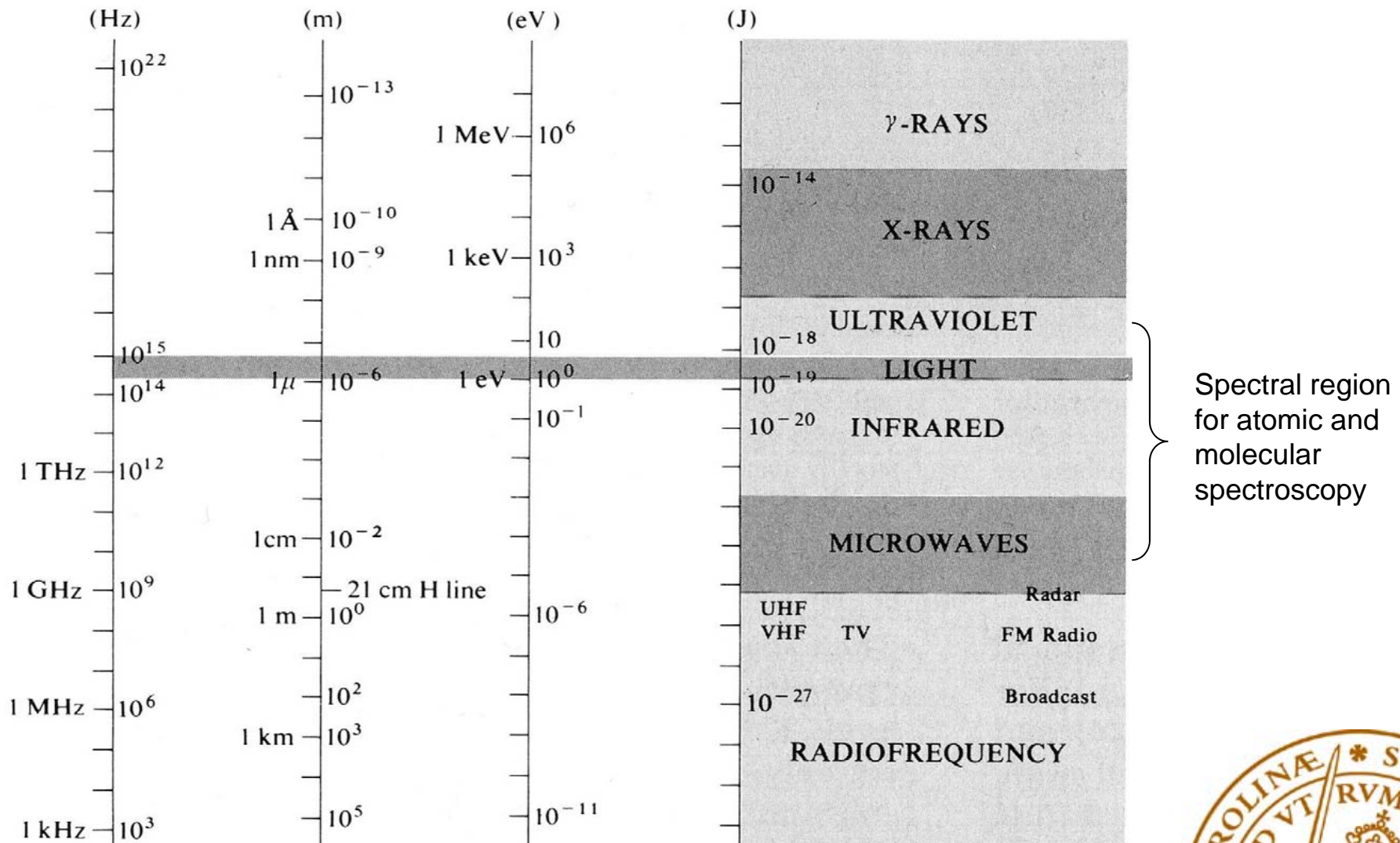


2. Molecular structure/Basic spectroscopy



The electromagnetic spectrum



*E. Hecht (2nd Ed.) Optics,
Addison-Wesley Publishing
Company, 1987*



Per-Erik Bengtsson

Spectral regions

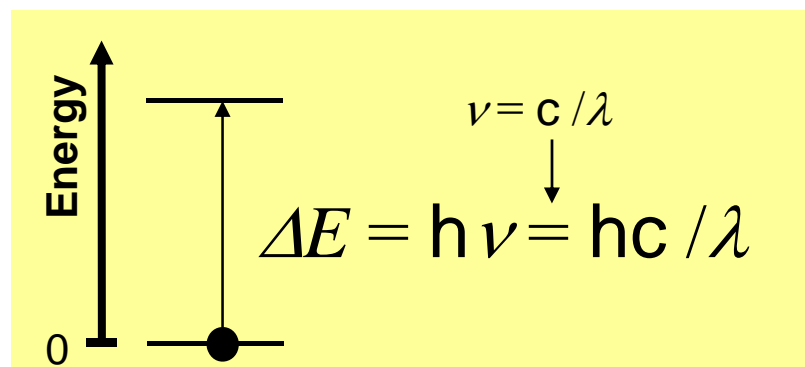
Molecular spectroscopy often deals with radiation in the ultraviolet (UV), visible, and infrared (IR) spectral regions.

- The visible region is from 400 nm – 700 nm
- The ultraviolet region is below 400 nm
- The infrared region is above 700 nm.



Spectroscopy: That part of science which uses emission and/or absorption of radiation to deduce atomic/molecular properties

Some basics about spectroscopy



ΔE = Energy difference

h = Planck's constant, 6.63×10^{-34} Js

ν = Frequency

c = Velocity of light, 3.0×10^8 m/s

λ = Wavelength

Often the wave number, σ , is used to express energy. The unit is cm^{-1} .

$$\sigma = \Delta E / hc = 1/\lambda.$$

Example

The energy difference between two states in the OH-molecule is 35714 cm^{-1} . Which wavelength is needed to excite the molecule?

Answer

$$\sigma = 1/\lambda = 35714 \text{ cm}^{-1} \Rightarrow \lambda = 1/\sigma = 280 \text{ nm}.$$

Other ways of expressing this energy:

$$\Delta E = hc/\lambda = 6.5 \times 10^{-19} \text{ J}$$

$$\Delta E / h = c/\lambda = 9.7 \times 10^{14} \text{ Hz}$$



Species in combustion

Combustion involves a large number of species

Atoms

oxygen (O), hydrogen (H), etc.

formed by dissociation at high temperatures

Diatomic molecules

nitrogen (N₂), oxygen (O₂)

carbon monoxide (CO), hydrogen (H₂)

nitric oxide (NO), hydroxyl (OH), CH, etc.

Tri-atomic molecules

water (H₂O), carbon dioxide (CO₂), etc.

Molecules with more than three atoms

fuel molecules such as methane, ethene, etc.

also molecules formed in rich flames



Quantum mechanics

According to quantum mechanics all energy levels in atoms and molecules are discrete and are given by the solution to the Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \psi = E \psi$$

Ψ = wavefunction

$\hbar = h/2\pi$ (h = Plancks constant)

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{reduced mass}$$

E = energy levels

V = potential energy

Since the selections rules only permit certain transitions a spectrum can be very precisely calculated



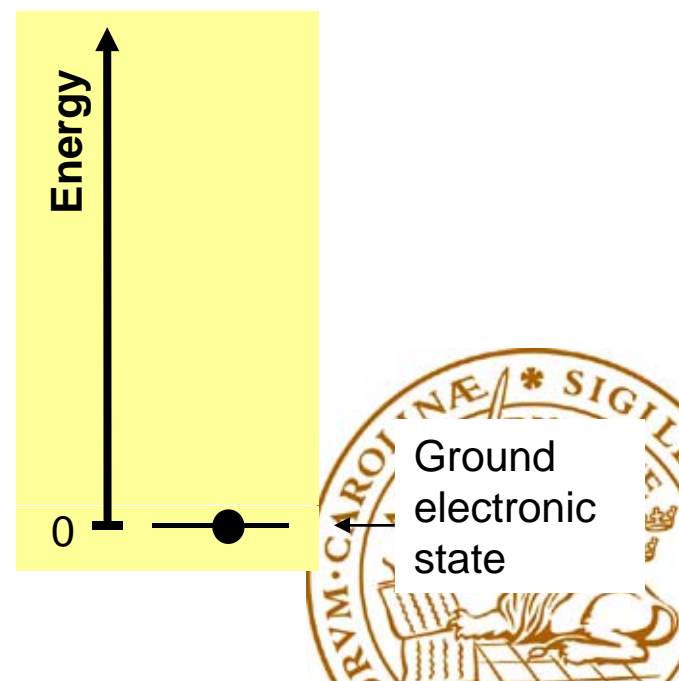
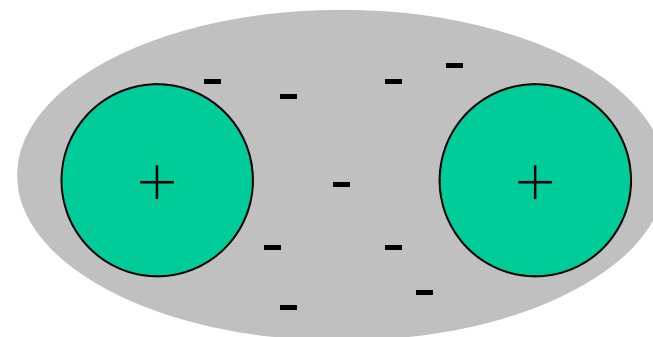
Diatomic molecules: Structure

A diatomic molecule consists of two nuclei and an electron cloud.

