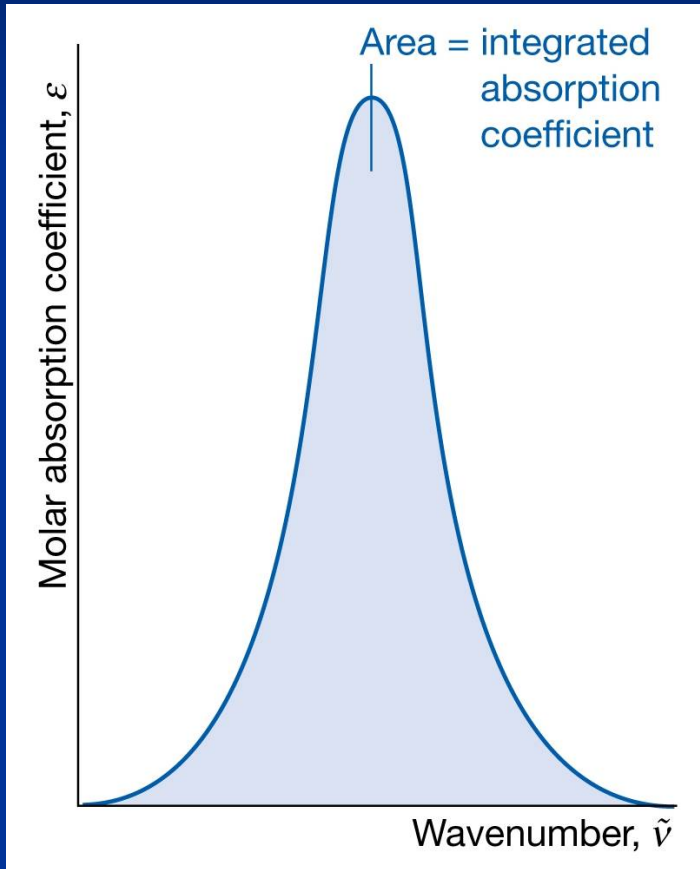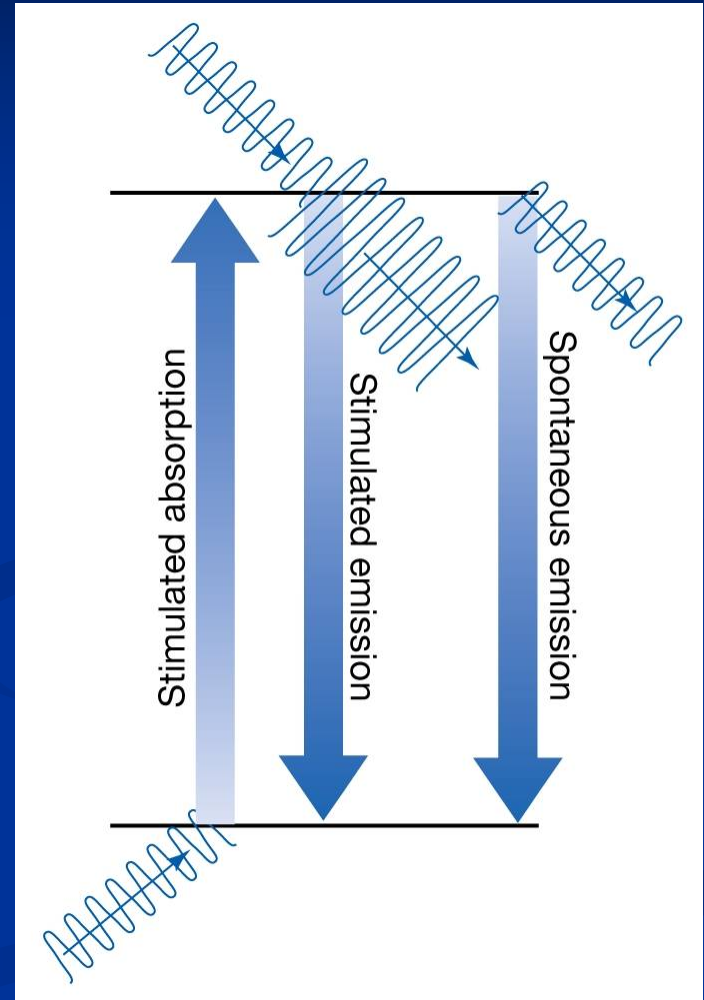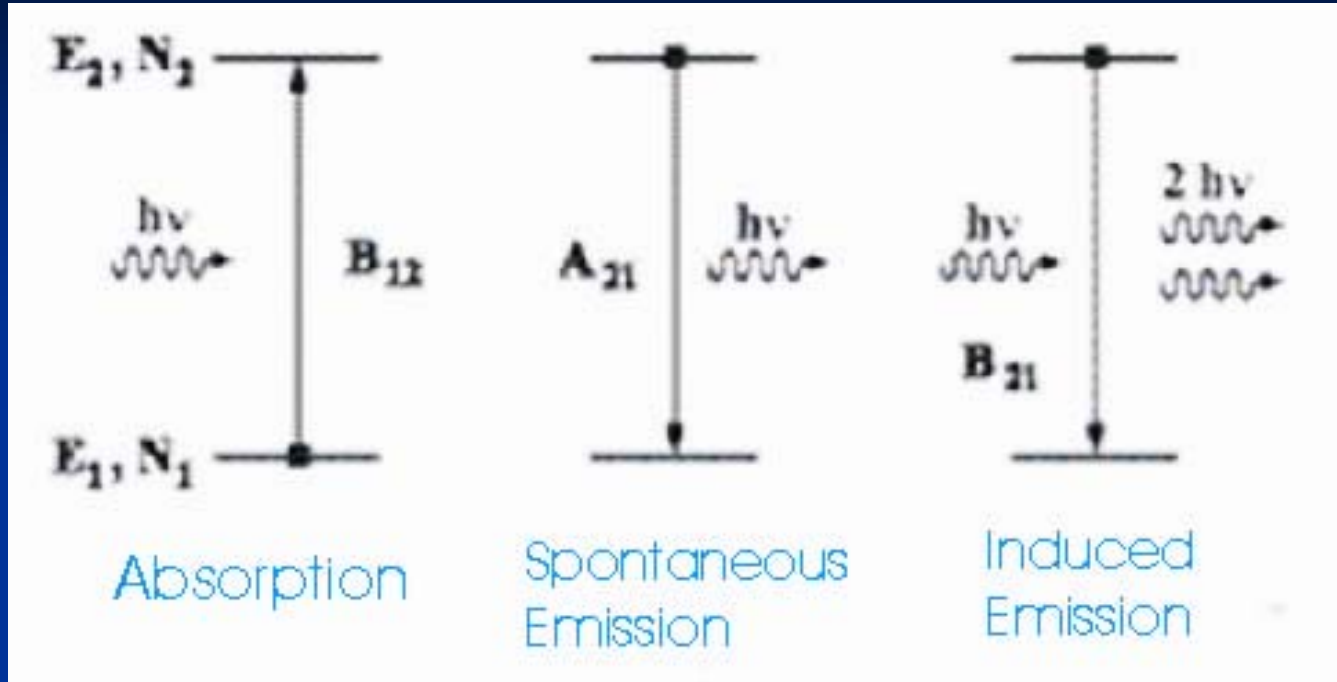# Optical Transitions

The integration absorption coefficient

Transitions

Einstein Coefficients

$$^{dN_2}/_{dt} = B_{12} \cdot u(\nu) \cdot N_1 \qquad ^{dN_2}/_{dt} = -A_{21} N_2 \qquad ^{dN_2}/_{dt} = -B_{21} \cdot u(\nu) \cdot N_2$$

$$B_{21}/B_{12} = g_2/g_1 \qquad\qquad A_{21}/B_{12} = 8\pi h\, ^{\nu\,^3}/_{c^3}$$

Lambert-Beer Law

Transmittance of the sample::

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

where σ [cm^2] is an absorption cross section, N[cm^{-3}], and l [cm]

The form which widely used in laboratory practice:

$$T = 10^{-\varepsilon C l},$$

where ε [L mol^{-1} cm^{-1}] is an extinction coefficient and **C** [mol L^{-1}] is a molar concentration:

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

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

Low Optical Density

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

$$I = I_0(1 - \sigma N l)$$

Integrating the cross section $\sigma = \sigma(v)$ over the light frequency v within the absorption peak, one obtains the integrated cross section $\langle \sigma(v) \rangle$:

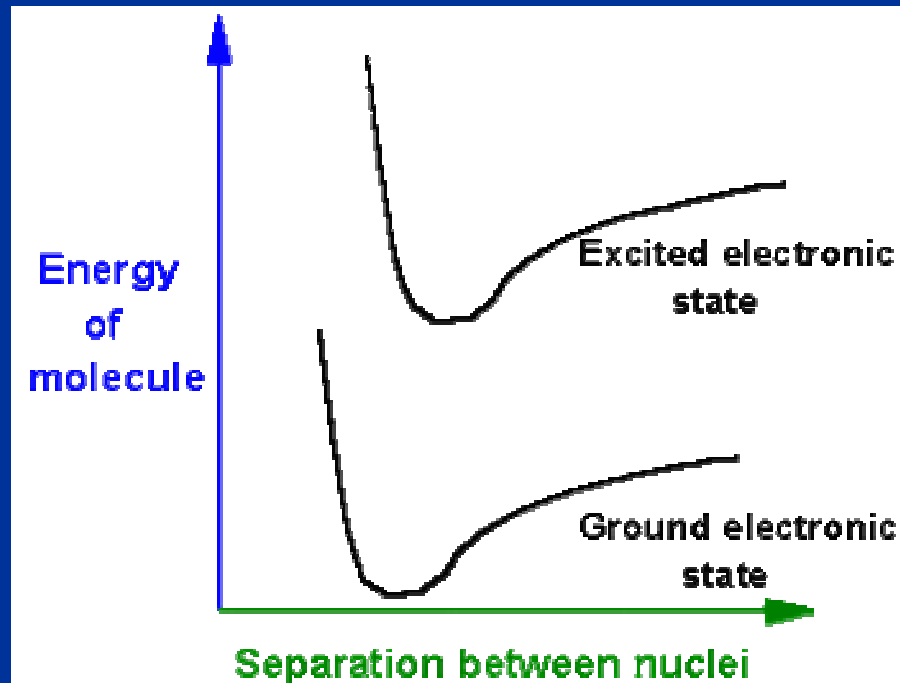$$\langle \sigma \rangle = \int \sigma(v)\, dv = B_{mn} \frac{h v_0}{c}$$

where B_{mn} is the Einstein absorption coefficient and v_0 is the center of the molecular absorption line. Thus, the Einstein coefficient B_{mn} can be directly determined from experiment.

Born-Oppenheimer Approximation

$$\Psi_{tot} = \Psi_{el}\, \Psi_{vib}\, \Psi_{rot}$$

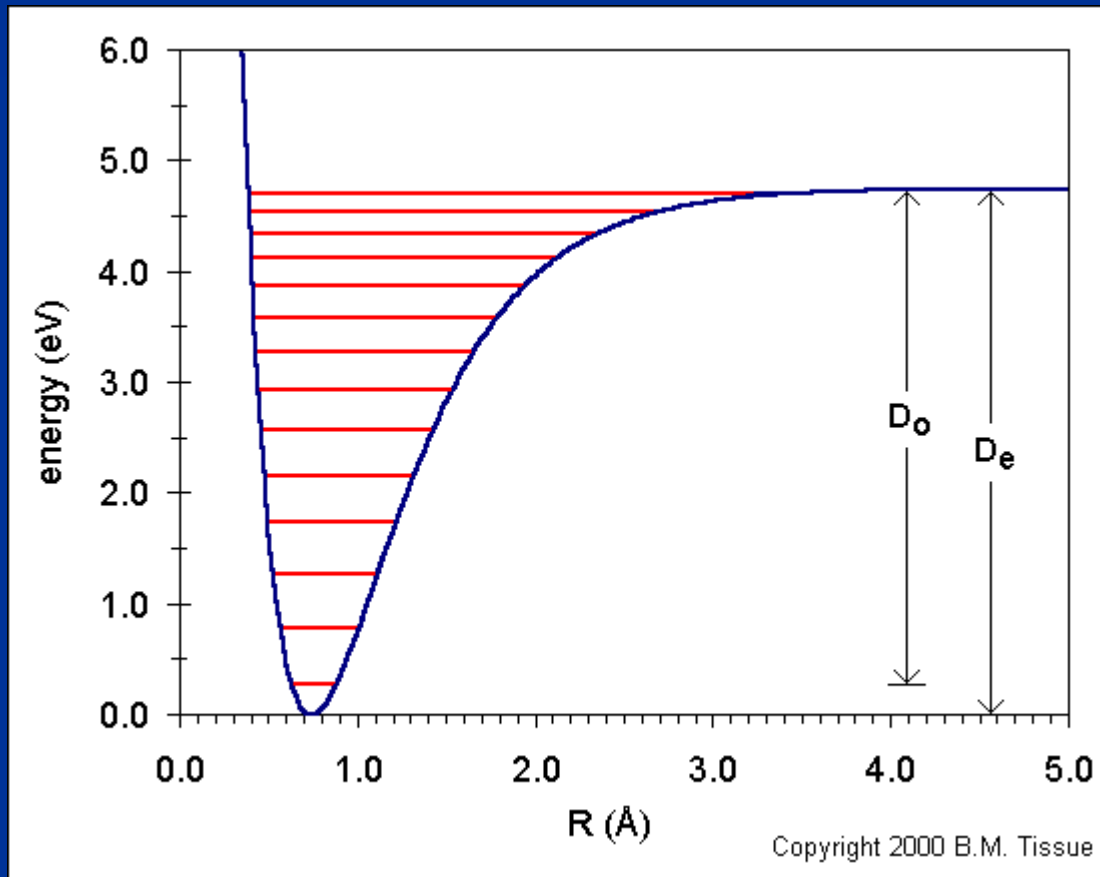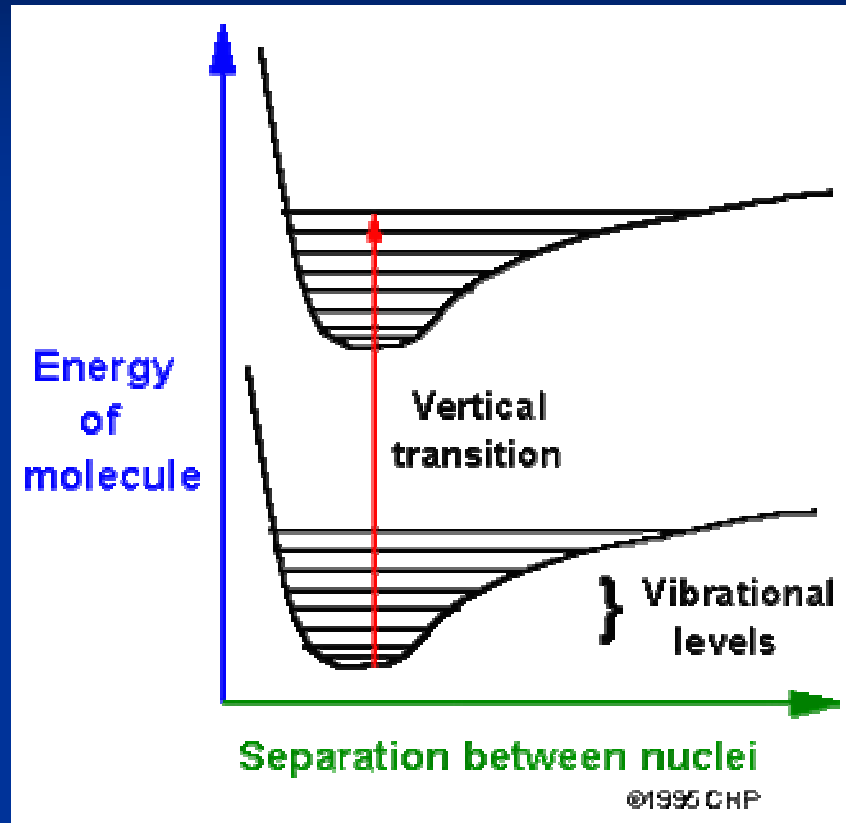$$E_{tot} = E_{el} + E_{vib} + E_{rot}$$

Potential energy curves

Morse Potential

$$V(R) = D_e \left(1 - 2^{-\beta(R-R_0)} \right) \qquad \beta = \pi \nu_e \sqrt{\dfrac{2\mu}{D_e}}$$
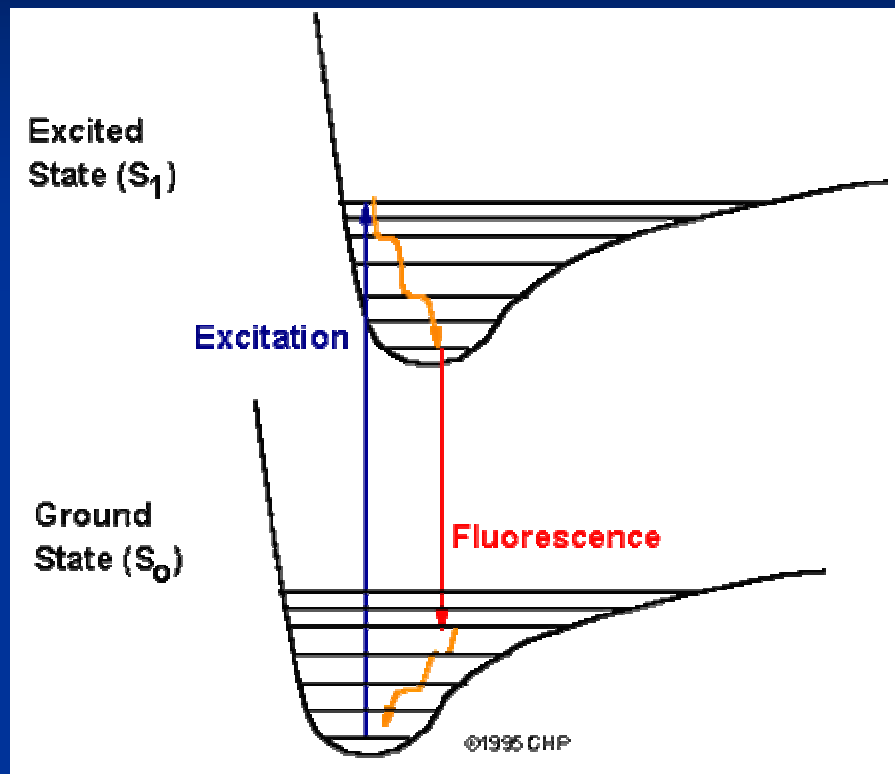
$E_v = (v + \tfrac{1}{2})\,\omega_e - (v + \tfrac{1}{2})^2\,\omega_e^2\,x_e^2 + (v + \tfrac{1}{2})^3\,\omega_e^3\,y_e^3 + \text{higher terms,} \qquad v = 0,1,2\ldots$
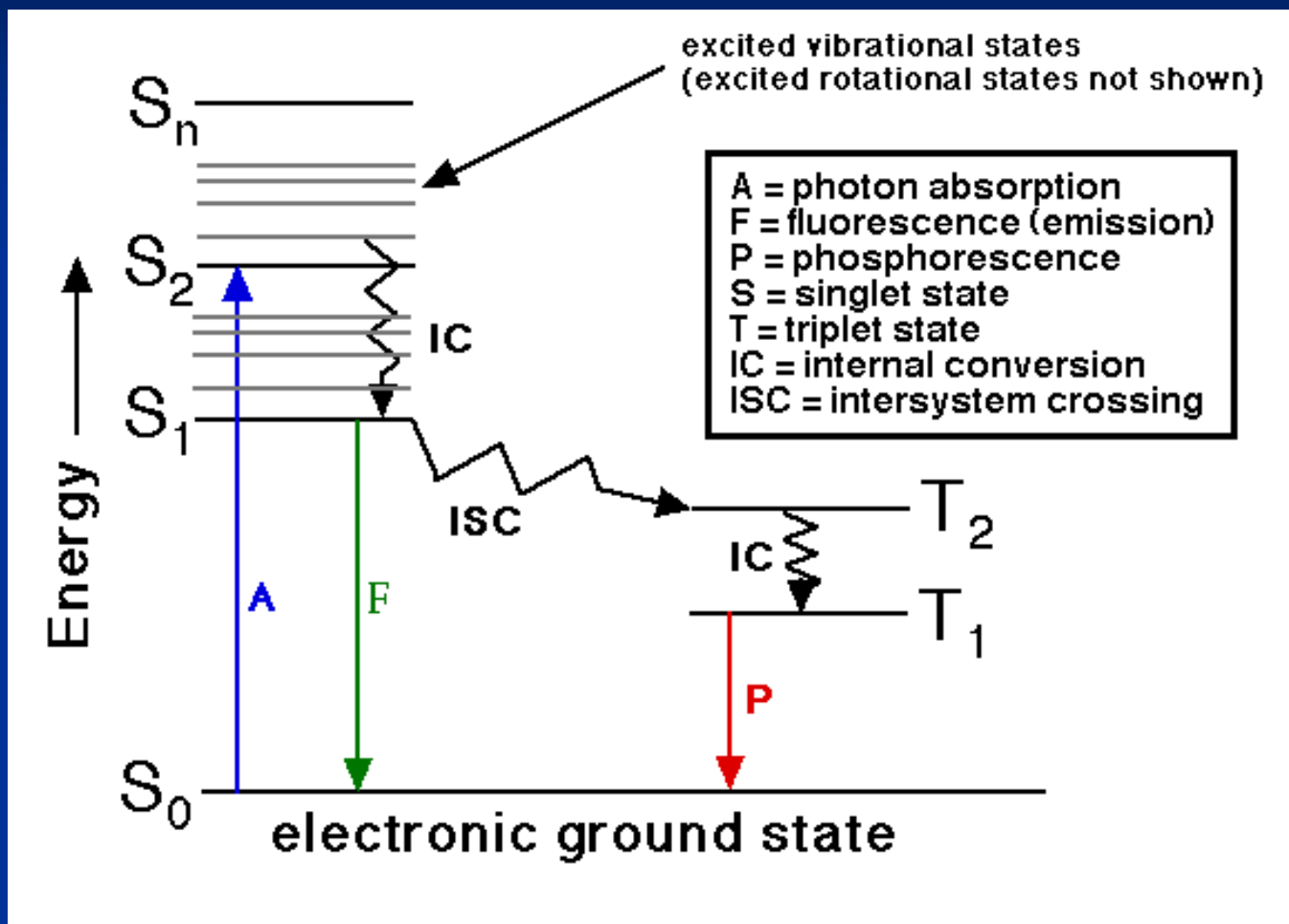

