Laser Detection Techniques

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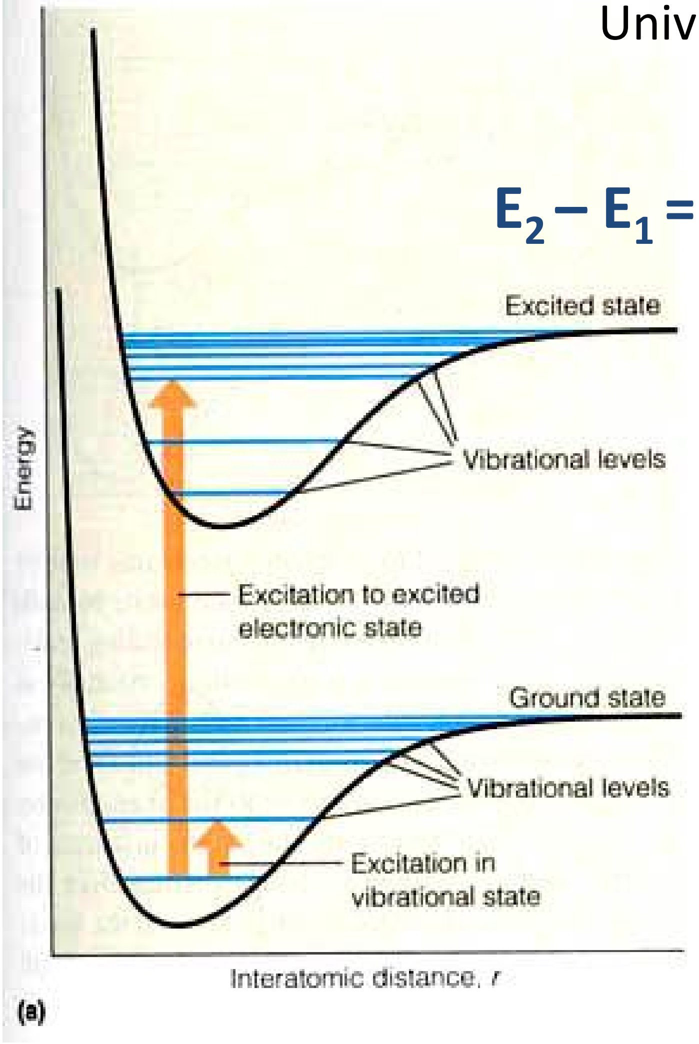
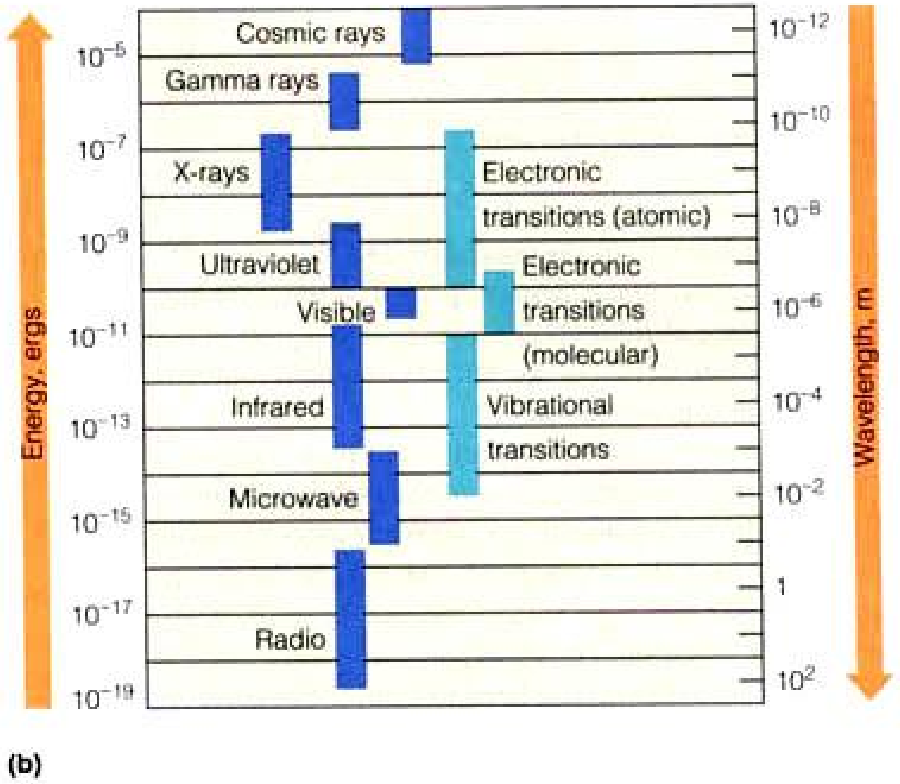
$E_2 - E_1 = hn, \quad \lambda = {}^{c}/_{n}$





Lambert-Beer Law

Transmittance of the sample::

$$T = I / I_0 \qquad T = e^{-s N l} = e^{-\alpha},$$

where s [cm^2] is an absorption cross section, N[cm^{-3}] is a concentration, and *l* [cm] is a sample length**.**

The form which widely used in laboratory practice:

$$T = 10^{-ecl},$$

where e [L mol^{-1} cm^{-1}] is the extinction coefficient
and c [mol L^{-1}] is the molar concentration:

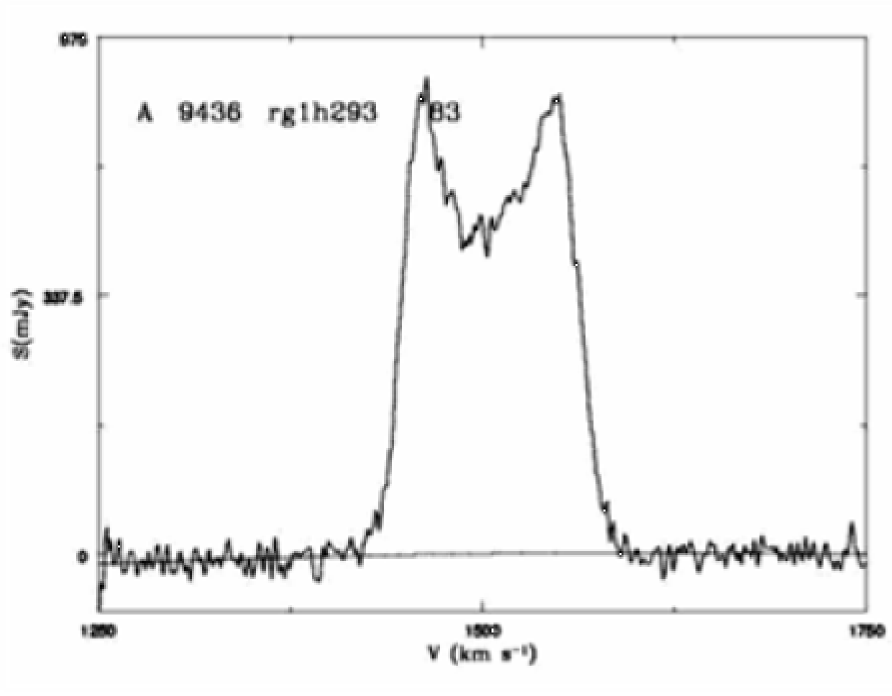
$$C = \frac{Number\ of\ molecules}{N_A V} = \frac{N}{N_A}$$

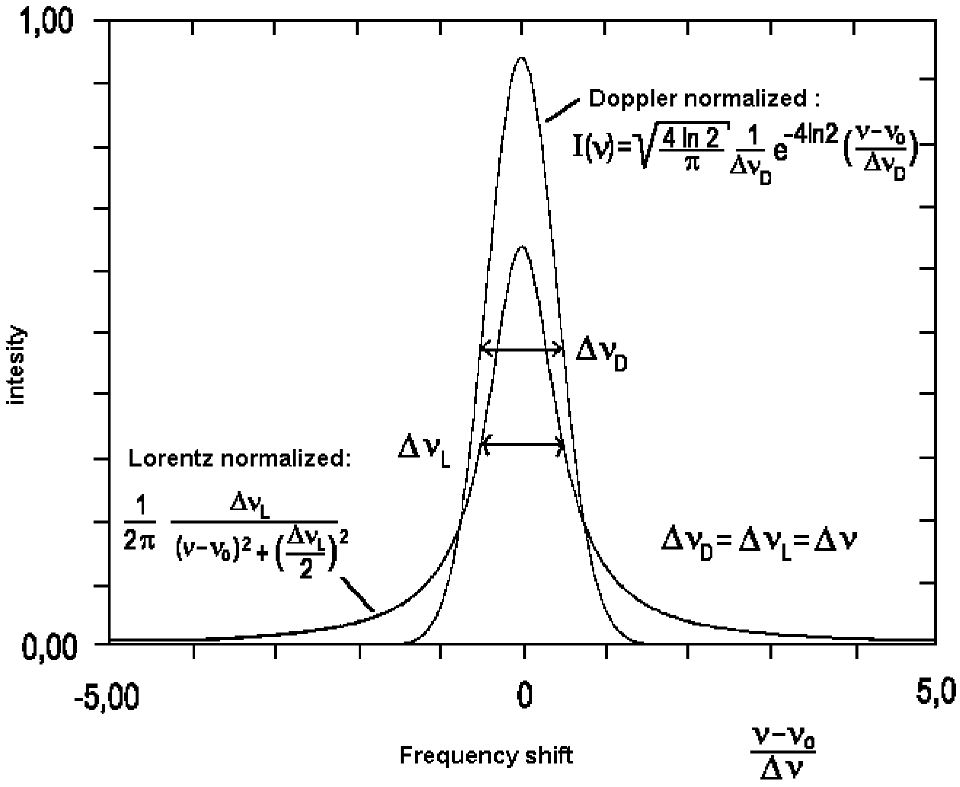
N_A is Avogadro number, $N_A = 6.022\ 10^{-23}$ mol^{-1}

Low Optical Density Approximation

In case if the exponent factor $a = s N l$ is small compared to unity, $a \ll 1$, the exponential function can be expanded over a. Keeping in this expansion only first two terms one comes to the important for practice particular case called low optical density of the sample:

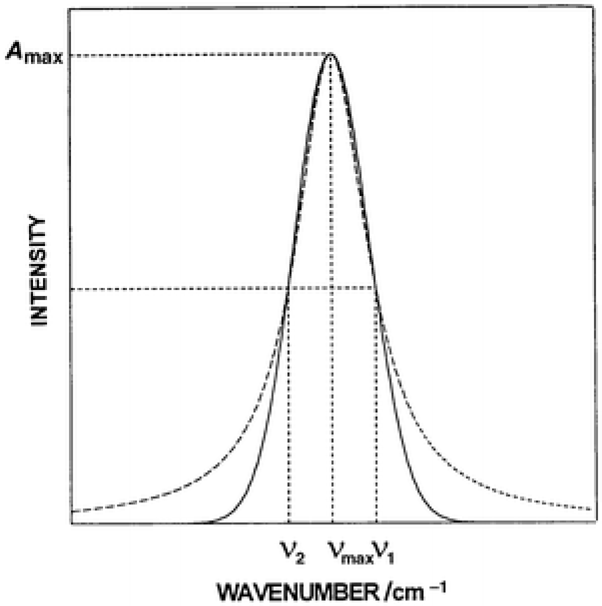
$$I = I_0(1 - \sigma N l) \rightarrow \quad (I - I_o)/I_o = s N l$$



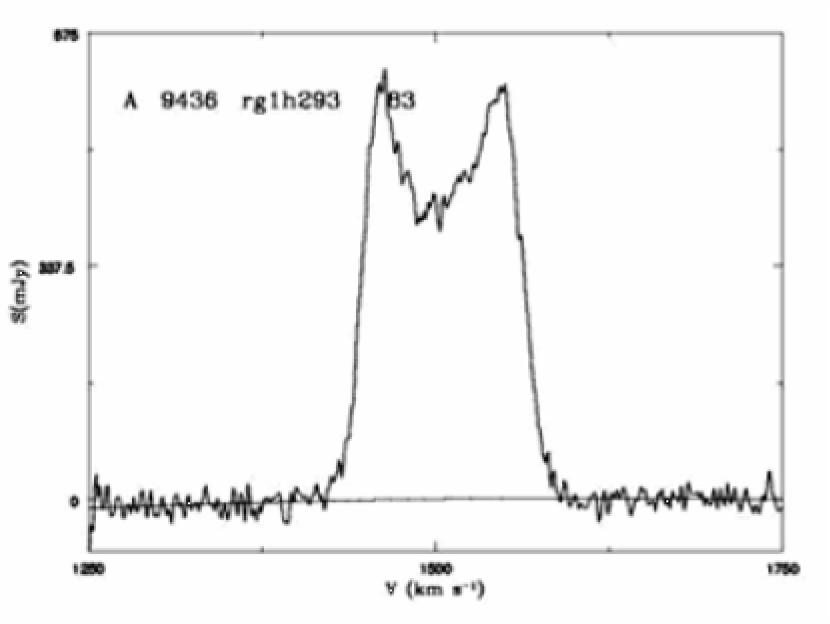


Why integrated cross section ?

Integrating the cross section <σ> = òσ(ν)dν over the light frequency ν within the absorption peak, one obtains the integrated cross section <σ>:



Gauss (dashed) and Lorentz line profiles

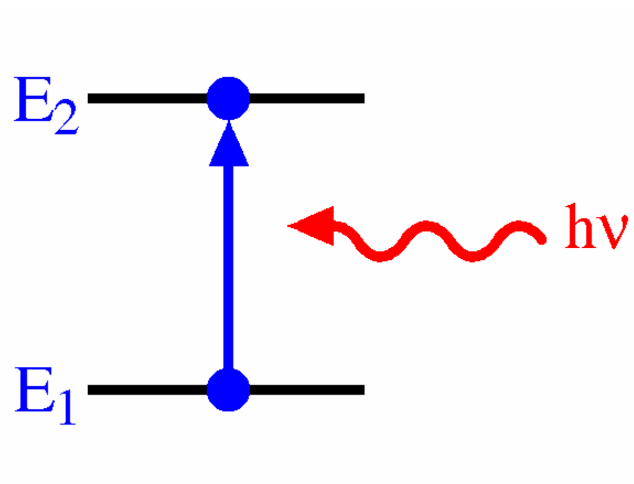


H atom line after photodissociation of HI

$$\left\langle s \right\rangle = \int s\,(n)\,dn = B_{12}\,\frac{hn_0}{c}$$

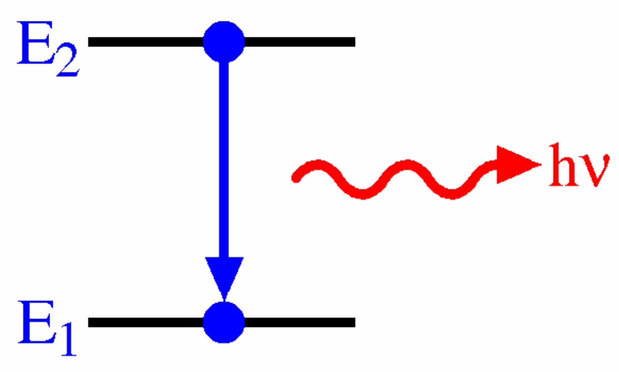
B_{12} is the Einstein absorption coefficient and ν_0 is the center of the molecular absorption line. Thus, the Einstein coefficient B_{12} can be directly determined from experiment.

Einstein Coefficients



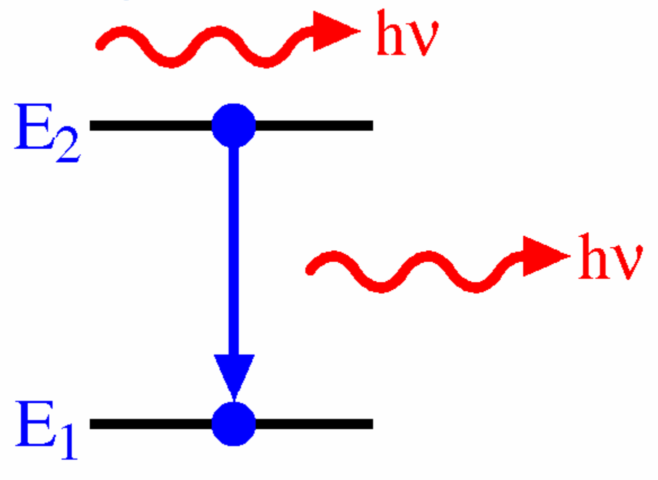
Absorption

$^{dN}{}_{2}/_{dt} = B_{12} \cdot u(n) \cdot N_1$



Spontaneous Emission

$^{dN}{}_{2}/_{dt} = - A_{21} N_2$



Induced Emission

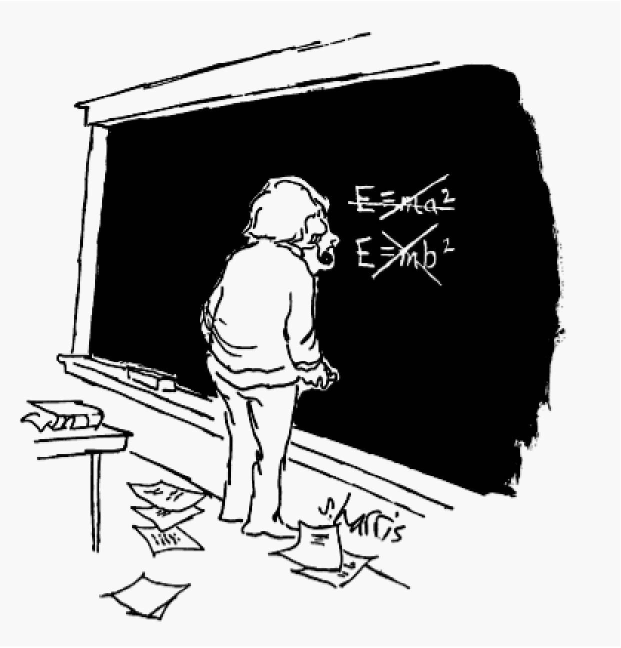
$^{dN}{}_{2}/_{dt} = - B_{21} \cdot u(n) \cdot N_2$

Fluorescence lifetime $t = 1/_{A_{21}}$:

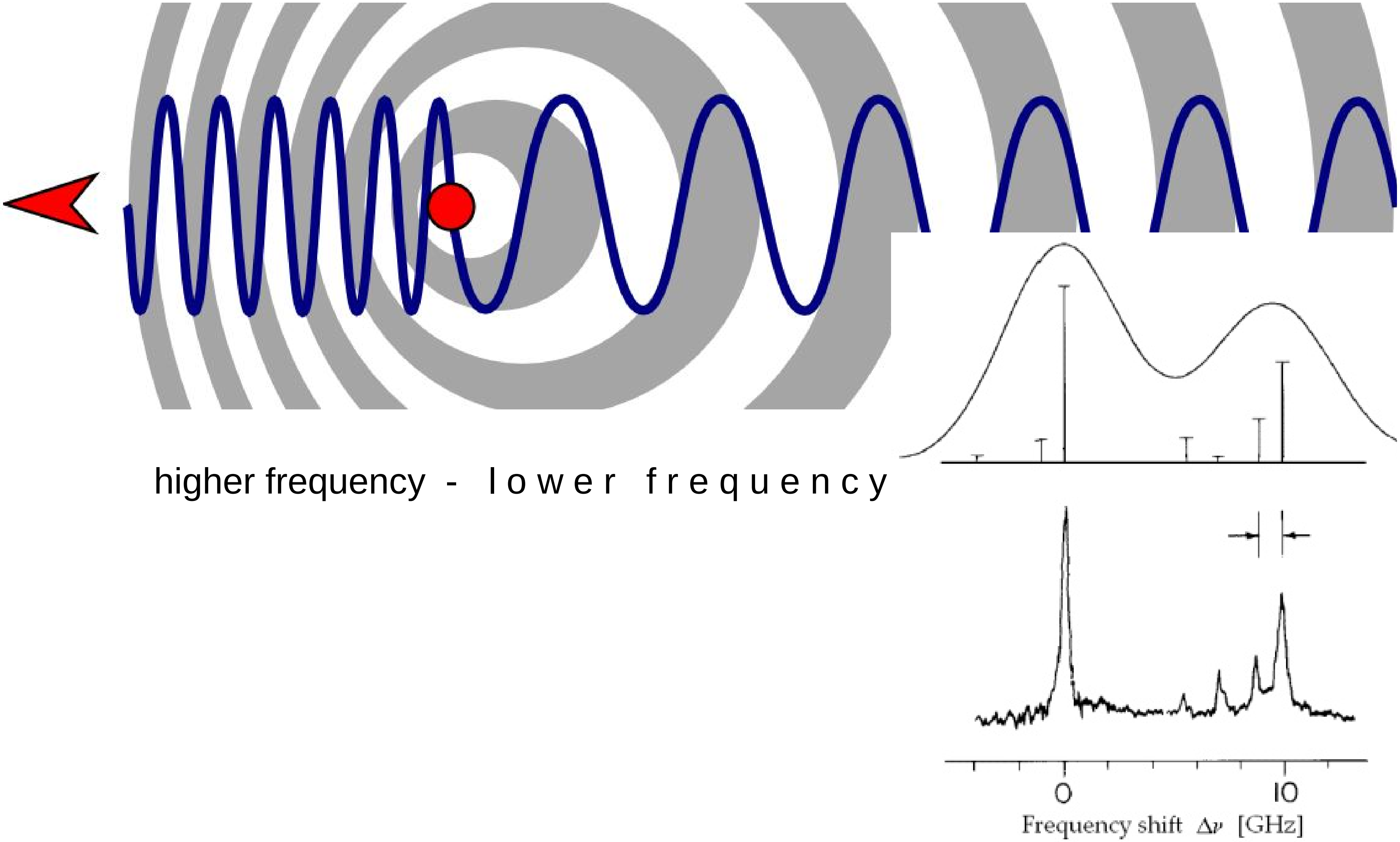
$I = I_o e^{-t/\tau}$

This causes a Lorentz type line shape.

