

Experimental Techniques: Sources of Radiation

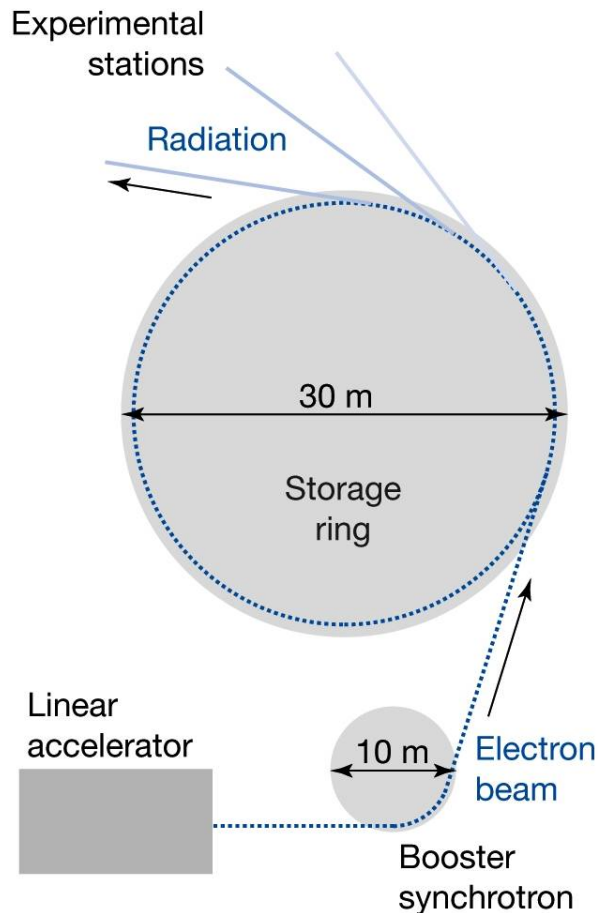
Polychromatic sources.

- a. Far-infrared range of spectrum ($\nu = 35 \text{ cm}^{-1} - 200 \text{ cm}^{-1}$): **high pressure mercury arc**
- b. Mid-infrared range of spectrum ($\nu = 200 \text{ cm}^{-1} - 4000 \text{ cm}^{-1}$): **Nernst Filament** (ceramics with ZrO₂Y₂O₃TiO₂), **Globar** (SiC).
- c. Near Infrared and Visible range of spectrum ($\lambda = 320 \text{ nm} - 2500 \text{ nm}$): **Tungsten filament**
- d. Ultraviolet and Visible range of spectrum ($\lambda = 180 \text{ nm} - 800 \text{ nm}$): **gas discharge lamps** (Xenon, Deuterium, Mercury, Neon, Krypton). Particularly, the output of a **high pressure xenon lamp** consists of sharp lines superimposed on a broad intense background due to emission from plasma which is widely used as a source of radiation which is similar to the black body radiation at 6000 K.
- e. **Synchrotron radiation.**

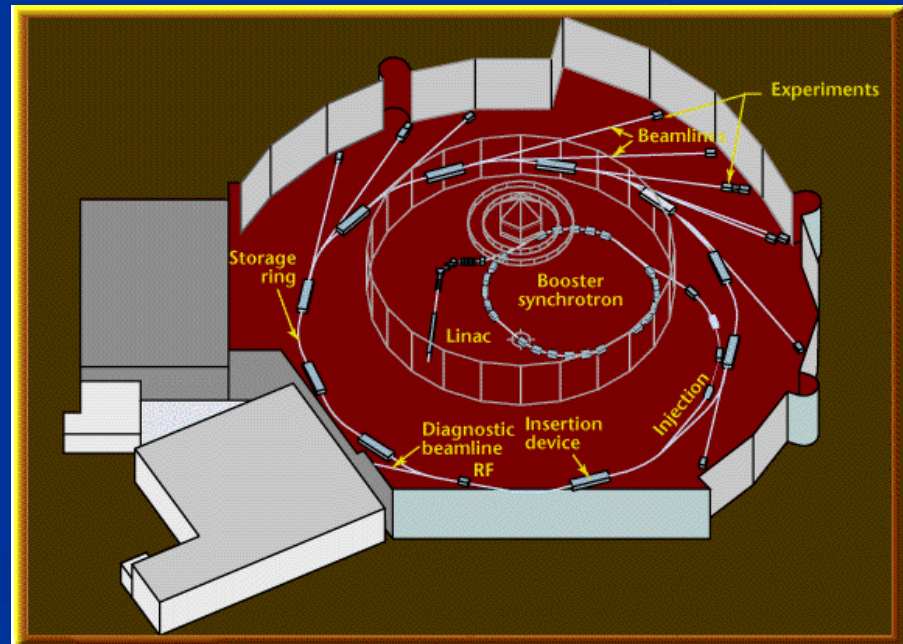
Synchrotron Radiation



ALS Berkeley, USA

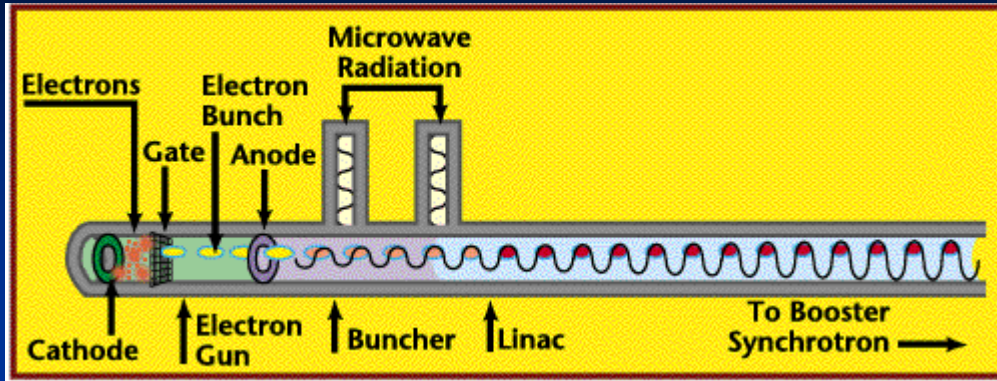


The electrons velocity in the Storage Ring is close to the speed of light. Moving along a curvilinear trajectory the electrons emit light in the very wide spectral range: from IR to X-rays. This is called **Synchrotron Radiation**.

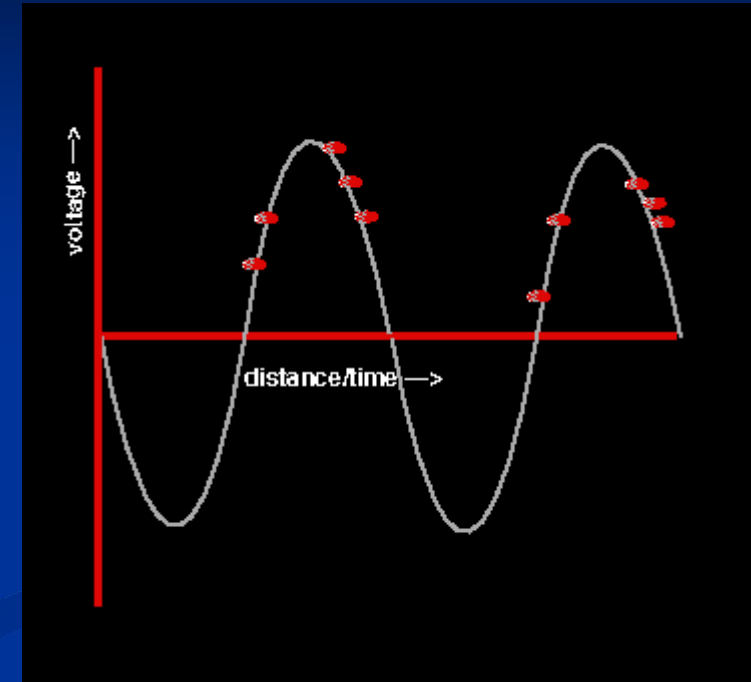
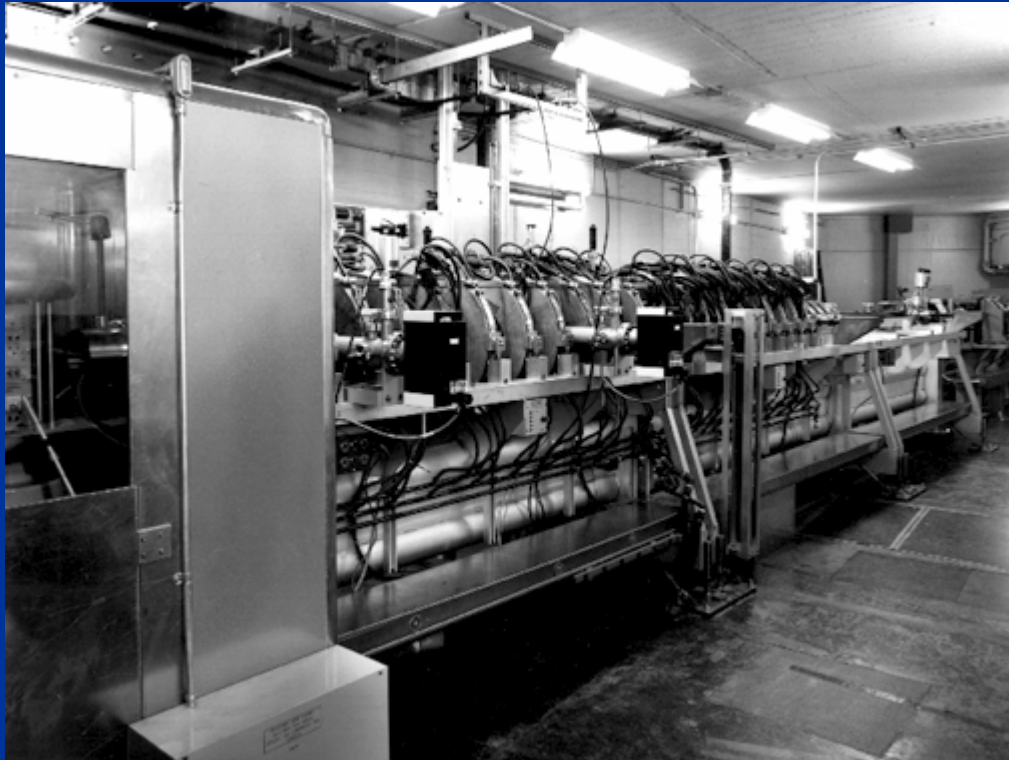


Linear Accelerator

$F \sim 500 \text{ МГц}$

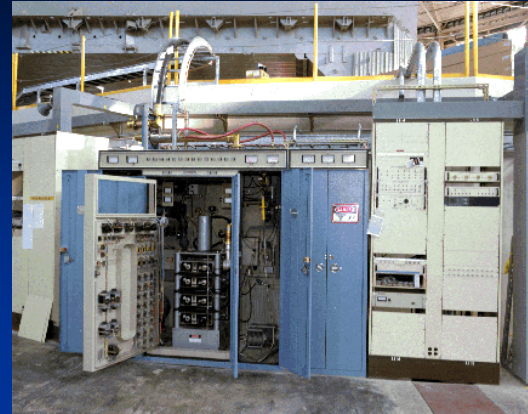
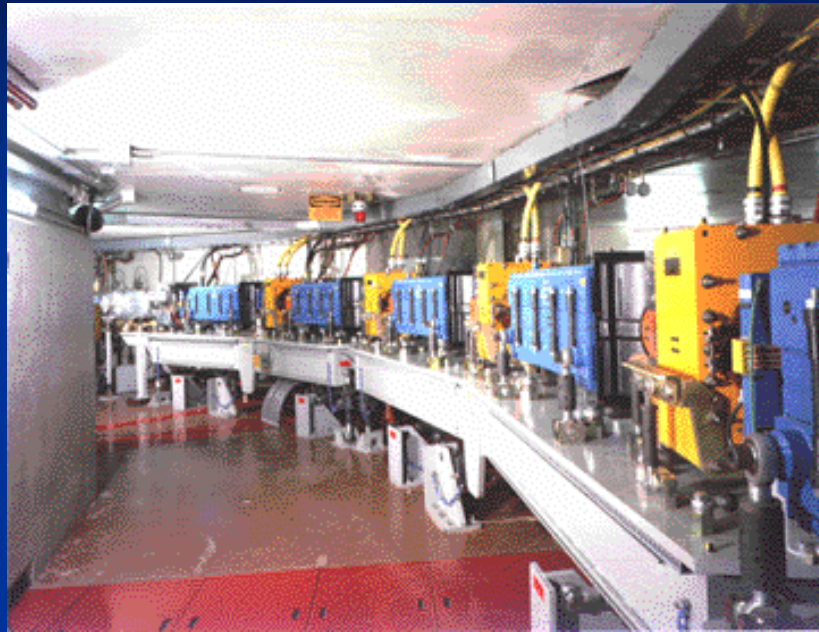


Длина около 4 метров



In the exit of the Linear Accelerator the electron bunches have velocity of about 0,6 c.

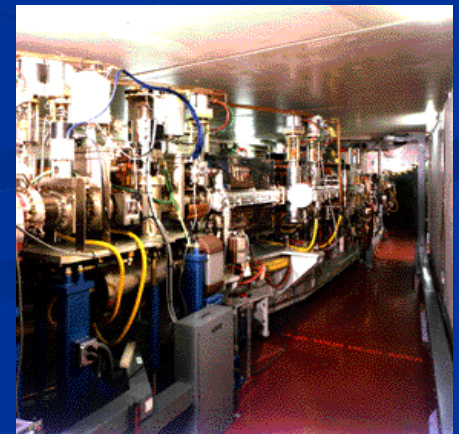
The Booster and the Storage Ring



The electron bunches in the Booster are accelerated by the radiofrequency field in a gap. The r.f. field is synchronized with the arrival of each next bunch. After passing of about 10^6 rings, the bunches reach the velocity of about **0,99999994 c** and the energy of about **1500000 eV**

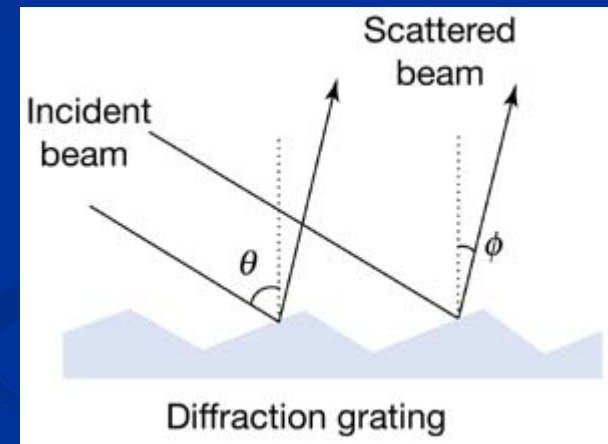
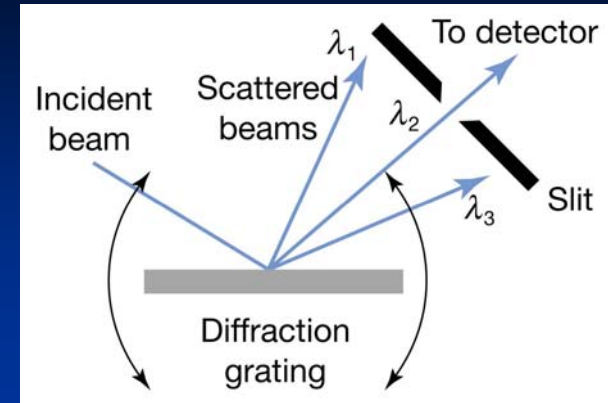
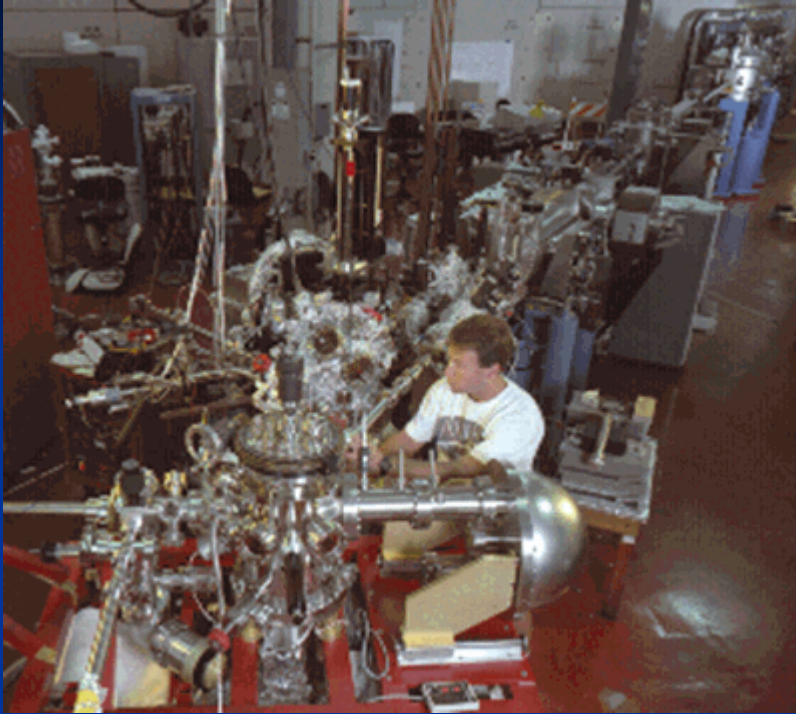
After that, they enter the Storage Ring.

The Storage Ring has the diameter of several dozens of meters. The ultra-high vacuum of 10^{-10} Torr provides the time of life of the electrons of about several hours.