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Born-Oppenheimer Approximation: Electronic transitions in molecules

Molecular Fluorescence Spectroscopy

Jablonski Diagram

Spectral Line Shape

Uncertainty relation for energy:

$$\Delta E \approx \frac{\hbar}{\tau}$$

Two main processes which are responsible to the finite lifetime of excited states:

1. Spontaneous decay which is proportional to the corresponding Einstein coefficient A_{nm}. The intensity the spontaneous decay is proportional to the square of the matrix element of interaction with electromagnetic modes of vacuum.

2. Interaction between the molecular quantum states and other particles and fields. In the gas phase this interaction is mostly inelastic collisions with surrounding particles. In the condensed matter there can be interaction with phonons (vibration of the surrounding lattice).

The corresponding line has the Lorentz shape:

$$I(v) = \frac{1}{\pi} \frac{\gamma/2}{(v - v_L)^2 + \left(\gamma/2\right)^2}$$

where $\gamma = 1/2\pi\tau$ is the decay rate

and $\Delta v_L = \gamma$

Homogeneous (Lorentz) Broadening

	Condition	$\Delta\nu_L$ (Hz)	$\Delta\nu_L$ (cm^{-1})
Natural lifetimes	Gas phase, electronic transitions	$\sim 10^7$	$\sim 10^{-4}$
Natural lifetimes	Gas phase, rotational transitions	$\sim 10^{-4}$	$\sim 10^{-15}$
Collisional lifetimes	Gas, atmospheric pressure	$\sim 10^9$	$\sim 10^{-2}$
Collisional lifetimes	Liquid, electronic transitions	$\sim 10^{12}$	$\sim 10^1$

Doppler Broadening

The Doppler effect results in light frequency shift when the source is moving toward, or away from the observer. When a source emitting radiation with frequency v_0 moves with a speed v, the observer detects radiation with frequency:

$$v = v_0 \left(1 \pm \frac{v_Z}{c} \right)$$

Molecules in a gas chaotically move in all directions. In case of the thermal equilibrium, the distribution of molecular velocities along the line of detection, which we designate as Z axis. this velocity distribution is known as **Maxwell-Boltzmann distribution**:

$$n(v_Z)\, dv_Z = \sqrt{\frac{2kT}{\pi m}} \exp\left[-\frac{m\, v_Z^2}{2kT} \right]$$

The observer detects the corresponding **Doppler-broadened spectral line profile**:
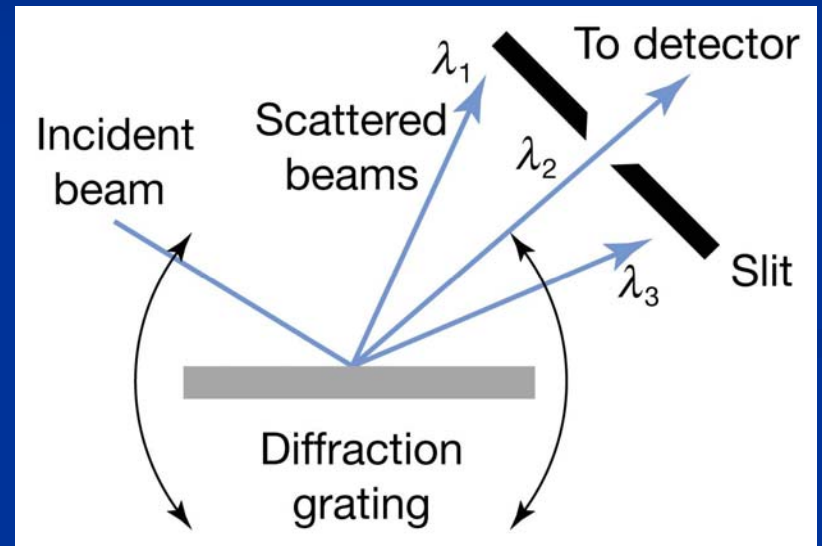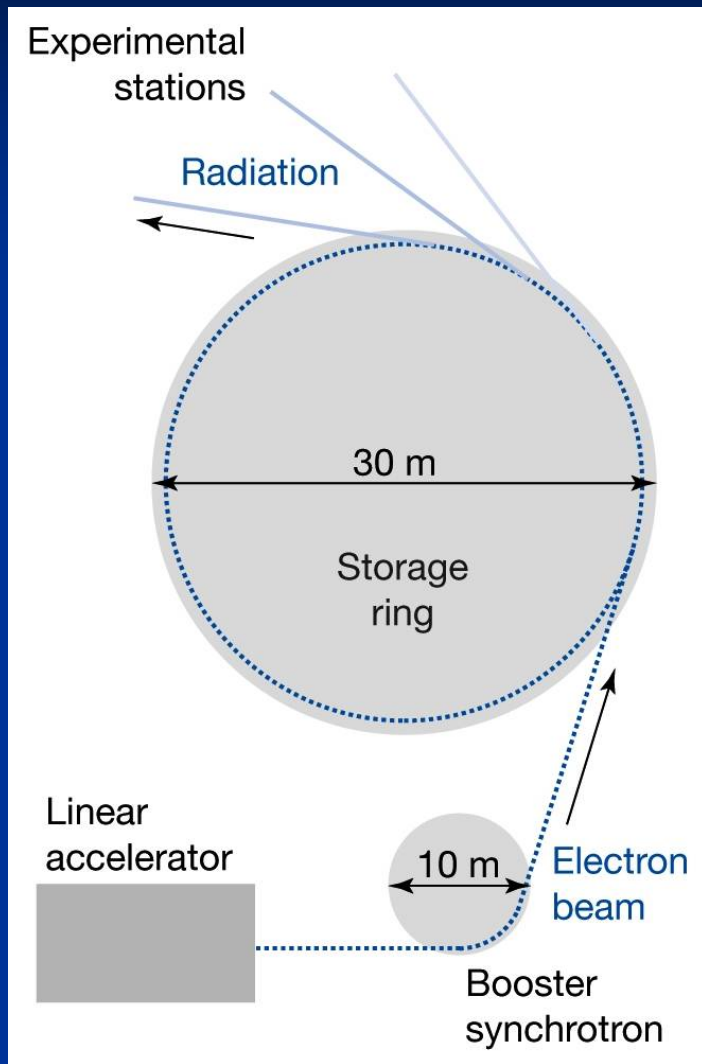
$$I(v) = \sqrt{\frac{4\ln 2}{\pi}} \frac{1}{\Delta v_D} \exp\left[-4\ln 2 \frac{(v - v_0)^2}{\Delta v_D^2} \right]$$

where

$$\Delta v_D = \frac{2 v_0}{c} \sqrt{\frac{2\ln 2\, kT}{m}}$$

For transitions which belong to the visible or the near-UV spectral range when the gas temperature is around 300 K, the **Doppler width** is typically within **one GHz**. For the visible part of the spectrum the **Doppler line broadening is usually much larger than the lifetime broadening.**
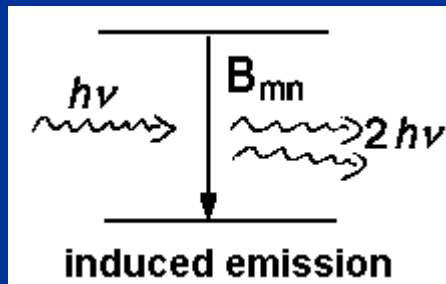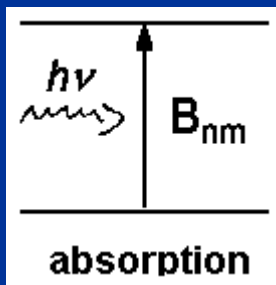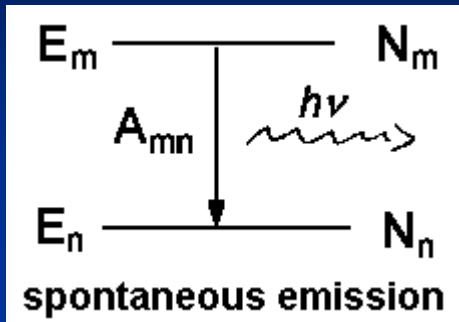
Lorentz and Doppler Line Shapes

Doppler normalized :

$$I(\nu)=\sqrt{\frac{4\ln 2}{\pi}}\ \frac{1}{\Delta\nu_D}\ e^{-4\ln 2\left(\frac{\nu-\nu_0}{\Delta\nu_D}\right)}$$

Lorentz normalized:

$$\frac{1}{2\pi}\ \frac{\Delta\nu_L}{(\nu-\nu_0)^2+\left(\frac{\Delta\nu_L}{2}\right)^2}$$

$$\Delta\nu_D=\Delta\nu_L=\Delta\nu$$

$\Delta\nu_D$

$\Delta\nu_L$

intesity

Frequency shift

$\frac{\nu-\nu_0}{\Delta\nu}$

Synchrotron Radiation

Experimental stations

Radiation

30 m

Storage ring

Linear accelerator

10 m   Electron beam

Booster synchrotron

To detector

Incident beam

Scattered beams

λ_1

λ_2

λ_3

Slit

Diffraction grating
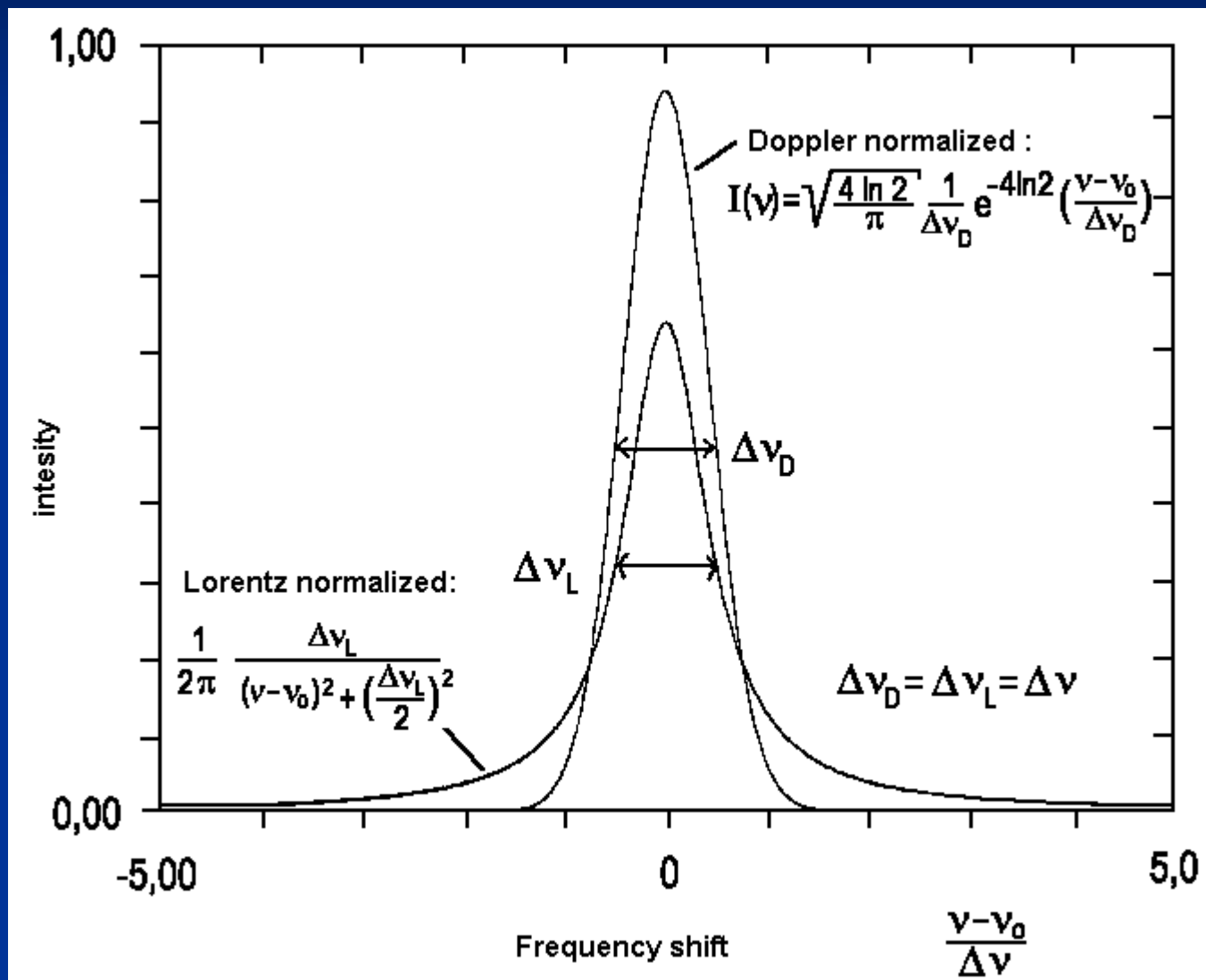
LASER

Light Amplification by Stimulated Emission

E_m ——— N_m

A_{mn} $h\nu$

E_n ——— N_n

spontaneous emission

$h\nu$ | B_{nm}

absorption

$h\nu$ | B_{mn} $2h\nu$

induced emission

(a) Thermal equilibrium

Pump

(b) Population inversion

(c) Laser action

**Nobel Prize, 1964
C.H. Townes,
N.G. Basov,
and A.M. Prokhorov**
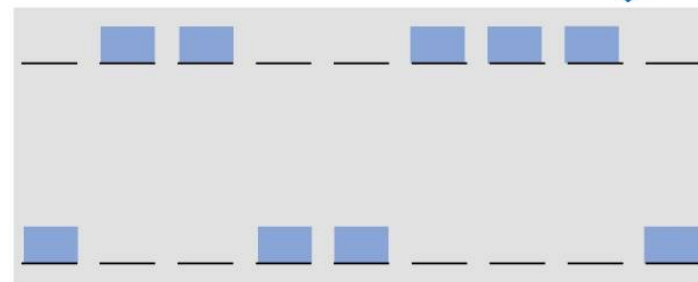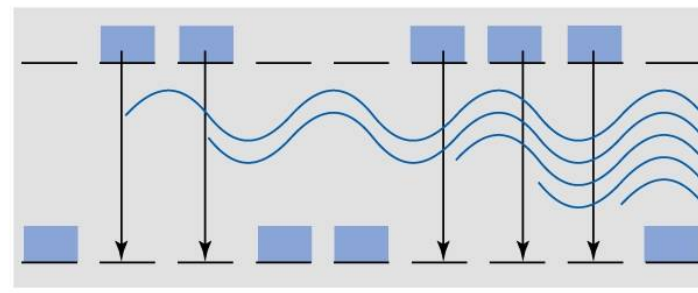
Properties of Laser Radiation

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:

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

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

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

   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 pick power from **10^9 to 10^{12} Watt.** High power pulsed lasers are widely used for investigation of **nonlinear** and **multiple photon processes**.

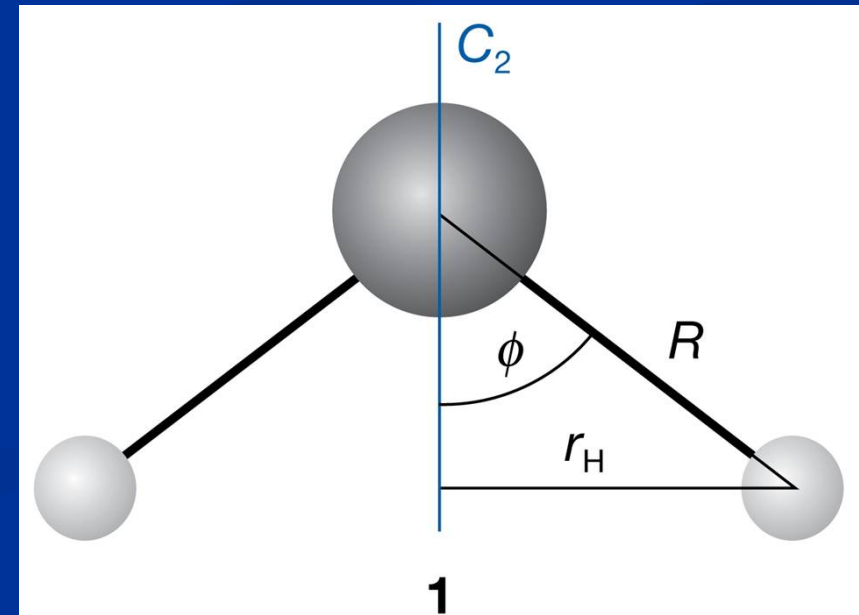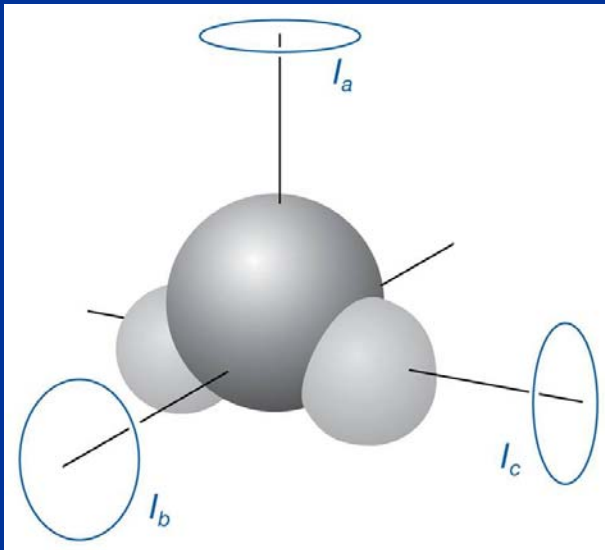# Rotational Spectra: Moment of Inertia

Energy of Rotation: $E_{rot} = \frac{1}{2} I \omega$, where I is the moment of inertia: $I = m\, r^2$.

