Molecular Spectroscopy
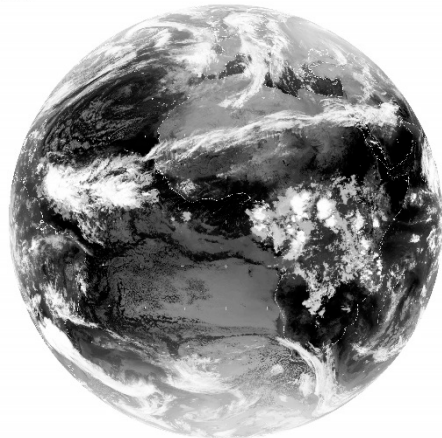
Prof. Hartmut Boesch

EOS, Dept. of Physics and Astronomy, University of Leicester, U.K.

http://www2.le.ac.uk/departments/physics/research/earth-observation-science

TRANSMISSION (Purely Absorbing Case)

$$I_o(\lambda) \rightarrow \boxed{\textbf{GAS: } \kappa(\lambda)} \rightarrow I_\tau(\lambda)$$
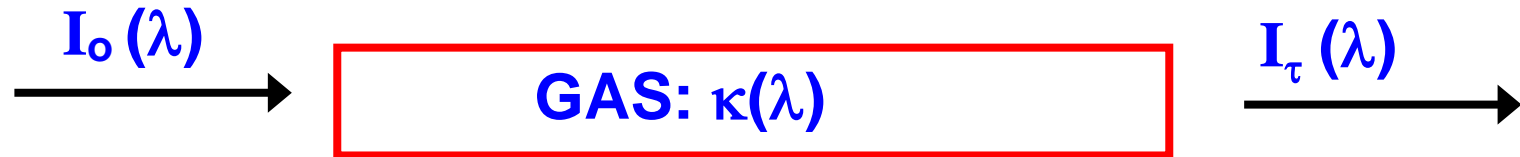
$$dI(\lambda) = -\ k(\lambda)\ dL$$

$$\mathcal{T}(\lambda) = \exp[-\sigma(\lambda)\ c\ L]$$
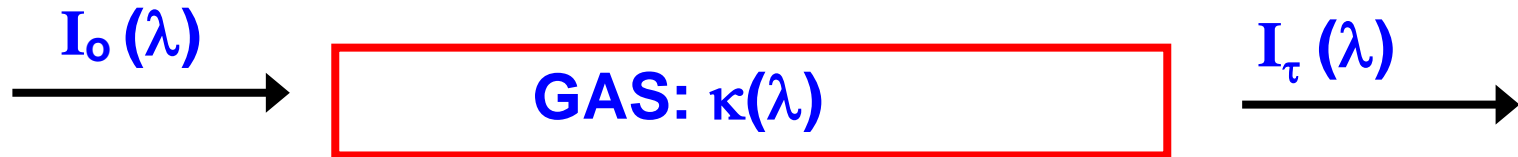
with c = the density of molecules per unit volume.

Three factors matter:

➢ **Spectroscopy**: absorption cross section $\sigma(\lambda)$ [cm^2/molecule]

➢ **Composition/density**: $c = \chi\ c_{air}$ [molecules/cm^3]

➢ **Photon pathlength**: geometrical distance = L [km]

TRANSMISSION (Purely Absorbing Case)

$$I_o(\lambda) \rightarrow \boxed{\textbf{GAS: } \kappa(\lambda)} \rightarrow I_\tau(\lambda)$$

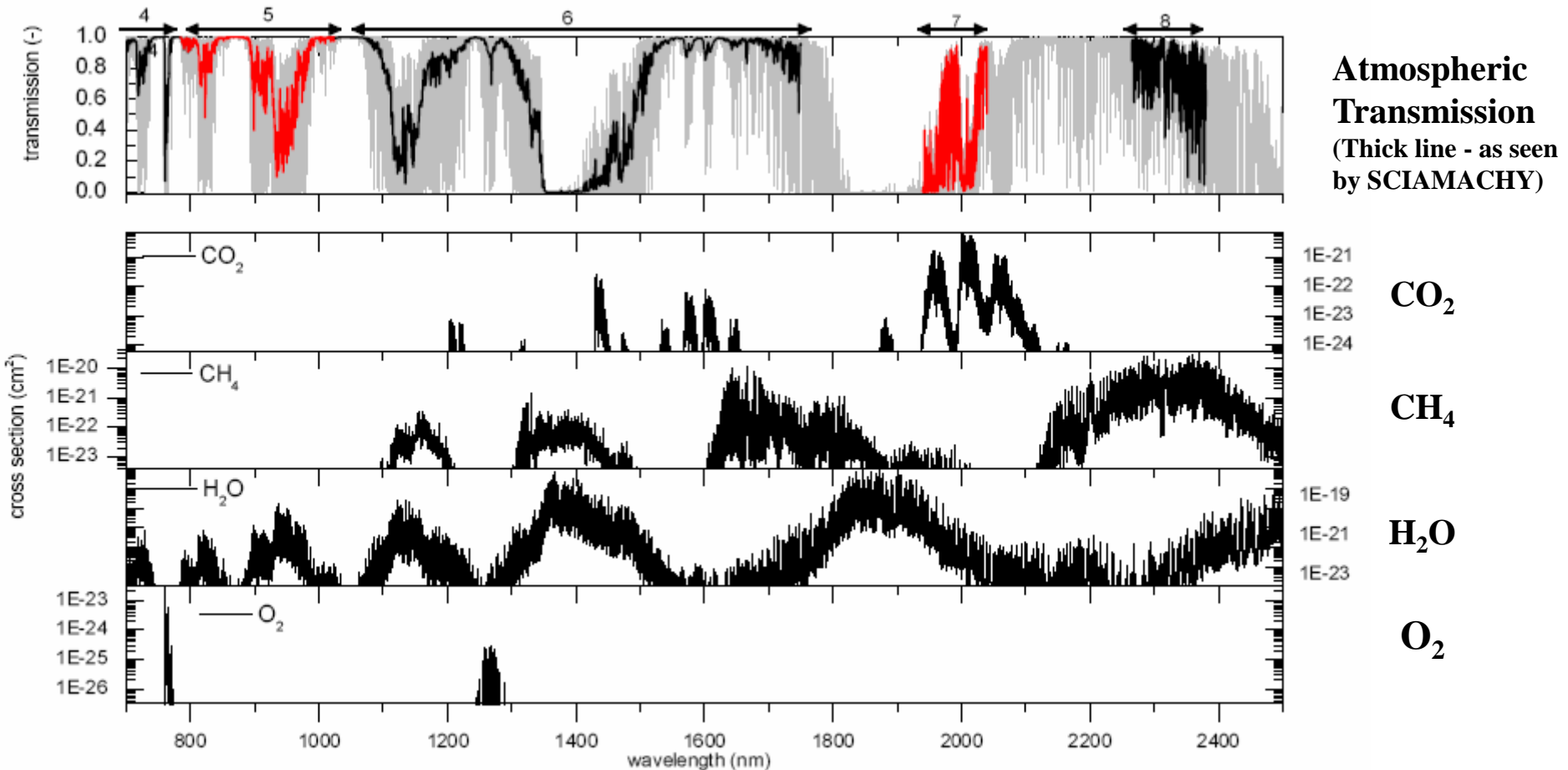$$dI(\lambda) = - k(\lambda) \, dL$$

$$\mathcal{T}(\lambda) = \exp[-\sigma(\lambda) \, c \, L]$$

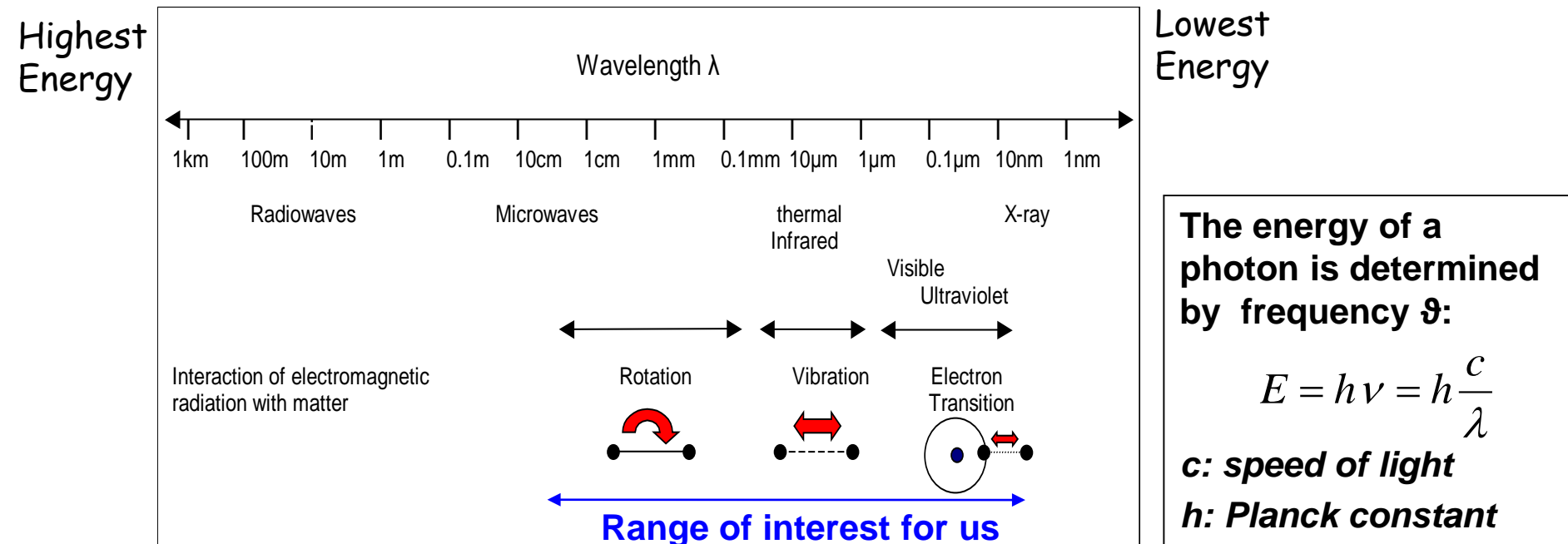with c = the density of molecules per unit volume.

