# Molecular spectroscopy

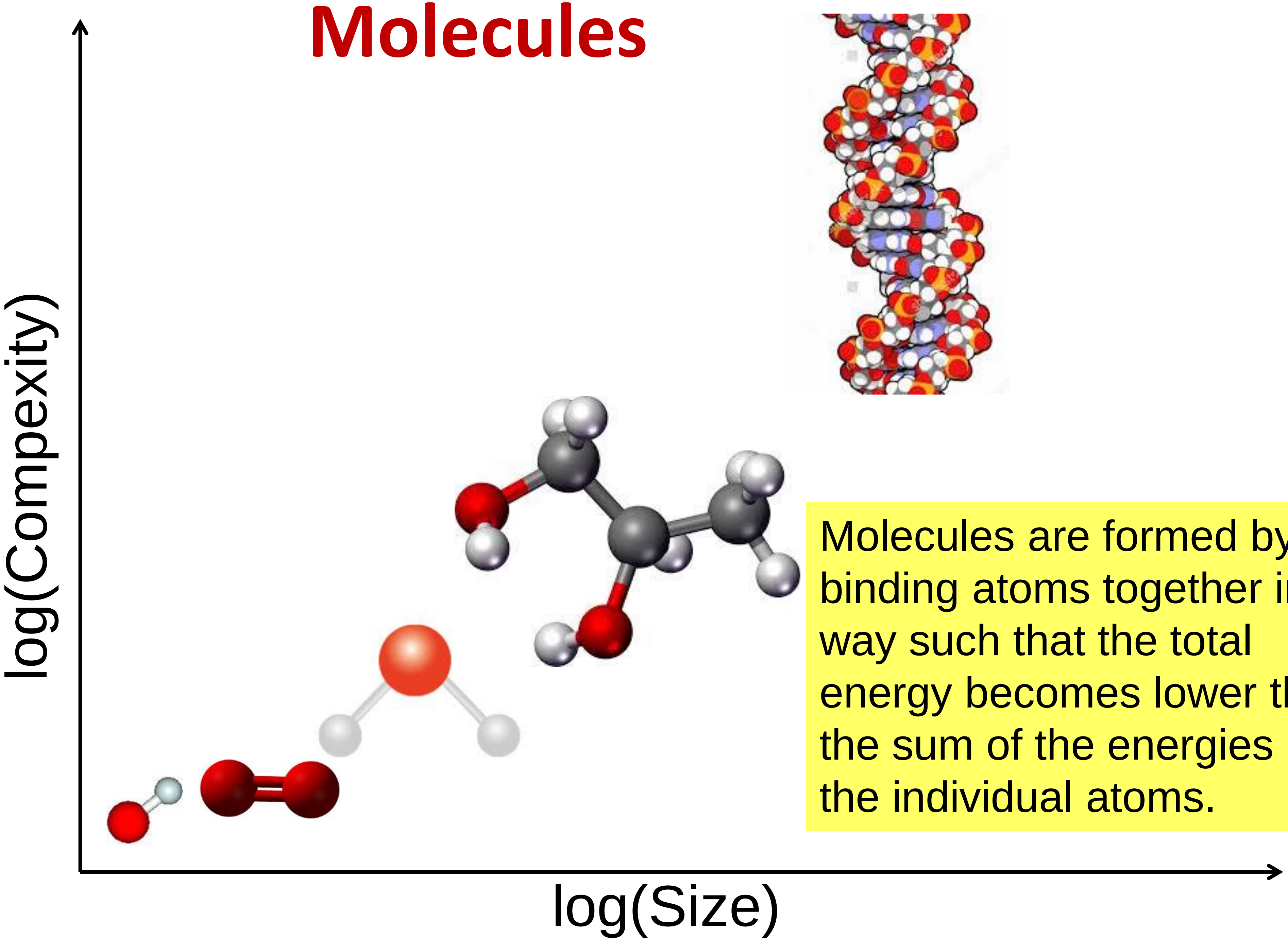
## Multispectral imaging (FAFF 020, FYST29)
## fall 2017

Lecture prepared by Joakim Bood
joakim.bood@forbrf.lth.se

# Outline

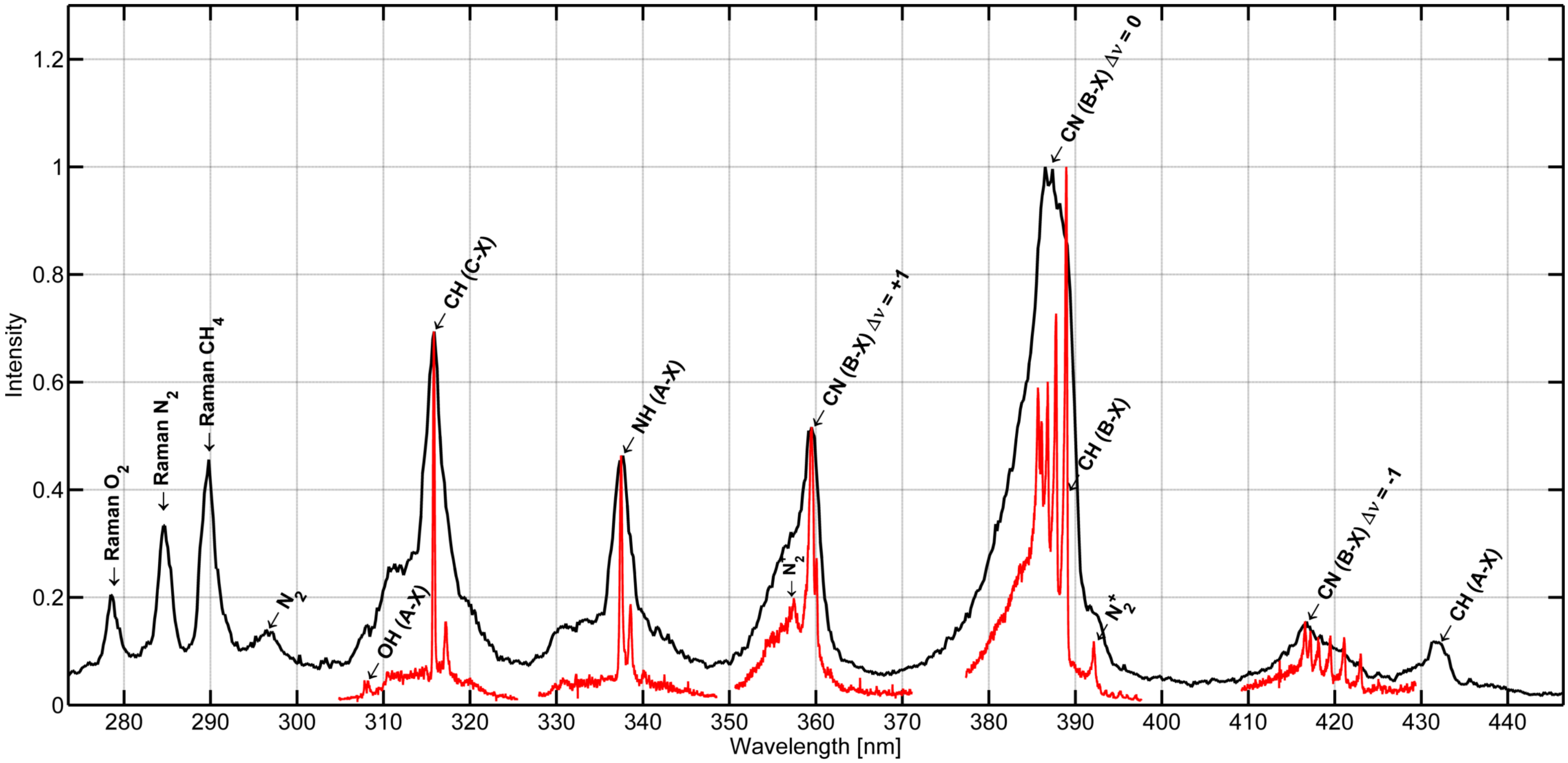
- **Molecular structure**
  - Electronic structure
  - Rotational structure
  - Vibrational structure
- **Molecular transitions**
  - Rotational transitions (pure rotational)
  - Rovibrational transitions (rotation + vibration)
  - Rovibronic transitions (rotation + vibration + electronic)
- **Population distributions**

# Molecules



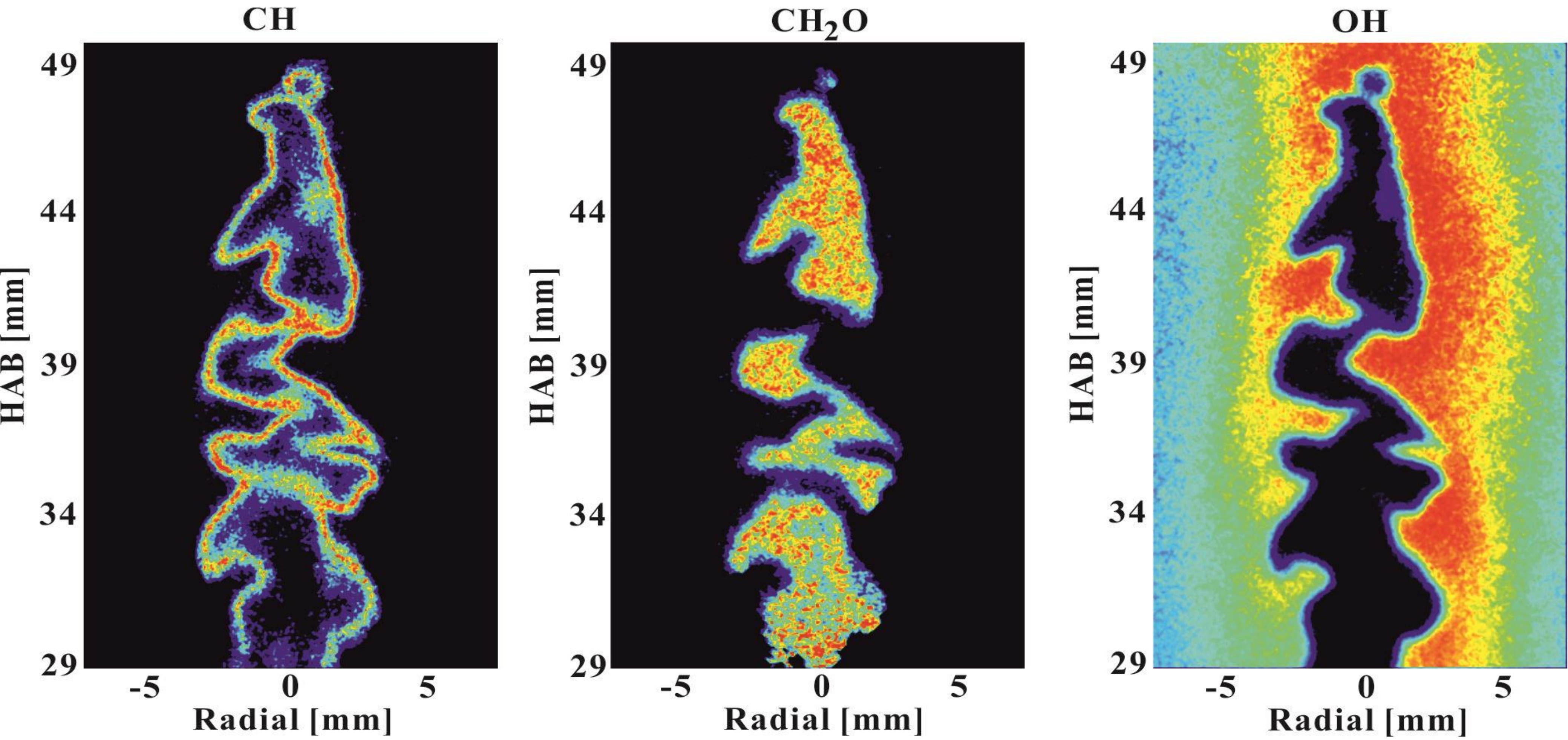
Molecules are formed by binding atoms together in a way such that the total energy becomes lower than the sum of the energies of the individual atoms.

# Example of a molecular spectrum



M. Jonsson, J. Borggren, M. Aldén, J. Bood, Appl. Phys. B **120**, 587-599 (2015)

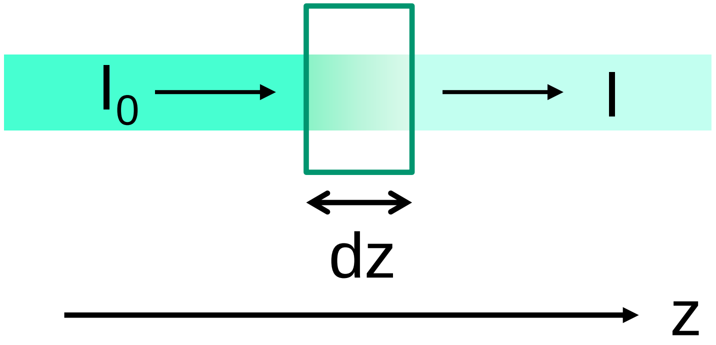
# Multispectral imaging of species distributions in turbulent flames

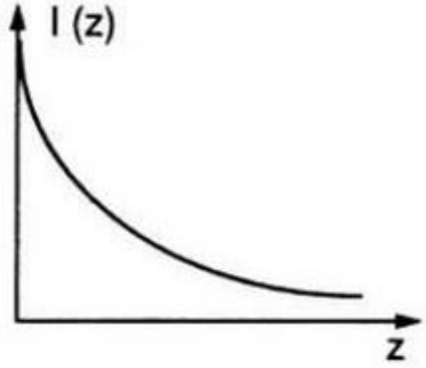


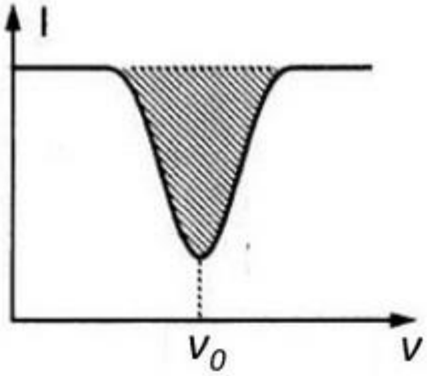
**Selectivity from excitation and emission wavelengths**