$A_{21} / B_{12} = 8$



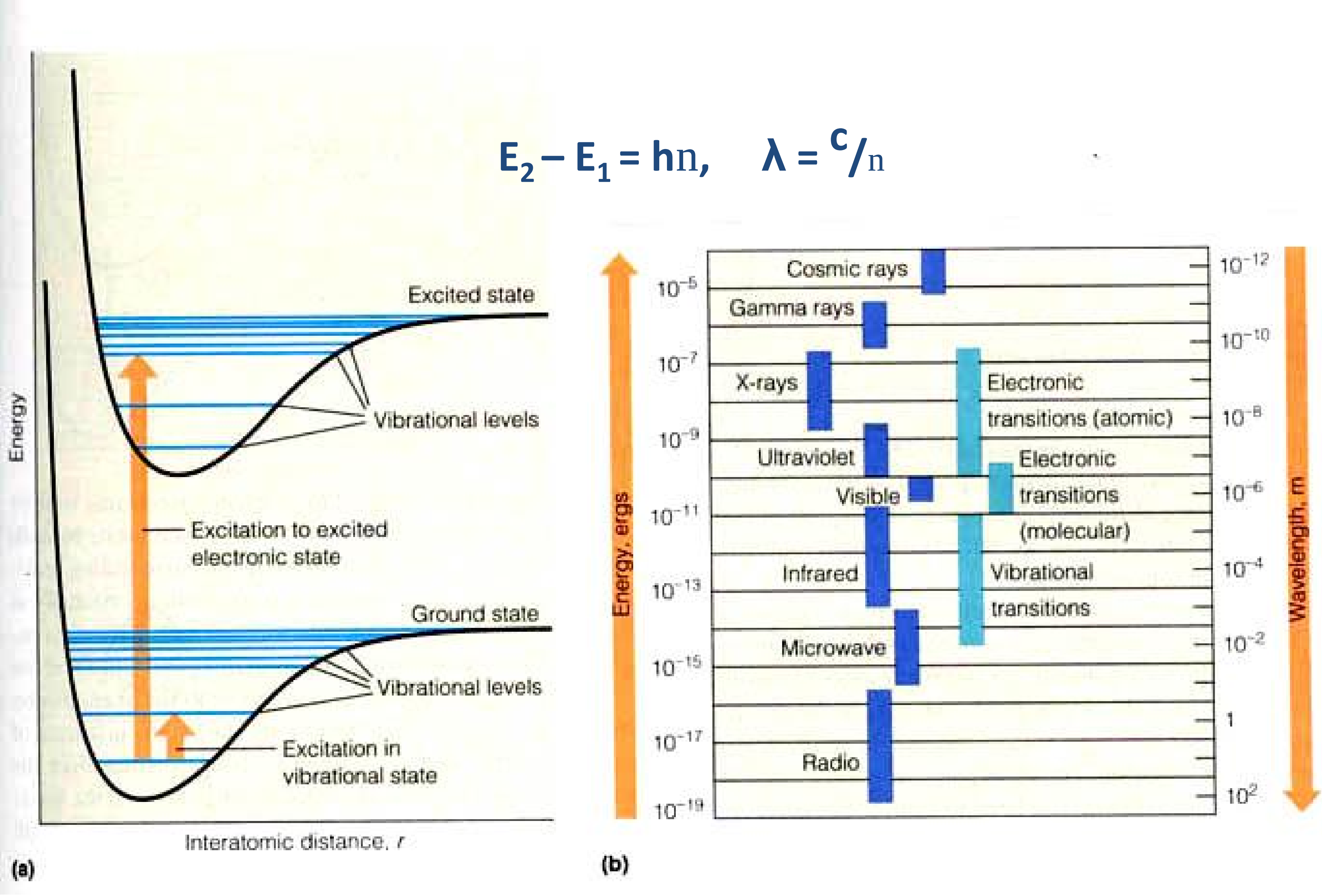
Doppler effect



higher frequency - lower frequency

Molecular motion – frequency (wavelength)

$E_2 - E_1 = h\nu, \quad \lambda = {}^{c}/\nu$



Detection Techniques

- Sensitivity
- Dynamic range
- Selectivity
- Interference (with surounding)
- Time resolution

Laser

Properties of Laser Radiation

1. The laser light can be very monochromatic 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 divergent (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:

$$q \approx 2l \,/\, pd$$

Using a lens, it is possible to focus a laser beam on a spot of the diameter:

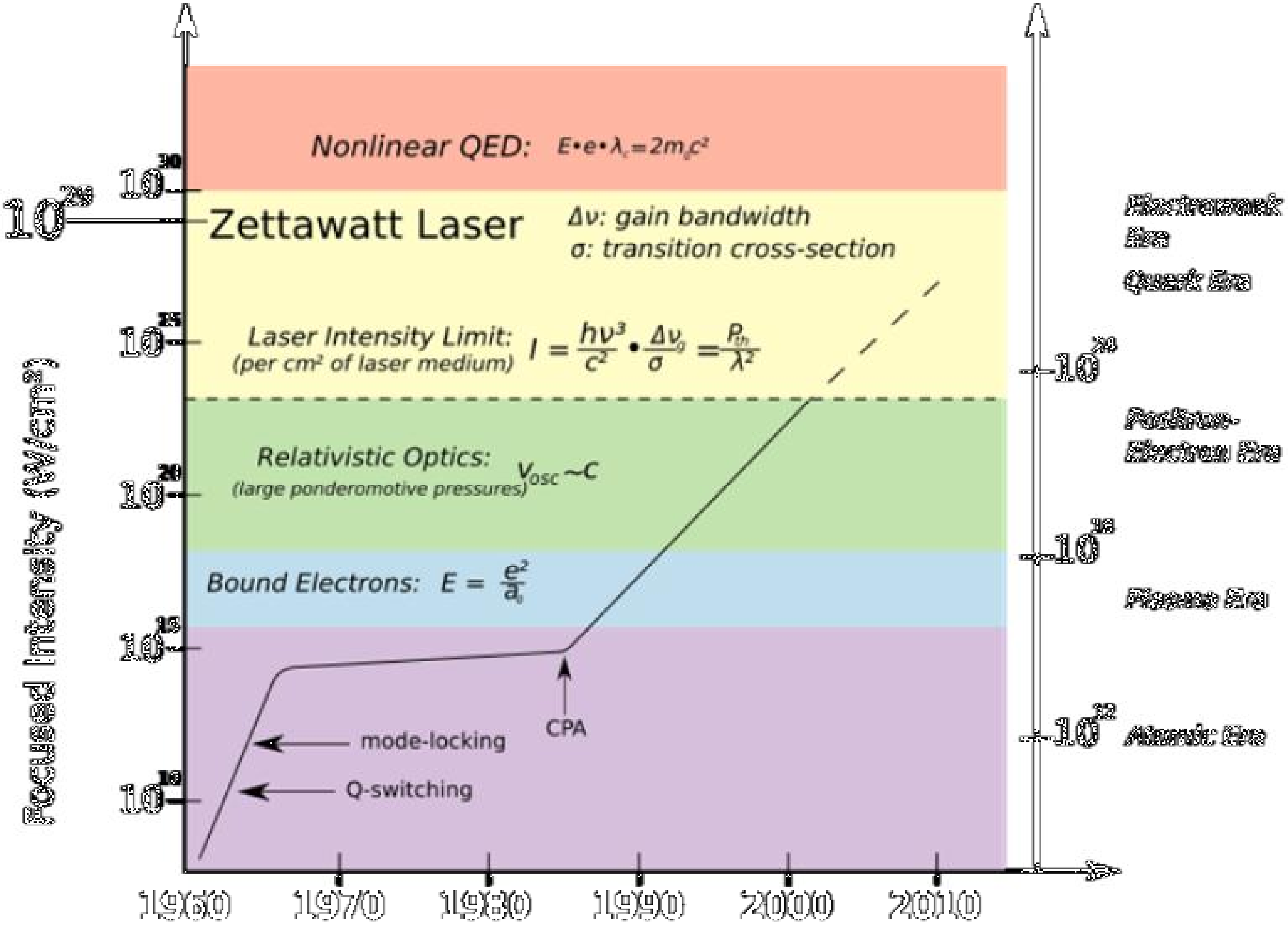
$$d \approx 2lf \,/\, p\,D \approx l/\,2$$

where, f denotes the focal distance of the lens.

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 the real-time domain**.

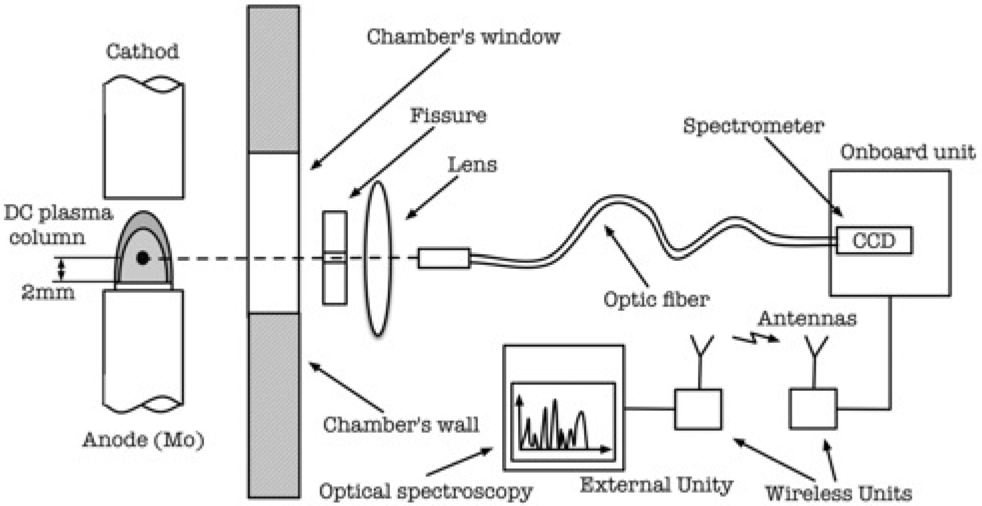
4. High power output. The continuous CO_2 lasers are now can produce the high power output up to 100 kW. These technological lasers are now widely used in industry and for military. The pulsed lasers, especially those operating in the pico- and femtosecond time-domain can have the peak power from **10^9 to 10^{12} Watt.** High power pulsed lasers are widely used for investigation of **nonlinear** and **multiple photon processes**.

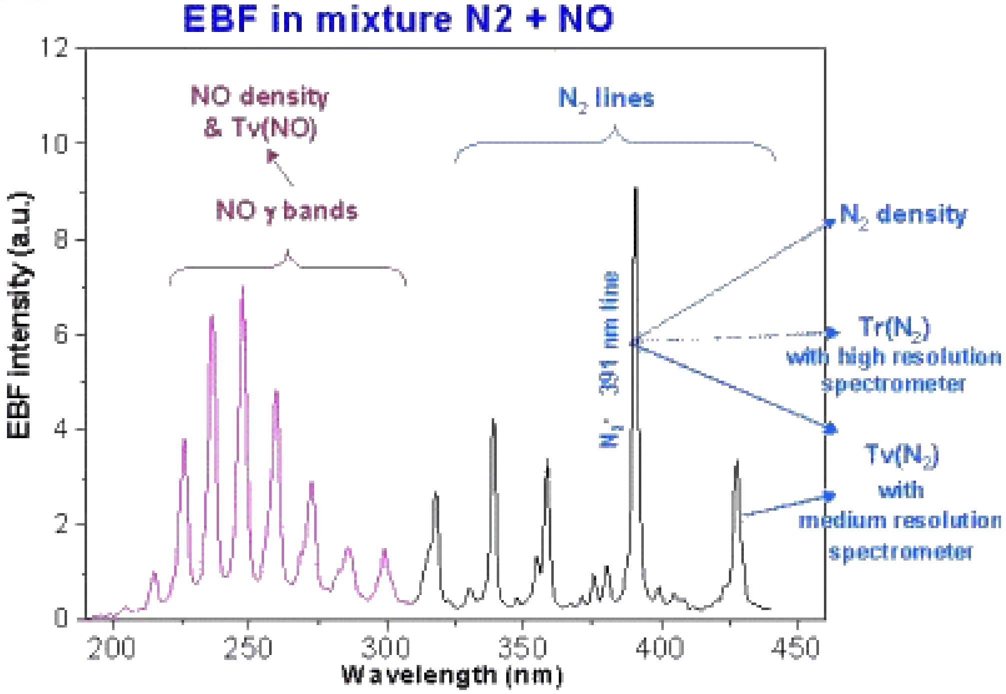
Laser (pulse) power



Detection Techniques

OES: Optical Emission Spectroscopy

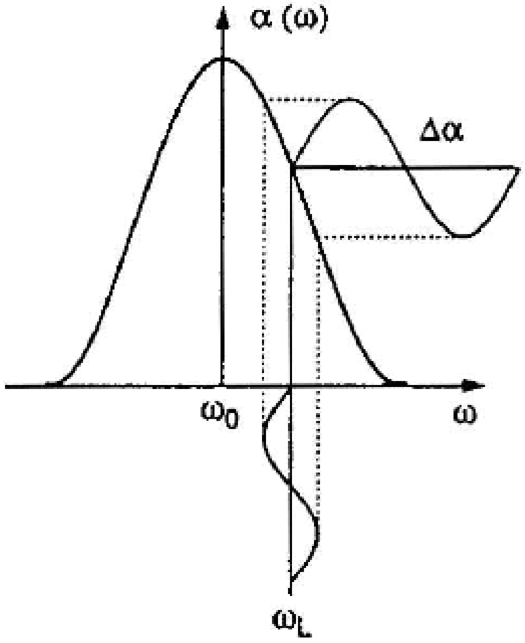


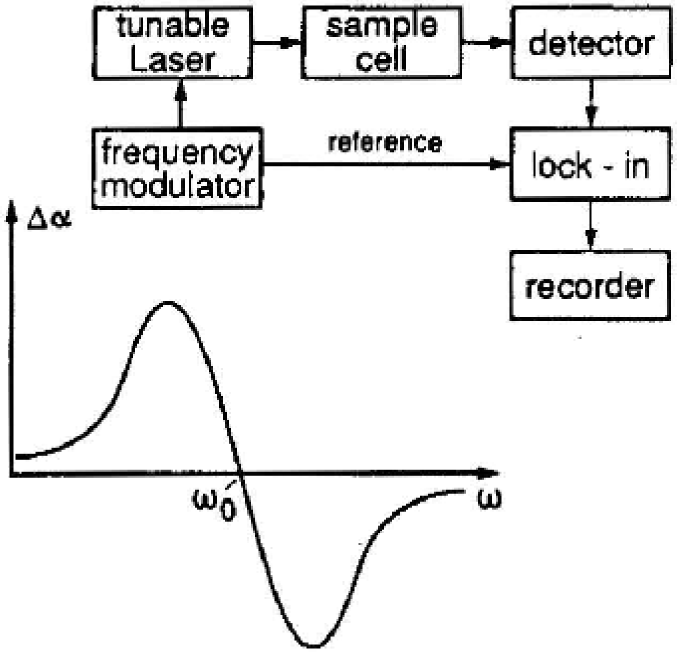


Absorption Spectroscopy with a Frequency Modulated Laser

$(I-I_o)/I_o$ = s N l = *Absorbance*   Detection limit $A=10^{-3}$

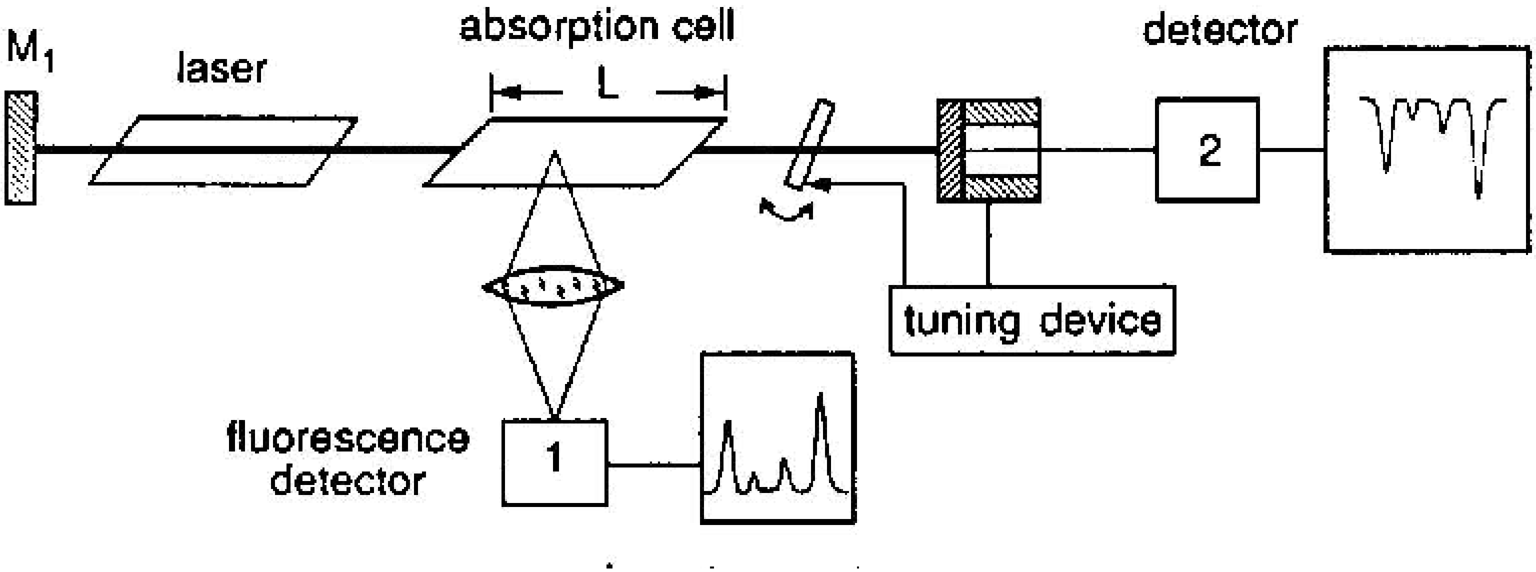
s $= 10^{-18} cm^2$ $l = 10$ cm Þ $N = 10^{-3} / (10^{-18} \cdot 10) = 10^{14}$ *molecules/cm³*





Detection limit $A=10^{-6}$

Intracavity Absorption Technique



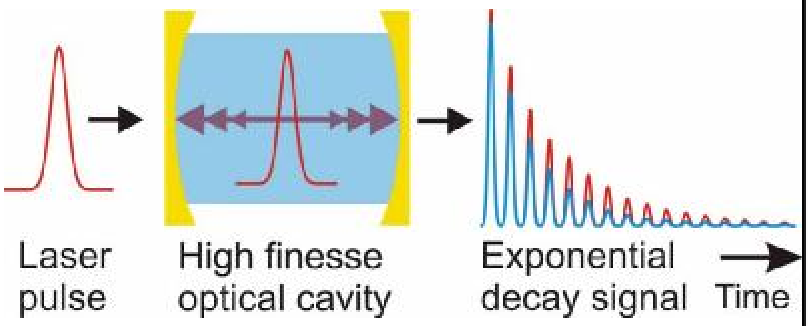
Operation close to laser threshold

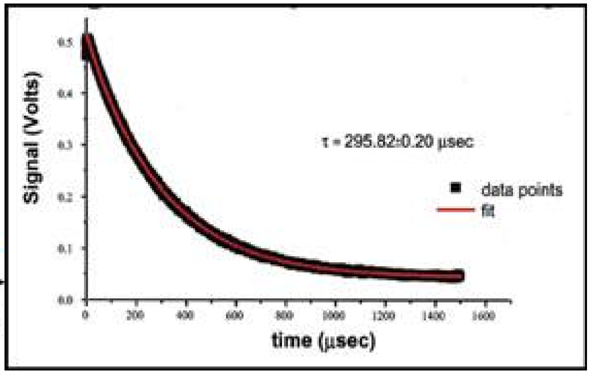
+ high sensitivity ($A=10^{-8}$)

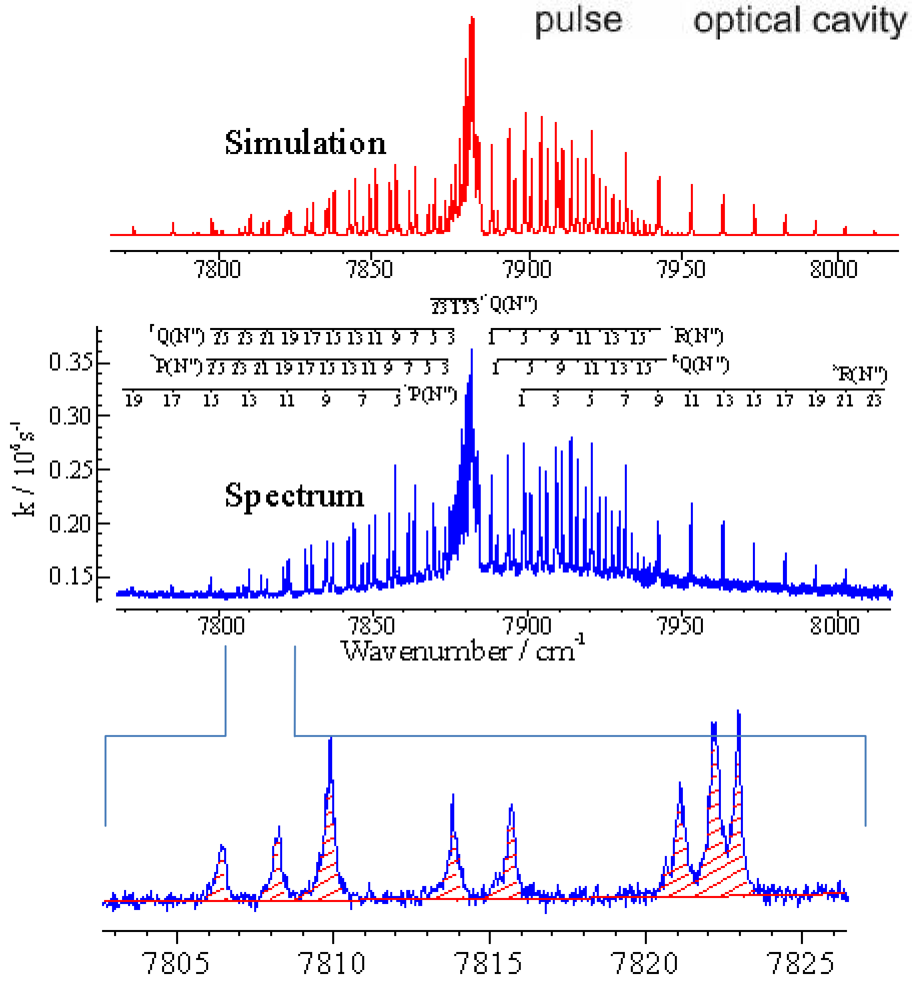
- non linear response
- interference with other absorber within resonator

CRD: Cavity Ring Down Spectroscopy

CRD spectroscopy is a highly sensitive direct absorption technique.