Three factors **This Lecture**

- **Spectroscopy**: absorption cross section $\sigma(\lambda)$ [cm^2/molecule]
- **Composition/density**: $c = \chi \, c_{air}$ [molecules/cm^3]
- **Photon pathlength**: geometrical distance = L [km]

Recap: GAS TRANSMISSIONS AND ABSORPTION CROSS SECTION – NEAR-IR

Atmospheric Transmission
(Thick line - as seen by SCIAMACHY)

CO_2

CH_4

H_2O

O_2

Highly-structured molecule-specific absorption coefficient

Electromagnetic spectrum

Highest Energy

Wavelength λ

Lowest Energy

| 1km | 100m | 10m | 1m | 0.1m | 10cm | 1cm | 1mm | 0.1mm | 10µm | 1µm | 0.1µm | 10nm | 1nm |

Radiowaves Microwaves thermal Infrared X-ray

Visible
Ultraviolet

Interaction of electromagnetic radiation with matter

Rotation Vibration Electron Transition

Range of interest for us

The energy of a photon is determined by frequency ϑ:

$$E = h\nu = h\frac{c}{\lambda}$$

c: speed of light
h: Planck constant

- **UV/Vis and near-IR:**   **Electronic and vibrational transitions**

- **Thermal IR:**   **Vibrational transitions**

- **Microwaves:**   **Rotational transitions**

**Electronic, vibrational and rotational transitions will be focus of this lecture!**

Dipole Moment

$$p = qr$$

☐ **Electric dipole moment:**

- **Parameter important to how EM radiation interacts with matter**

- **Displacement or oscillation of charge in dipole creates time varying dipole moment (ie. dp/dt) and in turn a time varying E-field and thus EM radiation**

☐ **Whether a molecule absorbs radiation is determined by how atoms are arranged to form the molecule and its associated ability to create charge separation (permanent dipole or induced dipole)**
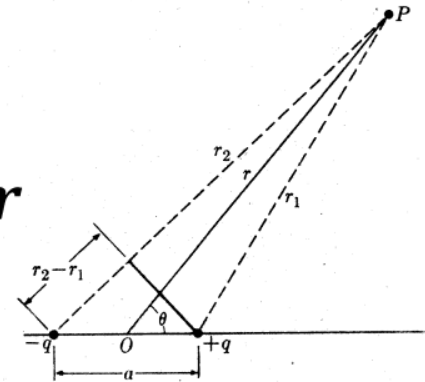
	Formula	Description	Example
Polar	AB	Linear Molecules	CO
	HA_x	Molecules with a single H	HF
	A_xOH	Molecules with an OH at one end	C_2H_5OH
	O_xA_y	Molecules with an O at one end	H_2O
	N_xA_y	Molecules with an N at one end	NH_3
Non-polar	A_2	Diatomic molecules of the same element	O2
	C_xA_y	Most carbon compounds	CO_2

Electronic States

❑ **Atoms/molecules are quantum mechanical systems with discrete energy levels described by a set of quantum numbers**

❑ **System needs to be described by time-dependent Schroedinger equation**

$$H\psi(r,t) = i\hbar \frac{\partial}{\partial t}\psi(r,t)$$

❑ **Electron is described by wave function $\psi(r,t)$**

❑ **We observe transitions between different energy levels (of outer loosely bond electrons): $\Delta E = E_2 - E_1 = h\nu$**

❑ **Transition dipole moment is the electric dipole moment associated with the transition between the two states a and b. Transition dipole moment (and its orientation) is useful for determining if transitions are allowed under the electric dipole interaction**

Compare classical dipole: $\boldsymbol{\tau} = |q\boldsymbol{r}||\boldsymbol{E}|sin\theta$

Basic QM: Hydrogen Atom

❑ **H-atom is a simple quantum mechanical system**

❑ **Hamiltonian is known (and given by Coulomb potential** $V(r) = kZe^2/r$ **):**

$$H = -\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{r})$$
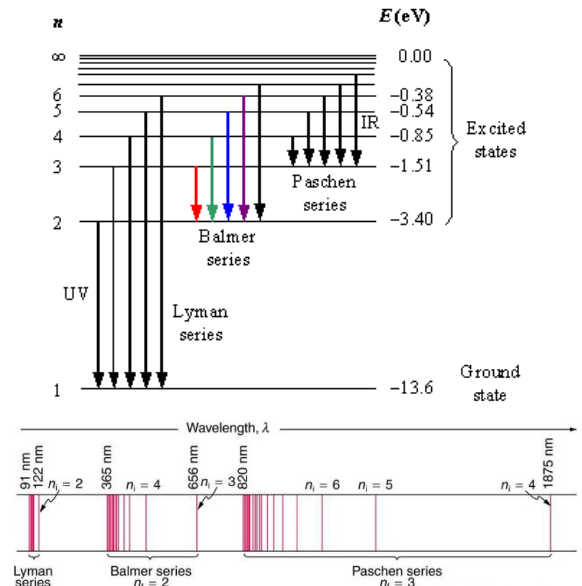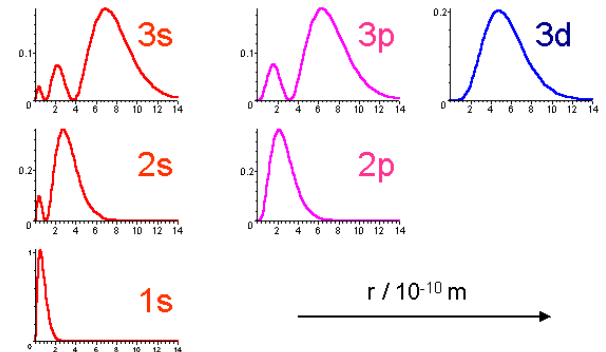
❑ **Analytic solution possible:**

- **Energy levels:** $E_n = -\dfrac{R}{n^2}$

- **With Rydberg constant R = 13.6 eV**

❑ **Series of spectral lines**

$$E_n = -R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu$$

Radial probability of electrons

Electron density in atomic hydrogen w(r) = r² [R_nl(r)]²

3s   3p   3d
2s   2p
1s   r / 10⁻¹⁰ m

A simple Molecule: H_2^+

- **Simplest possible molecule: 1 electron and 2 protons**

- **Hamiltonian includes 2 potential terms**

$$H = -\frac{\hbar^2}{2m}\Delta + V(r_a) + V(r_b)$$

  + Coulomb repulsion between protons

- **Wavefunction will be given by combinations of individual wave function: symmetric and asymmetric solution possible**

- **This results in 2 energy levels: binding and anti-binding state**

- **Multi-electron systems much more complicated !**

symmetric   *asymmetric*
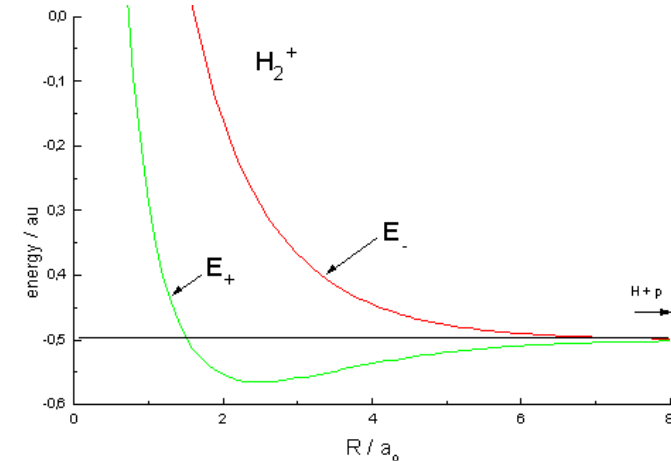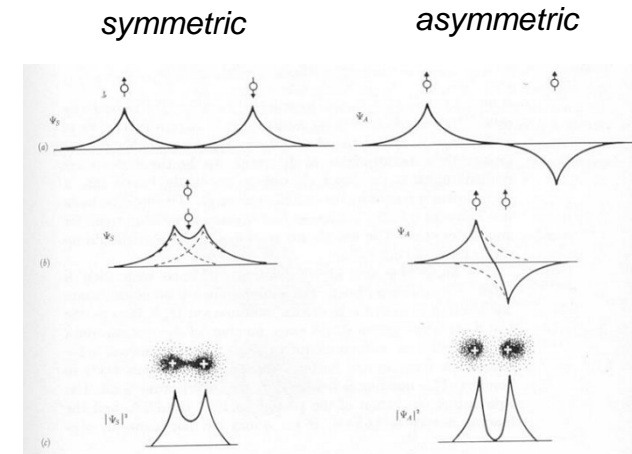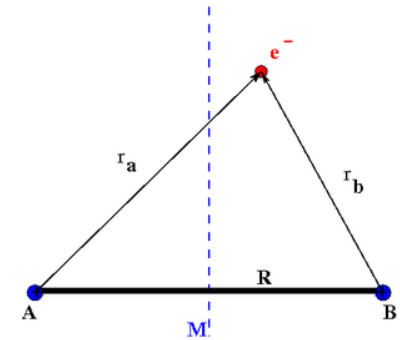
Molecular motions