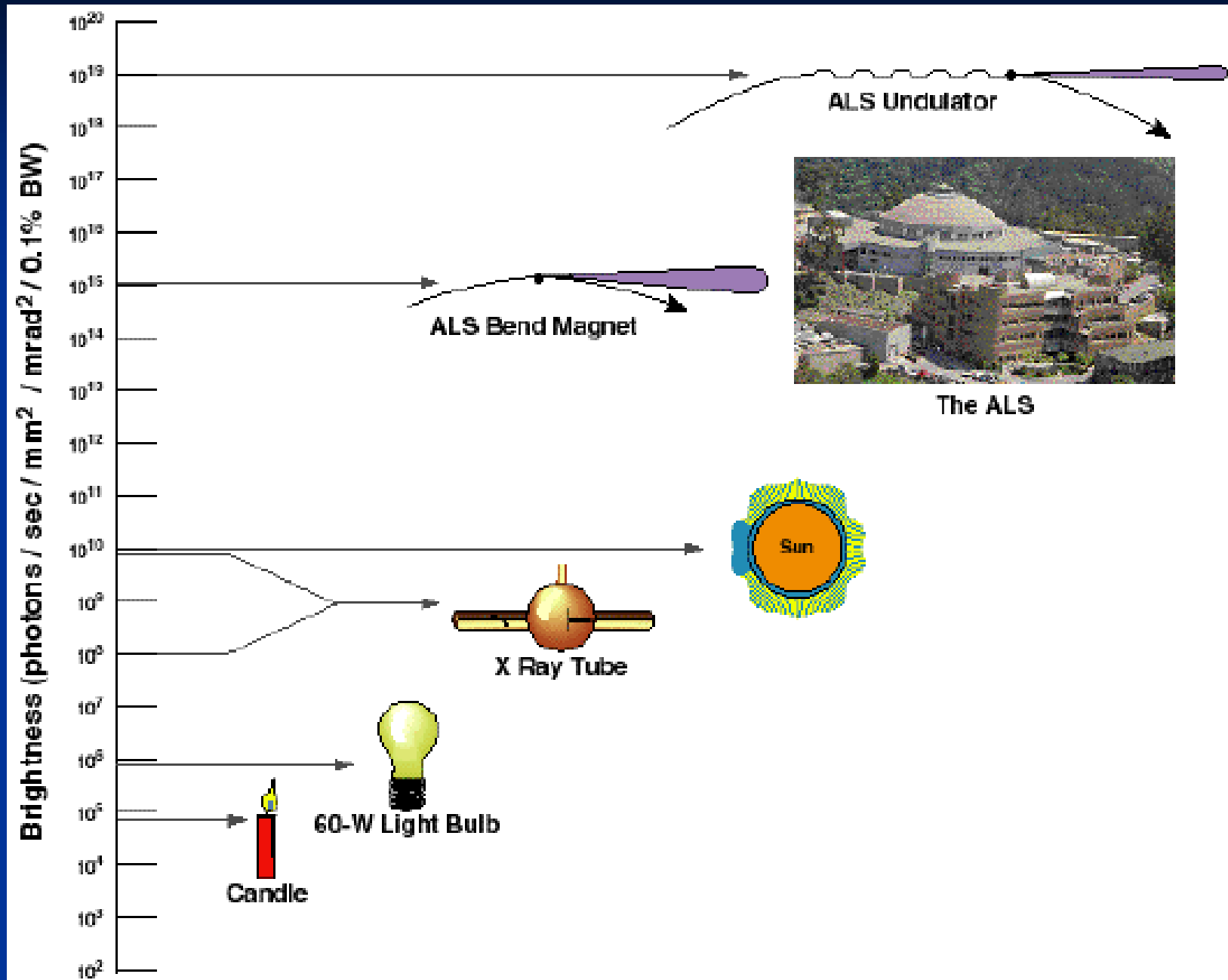
The Storage Ring contains also **Ondulators** and **Wigglers** which are the series of magnets forcing electrons to move along a S-turn and dramatically increasing the brightness of the emitted synchrotron radiation.

Workstations



The **Synchrotron Radiation** is monochromated by **Diffraction Gratings** and then used for experiments at the **Workstations**.

Brightness of different non-coherent light sources

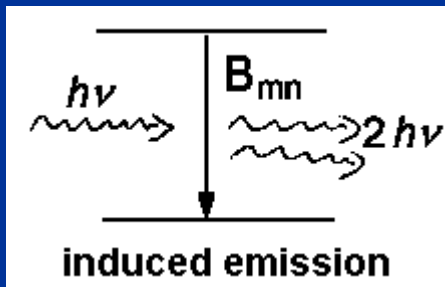
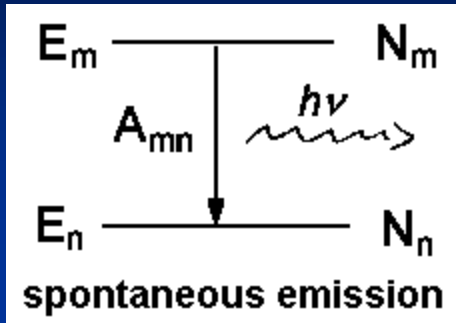


Monochromatic light sources

1. Near IR-UV spectral range ($\lambda = 180 \text{ nm} - 800 \text{ nm}$): **electrodeless lamps** containing a small amount of a chemical element (Cs, Rb, K, Na, Ag, Hg, Sn, Be, Sr, etc.) at the pressure of about 10^{-3} Pa and a few Pa of inert gas (Ne, Ar, Xe).
2. **Lasers.** The basic principle of laser operation is stimulated emission from a medium with **population inversion**. Independent from the construction details, lasers contain the following important components: **an active medium** with an upper and a lower working energy levels, a **pumping source**, and a **resonator**.

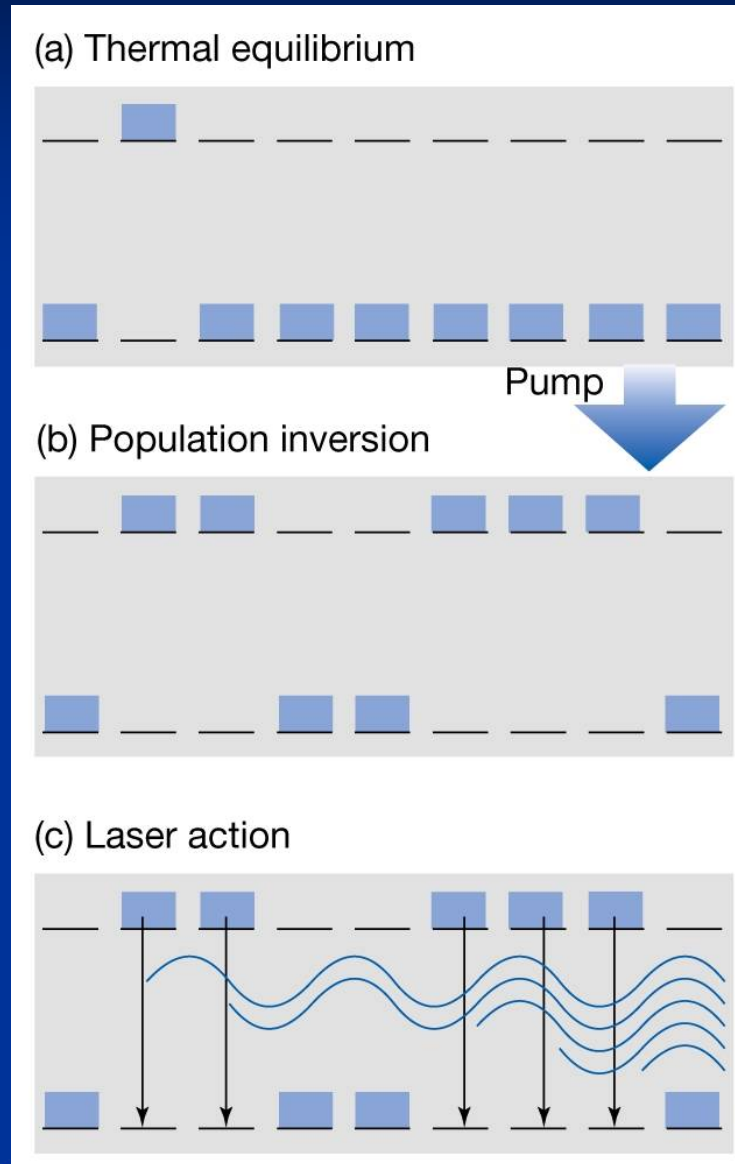
LASER

Light Amplification by Stimulated Emission

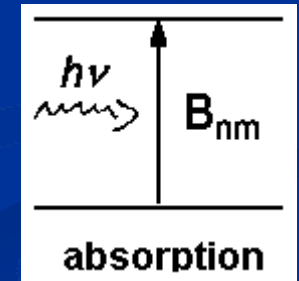


$$A_{21} / B_{12} = 8\pi h \nu^3 / c^3$$

For instance, for the wavelength of 500 nm the ratio between the intensities of the spontaneous and stimulated transitions is $F = e^{96} = 5 \cdot 10^{41}$!



Nobel Prize, 1964
C.H. Townes,
N.G. Basov,
A.M. Prokhorov



Properties of Laser Radiation

1. The laser light can be **very monochromatic** (temporal coherence), and can be effectively used for **high resolution spectroscopy**. The best results have been obtained for the low pressure gas lasers: $\Delta\lambda/\lambda \approx 10^{-15}$.
2. The laser beam can be of **very low divergence** (spatial coherence), which means that its diameter is increased only slowly in space. In principle, with laser beams it is possible to reach the diffraction limit:

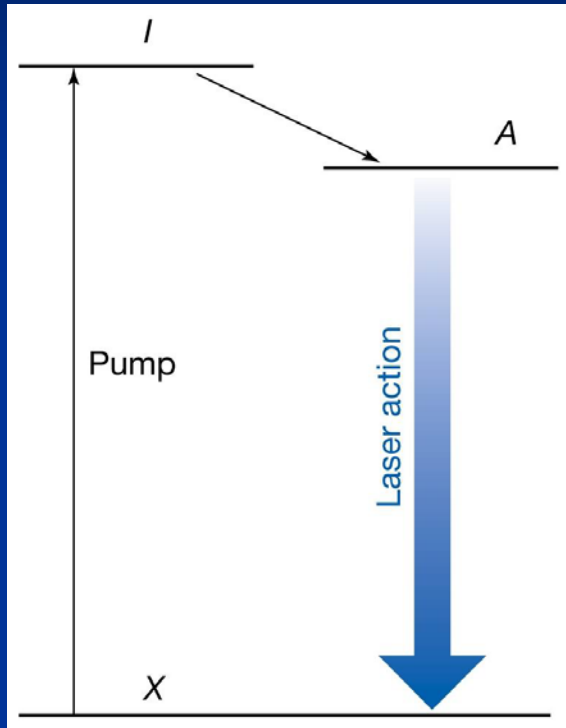
$$\theta \approx 2\lambda / \pi d$$

Using a lens of focal length f , it is possible to focus a laser beam (of diameter D) on a spot of the diameter:

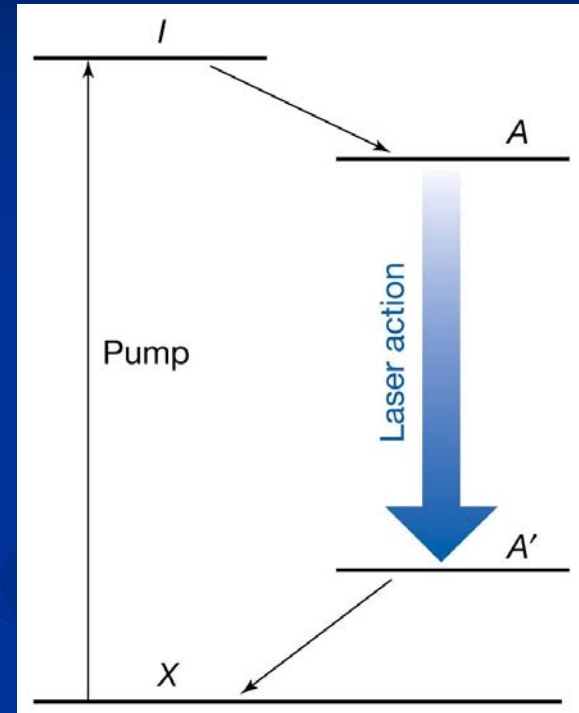
$$d \approx 2\lambda f / \pi D \approx \lambda / 2$$

3. **Extremely short laser pulses** can be produced. The pulse duration in the **nanosecond** (10^{-9}), **picosecond** (10^{-12}), and **femtosecond** (10^{-15}) range are now available commercially. Particularly, **femtosecond** laser pulses are of great importance, because they allow to investigate chemical reactions **in real-time**.
4. **High output power**. The continuous CO_2 lasers can produce a high power output of up to 100 kW. These lasers are nowadays widely used in industry and for military. Pulsed lasers, especially those operating in the pico- and femtosecond time-domain can have peak powers from **10^9 to 10^{12} Watt**. High power pulsed lasers are widely used for investigation of **nonlinear** and **multiple photon processes**.

Principles of LASER radiation

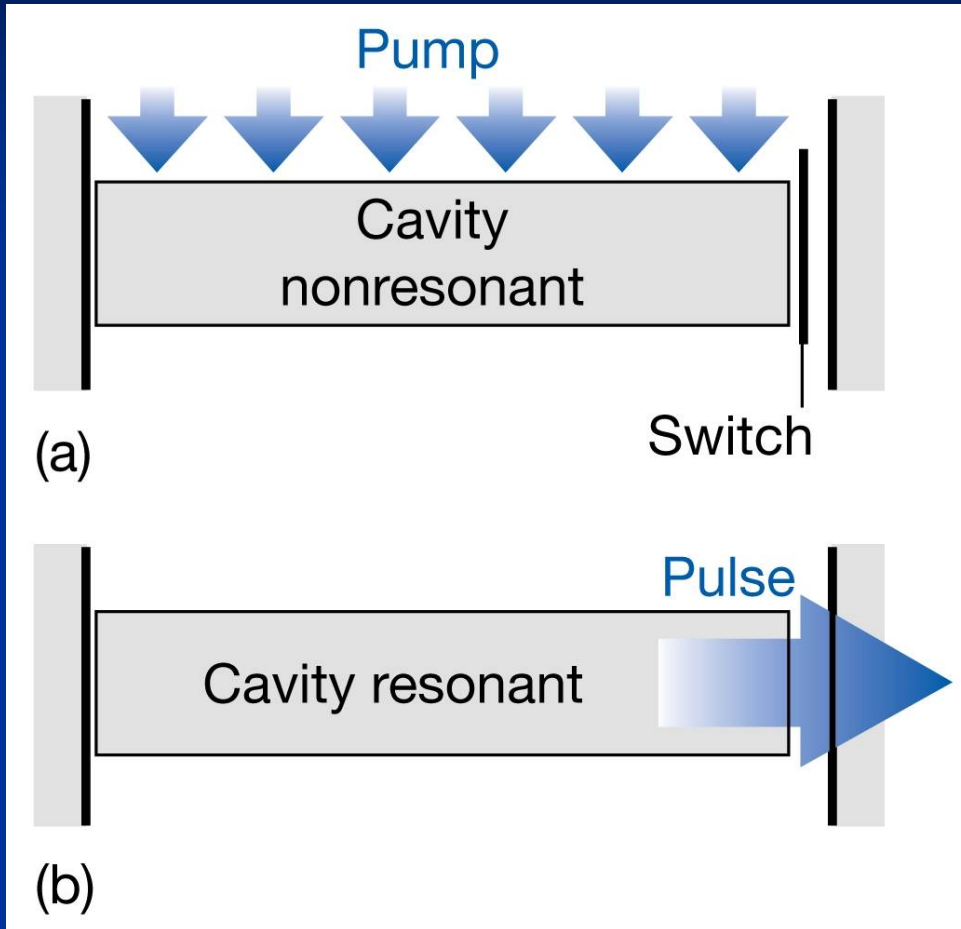


3-level laser scheme

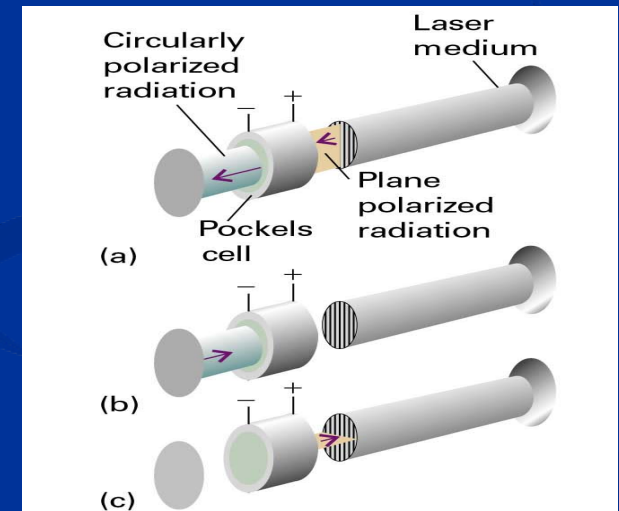


4-level laser scheme

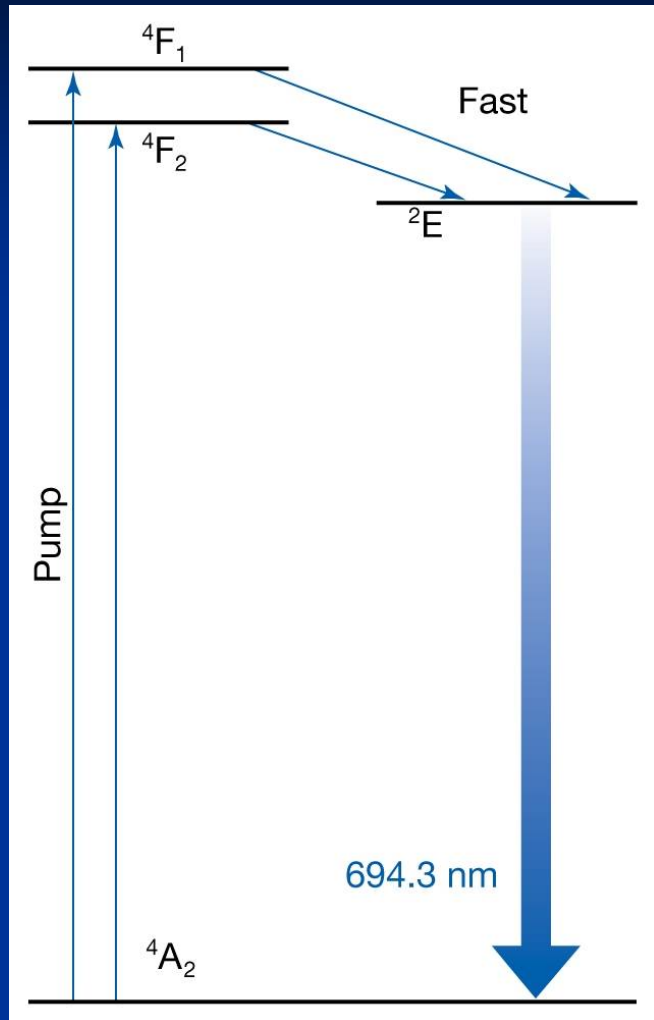
LASER: Q-switching



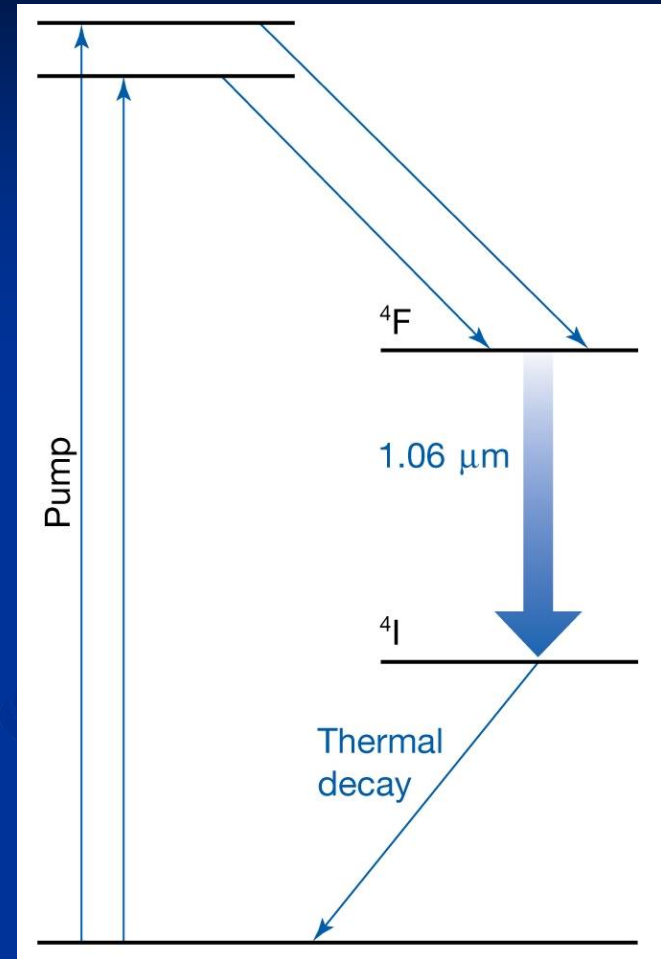
The switching may be achieved by impairing the resonance characteristics of the cavity in the same way while the pumping pulse is active and then suddenly to improve them. One technique is to use a **Pockels cell**.



