Molecular spectroscopy

Multispectral imaging (FAFF 020, FYST29)
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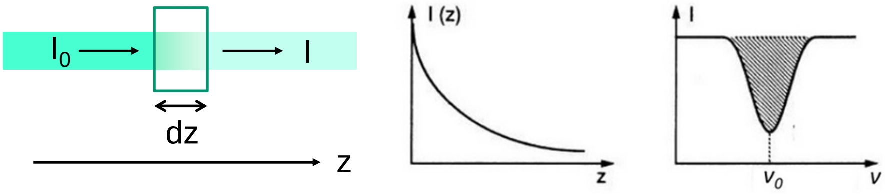
Outline

- Brief introduction to molecular spectroscopy
- Atomic structure (recap)
- Molecular structure
  - Electronic structure
  - Rotational structure
  - Coupling of rotational and electronic modes
  - Vibrational structure
  - Vibrational-rotational interaction
- Population distributions

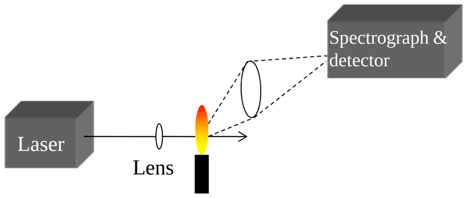
Major types of molecular spectroscopy

Absorption

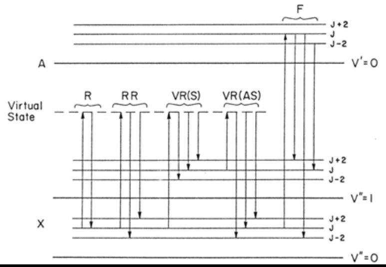


$$I(z,\nu) = I_0 e^{-\sigma(\nu)Nz}$$ (Beer-Lambert law)

Emission (e.g. fluorescence)

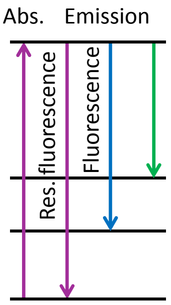


Scattering

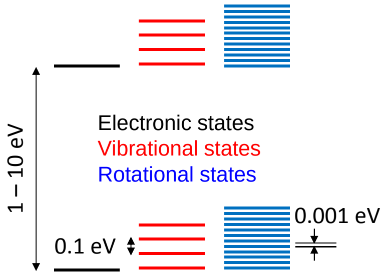


Liquid and solid phase → broad energy bands

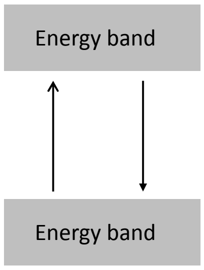
Free atoms



Free molecules

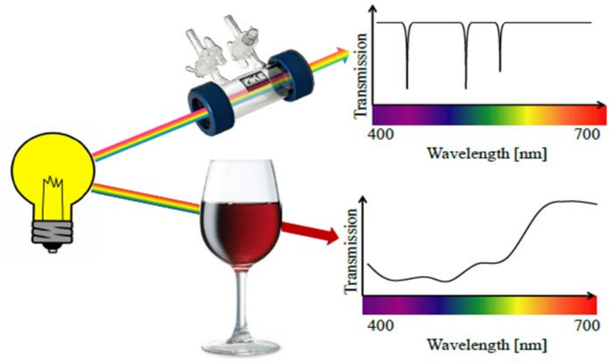


Condensed matter



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



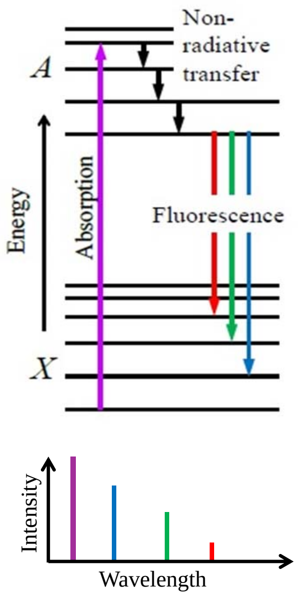
Gas absorption
Gives rise to sharp spectral lines. Most light is transmitted.

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.