Translation: Motion of the complete molecule in three dimensions

Rotation: Rotation of the complete molecule around three axes

Vibration: Periodic motion of individual atoms relative to each other
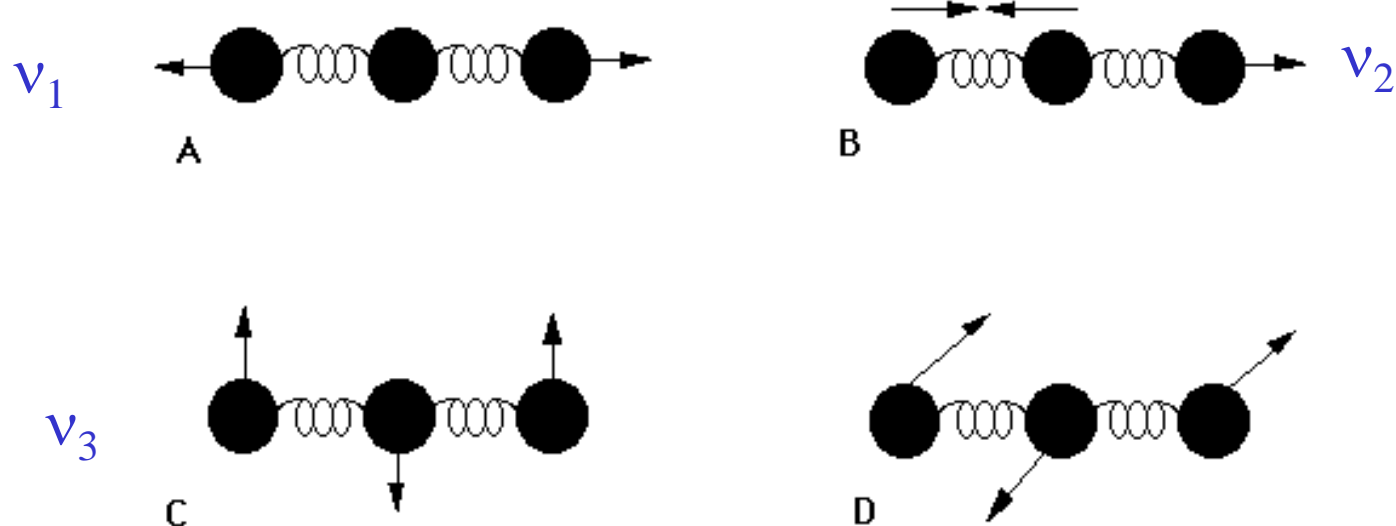
Degrees of freedom: A molecule with N atoms has 3N degrees of freedom

- Translation: $f_T = 3$
- Rotation: $f_R = 3$ ($f_R = 2$ for linear molecules)
- Vibration: $f_V = 3N - 6$ ($f_V = 3N-5$ for linear molecules)

- 2 atomic molecule: $f = 6$

   $f_T = 3$; $F_R = 2$ and $f_V = 1$

CO$_2$ Vibrations
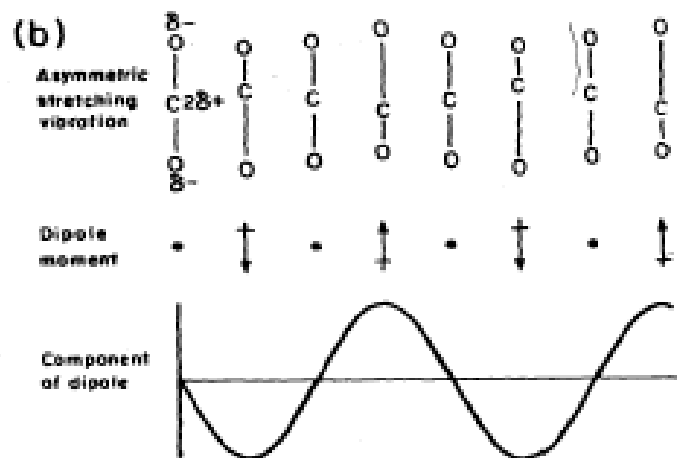

ν_1 A

ν_2 B

ν_3 C

D

❑ **(A) & (B) stretching of chemical bonds**
- **(A) symmetrical (not IR active - no change in dipole moment**
- **(B) asymmetrical (IR active - change in dipole moment)**

❑ **(C) & (D) bending vibrations**
- **one in plane of paper; one out of plane of paper**
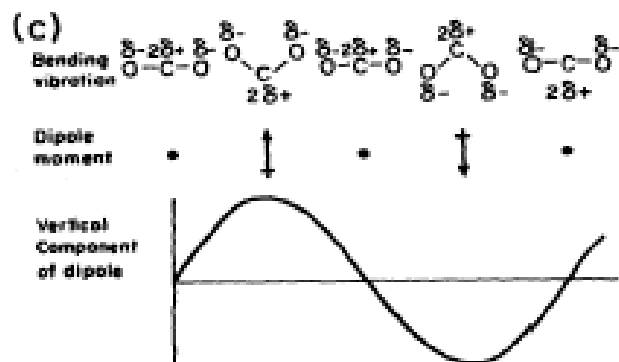- **equal in energy**

Optically active modes

ν_1 **does not originate any electrical dipole** ➜ **optically inactive**

For the same reason O_2 and N_2 are optically inactive

ν_2 **and** ν_3 **originate an electrical dipole** ➜ **optically active**

All molecules with three or more atoms absorb IR radiation because they all have some vibrations that change the polarity of the molecule

Vibration

❑ **Analogy to classical mechanic**

- ▪ **Molecules vibrate since the atoms are not fixed but are elastically coupled (like with mechanical springs)**
- ▪ **Hooks law can be applied:** $\text{F} = m\dfrac{\partial^2 x}{\partial t^2} = -kx$
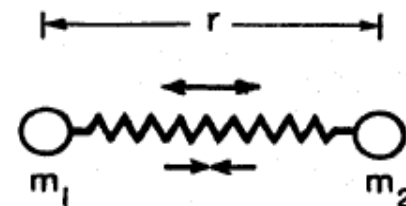
❑ **Classic Solution (harmonic oscillator) :**

Oscillator frequency $\quad v_0 = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m'}}$ or $\quad \omega_o = \sqrt{\dfrac{k}{m'}}$

Reduced mass $\quad m' = \dfrac{m_1 m_2}{m_1 + m_2}$

All energies possible

❑ **General rule:**

- ▪ **The lighter the masses of atoms, the higher the vibrational frequency**
- ▪ **The stronger the bond, the higher the vibrational frequency**

Vibration

❑ **Quantum mechanics: energy values must be discrete:**
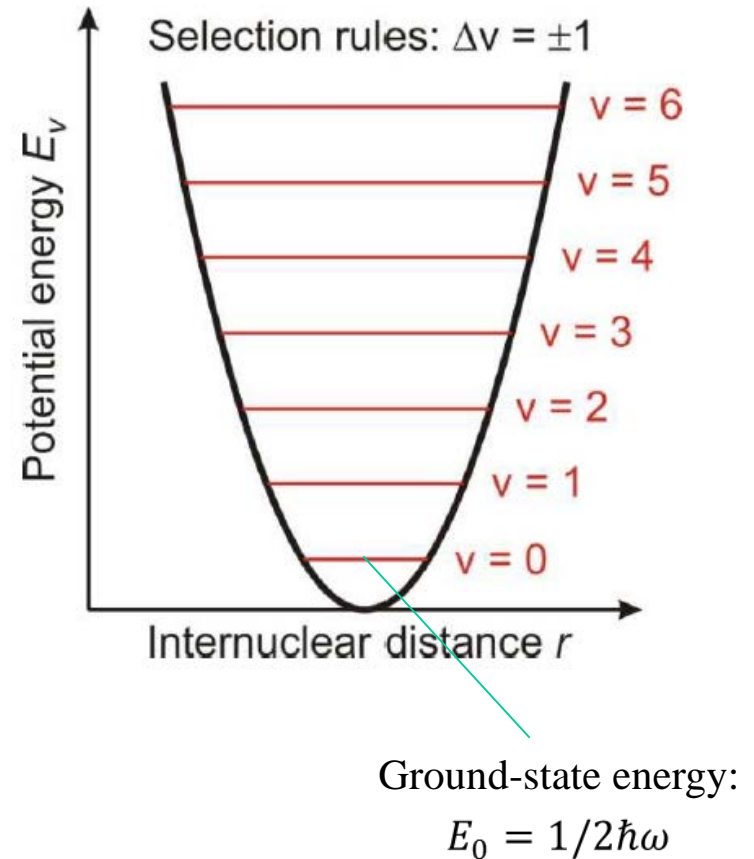
$$E = \hbar\omega\left(v + \frac{1}{2}\right)$$