Practical Lasers

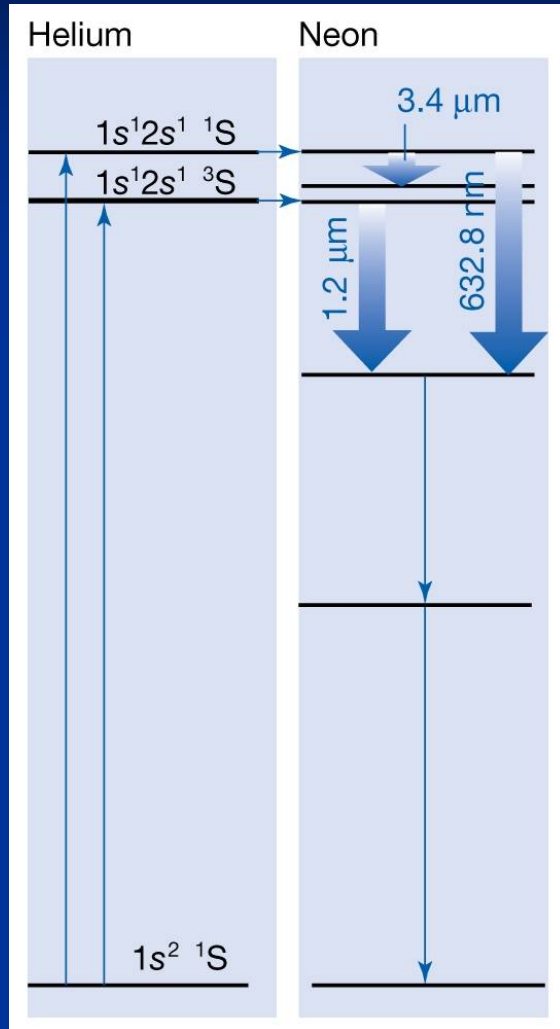


Ruby laser
 Al_2O_3 doped with Cr^{3+} ions

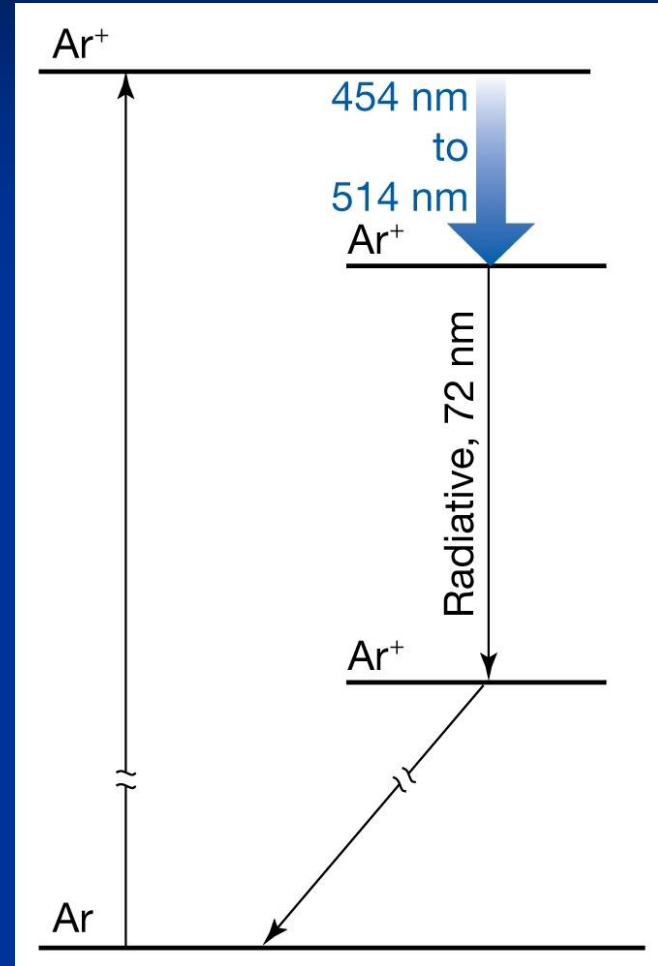


Nd: YAG laser
Yttrium aluminium garnet ($Y_3Al_5O_{12}$)
doped with Nd^{3+} ions

Practical Lasers

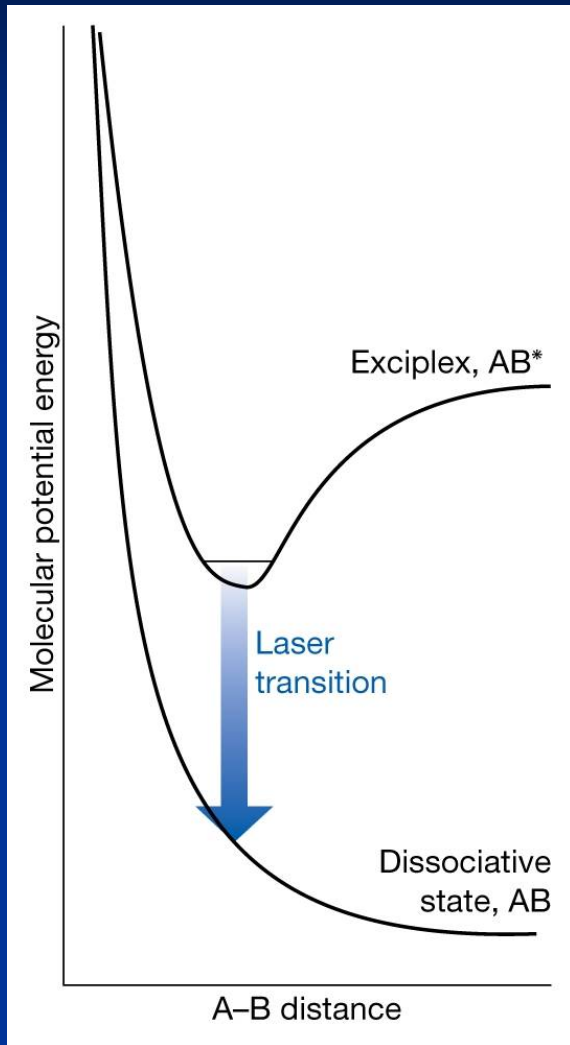


He-Ne laser



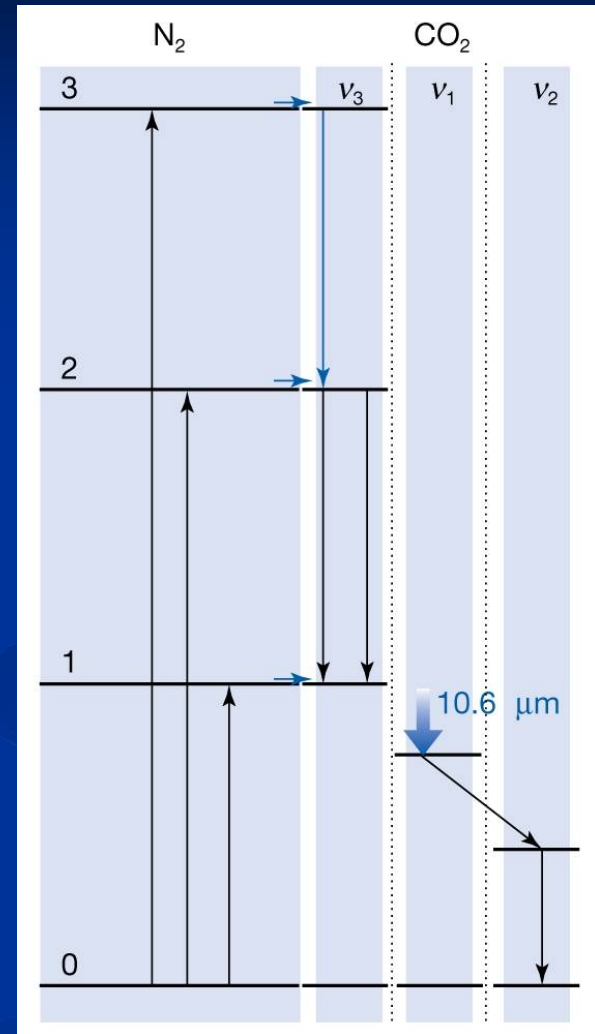
Ar^+ laser

Practical Lasers



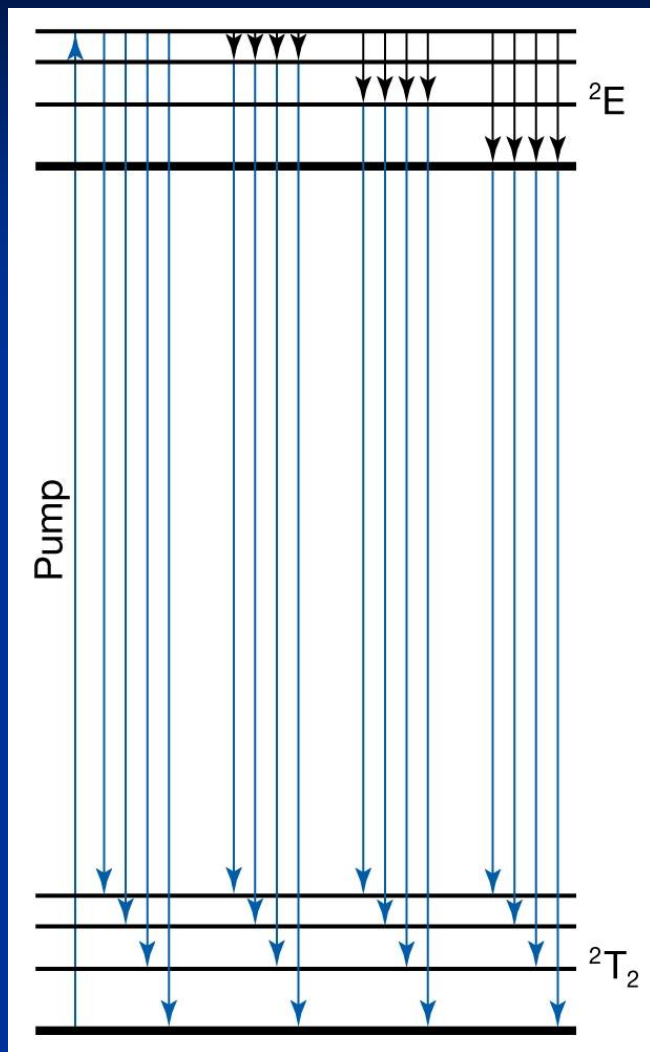
Excimer laser

Active media: XeCl, ArF, ArCl, etc.

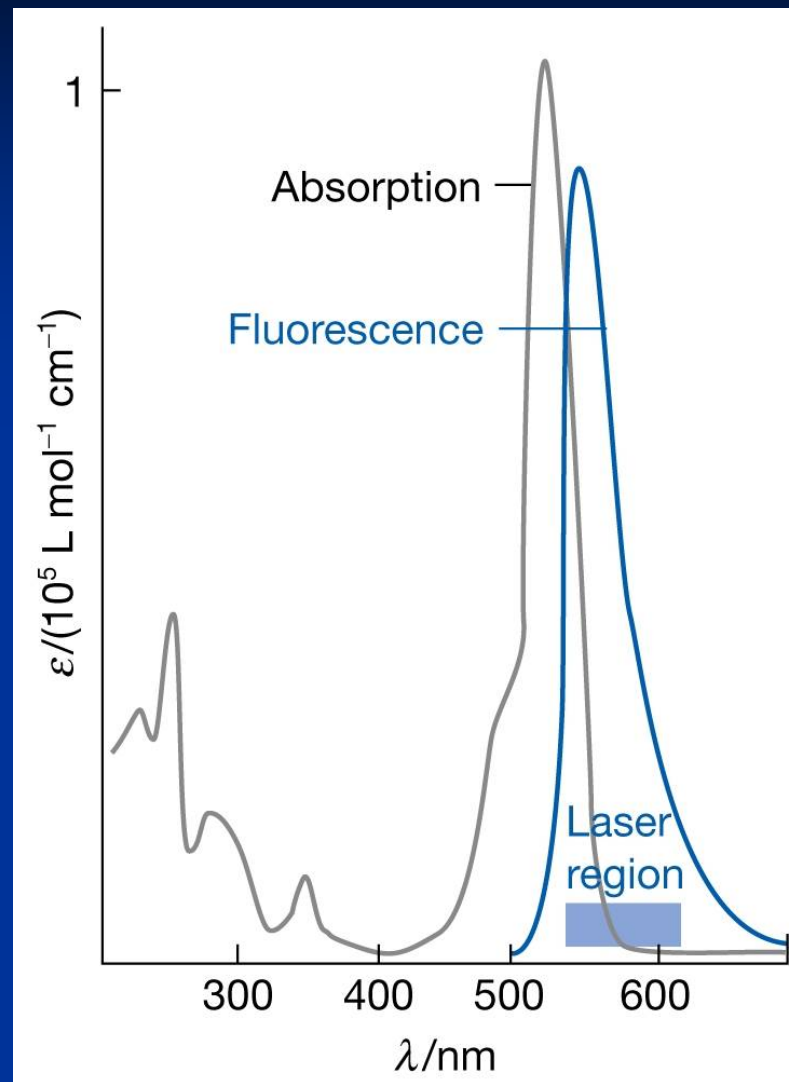


CO₂ laser

Practical Lasers

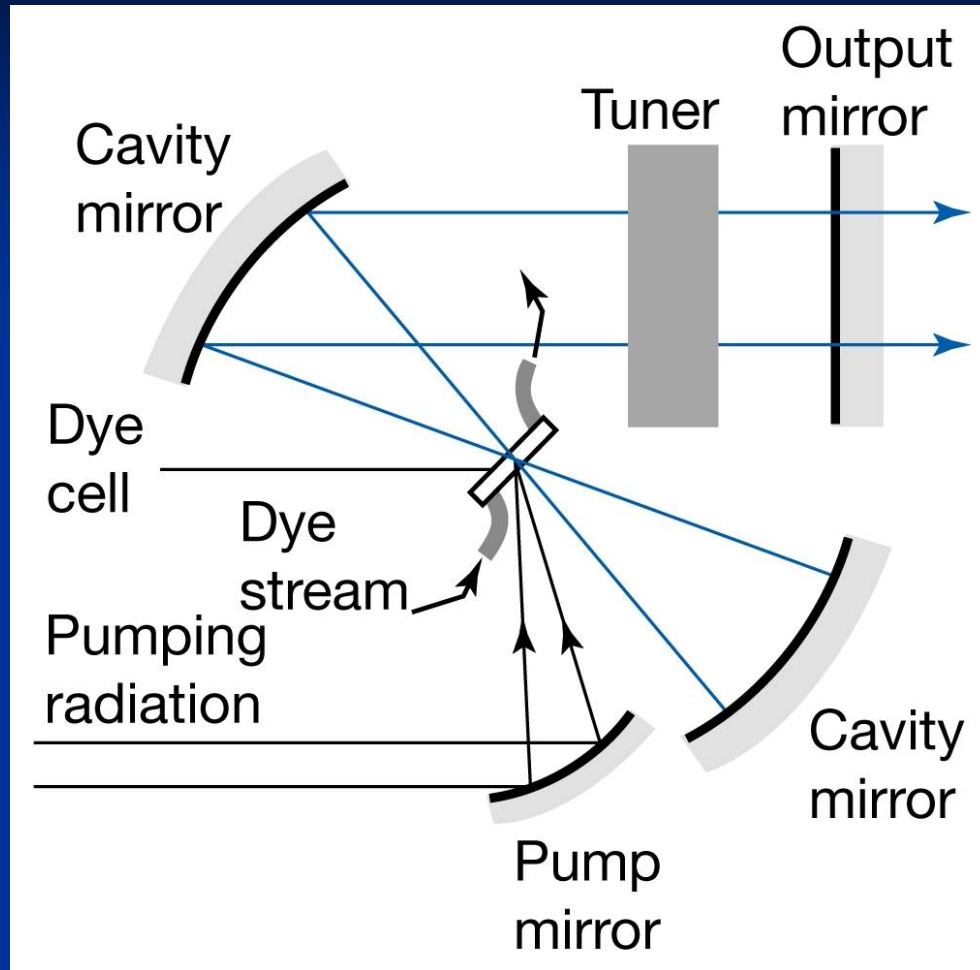


Titanium Sapphire laser,
 Ti^{3+} ions in sapphire (Al_2O_3)