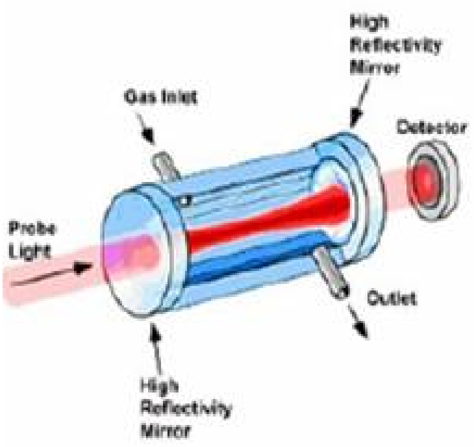


$I = I_o e^{-t/\tau}$ → absorption cross section

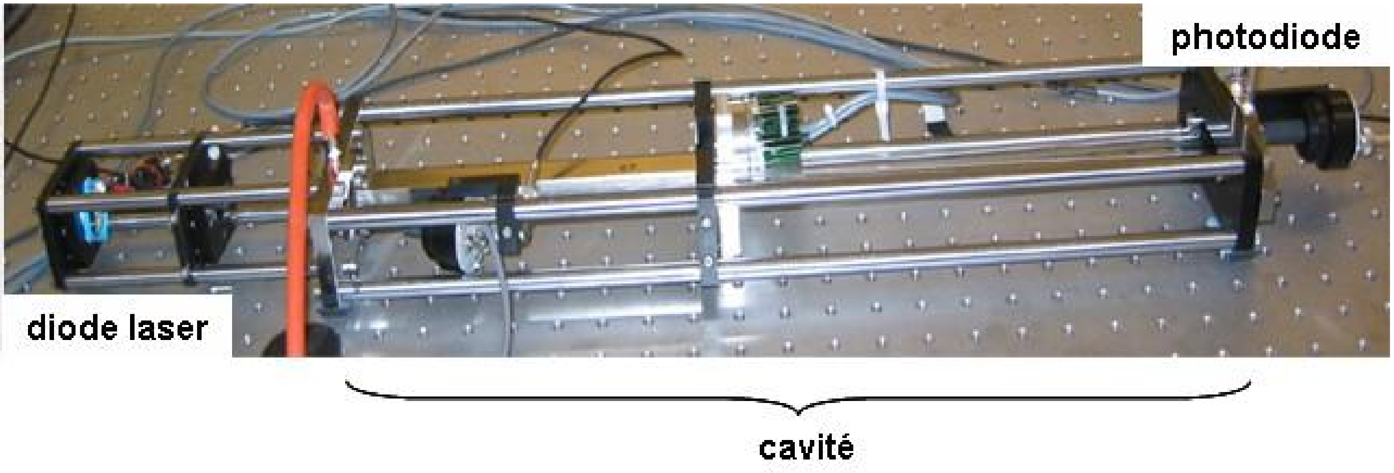
CRD of O_2: $a^1\Delta_g - X^3\Sigma_g^-$ (0,0)

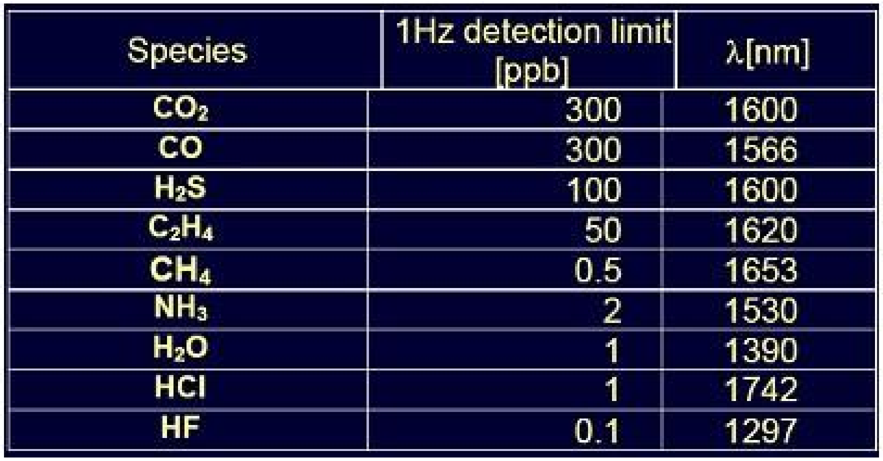
Integrated absorption → B → A → lifetime 0.2 ms

CRD: Cavity Ring Down



Schematic drawing of the optical nose components (NIST)





Species	1Hz detection limit [ppb]	λ[nm]
CO_2	300	1600
CO	300	1566
H_2S	100	1600
C_2H_4	50	1620
CH_4	0.5	1653
NH_3	2	1530
H_2O	1	1390
HCl	1	1742
HF	0.1	1297

Improvement: $^{1}/_{(1\text{-Reflectivity of mirrors})}$

R=99.999%

Photoacoustic Spectroscopy

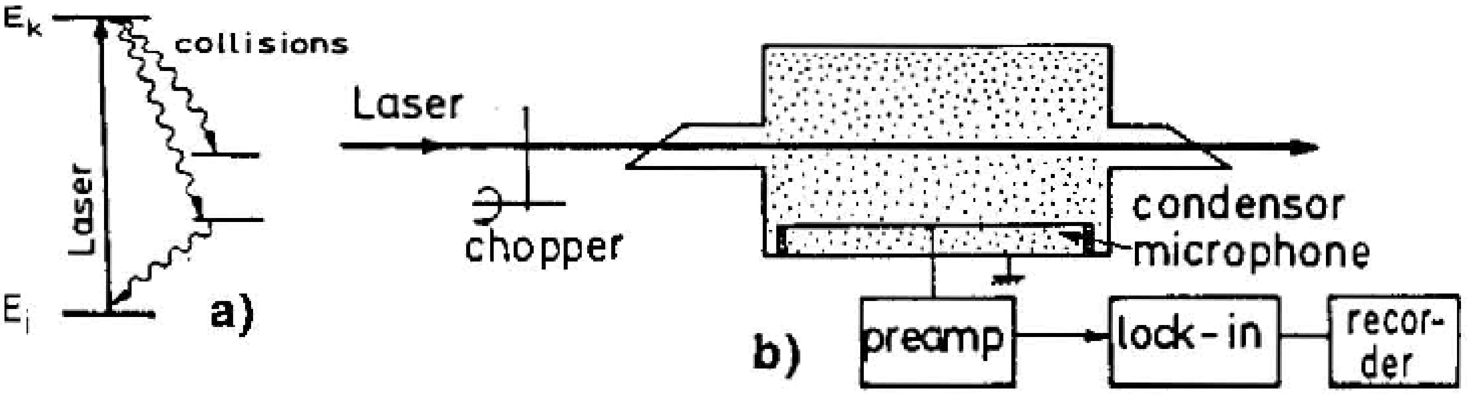


Fig.6.13. Photoacoustic spectroscopy (a) level scheme (b) schematic experimental arrangement

Photoacoustic Spectroscopy: C_2H_2

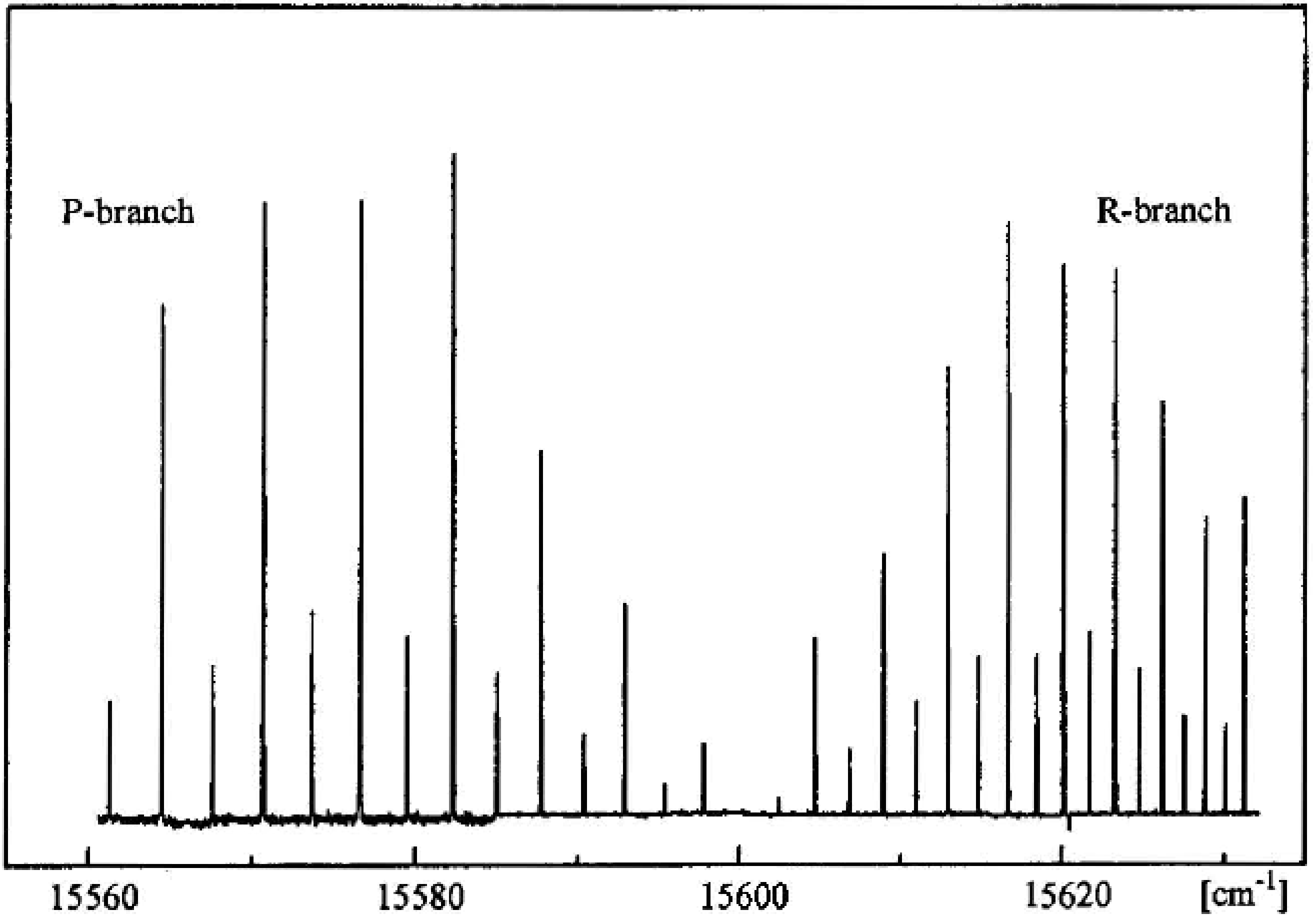
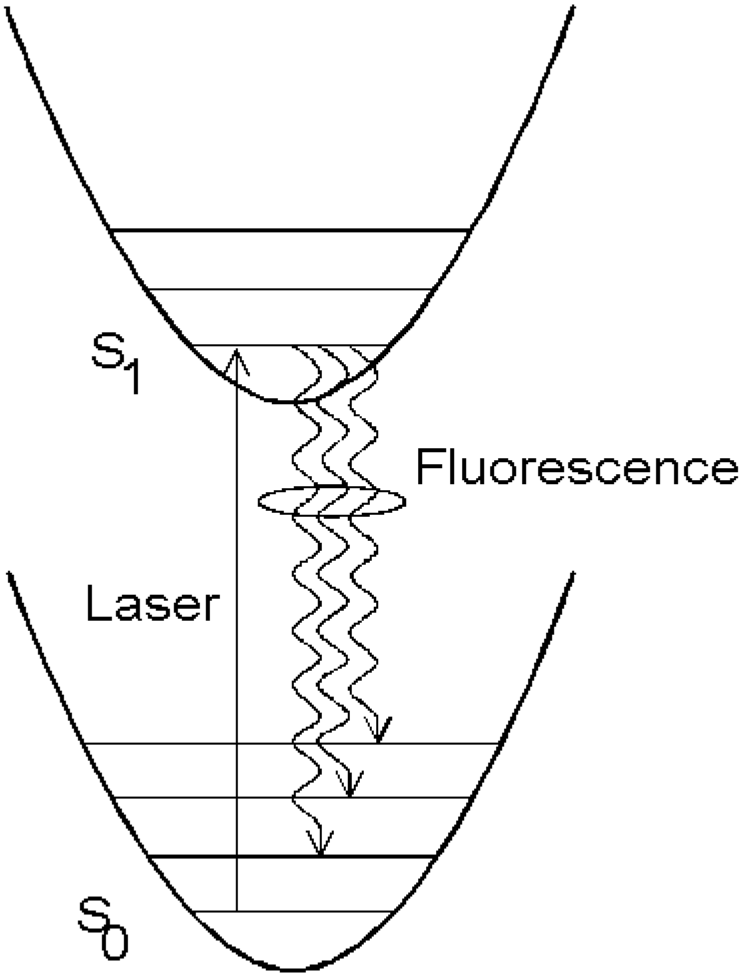
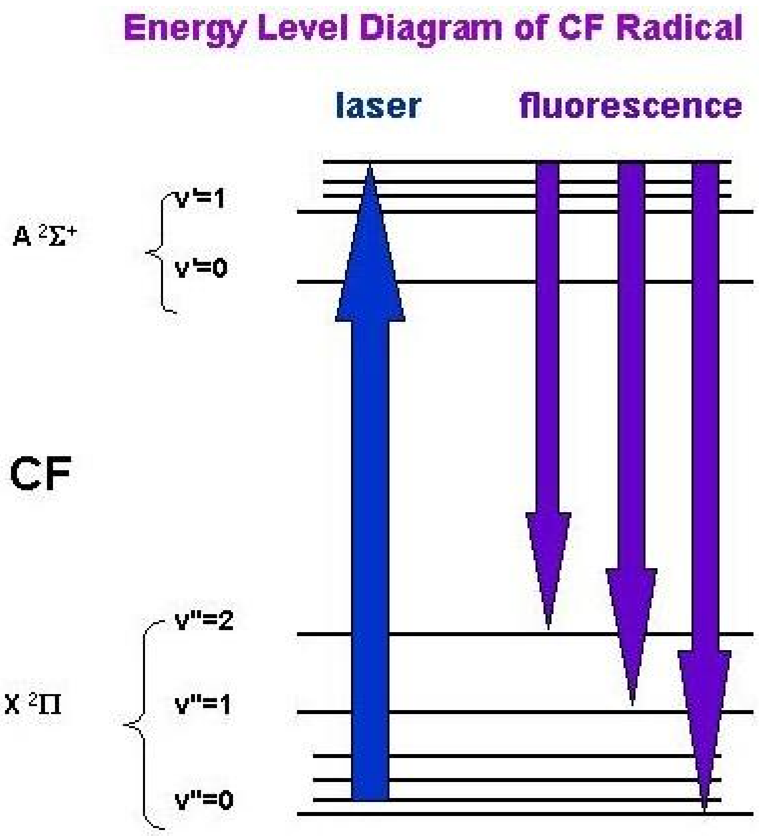


Fig.6.15. Optoacoustic overtone absorption spectrum of acethylene around $\bar{\nu}$ = 15600 cm^{-1} corresponding to the excitation of a local mode by 5 quanta vibrations [6.45]

Laser induced fluorescence (LIF)