with vibrational quantum number v

and $\quad \omega = \sqrt{\dfrac{k}{m'}}$

❑ **All energy levels are equidistant**

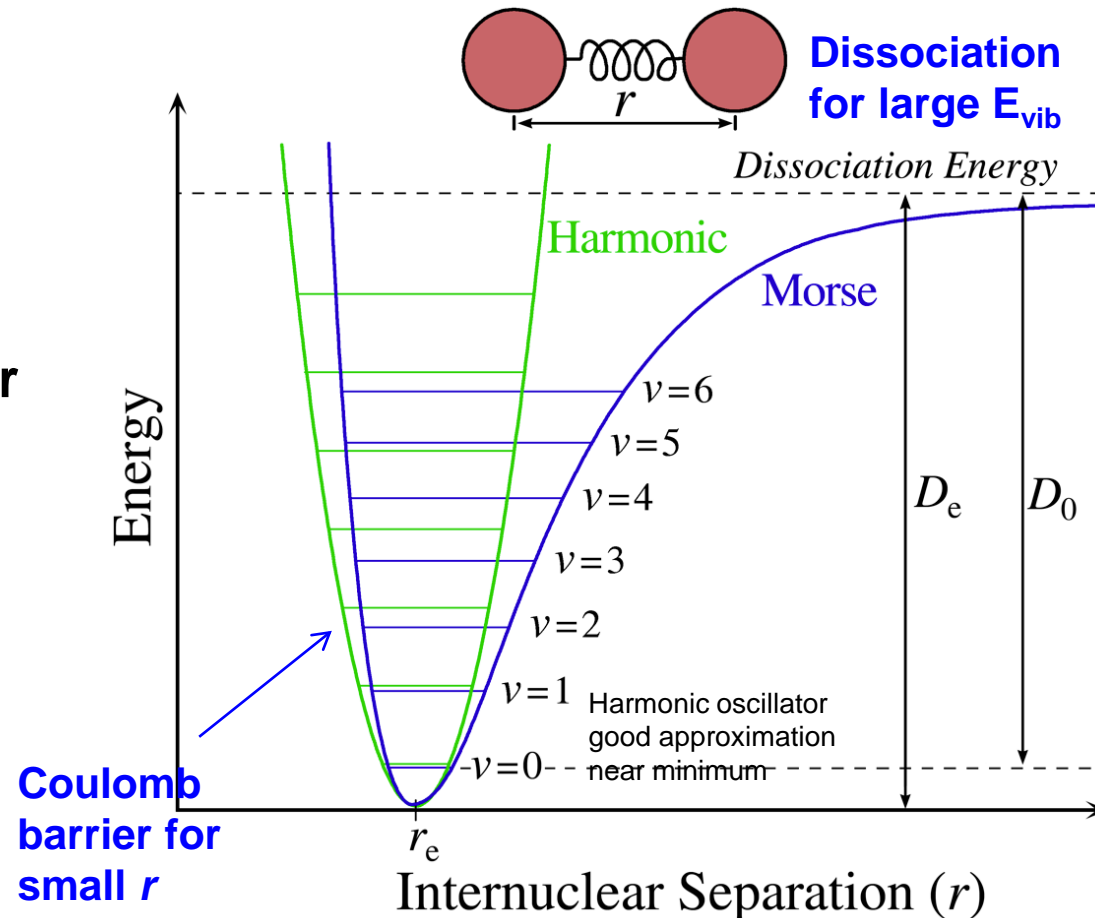❑ **Selection rule: $\Delta v = +/- 1$**

➢ **Only 1 line will be observed !**

Selection rules: $\Delta v = \pm 1$

Potential energy E_v

Internuclear distance r

v = 6
v = 5
v = 4
v = 3
v = 2
v = 1
v = 0

Ground-state energy:
$$E_0 = 1/2\hbar\omega$$

Anharmonic oscillator

Morse potential

D: Dissociation energy
A: molecule specific parameter
r_e : equilibrium distance

$$V(r) = D \left(1 - e^{-a(r-r_e)^2}\right)^2$$

☐ **Classic oscillator is not sufficient to describe molecular oscillations**

☐ **Anharmonic oscillator is better model for molecular vibrations**

Dissociation for large E_{vib}

Dissociation Energy

Harmonic

Morse

$v=6$
$v=5$
$v=4$
$v=3$
$v=2$
$v=1$
$v=0$

D_e D_0

Harmonic oscillator good approximation near minimum

Coulomb barrier for small r

r_e

Energy

Internuclear Separation (r)

Vibration Spectra

- **Selection rule: Δv=+/- 1, +/-2, +/-3 ...**

✦ Vibrational spectra

- Approximately equidistant bands
- $\Delta v = \pm 1$ most intense
- $v = 1 \leftarrow 0$ fundamental transition
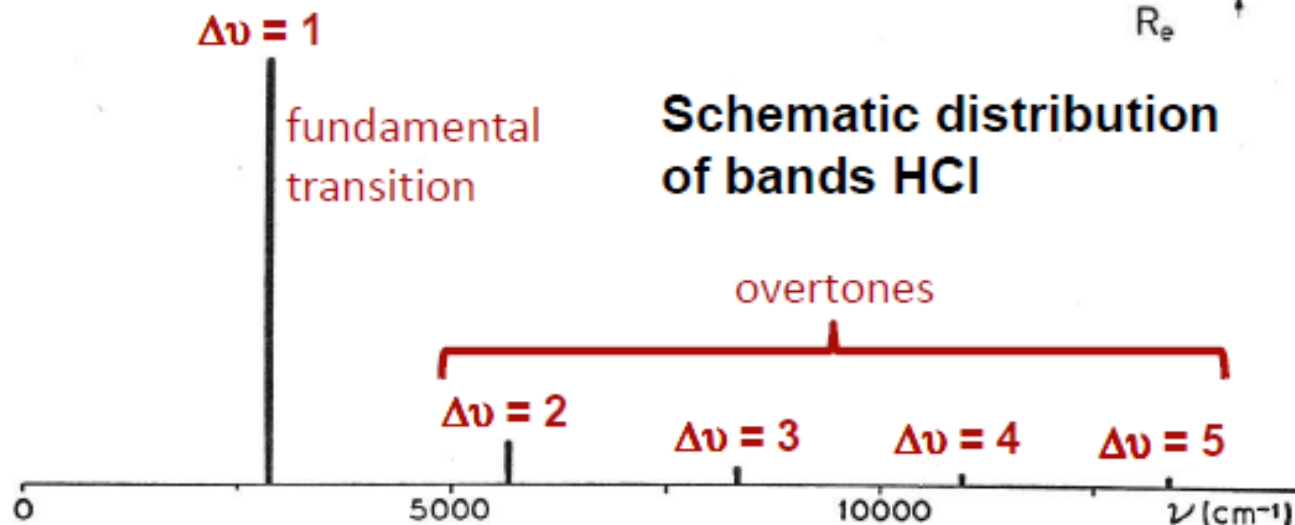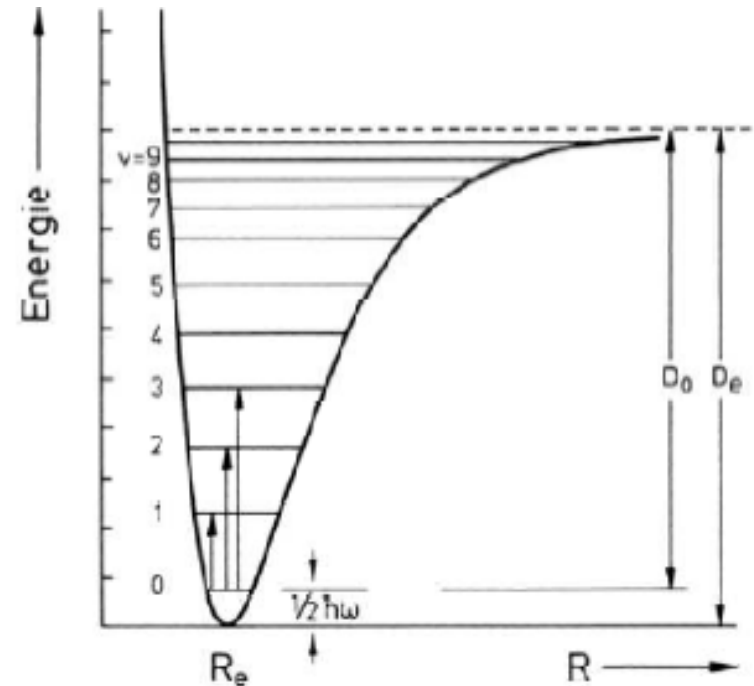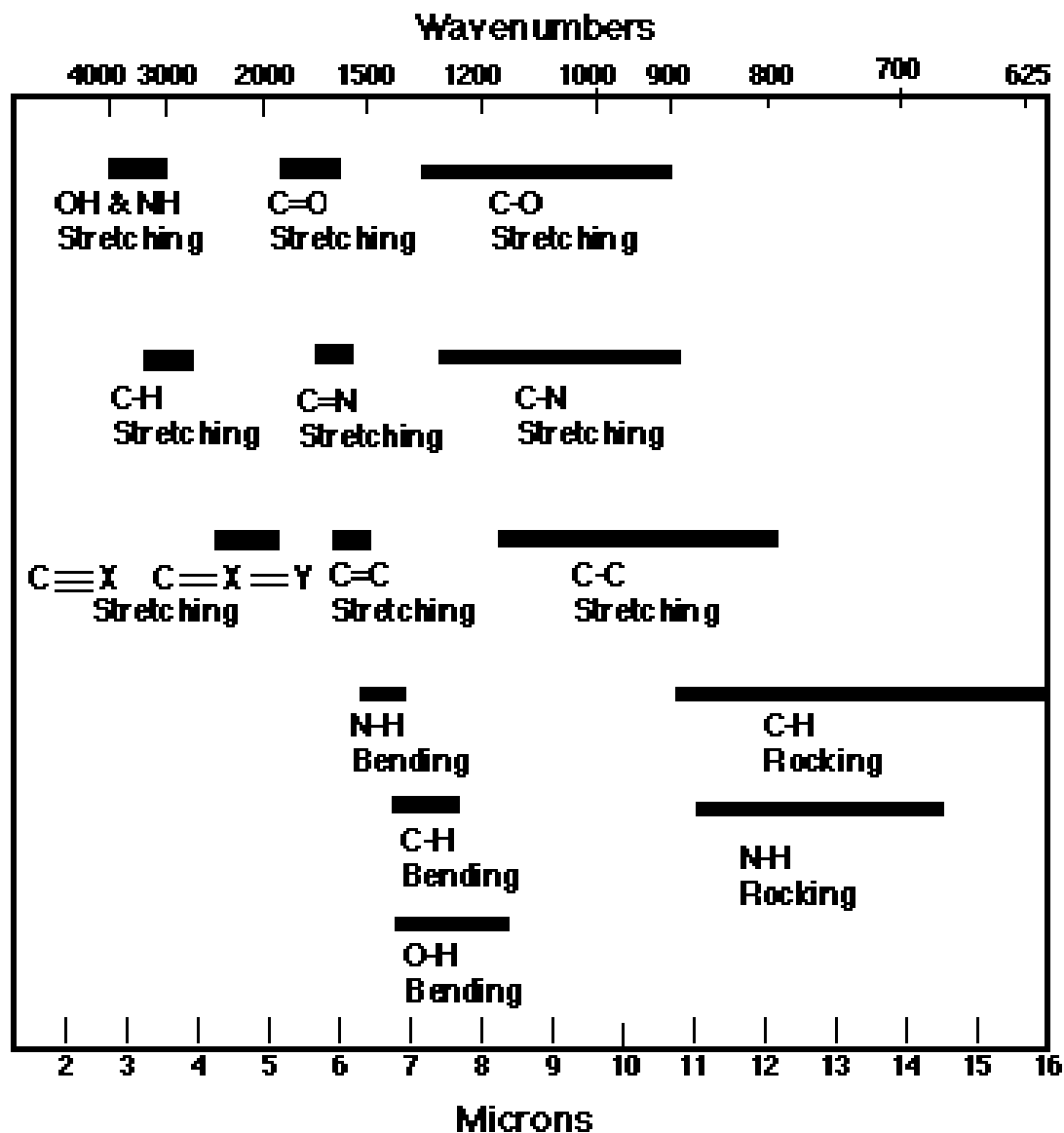- For increasing v, the distance between energy level decreases