For arbitrary object rotation energy is written as:

$$E_{rot} = \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2 = \frac{J_A^2}{2I_A} + \frac{J_B^2}{2I_B} + \frac{J_C^2}{2I_C}$$

where A, B, and C are **principale axes of rotation** and
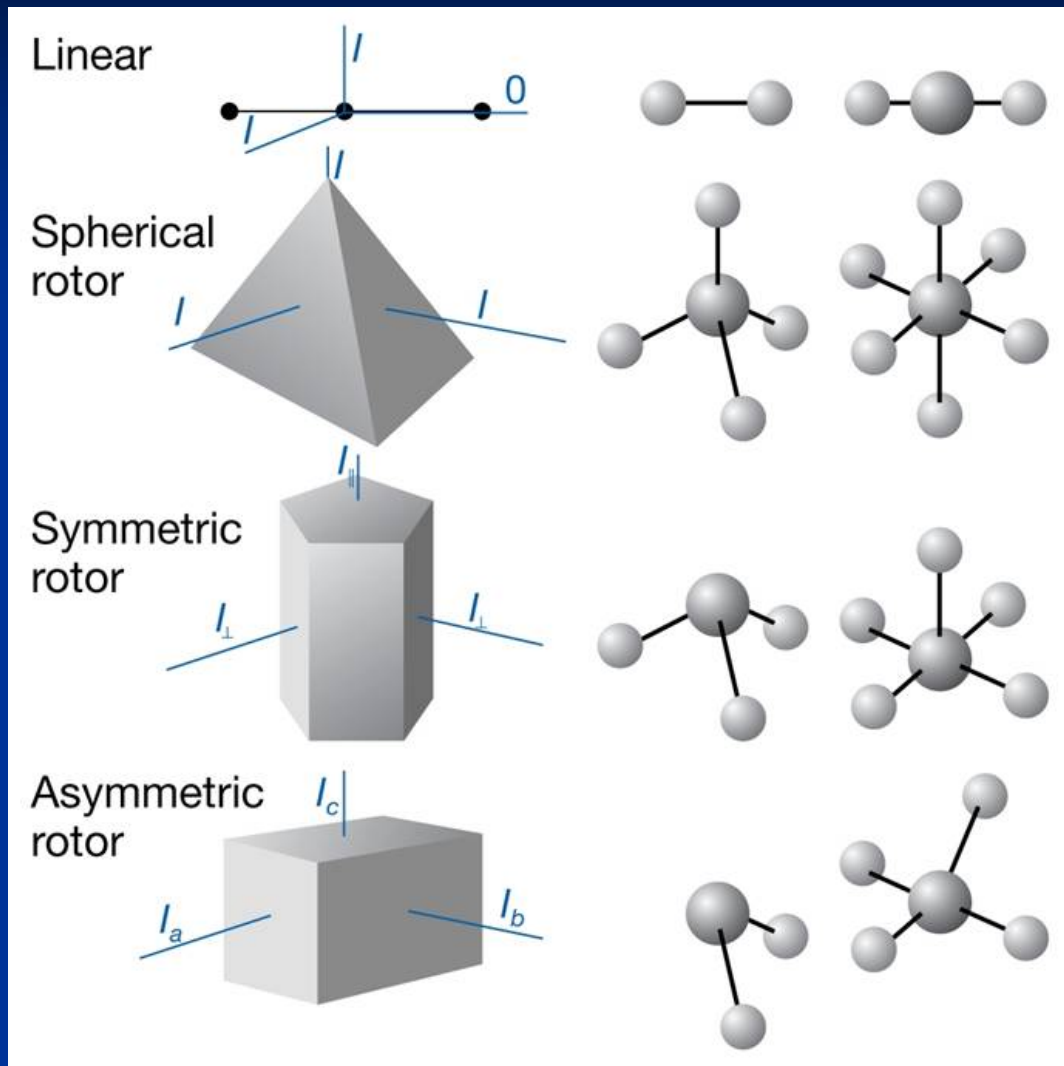
$J_i = I_i \omega_I$ is angular momentum

H_2O

Rigid Rotator: examples

$$E_{rot} = \frac{J_A^2}{2I_A} + \frac{J_B^2}{2I_B} + \frac{J_C^2}{2I_C}$$

Sperical Top	$I_A = I_B = I_C = I$	CH_4, CCl_4, CF_6
Symmetric Top	$I_A = I_A = I_\perp, \quad I_C = I_\parallel$ $I_\perp < I_\parallel$ **oblate** $I_\perp > I_\parallel$ **prolate**	C_6H_6, CH_3I, NH_3
Linear Rotor	$I_A = 0, \quad I_B = I_C$	All diatomic molecules, CO_2, N_2O, C_2H_2
Asymmetric Top	$I_A \neq I_B \neq I_C$ $I_C \geq I_B \geq I_A$	$H_2O, NO_2, H_2CO,$ CH_3OH

Moments of Inertia

Linear — Diatomics, CO_2, N_2O, C_2H_2

Spherical rotor — CH_4, CCl_4, SF_6

Symmetric rotor — NH_3, CH_3I, C_6H_6

Asymmetric rotor — H_2O, NO_2, H_2CO, CH_3OH

Sperical Top: Energy States
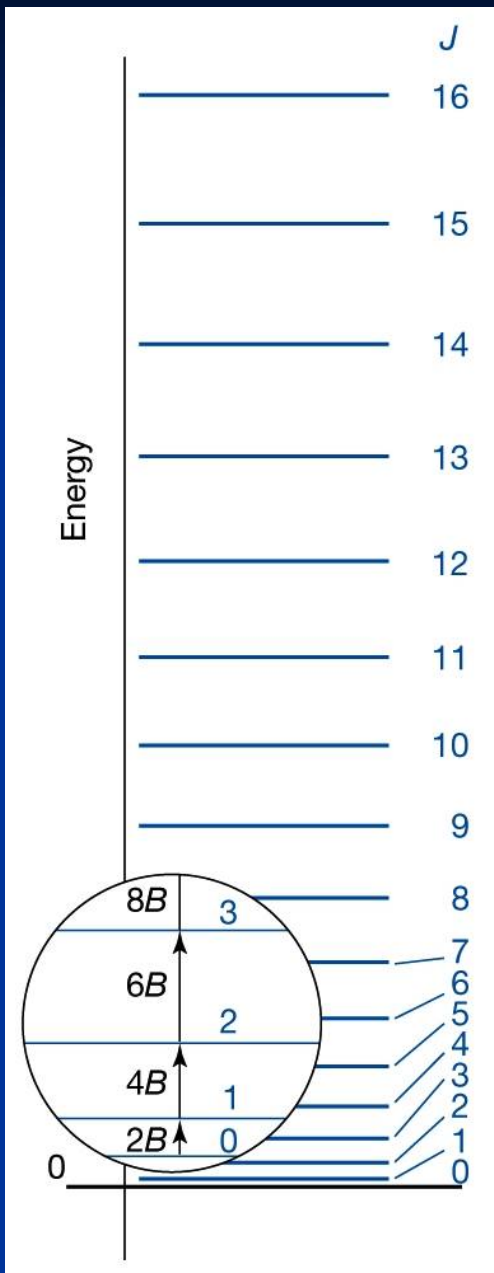
$$E_{rot} = \frac{J_A^2}{2I} + \frac{J_B^2}{2I} + \frac{J_C^2}{2I} = \frac{\mathbf{J}^2}{2I}$$

The corresponding quantum mechanical expression:

$$E_{rot} = \frac{\mathbf{J}^2}{2I} = \frac{\hbar^2}{2I} J(J+1)$$

because the eigenvalue of the operator J² is

$$\mathbf{J}^2 \Psi = \hbar^2 J(J+1)\Psi$$

In spectroscopy the rotational energy is usually written as:

$$E_{rot} = hcB \cdot J(J+1)$$

where the rotational constant $\mathbf{B}$ in cm⁻¹

$$B = \frac{\hbar}{4\pi cI}$$

The rotational term:

$$F(J) = B \cdot J(J+1)$$

Symmetric Top

$$E_{rot} = \frac{J_A^2}{2I_\perp} + \frac{J_B^2}{2I_\perp} + \frac{J_C^2}{2I_\parallel} = \frac{J_A^2 + J_B^2}{2I_\perp} + \frac{J_C^2}{2I_\parallel}$$

where

$$J_A^2 + J_B^2 + J_C^2 = \mathbf{J}^2$$

$$E = \frac{\mathbf{J}^2}{2I_\perp} + J_C^2 \left(\frac{1}{2I_\parallel} - \frac{1}{2I_\perp} \right)$$

using $\mathbf{J}^2 \rightarrow J(J+1)\,\hbar^2$ and $J_C \rightarrow K\,\hbar$

We get the corresponding quantum mechanical expression for the rotational term:

$$F_{JK} = B\,J(J+1) + (A-B)K^2$$

Oblate top: A - B < 0

where $J = 0, 1, 2 \ldots$ and $K = 0, \pm 1, \pm 2, \pm J$.

Prolate top: A - B > 0

$$A = \frac{\hbar}{4\pi c I_\parallel} \qquad B = \frac{\hbar}{4\pi c I_\perp}$$

Symmetric Top: $F(J) = B\,J(J+1) + (A - B)K^2$

(a)

$K \approx J$

(b)

$K = 0$
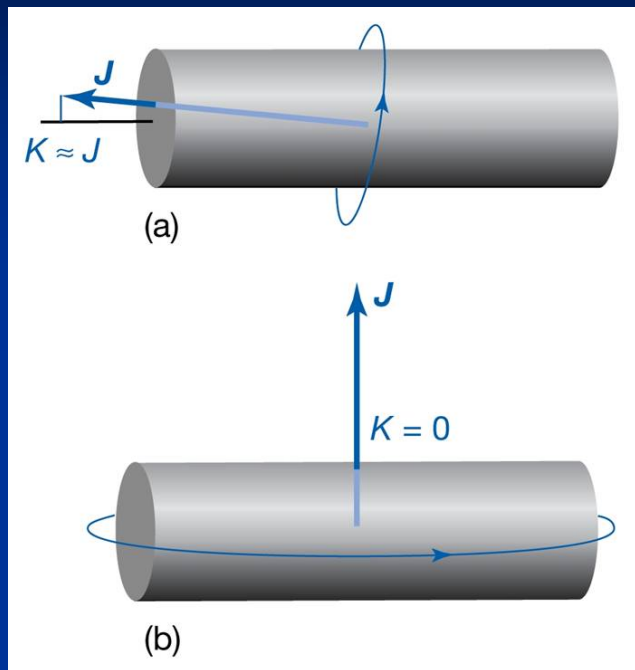
Role of the quantum number K:

if $K = J \gg 1$, $F(J) \approx A\,K^2$

if $K = 0$, $F(J) = B\,J(J+1)$

(a)

(b)

(c)

$M_J = 0$
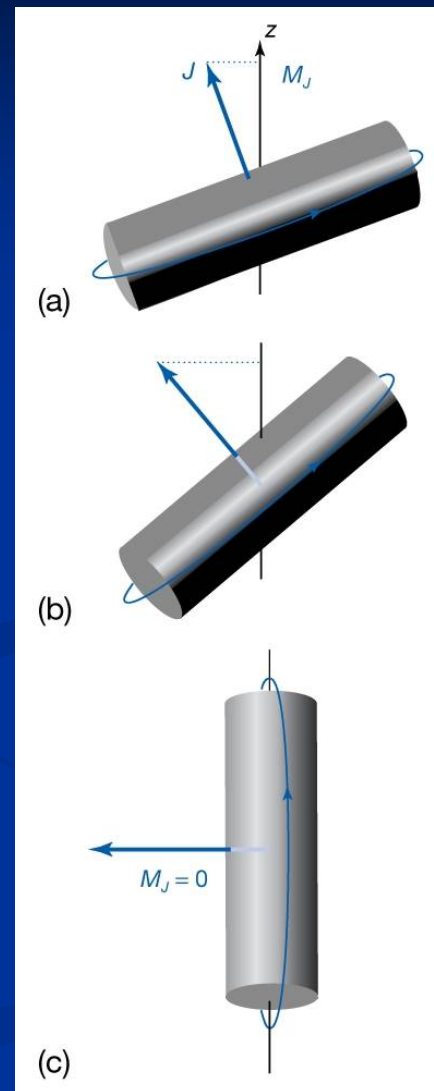
Role of the quantum number M_J

Asymmetric Top
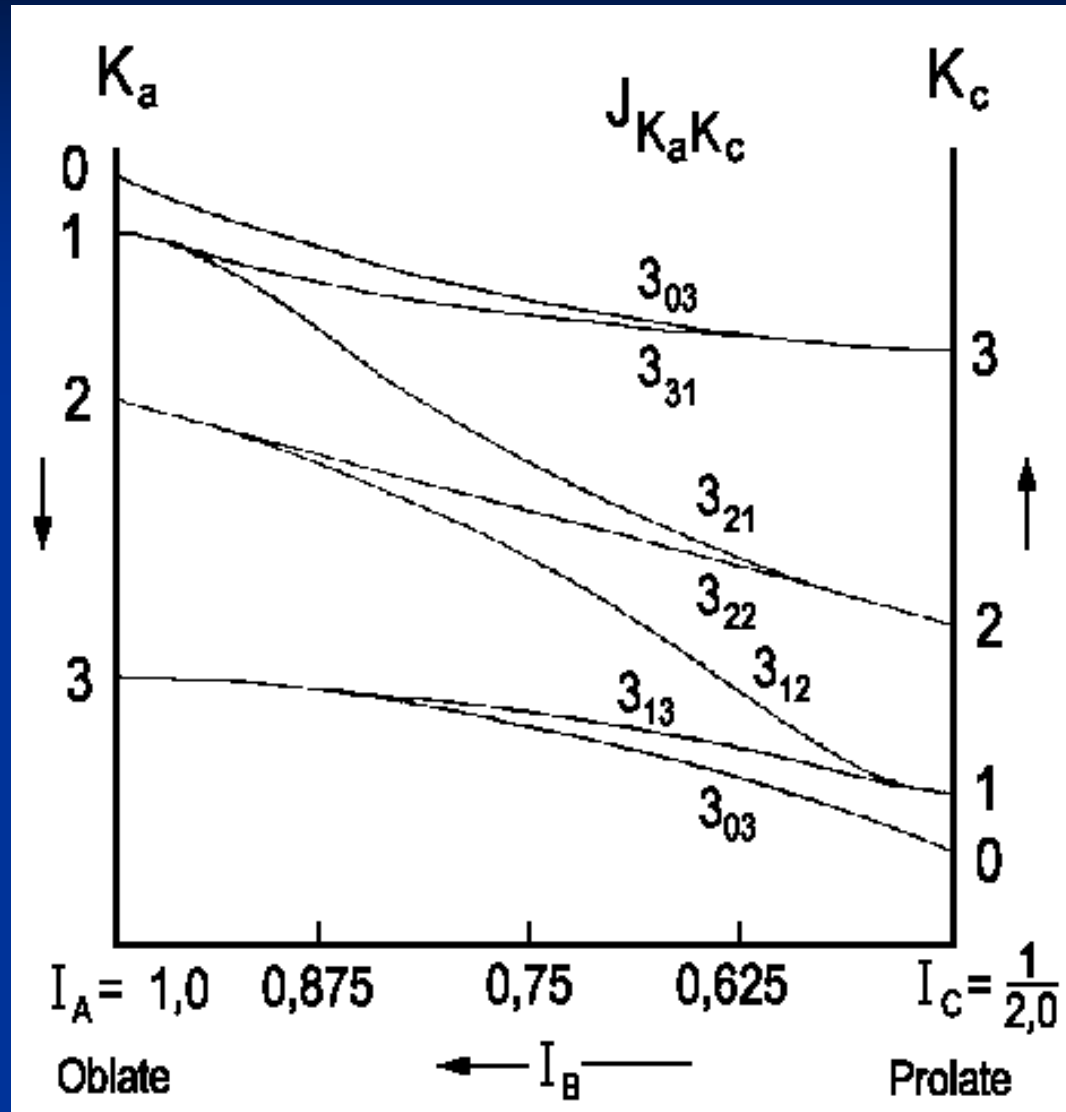
Elastic Rotator: Centrifugal Distortion

So far, we assumed that rotation does not affect the shape of a molecule (rigid rotor). However, in general there are centrifugal forces that stretch the bonds of a rotating molecule.

An increased length of the bond corresponds to a higher moment of inertia ($I = \mu \, r^2$). In turn, the rotational constant B decreases ($B \sim I^{-1}$), i.e. we would expect a rotational energy in the form:

$$F(\, J\,) \approx B \, J\,(\, J + 1) - D \, J^2 (\, J + 1)^2 \; + \; \dots$$

where the coefficient **D** is a small correction, which is called **centrifugal distortion constant**.

Pure Rotational Transitions

The pure rotational transitions are possible in **polar molecules** which have a **permanent dipole moment** and a transitional dipole moment within a pure rotational spectrum is not equal to zero.

In contrast, **no rotational spectra** exists for **homonuclear diatomics**; the same is true for **spherical tops**.