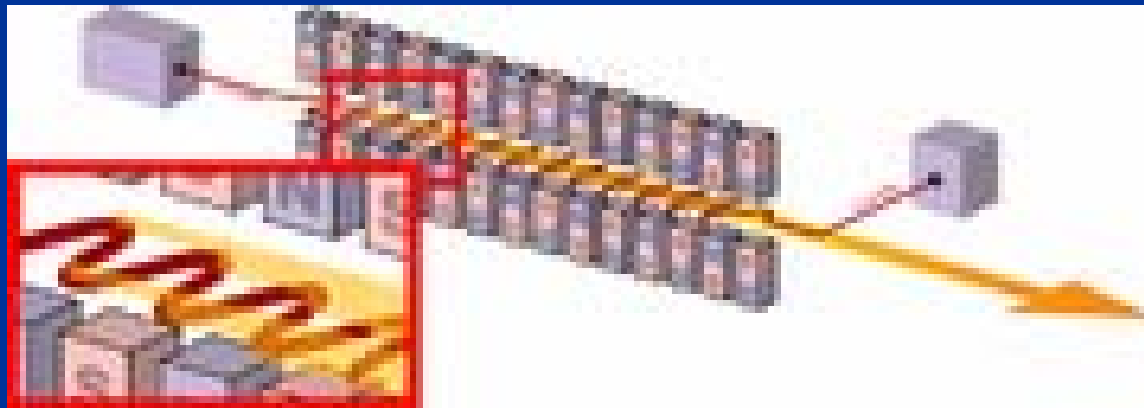
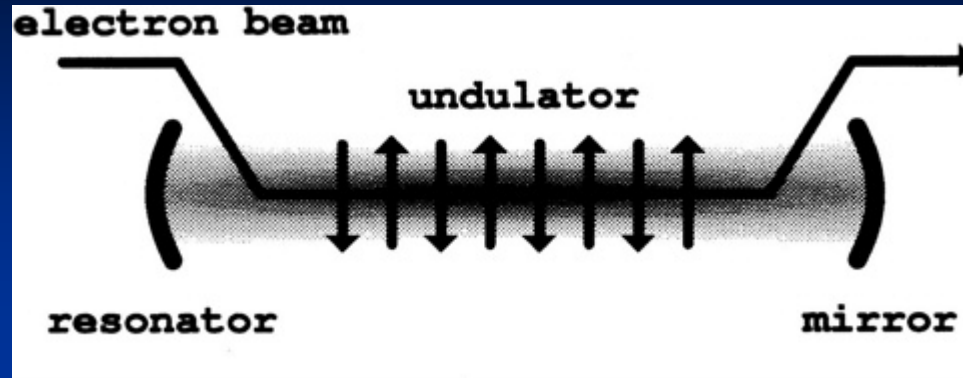
Dye laser

Practical Lasers



Typical construction of the dye laser

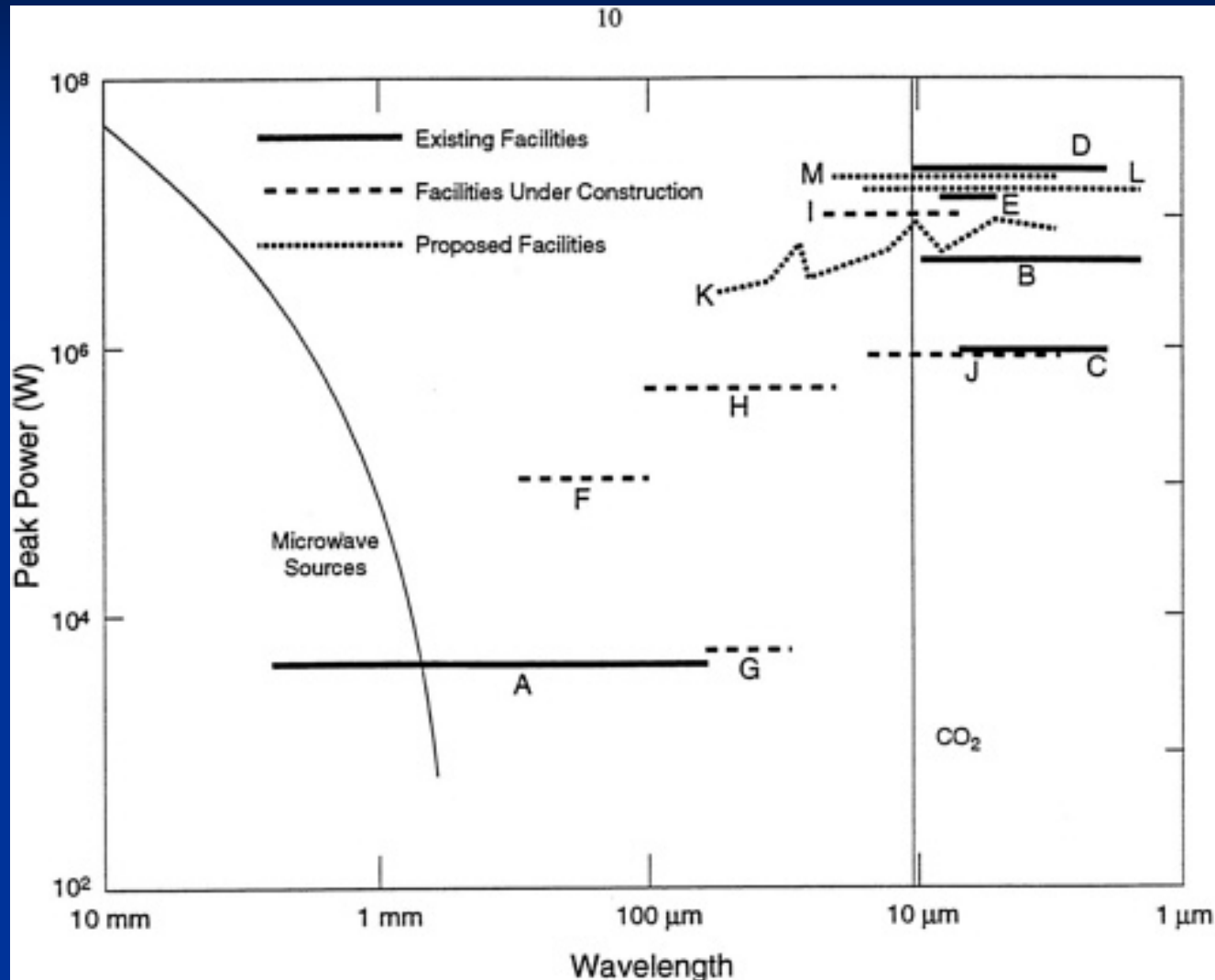
Free Electron Laser (FEL)



Free Electron Lasers were invented in 1971. Unlike all other lasers, they explore a flux of relativistic electrons as an active medium. The advantage of FEL is that they have the most wide spectral tuning band, from the microwave spectral range ($\lambda \sim 1 \text{ mm}$) and up to the X-rays spectral range ($\lambda \sim 1 \text{ nm}$). The electron energy ranges from 10 MeV to 10 GeV

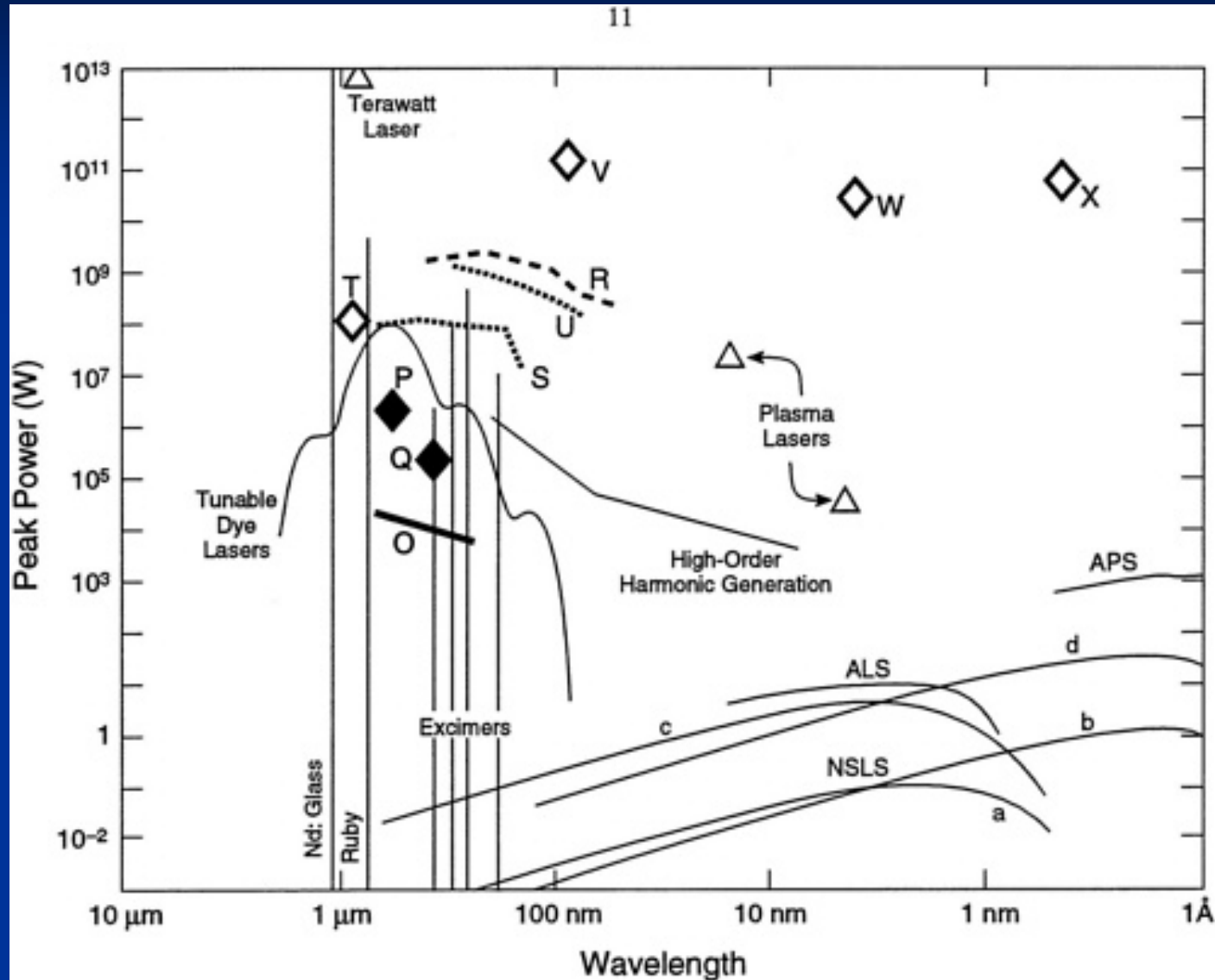
Various types of Free Electron Lasers

IR spectral range $\lambda = 1000 \mu\text{m} - 1 \mu\text{m}$



Various types of Free Electron Lasers

Near-IR, visible, and UV spectral ranges $\lambda = 1 \mu\text{m} - 200 \text{ nm}$



Various types of Free Electron Lasers

VUV spectral range $\lambda = 200 \text{ nm} - 0,1 \text{ nm}$

DESY, Hamburg, Germany

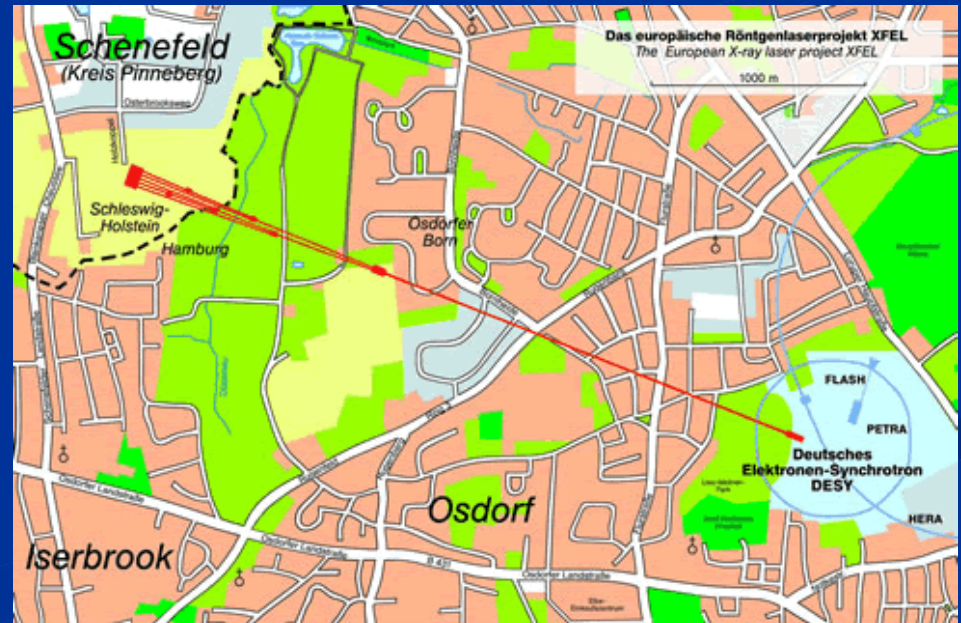
Length – 3,4 km, Cost more than 10^9 Euro,

Electron beam energy 10 - 20 GeV

Radiation line length 0,085 – 6 nm

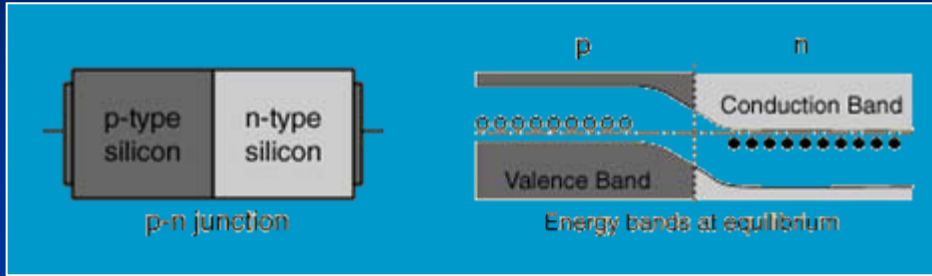
Radiation pulse duration 100 fsec

Brightness: 10^9 times more than the brightness of conventional X-rays sources



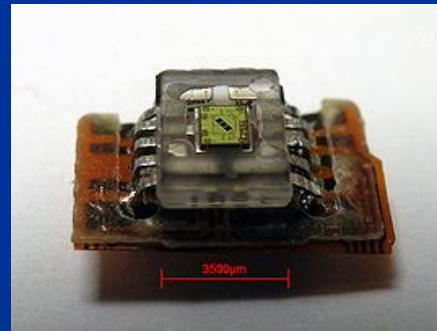
Radiation detectors: photodiodes

p-n junction

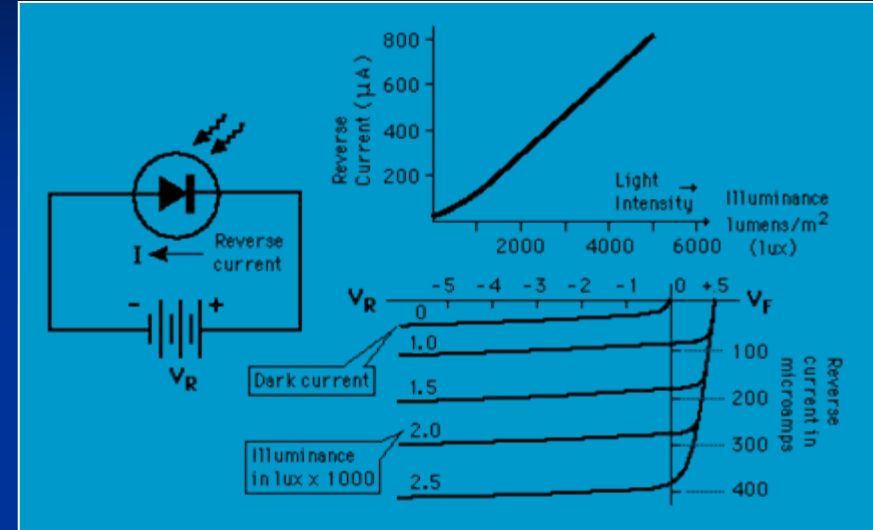


Photodiode Materials

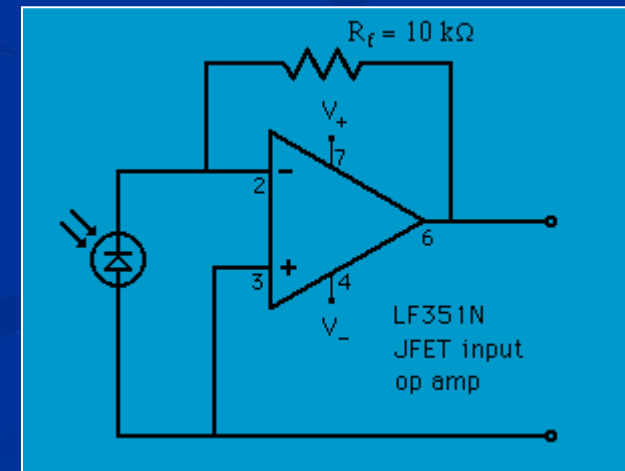
Material	Spectral range
Si	190-1100 nm
Ge	400-1700 nm
InGaAs	800-2600 nm