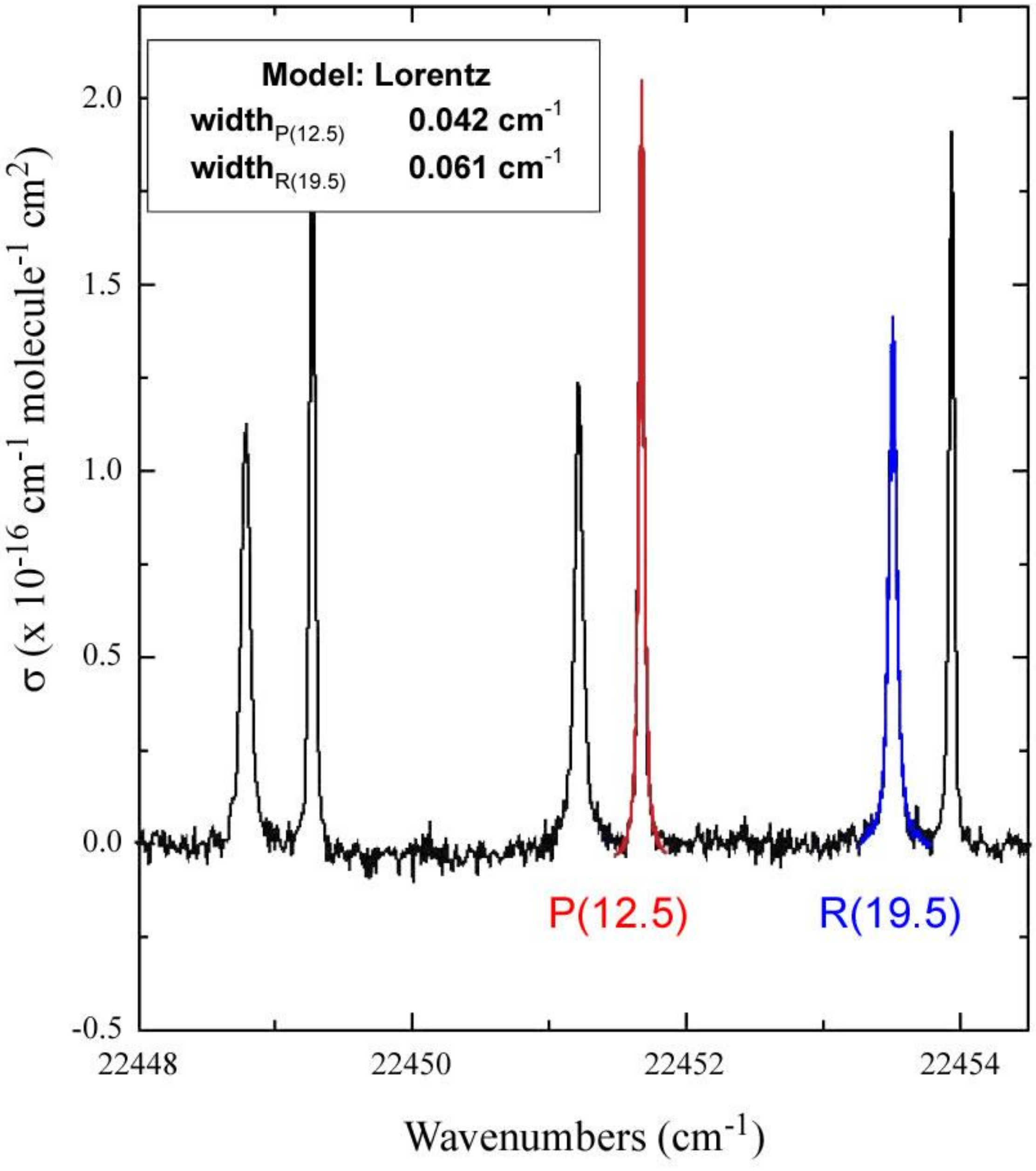




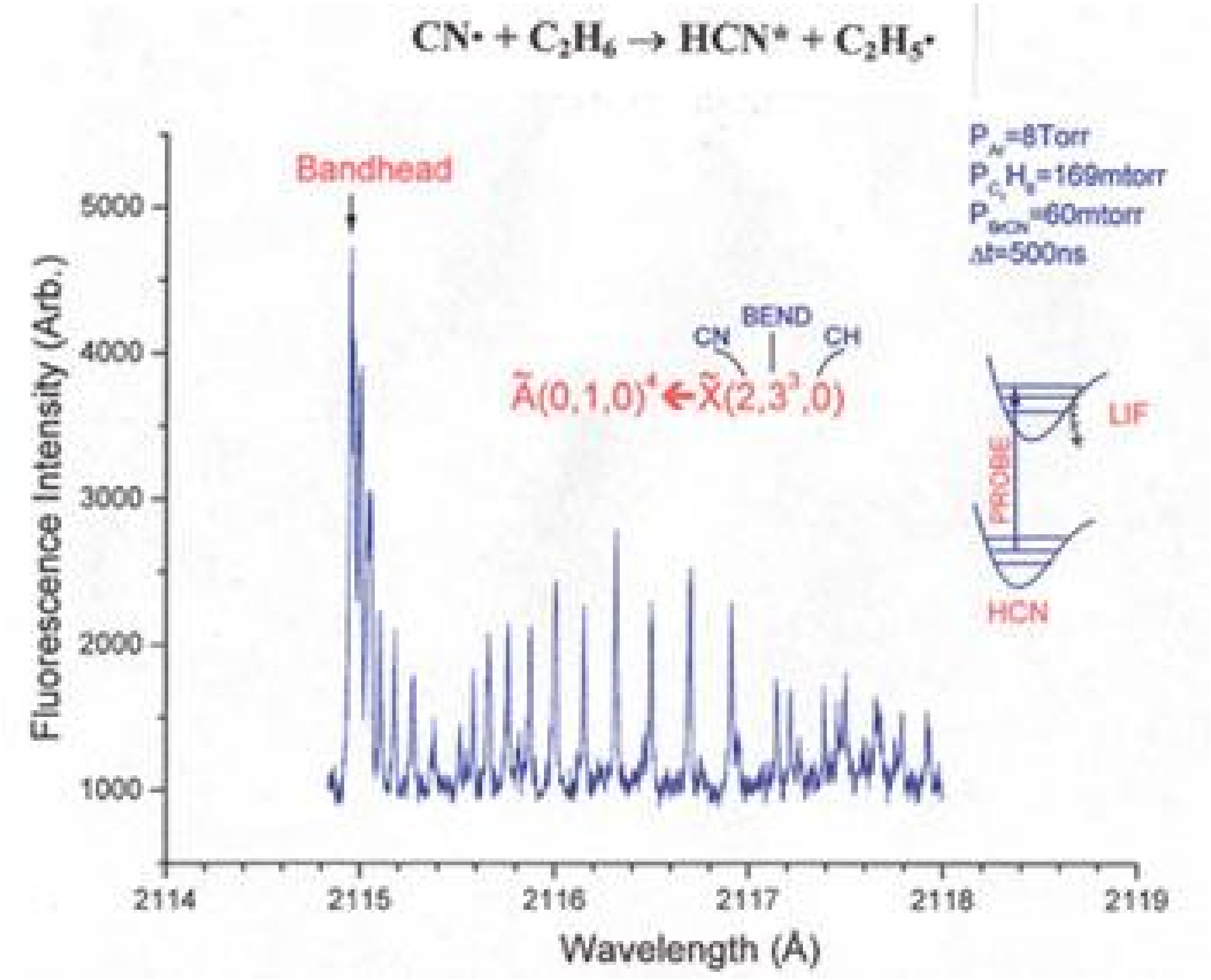
LIF

+ extremely sensitive
+ selective
- calibration
- handling
- costs

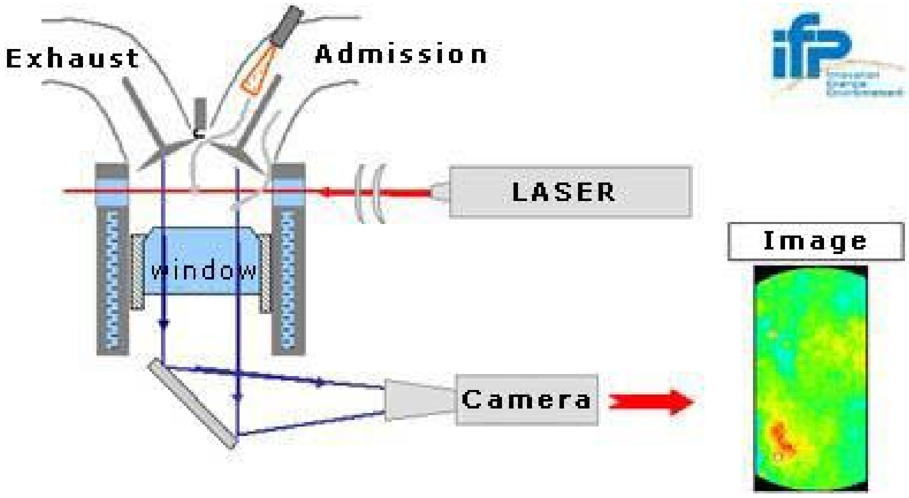
IO(v‘=2-v‘‘=0) around 445 nm



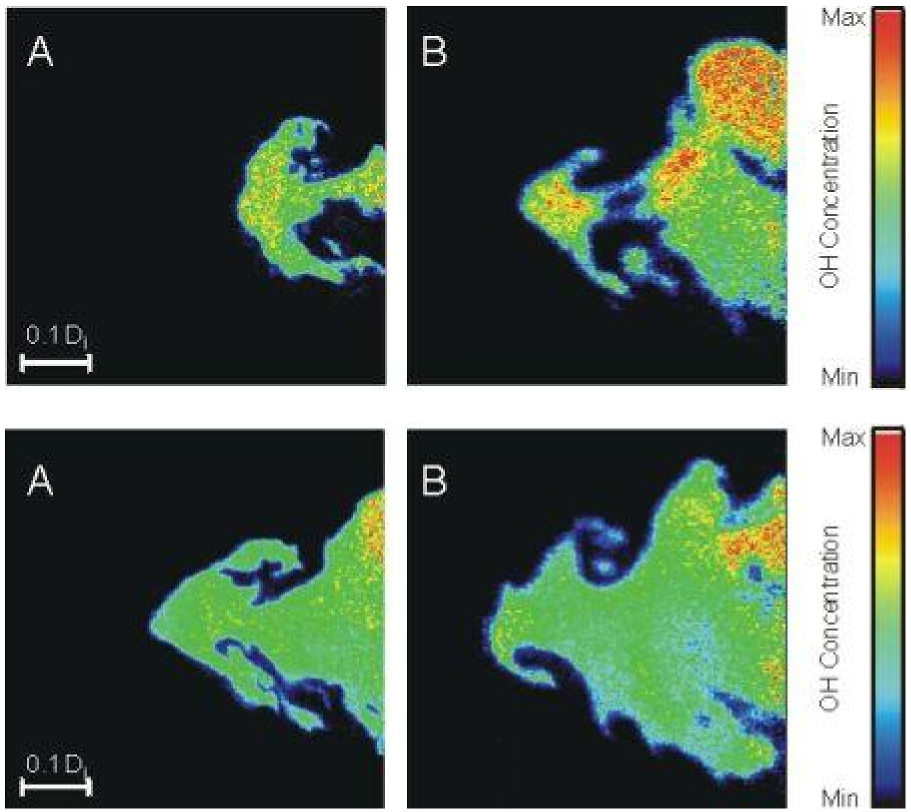
Laser induced fluorescence (LIF)



Laser induced fluorescence (LIF)



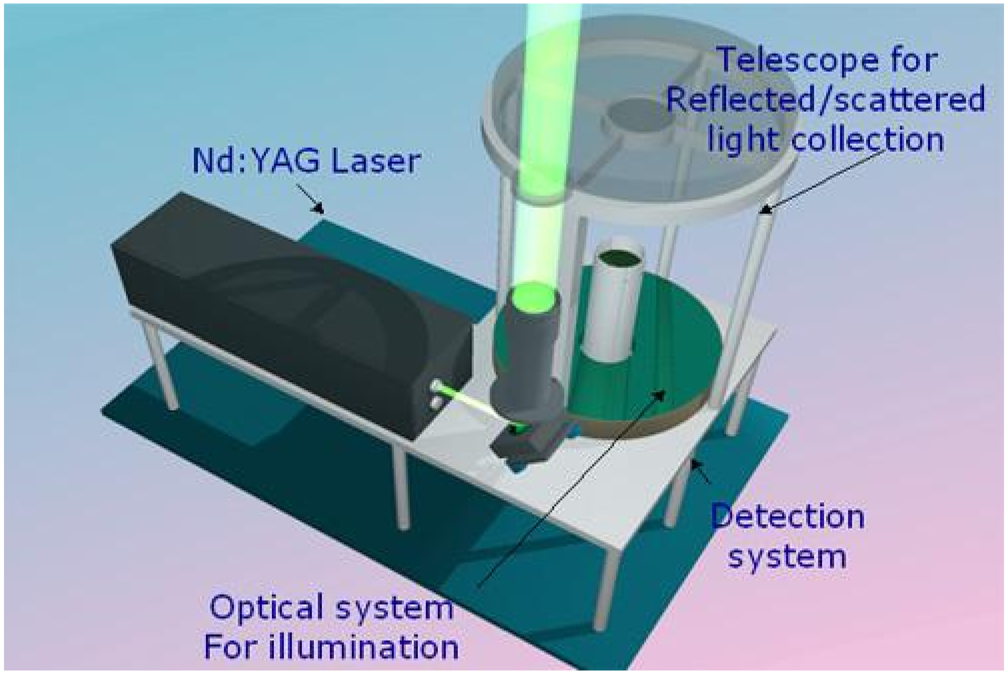
LIF in a running engine of a car

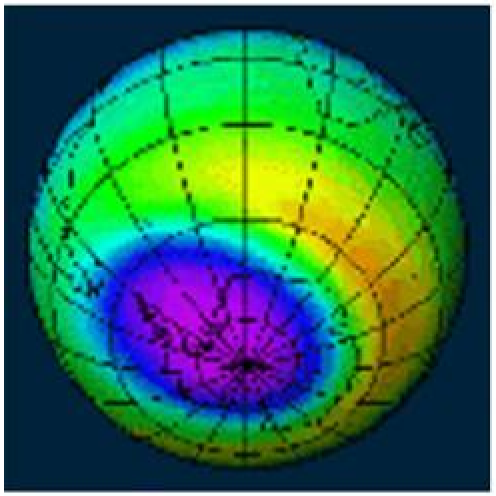


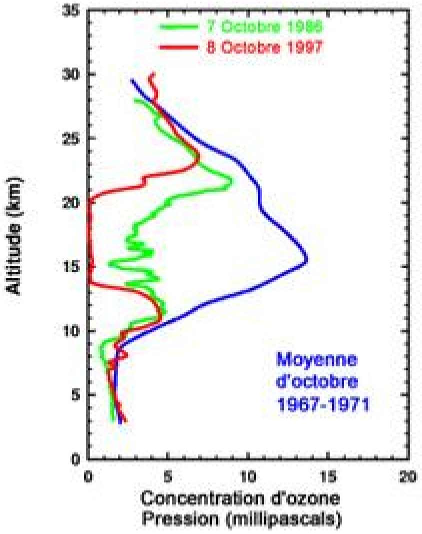
LIDAR: Light Detection And Ranging

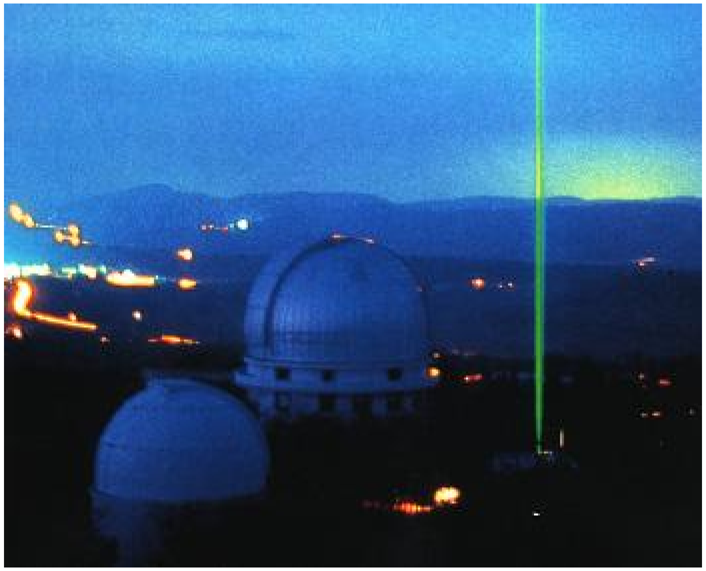
LIDAR: A remote-sensing technique that uses a laser light source to probe the characteristics of a target:

- Atmosphere control
    - Density
    - Temperature
    - Wind
    - Pollution
- Distance, speed measurement
- Rayleigh, Mie scattering
- Raman scattering
- Fluorescence
- Doppler shift









Atmospheric OH

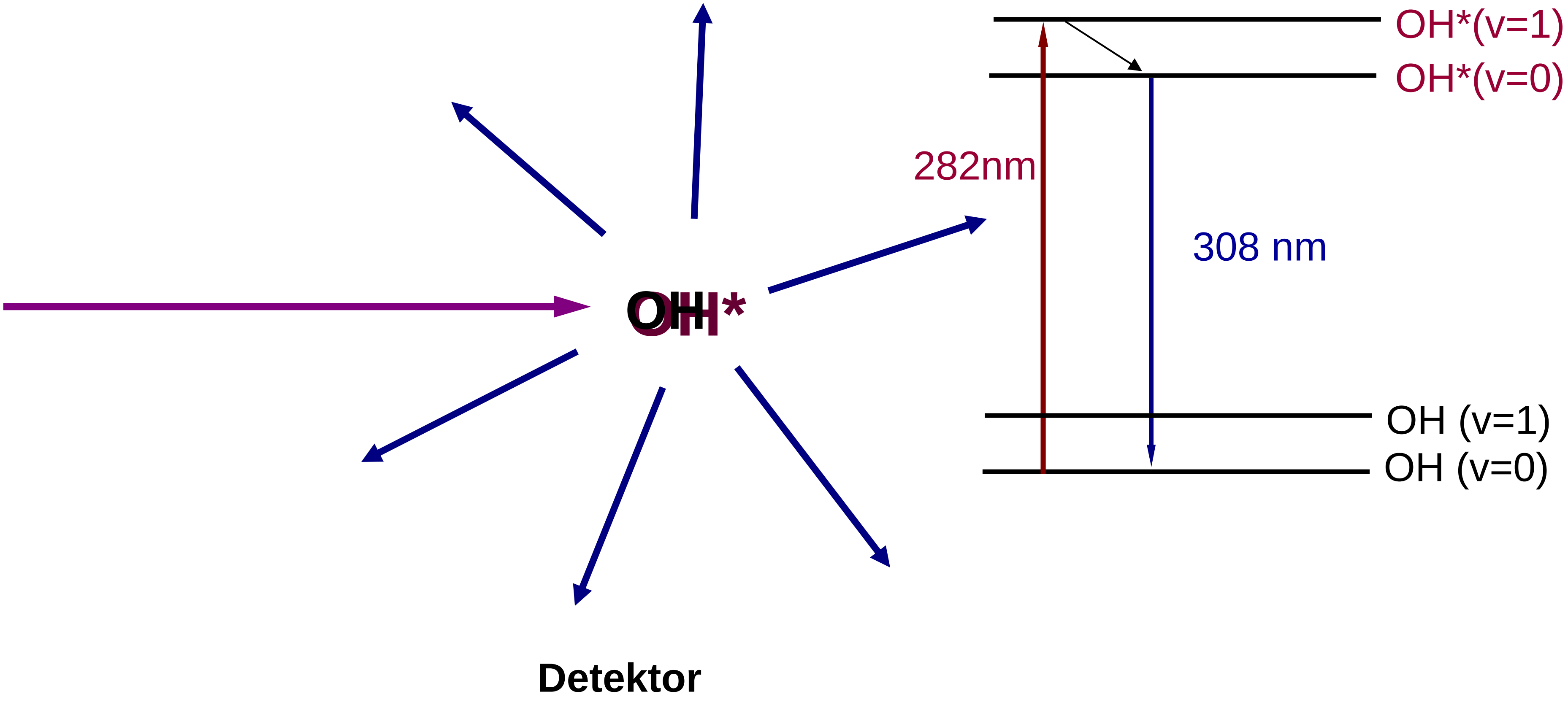
- OH is the detergent of the atmosphere (Crutzen)
- For example hydrocarbon [HC]:

$^{d[HC]}/_{dt} = -k\ [HC] \cdot [OH]$

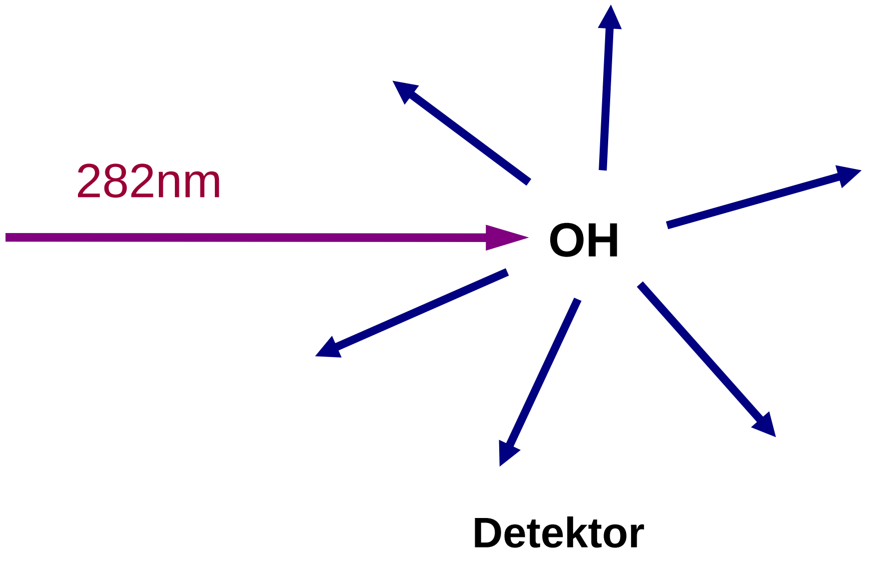
lifetime of HC in the atmosphere: $\tau = {}^{1}/_{k\ [OH]}$

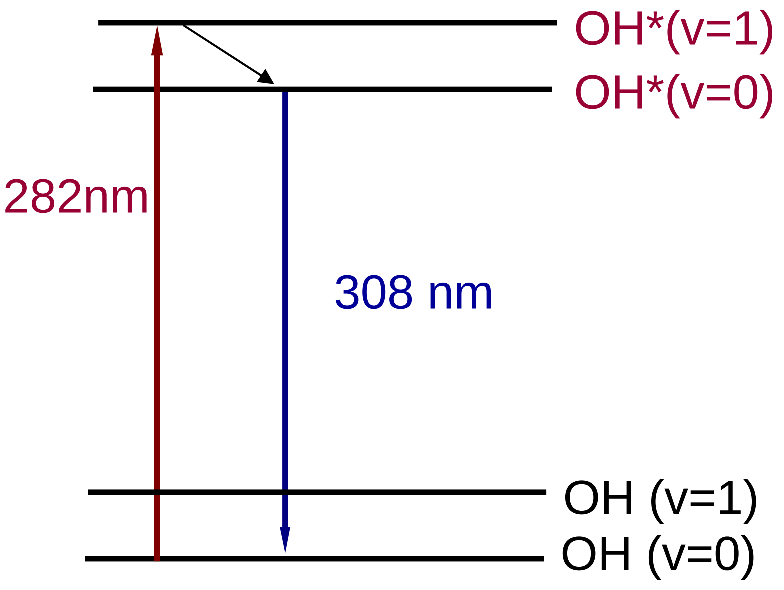
However, OH concentration around 10^5-10^6 /cm^3

OH detection in the lab via LIF



OH detection in the atmosphere ?