# Major types of molecular spectroscopy

## Absorption



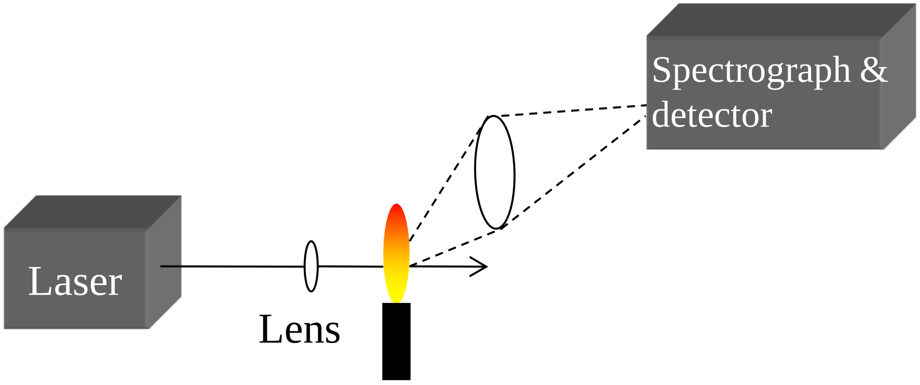




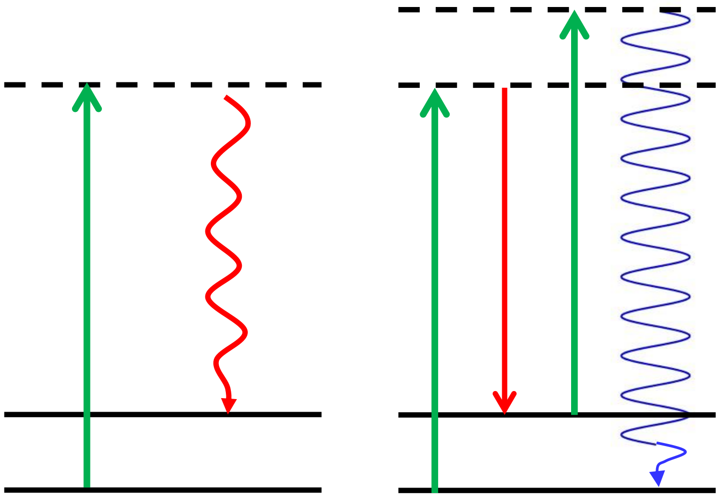
$$I(z,\nu) = I_0 e^{-\sigma(\nu)Nz}$$

(Beer-Lambert law)

## Emission (e.g. fluorescence)

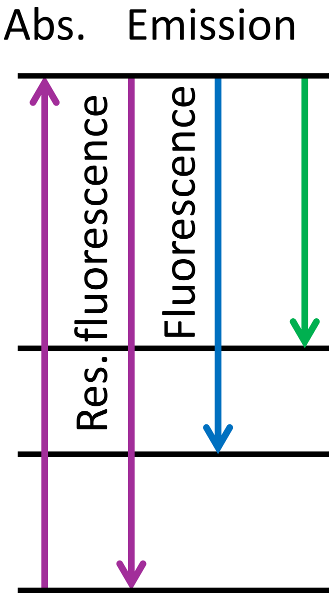


## Scattering

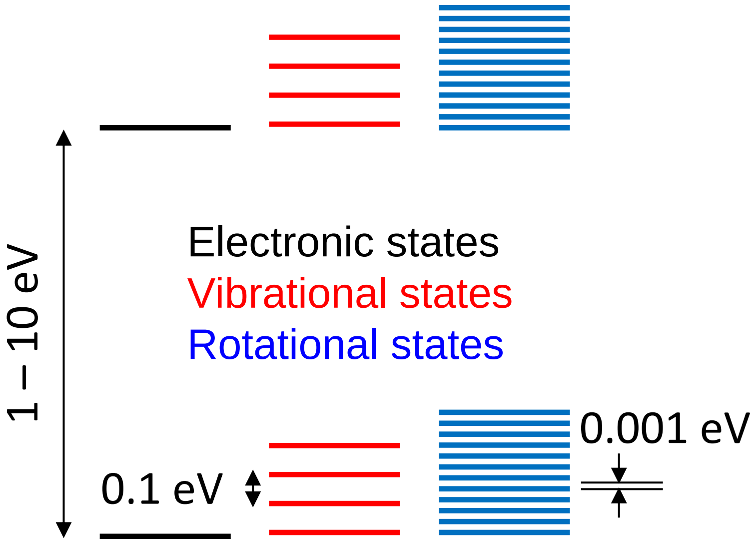


# Liquid and solid phase → broad energy bands

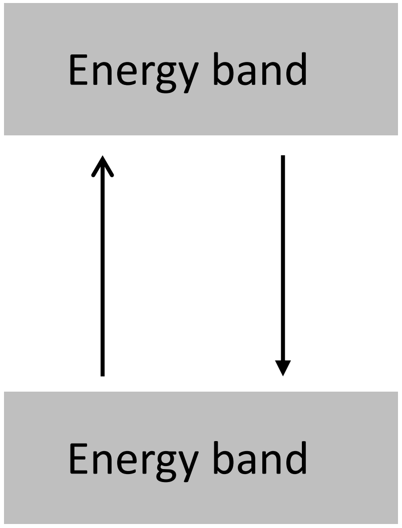
## Free atoms



## Free molecules

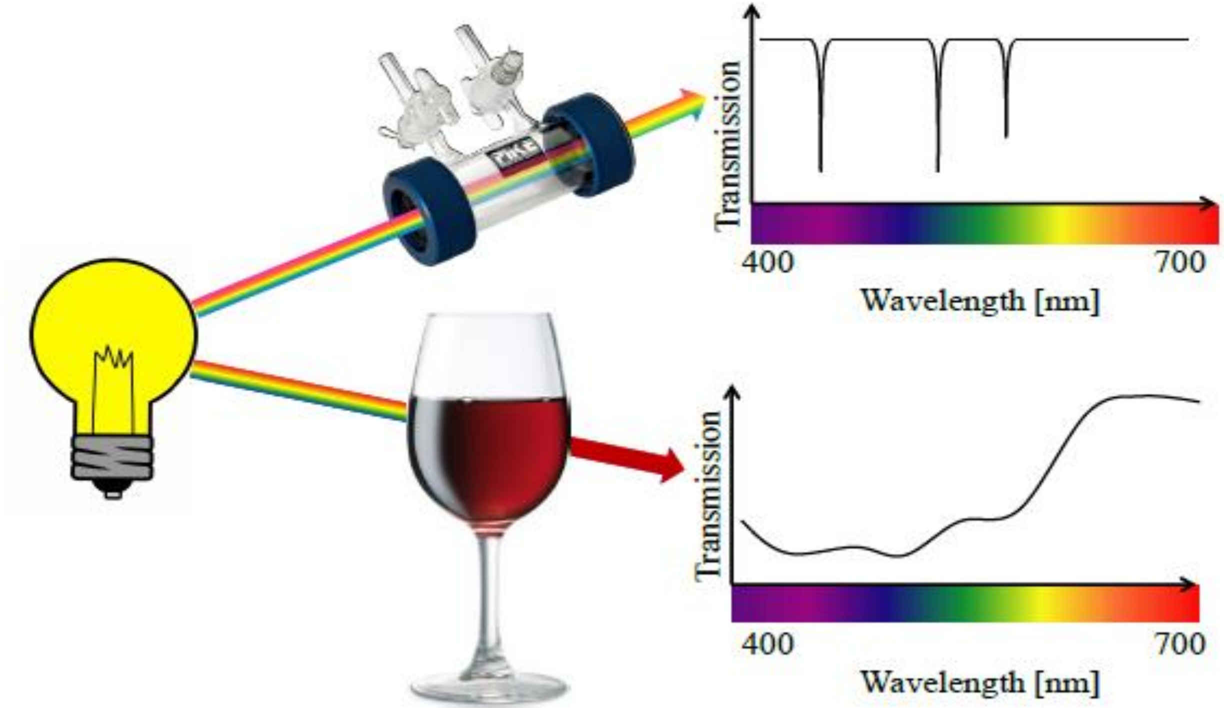


## Condensed matter



Human tissue contains a lot of water, lipids and proteins → broad energy bands instead of the sharp energy levels of free atoms and molecules.

# Light absorption in gases, liquids, and solids



**Gas absorption**

Gives rise to sharp spectral lines. Most light is transmitted.

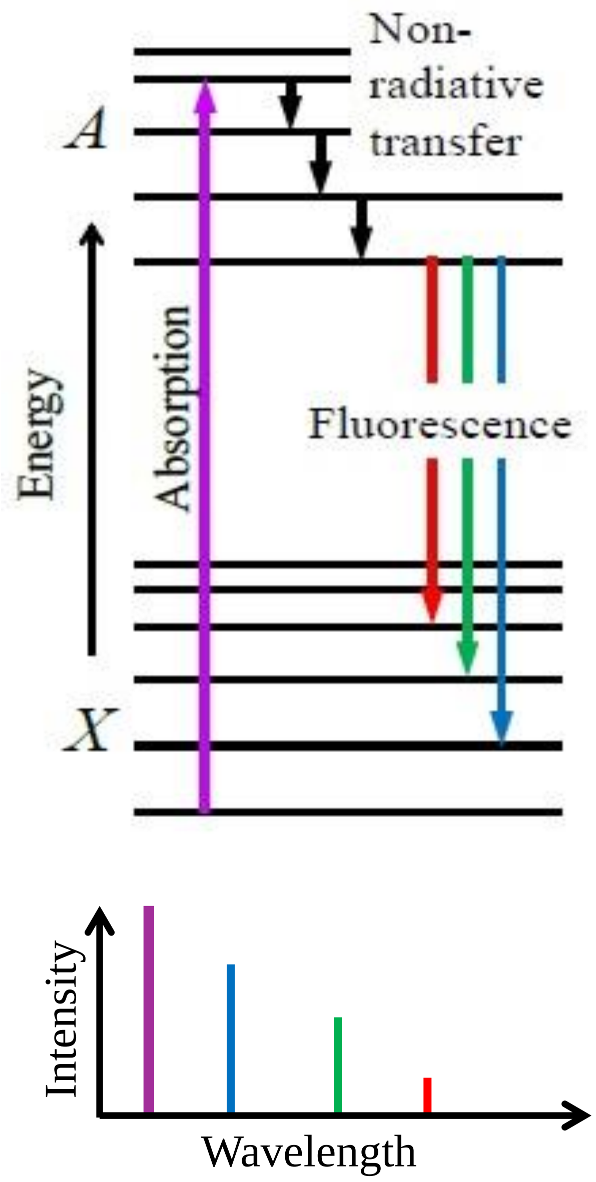
**Absorption in liquids and solids**

Gives rise to broad spectral features. The transmitted light from wine is red, while blue, green, and yellow light is absorbed.

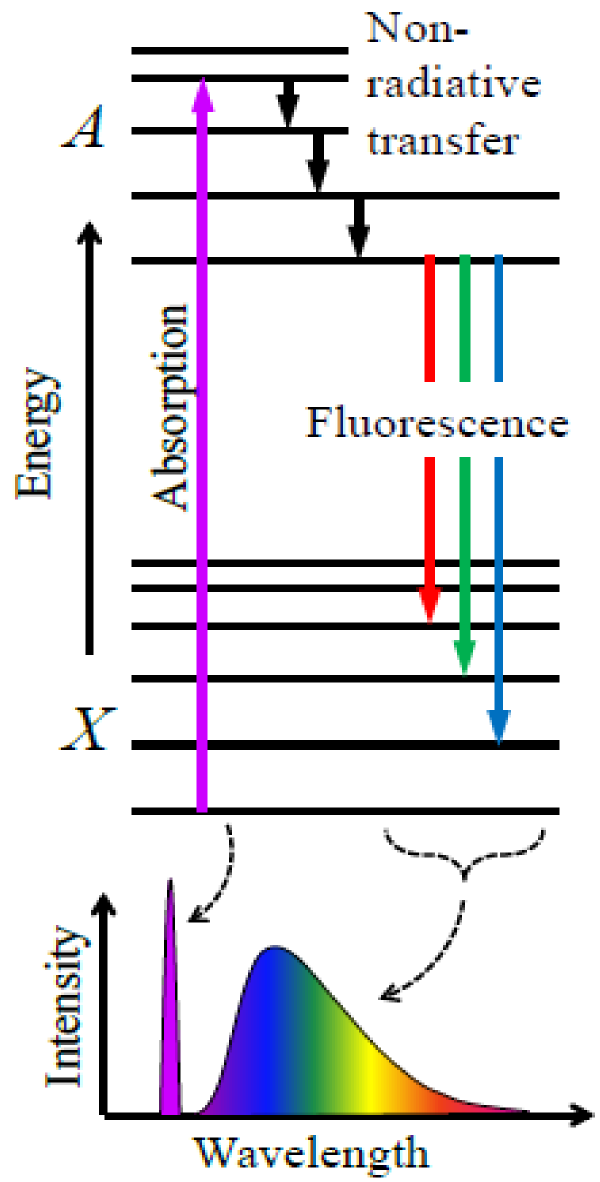
P. Lundin, Doctoral Thesis, LRAP-488, Lund University, 2014

# Fluorescence in gases, liquids, and solids

## Gases



## Liquids and solids



# The electromagnetic spectrum

Nuclear state changes

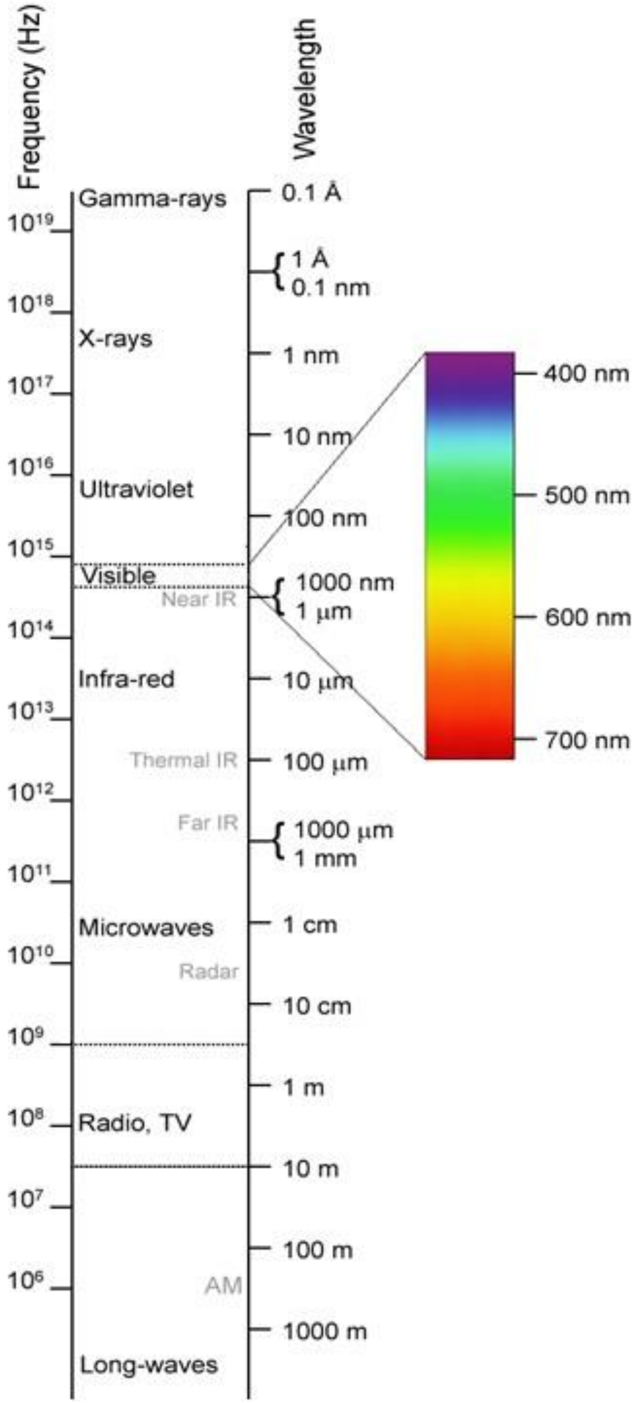
Inner electron transitions

Outer electron transitions

Vibrational state changes

Rotational state changes

Spin state changes, NMR



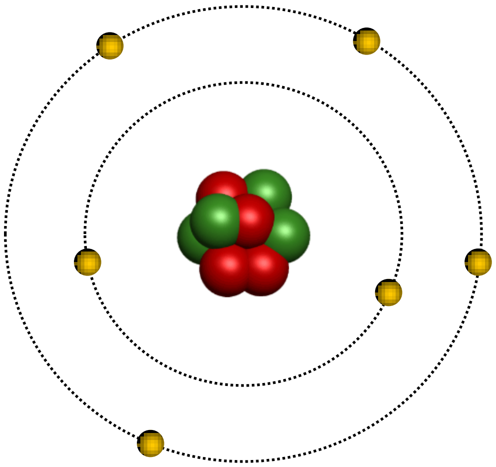
# Spectral quantities and units

| Quantity | Formula | SI unit | Comment |
|---|---|---|---|
| Frequency | $\nu = c/\lambda$ | Hz or $s^{-1}$ | |
| Wavelength | $\lambda = c/\nu$ | m | often nm or Å |
| Wavenumber | $\tilde{\nu} = 1/\lambda$ | $m^{-1}$ | Sometimes $\sigma$ instead of $\tilde{\nu}$ (often $cm^{-1}$) |
| Energy | $E = h\nu = hc/\lambda$<br>$= hc\tilde{\nu}$ | J | |

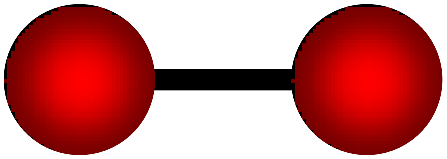
The formulas above are only strictly valid for $n = 1$

In spectroscopy, and in particular Raman spectroscopy, it is very common to work with wavenumbers in $cm^{-1}$. It is convenient as it is directly proportional to energy.