The positive nuclei repel each other.

The negative electrons attract the positive nuclei and prevent them from separation.

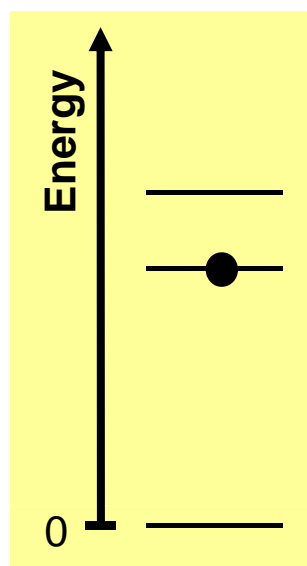
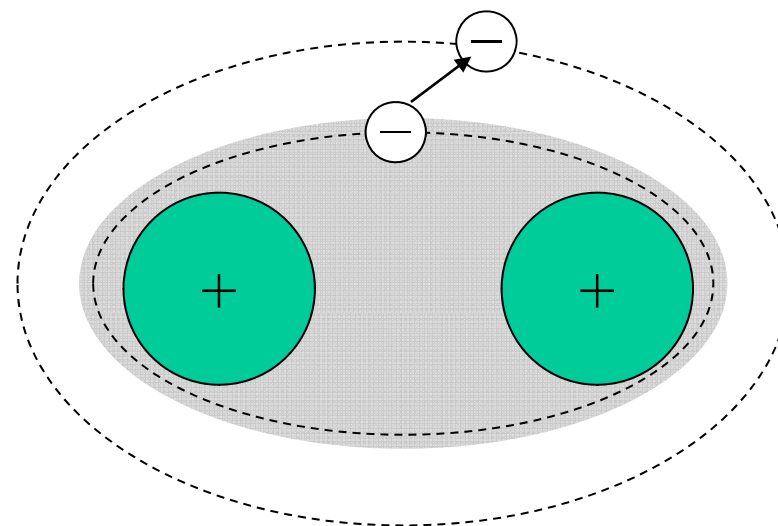
When all electrons have their lowest possible energies, the molecule is in its **ground electronic state**.



Diatomic molecules: electronic states

We observe an outer loosely bound electron.

By the addition of energy, it can be moved to another "orbit" at higher energy, and the molecule end up in an excited electronic state.



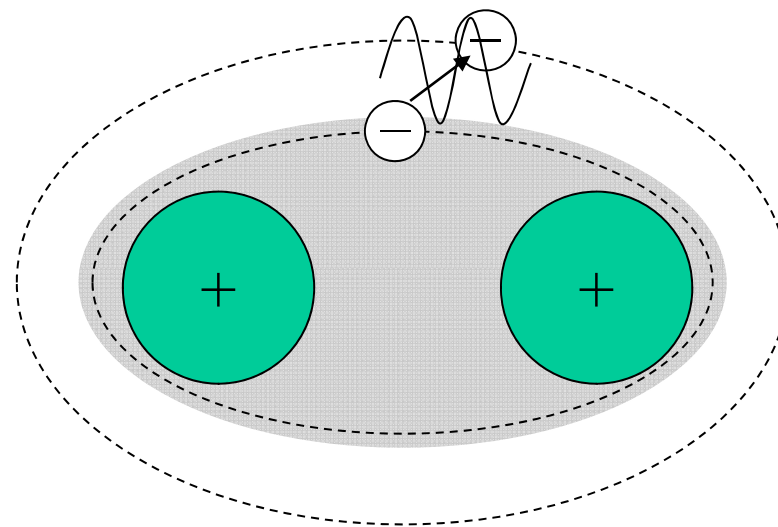
Different electronically excited states

Ground electronic state

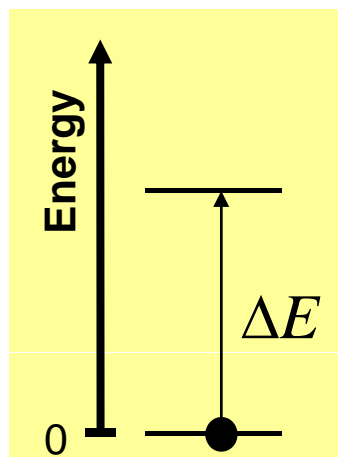


Absorption

For many molecules of interest in combustion, absorption of radiation in the ultraviolet and visible spectral region can lead to electronic excitation of a molecule.



This absorption process can be represented in an energy level diagram:



The energy levels are discrete, and the energy difference can be used to calculate the exact wavelength of the radiation needed for absorption:
$$\Delta E = hc/\lambda$$



Diatomic molecules: Structure

The electronic states of molecules are in analogy with electronic states of atoms.

In addition molecules can vibrate and rotate. In the Born-Oppenheimer approximation these motions are initially treated separately:

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

To more easily describe vibrational and rotational energies, a simpler model for the molecule will be used.

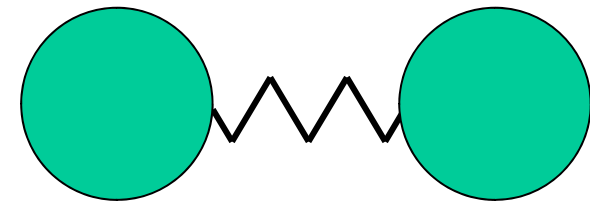
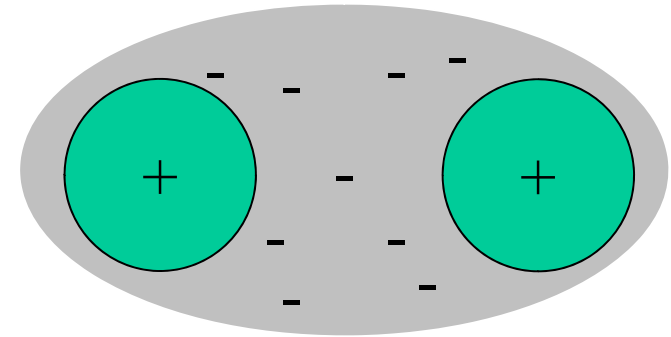
Consider the diatomic molecule as two atoms joined by a string.

Time scales:

Electronic interaction $\sim 10^{-15} \text{s}$

Vibrations $\sim 10^{-14} \text{s}$

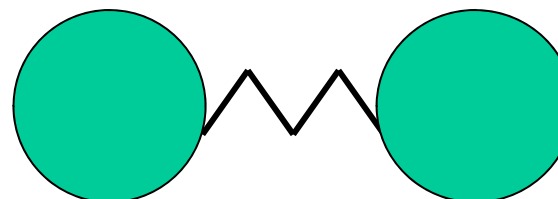
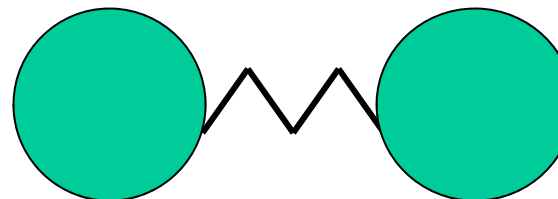
Rotations $\sim 10^{-13} - 10^{-12} \text{s}$



Diatomic molecules: vibrations

Molecules can also vibrate at different frequencies.

But only specific discrete vibrational frequencies occur, corresponding to specific energies.