Operation Principle



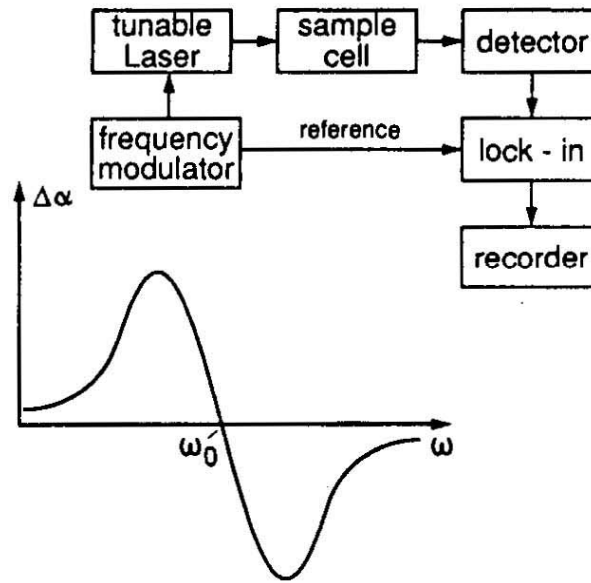
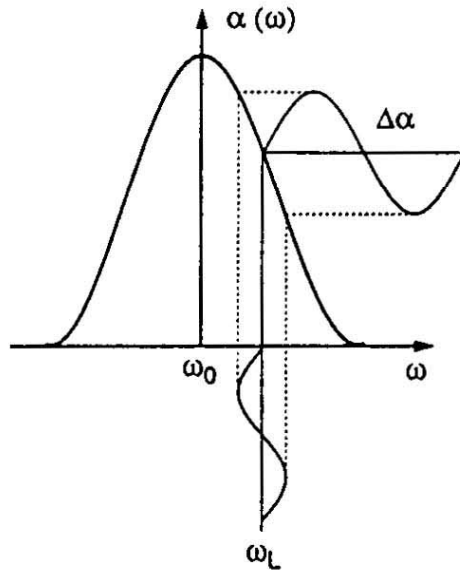
Schematic circuit



Absorption Spectroscopy with a Frequency Modulated Laser

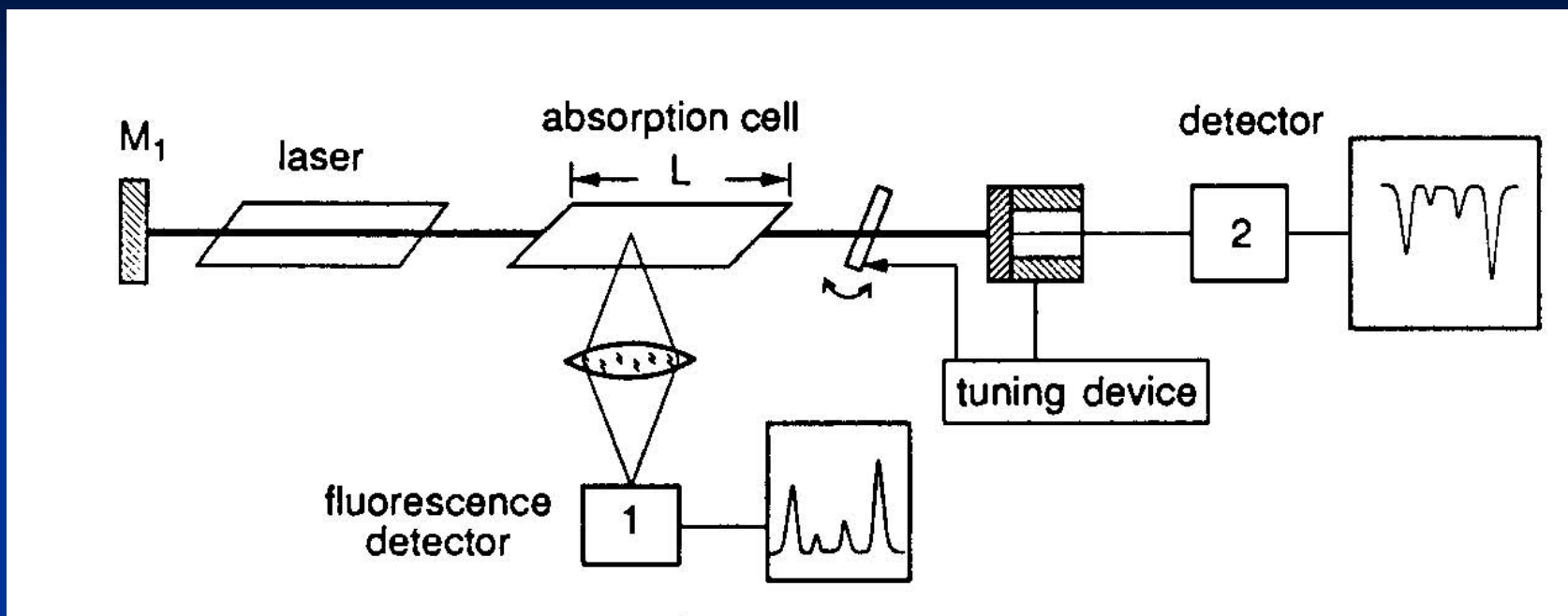
$$I(\omega) = I_0 e^{-k(\omega)l}$$

Thin optical layer: $k(\omega) = [I_0 - I(\omega)] / I(\omega)$



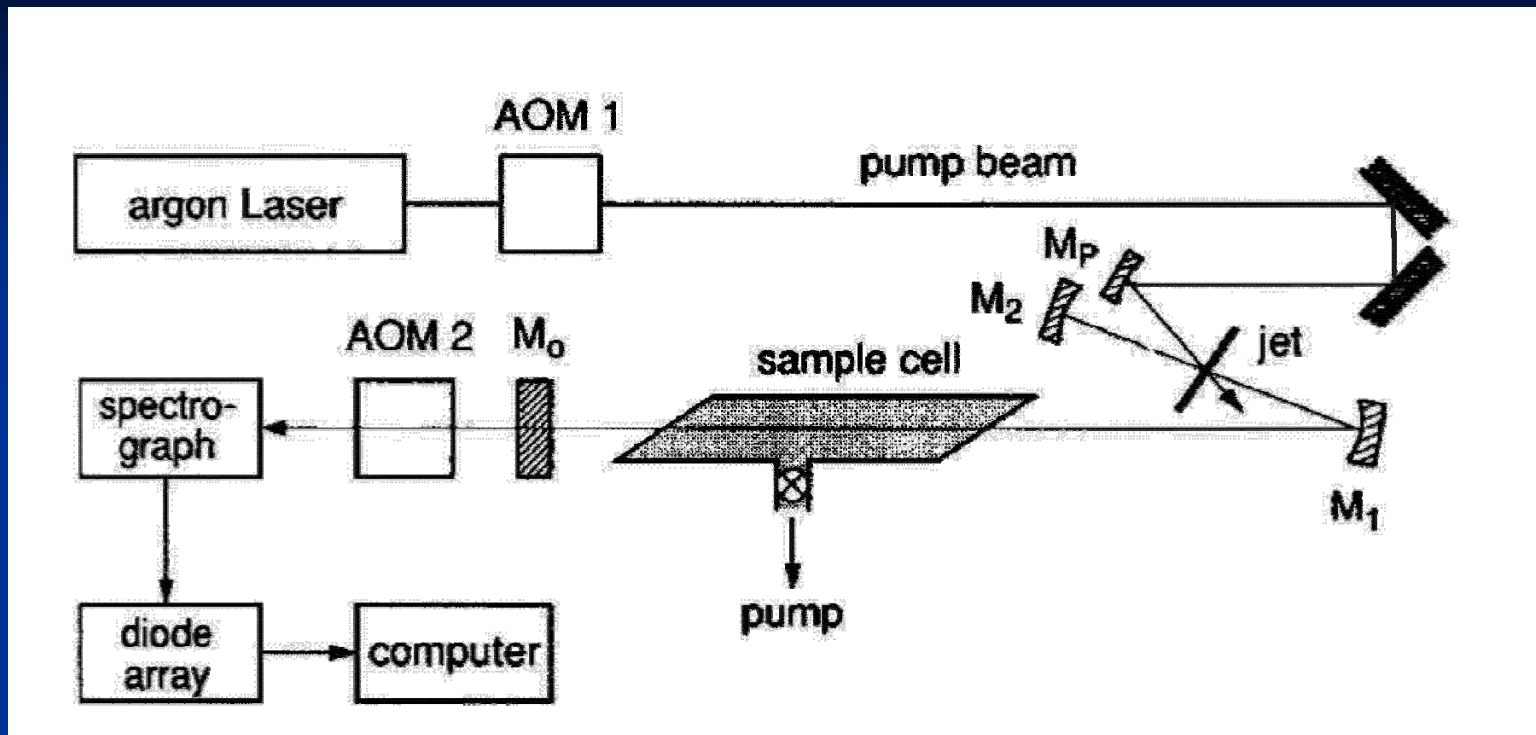
$$\frac{dk(\omega)}{d\omega} = -\frac{1}{I_0 l} \frac{dI(\omega)}{d\omega}$$

Intracavity Absorption Technique



As the photons pass the resonator many times, $q \gg 1$, the effective length of the absorbing layer also dramatically increases: $\ell = q L$. The obtained ultra-high sensitivity allows to determine either very low molecular concentration, or to excite forbidden transitions in molecules.

Cavity Ring-Down Spectroscopy



Example: a vibrational harmonic $\Delta\nu = 6$ in SH_4 can be detected with effective absorption length of 5,25 km with high spectral resolution allowing to resolve the molecular rotational structure.

Photoacoustic Spectroscopy

Allows to detect a small admixture of molecules at high pressures (other gases at atmospheric pressure).

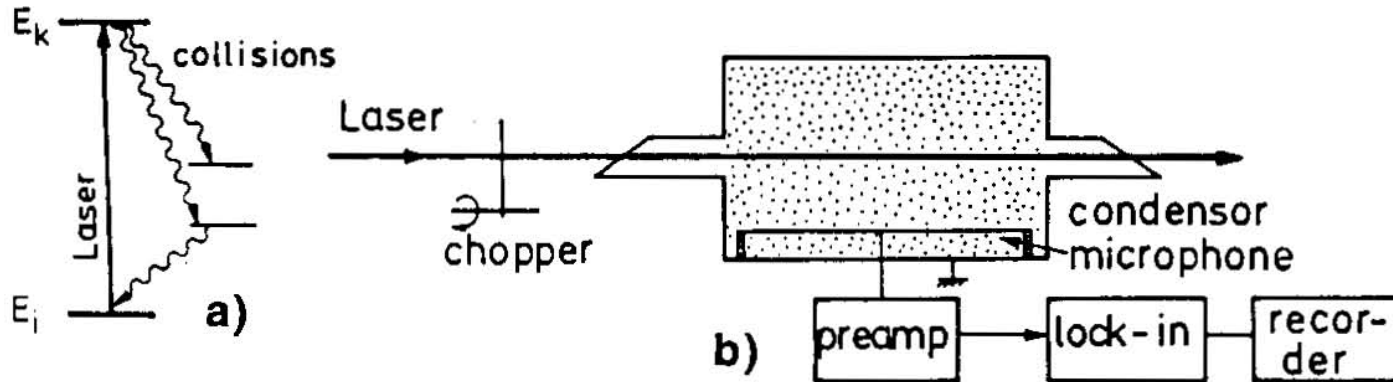


Fig.6.13. Photoacoustic spectroscopy (a) level scheme (b) schematic experimental arrangement

Amplitude modulation ($f \sim 20$ KHz) of the output of an IR laser produces the sound oscillations in the cell which are detected by a sensitive microphone.

$$S \propto \Delta W = N_i \sigma_{ik} l (1 - \eta_k) P_L \Delta t$$

Photoacoustic Spectroscopy: C₂H₂

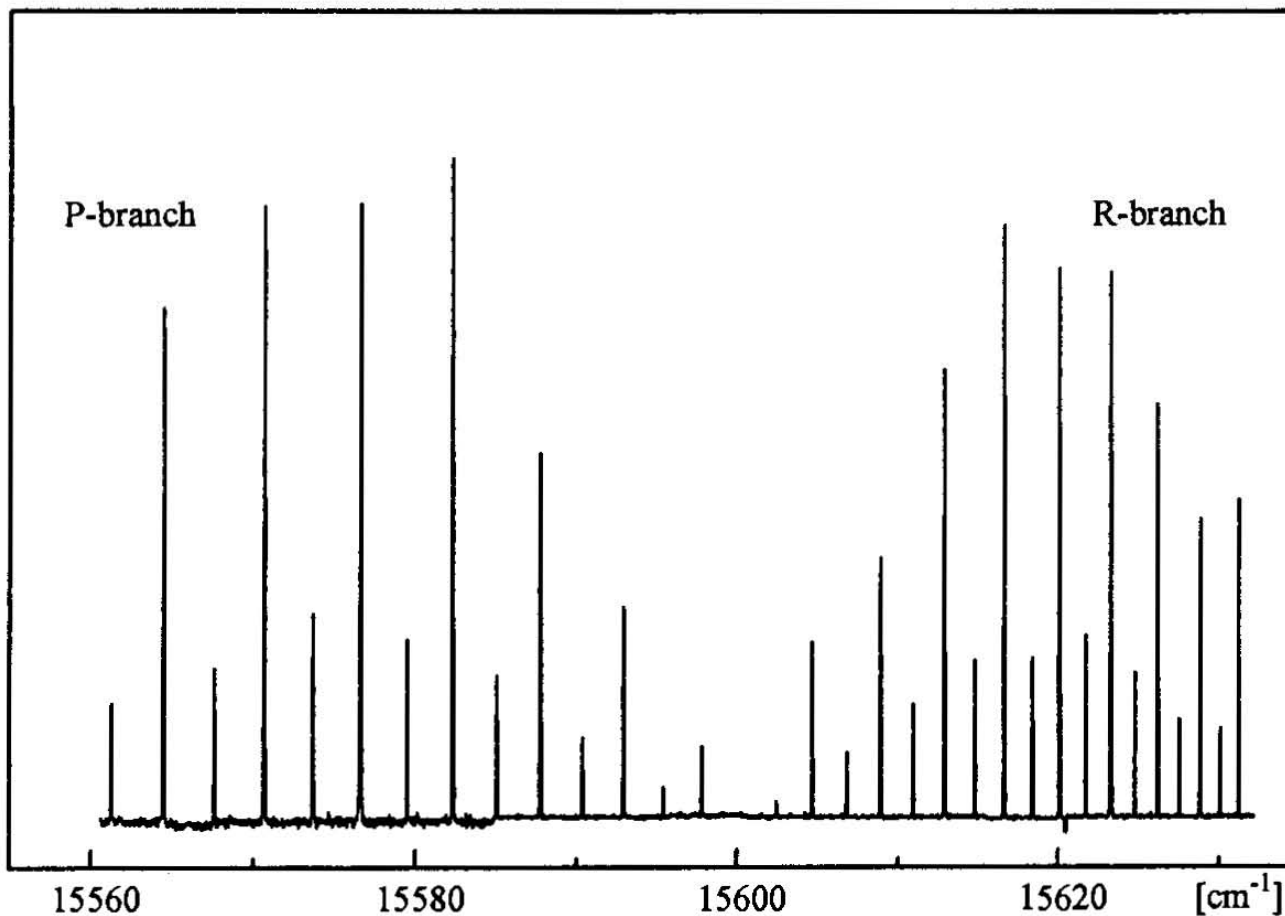


Fig.6.15. Optoacoustic overtone absorption spectrum of acetylene around $\bar{\nu} = 15600$ cm⁻¹ corresponding to the excitation of a local mode by 5 quanta vibrations [6.45]

Laser Induced Fluorescence (LIF)

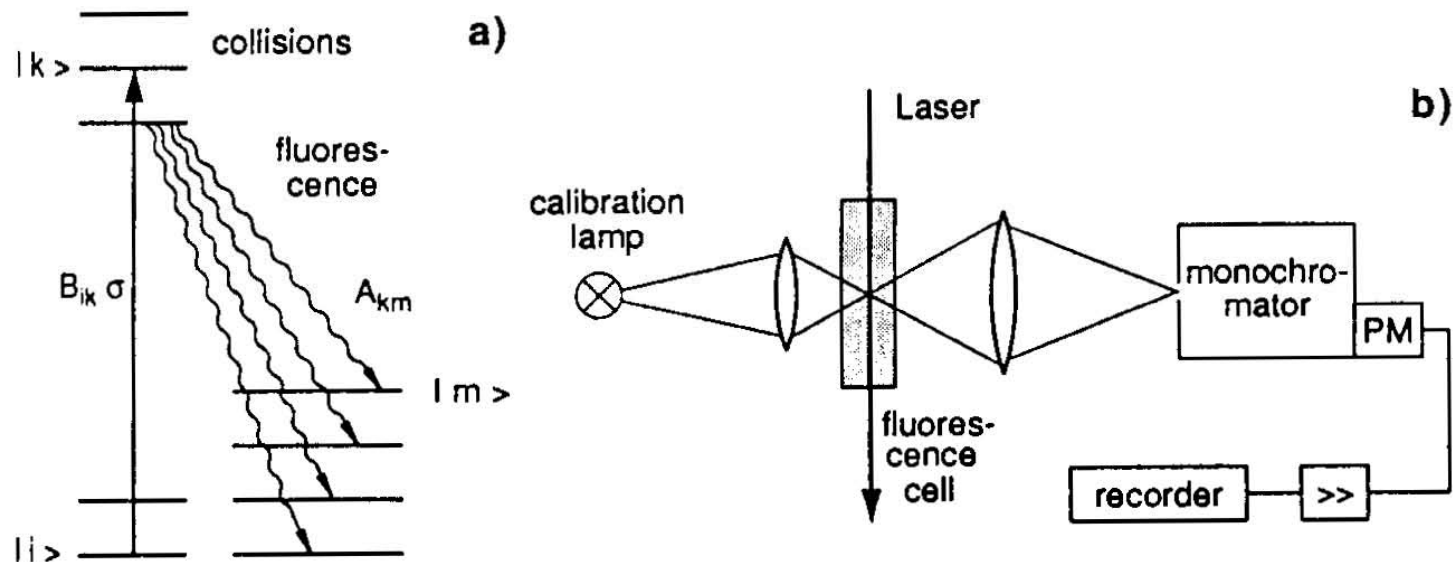


Fig.6.33a,b. Laser-induced fluorescence: (a) Level scheme and (b) experimental arrangement for measuring LIF spectra