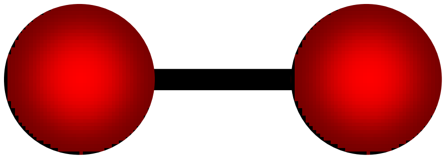
# Molecular energy structure



Electronic energy

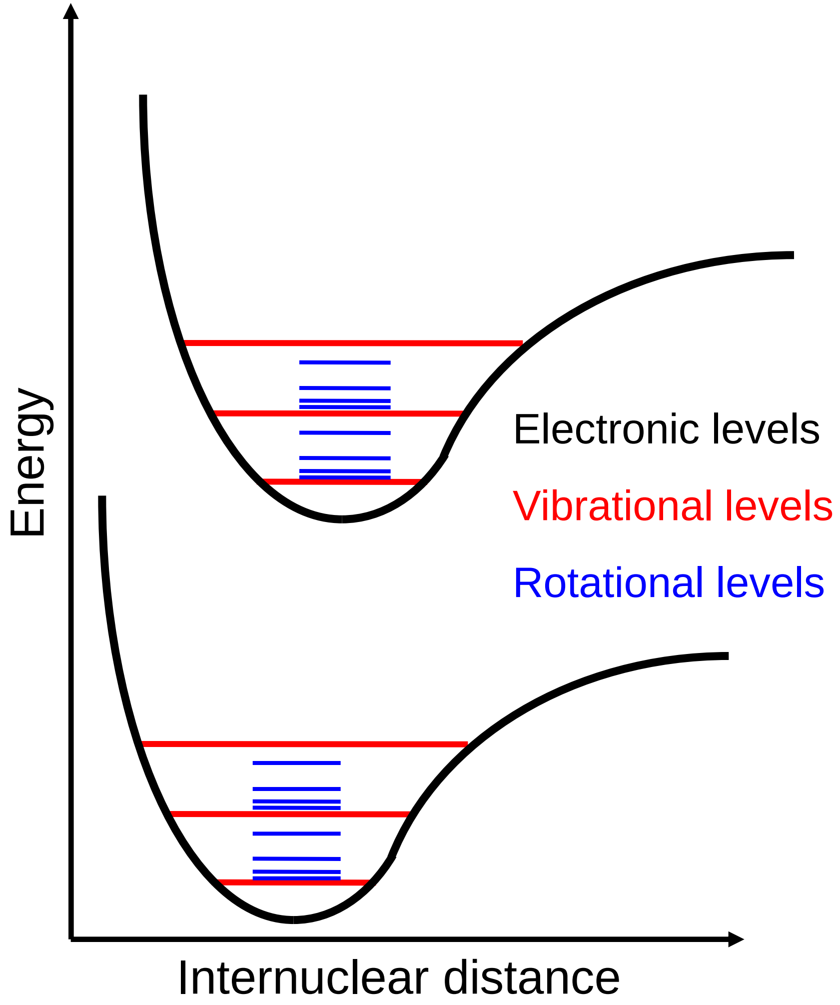


Vibrational energy



Rotational energy

## Energy level diagram



# Quantum mechanics - Molecules

The Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n(\vec{r})+V(\vec{r})\psi_n(\vec{r})=E_n\psi_n(\vec{r})\Leftrightarrow \mathbf{H}\psi_n(\vec{r})=E_n\psi_n$$

- Born-Oppenheimer approximation
- Vibrational motion is much faster than rotational motion

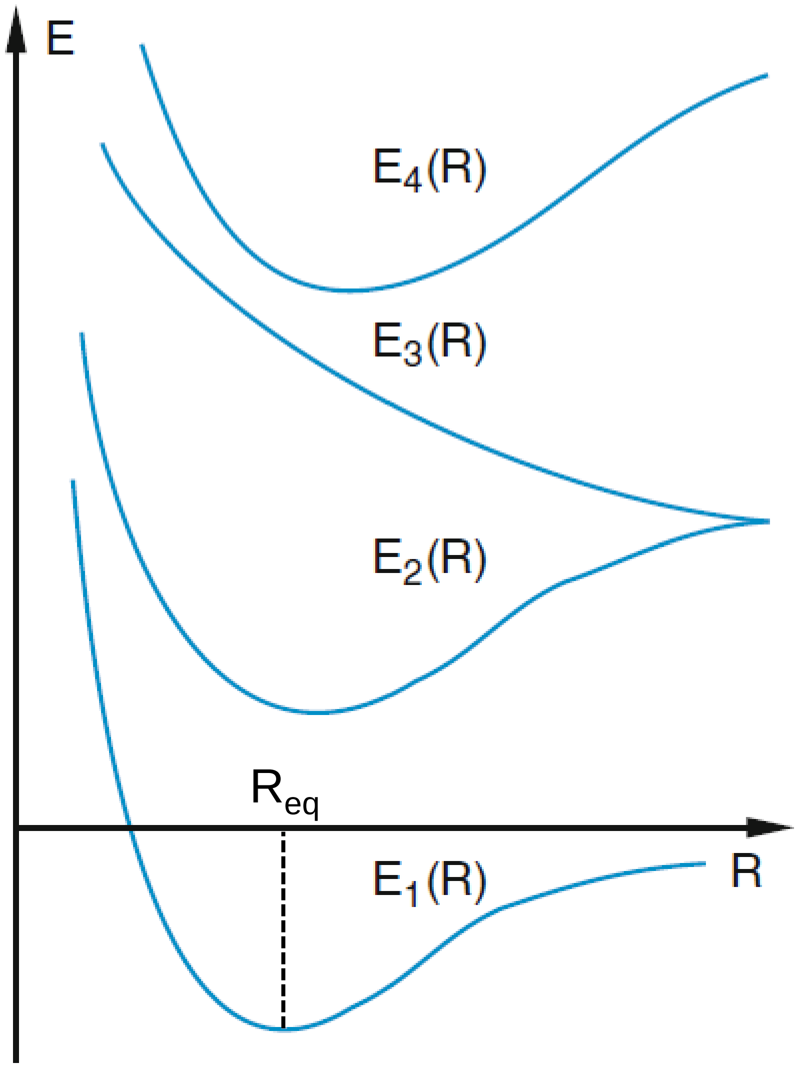
$$\Rightarrow \quad \begin{aligned} \Psi_{\mathrm{tot}} &= \Psi_{\mathrm{el}}\Psi_{\mathrm{vib}}\Psi_{\mathrm{rot}} \\ \mathrm{E}_{\mathrm{tot}} &= \mathrm{E}_{\mathrm{el}}+\mathrm{E}_{\mathrm{vib}}+\mathrm{E}_{\mathrm{rot}} \end{aligned}$$

$$E_{tot} = T_e + G(v) + F(J)$$

# Electronic structure

## Svanberg: 3.1

# Potential energy curves (PECs)



$E_1(R)$, $E_2(r)$, and $E_4(R)$ are bound (stable) states

$E_2(R)$ is an unbound (unstable/repulsive) state

B-O approx. $\Rightarrow E_{molecule} = E_{e-} + E_{nuclei}$

It also means $\psi_{molecule} = \psi_{e-} \cdot \psi_{nuclei}$

Going beyond the approximation of clamped nuclei, the PECs describe the potentials in which the nuclei can vibrate (more about this later).

**B-O approximation**: $m_p \sim 2000\ m_e \Rightarrow$ The electrons are moving much faster than the nuclei $\Rightarrow$ The electronic states are at any moment essentially the same as if the nuclei were fixed. Thus, in the B-O approximation **R is fixed**.

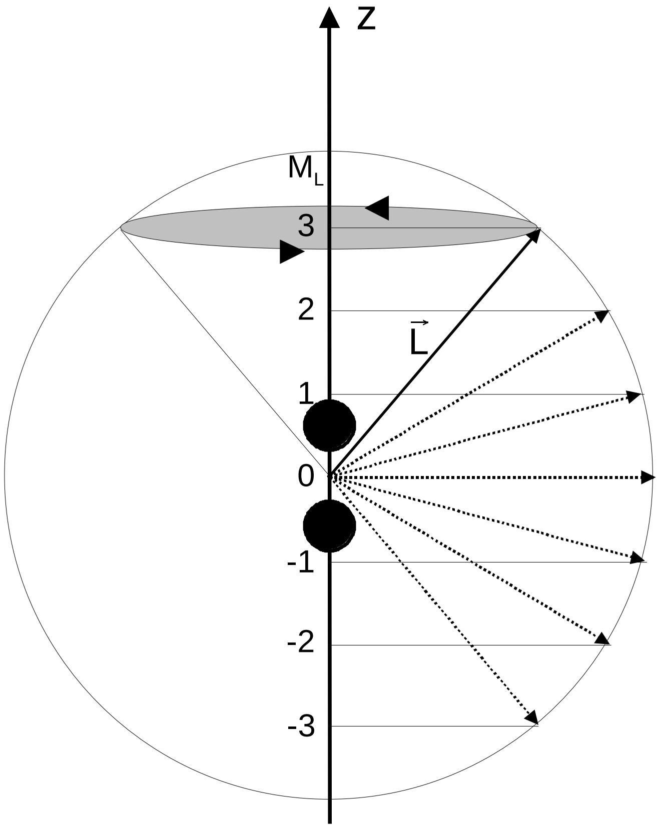
# The electronic orbital angular momentum

- Electron orbital angular momentum, L, of molecules is quantized

- Only the component along the internuclear axis, $L_z$, is a constant of motion ⇒ quantum numbers: $M_L$=L, L-1, ….., -L

- Quantum number Λ introduced: Λ=|$M_L$|, Λ=0,1,2,..,L Λ=0,1,2,…

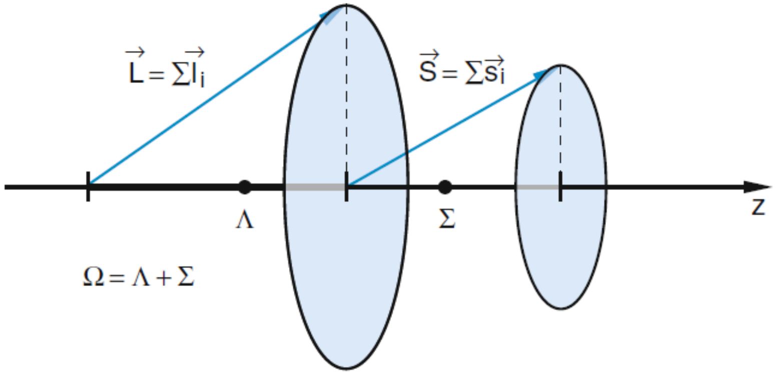
Λ=0 means a Σ-state
Λ=1 means a Π-state
Λ=2 means a Δ-state



**Svanberg: 3.1 and Fig. 3.2**

# Electronic spin

- Molecules also have spin angular momentum. S precesses around the internuclear axis
- S can have 2S+1 different projections, Σ, on the internuclear axis
- 2S+1 = multiplicity of the state
- Total angular momentum: $\Omega = \Lambda + \Sigma$



Projections on the z-axis:

$S_z = \Sigma \cdot \hbar$ $\qquad$ Σ = S,S-1,…,-S

$L_z = \Lambda \cdot \hbar$ $\qquad$ Λ = 0, 1, 2, …

$\Omega = \Lambda + \Sigma$ $\qquad$ Σ, Π, Δ, …

Svanberg: 3.1

# Term symbols for diatomic molecules

For an atom: $^{2S+1}L_J$    For a diatomic: $^{2S+1}\Lambda_\Omega$

$\vec{\Lambda}$:

Projection of orbital angular momentum onto the internuclear axis.

Magnitude: $|\vec{\Lambda}| = \Lambda \cdot \hbar$

Symbols:

| $\Lambda$ | 0 | 1 | 2 |
|---|---|---|---|
| Symbol | $\Sigma$ | $\Pi$ | $\Delta$ |

Atoms:

| L | 0 | 1 | 2 |
|---|---|---|---|
| Symbol | S | P | D |

$\vec{S}$:

Total electronic spin (sum of spins in unfilled shells).