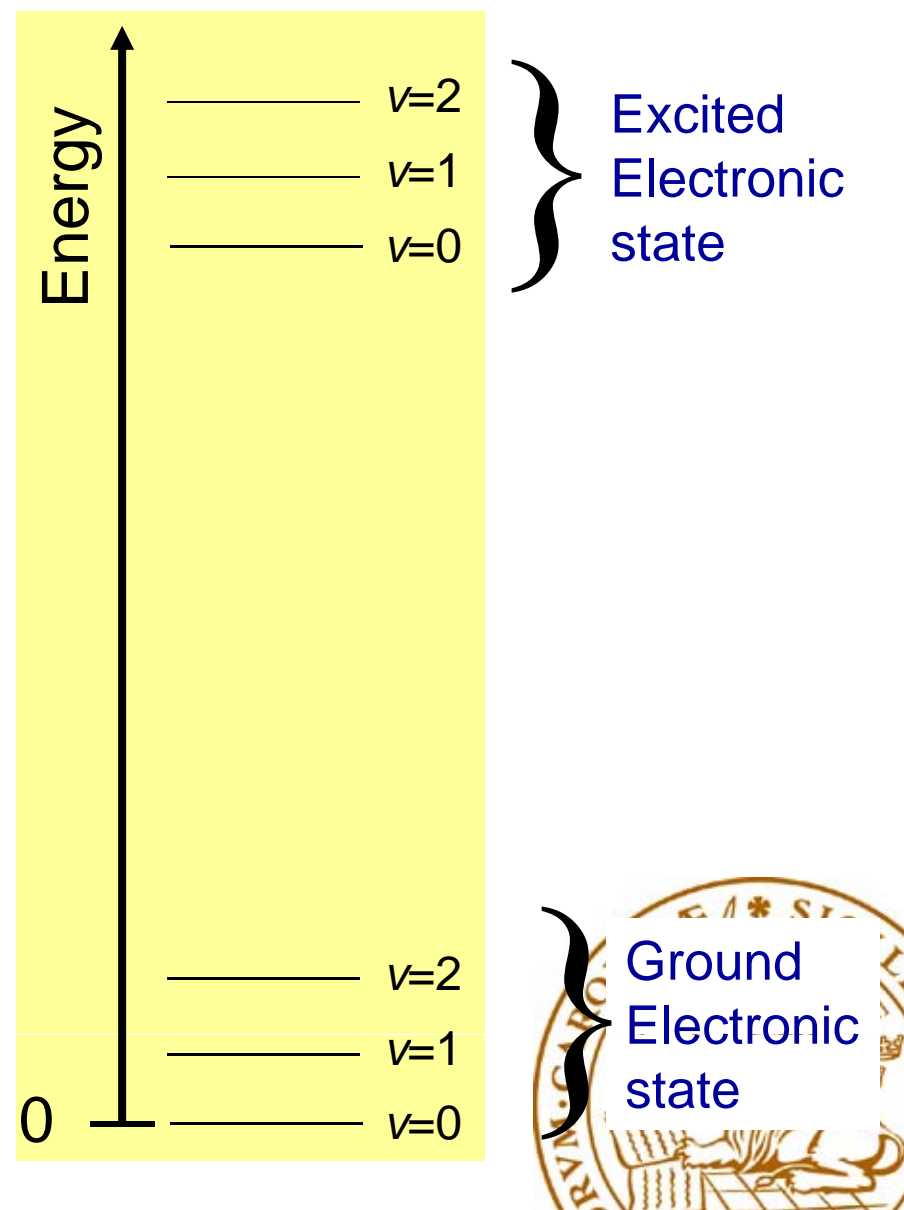


Vibrational energy levels

The vibrational energy states give a fine structure to the electronic states.

$v=0$ is the lowest vibrational frequency, then higher v numbers correspond to higher vibrational frequencies.

While the separation between electronic energy states is around 20000 cm^{-1} , the separation between vibrational energy states is on the order of 2000 cm^{-1} .

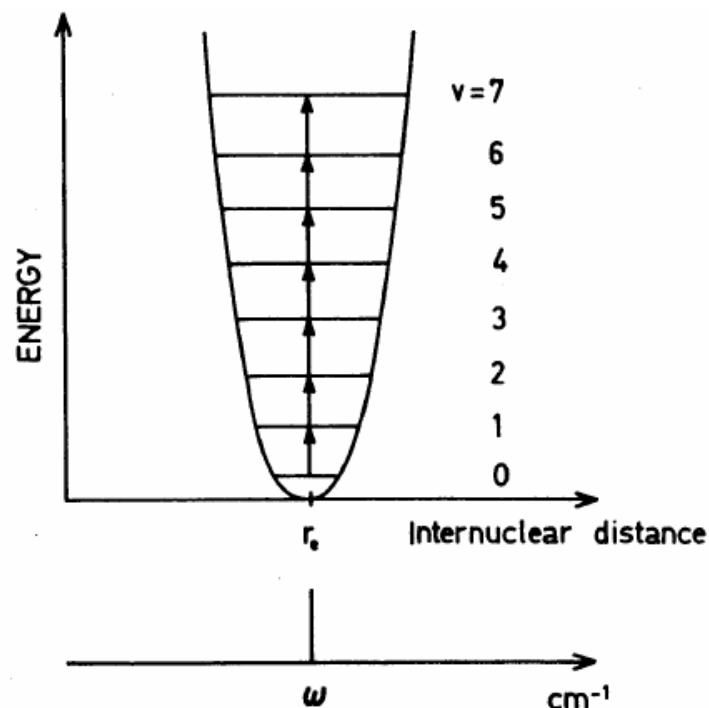


Vibrational energy levels

Solutions to Schrödinger equation for harmonic oscillator with $V(r) = \frac{1}{2} k (r_e - r)^2$ give

$$E_v/hc = G_v = \omega(v + 1/2) \quad [\text{cm}^{-1}] \quad G_0 = 1/2 \omega, \quad G_1 = 3/2 \omega, \quad G_2 = 5/2 \omega$$

$$\Delta v = \pm 1 \rightarrow \sigma = G(v') - G(v'') = \omega(v + 1 + 1/2) - \omega(v + 1/2) = \omega$$



v' - corresponds to levels in the excited state

v'' - corresponds to levels in the ground state

Vibrational energy levels

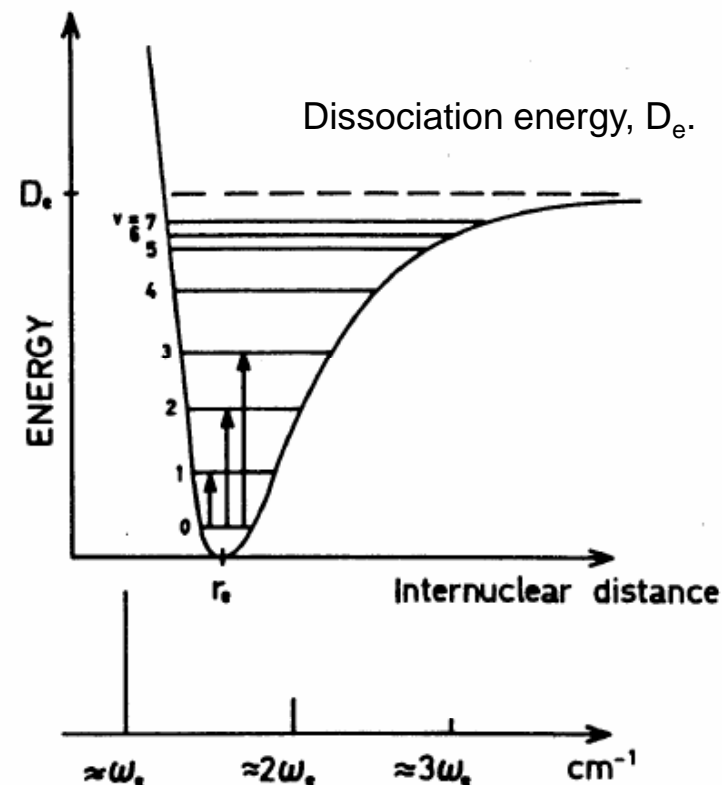
A better description of the energy is given by the Morse function:

$$V = D_{eq.} [1 - \exp \{a(r_{eq.} - r)\}]^2$$

where a is a constant for a particular molecule. Energy corrections can now be introduced.

$$G_v = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 \quad [\text{cm}^{-1}]$$

$$\Delta v = \pm 1, \pm 2,$$



Vibrational population

The transition from $v=0$ to $v=1$ then occurs at;

$$G(v=1) - G(v=0) = \omega_e(1+1/2) - \omega_e x_e(1+1/2)^2 - \left\{ \omega_e \cdot 1/2 - \omega_e x_e(1/2)^2 \right\} = \omega_e(1 - 2x_e) \text{ cm}^{-1}$$