Selection rules: $\Delta J = \pm 1$; $\Delta M_J = 0, \pm 1$

For a symmetric top, an existing dipole moment is always parallel to the molecular axis:

$$\Delta K = 0$$

Pure Rotational Spectrum
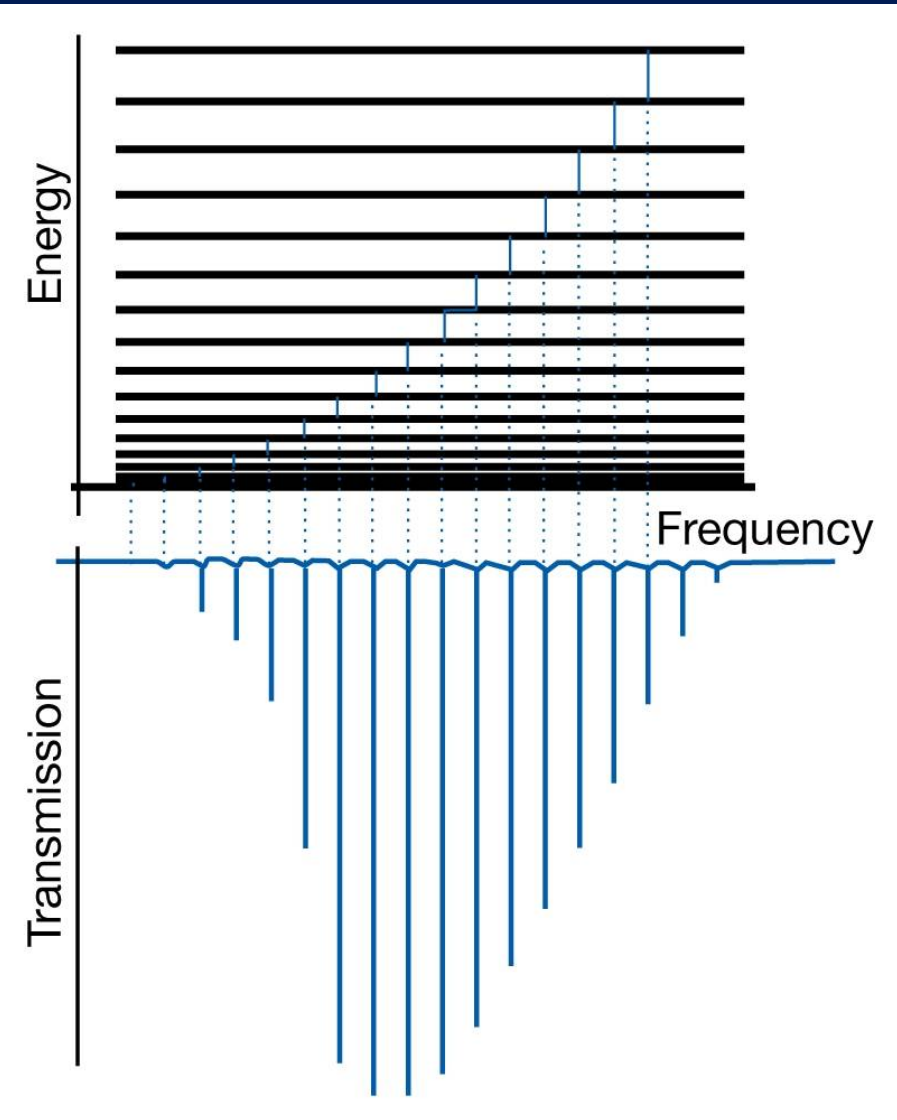
$$\nu(J) = B(J+1)(J+2) - B\,J(J+1)$$

$$= 2B(J+1)$$

$$\Delta\nu = \nu(J+1) - \nu(J) = 2B$$

That is, the spectrum consists of **equidestant lines.**

The **intensities of spectral lines** first increase with increasing J and pass through a **maximum**. The reason for the maximum in intensity is the existence of a maximum in the population of rotational levels. According to the **Boltzmann distribution** the population of a rotational level at temperature T is given by:

$$N(J) = N_0\, g_J \exp(-E_J/kT)$$

Vibrational Levels
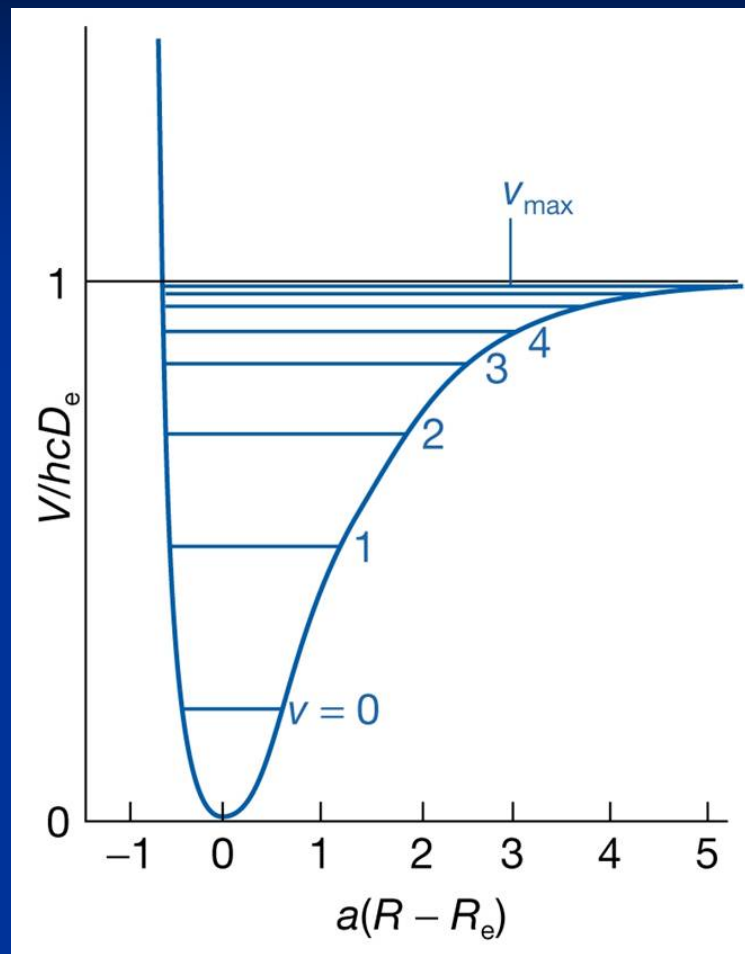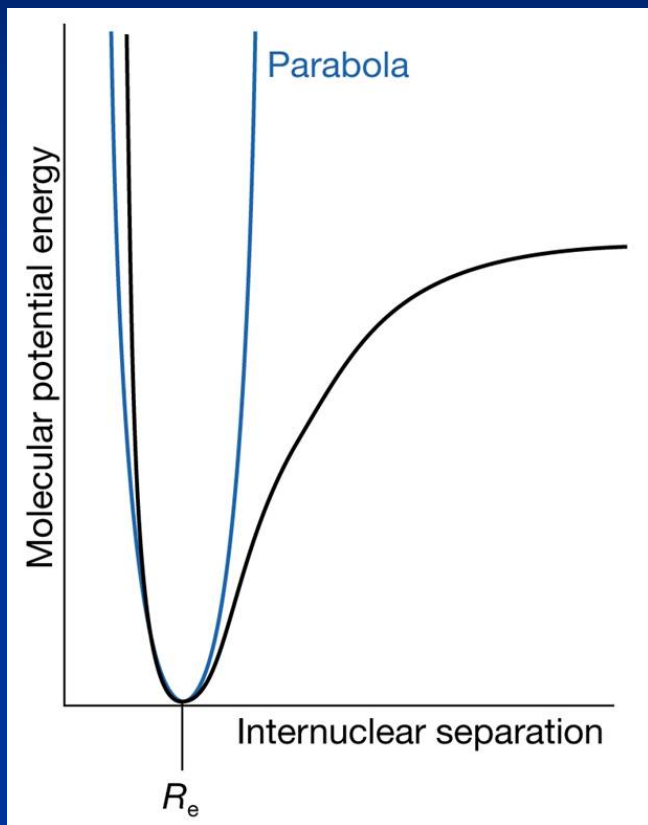
$$E_v = (v+\tfrac{1}{2})\, \omega_e$$

$$v = 0, 1, 2, \ldots$$

$$E_v = (v+\tfrac{1}{2})\, \omega_e - (v+\tfrac{1}{2})^2\, \omega_e^2\, x_e^2 + (v+\tfrac{1}{2})^3 \omega_e^2\, y_e^2 + \ldots$$

Vibrational Transitions

If the molecule in its equilibrium position has a dipole moment, as is always the case for the heteroatomic molecules, this dipole moment will in general change if the internuclear distance changed. The molecular vibration would lead to the emission of light at the oscillation frequency. Therefore, all heteroatomic molecules in principle are said to be infrared active, that is they can absorb or emit infrared radiation. Contrary, all homoatomic diatomic molecules do not have any dipole moment and cannot set in vibration by absorption the infrared light. These molecules are said to be infrared inactive. The selection rules for the vibrational transitions in a harmonic oscillator-like molecule are:

$$\Delta v = v' - v'' = \pm 1$$

As the energy difference between each two neighbor vibrational energy levels is $\hbar\omega$, the vibrational spectrum would contain only one line. This line is called fundamental line. The wavelength of this line for different diatomic molecules usually lies in near IR spectral range $\lambda = 2 \ldots 20$ mkm .

However, for high lying vibrational energy states the harmonic oscillator approximation in is not valid any more. For anharmonic oscillator the selection rule above is not valid and additional lines appear in the molecular vibration spectra corresponding to transitions $\Delta v = v' - v'' = \pm 1, \pm 2, \pm 3$ and so on. These transitions are called second harmonic, third harmonic, and so on. The intensity of the harmonic transitions transitions is usually much smaller than the intensity of the fundamental line.

Vibrational–Rotational Transitions
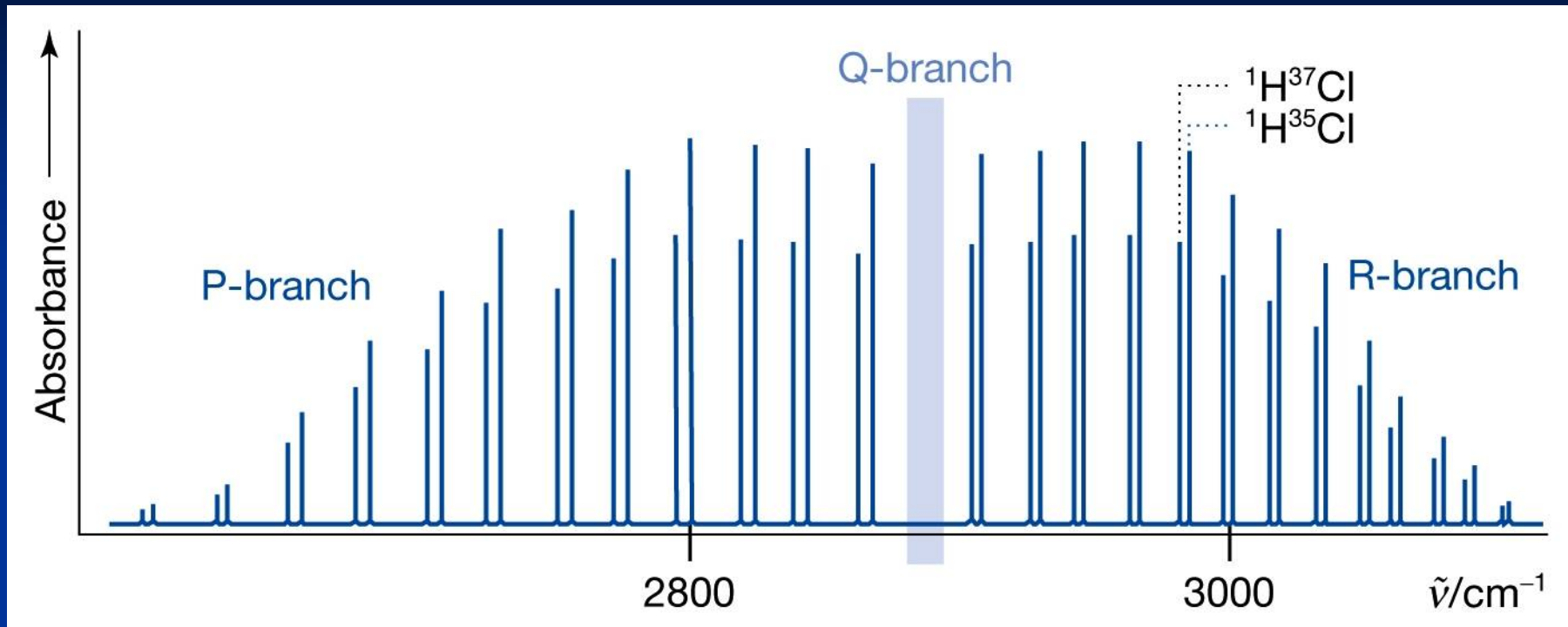
The quantum mechanical analysis of **simultaneous vibrational and rotational** transitions shows that the rotational quantum number J **changes by** ± 1 during the vibrational transition. If the molecule also possesses **angular momentum** about its axis, (for instance, $NO(^2\Pi)$), then the selection rule also allows $\Delta J = 0$. In general, the vibrational-rotational spectrum of the $v' \rightarrow v'' \pm 1$ transition can contains three rotational branches: $\Delta J = -1$, $\Delta J = 0$, and $\Delta J = 1$ branches which are called **P**, **Q**, and **R** branches, respectively.

Electronic Transitions
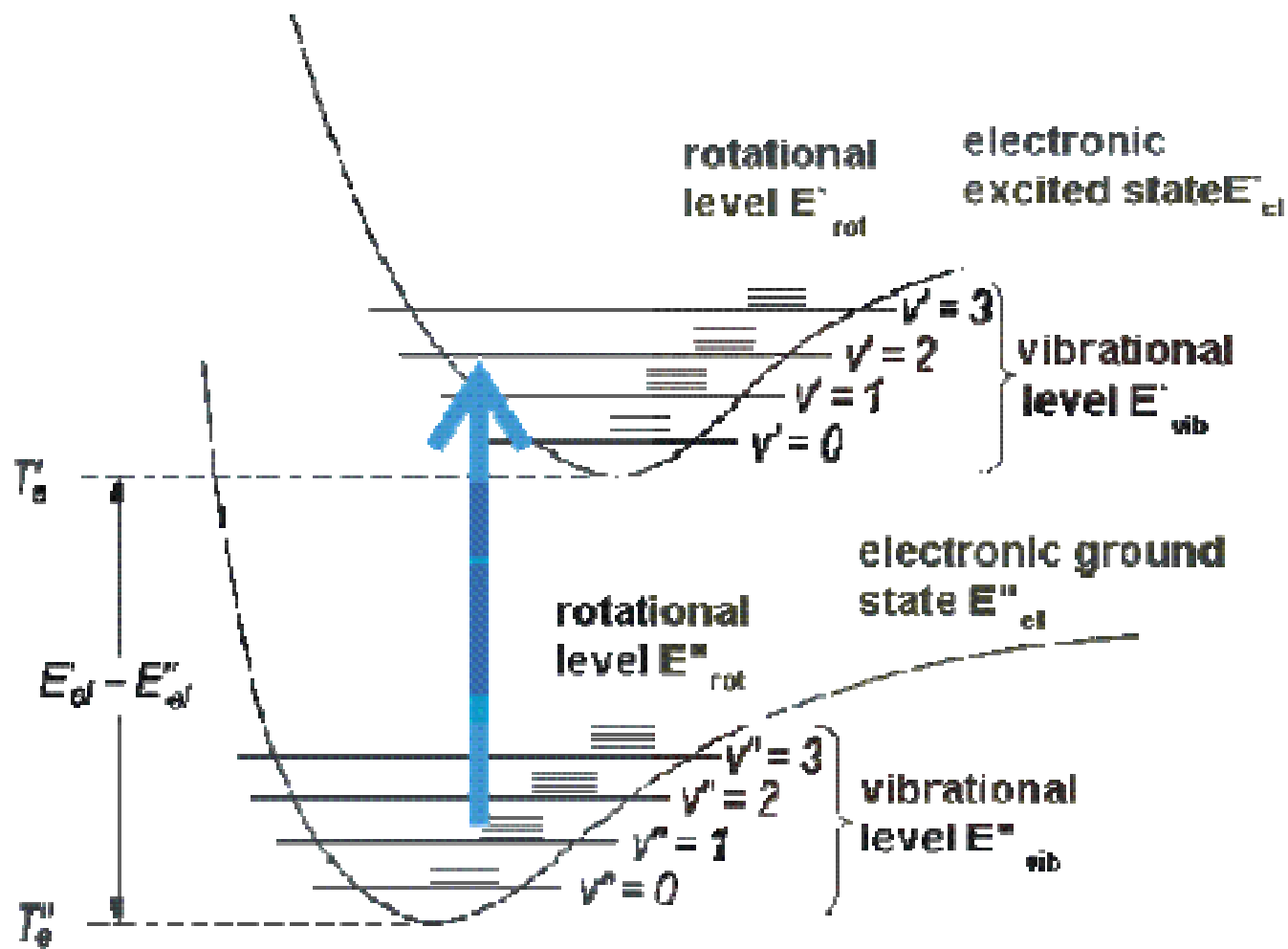
Electronic Transitions

In the Born-Oppenheimeer Approximation:

Wavefunction:

$$\Psi(\mathbf{r}_e, \mathbf{R}(\theta, \phi)) \approx \Psi_{el}(\mathbf{r}_e, R)\, \Psi_{vib}(R)\, \Psi_{rot}(\theta, \phi)$$

Energy: $E = E_{el} + E_{vib} + E_{rot}$

Term [cm^{-1}]: $F = T_e + \omega_e (v + \frac{1}{2}) + B_e\, J\,(J+1)$

where $T_e \gg \omega_e \gg B_e$

$\Delta F = T_e' - T_e'' + \omega_e' (v' + \frac{1}{2}) - \omega_e'' (v'' + \frac{1}{2}) + B_e'\, J'(J'+1) - B_e''\, J''(J''+1)$

Electronic Transitions: Franck–Condon factors

Transition dipole moment:

$$\left\langle \Psi' \middle| d_q \middle| \Psi'' \right\rangle \approx \left\langle \Psi'_{el} \Psi'_{vib} \Psi'_{rot} \middle| d_q \middle| \Psi''_{el} \Psi''_{vib} \Psi''_{rot} \right\rangle \approx \left\langle \Psi'_{rot} \middle| \Psi''_{rot} \right\rangle \left\langle \Psi'_{vib} \middle| \Psi''_{vib} \right\rangle \left\langle \Psi'_{el} \middle| d_q \middle| \Psi''_{el} \right\rangle$$
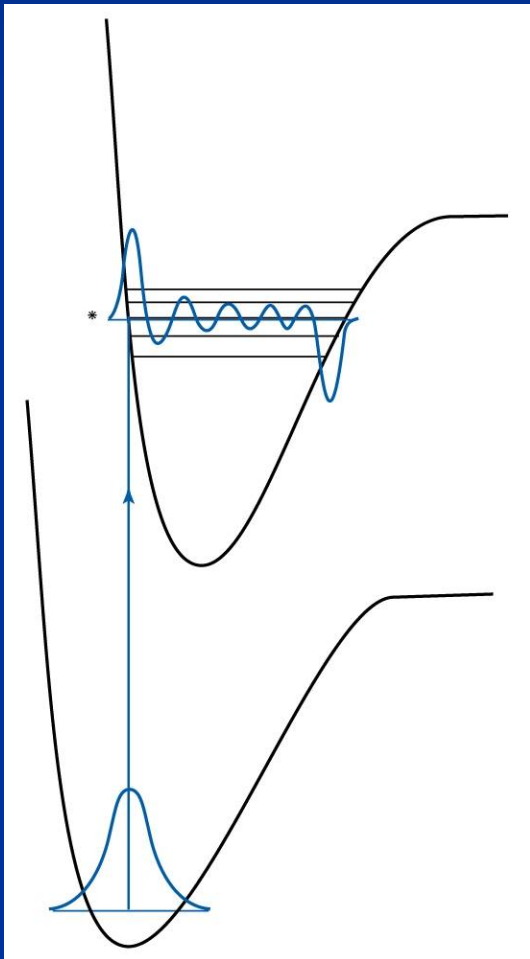
Where

$$\left\langle \Psi'_{vib} \middle| \Psi''_{vib} \right\rangle$$

is a Frank-Condon Factor

and

$$\left\langle \Psi'_{el} \middle| d_q \middle| \Psi''_{el} \right\rangle$$

is an electronic transition dipole moment

Electronic Transitions: selection rules

Diatomic Molecule Electronic Terms:

$$^{2S+1}\Lambda_{\Omega}$$

Additional quantum numbers:

g , **u** for homonuclear molecules

± for Σ states

Examples: $^{1}\Sigma_{0}^{+}$, $^{3}\Sigma_{1u}^{+}$, $^{1}\Pi_{1}$, $^{1}\Pi_{1g}$
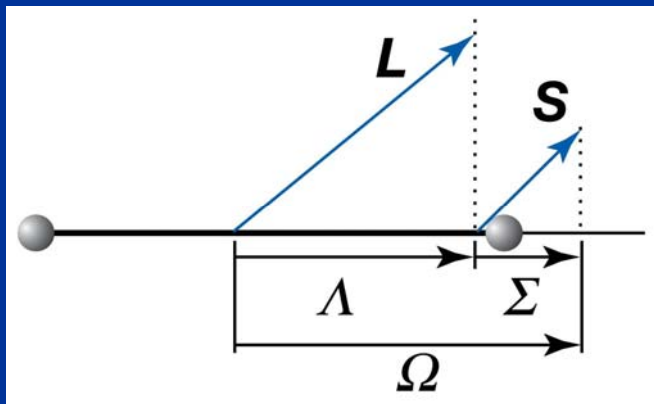
$$\Lambda = \sum_{i} \lambda_i \quad \Sigma = \sum_{i} \sigma_i \quad \Omega = \Lambda + \Sigma$$