Magnitude: $|\vec{S}| = S \cdot \hbar$

$\vec{\Sigma}$:

Projection of $\vec{S}$ onto the internuclear axis (only defined when $\Lambda \neq 0$)

Magnitude: $|\vec{\Sigma}| = \Sigma \cdot \hbar$

Allowed values: $\Sigma$ = S,S-1,…,-S (2S+1 values)

$\vec{\Omega}$:

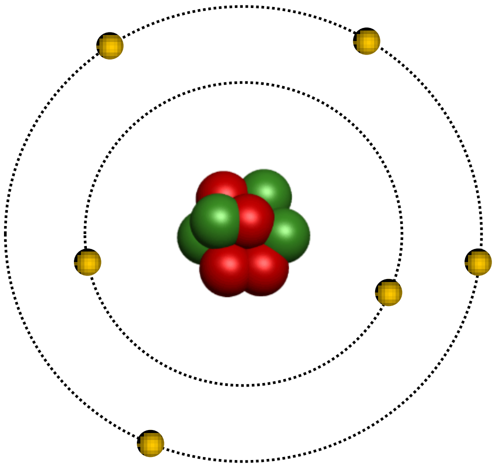
Sum of projections along the internuclear axis of electron spin and orbital angular momentum. $\vec{\Omega} = \vec{\Lambda} + \vec{\Sigma}$

$\Omega = \Lambda+\Sigma, \Lambda+\Sigma-1, \ldots, |\Lambda-\Sigma|$ (2S+1 values for $\Lambda \geq$ S)

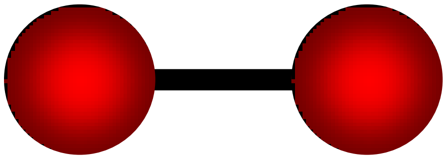
# Rotation and vibration of molecules

Svanberg: 3.2 - 3.4

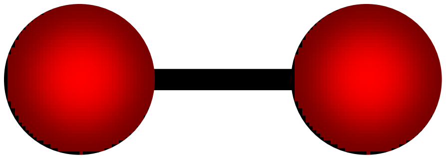
# Molecular energy structure



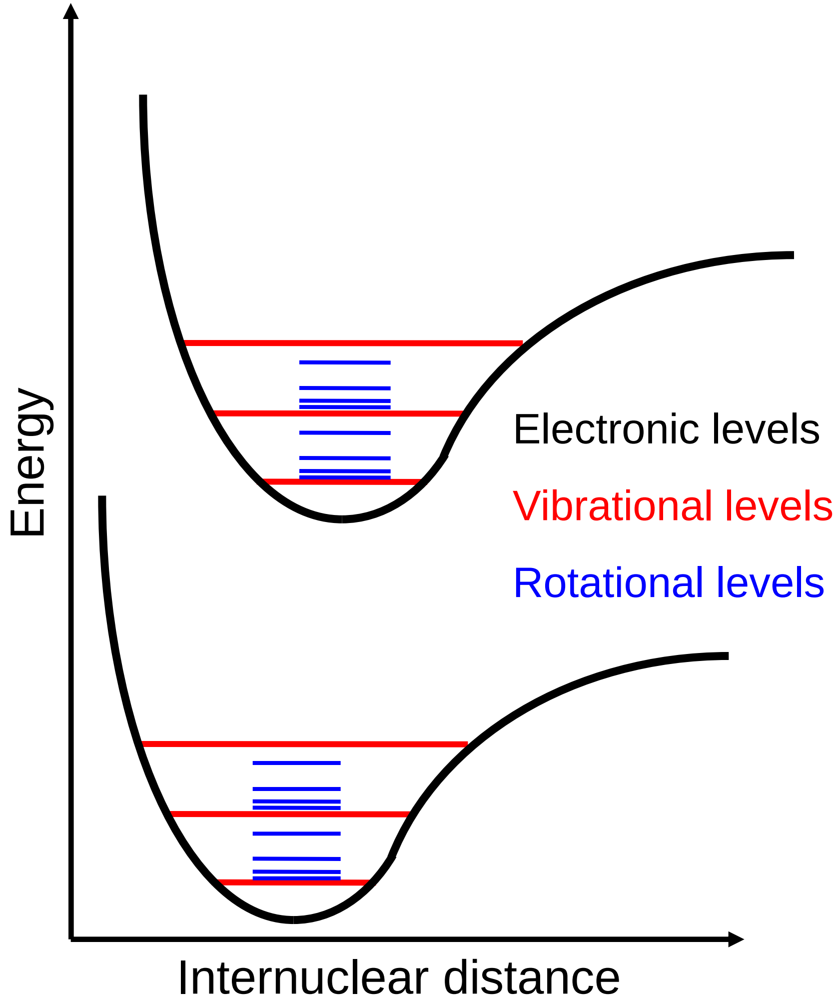
Electronic energy



Vibrational energy



Rotational energy



Energy level diagram

# Quantum mechanics - Molecules

The Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n(\vec{r})+V(\vec{r})\psi_n(\vec{r})=E_n\psi_n(\vec{r})\Leftrightarrow \mathbf{H}\psi_n(\vec{r})=E_n\psi_n$$

- Born-Oppenheimer approximation
- Vibrational motion is much faster than rotational motion

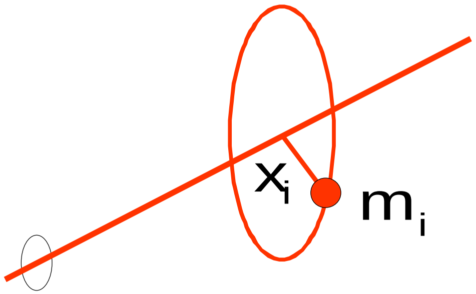
$$\Rightarrow \quad \begin{aligned}\Psi_{\mathrm{tot}} &= \Psi_{\mathrm{el}}\Psi_{\mathrm{vib}}\Psi_{\mathrm{rot}}\\ \mathrm{E}_{\mathrm{tot}} &= \mathrm{E}_{\mathrm{el}}+\mathrm{E}_{\mathrm{vib}}+\mathrm{E}_{\mathrm{rot}}\end{aligned}$$

# Molecular rotation

## Classical picture

Moment of inertia:

$$I_{qq} = \sum_i m_i x_i^2(q)$$



Reduced mass (diatomic molecule):

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B} \Leftrightarrow \mu = \frac{m_A m_B}{m_A + m_B} \Rightarrow I = \mu R^2$$

where R is the equilibrium bond length (internuclear distance) of the molecule

**Svanberg: 3.2**

# Molecular rotation

## Quantum mechanical picture

Classical mechanics:

$$T = \frac{1}{2}\sum_q I_{qq}\omega_q^2 = \sum_q \frac{J_q^2}{2I_{qq}} \quad \text{where} \quad J_{qq} = I_{qq}\omega_q$$

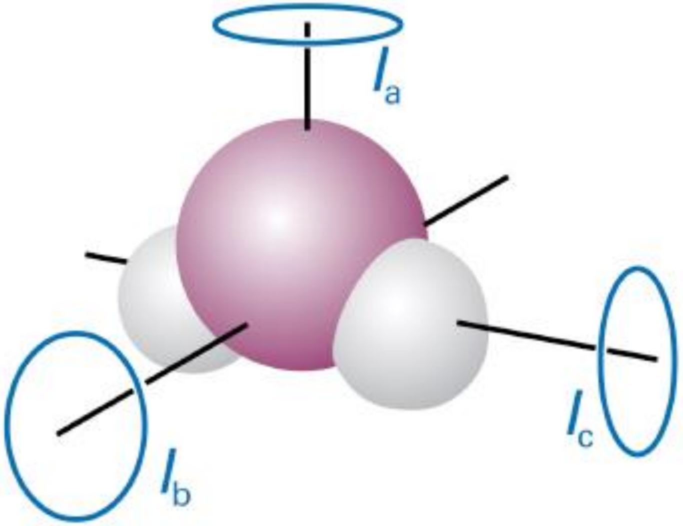
Quantum mechanics: (J$_q$ is an operator of the angular momentum)

$$\Rightarrow \mathbf{H} = \frac{\mathbf{J}_x^2}{2I_{xx}} + \frac{\mathbf{J}_y^2}{2I_{yy}} + \frac{\mathbf{J}_z^2}{2I_{zz}}$$

There is no potential energy associated with pure rotational motion

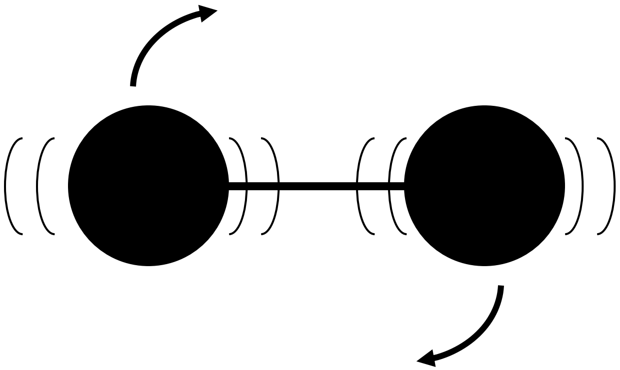
# Four types of rigid rotors

- **Linear rotors**
  - One moment of inertia is zero (e.g. $CO_2$, HCl)
- **Symmetric rotors**
  - Two equal moments of inertia, one different (e.g. $NH_3$)
- **Spherical rotors**
  - Three equal moments of inertia (e.g. $CH_4$)
- **Asymmetric rotors**
  - Three different moments of inertia (e.g. $H_2O$)



# Diatomic molecules - Basics

A diatomic molecule has a total wave function consisting of an electronic wave function, and a nuclear wave function.



The nuclear wave function can be separated into a rotational wave function and a vibrational wave function.

In the Born-Oppenheimer approximation these are initially treated separately:

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

**Time scales**

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

*Vibrations:* $\sim 10^{-14}$ *s*

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

# Diatomic molecules

$$\mathbf{H} = \frac{\mathbf{J}^2}{2I} \quad \Rightarrow \text{eigenvalues:} \quad E(J, M_J) = \frac{J(J+1)\hbar^2}{2I}$$

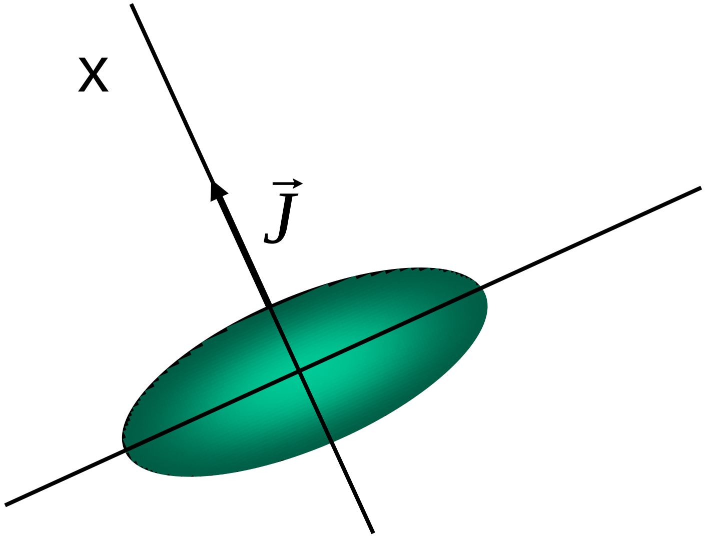
Eigenfunctions: $Y_{J,M_J}(\theta, \phi)$ (Spherical harmonics, known from the atomic structure)

$$\mathbf{J}^2 = \mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2$$

( J = 0,1,2,…. $M_J$ = J, J-1,…., -J )

2J+1 possible $M_J$ values for each rotational level

⇒ 2J+1-fold degenerate.



The rotational constant, B:

$$B[Joule] = \frac{\hbar^2}{2I} \qquad B[cm^{-1}] = B = \frac{\hbar}{4\pi c I}$$

$$\boxed{F(J) = BJ(J+1)} \quad (\text{cm}^{-1})$$

**Svanberg: 3.2**

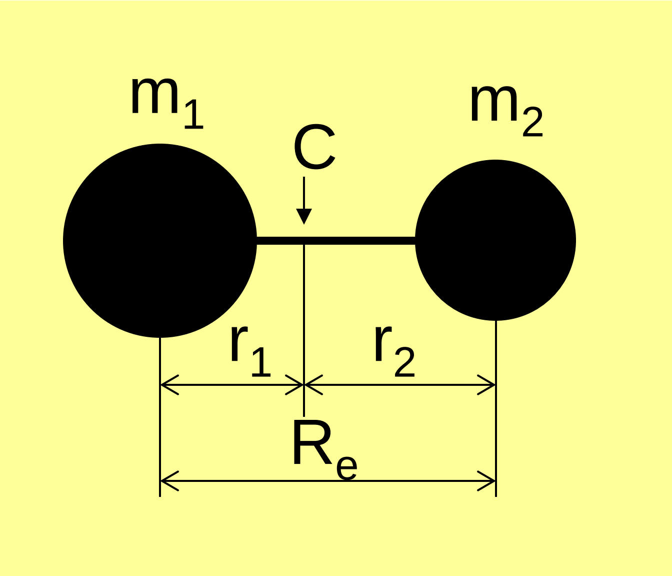
# Rotational energy levels for a diatomic molecule

Solutions to the Schrödinger equation:

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

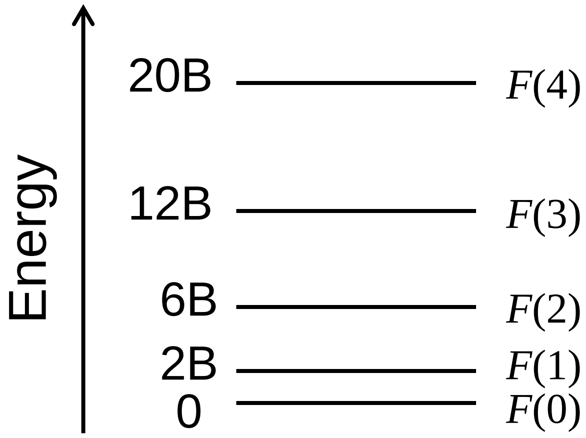
$$I = \mu R_e^2$$

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



$$F(J) = \frac{E_J}{hc} = \frac{h}{8\pi^2 cI} J(J+1) = BJ(J+1) \quad [cm^{-1}]$$

J=0, 1, 2, .... ⇒



The energy separation increases with increasing J

**Svanberg: 3.2**

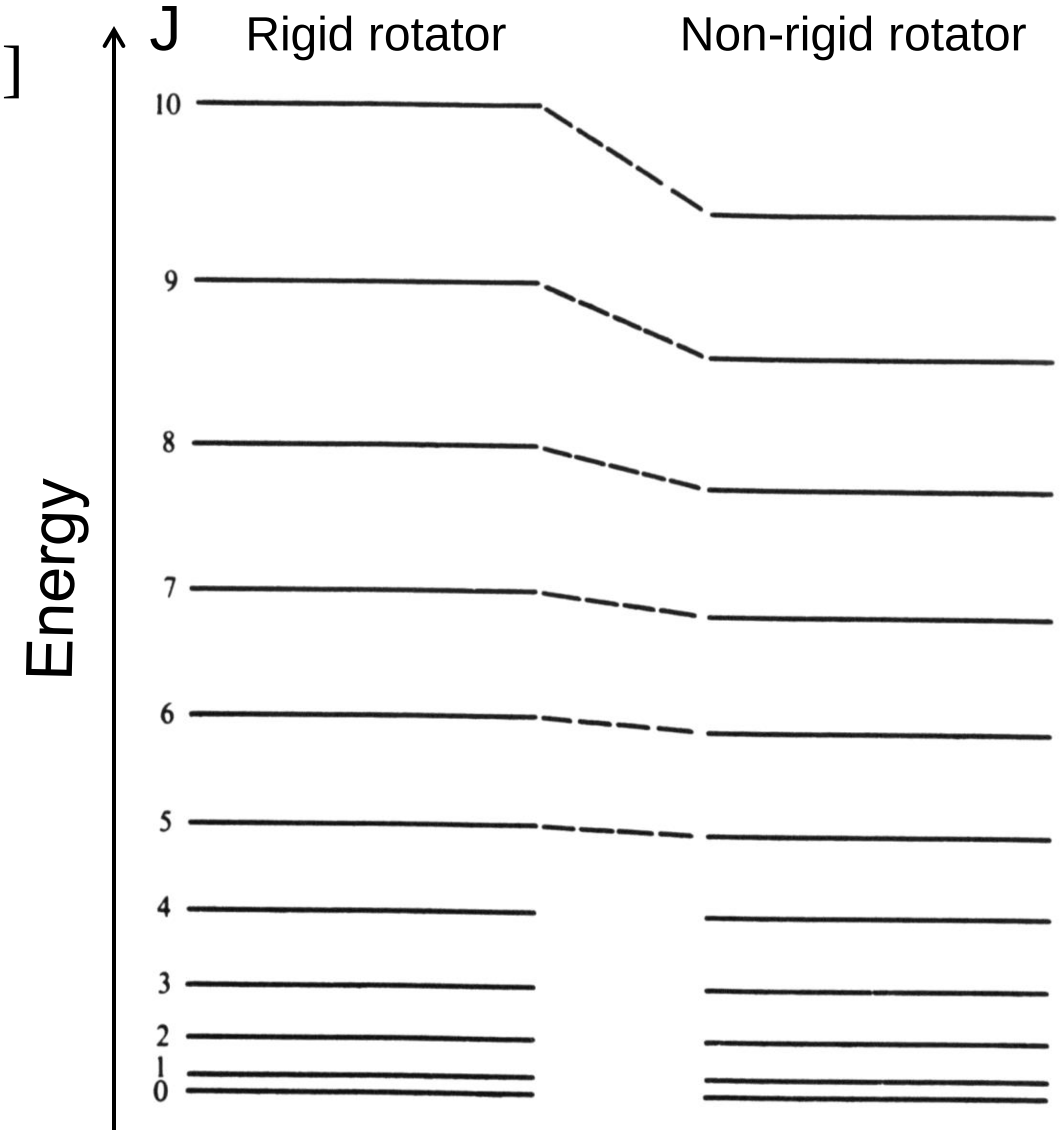
# Energy levels for non-rigid rotator

$$F(J) = BJ(J+1) - DJ^2(J+1)^2[cm^{-1}]$$

D centrifugal distortion constant

F(18) = 683,40 $cm^{-1}$ for $N_2$
without D-correction

F(18) = 682,72 $cm^{-1}$ for $N_2$
with D-correction



Svanberg: Fig 3.6

# Vibrational energy levels

Solutions to Schrödinger equation for harmonic oscillator:

$$G(v) = \omega_e \left(v + \frac{1}{2}\right) \quad (\text{cm}^{-1})$$

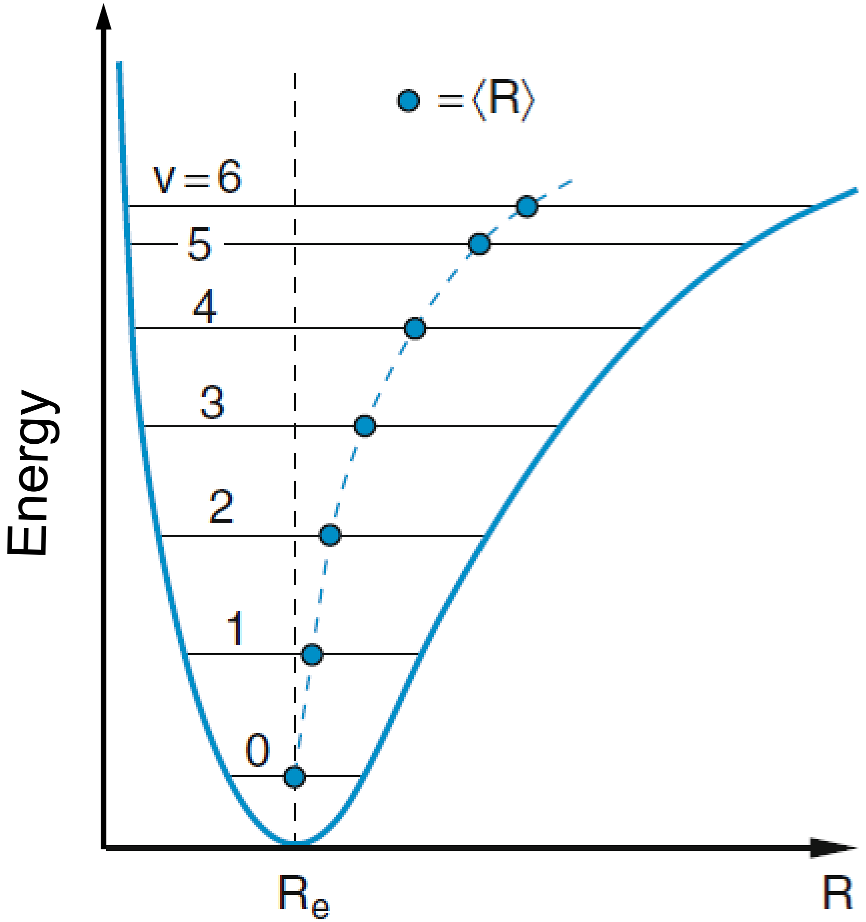
$G(0) = 0.5\omega_e$, $G(1) = 1.5\omega_e$, $G(2) = 2.5\omega_e$

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

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

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

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



**Svanberg: 3.3**

# Interaction between rotation and vibration

The vibrational and rotational energies can not be treated quite independent. A molecule can vibrate 100-1000 times during a rotation.

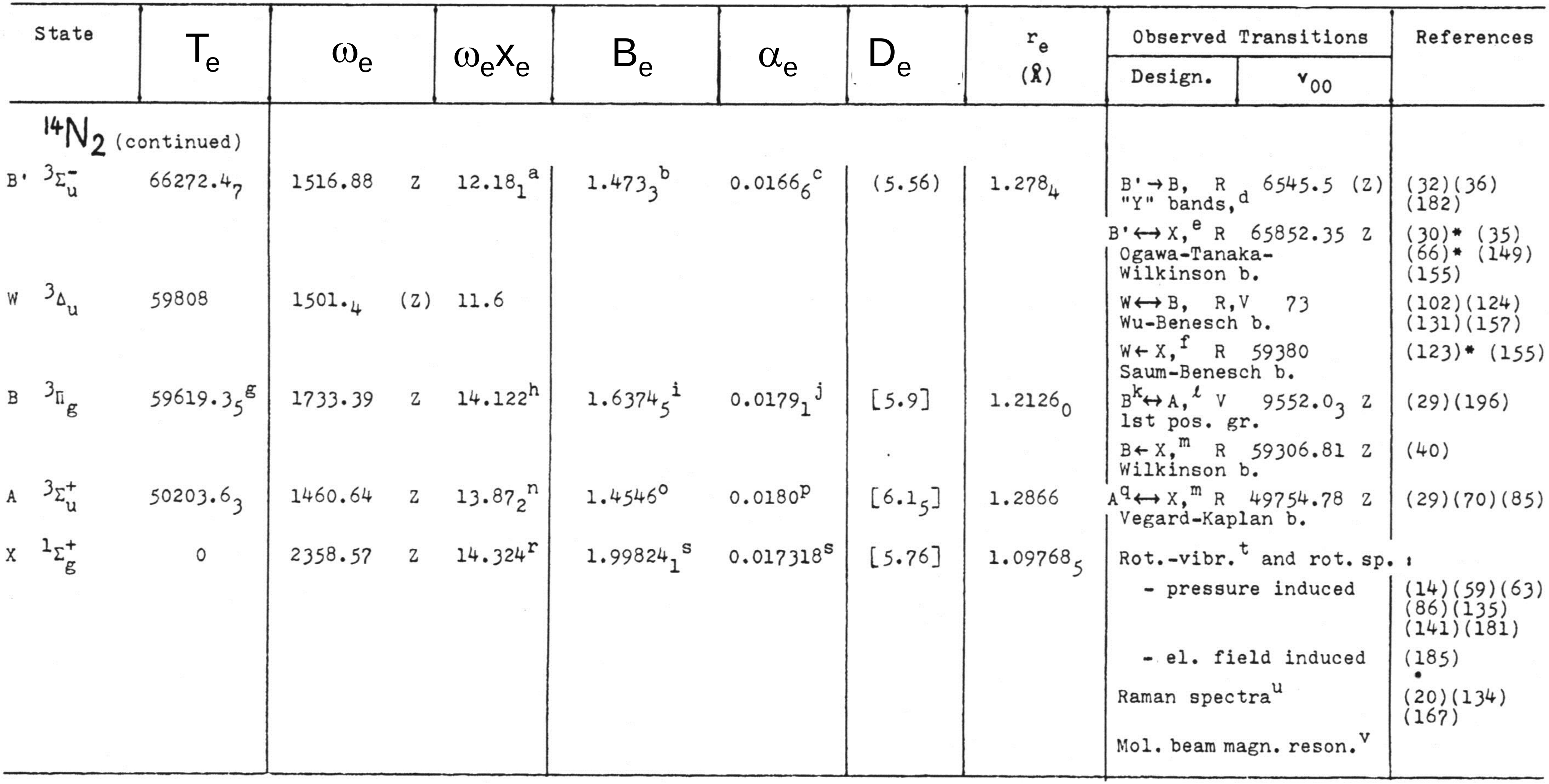
The rotational constant $B_v$ in a vibrational state v, can be expressed as

$$B_v = B_e - \alpha_e (v + 1/2) \quad [cm^{-1}]$$

The centrifugal distortion constant $D_v$ in a vibrational state v, can be expressed as

$$D_v = D_e + \beta_e (v + 1/2) \quad [cm^{-1}]$$

# Molecular constants



| State | $T_e$ | $\omega_e$ | $\omega_e x_e$ | $B_e$ | $\alpha_e$ | $D_e$ | $r_e$ (Å) | Observed Transitions | | References |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Design. | $\nu_{00}$ | |
| $^{14}N_2$ (continued) | | | | | | | | | | |
| B' $^3\Sigma_u^-$ | $66272.4_7$ | 1516.88 Z | $12.18_1{}^{a}$ | $1.473_3{}^{b}$ | $0.0166_6{}^{c}$ | (5.56) | $1.278_4$ | B' → B, R<br>"Y" bands,$^{d}$ | 6545.5 (Z) | (32)(36)<br>(182) |
| | | | | | | | | B' ↔ X,$^{e}$ R<br>Ogawa-Tanaka-Wilkinson b. | 65852.35 Z | (30)* (35)<br>(66)* (149)<br>(155) |
| W $^3\Delta_u$ | 59808 | $1501._4$ (Z) | 11.6 | | | | | W ↔ B, R,V<br>Wu-Benesch b. | 73 | (102)(124)<br>(131)(157) |
| | | | | | | | | W ← X,$^{f}$ R<br>Saum-Benesch b. | 59380 | (123)* (155) |
| B $^3\Pi_g$ | $59619.3_5{}^{g}$ | 1733.39 Z | $14.122^{h}$ | $1.6374_5{}^{i}$ | $0.0179_1{}^{j}$ | [5.9] | $1.2126_0$ | B$^{k}$ ↔ A,$^{\ell}$ V<br>1st pos. gr. | $9552.0_3$ Z | (29)(196) |
| | | | | | | | | B ← X,$^{m}$ R<br>Wilkinson b. | 59306.81 Z | (40) |
| A $^3\Sigma_u^+$ | $50203.6_3$ | 1460.64 Z | $13.87_2{}^{n}$ | $1.4546^{o}$ | $0.0180^{p}$ | $[6.1_5]$ | 1.2866 | A$^{q}$ ↔ X,$^{m}$ R<br>Vegard-Kaplan b. | 49754.78 Z | (29)(70)(85) |
| X $^1\Sigma_g^+$ | 0 | 2358.57 Z | $14.324^{r}$ | $1.99824_1{}^{s}$ | $0.017318^{s}$ | [5.76] | $1.09768_5$ | Rot.-vibr.$^{t}$ and rot. sp.: | | |
| | | | | | | | | - pressure induced | | (14)(59)(63)<br>(86)(135)<br>(141)(181) |
| | | | | | | | | - el. field induced | | (185) |
| | | | | | | | | Raman spectra$^{u}$ | | (20)(134)<br>(167) |
| | | | | | | | | Mol. beam magn. reson.$^{v}$ | | |

*From Huber and Herzberg: "Constants of diatomic molecules"*

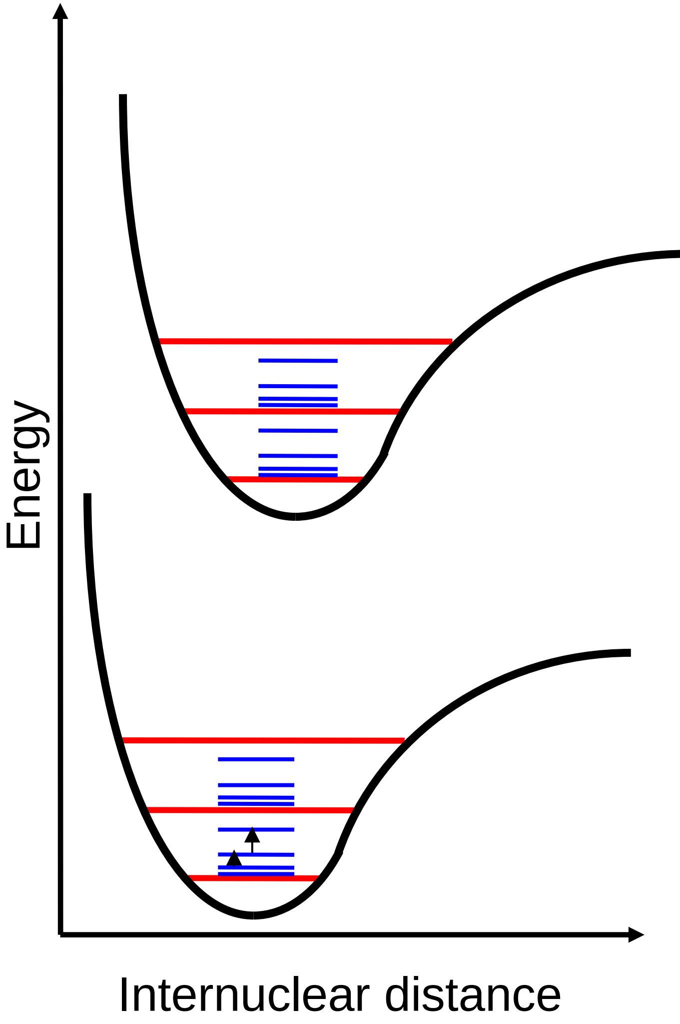
Molecular constants are available at: http://webbook.nist.gov/chemistry/form-ser.html