Laser Induced Fluorescence: Na₂

B¹Π_u

X¹Σ_g

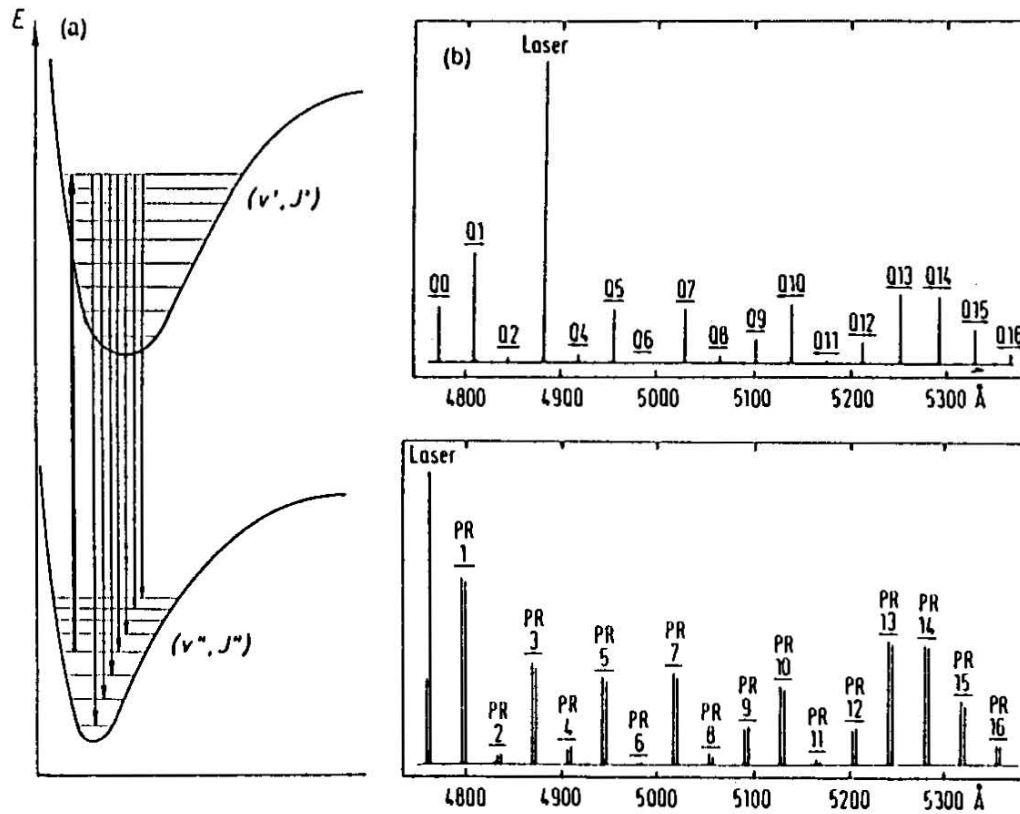
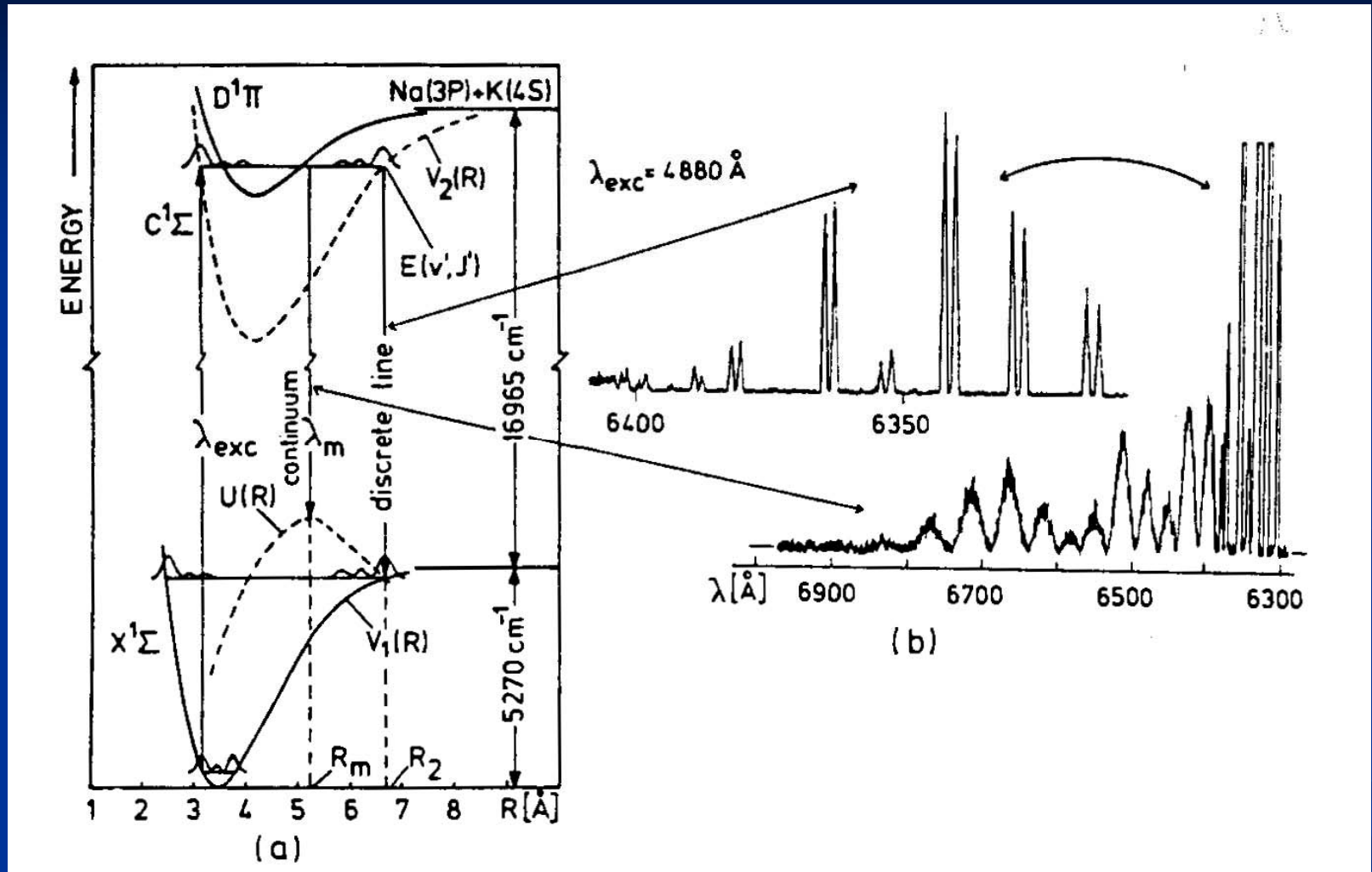


Fig.6.34. Laser-induced fluorescence of the Na₂ molecule excited by argon laser lines (a) term diagram (b) fluorescence lines with $\Delta J = 0$ (Q-lines) emitted from the upper level ($v'=3, J'=43$) of the B¹Π_u state, excited at $\lambda = 488$ nm. (c) P and R doublets, emitted from the upper level ($v'=6, J'=27$)

Advantage: very high selectivity. 488 nm line excites a positive Λ component of the $v' = 6, J' = 43$ which emits only Q lines. 476,5 nm line excites a negative Λ component of the $v' = 6, J' = 27$ level which emits P and R lines.

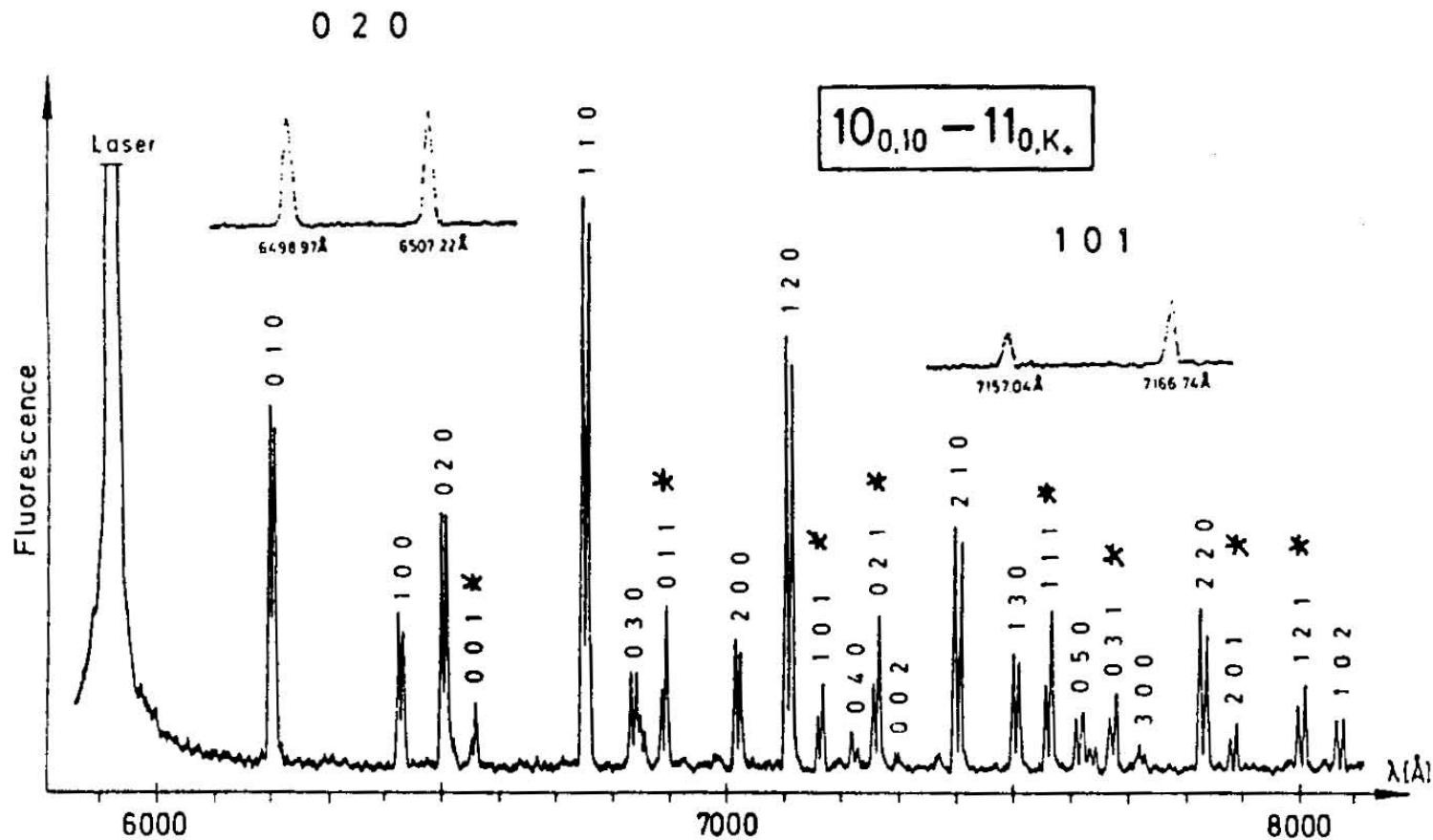
Laser Induced Fluorescence: NaK

Transitions between high vibrational levels of two bound states.



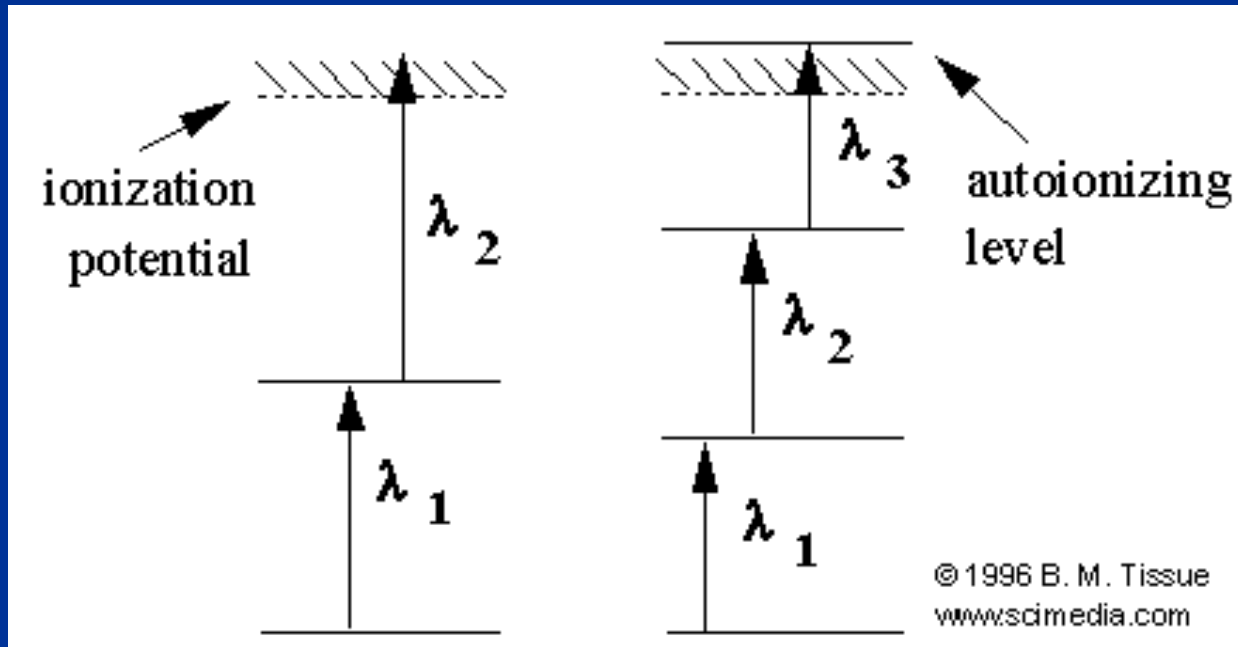
The line intensities are proportional to the values of the **Franck-Condon integrals** and allow the determination of one of the potential curves if the other is known.

Laser Induced Fluorescence: NO₂



Ionization Spectroscopy

Absorption of photons on the molecular transition $E_i \rightarrow E_k$ is monitored by detection of the ions or electrons, produced by some means from the molecular excited state E_k . The ionization of the excited molecule may be performed by photons, by collisions, or by an external electric, or magnetic field.

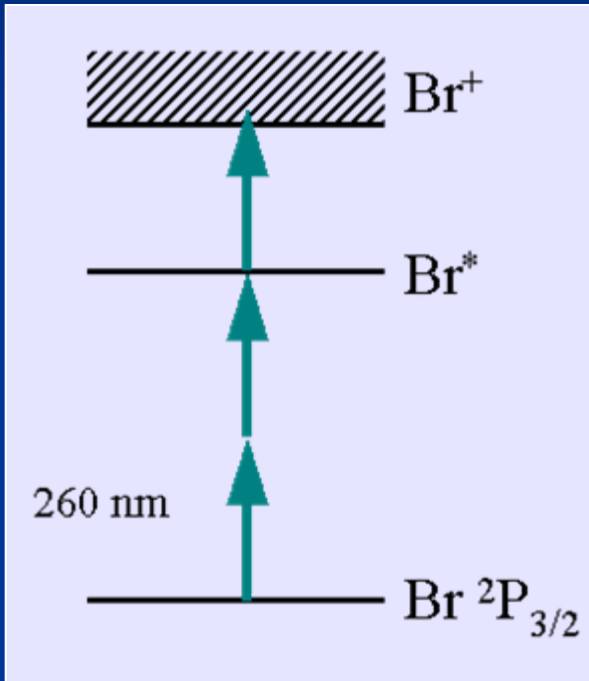


The ionization methods used in molecular spectroscopy and particularly, for determination of the internal-state distribution in reaction products of chemical reactions are in general called resonance-enhanced multiphoton ionization (**REMPI**).

REMPI 2+1

The probability of two-photon excitation is given by the expression:

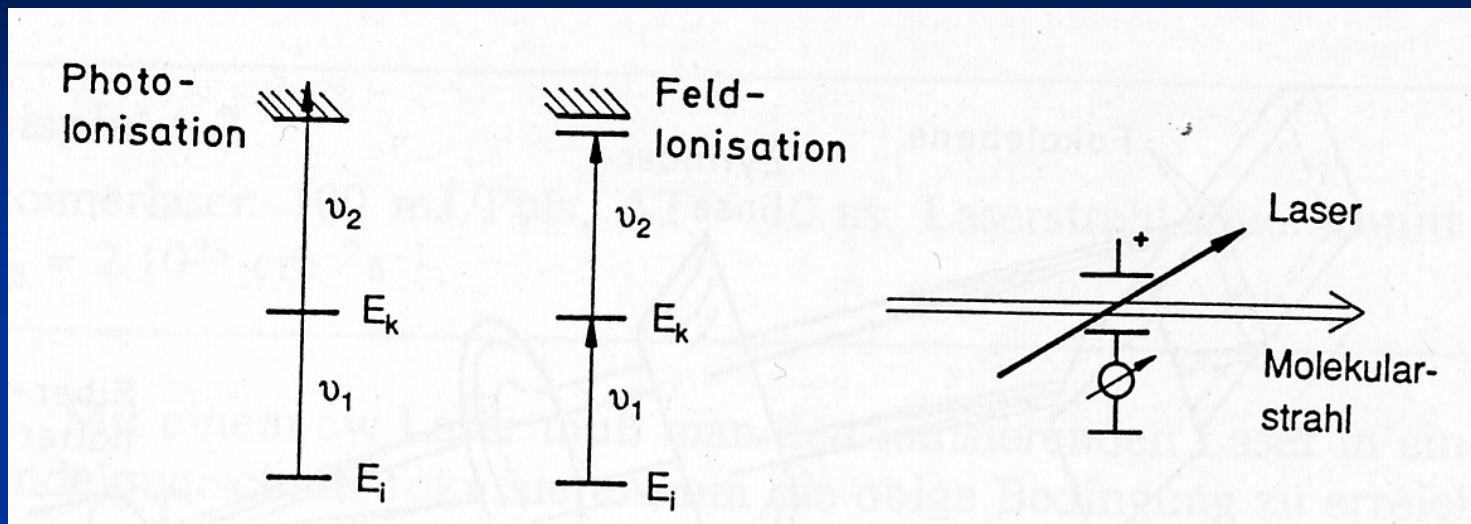
$$W(2ph) = C_2 \sum_{e,i,i',g} \frac{\langle e|\mu|i\rangle^* \langle i|\mu|g\rangle^* \langle e|\mu|i'\rangle \langle i'|\mu|g\rangle}{(\omega_{ig} - \omega + i\Gamma_i/2)(\omega_{ig} - \omega - i\Gamma_i/2)}$$



Where ω is the light frequency, Γ_i is the the intermediate state spontaneous radiation rate, and constant C_2 depends on the **square** of the light intensity, I^2 .