Δv = 1

fundamental transition

Schematic distribution of bands HCl

overtones

Δv = 2   Δv = 3   Δv = 4   Δv = 5

Chart of Characteristic Vibrations

Example CO molecule

Masses:

m(C) = 20 x10^{-27} kg
m(O) = 26.5 x10^{-27} kg
m'= 11.4 X10^{-27} kg

Fundamental transition at λ = 4.6µm

using $$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m'}}$$

-> k = 1907 kg/s^2

Wavelength (µm)

Line Strength (cm^{-1}/molecule cm^{-2})

CO (Carbon Monoxide)

rotational   Fundamental   overtones

Wavenumber (cm^{-1})
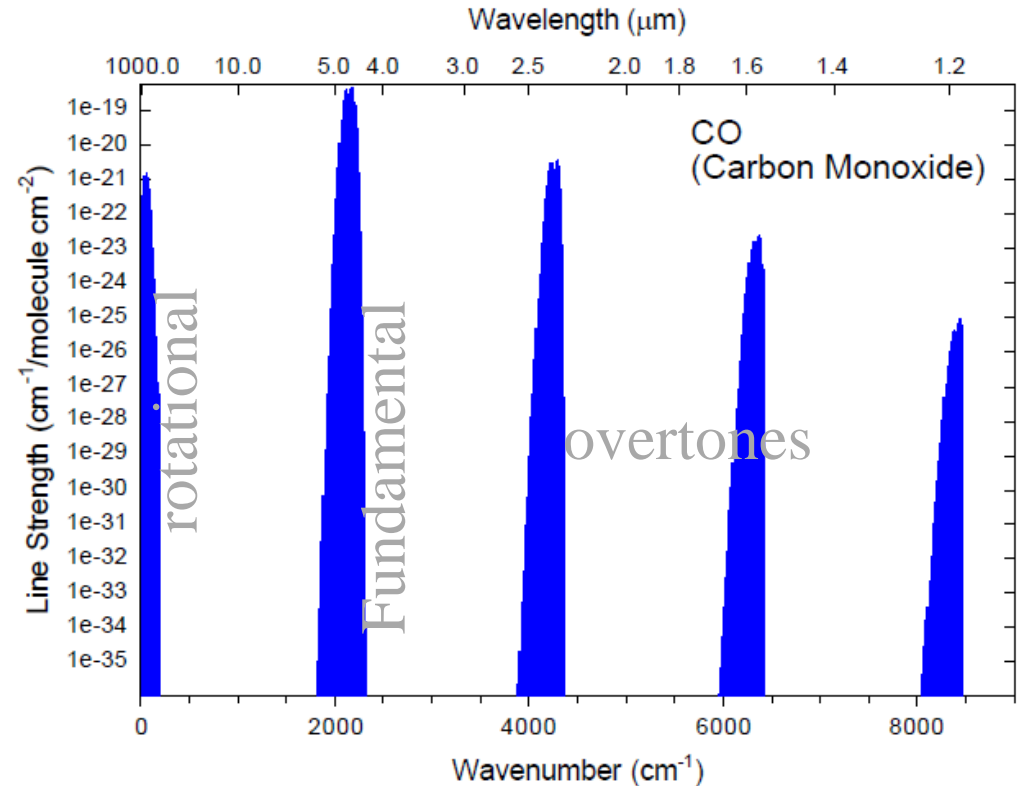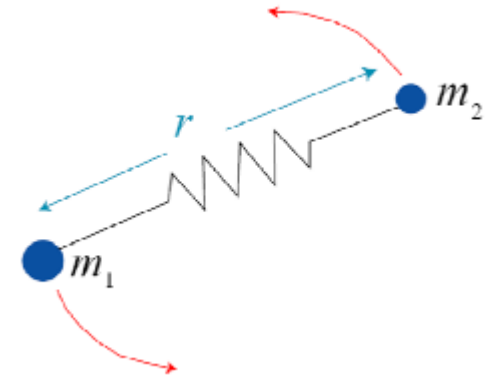
Compare HCl:

Fundamental transition at λ = 3.47µm

K = 4.78 kg/s2

Rotation

- **Rotating diatomic molecule with different atoms of mass m_1 and m_2, whose distance from the center of mass are r_1 and r_2 respectively**

- **The moment of inertia of the system about the center of mass is:**

$$I = m_1 r_1^2 + m_2 r_2^2$$

$$I = m' r^2 \qquad \text{With reduce mass } m'$$

- **The classical expression for energy of rotation is**

$$E_r = \frac{I\omega^2}{2} = \frac{L^2}{2I} \; where \; L = angular \; momentum$$

Rotation

❑ **Quantum Mechanics:**

$$L^2 \rightarrow \left(\frac{h}{2\pi} \right)^2 J(J+1)$$

where *J* is the rotational quantum number

❑ **Rotational energy:**

$$E(J) = \frac{1}{2I} \left(\frac{h}{2\pi} \right)^2 J(J+1) = h\,c\,B_v J(J+1)$$

$$B_v = \frac{h}{8\,\pi^2 c\,I} \quad \text{the rotational constant}$$

Rotation

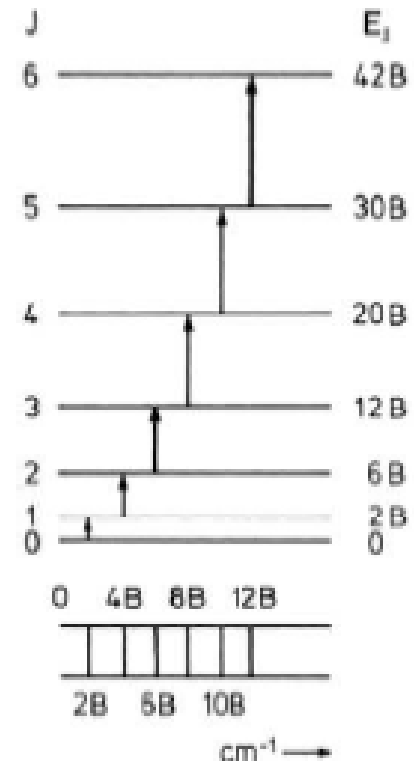❑ **Transition between 2 levels:**

$$J \rightarrow J+1$$

❑ **Energy difference:**

$$\Delta E = h\nu = hcB \,(J{+}1(J{+}2) - J(J{+}1))$$

$$\rightarrow \nu = 2cB\,(J{+}1)$$

In wavenumber: $\bar{\nu} = 2B(J+1)$

❑ **Thus rotational lines are equally spaced for a diatomic molecule:**

- ▪ **Distance depends only on B**

Non-Rigid Rotor

❑ **Non-rigid rotor: Nuclei connected by spring**

❑ **Fast non-rigid rotor: Stretching due to centrifugal force (moment of intertia increases)**

❑ **Rotational lines move closer for higher J**

❑ **Vibrating Rotor:**

  ▪ **Vibrations and rotations typically occur together**

  ▪ **Corrections for interaction between rotation and vibration:**

    • **Average internuclear distance increases with ν (quantum number for vibrations) -> smaller rotational constant B**
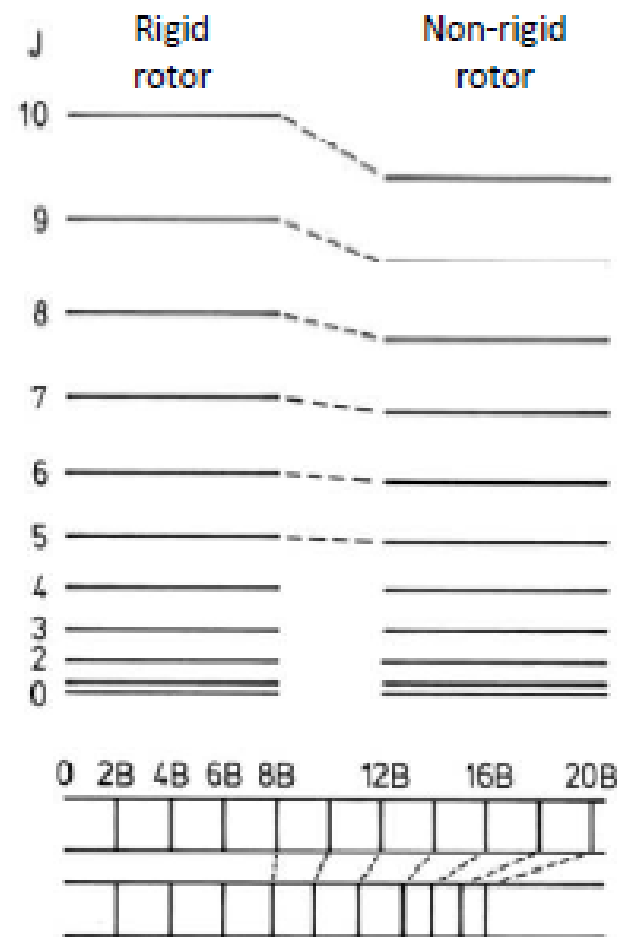
Rotation-vibration Spectra

❑ **Transitions between rotational levels of two vibrational levels (within an electronic state):**