Allowed Transitions	Examples
$\Delta\Lambda = 0, \pm 1$	$\Sigma \to \Sigma, \Pi \to \Pi,$ $\Sigma \to \Pi, \ \Delta \to \Pi$
$\Delta S = 0$	$^{1}\Sigma \leftrightarrow {}^{1}\Sigma, \ {}^{2}\Sigma \leftrightarrow {}^{2}\Pi,$ $^{3}\Pi \leftrightarrow {}^{3}\Pi, {}^{1}\Sigma \leftrightarrow {}^{1}\Pi$
$+ \leftrightarrow +$ $- \leftrightarrow -$	$\Sigma^{+} \leftrightarrow \Sigma^{+}$ $\Sigma^{-} \leftrightarrow \Sigma^{-}$
$g \leftrightarrow u$	$\Sigma_g^{+} \leftrightarrow \Sigma_u^{+}$ $\Sigma_u \leftrightarrow \Pi_g$

Rotational Structure of Electronic Transitions: Selection Rules

Electron Transition	Allowed Transitions	Name
$\Sigma \leftrightarrow \Sigma$	$\Delta J = -1$ $\Delta J = +1$	P branch R branch
All others	$\Delta J = -1$ $\Delta J = 0$ $\Delta J = +1$	P branch Q branch R branch

Rotational Structure of Electronic Transitions

(a) $B' < B$

(b) $B' > B$

P   R   P   R

band head   band head
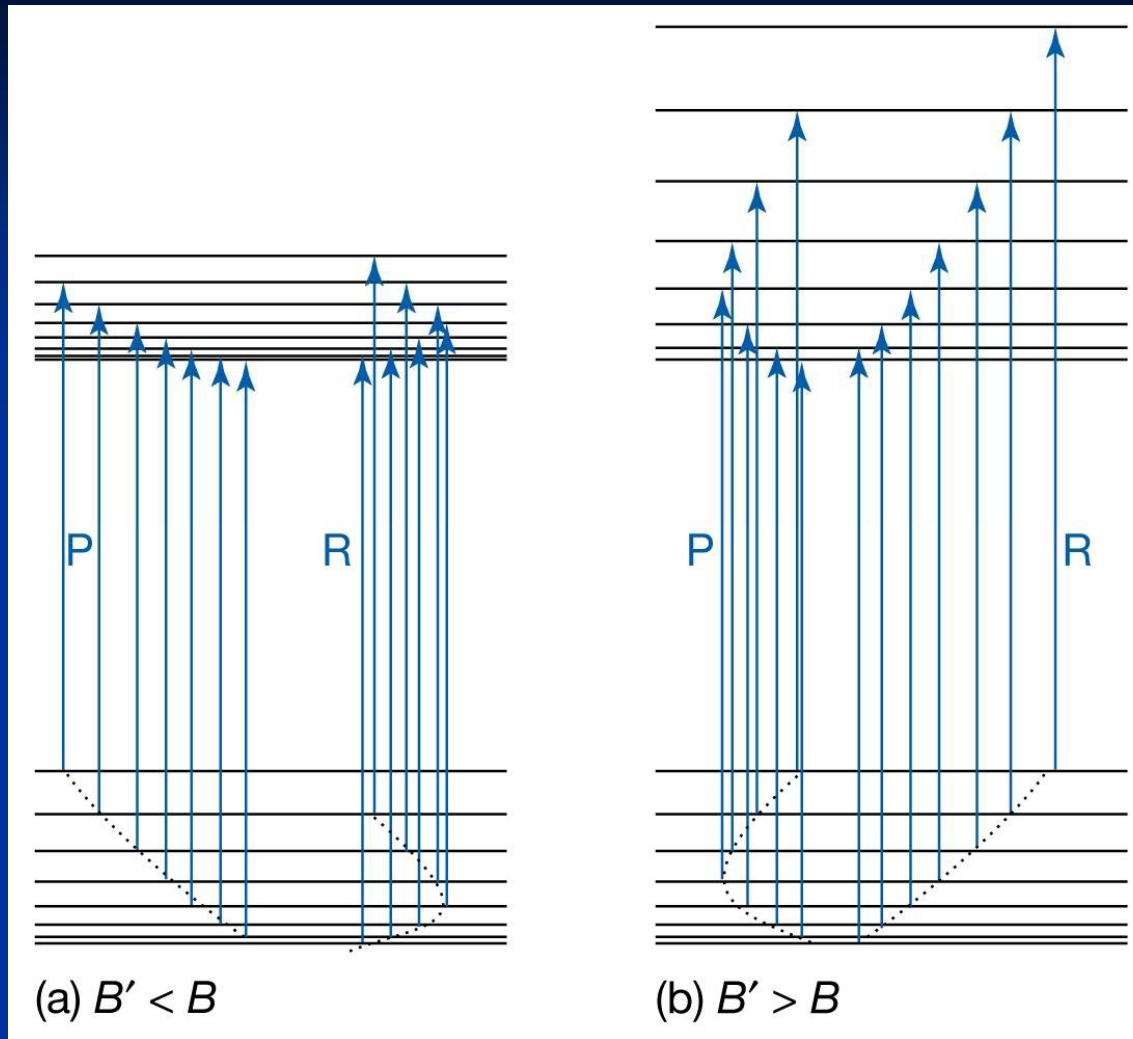
Red shadowed   **Blue shadowed**

Dissociation and Predissociation
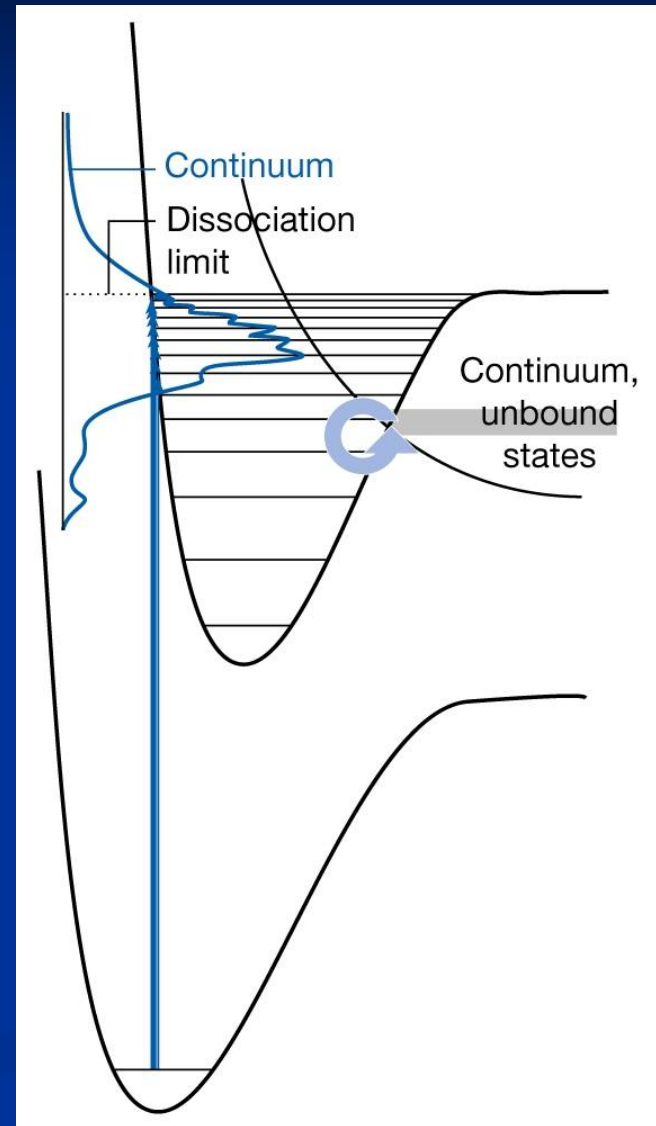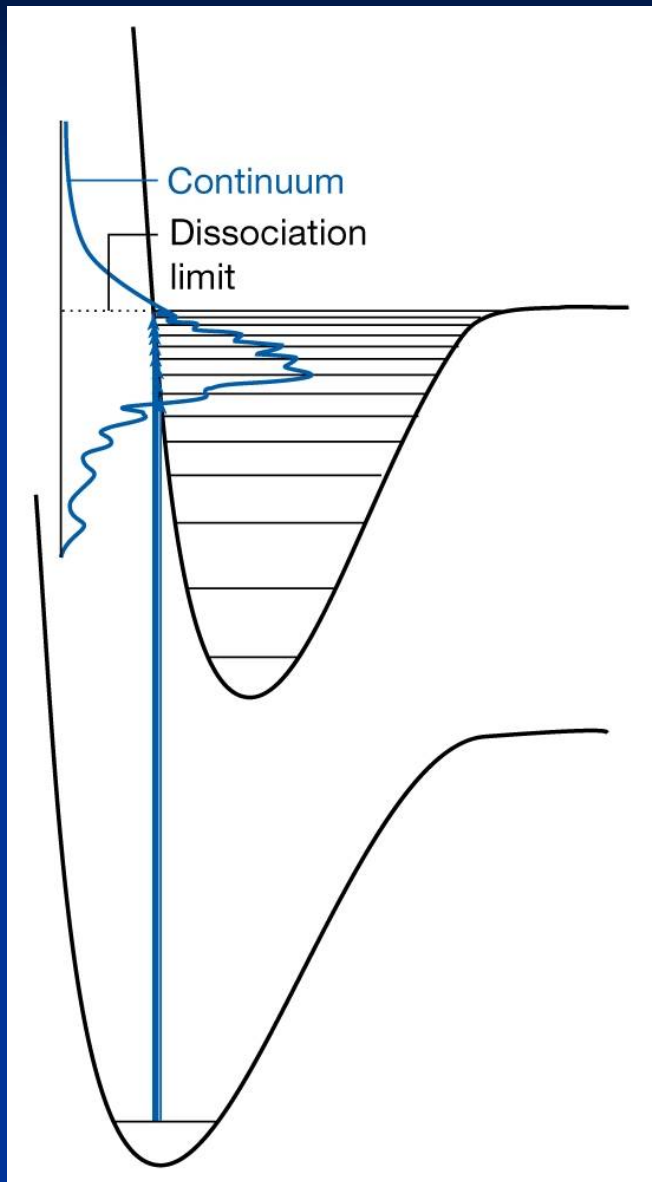
Photoelectron Spectroscopy: CO Molecule
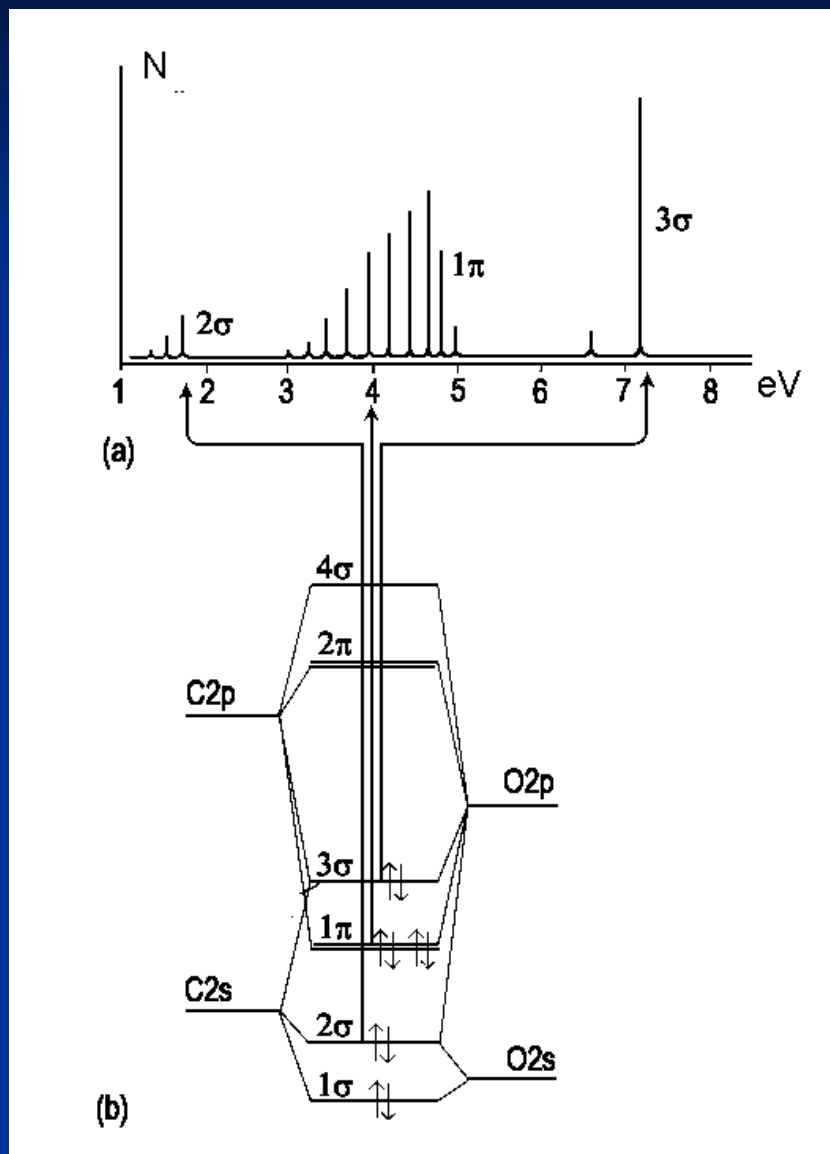
Absorption Spectroscopy with a Frequency Modulated Laser
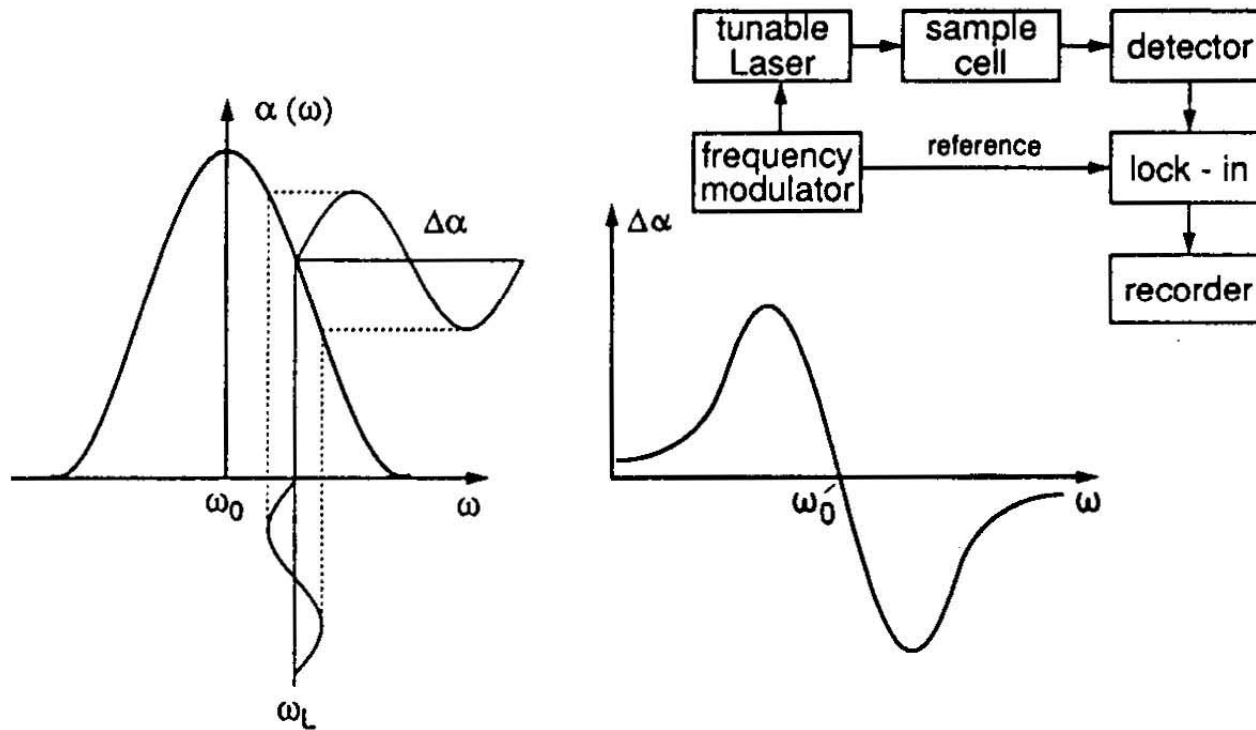
Intracavity Absorption Technique
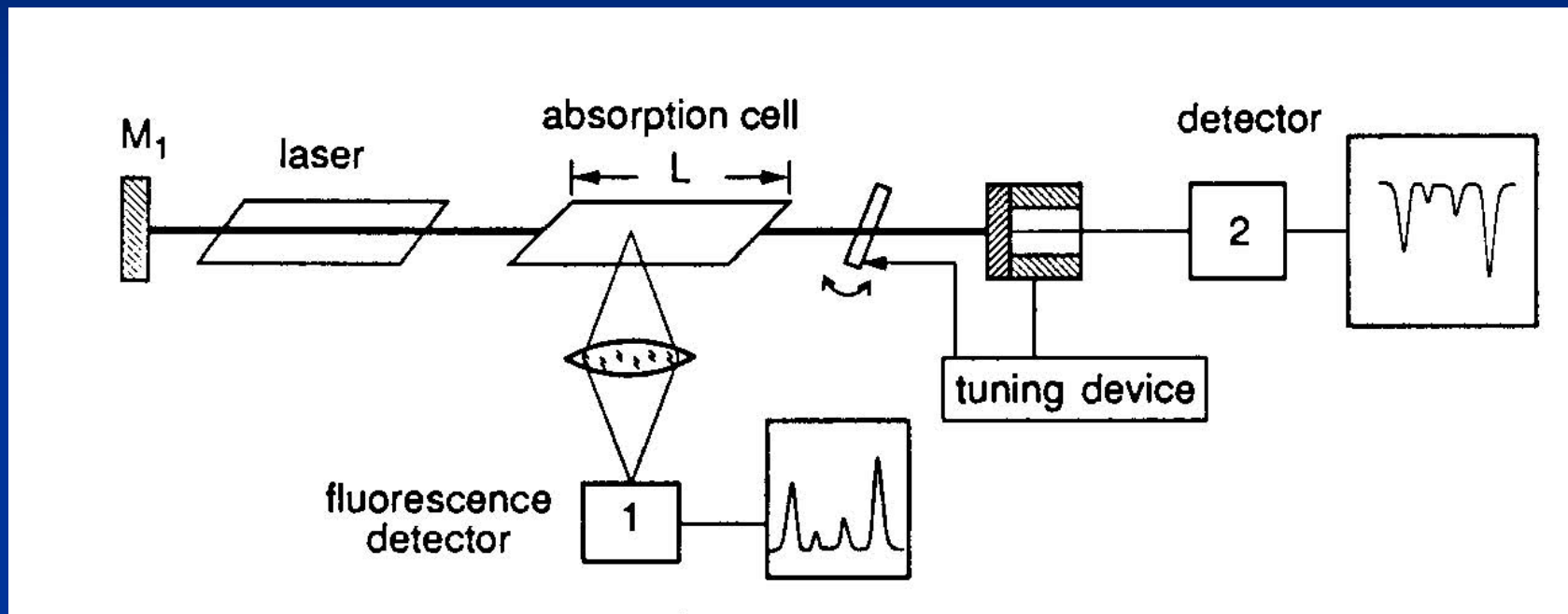
Cavity Ring–Down Spectroscopy
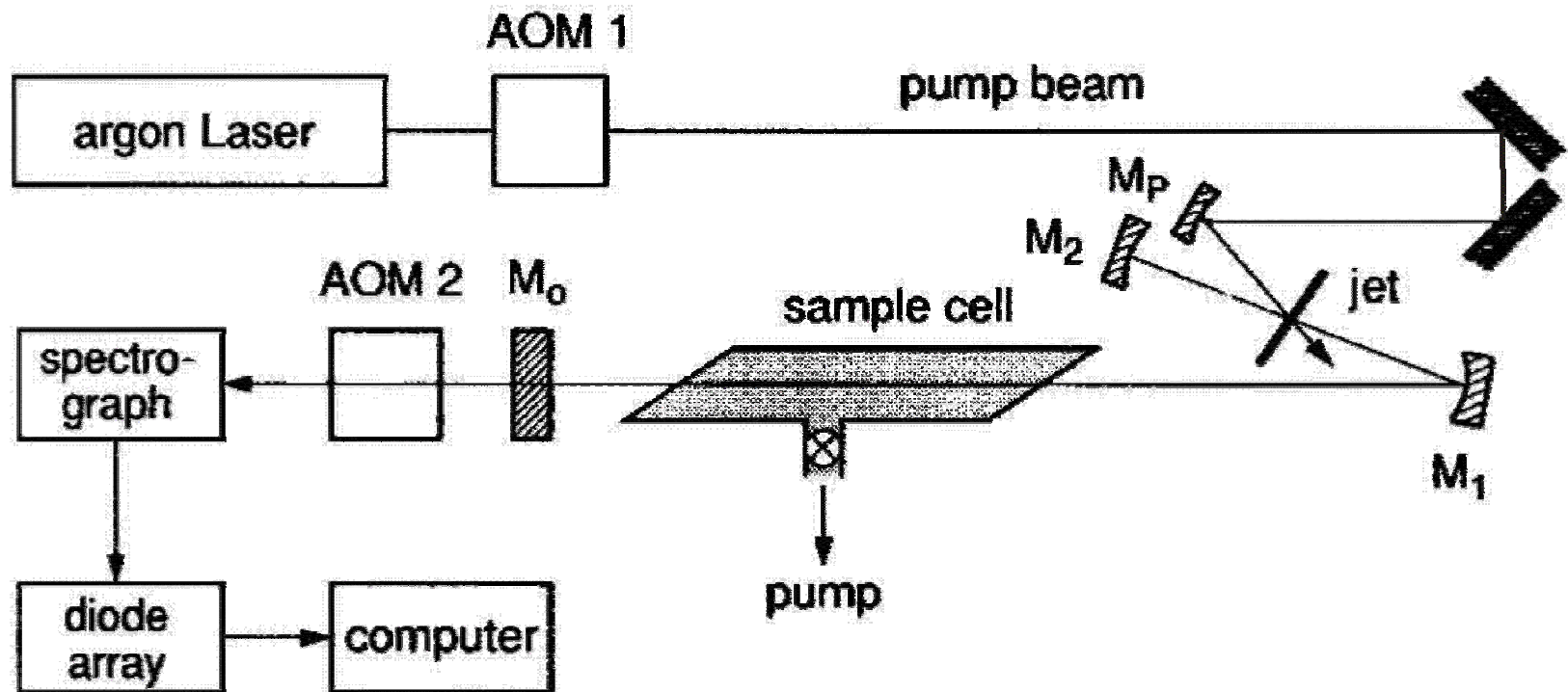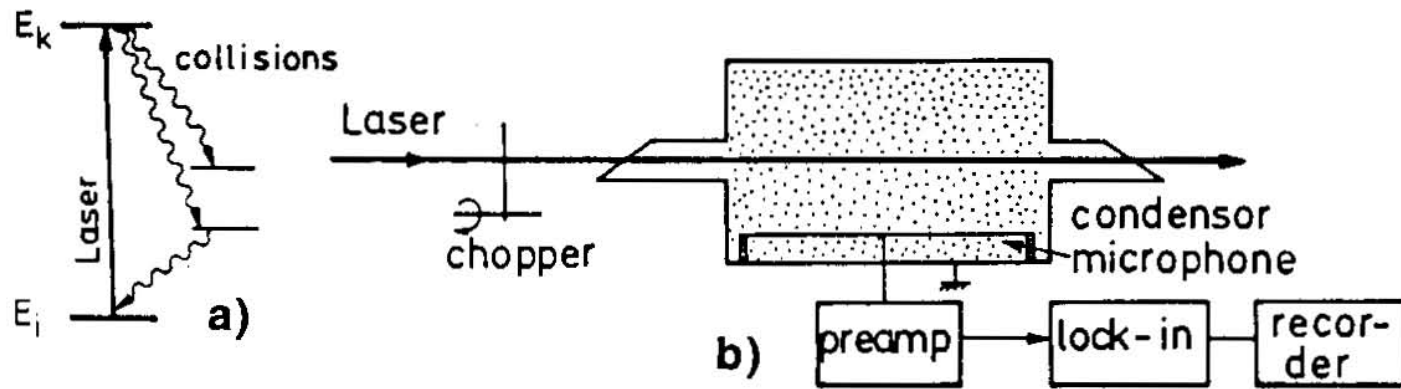
Fig.6.13. Photoacoustic spectroscopy (a) level scheme (b) schematic experimental arrangement