Note that the probability of a **two-photon transition** is usually several orders of magnitude smaller that the probability of a **one-photon transition** due to the large denominator. Therefore, in order to obtain sufficient intensity of the transition, one usually has to **focus the laser beam** down to a diameter of $d = 1 \dots 0.1$ mm.

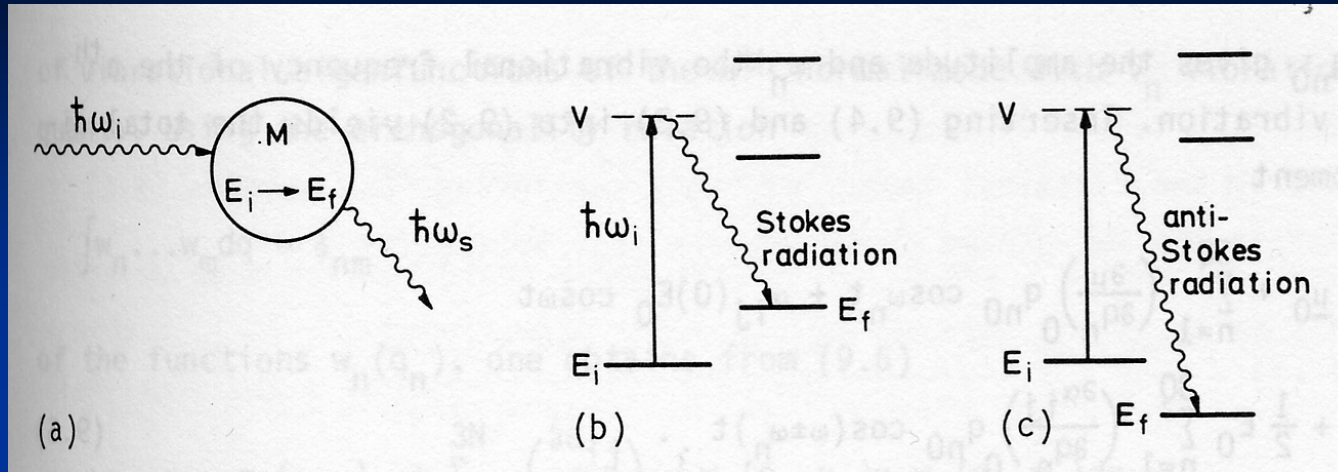
Rydberg State Ionization



A very efficient photoionization process is the excitation of high-lying Rydberg energy levels of atoms, or molecules in the vicinity of the ionization limit which then decay by themselves (this process is called **autoionization**), or by applying an external electric field (this process is called **field ionization**):



Raman Laser Spectroscopy



The necessary condition for a rotational Raman transitions is that the molecule must have **anisotropic polarizability**. This means that the molecule can acquire an **induced dipole moment** under the influence of an external laser electric field E :

$$\mu_{in} = \alpha E$$

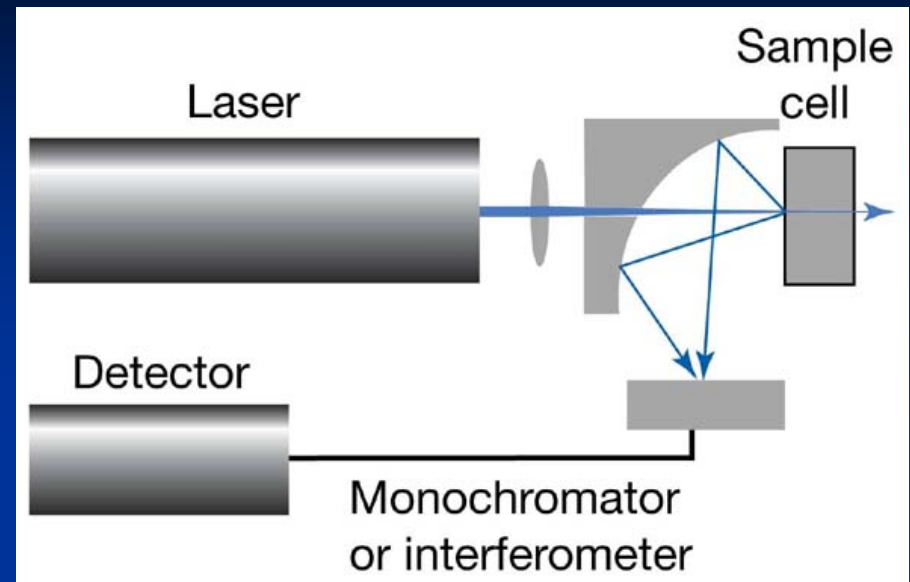
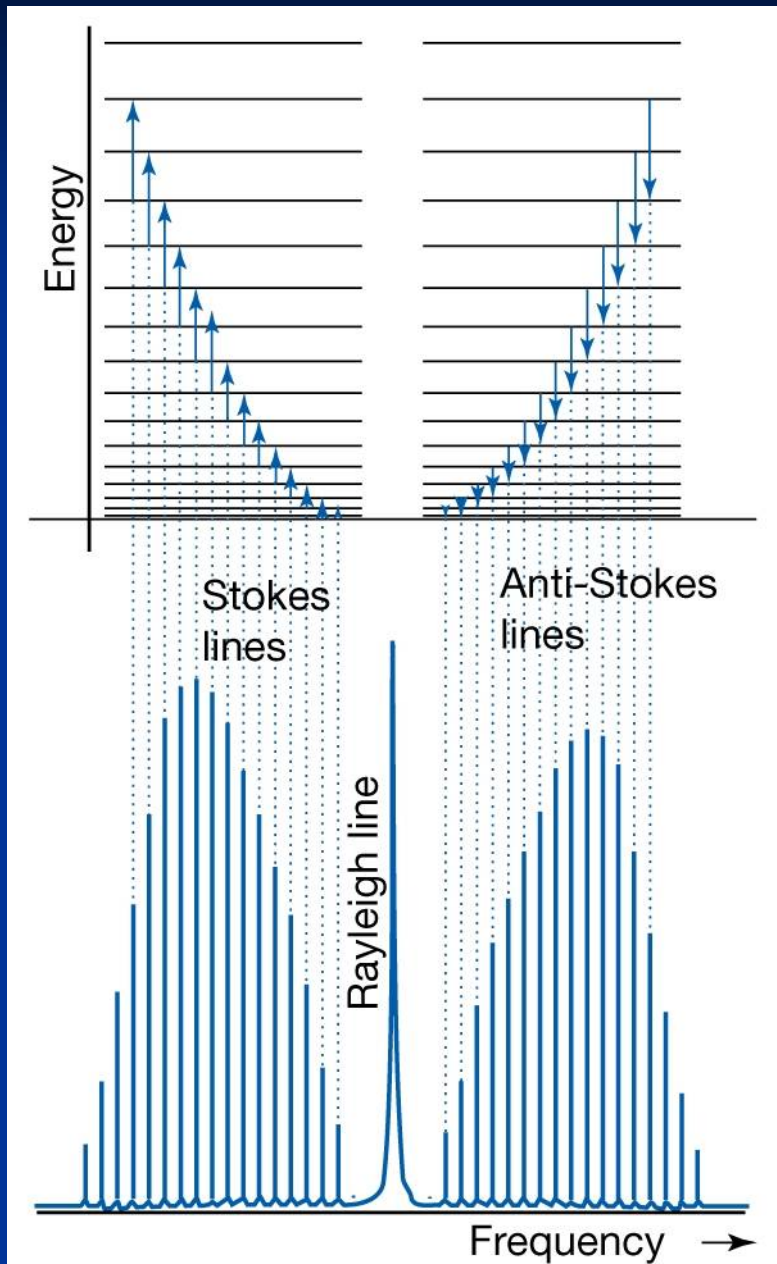
Most of the molecules, including all diatomic (both homonuclear and heteronuclear) have anisotropic polarizability, and so they are **rotationally Raman active**. The rotational Raman selection rules are:

Linear rotors: $\Delta J = 0, \pm 2$.

Symmetric rotors: $\Delta J = 0, \pm 1, \pm 2$; $\Delta K = 0$.

In addition, the $\Delta J = 0$ transition does not lead to any shift of the scattered photon frequency and contribute to the unshifted Rayleigh radiation.

Rotational Raman Spectroscopy



Rotational Raman Spectroscopy: C₂N₂

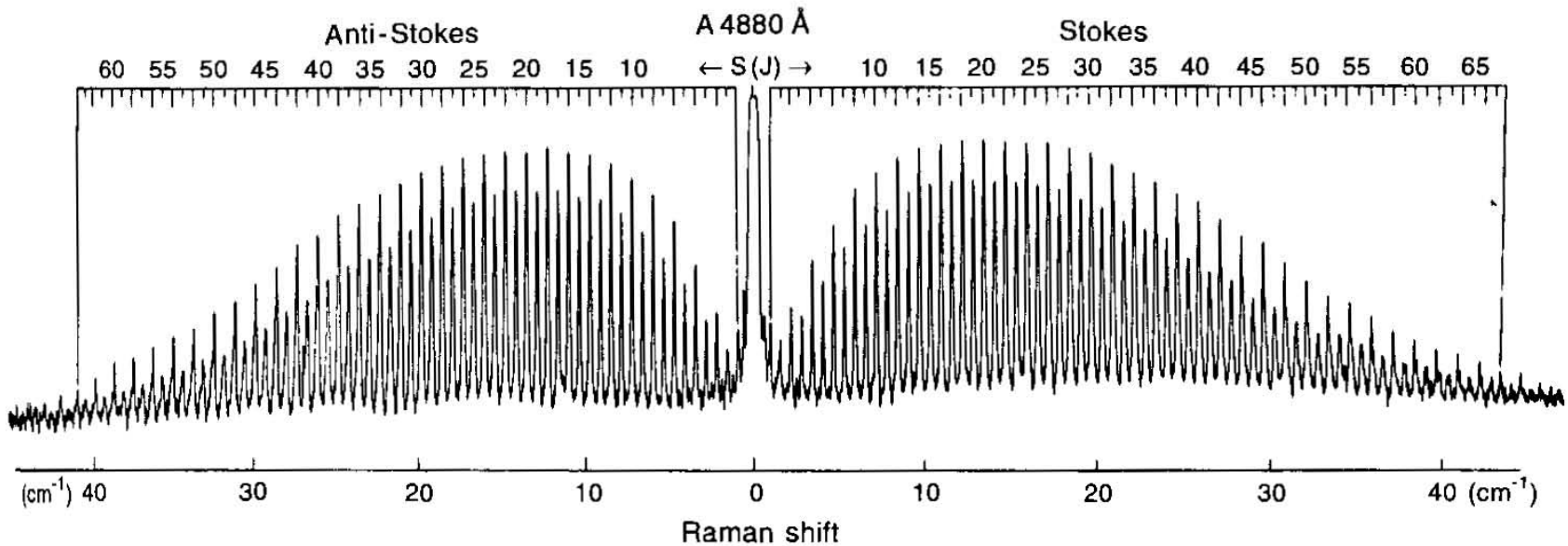
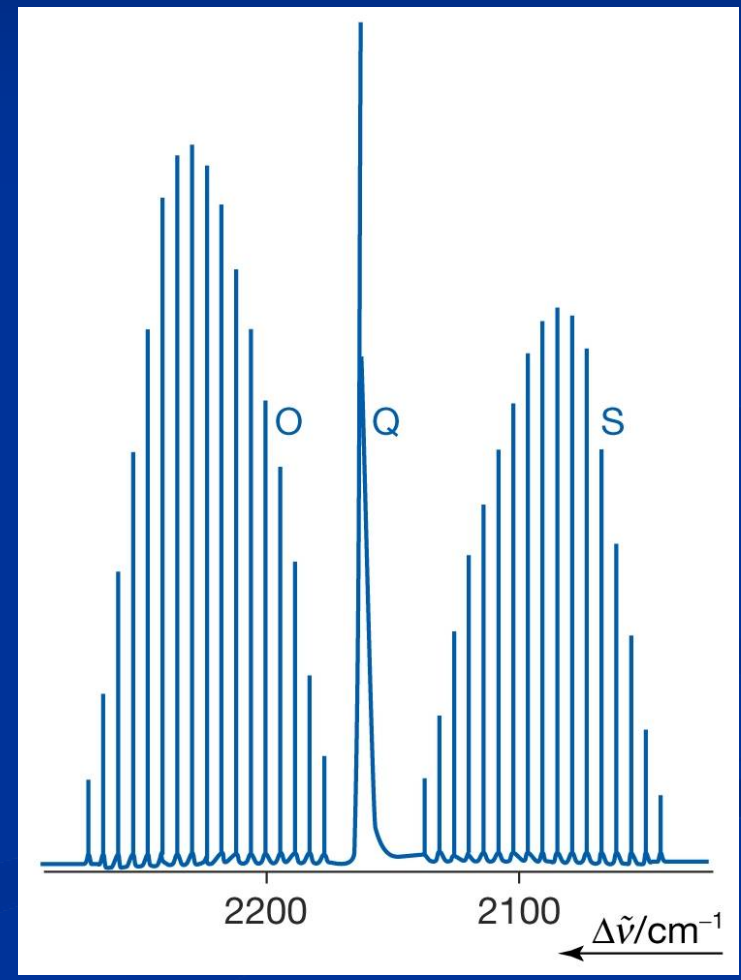
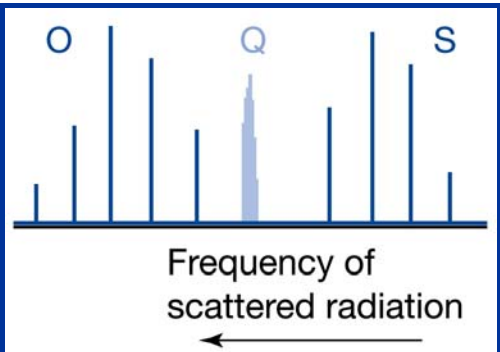
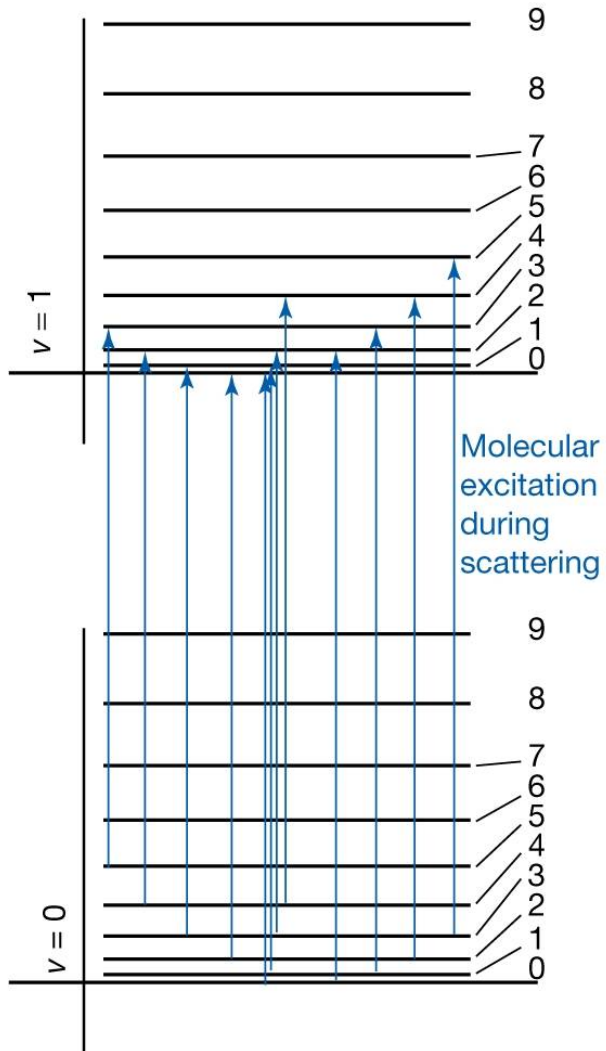


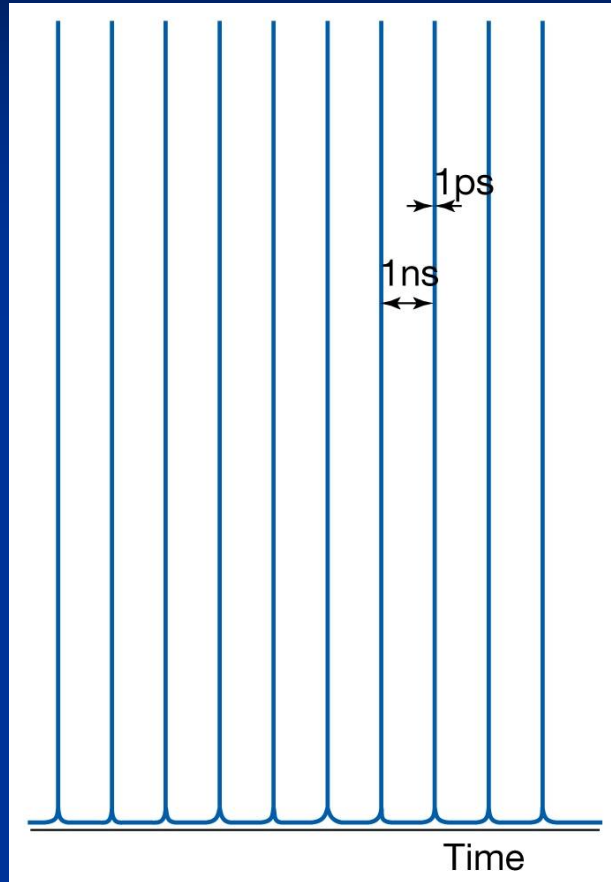
Fig.8.3. Rotational Raman spectrum of C₂N₂ excited with the 488 nm line of the argon laser in the experimental setup of Fig.8.2 and recorded on a photographic plate with 10 min exposure time [8.20]

The general disadvantage of the Raman spectroscopy is the very small scattering cross section which is about $\sigma_{sc} \sim 10^{-30} \text{cm}^2$. Therefore, the sensitivity of the method is not very high and the typical experimental problem is the detection of a weak signal in the presence of an intense background radiation.