# Molecular transitions

Svanberg: 4.2.2

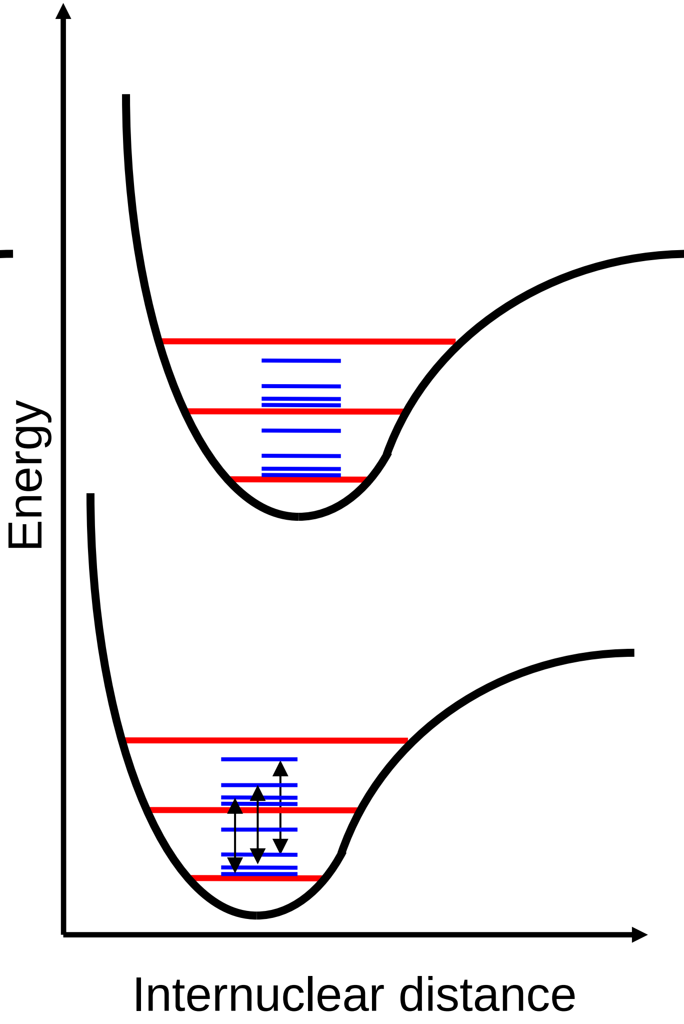
# Molecular transitions

## Rotational transitions



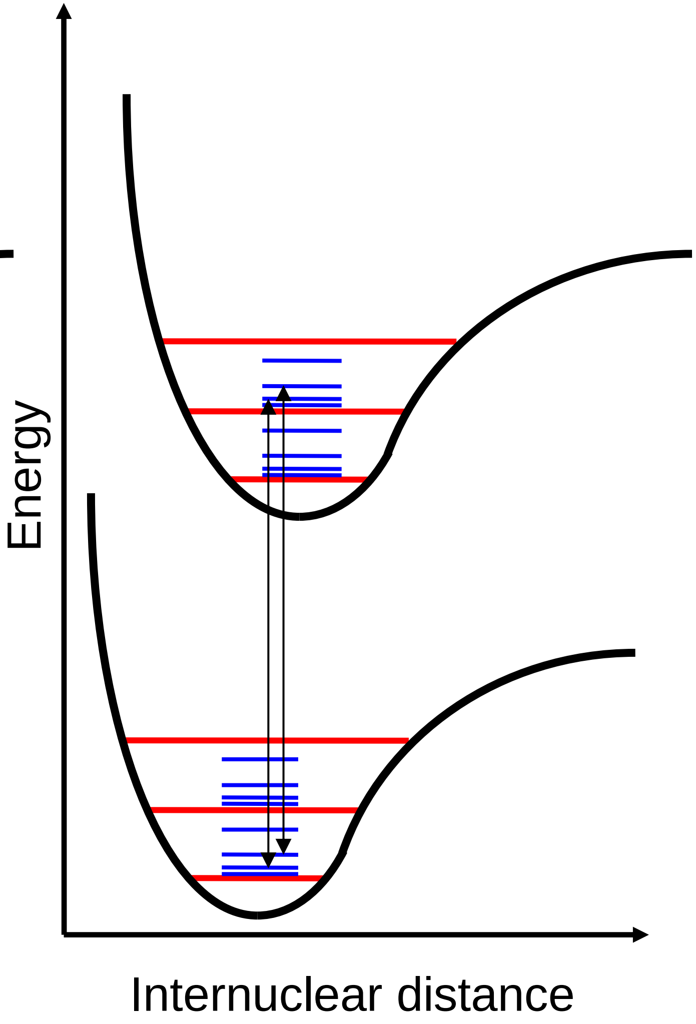
microwaves

## Rovibrational transitions



infrared (IR)

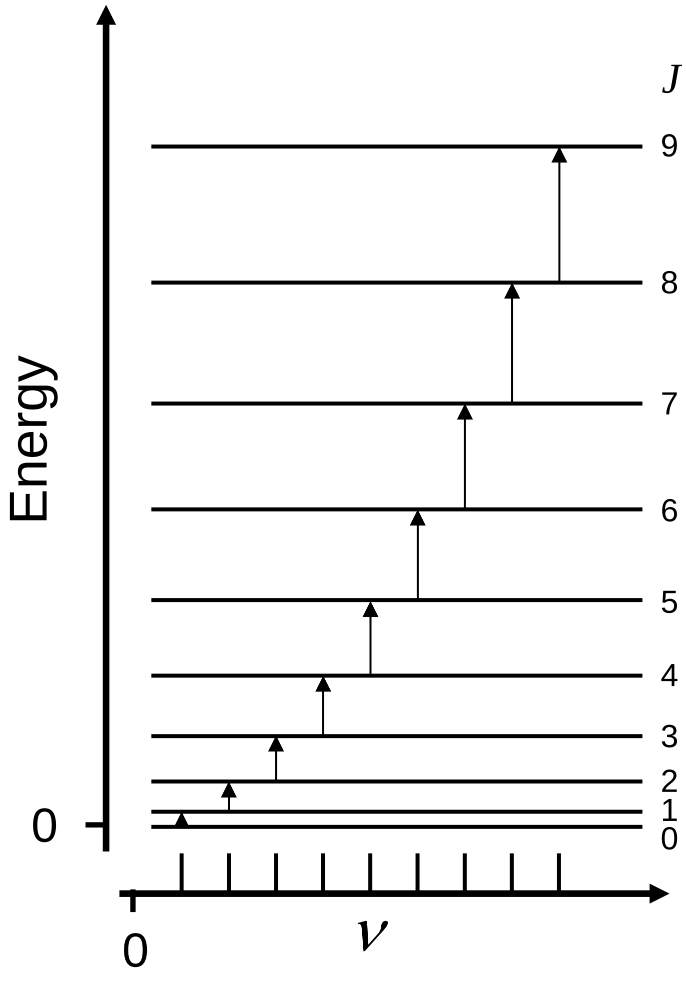
## Rovibronic transitions



vis – ultraviolet (UV)

# Pure rotational transitions

A heteronuclear diatomic molecule possesses a permanent dipole moment and therefore emits radiation when the rotation is changed. Selection rule: **ΔJ = ±1**



Rigid molecule: $F(J) = BJ(J+1)$

Transitions at the following wavenumbers:

$$\nu(J+1 \leftrightarrow J) = 2B(J+1)$$ J = 0,1,2,…

Elastic molecule:

$$F(J) = BJ(J+1) - DJ^2(J+1)^2$$

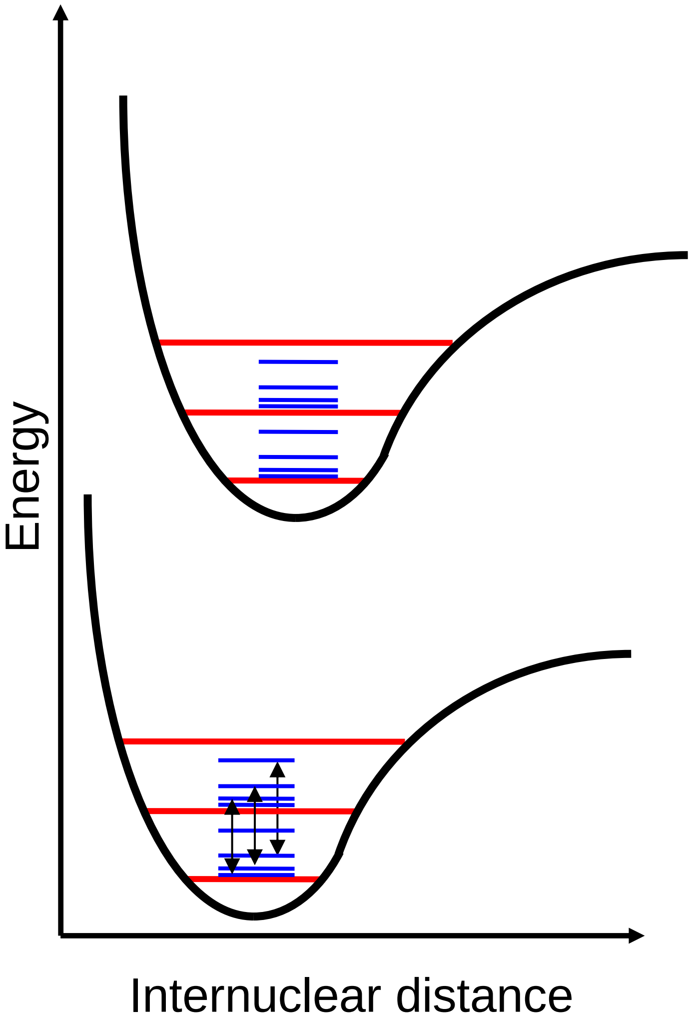
Transitions:

$$\nu(J+1 \leftrightarrow J) = 2B(J+1) - 4D(J+1)^3$$

J = 0,1,2,…

**Svanberg: 4.2.2, Fig. 4.10**

# Rovibrational transitions (IR transitions)



A vibration is **IR-active** only if it involves a **change in the dipole moment**. For diatomic molecules, therefore only heteronuclear molecules are IR-active. Thus, rovibrational transitions are not possible in homonuclear diatomics (since they are symmetric).

$\Delta v = \pm 1$ are by far strongest

$\Delta J = \pm 1$ (same as for pure rot. trans.)

# Rovibrational transitions

Total energy: $E(v,J) = G(v) + F(J)$

Upper state energy: $E' = G(v') + B'J'(J'+1)$

Lower state energy: $E'' = G(v'') + B''J''(J''+1)$

Expression for P-branch transitions:

$$P(J) = \boxed{G(v') - G(v'')} - (B' + B'')J + (B' - B'')J^2$$

$$\tilde{\nu}_{v'v''} = G(v') - G(v'') \quad \textit{(band origin)}$$

$$P(J) = \tilde{\nu}_{v'v''} - (B' + B'')J + (B' - B'')J^2$$

$$R(J) = \tilde{\nu}_{v'v''} + (B' + B'')(J+1) + (B' - B'')(J+1)^2$$

Both branches in a single formula: $\tilde{\nu} = \tilde{\nu}_{v'v''} + am + bm^2$

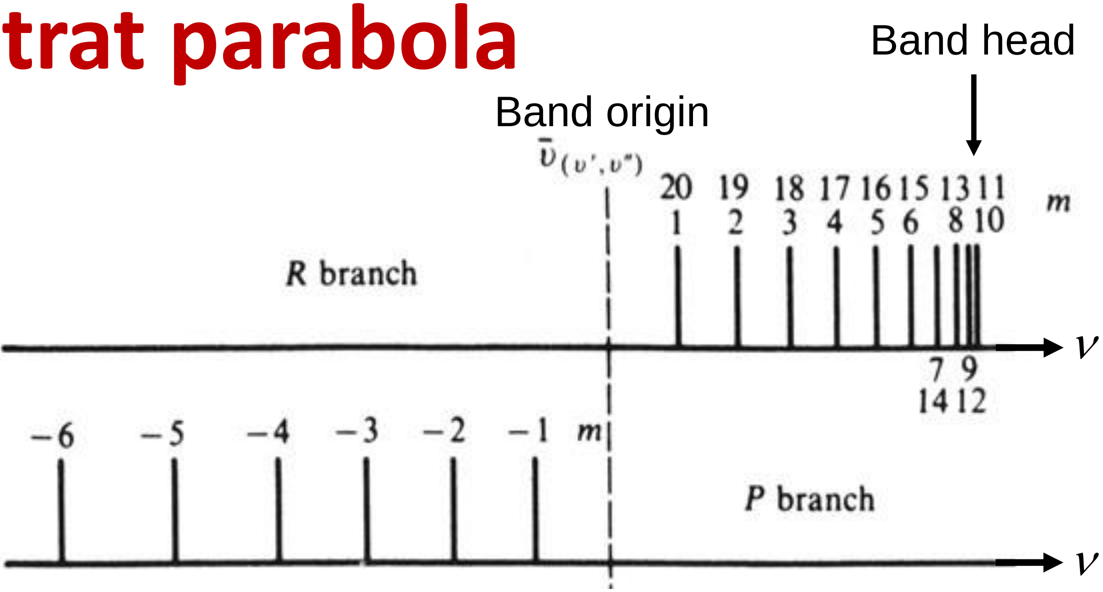
$m = -J$ for P-branch transitions

$m = J + 1$ for R-branch transitions

where $a = B' + B''$ and $b = B' - B''$

**Svanberg: page 57-58**

# The Fortrat parabola

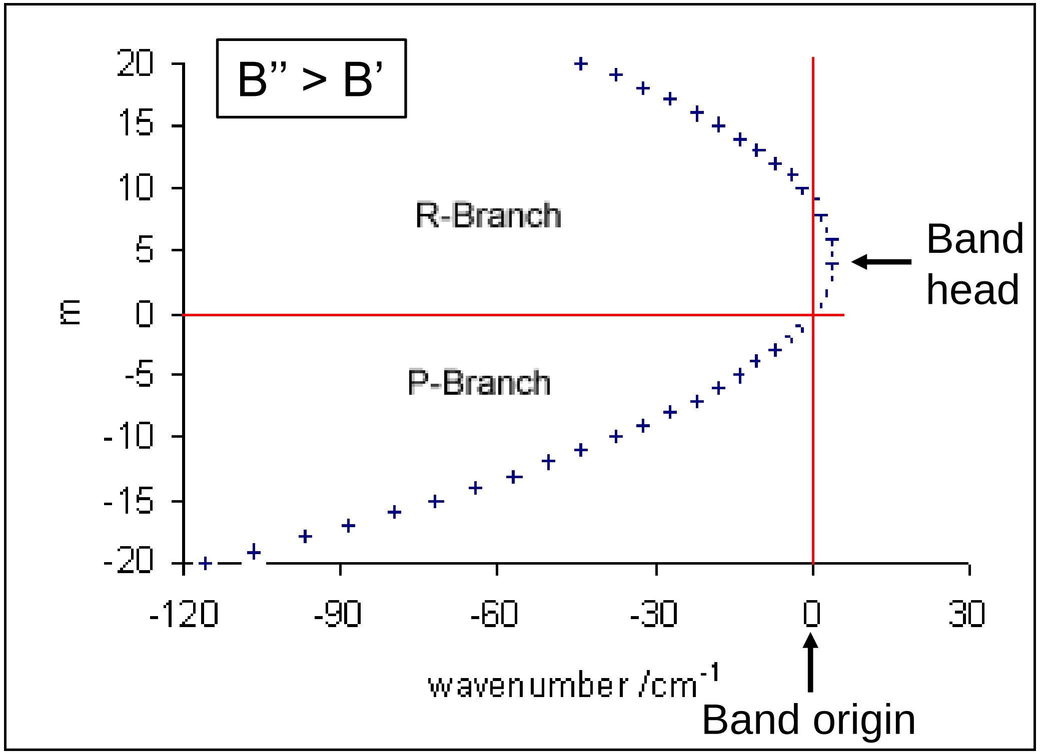


$$\tilde{\nu} = \tilde{\nu}_{v'v''} + am + bm^2$$

m= -1,-2,-3,… for P-branch

m= 1,2,3,… for R-branch

where $a = B' + B''$ and $b = B' - B''$



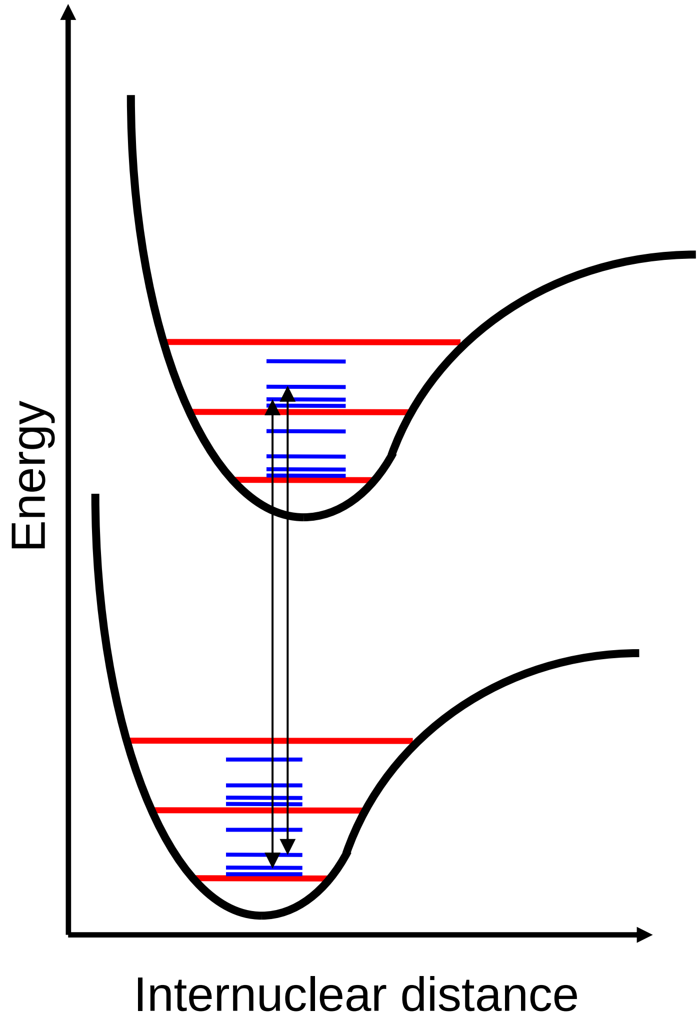
Plotting the result of the expression in a diagram with m vs $\tilde{\nu}$ results in a so-called **Fortrat daigram**.