$O_3 + hv \rightarrow O(^1D) + O_2$ 282nm: s huge, F = 0,9

$H_2O + O(^1D) \rightarrow OH + OH$

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IS UV LASER INDUCED FLUORESCENCE A METHOD TO MONITOR TROPOSPHERIC OH ?

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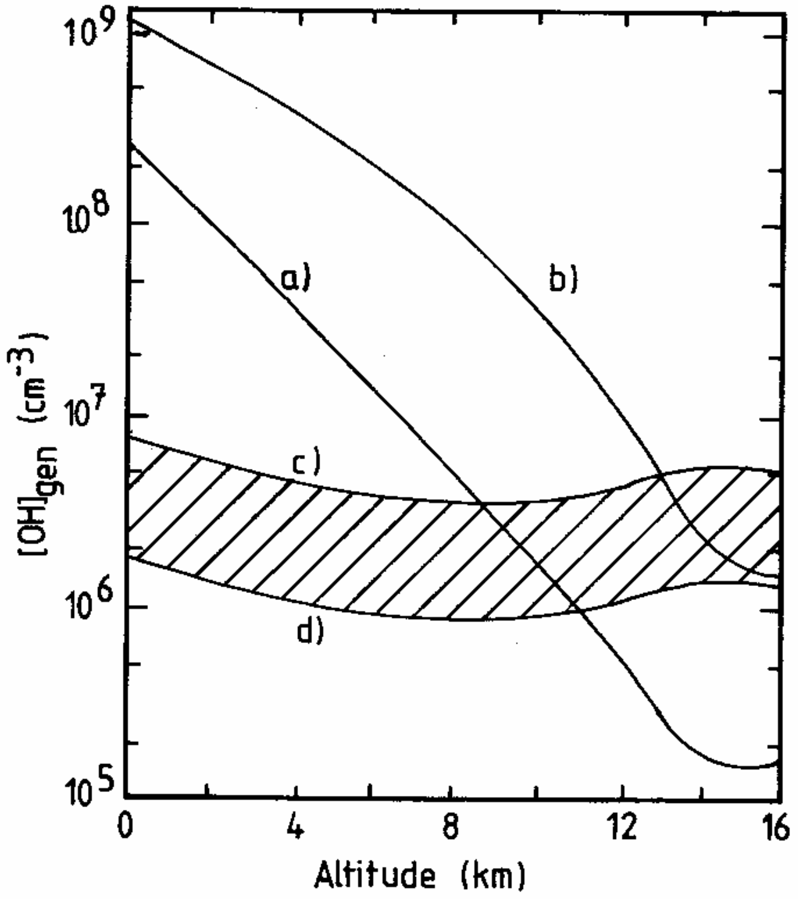


Laser Induced Fluorescence: Na$_2$

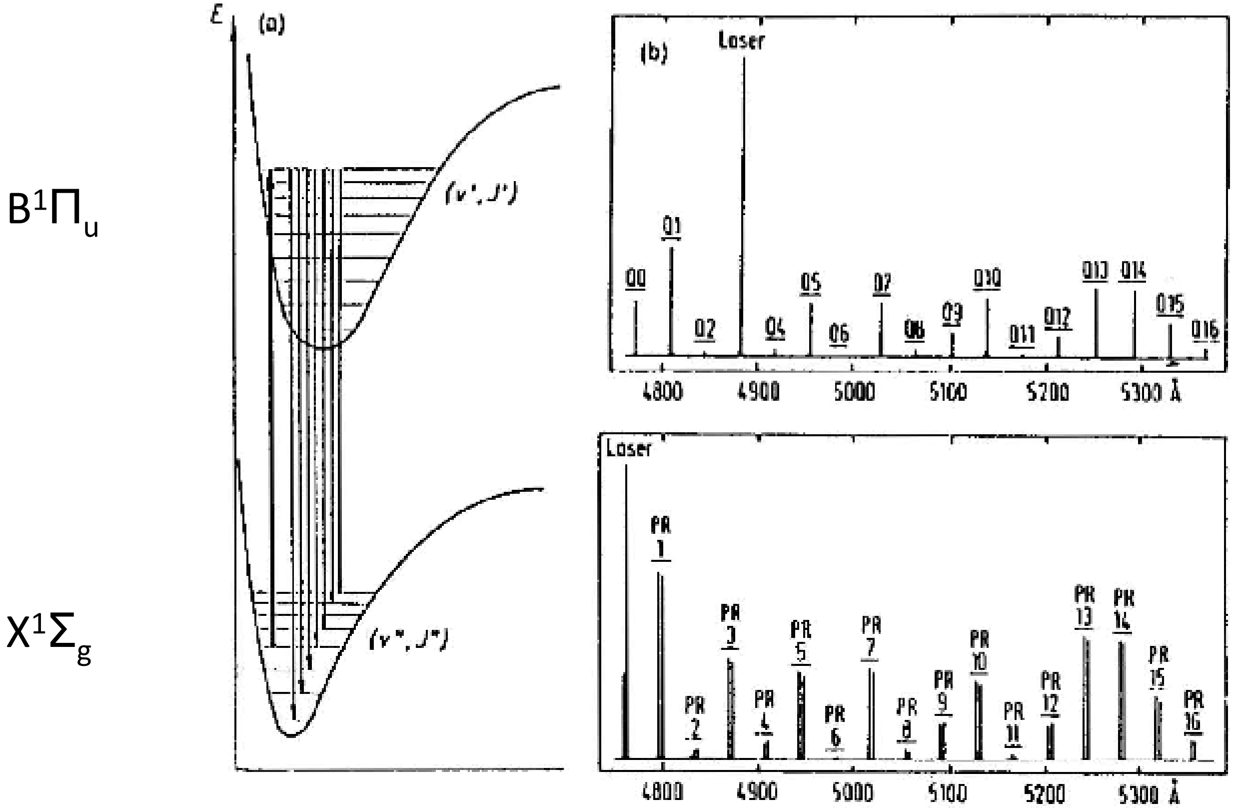
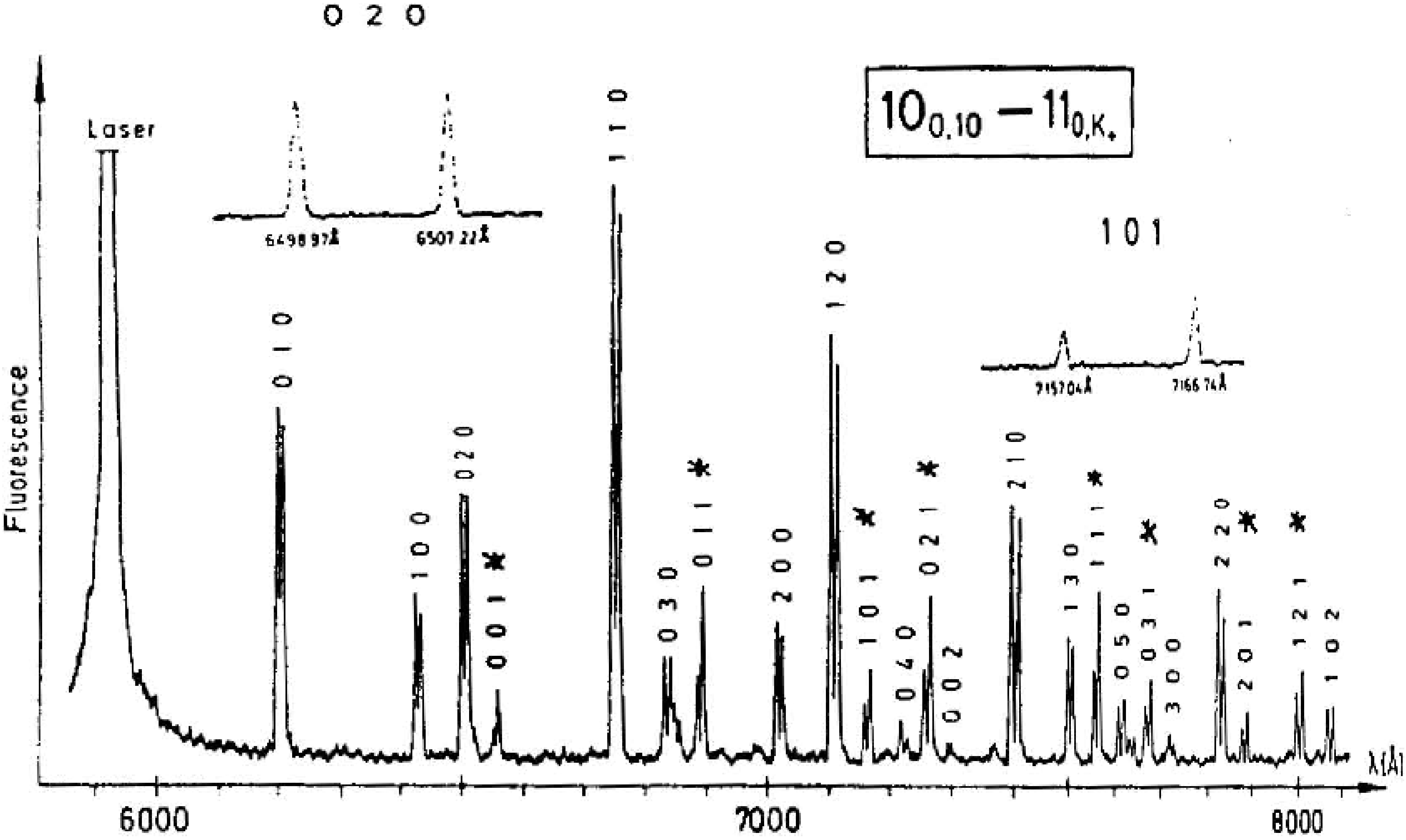


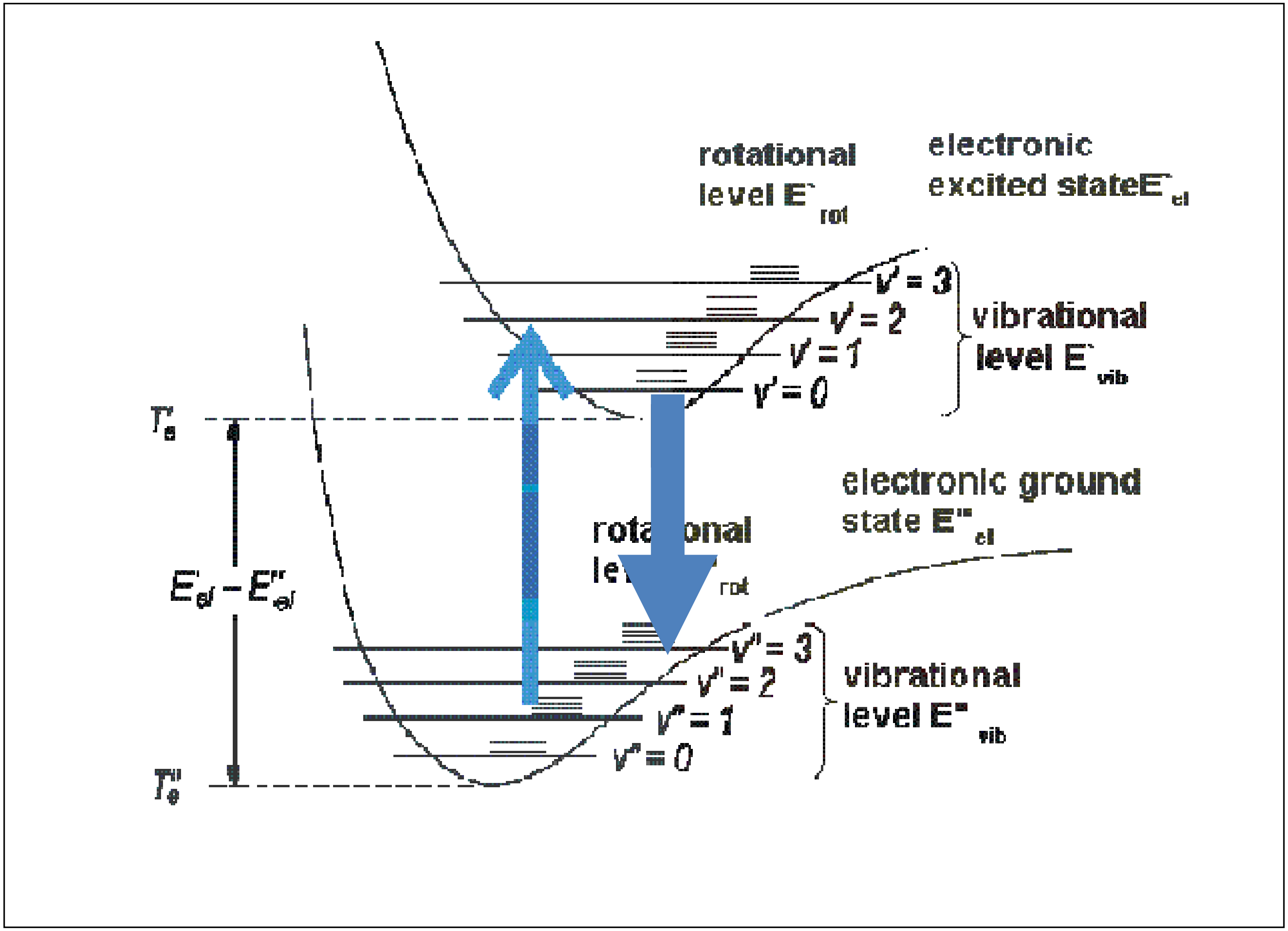
Fig.6.34. Laser-induced fluorescence of the Na$_2$ molecule excited by argon laser lines (a) term diagram (b) fluorescence lines with $\Delta J = 0$ (Q-lines) emitted from the upper level ($v'=3$, $J'=43$) of the B$^1\Pi_u$ state, excited at $\lambda = 488$ nm. (c) P and R doublets, emitted from the 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.