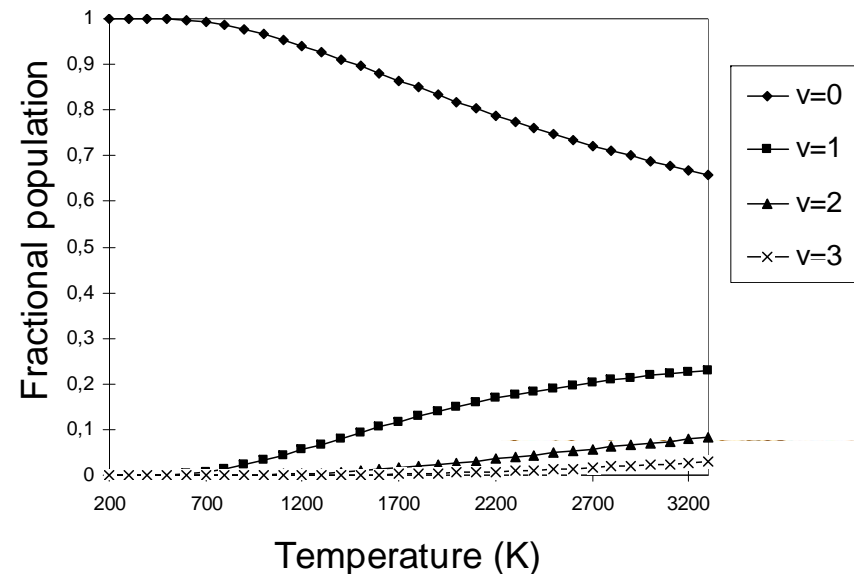
Whereas the transition from $v=1$ to $v=2$ (hot band) occurs at

$$G(v=2) - G(v=1) = \omega_e(1 - 4X_e) \text{ cm}^{-1}$$

Population N_v ;

$$N_v \sim \exp[-G(v)/kT]$$

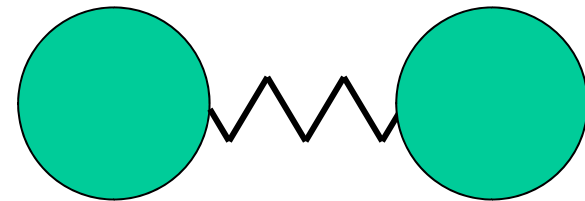
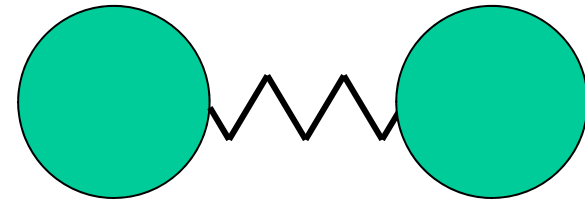
Population distribution of N_2



Diatomic molecules: rotations

Molecules can also rotate at different frequencies.

But only specific discrete rotational frequencies occur, corresponding to specific energies.

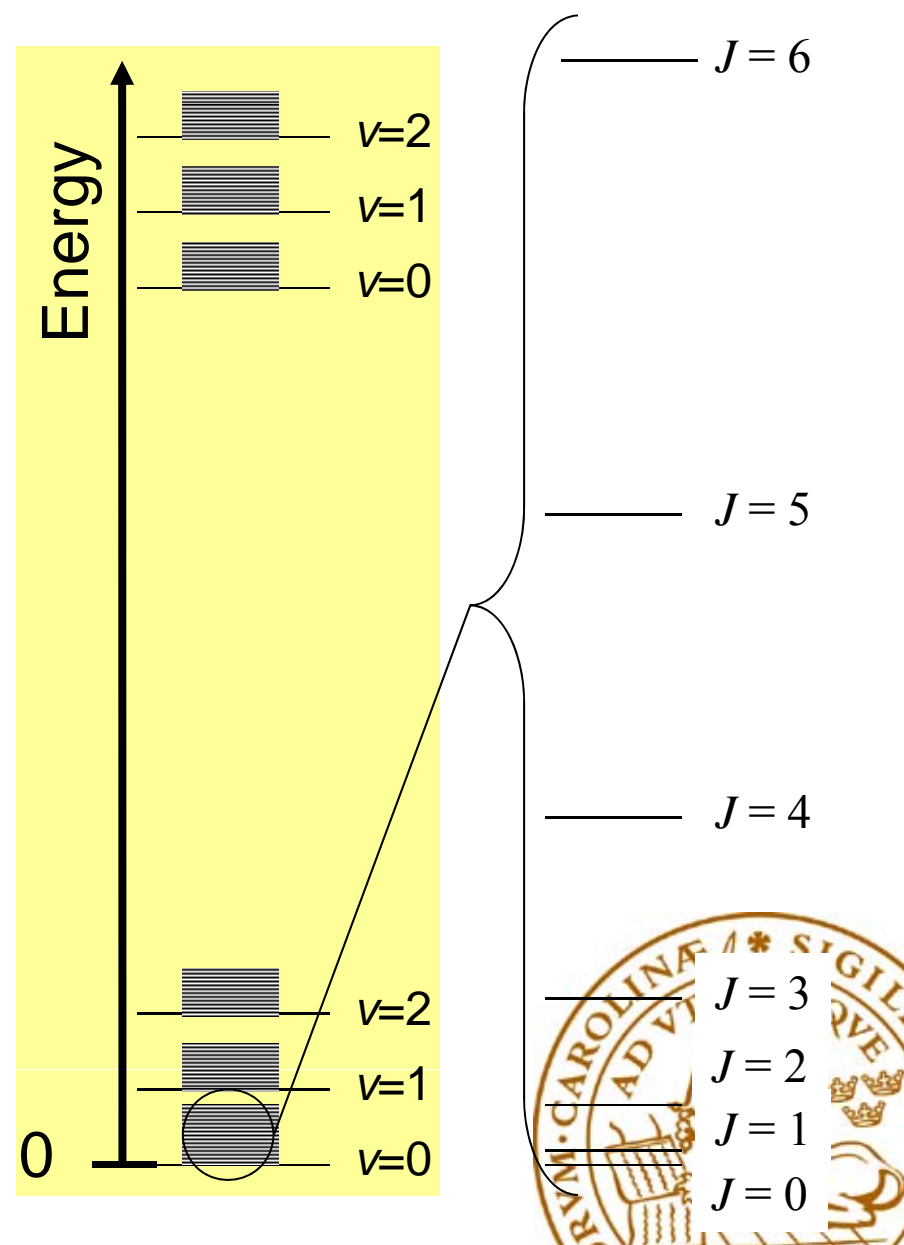


Rotational energy levels

The rotational energy states give a fine structure to the vibrational states.

$J=0$ is the lowest rotational energy state, then higher J numbers correspond to higher rotational states.

While the separation between vibrational energy states is around 2000 cm^{-1} , the separation between rotational energy states is on the order of a few to hundreds of cm^{-1} .



Energy levels for rigid rotator

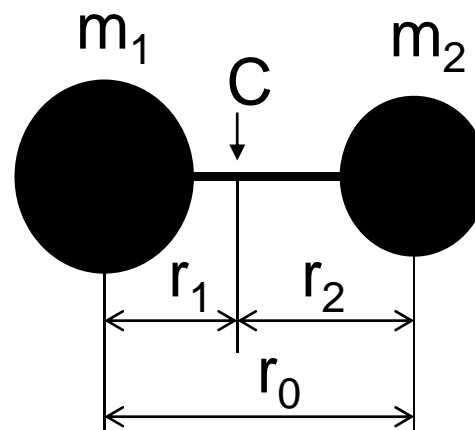
Solutions to Schrödinger equation
with $V(r) = 0$, gives

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$I = \mu r_0^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

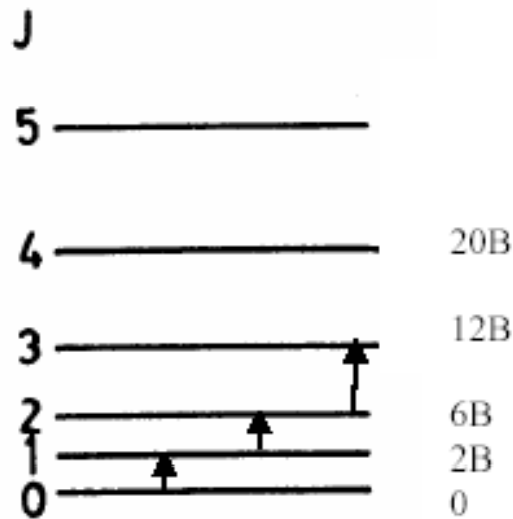
$$F_J = \frac{E_r}{hc} = \frac{h}{8\pi^2 c I} J(J+1) = B J(J+1) \quad [\text{cm}^{-1}]$$