Photoacoustic Spectroscopy: C_2H_2
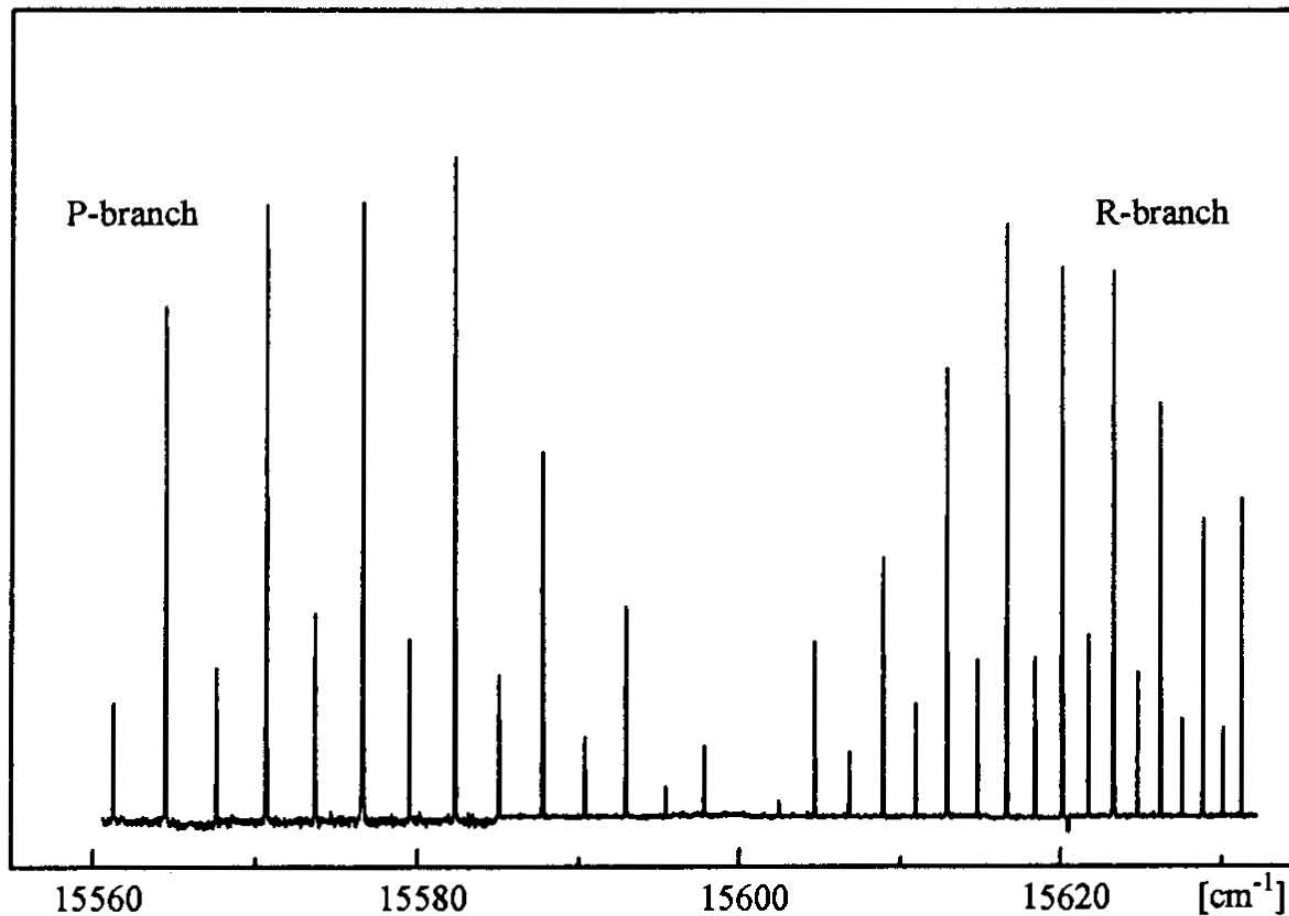
Fig.6.15. Optoacoustic overtone absorption spectrum of acethylene around $\bar{\nu} = 15600$ cm^{-1} corresponding to the excitation of a local mode by 5 quanta vibrations [6.45]

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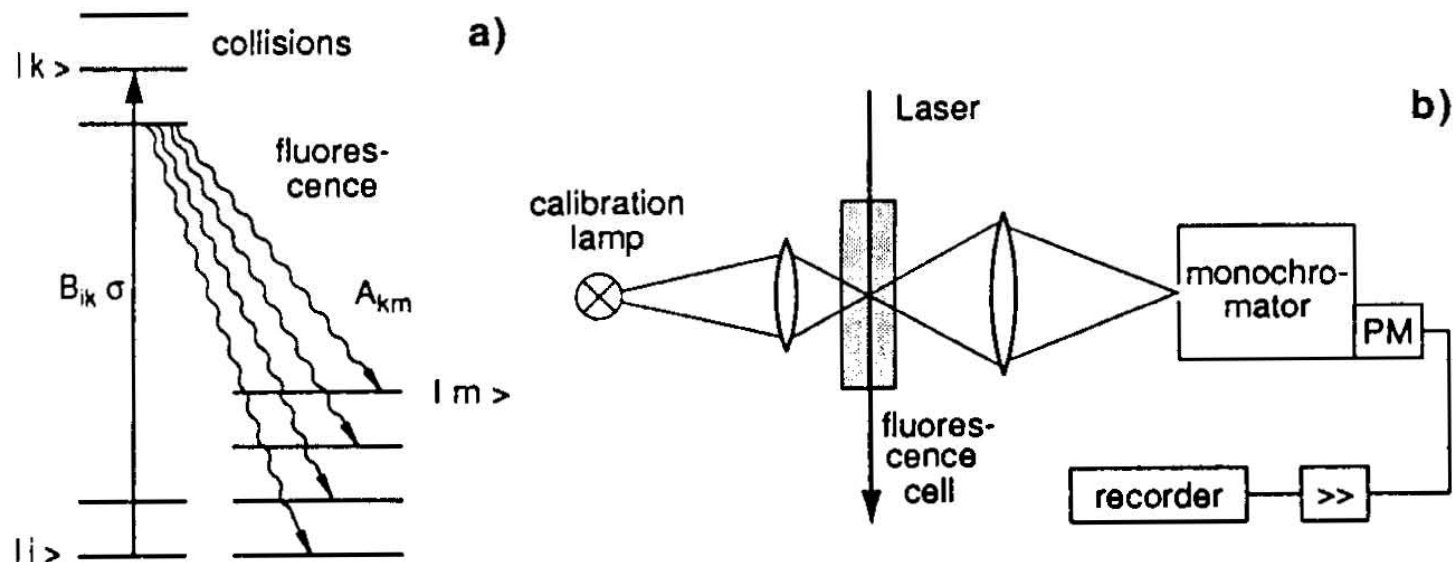
Fig.6.33a,b. Laser-induced fluorescence: (a) Level scheme and (b) experimental arrangement for measuring LIF spectra

Diffraction grating
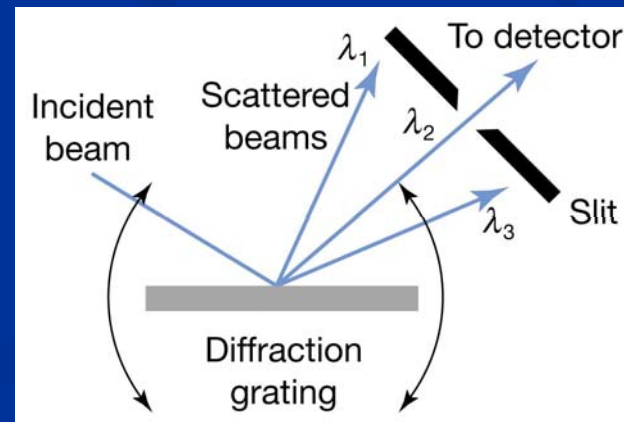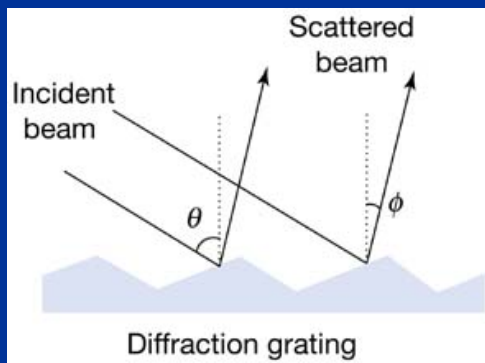
Laser Induced Fluorescence: Na$_2$
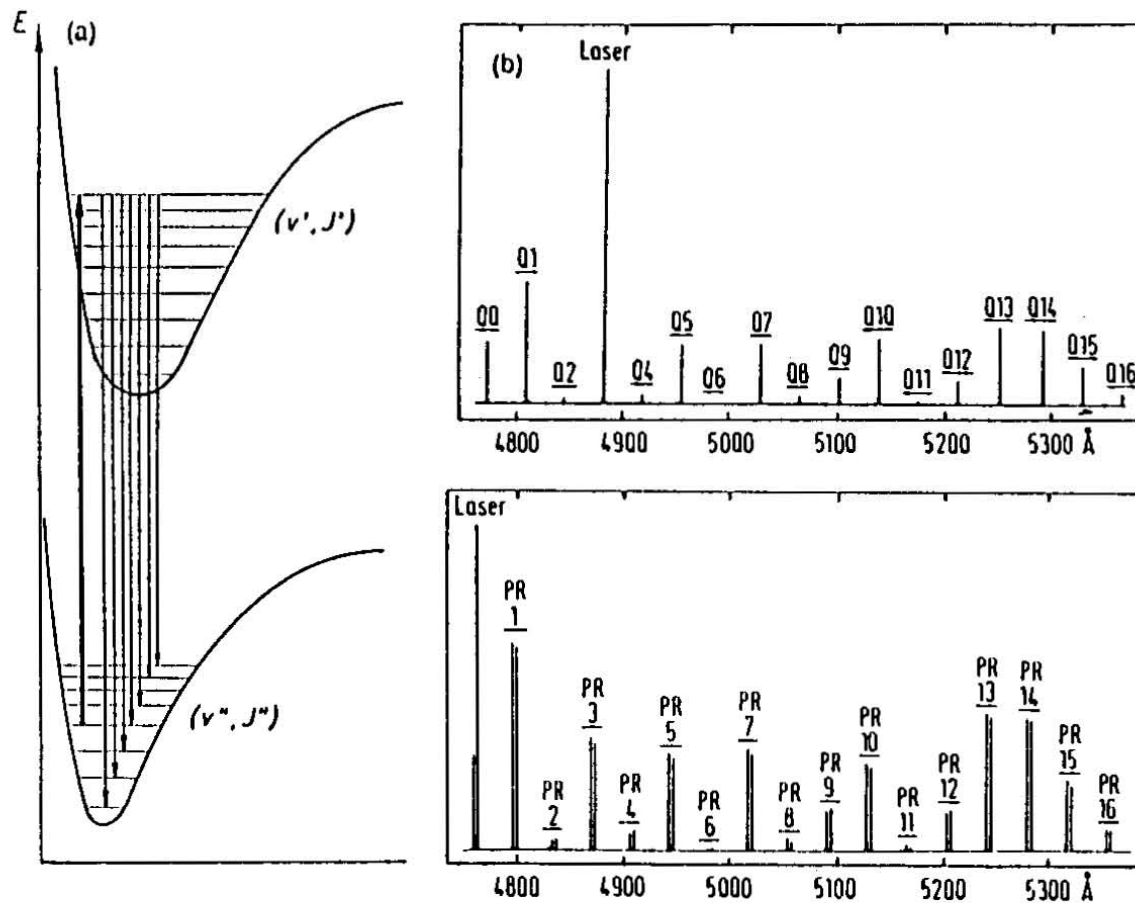
Fig.6.34. Laser-induced fluorescence of the Na$_2$ molecule excited by argon laser lines (a) term diagram (b) fluorescence lines with $\Delta J = 0$ (Q-lines) emitted from the upper level ($v'=3$, $J'=43$) of the B^1II_u state, excited at $\lambda = 488$ nm. (c) P and R doublets, emitted from the upper level ($v'=6$, $J'=27$)