- ▪ **Approximately equidistant vibrational bands**
- ▪ **v = 1->0 fundamental Transition**
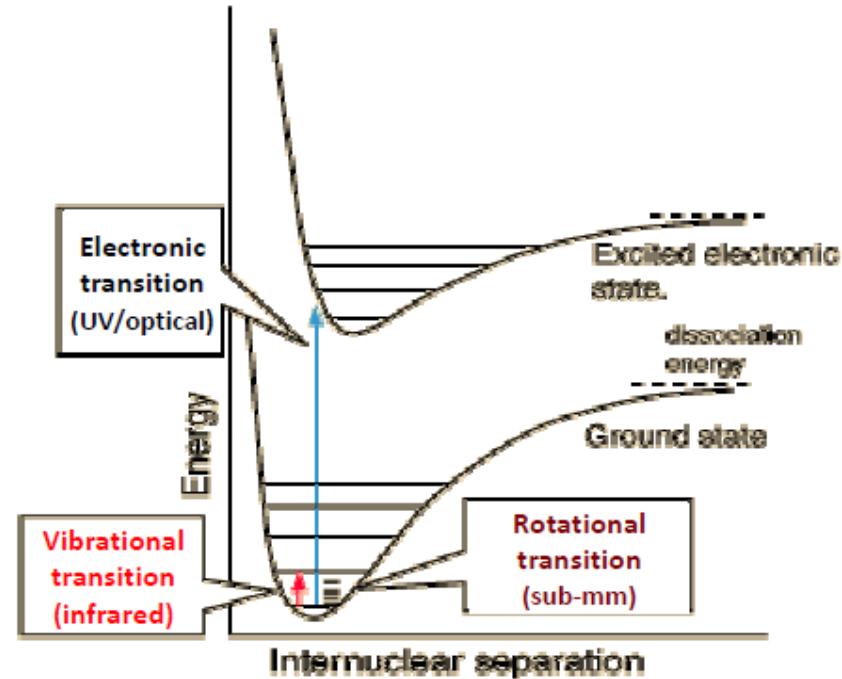- ▪ **Rotational structure ~equidistant lines**

❑ **Selection rules:**

- ▪ **$\Delta J = \pm 1$ if $\Lambda = 0$**
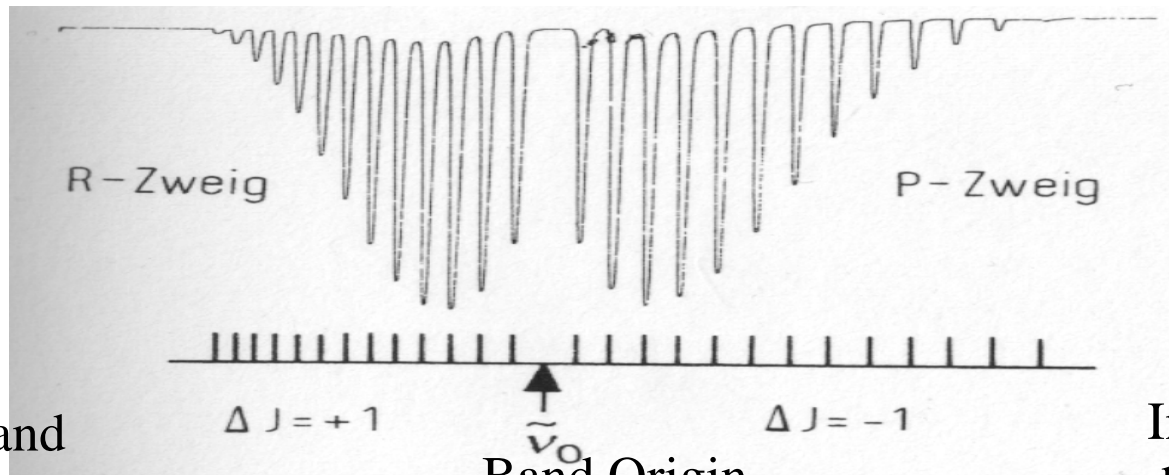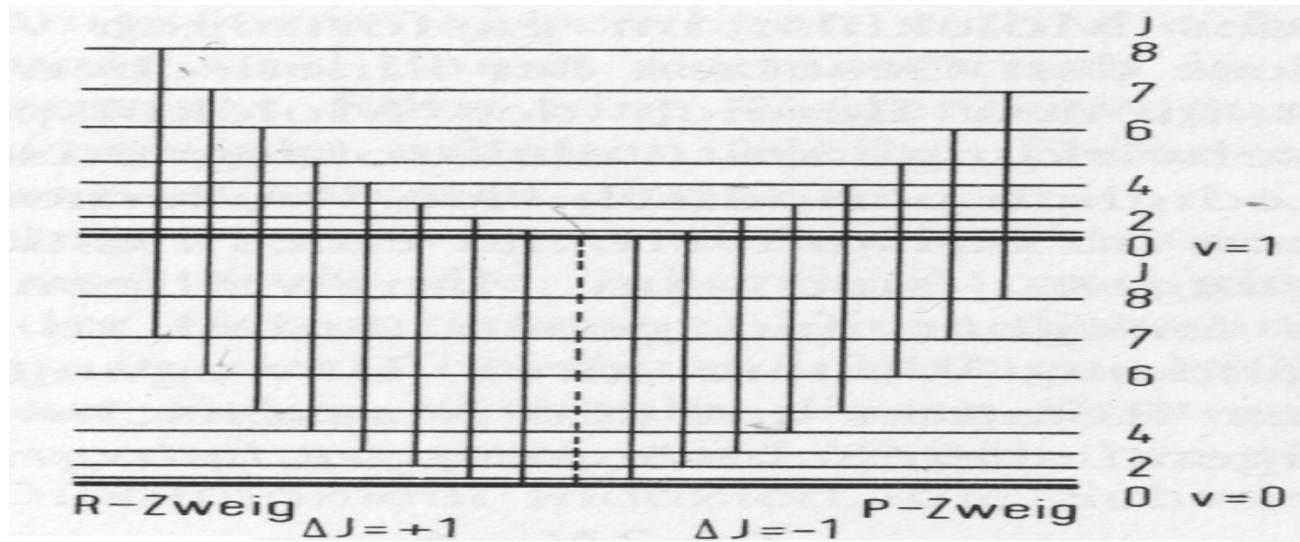- ▪ **$\Delta J = \pm 1, 0$ if $\Lambda \neq 0$**

  Λ: **Angular momentum quantum number**

❑ **Branches:**

- ▪ **R-Branch: $\Delta J = +1$**
- ▪ **P-Branch: $\Delta J = -1$**
- ▪ **Q-Branch: $\Delta J = 0$**

Electronic transition (UV/optical)

Excited electronic state.

dissociation energy

Ground state

Energy

Vibrational transition (infrared)

Rotational transition (sub-mm)

Internuclear separation

Rotation-vibration Spectra

Reduced distance (band head)

R-Zweig ΔJ = +1

$\tilde{\nu}_0$

Band Origin (zero lines) No Q branch

ΔJ = −1

Increased distance

Line Strength

Three important factors define the properties of an absorption line

- **Spectral position:** ν_0 ⟵ **Given by the energy levels**
- **Strength: S**
- **Shape:** $f(\nu - \nu_0)$

Lines are not sharp

The line strength (or intensity) is determined by <u>occupation of the initial state</u> and <u>transition probability</u> (given by Einstein coefficients).

In the case of a vibration-rotation band we define a band strength

Absorption cross section:

$$\sigma(\nu) = S(\nu_0)f(\nu - \nu_0)$$

Populations of Levels

❑ **Line strength of a individual transition depends on population of lowest level for each vibration/rotation level**

❑ **Electronic levels have a large energy difference, nearly all molecules are in 'ground' state**

❑ **Population of the rotational-vibrational levels is governed by the Boltzmann distribution -> T-dependence**

❑ **For rotational levels we have the complication that each level is 'degenerated'. For each rotational number *J* there are *(2J+1)* levels.**
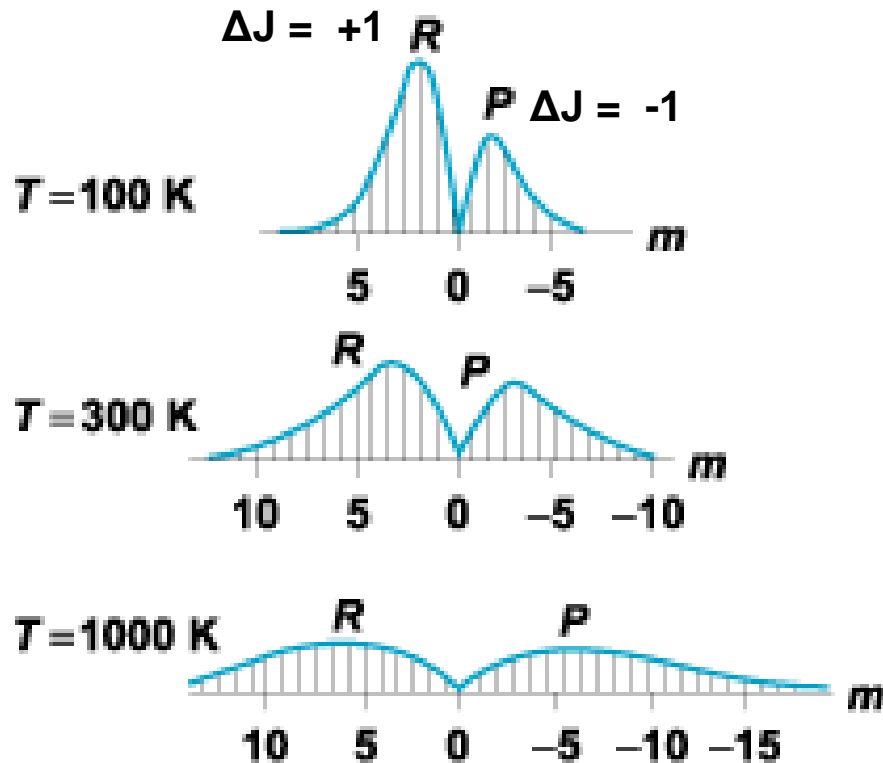
$$N(J) \propto (2J+1)\exp-\frac{E(J)}{k_B T}$$
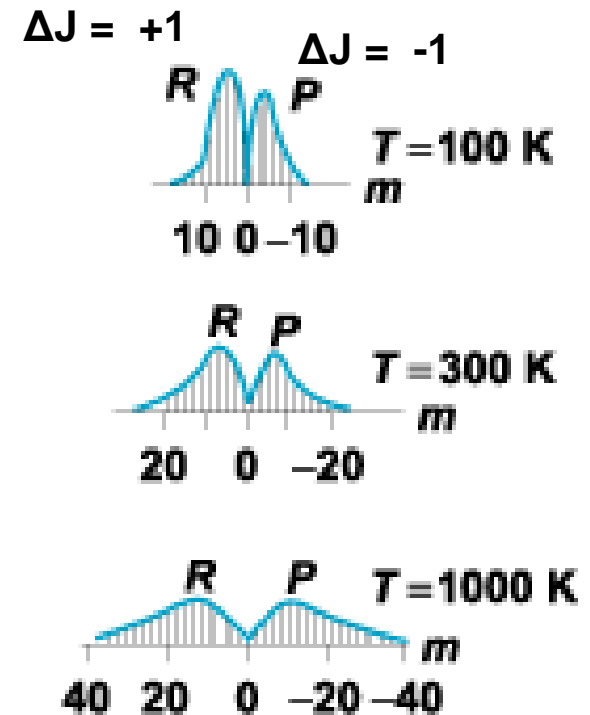
Statistical weight

