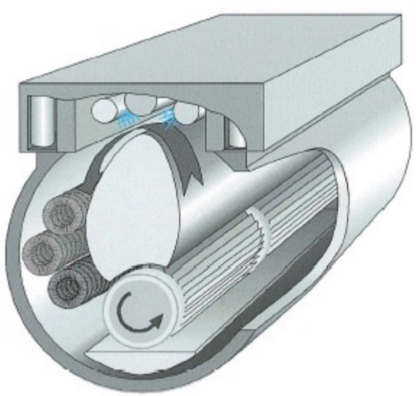
Most efficient laser(cheapest photons)
Most powerful industrial
Line-to line tunable in 9-10 μm region

Energy diagram of CO_2 excitation





(**a**) Some of the low-lying vibrational levels of the carbon dioxide (CO_2) molecule, including the upper and lower levels for the 10.6-μm



Most efficient laser(cheapest photons)
Most powerful industrial
Line-to line tunable in 9-10 μm region

Nd:YAG laser

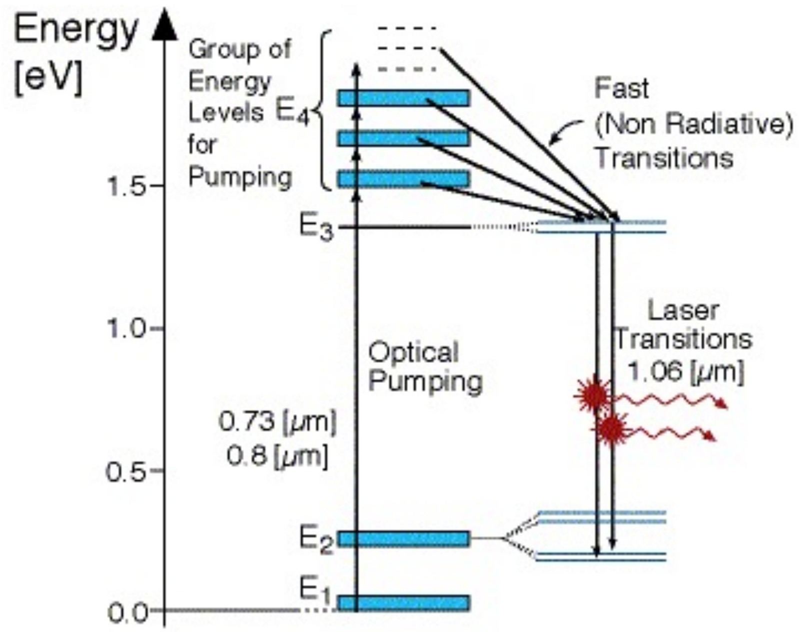
Neodymium-doped
Yttrium Aluminium Garnet

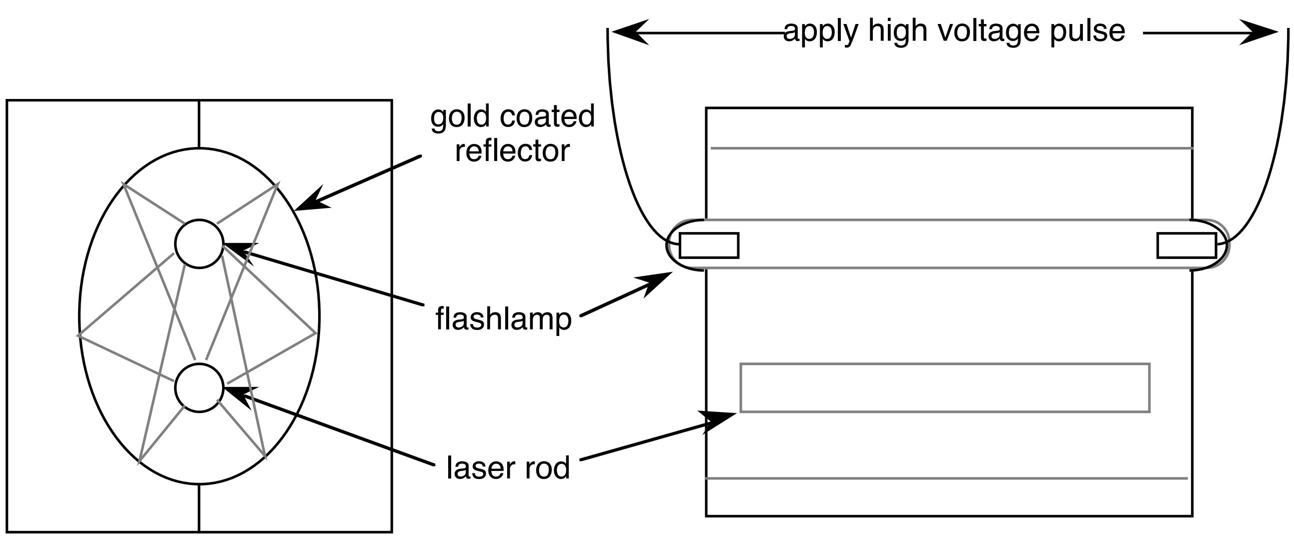
$Nd^{+3}:Y_3A_{l5}O_{12}$

Active centers: Nd^{3+};

Absorption bands:

720 nm, 830 nm.





Nd:YAG laser

Wavelengths:
Fundamental-1064 nm,
2-nd harmonic-532 nm (50%),
3-rd harmonic-355 nm, (30%)
4-th harmonic-266 nm, (10%)

Pulse energy: 0.5-2 J

Rep. Rate: 100Hz

Linewidth: <1.5 cm^{-1}

Mid-efficient (1.5%)