Rotational transitions

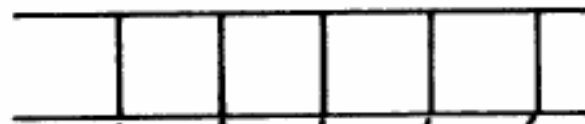
$$\Delta F = F(J') - F(J'') = B J'(J'+1) - B J''(J''+1)$$

$$\Delta J = \pm 1 \rightarrow \Delta F = 2BJ$$



J' - corresponds to levels in the excited state

J'' - corresponds to levels in the ground state



Spectrum

0 2B 4B 6B 8B 10B



Rotational population distribution

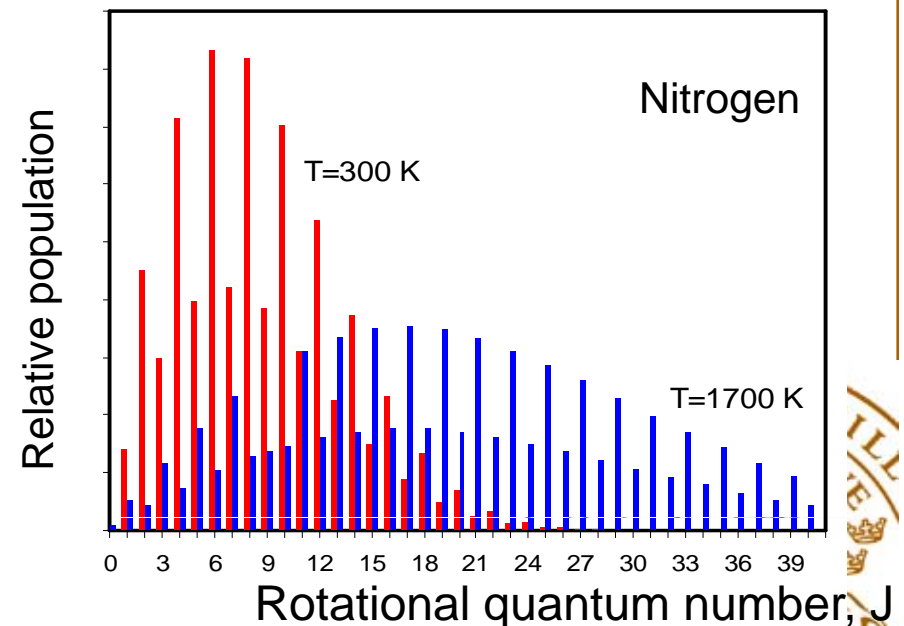
The rotational population distribution can be calculated as

$$N \propto (2J + 1) e^{-BJ(J+1)hc/kT}$$

If $f(J) = (2J + 1) e^{-BJ(J+1)hc/kT}$

then $\frac{\partial f(J)}{\partial T} = 0$

gives $J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$



A coupling rotation-vibration

Total energy $T_{v,j}$ given by:

$$T_{v,J} = G(v) + F(J) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + BJ(J + 1)$$

A transition from v' to v'' occurs at:

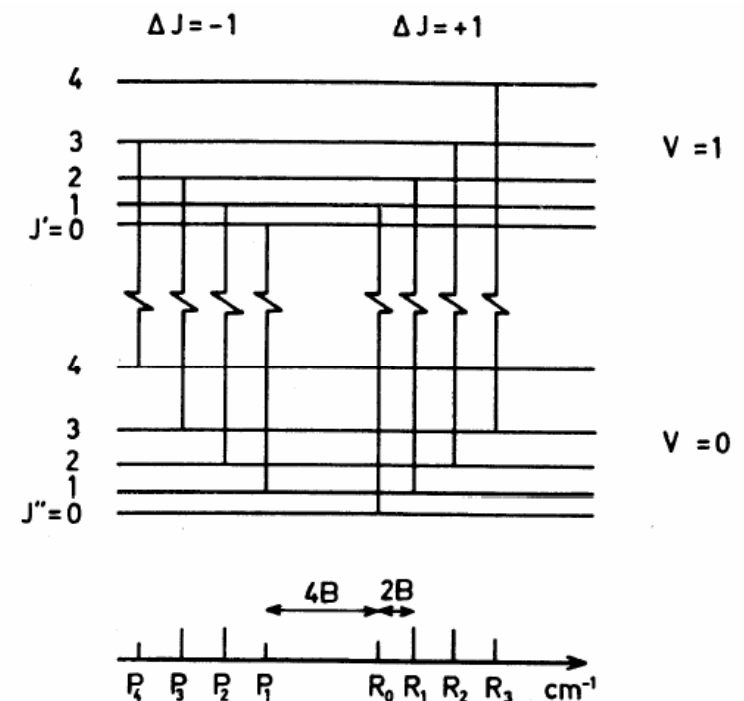
$$\sigma = \sigma_0 + BJ'(J'+1) - BJ''(J''+1)$$

$$\sigma_0 = G(v') - G(v'') = \omega_e(1 - 2x_e)$$

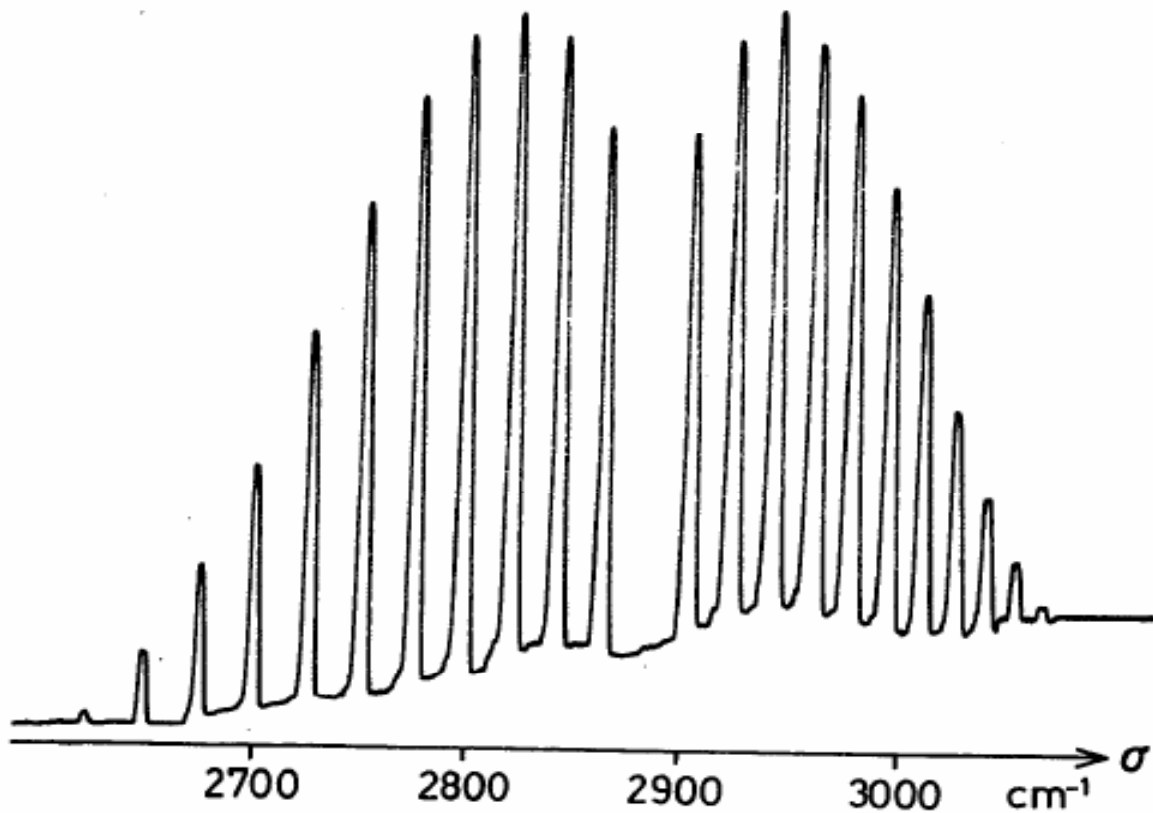
Consider two cases:

a) $\Delta J = +1, \sigma = \sigma_0 + 2B(J''+1) \quad J'' = 0, 1, 2,$

b) $\Delta J = -1, \sigma = \sigma_0 - 2BJ'' \quad J'' = 1, 2$



A coupling rotation-vibration: Example HCl absorption

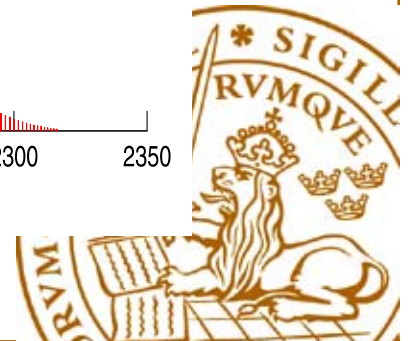
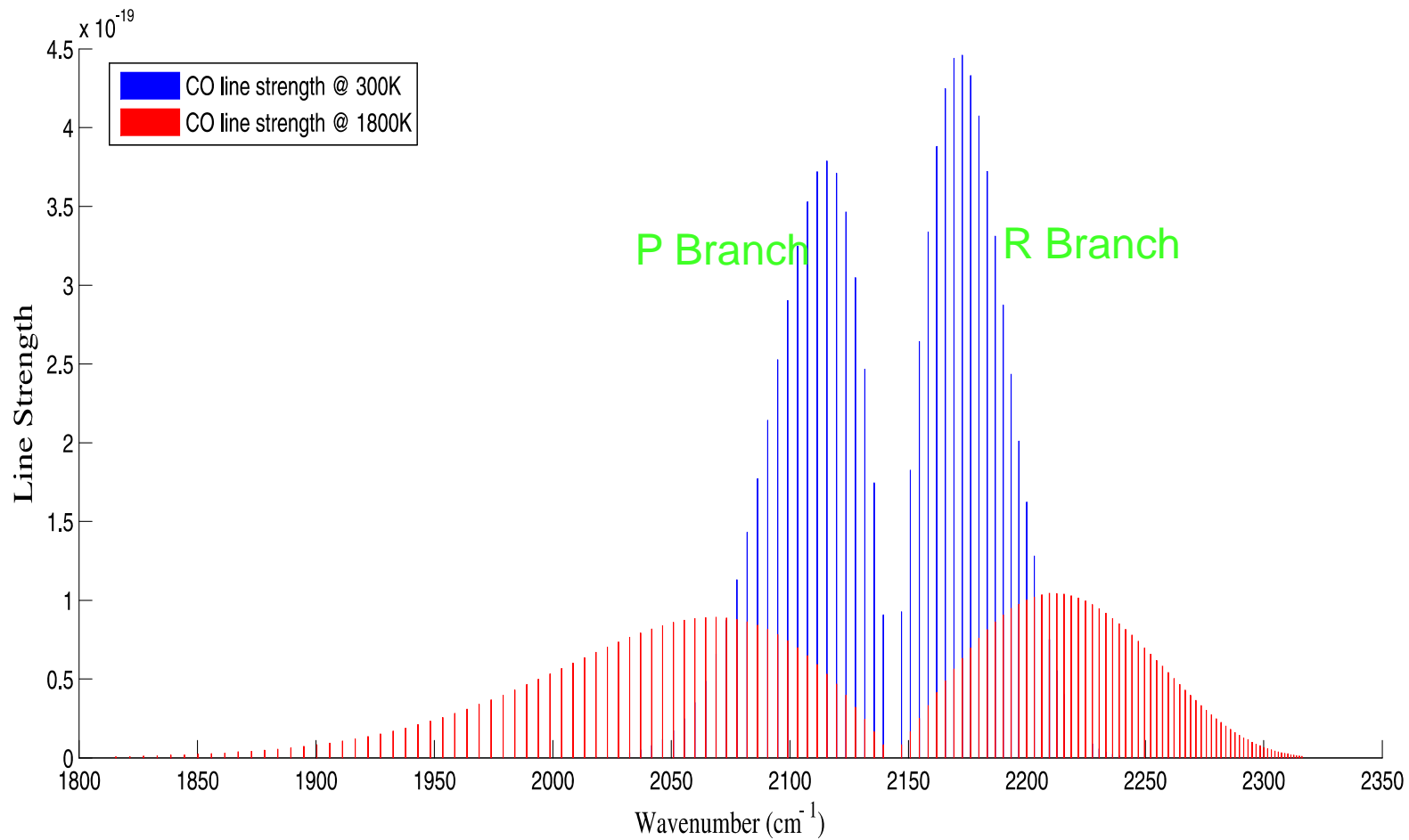


HITRAN

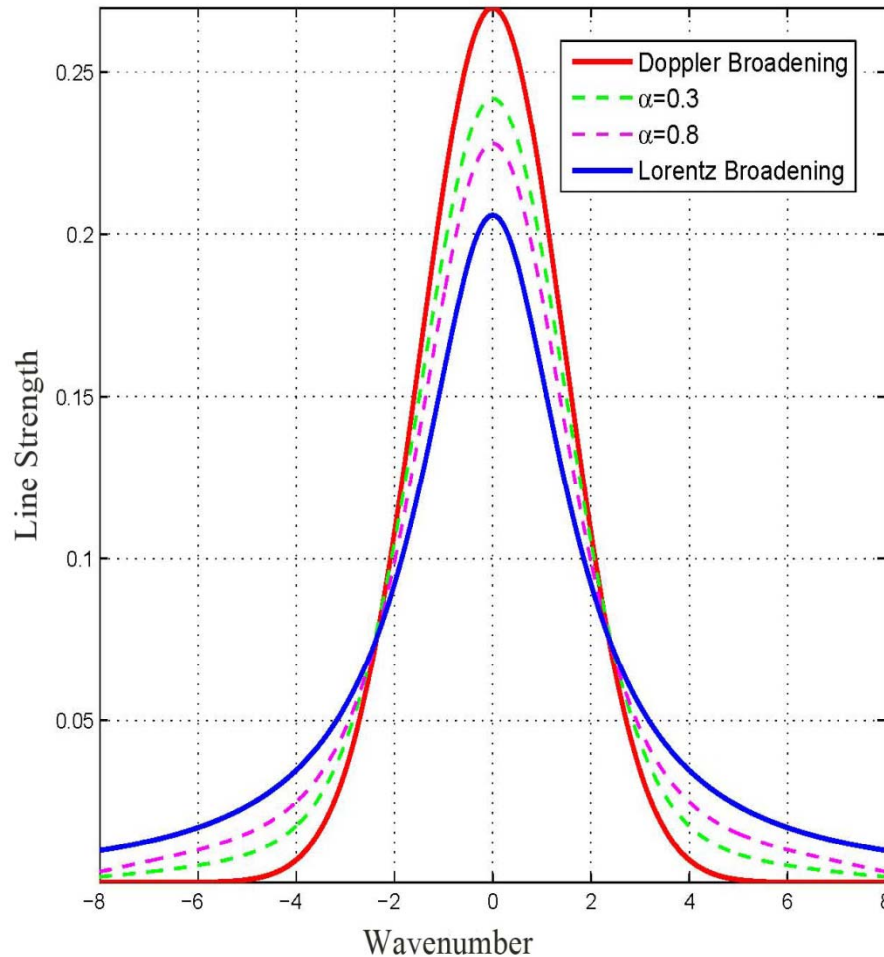
HITRAN is an acronym for **high-resolution transmission molecular ABSORPTION**, which is a database using spectroscopic parameters to predict and simulate the absorption spectra of different molecules



Example: The CO vibrational band (0-1)



Different broadening mechanisms: Collisional broadening and Doppler broadening



Lorentz profile:

$$g_L(\eta) = \frac{1}{\pi} \frac{b_L}{(\eta - \eta_0)^2 + b_L^2}$$

Doppler profile:

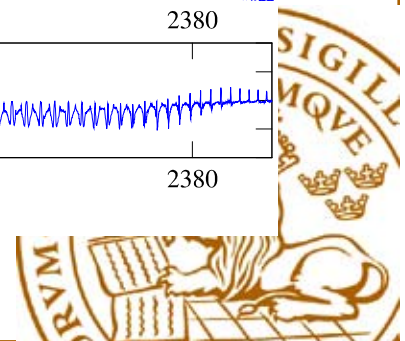
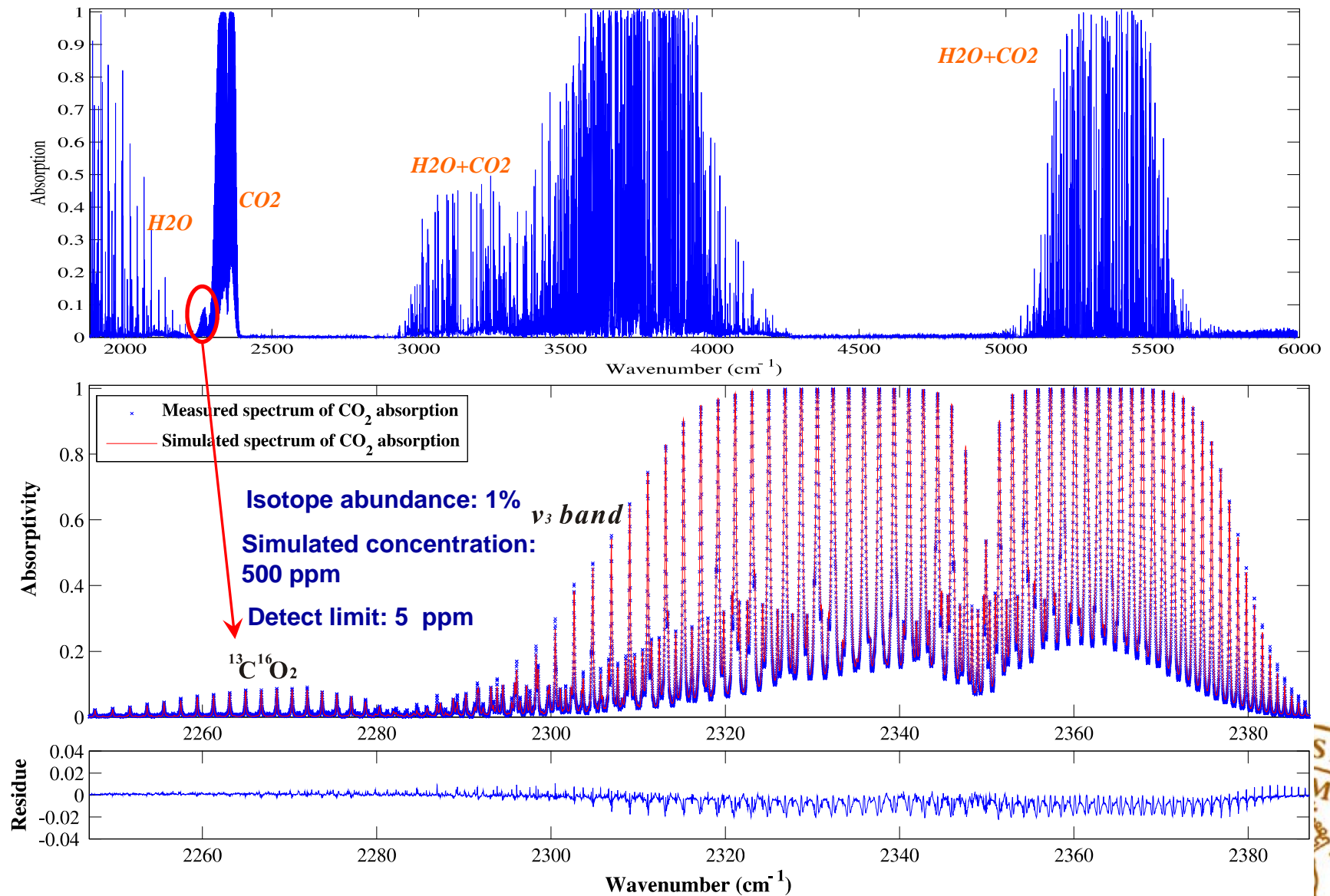
$$g_D(\eta) = \sqrt{\frac{\ln 2}{\pi}} \frac{\exp(-(\ln 2) \left(\frac{\eta - \eta_0}{b_D}\right)^2)}{b_D}$$

Voigt profile—convolution of Doppler and Lorentzian line shape function:

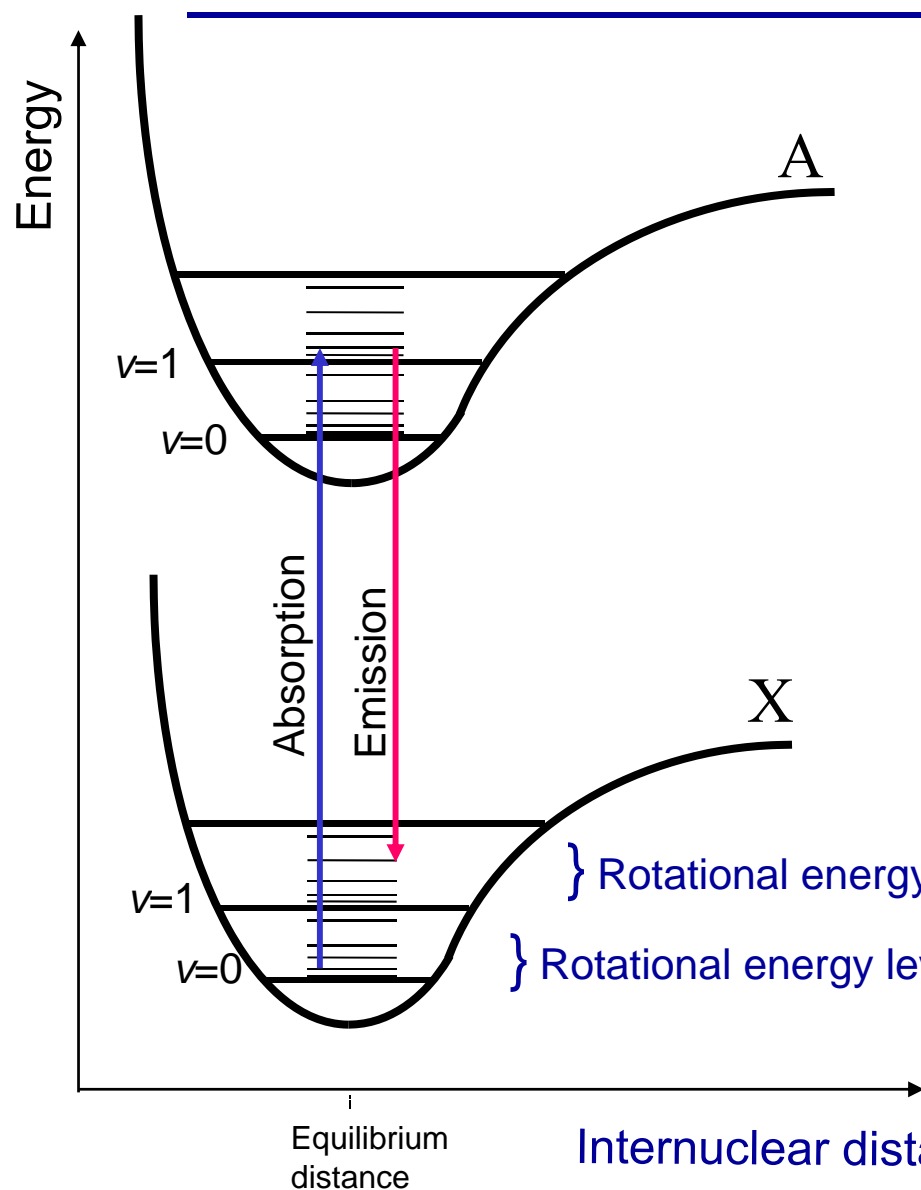
$$g_V(\eta) = \int_{-\infty}^{+\infty} g_D(\eta') g_L(\eta - \eta') d\eta'$$



Absorption simulation



Transitions between electronic states



Absorption and emission spectra are species specific

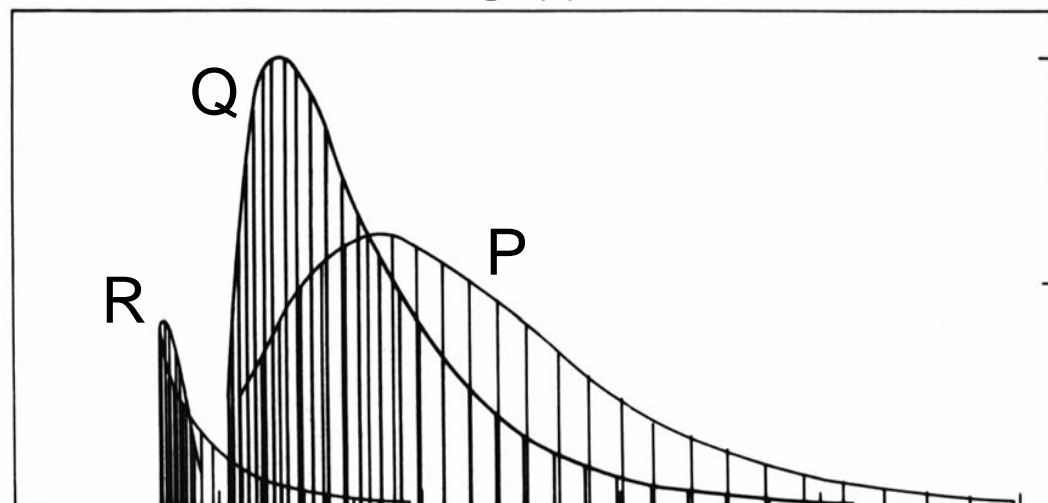
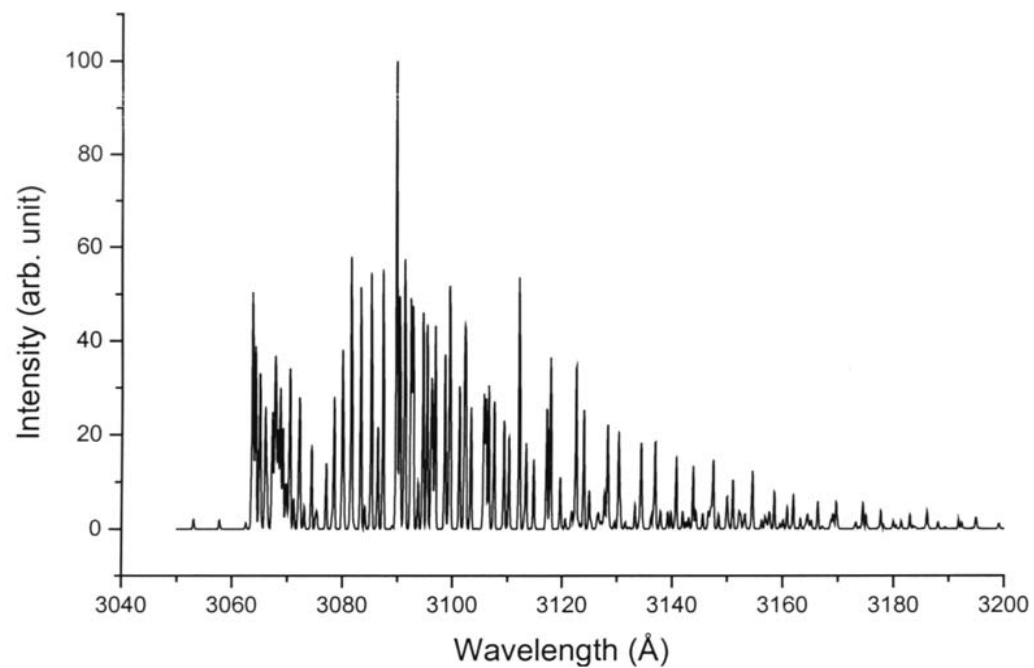
The energy difference (and thereby the wavelength) can be calculated using molecular parameters for the involved electronic states.