Boltzmann factor

2 competing effects !
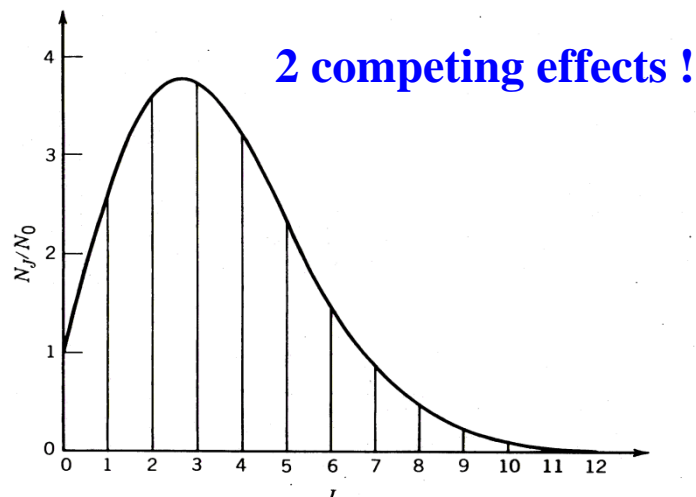
Intensity distribution for a diatomic absorption band

(a) HCl

(b) CO

Broadening

❑ **Several processes lead to a spectral broadening of the originally monochromatic, i.e. energetically sharp transition.**

❑ **Natural broadening:**

  ▪ **Intrinsic level of uncertainty associated with any energy level of the molecule**

  ▪ **Simple estimate:**

$$\Delta E \Delta t \leq h / 2\pi \qquad \text{Uncertainty relation}$$

$$\Delta E = h\Delta v \qquad \text{Photon energy}$$

$$\Rightarrow \qquad \Delta v \leq 1 / 2\pi\Delta t$$

Typical life time $\Delta t \sim 10^{-8}$ s $\quad \Delta v \sim 1.6 \times 10^7 \, s^{-1}$

For $\lambda = 500$ nm $\qquad \Delta\lambda = \dfrac{\lambda^2}{c} \, \Delta v \sim 1.3 \times 10^{-14} m = 0.013 \, pm$

Doppler Broadening

❑ **Frequency at which absorptions take place are shifted as a consequence of the motions of the molecules (Doppler effect)**

❑ **Frequency shift is proportional to molecular velocity v:**

$$\Delta \upsilon = \pm \frac{v}{c} \upsilon_0$$

❑ **Molecular velocity v is given by Maxwell distribution**

$$p(v) \sim \exp\{-mv^2 / 2kT\}$$

❑ **Lineshape is given by integral over distribution of frequency shifts:**

Gaussian Distribution $f(v - v_0) = \dfrac{1}{\alpha\sqrt{\pi}} \exp\left\{-\dfrac{(\upsilon - \upsilon_0)^2}{\alpha^2}\right\}$

with $\alpha = \upsilon_0 \sqrt{\dfrac{2kT}{mc^2}}$

and $FWHM = 2\sqrt{\ln 2}\,\alpha$

For O_2 at T~300 K and 765 nm:

α = 0.017cm^{-1} and FWHM ~ 0.03 cm^{-1} or 1.68 pm

Doppler broadening increases with increasing frequency

Pressure Broadening

❑ **Collisions between molecules will reduce the lifetime of an excited state and thus produce a broadening of the absorption line**

❑ **Pressure broadening is described by Lorentz model:**

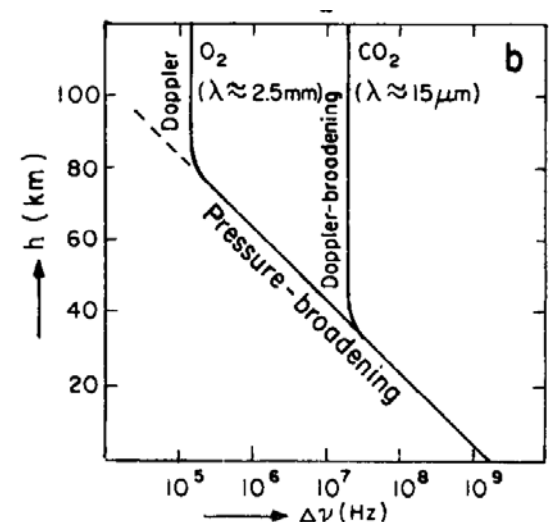$$f(\nu - \nu_0) = \frac{\alpha/\pi}{(\nu - \nu_0)^2 + \alpha^2}$$

❑ **α is HWHM of Lorentz line and is ~1/t with time between collision t (which depends on p and T):**

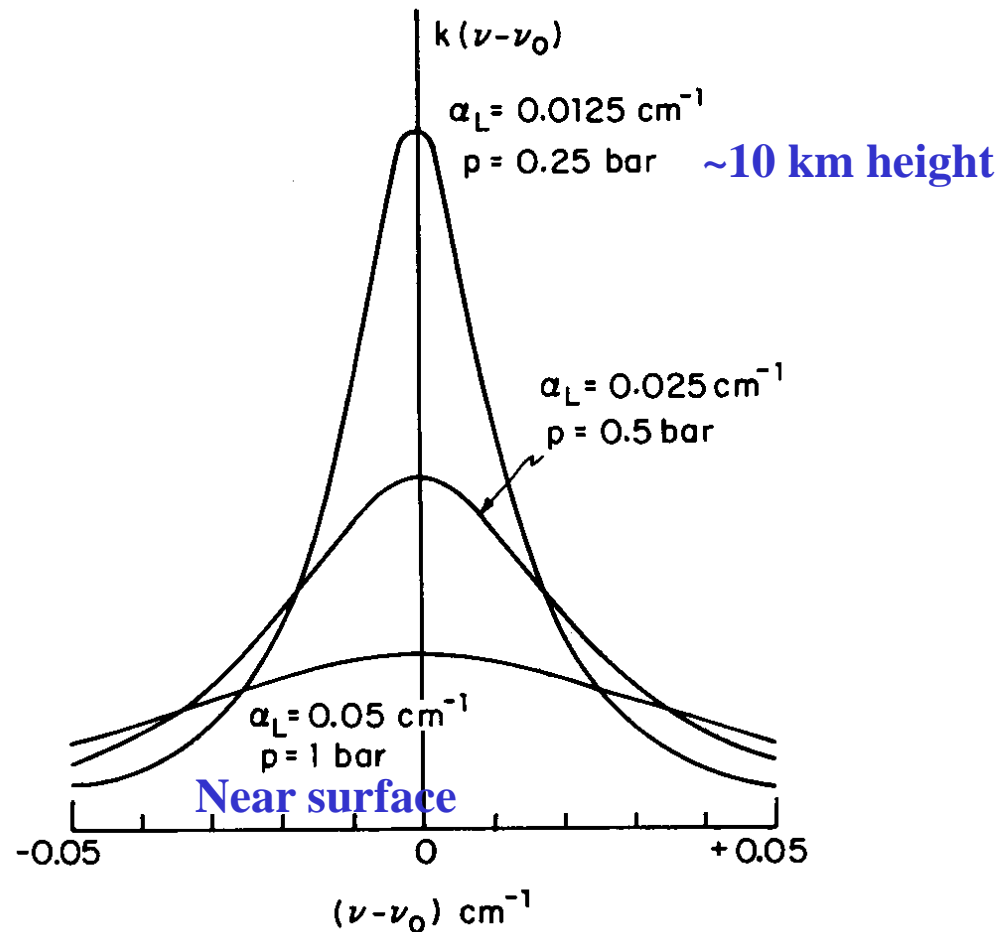$$\alpha = \alpha_0 \left(\frac{p}{p_0}\right)\left(\frac{T_0}{T}\right)^{1/2}$$

$\alpha_0 \sim 0.07$ cm^{-1} For air and normal conditions (1 atmosphere, 296 K)

Compare: Doppler HWHM ~ 0.015 cm^{-1}

❑ **Usually pressure broadening is the dominant broadening mechanism**

# Lorentz line shape profiles for different pressures

The proportionality of the line width on pressure is fundamental and has profound effect on lineshape

Voigt Profile

❑ **Under the assumption that Doppler and pressure broadening occur independently, they form the *Voigt* profile, given by the convolution of both profiles**

$$f(\nu - \nu_0) = \int\limits_{-\infty}^{\infty} f_G(x)\, f_L(\nu - \nu_0 - x)\, dx$$