Laser Induced Fluorescence: NaK
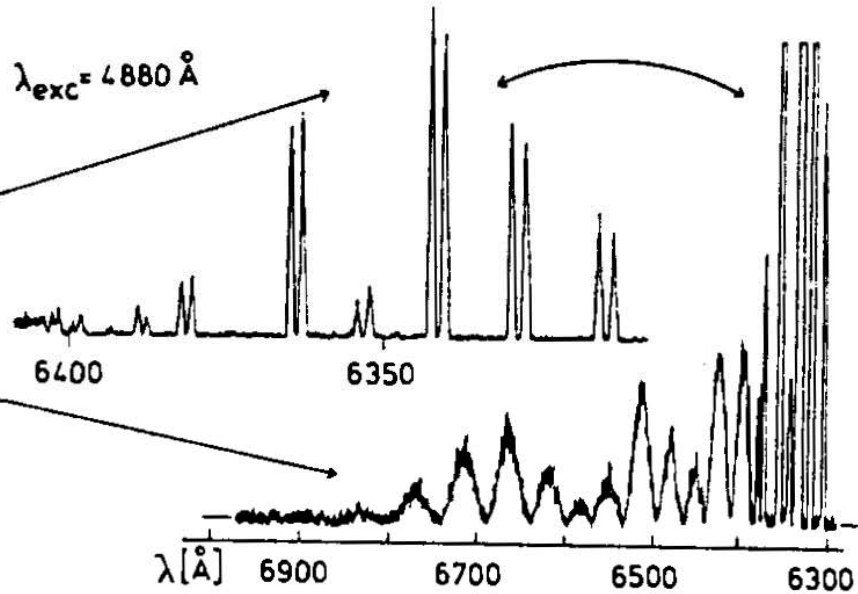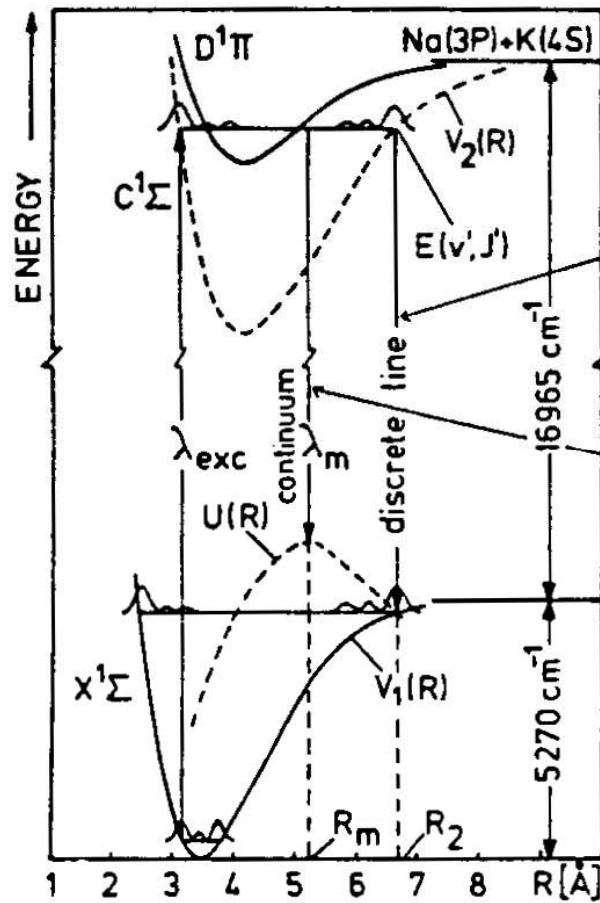
Laser Induced Fluorescence: NO$_2$
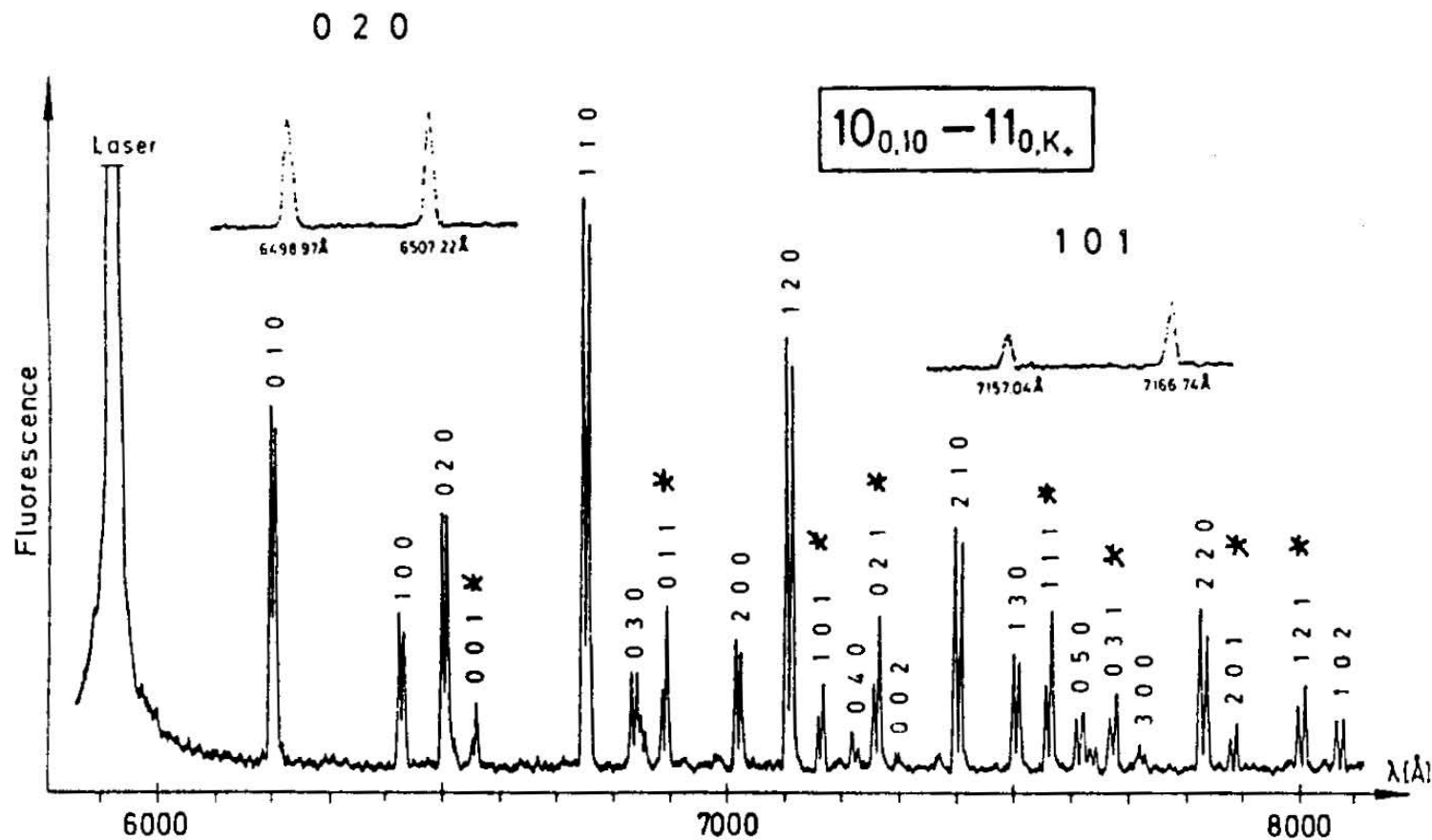
Ionization Spectroscopy
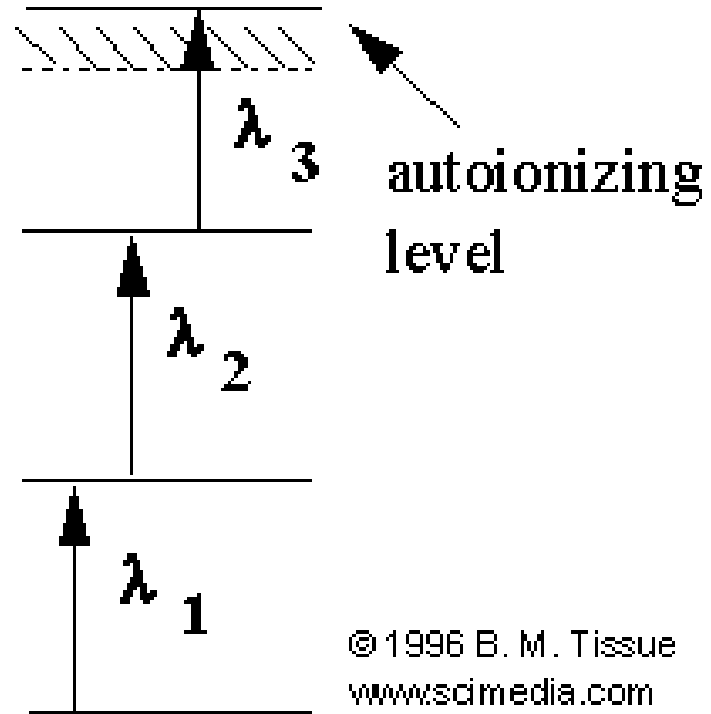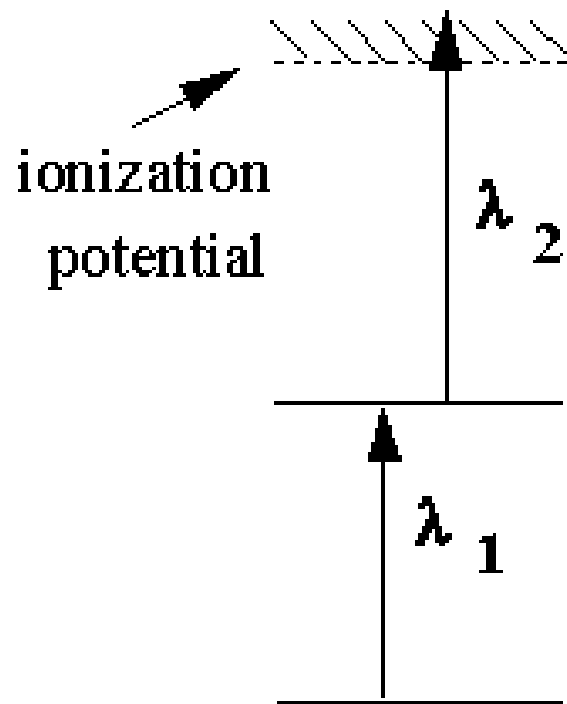
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Br$^+$