Vibrational Raman Spectroscopy: CO



Ultra Short Laser Pulses: Mode locking



The technique can produce pulses of picosecond duration and less. It can be accomplished using the optical Kerr effect.

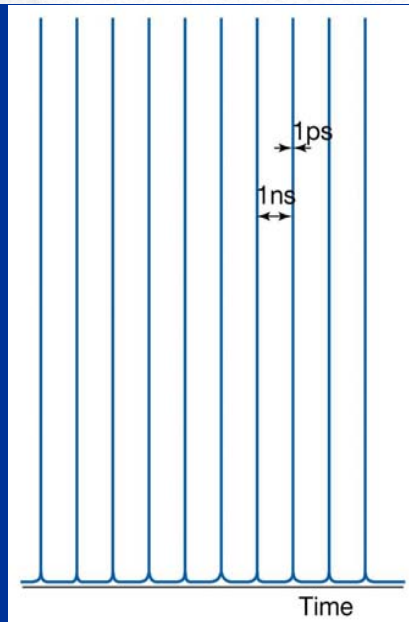
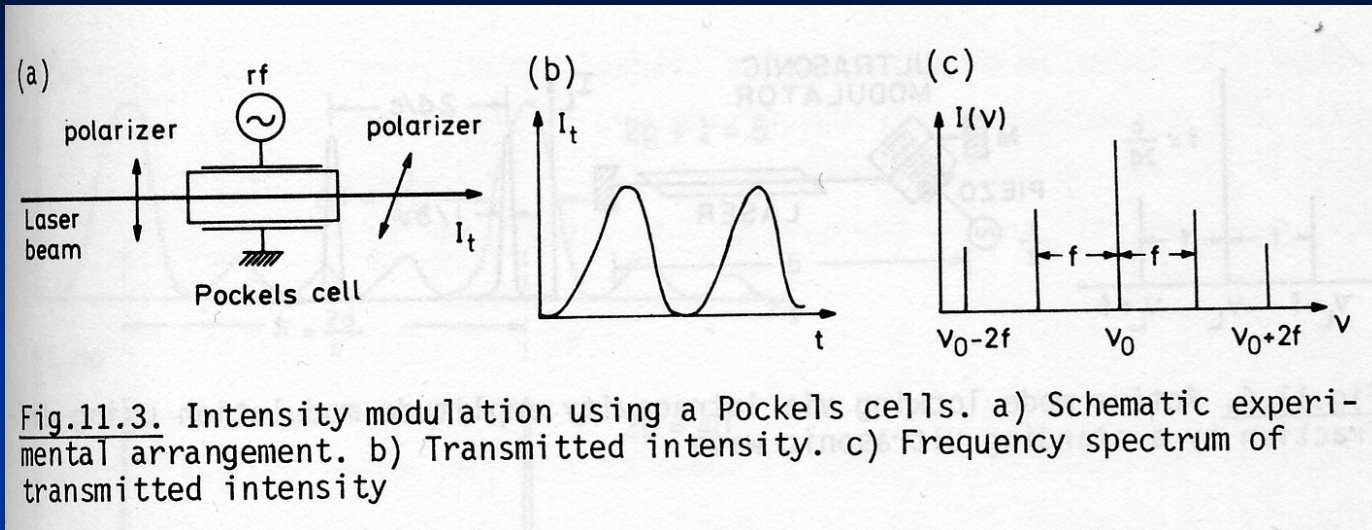
$$E_n(t) = E_0 e^{2\pi i(\nu + \frac{nc}{2L})t}$$

$$\begin{aligned} E(t) &= \sum_n E_n(t) = E_0 e^{2\pi i\nu t} \sum_{n=0}^{n=N-1} e^{i\pi nct/L} = \\ &= E_0 e^{2\pi i\nu t} \frac{\sin(N\pi ct / 2L)}{\sin(\pi ct / 2L)} e^{(N-1)i\pi ct / 2L} \end{aligned}$$

$$I \propto E^* E = E_0^2 \frac{\sin^2(N\pi ct / 2L)}{\sin^2(\pi ct / 2L)}$$

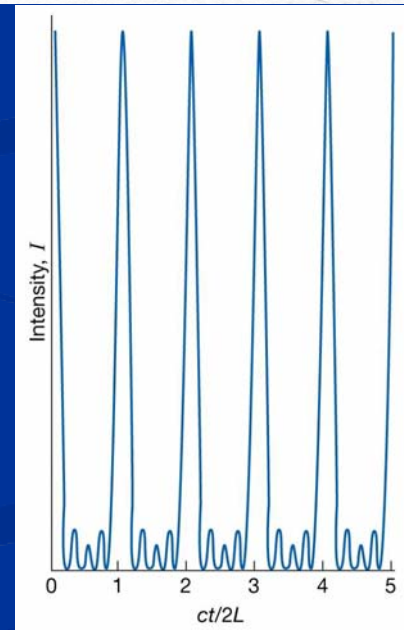
If $N = 1000$, then $\tau = 4$ ps

Ultra Short Laser Pulses: mode locking



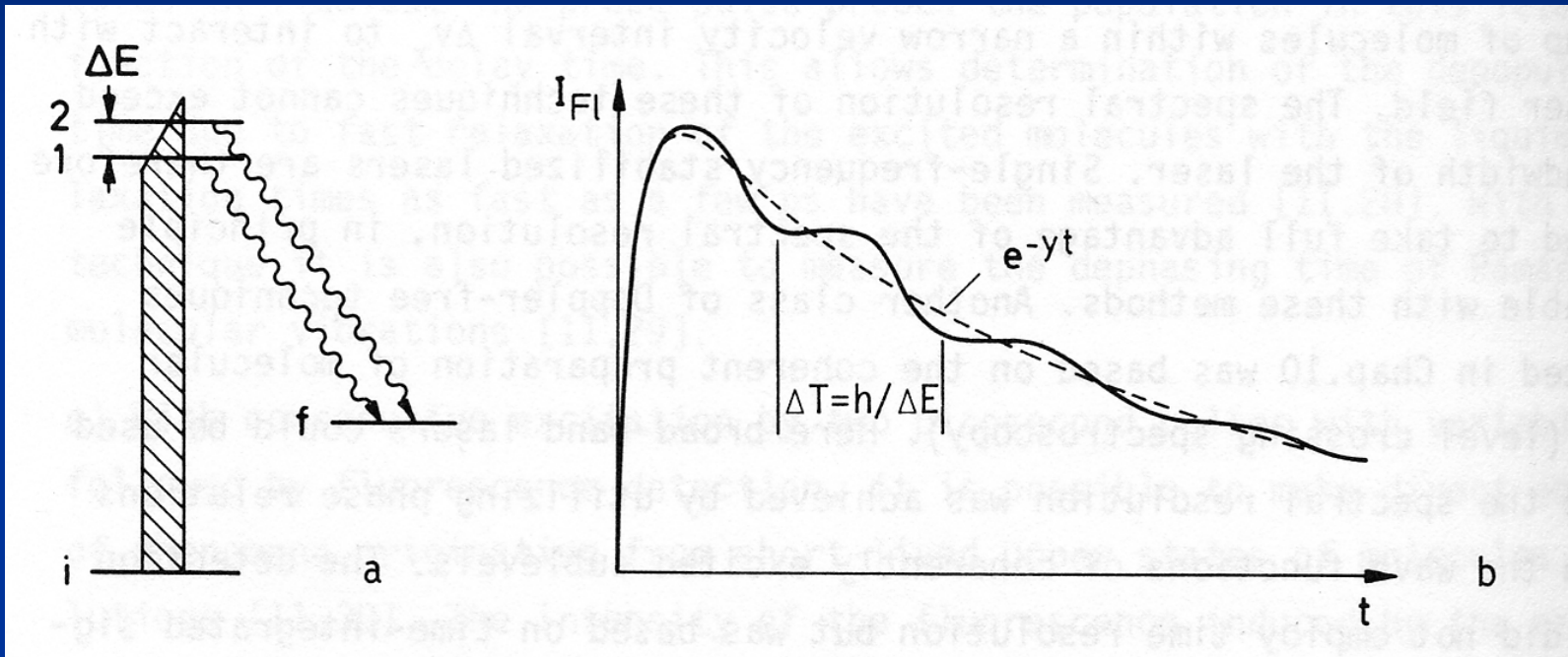
$$2p=50$$

Time scale



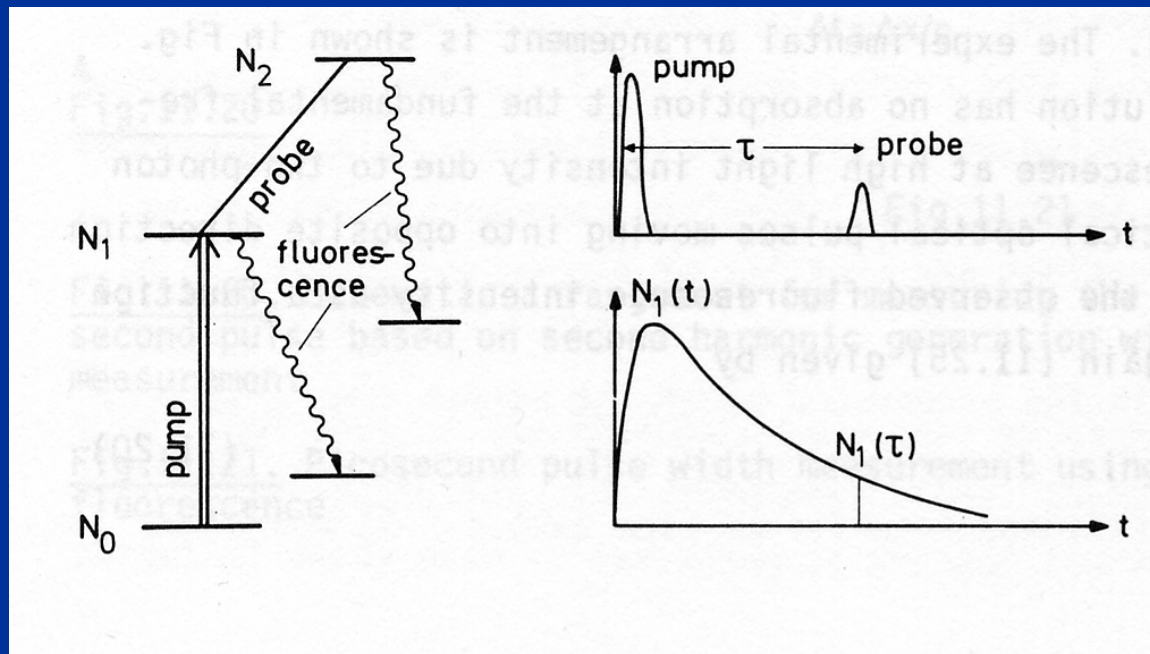
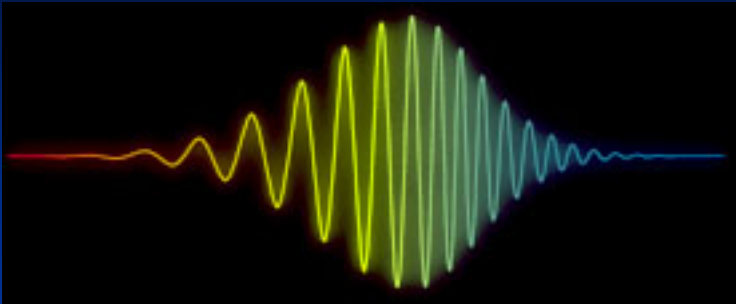
$$2p+1=5$$

Quantum Beat Spectroscopy



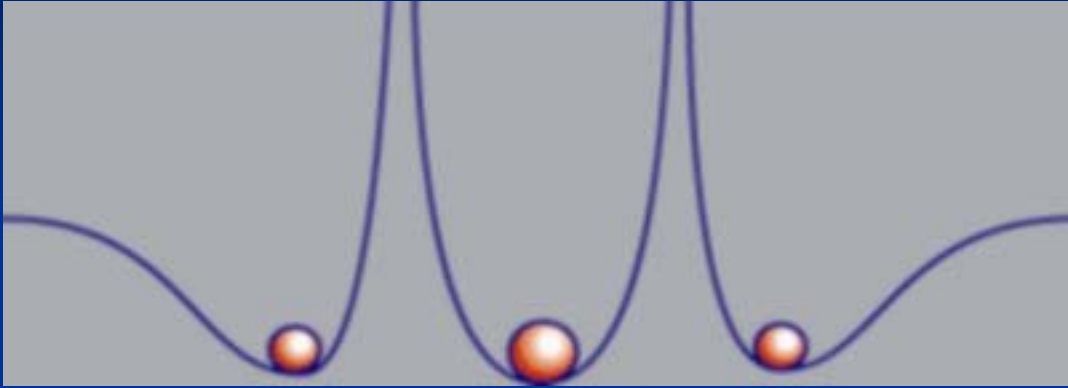
Femto-Second Laser Spectroscopy

1999 Nobel Prize
Ahmed Zewail

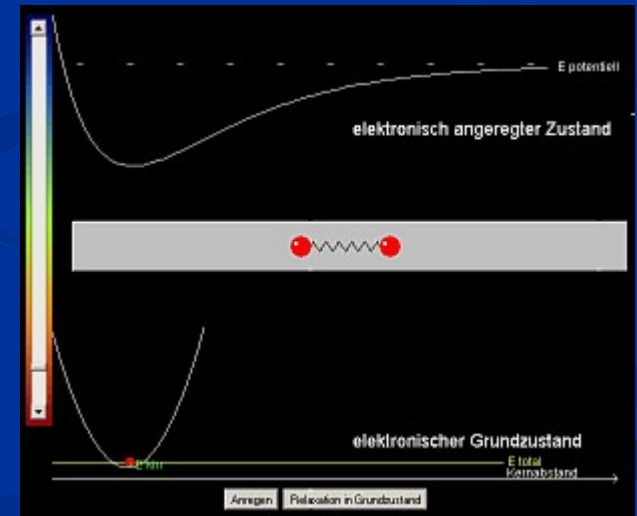


Pump-and-probe Technique

Femto-Second Laser Spectroscopy



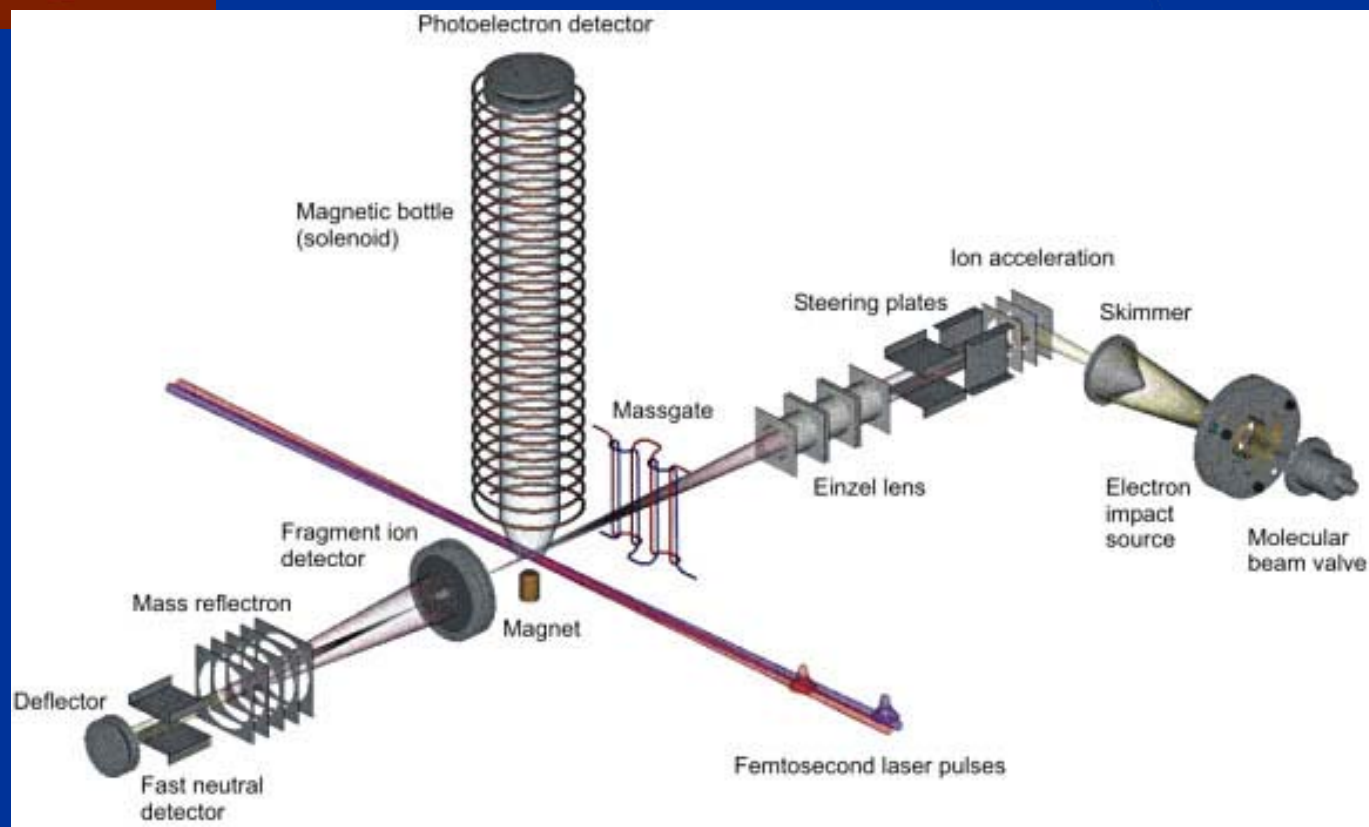
H₂O



Pump-and-probe technique

Spectroscopy of size-selected molecular clusters: $(O_n)^-$

Ahmed Zewail Lab



Spectroscopy of size-selected molecular clusters