**When B'' > B'** there is a **bandhead in the R-branch** and the band is said to be **degraded towards red** because the parabola has its vertex towards higher frequencies (like in this example)

When **B'' < B'** there is a **bandhead in the P-branch** and the band is **degraded towards violet**.

Svanberg: Fig. 4.13

# Rovibronic transitions



## Selection rules (diatomics):

Electronic: (major) $\Delta\Lambda = 0, \pm 1$

$\Delta S = 0$

$\Delta\Sigma = 0$

$\Delta\Omega = 0$

Vibrational: No strict rule, dependent on Franck-Condon overlap (more about this later)

Rotational: $\Delta J = -1, 0, \text{or} +1$ (P, Q, R branch) (not J = 0 to J = 0)

# Rovibronic transitions

Total energy: $E(T_e, v, J) = T_e + G(v) + F(J)$

Upper state energy: $E' = T'_e + G(v') + B'J'(J' + 1)$

Lower state energy: $E'' = T''_e + G(v'') + B''J''(J'' + 1)$

$$P(J) = \underbrace{T'_e - T''_e + G(v') - G(v'')}_{\tilde{\nu}_{v'v''}\ \text{(band origin)}} - (B' + B'')J + (B' - B'')J^2$$

$$P(J) = \tilde{\nu}_{v'v''} - (B' + B'')J + (B' - B'')J^2$$

$$R(J) = \tilde{\nu}_{v'v''} + (B' + B'')(J + 1) + (B' - B'')(J + 1)^2$$

$$Q(J) = \tilde{\nu}_{v'v''} + (B' - B'')J + (B' - B'')J^2$$

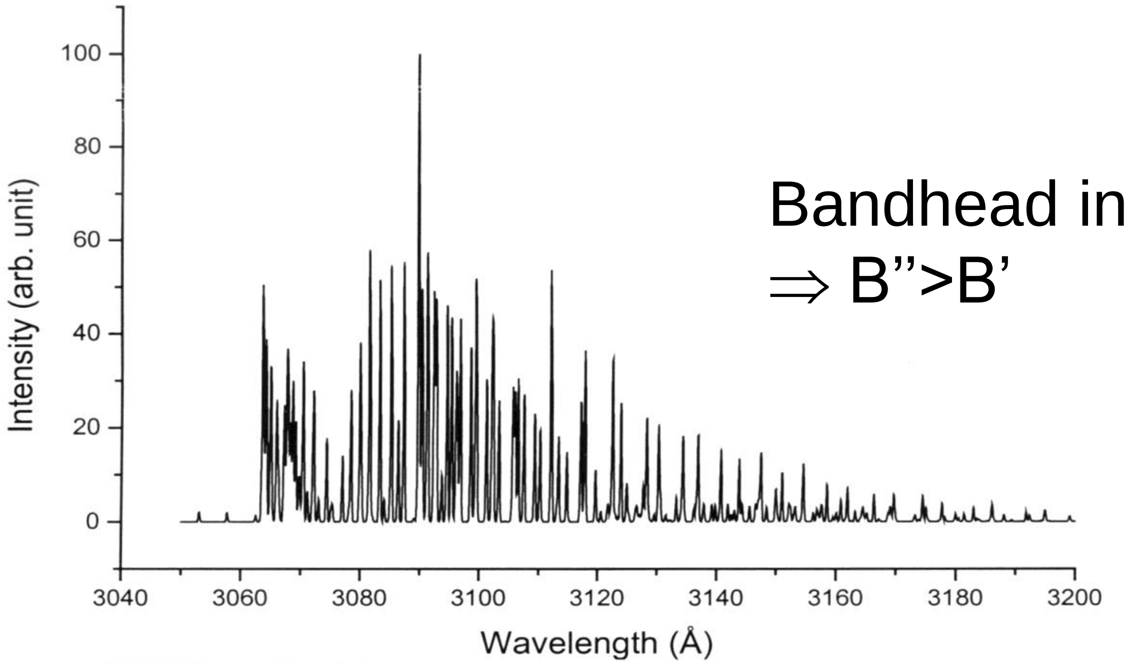
**Q-branch is possible for electronic trans.**

**P and R branches**: $\tilde{\nu} = \tilde{\nu}_{00} + am + bm^2$
**Q branch**: $\tilde{\nu} = \tilde{\nu}_{00} + bm + bm^2$
where $a = B' + B''$ and $b = B' - B''$

$m = -J$ for P-branch transitions
$m = J + 1$ for R-branch transitions
$m = J$ for Q-branch transitions

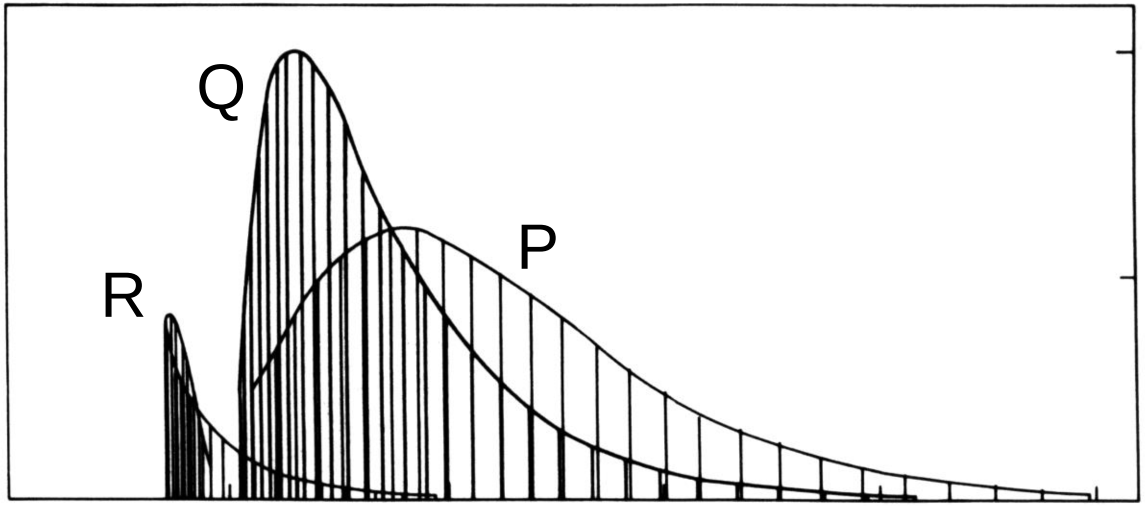
→ Fortrat diagrams

# Absorption spectrum of OH

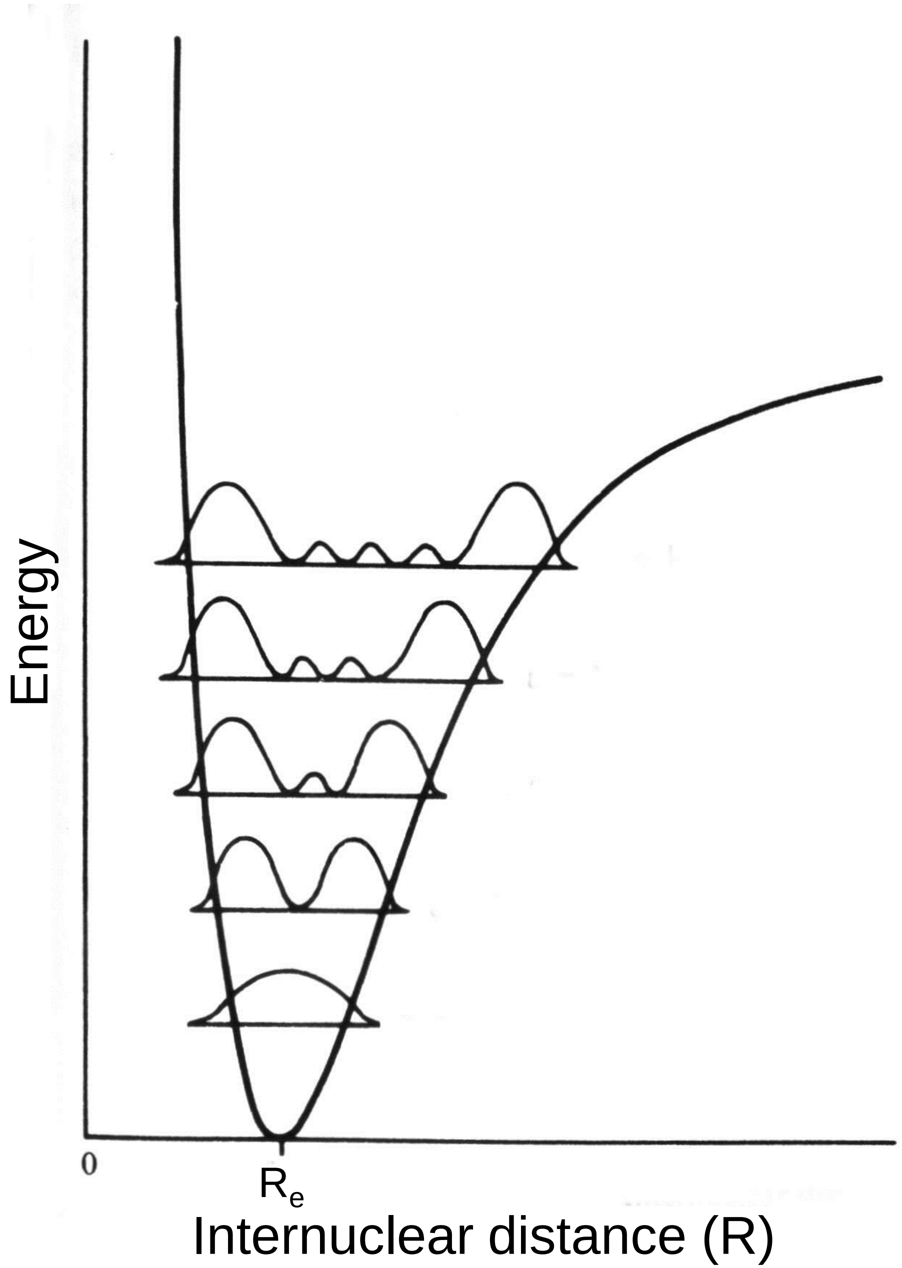


Bandhead in the R-branch

$\Rightarrow$ B''>B'



# Probability distributions for vibrational states

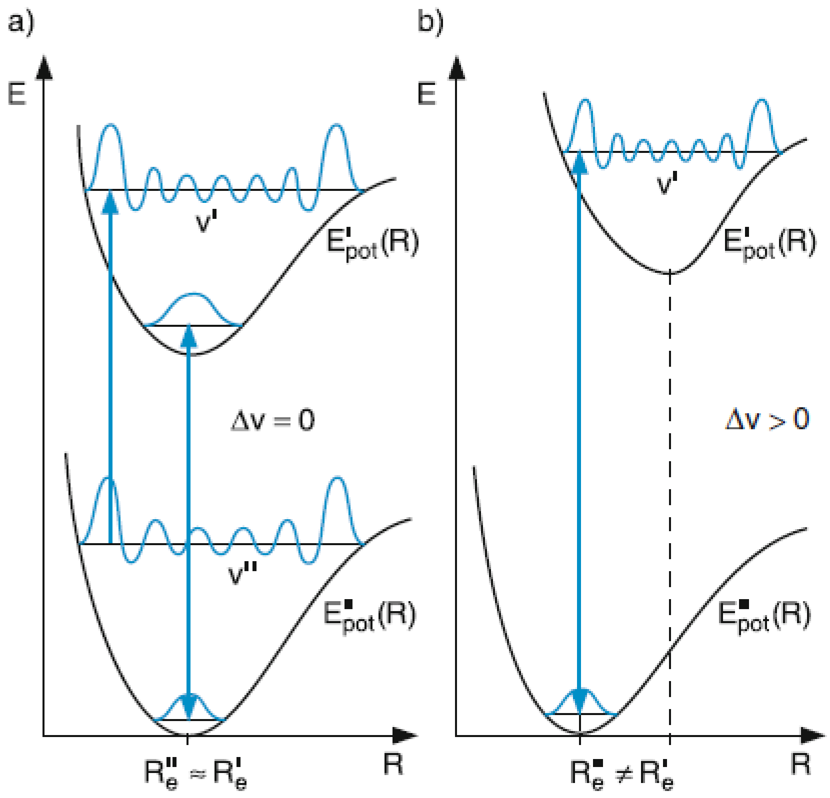


It is more probable to find a molecule at the end positions than at the equilibrium position for excited vibrational states!

# Strength of rovibronic transitions

The strength of a vibrational transition depends on the overlap between the vibrational wave functions in the two states (Franck-Condon Factor, FCF).