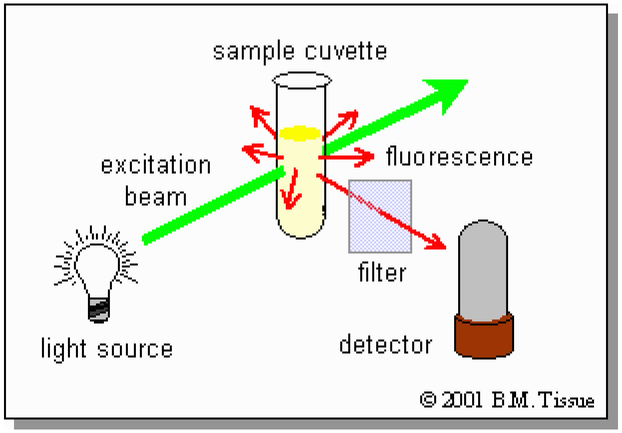
Laser Induced Fluorescence: NO_2

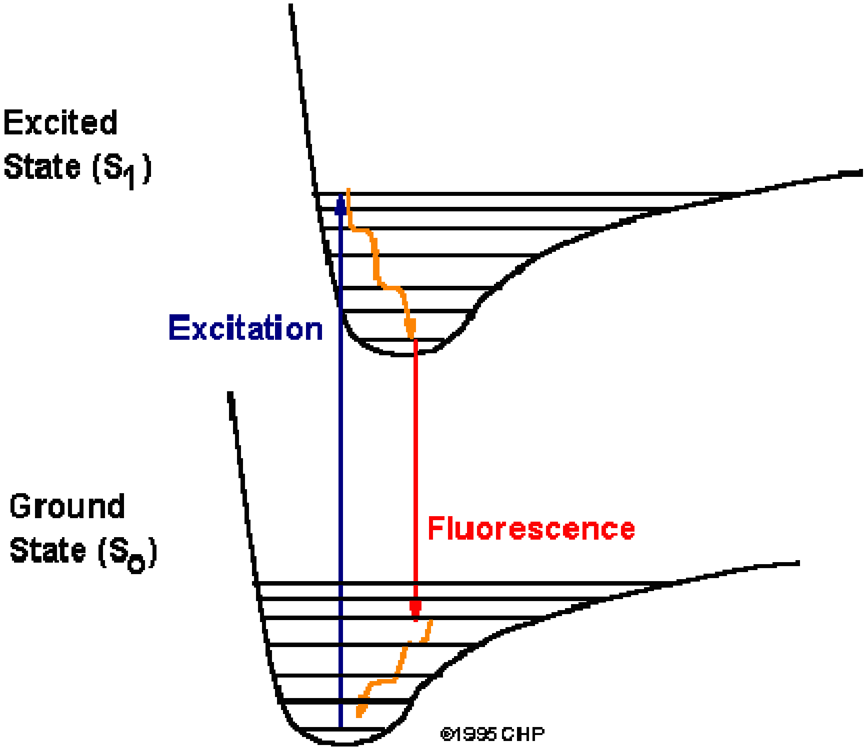


Transitions

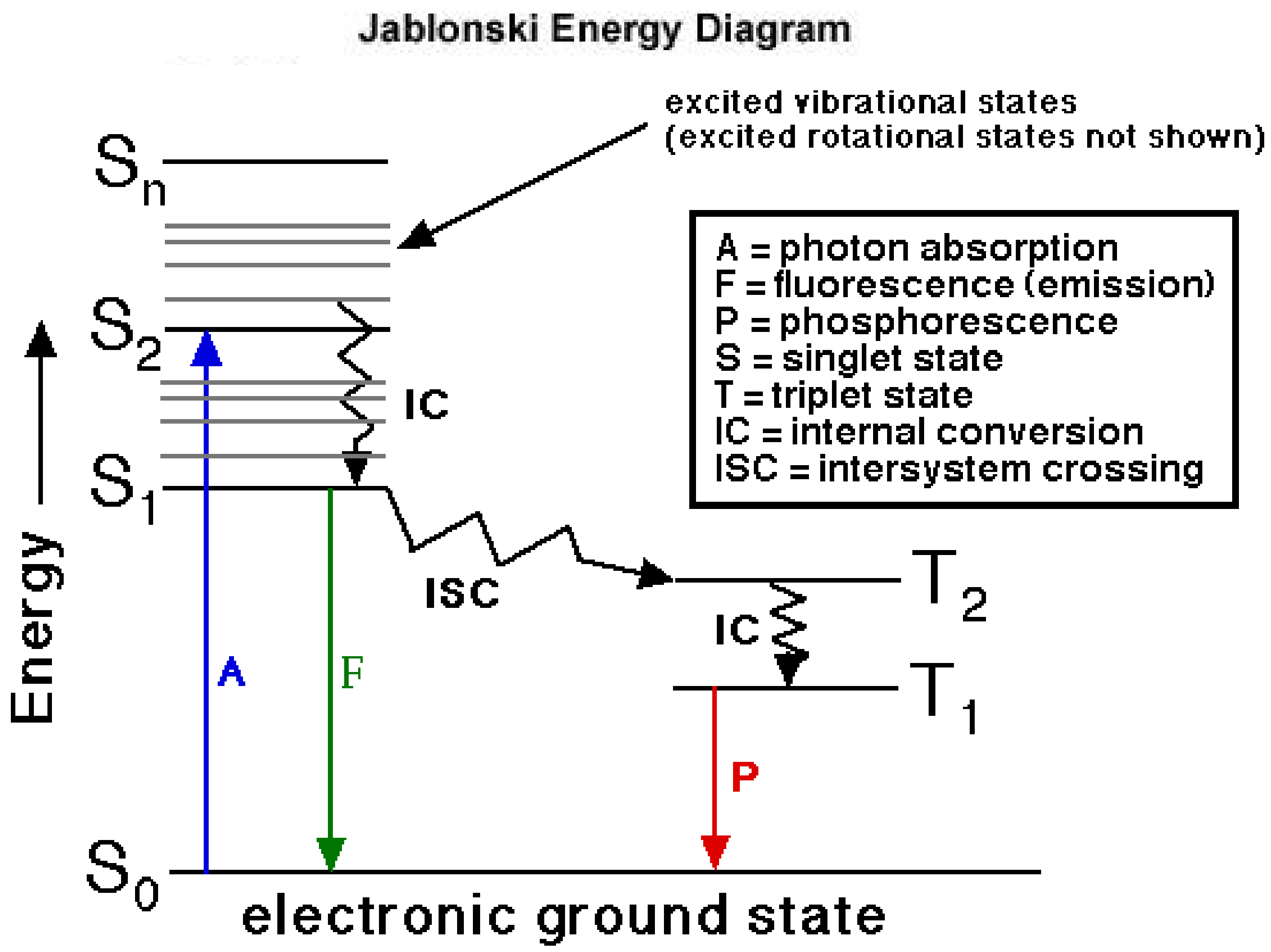


Molecular Fluorescence Spectroscopy





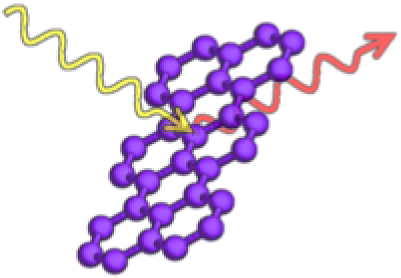
Jablonski Diagram

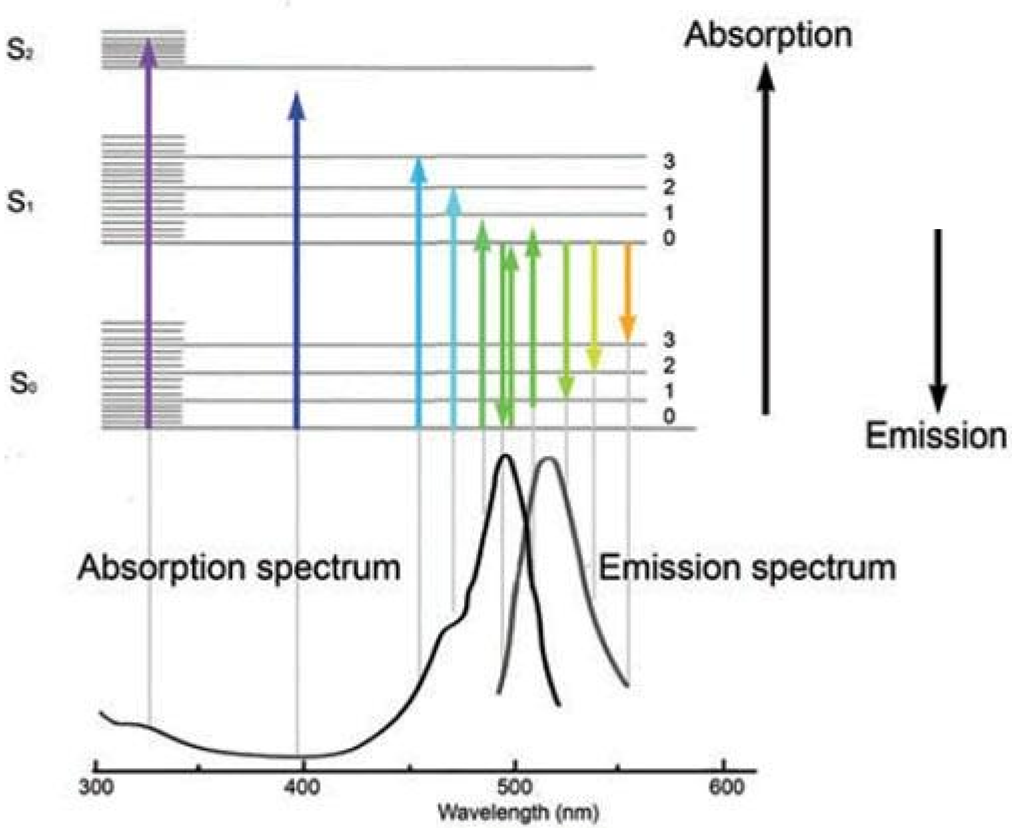


Jablonski Energy Diagram

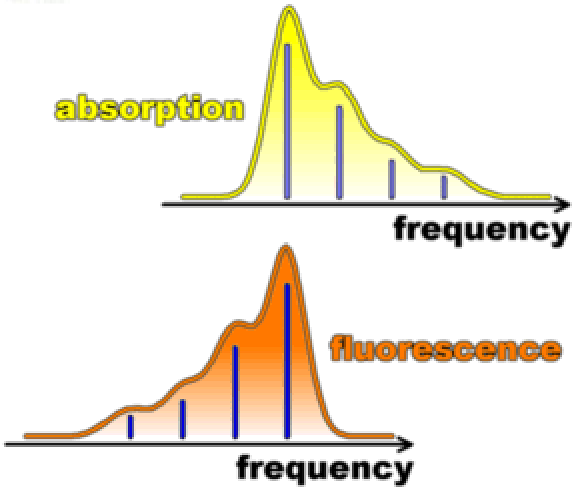
A = photon absorption
F = fluorescence (emission)
P = phosphorescence
S = singlet state
T = triplet state
IC = internal conversion
ISC = intersystem crossing

That‘s what you usually find in text books about absorption/fluorescence of a molecule:

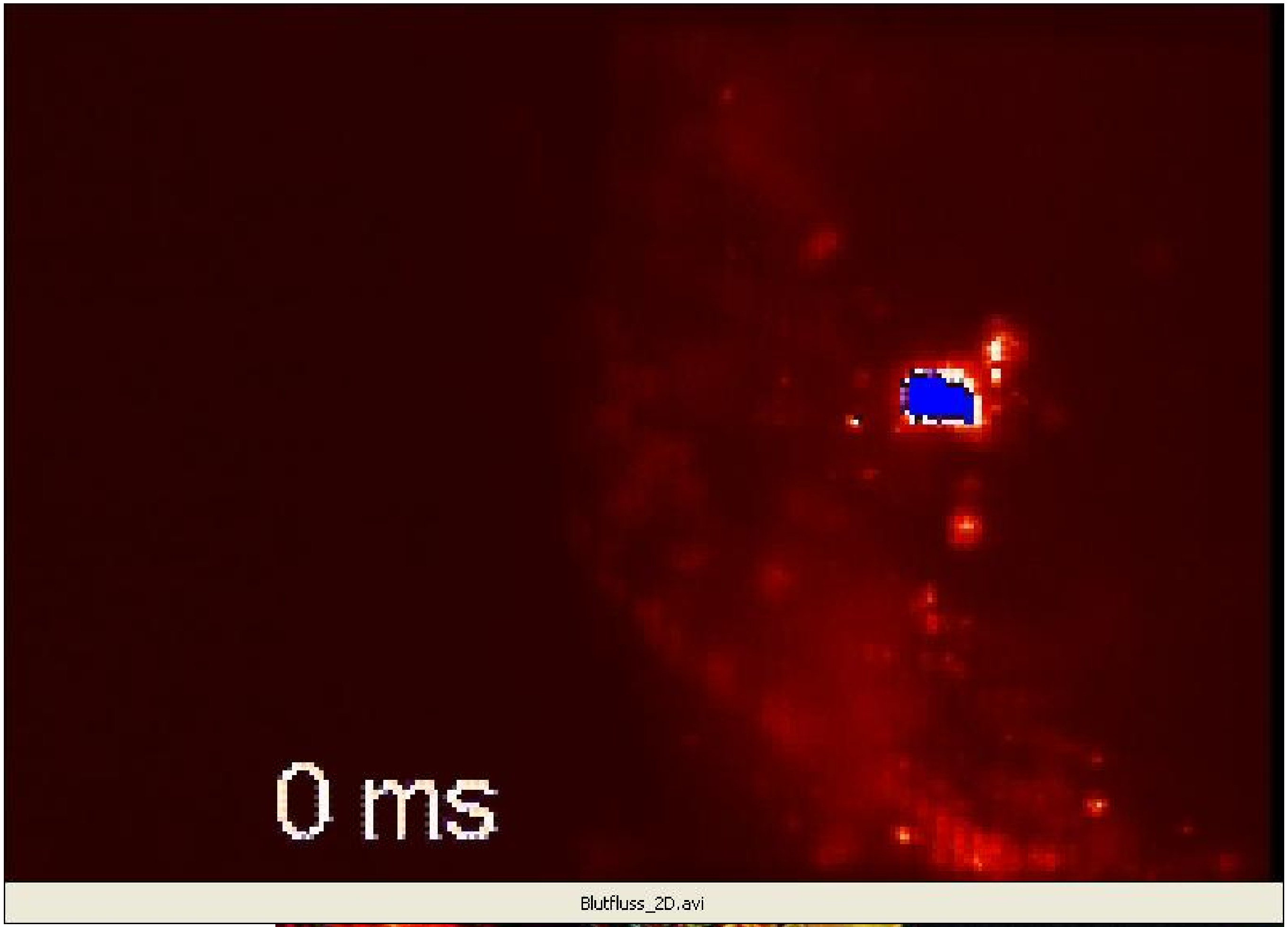




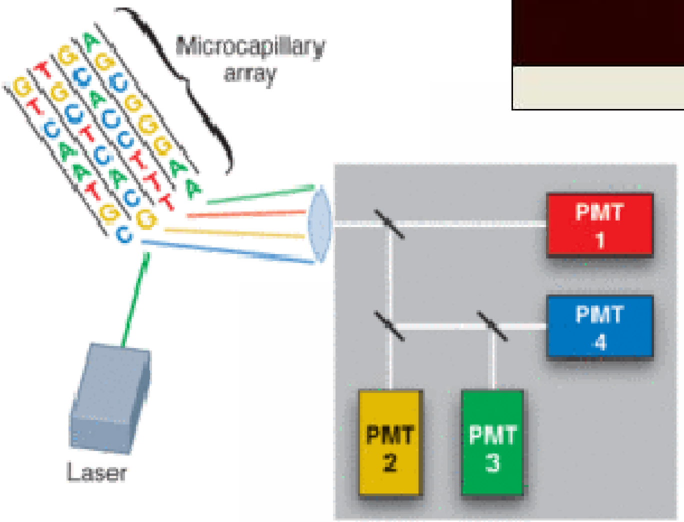
What‘s wrong?

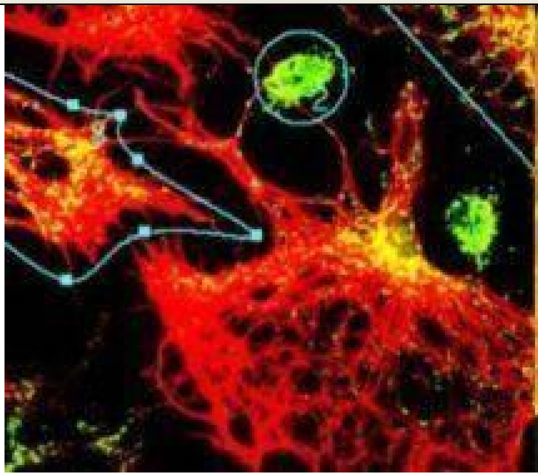


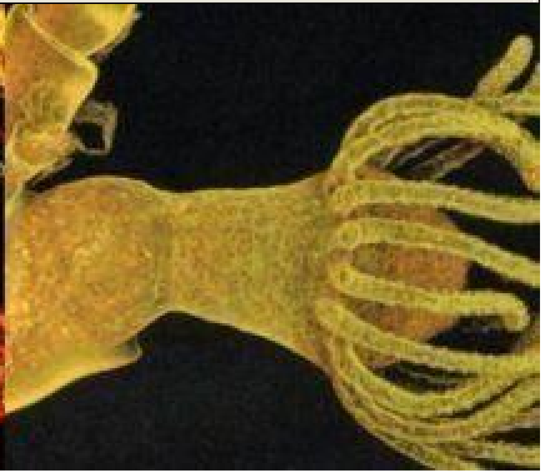
Modern Microscopy is LIF



Blutfluss_2D.avi

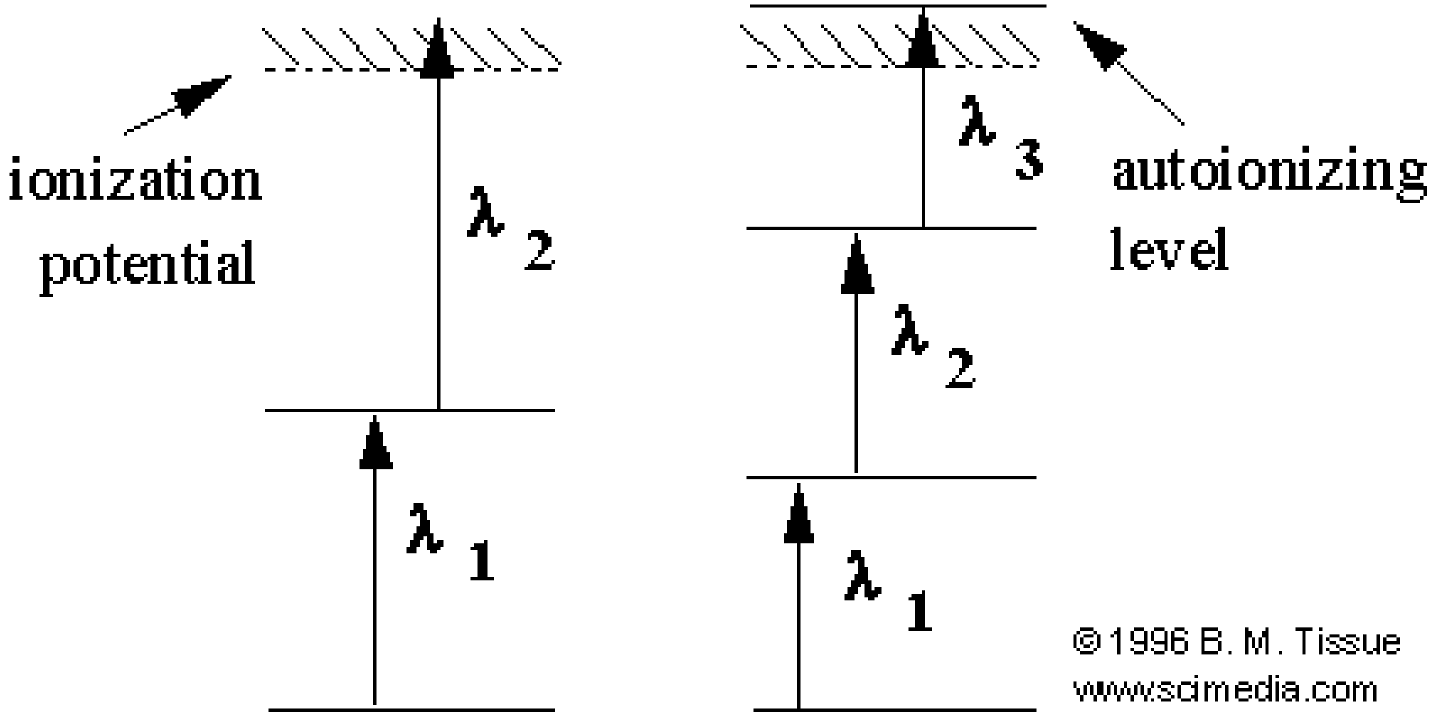






Ionization Spectroscopy

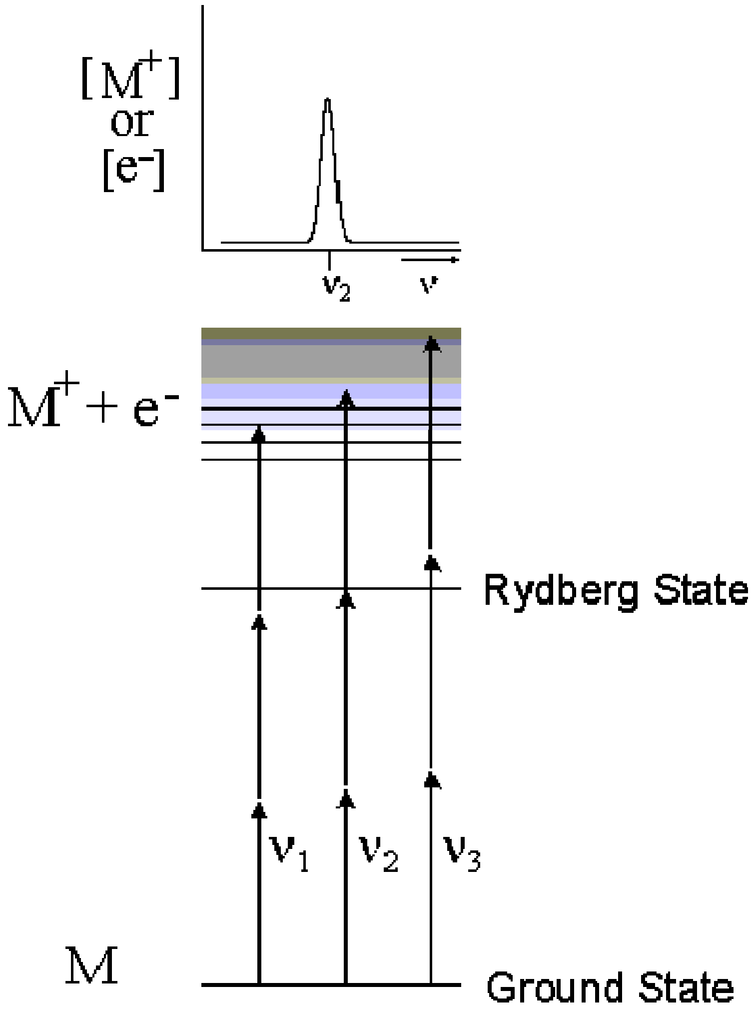
Absorption of photons on the molecular transition $E_i \rightarrow E_k$ is monitored by detection of the ions or electrons, produced by some means from the molecular excited state E_k. The ionization of the excited molecule may be performed by photons, by collisions, or by an external electric, or magnetic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

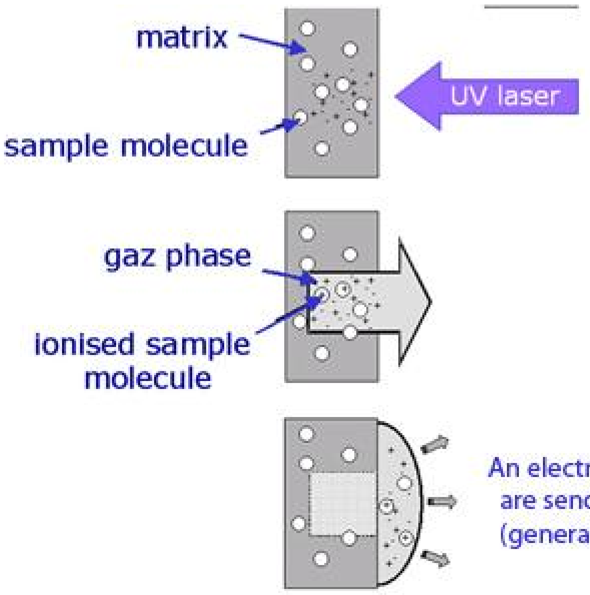
REMPI: Resonant Enhanced Multi-Photon Ionisation

REMPI involves a resonant single or multiple photon absorption to an electronically excited intermediate state followed by another photon which ionizes the atom or molecule.