} Rotational energy levels in the first excited vibrational state.

} Rotational energy levels in the ground vibrational state.



Molecular structure - OH

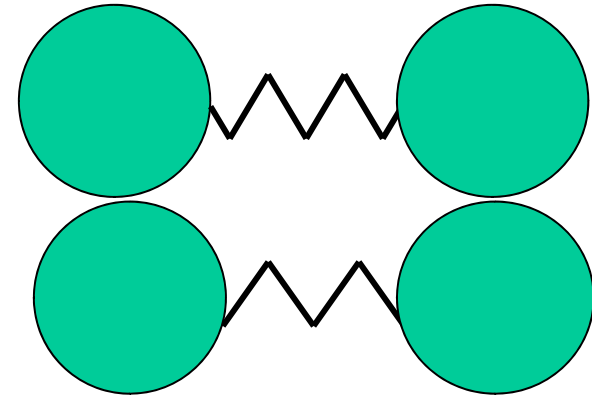


Summary 1: Temperature effects

At low temperature (room- T)

Molecules generally

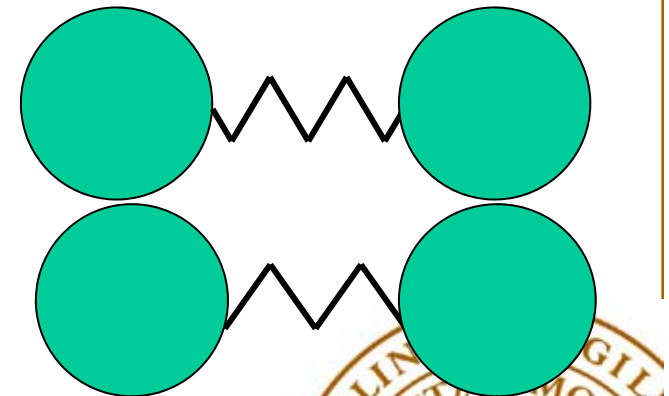
- rotate at lower frequencies.
- vibrate at lower frequencies



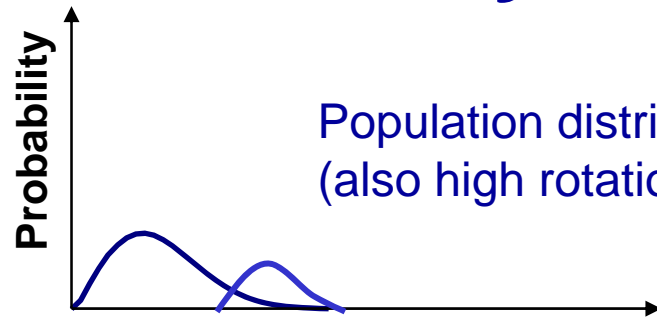
At high temperature (flame- T)

Molecules generally

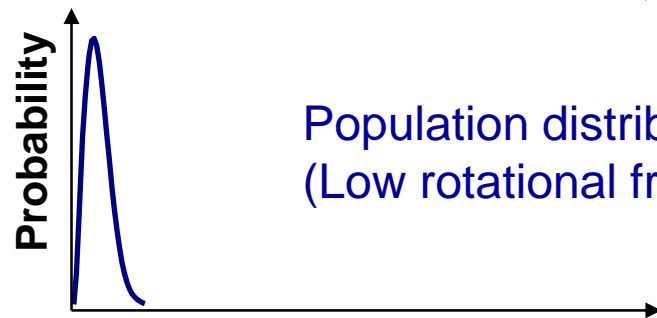
- rotate at higher frequencies.
- vibrate at higher frequencies



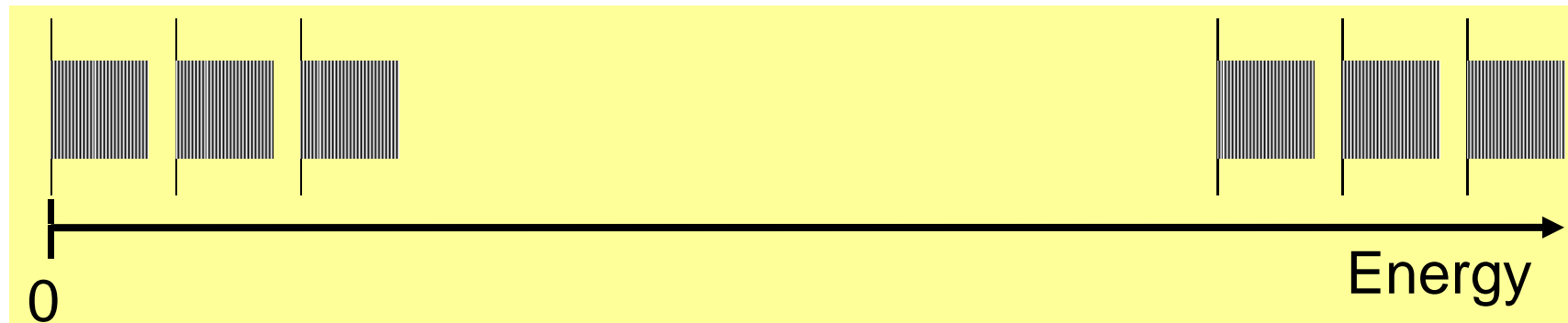
Summary 2: Temperature effects



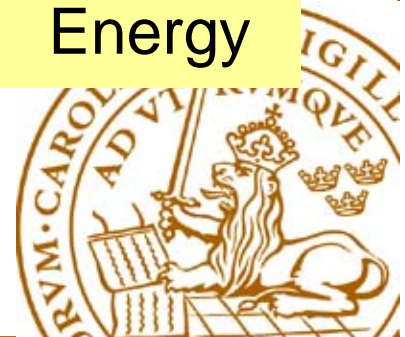
Population distribution over energy states at **flame temperature**,
(also high rotational frequencies, not only lowest vibrational frequency)



Population distribution over energy states at **room temperature**,
(Low rotational frequencies, lowest vibrational frequency)



The population distribution is often what is probed
when temperatures are measured



Summary: Molecular physics

Each molecule is at a certain time in a specific rotational state, J , in a specific vibrational energy level, v , and in a specific electronic energy level.

There is a high probability that a molecule changes state as a result of a molecular collision. However, the population distribution over all possible states is the same at a constant temperature (because of the large number of molecules).

To excite an atom or a diatomic molecule a laser must be tuned to an exact wavelength for the excitation.

A larger molecule, such as a 3-pentanone or acetone, has many more close-lying states. To excite such a molecule, any wavelength within a range can be used for the excitation.



Summary

- Molecules have different energies; rotational energies, vibrational energies, and electronic energies.
- Information about the energy levels for molecules is used to interpret spectroscopic information from laser-based techniques and other optical techniques.
- Absorption and laser-induced fluorescence are techniques for which we need to know at which wavelength a certain species can be excited.
- Temperatures can be measured by probing the population distribution over different energy levels, for example in Raman and CARS techniques.