Br*

260 nm

Br ^{2}P$_{3/2}$
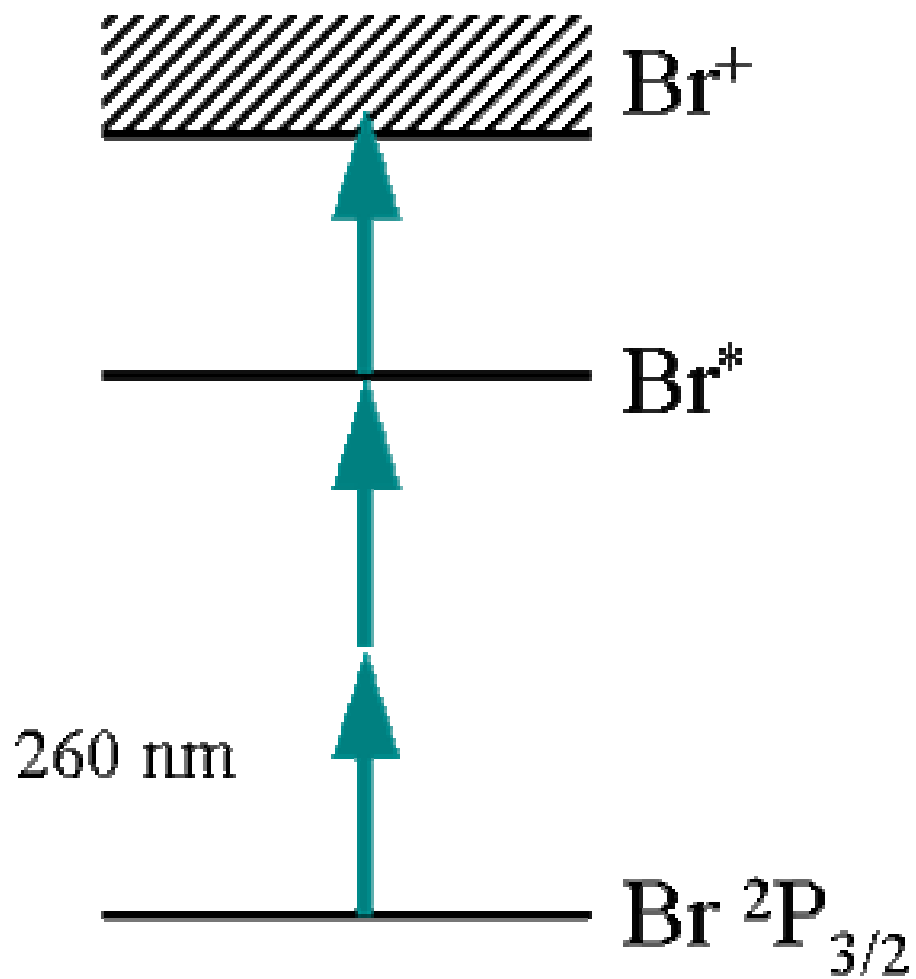
Rydberg States Ionization
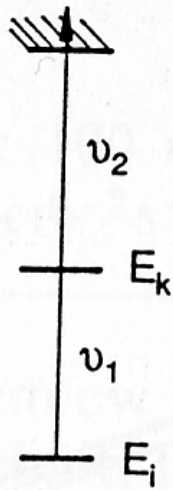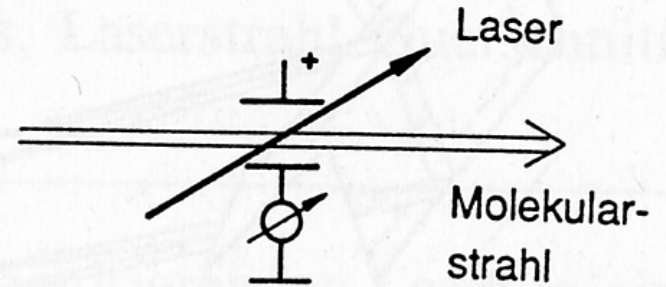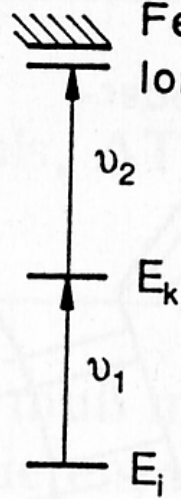
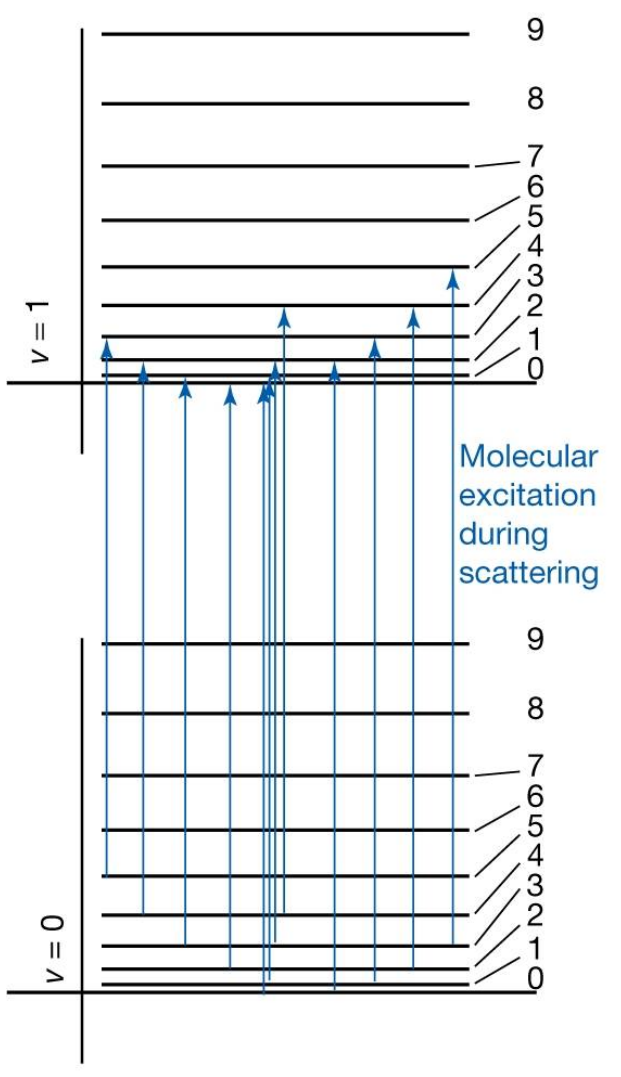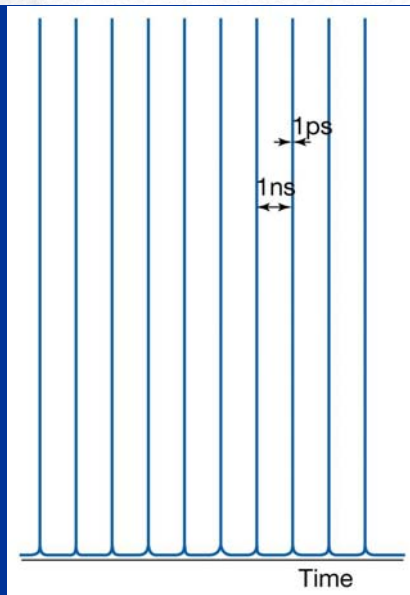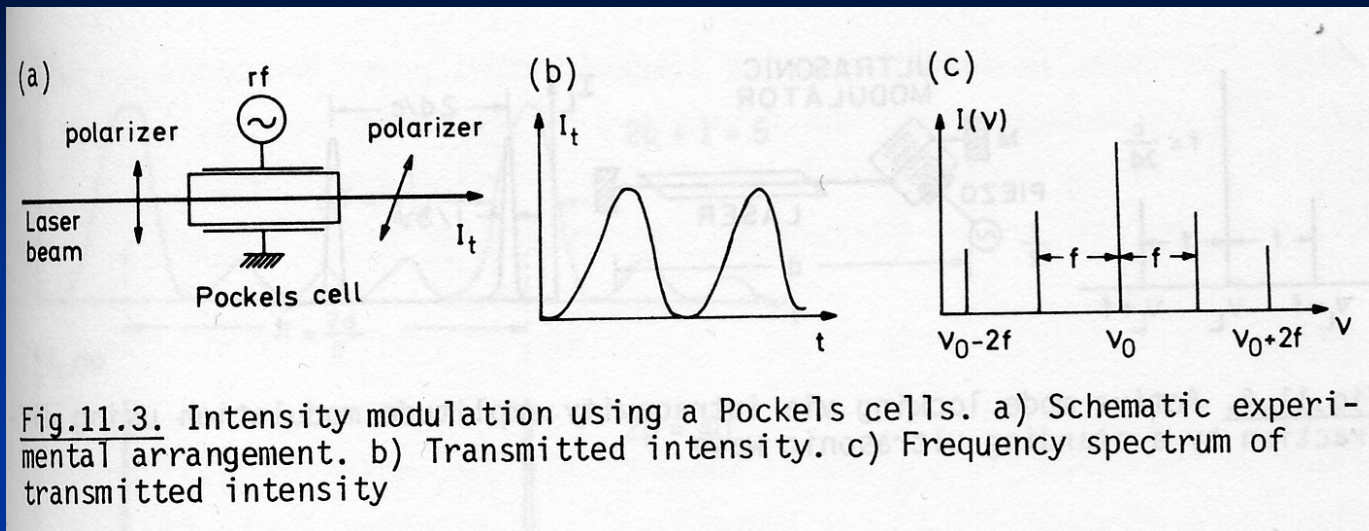# Raman Laser Spectroscopy
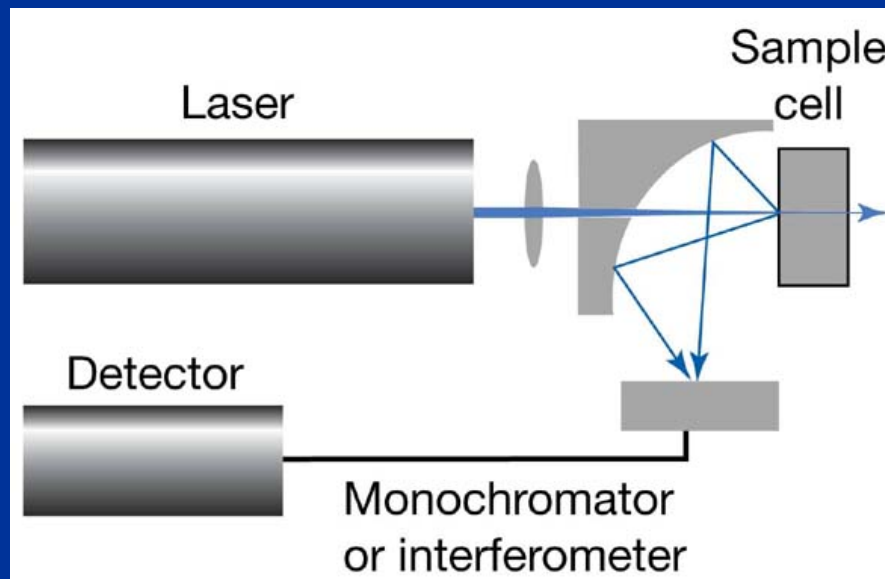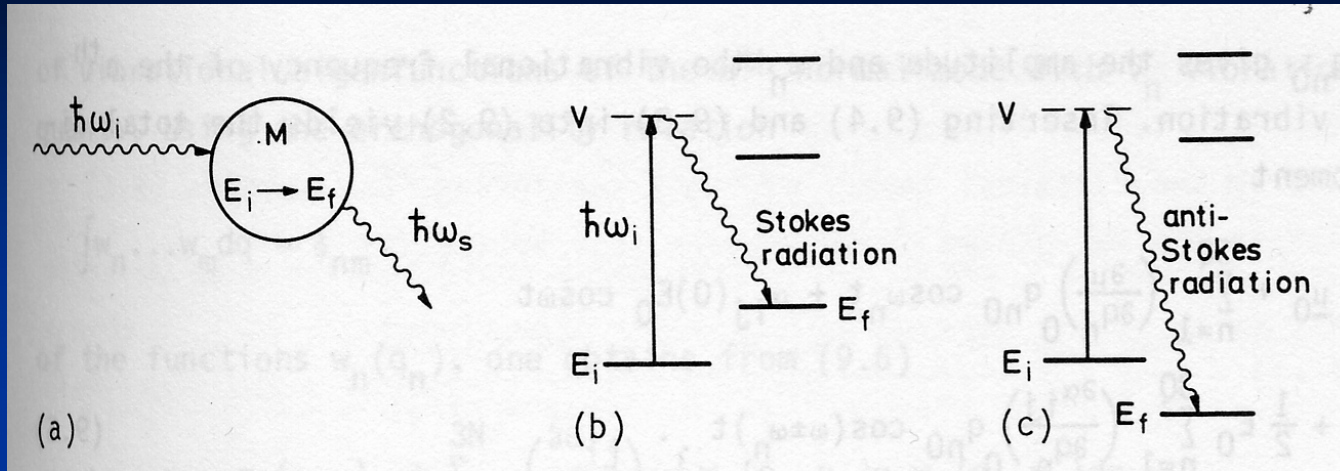
Rotational Raman Spectroscopy
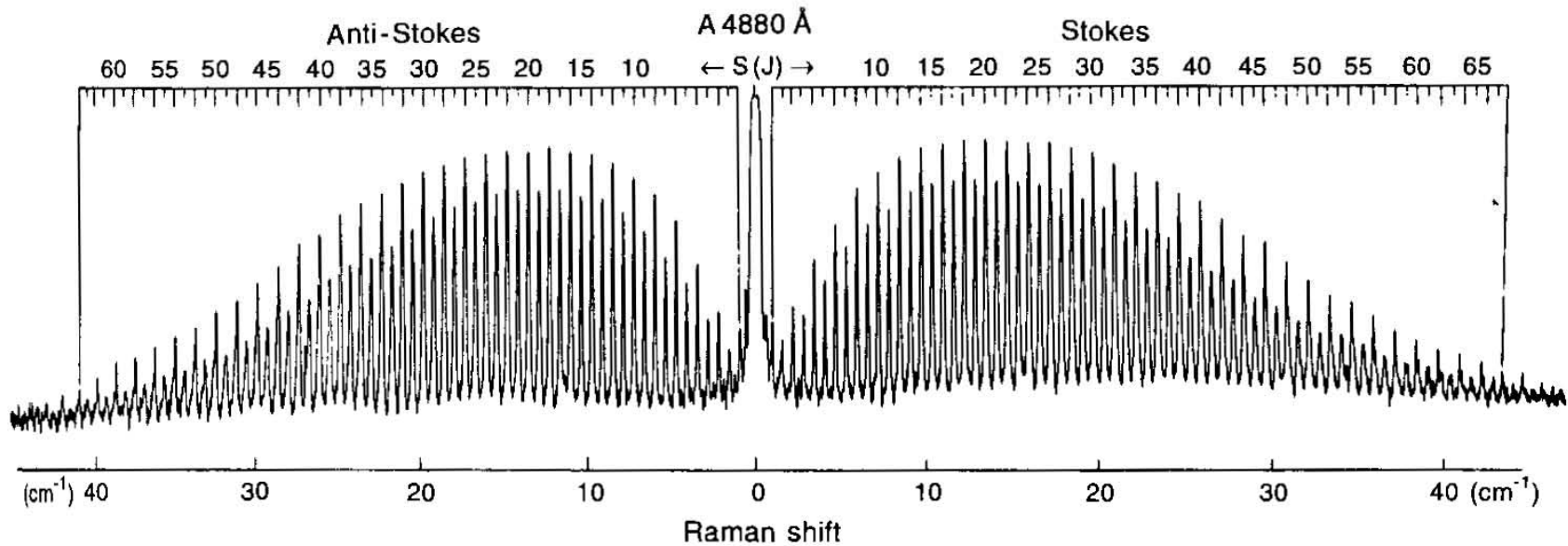
Fig.8.3. Rotational Raman spectrum of C_2N_2 excited with the 488 nm line of the argon laser in the experimental setup of Fig.8.2 and recorded on a photographic plate with 10 min exposure time [8.20]
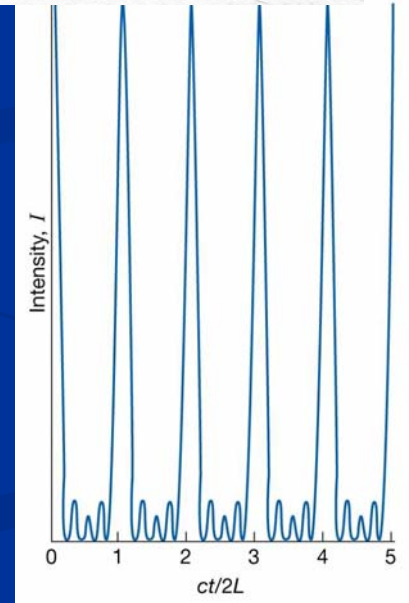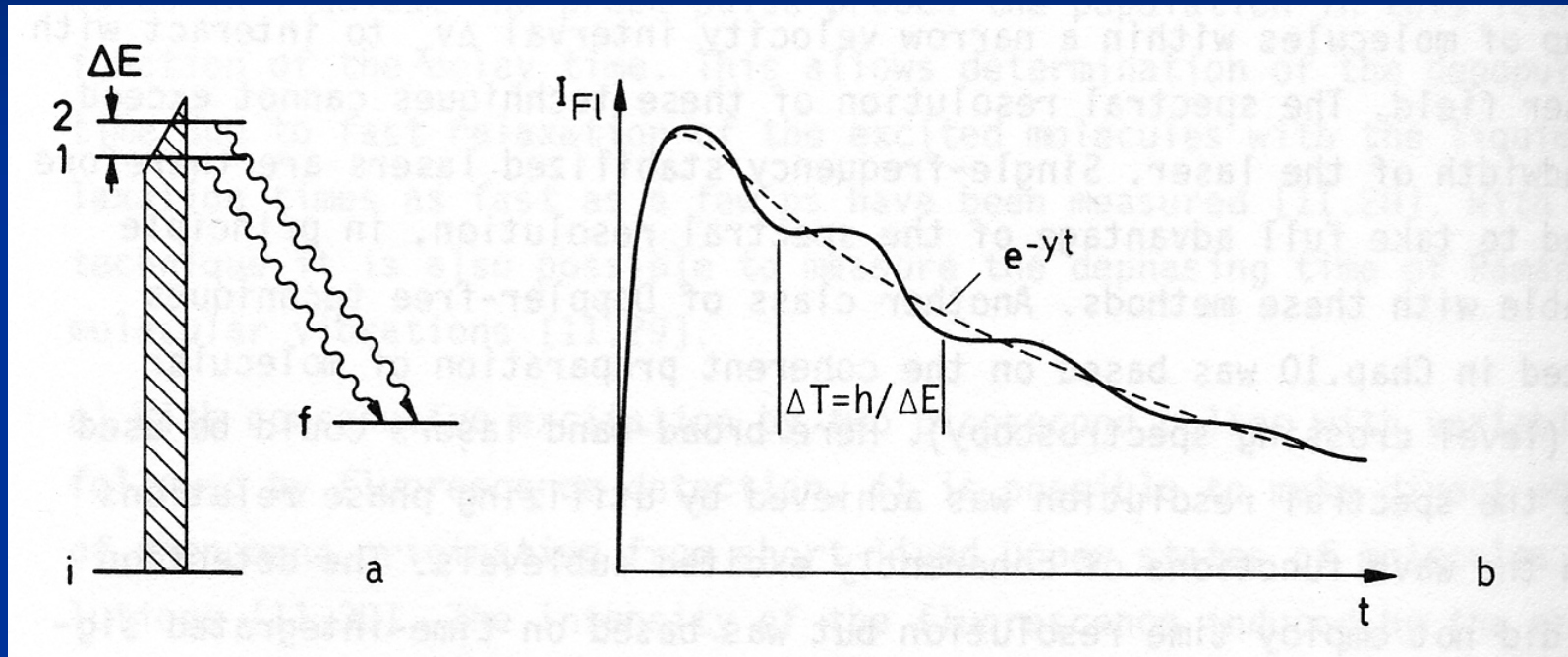
Vibrational Raman Spectroscopy: CO

Molecular excitation during scattering

O   Q   S

2200   2100 $\Delta\tilde{v}/cm^{-1}$

O   Q   S

Frequency of scattered radiation
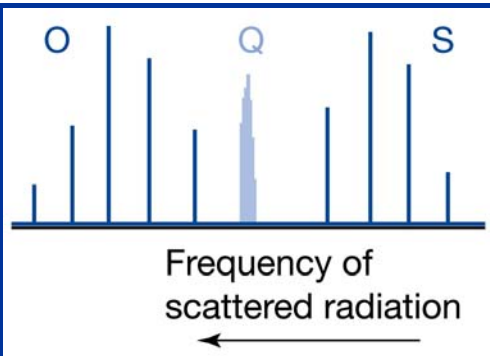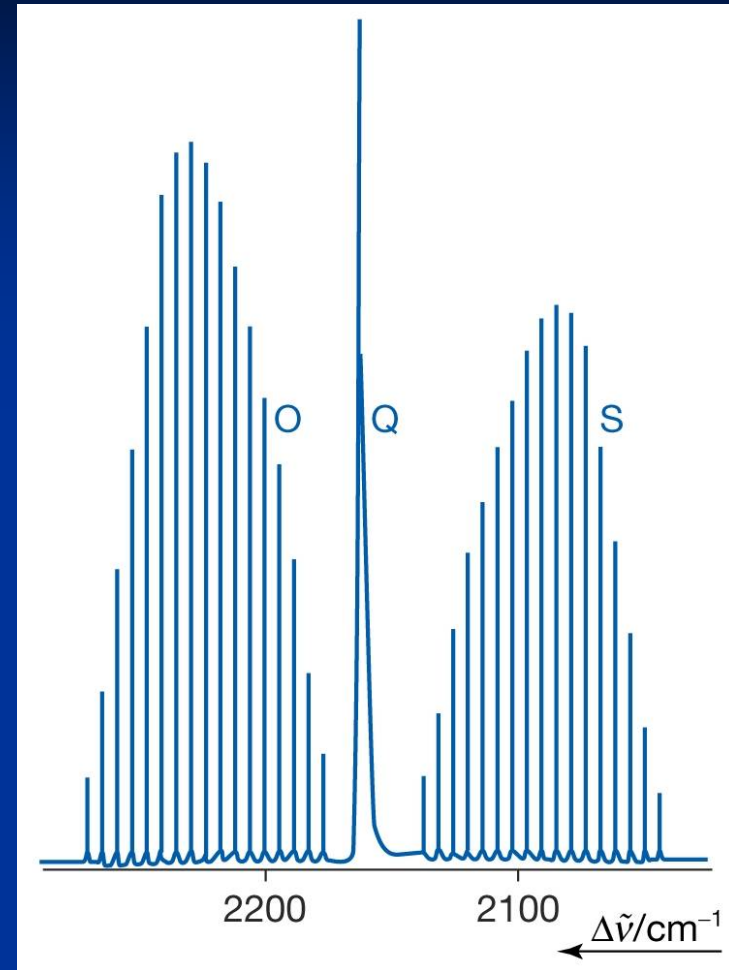
Ultra Short Laser Pulses: mode locking

Fig.11.3. Intensity modulation using a Pockels cells. a) Schematic experimental arrangement. b) Transmitted intensity. c) Frequency spectrum of transmitted intensity
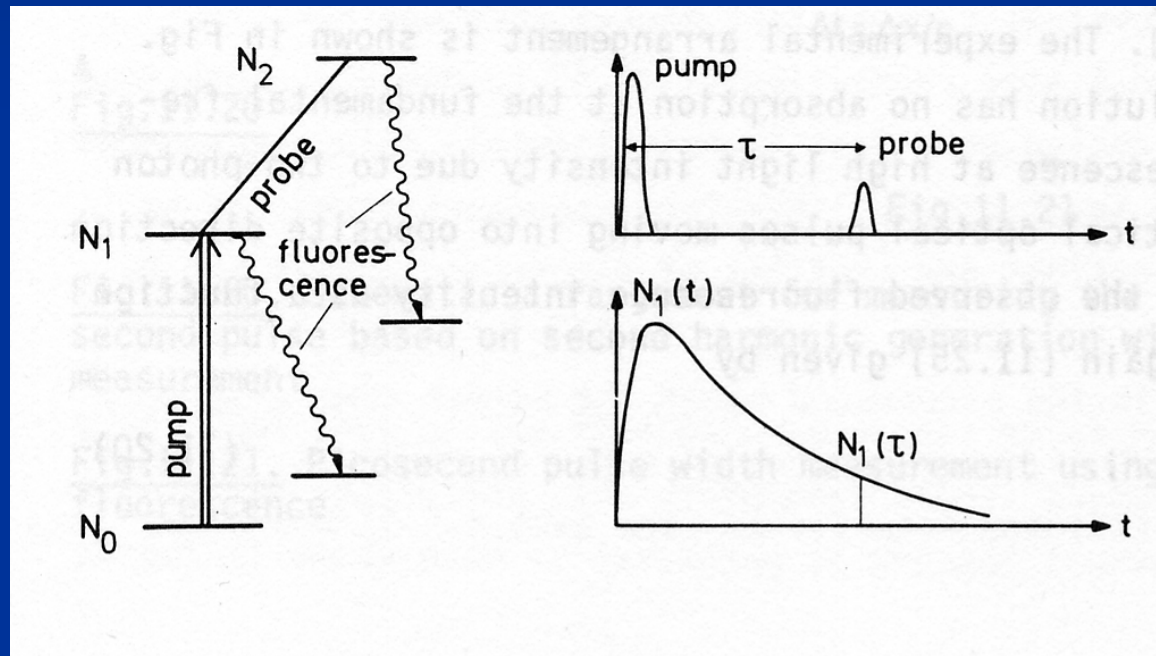
Time scale

2p=50

2p+1=5

Quantum Beat Spectroscopy

Femto-Second Laser Spectroscopy
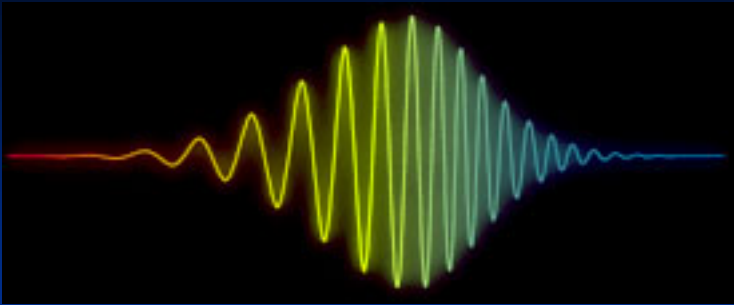
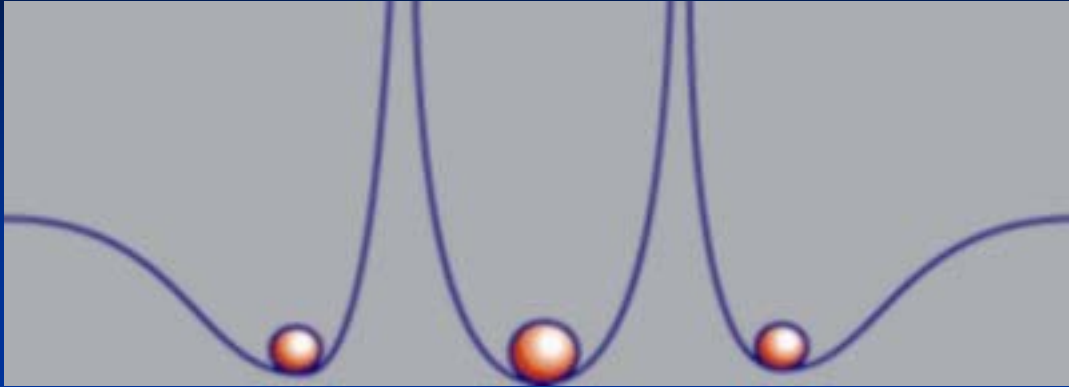**1999 Nobel Prize
Ahmed Zewail**

Pump-and-probe Technique

H$_2$O
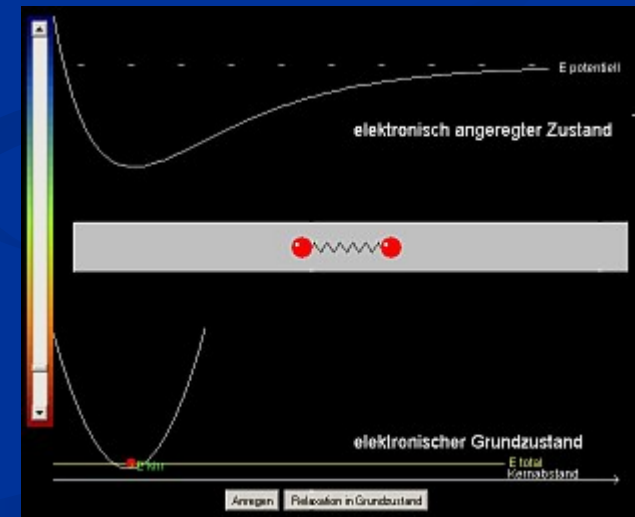
Pump-and-probe technique

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

Ahmed Zewail Lab

Spectroscopy of size–selected molecular clusters