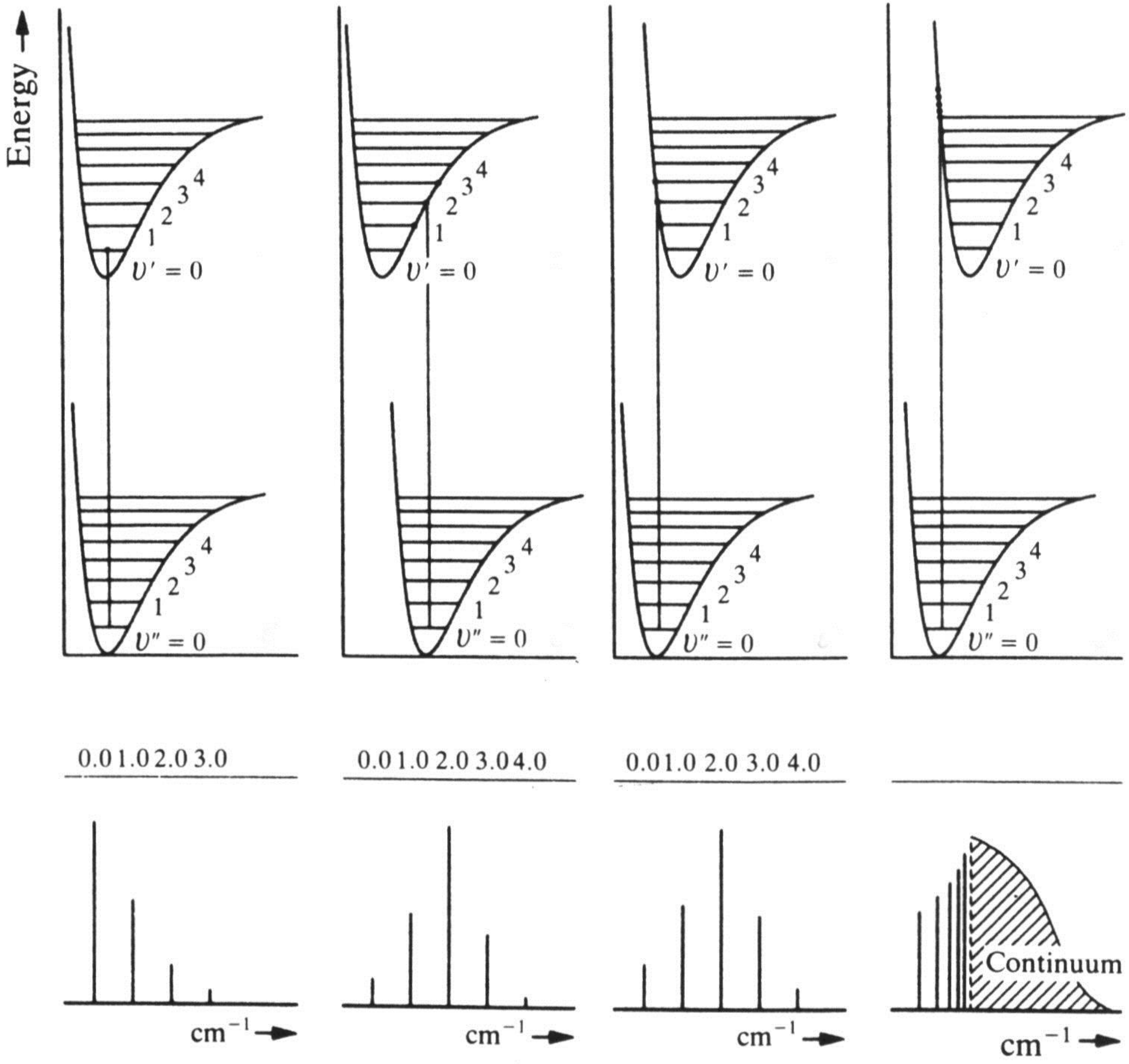
**Franck-Condon principle:**
An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciable during the transition. This means that **the transitions can be represented by vertical arrows**.



a) FCF maximum for $\Delta v = 0$ transitions
b) FCF maximum for $\Delta v > 0$ transitions

Svanberg: page 60

# Vibrational band structure

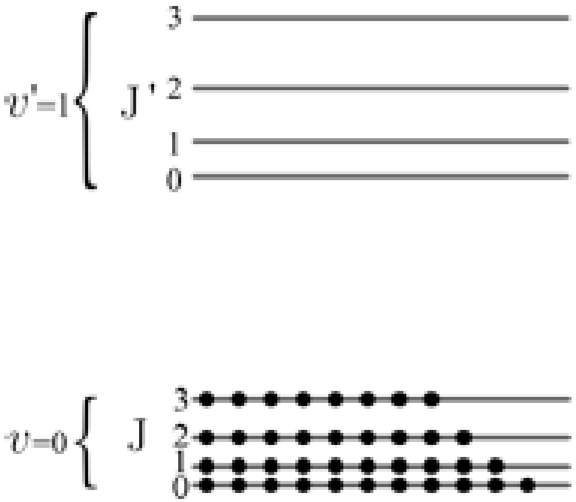


There is essentially no selection rule for vibrational states when undergoing electronic transitions.

**Svanberg: page 60**

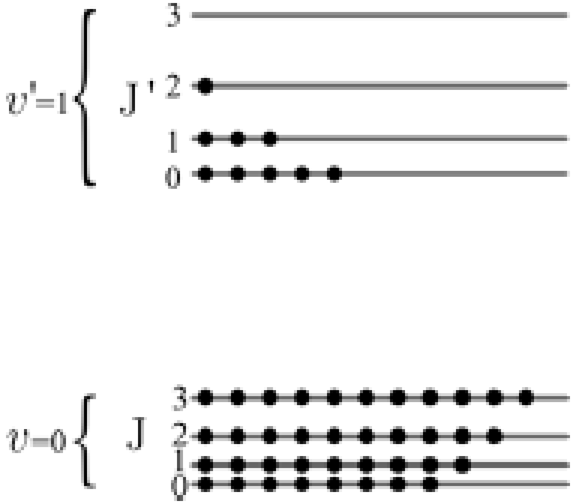
# Population distributions

**T ~ 300 K**



(a)

**T > 1000 K**



(b)

# Vibrational population distributions

The population distribution may generally be written

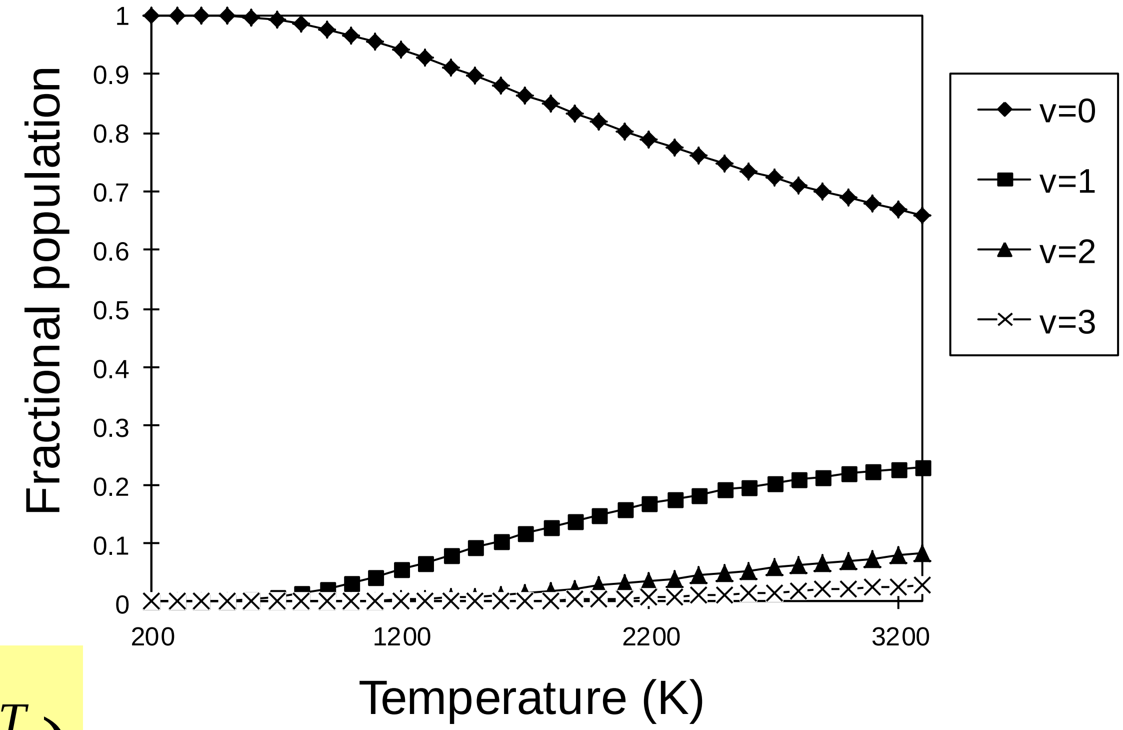
$$\frac{N_j}{N} = \frac{g_j e^{-\varepsilon_j / kT}}{\sum_j g_j e^{-\varepsilon_j / kT}}$$

($\varepsilon_j$ is the energy of a state j)

The vibrational population distribution can be written:

$$\frac{N_v}{N} = e^{-vhc\omega_e / kT}\left(1 - e^{-hc\omega_e / kT}\right)$$

$N_v$: Population in state v
N: Total population



**Population distribution of $N_2$**

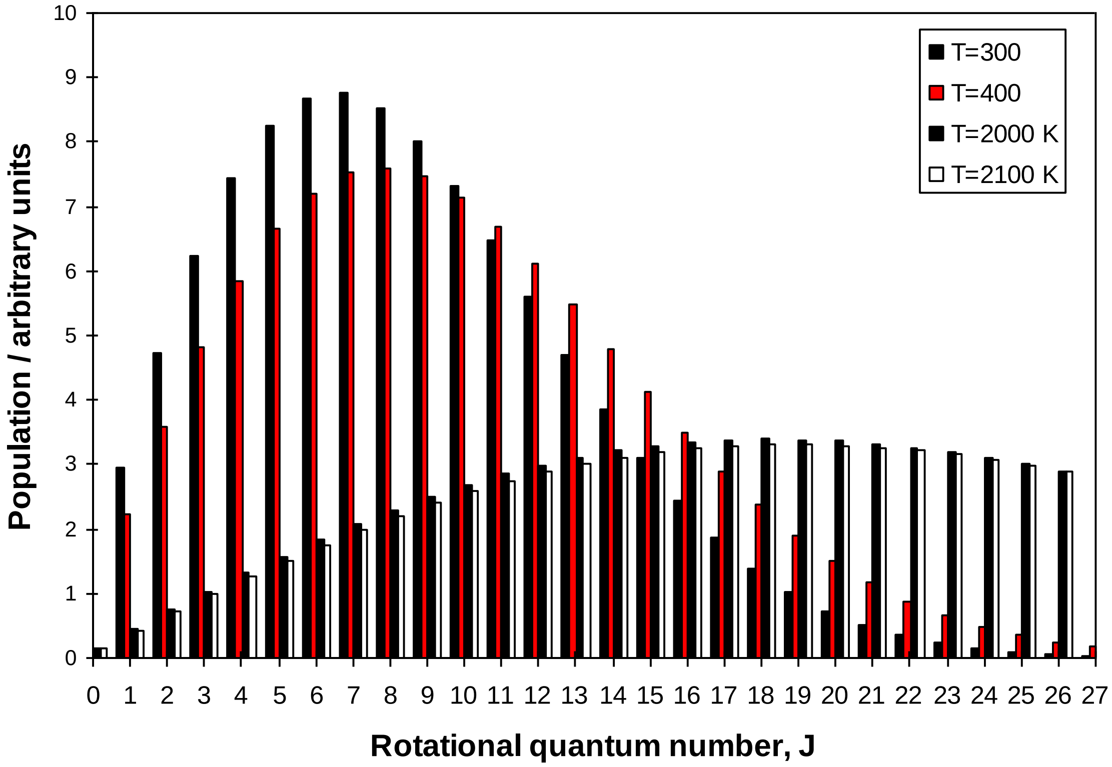
**Svanberg: page 59**

# Rotational population distributions

The rotational pop. distribution can be written:

$$\frac{N_J}{N} = \frac{1}{Q_{rot}}(2J+1)\,e^{-BJ(J+1)hc/kT}$$

$$Q_{rot} \approx \frac{kT}{hcB}$$



Where is max. population?

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

$$\frac{\partial f(J)}{\partial J} = 0 \quad \Rightarrow$$

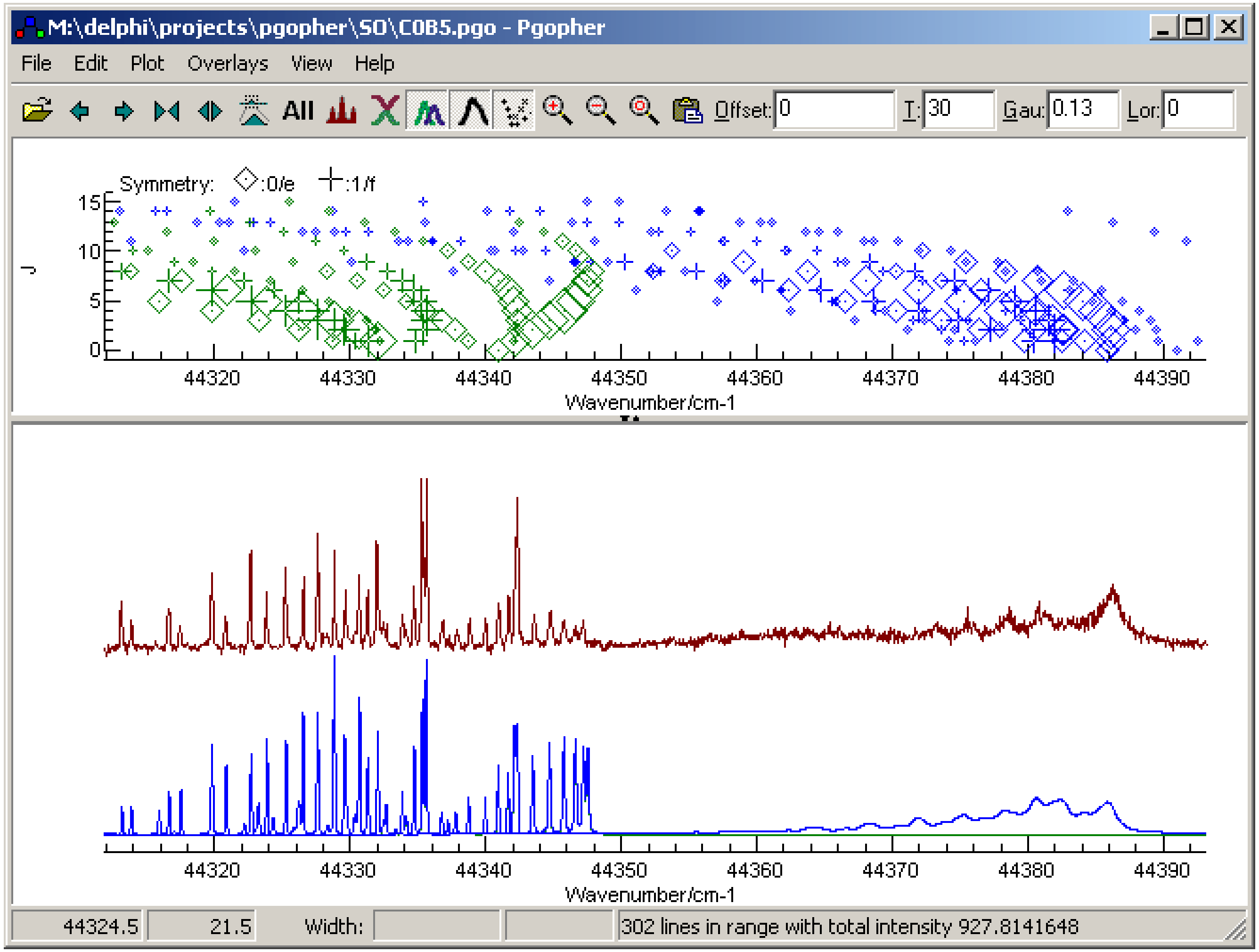
$$J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

**Svanberg: page 59**

# Data bases and simulation tools

HITRAN/HITEMP: http://hitran.org/

PGOPHER: http://pgopher.chm.bris.ac.uk/



Offset: 0 T: 30 Gau: 0.13 Lor: 0

44324.5 | 21.5 | Width: | 302 lines in range with total intensity 927.8141648

*PGOPHER, a program for rotational, vibrational and electronic spectra.*

# The End