❑ **In the line wings the Voigt profile has a Lorentz shape. At the line centre or core, it has a Doppler behaviour**
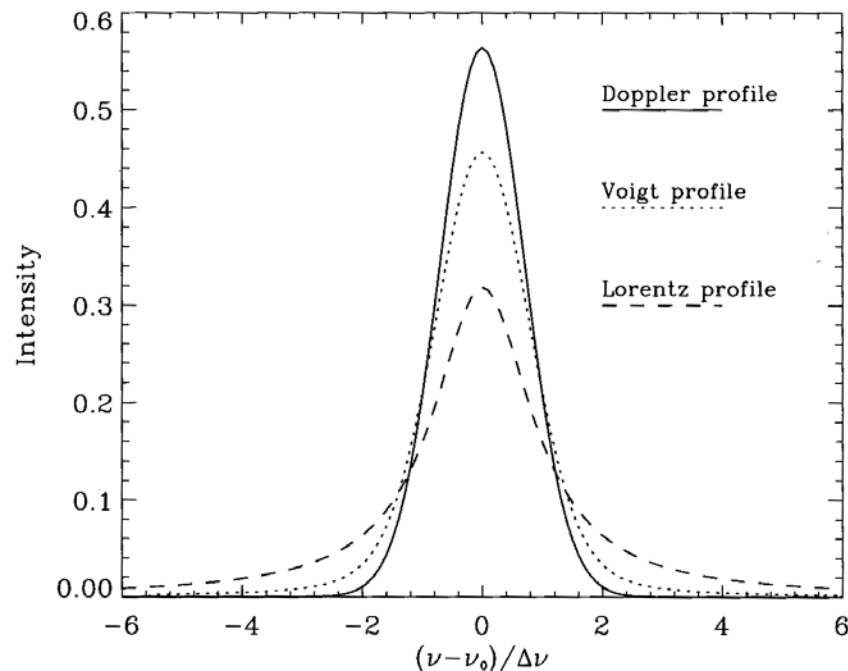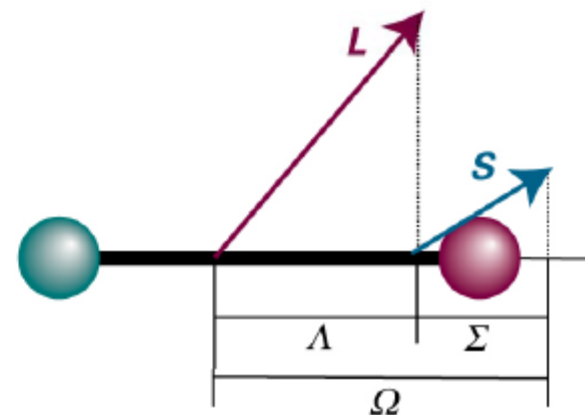
Molecular term symbols

Electronic terms are classified according to their overall angular momentum on the internuclear axis, Λ:

$$\Lambda = \sum_i \lambda_i = \lambda_1 + \lambda_2 + \lambda_3 + \dots$$

By analogy with atoms we use term symbols:

"Spin multiplicity"= $2S+1$

(S is the total spin quantum number for the molecule)

$$^2\Pi^{+/-}_{3/2}$$

Gives Λ, according to:

Σ for $\Lambda = 0$

Π for $\Lambda = \pm 1$

Δ for $\Lambda = \pm 2$

Spin-orbit levels
$$\Omega = |\Lambda + \Sigma|$$

Projection of S on internuclear axis

Also, denoted it symmetry (+/-) with respect to reflection in a plane containing internuclear axis

For homonuclear diatomics also symmetry (u/g) of orbitals is given

Example: O$_2$

Electronic transition	Vibrational transition	Band center [nm]	Band strength [cm/molec]	Name
$B^3\Sigma_g^- \leftarrow X^3\Sigma_g^-$	-	UV 175.9	-	Schumann-Runge
$A^3\Sigma_g^+ \leftarrow X^3\Sigma_g^-$	-	UV 242-286	-	Herzberg I
$b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$	$(0 \leftarrow 0)$	762.19	2.24E-22	$A - band$
$b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$	$(1 \leftarrow 0)$	688.47	1.49E-23	$B - band$
$b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$	$(2 \leftarrow 0)$	628.85	4.63E-25	$\gamma - band$
$b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$	$(1 \leftarrow 1)$	771.07	9.53E-26	
$b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$	$(0 \leftarrow 1)$	864.75	7.88E-27	
$a^1\Delta_g \leftarrow X^3\Sigma_g^-$	$(0 \leftarrow 0)$	1268.6	3.68E-24	
$a^1\Delta_g \leftarrow X^3\Sigma_g^-$	$(1 \leftarrow 0)$	1067.7	9.53E-27	
$a^1\Delta_g \leftarrow X^3\Sigma_g^-$	$(0 \leftarrow 1)$	1580.8	2.75E-28	
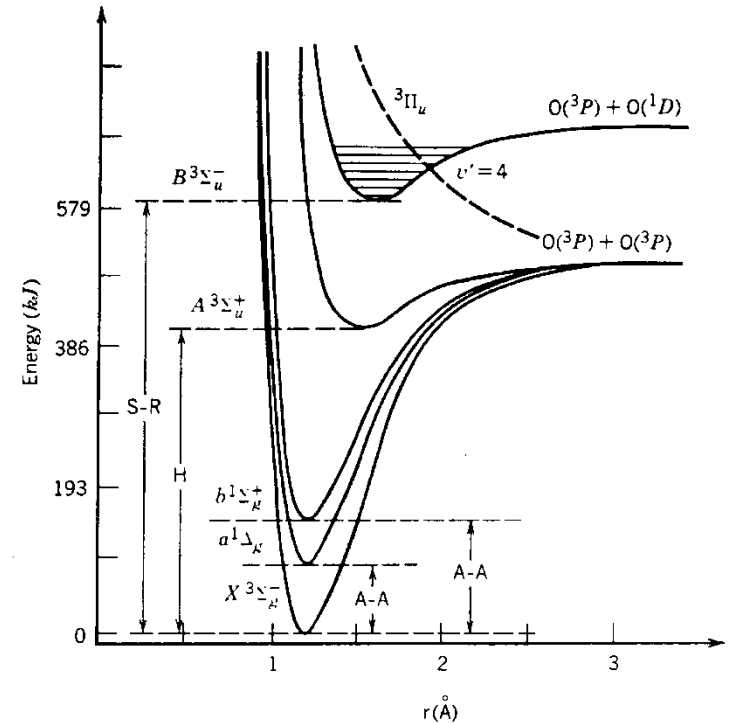
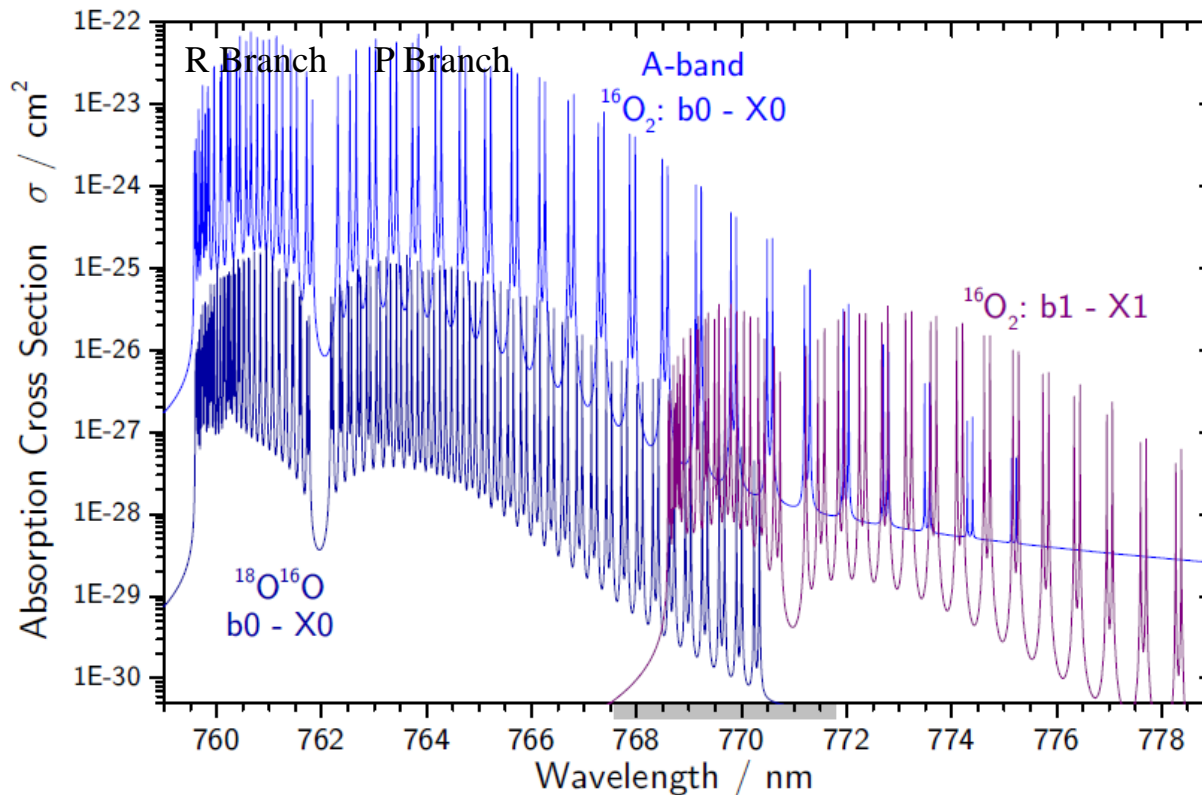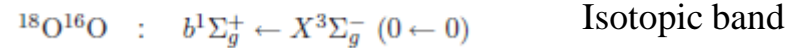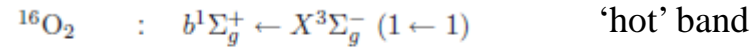

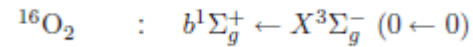**O$_2$ has no permanent electric dipole moment**

Vibrations are optically inactive

Transitions are electric dipole-forbidden by symmetry selection rules

Transitions are magnetic dipole (and electric quadruple) transitions

O$_2$ A Band

O$_2$ A Band consists of 3 transitions:

$^{16}O_2$: $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ $(0 \leftarrow 0)$

$^{16}O_2$: $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ $(1 \leftarrow 1)$ 'hot' band

$^{18}O^{16}O$: $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ $(0 \leftarrow 0)$ Isotopic band

Summary

Absorption and emissions is driven by vibrational, rotational and electronic transitions governed by QM

Certain molecules absorb because of the existence of a permanent dipole (e.g H_2O) or an induced dipole(CH_4, CO_2)-the latter have no pure rotational spectra

Line strength (or intensity) is determined by occupation of the initial state and transition probability

Lines are broadened by Doppler and pressure broadening

Spectroscopy is rather complicated !