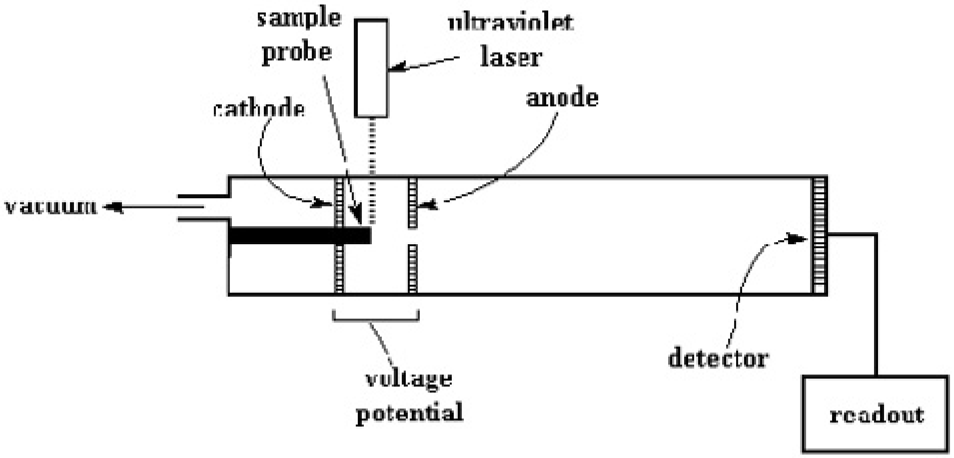


MALDI: Matrix Assisted Laser Desorption/Ionisation

A time of flight spectrometry technique, allowing the analysis of biomolecules and large organic molecules



An electrical field is applied and ions are send to a detector (generally but not only TOF)



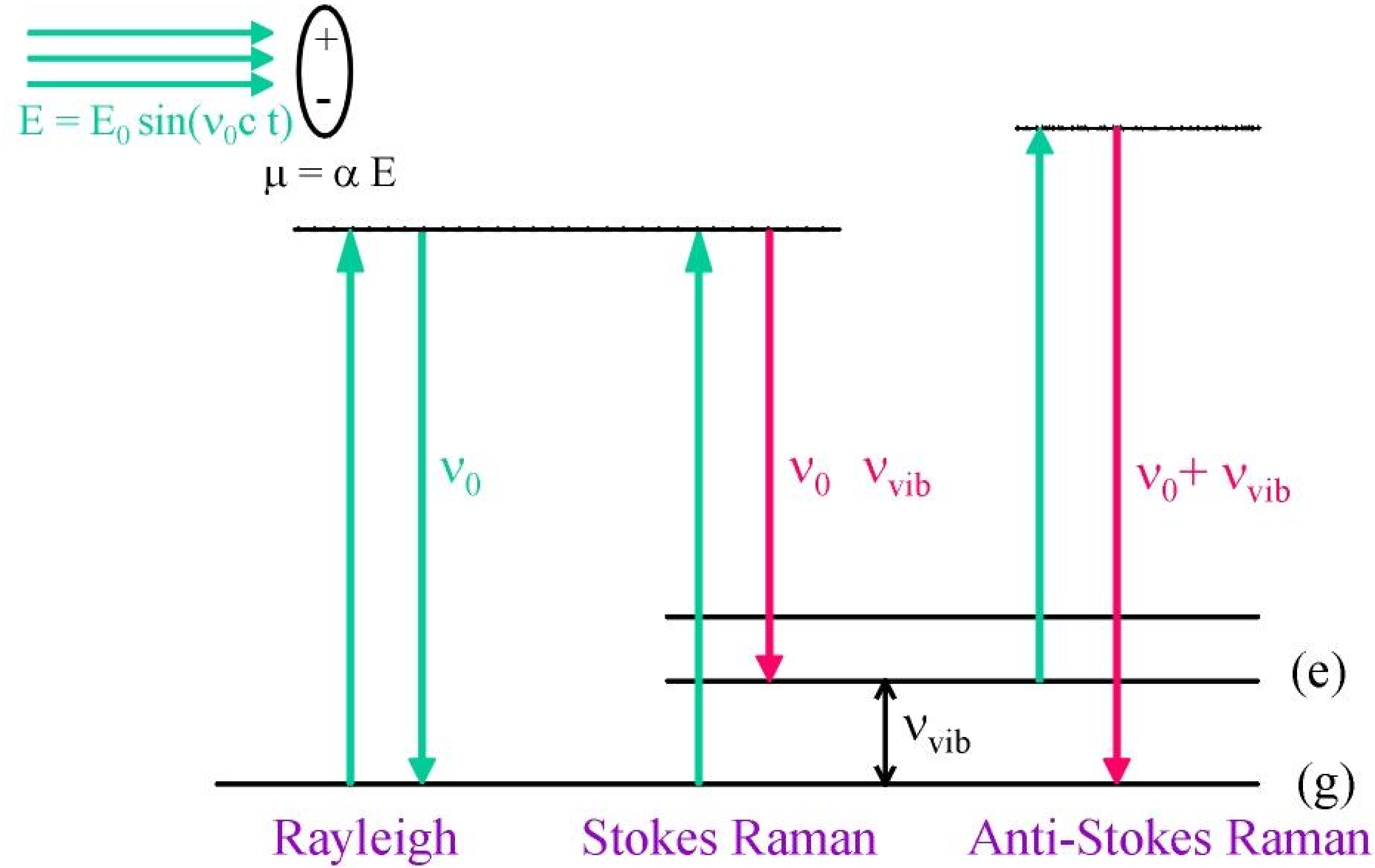
A simplified diagram of a MADLI apparatus
(After Creel, H., *Trends in Polym. Sci.*, 1993, *1(11)*, 336-342.)

AND MUCH MORE TECHNIQUES.....

Enough is enough

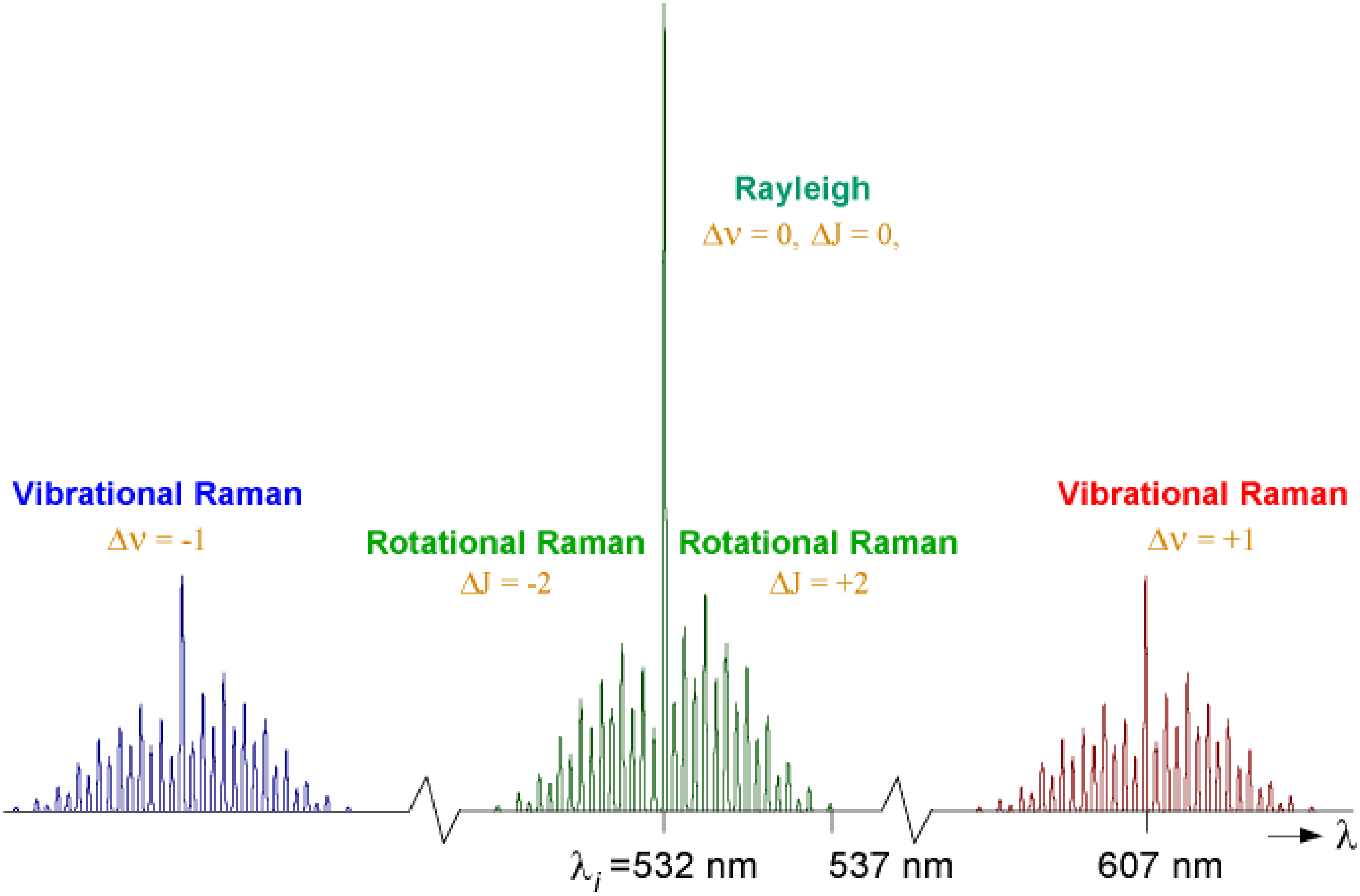
Thank you

Raman

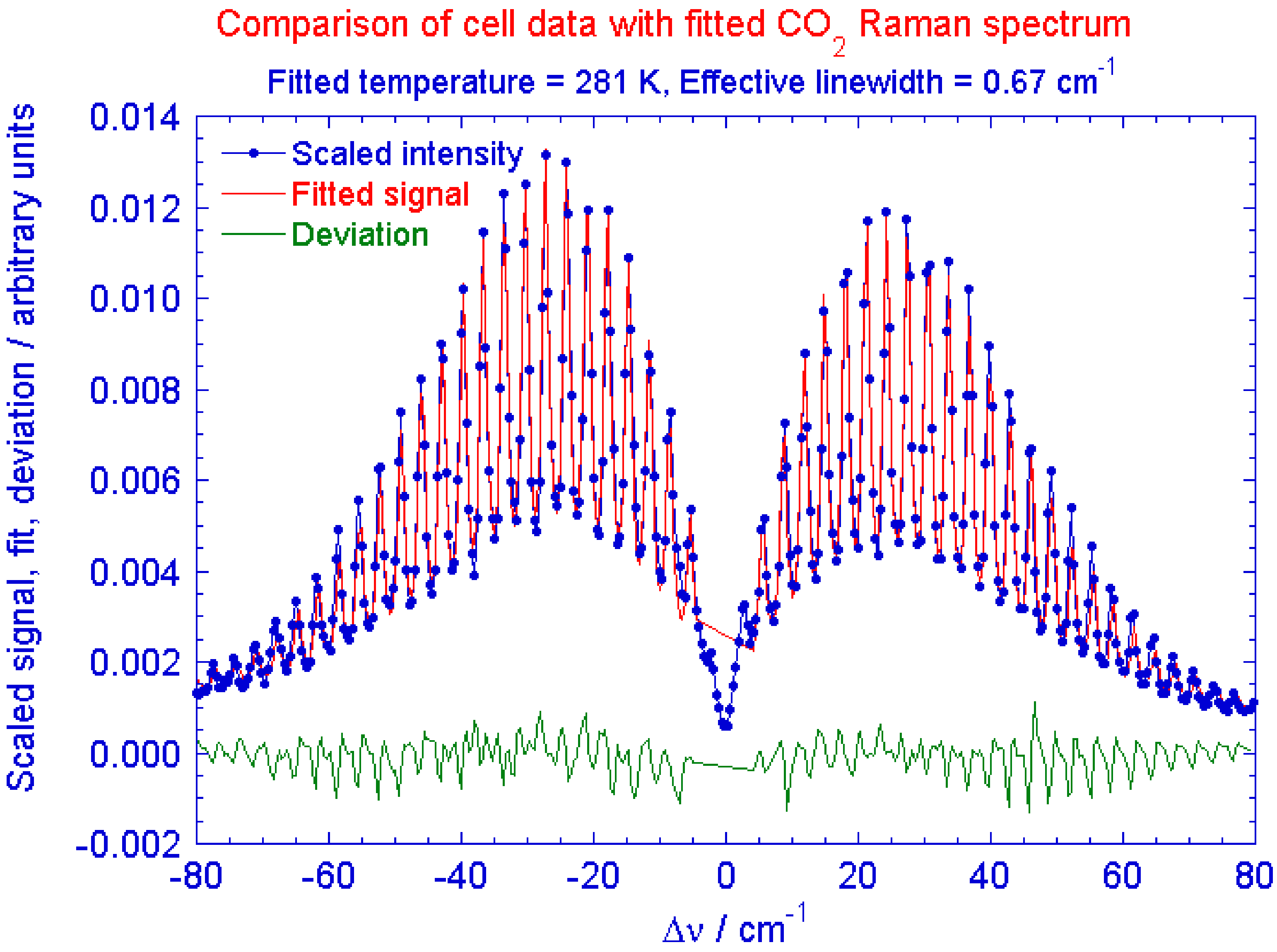


$E = E_0 \sin(\nu_0 c\, t)$
+
-
$\mu = \alpha E$
ν_0
$\nu_0 \quad \nu_{vib}$
$\nu_0 + \nu_{vib}$
(e)
ν_{vib}
(g)
Rayleigh
Stokes Raman
Anti-Stokes Raman

Raman spectrum of N_2



Raman spectrum



Rotational Raman Spectroscopy: C_2N_2

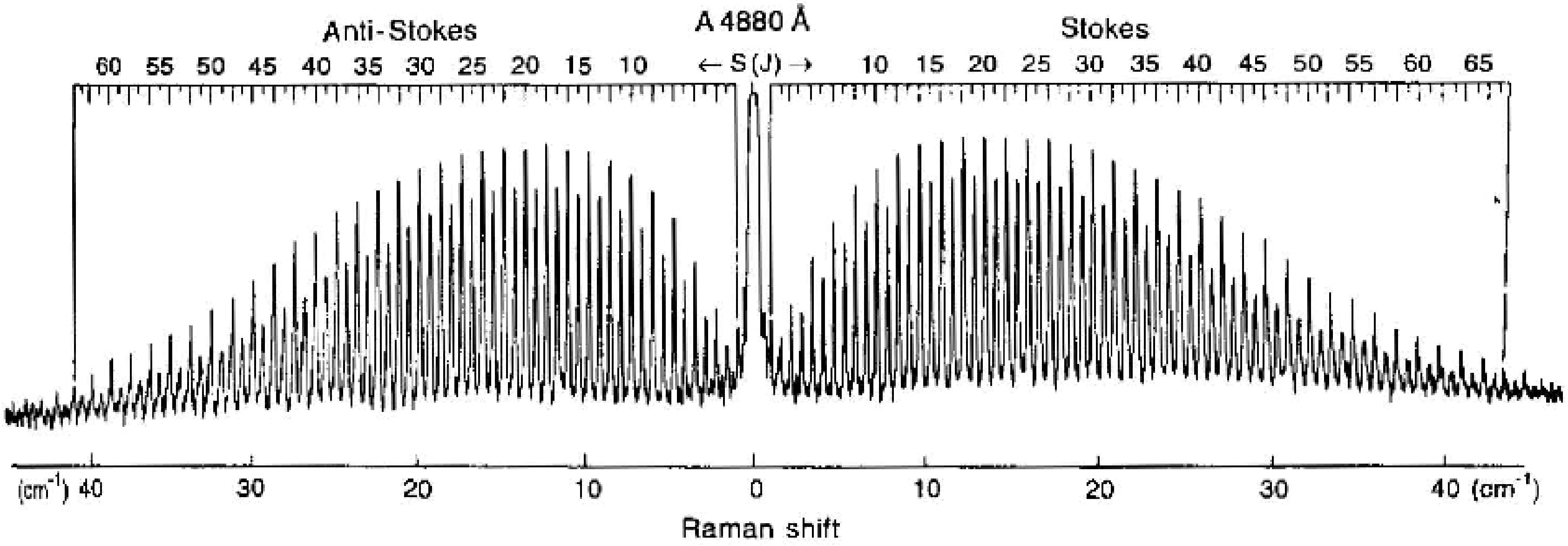
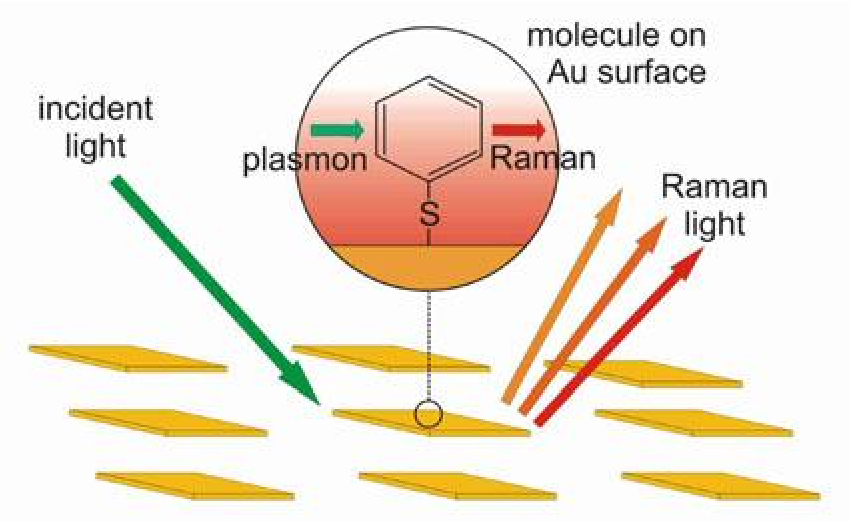


Fig.8.3. Rotational Raman spectrum of C_2N_2 excited with the 488 nm line of the argon laser in the experimental setup of Fig.8.2 and recorded on a photographic plate with 10 min exposure time [8.20]

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

Surface Enhanced Raman Scattering (SERS)

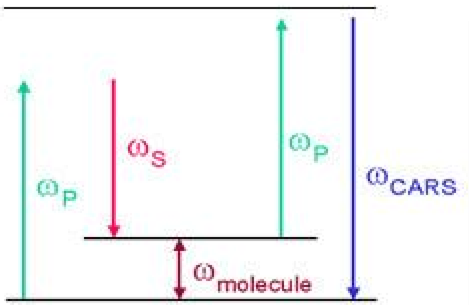
SERS is a surface sensitive technique that results in the enhancement of Raman scattering by molecules adsorbed on rough metal surfaces. Improvement of the detection limits by a factor of 10^{12} - 10^{14}.



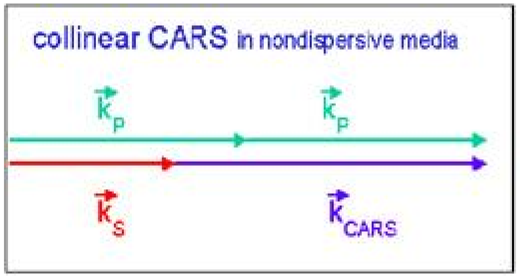
The excitation laser is selected to be in resonance with the surface absorption band, or surface plasmon associated with the metal surface. The analyte that adsorbs in the interaction region is perturbed, leading to enhanced spectral features. Since SERS is a direct measure of the analyte's bonding structure, unique spectral signatures are collected and false positives are minimized. SERS techniques have permitted trace level detection and identification of pollutants such as cyanide and pesticides in water supplies.

CARS: Coherent Antistoke Raman Scattering

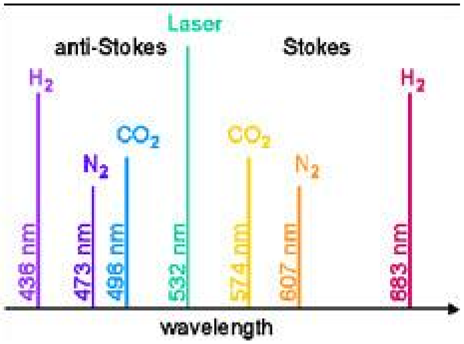
A (coherent non linear 4 wave mixing) diagnostic technique used to determine temperature and concentration in combustion processes.

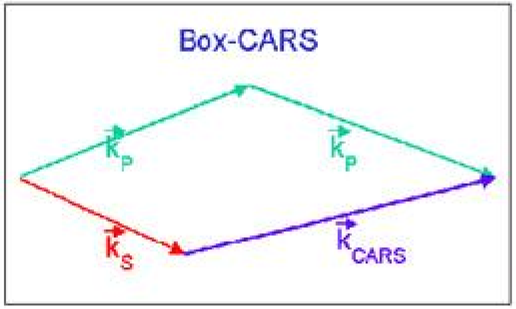


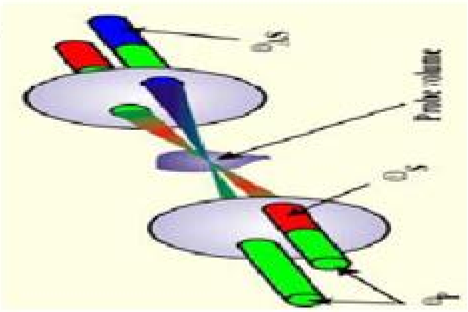
ω_P: **pump laser frequency**
ω_S: **stokes**
ω_{CARS}: **raman frequency of a molecular transition**



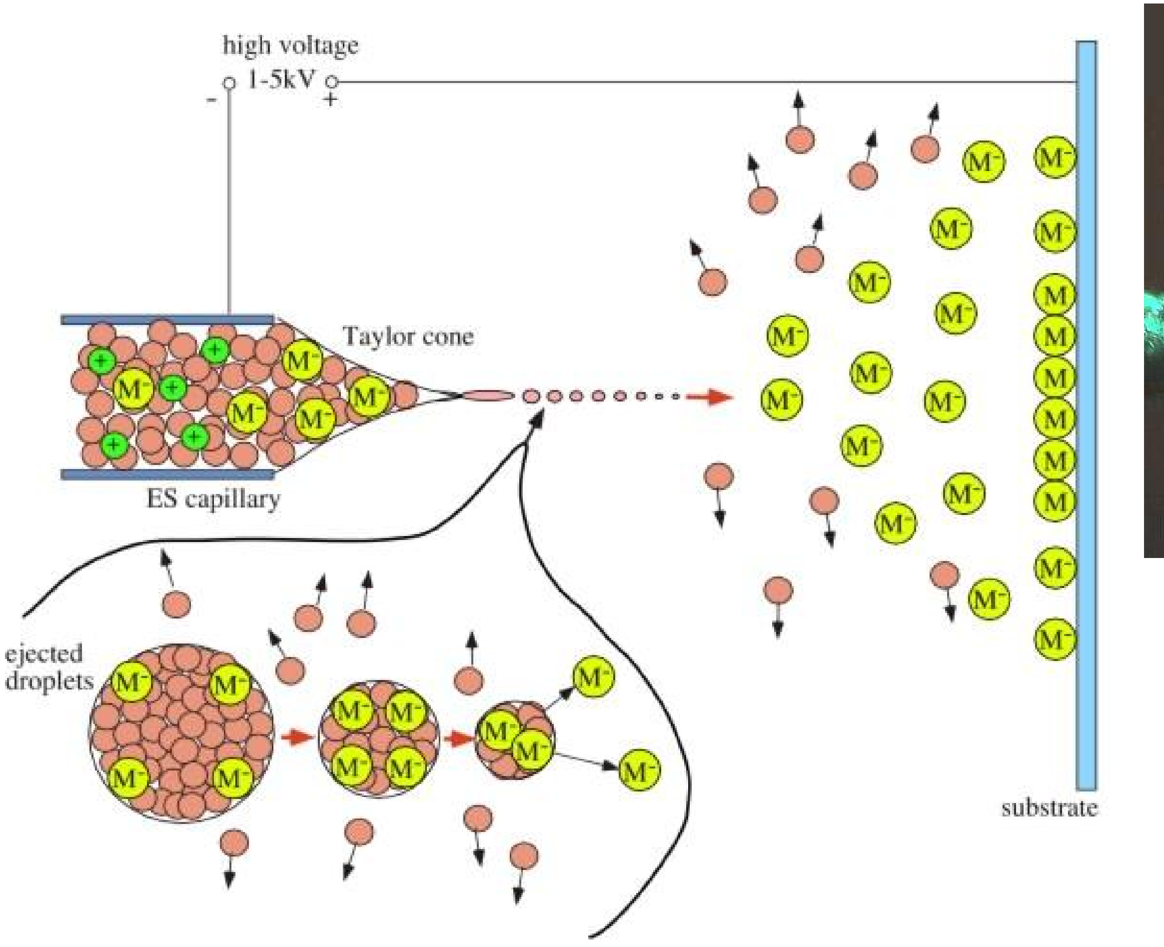
$$\vec{k}_P + \vec{k}_P = \vec{k}_S + \vec{k}_{CARS}$$







Electrospray

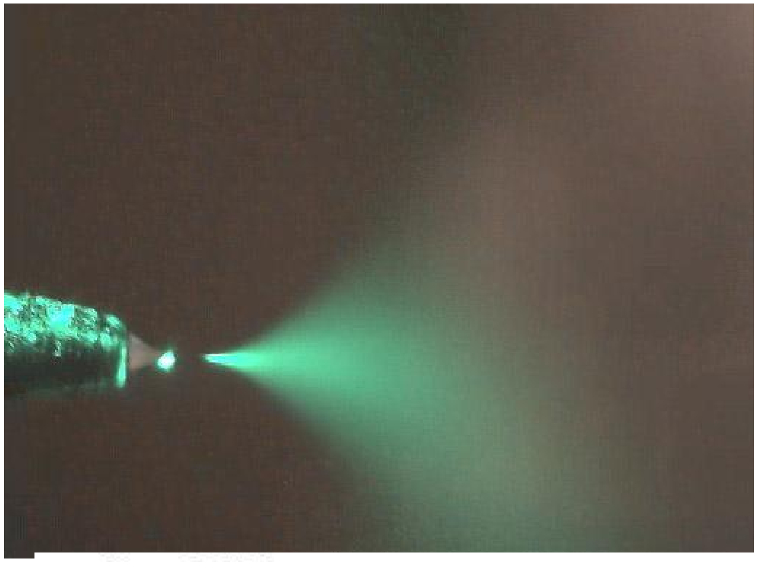


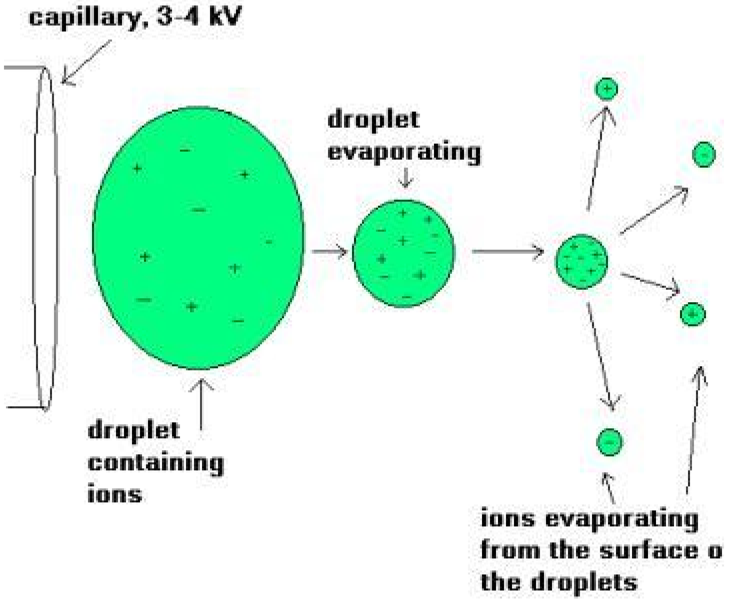
a) strong electric field extracts droplets from Taylor cone containing solute ions M^-; most counter ions + remain in capillary

b) Solvent ● evaporates, droplets shrink, charge density increases

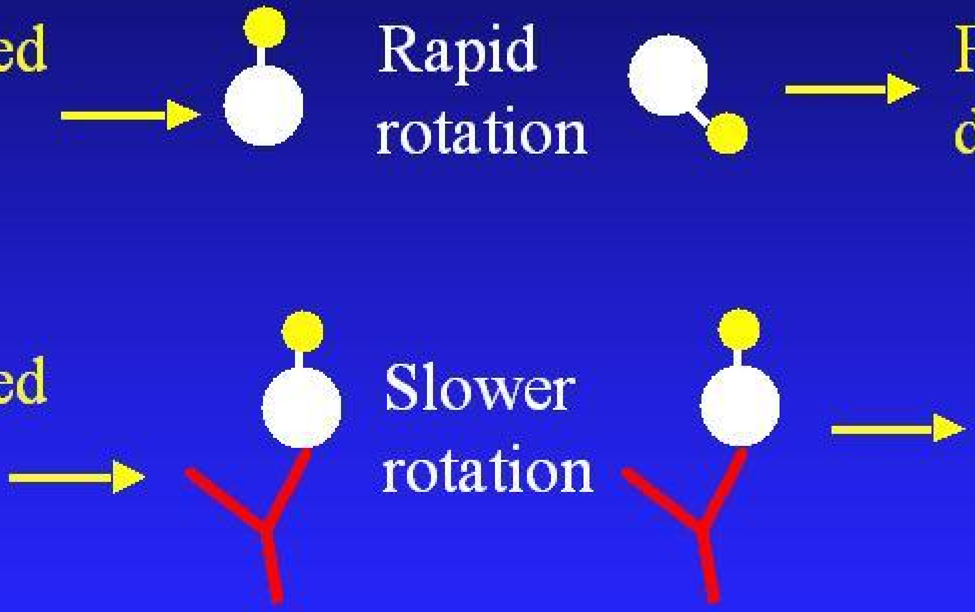
c) solute ions are ejected from the shrinking droplets; Space charge causes a plume

d) solute molecules form thin film on substrate





Fluorescence Polarization (FP)



Small unbound molecule

Polarized light → Rapid rotation → Fluorescence de-polarized

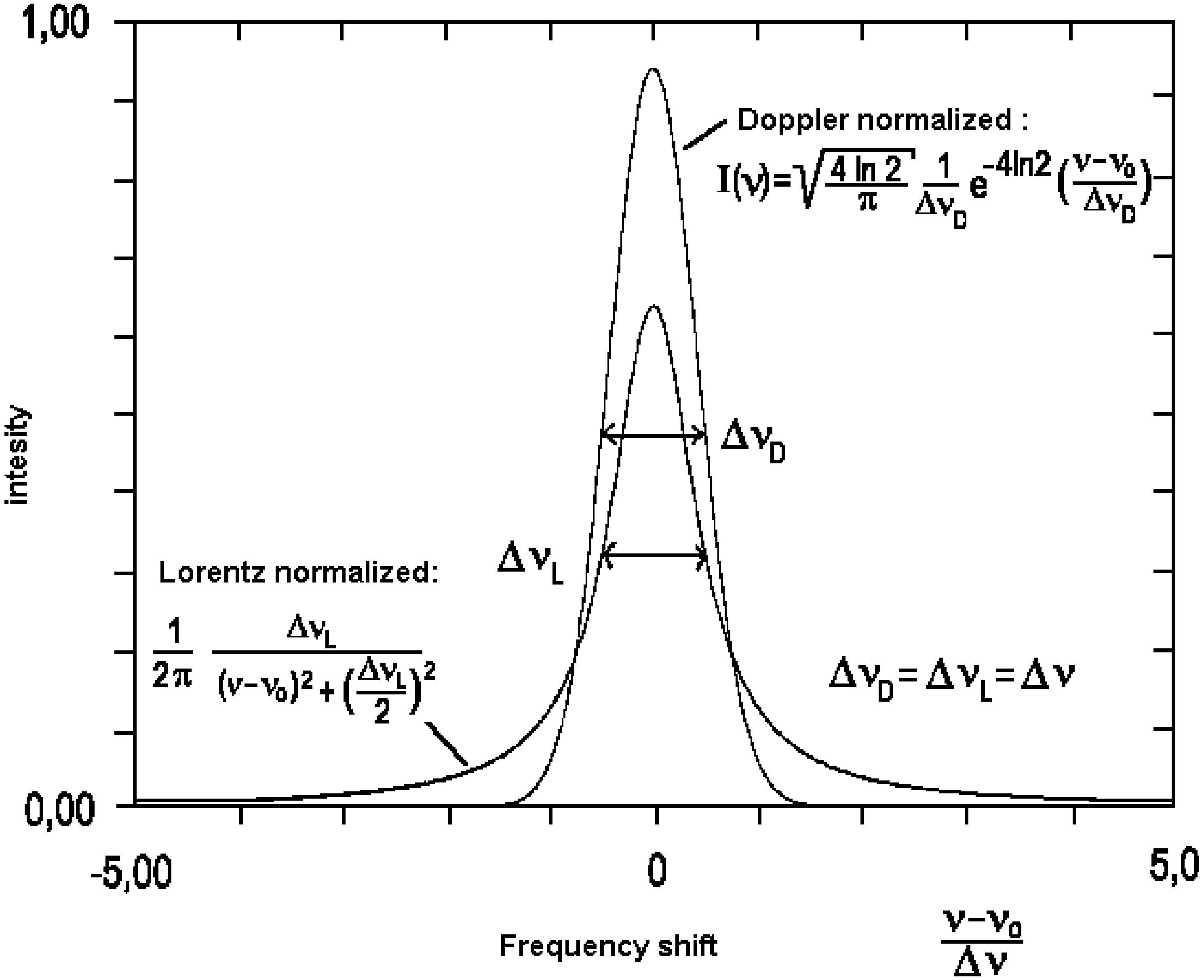
Polarized light → Slower rotation → Fluorescence polarized

Large complex molecule

Heterodyne detection

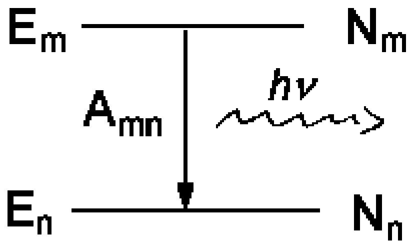
Heterodyne detection is a method of detecting radiation by non-linear mixing with radiation of a reference frequency. It is commonly used in telecommunications and astronomy for detecting and analysing signals.

Lorentz and Doppler Line Shapes

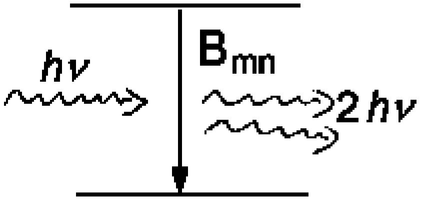


LASER

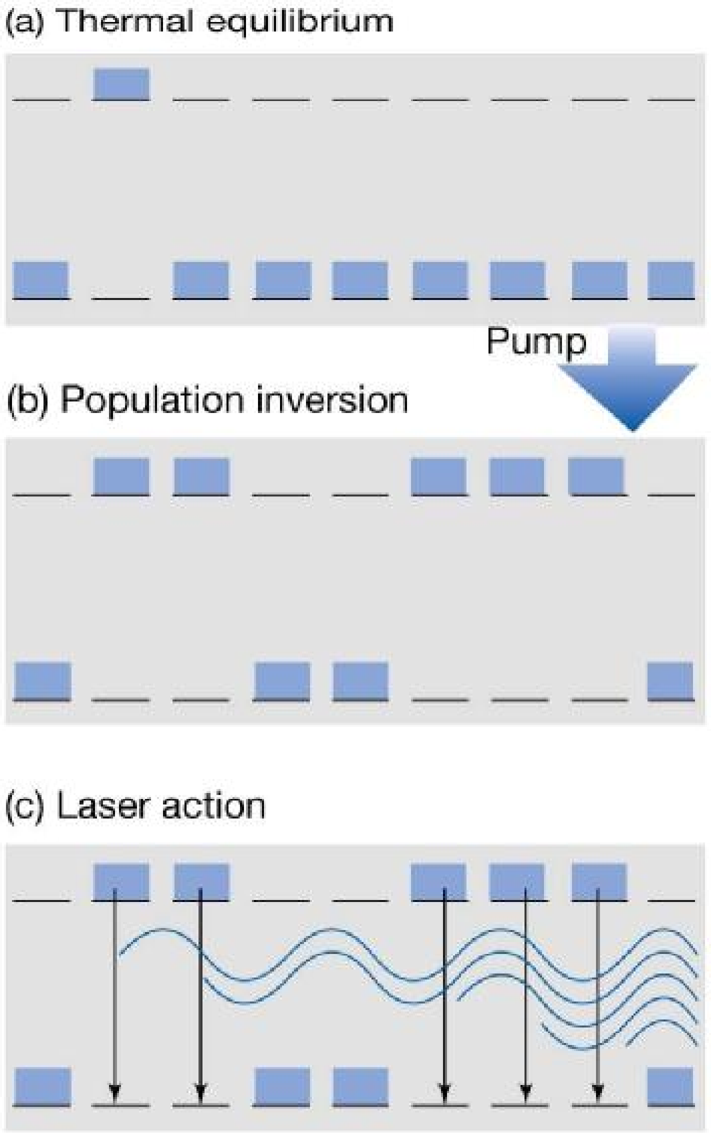
Light Amplification by Stimulated Emission



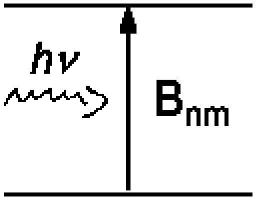
spontaneous emission



induced emission



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

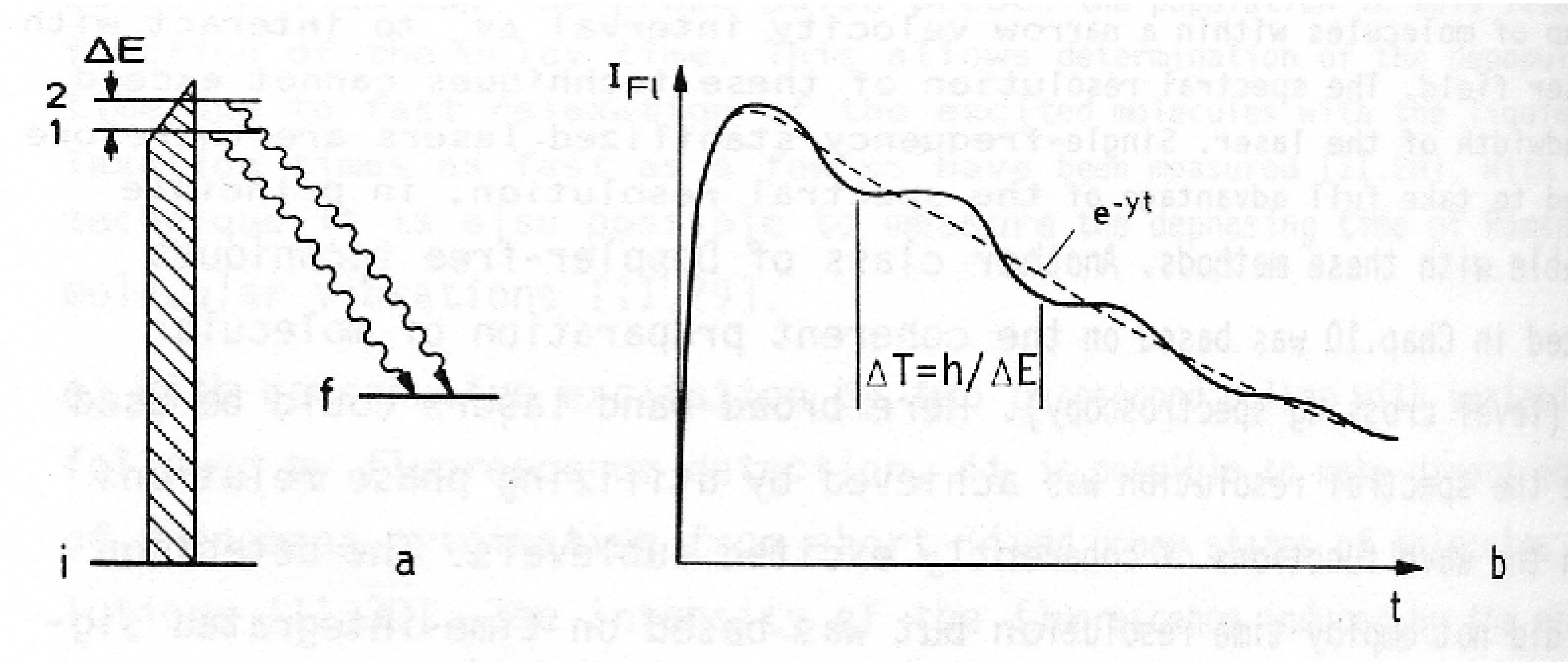


absorption

$A_{21} / B_{12} = 8ph\,{}^{n\,3}/_{c^3}$

For instance, for the wavelength of 500 nm the ratio between the intensities of the spontaneous and stimulated transitions is
F = e^{96} = 5½10^{41} !

Quantum Beat Spectroscopy



Laser Induced Fluorescence (LIF)

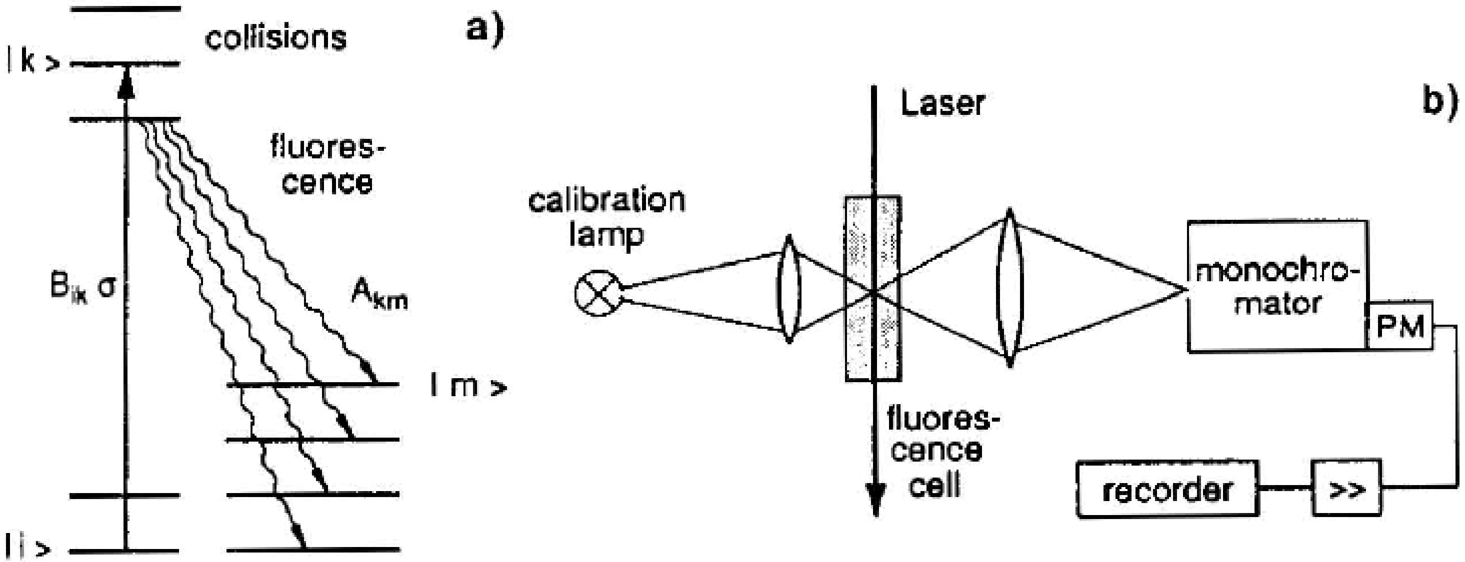


Fig.6.33a,b. Laser-induced fluorescence: (a) Level scheme and (b) experimental arrangement for measuring LIF spectra