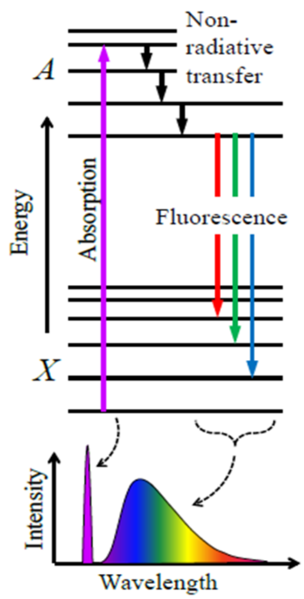
P. Lundin, Doctoral Thesis, LRAP-488, Lund University, 2014

Fluorescence in gases, liquids, and solids

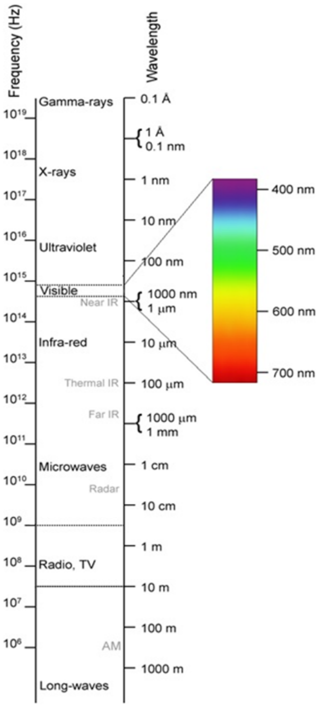
Gases



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 terms

Frequency: $\nu = \frac{v}{\lambda}$ (Hz or s^{-1}) $\omega = 2\pi\nu$ (rad/s)

ω is angular frequency

Wavelength: $\lambda = \frac{v}{\nu}$ (m) (most often given in nm or Å)

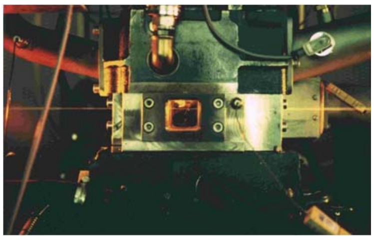
Speed: $v = \frac{c}{n}$ (m/s)

"Vacuum wavelength" $\lambda_0 = \frac{c}{\nu}$ (m)

Energy: $E = h\nu = \frac{hc}{\lambda_0} = E_{upper} - E_{lower}$ (J)

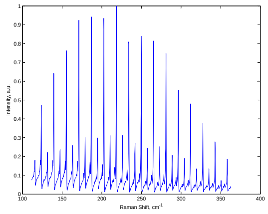
Wavenumber: $\varepsilon = \frac{E}{hc} = \frac{1}{\lambda_0}$ (m^{-1}) (most often it is given in cm^{-1})

Molecular spectrometry concept

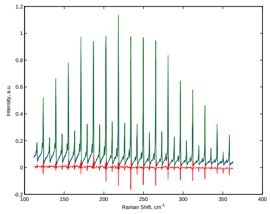


Temperature measurement using Rotational-CARS

Measure



Analyze

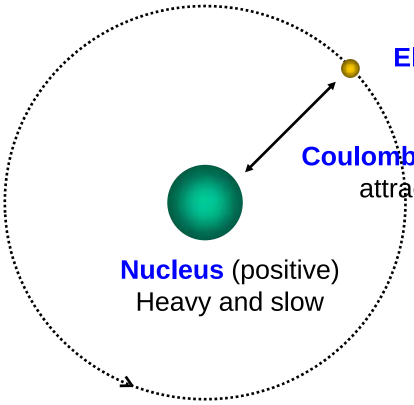


Predict

T = 1800 K

Atomic structure basics

Hydrogenic system



Electron (negative)
light and mobile

Coulomb (electric)
attraction

Nucleus (positive)
Heavy and slow

Summary: Atomic structure

The energy levels and wavefunctions are calculated by solving Schrödinger's equation:

Hamiltonian

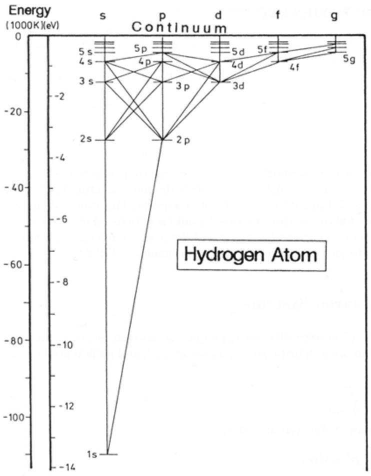
$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi_{n,l}}_{\text{Kinetic energy term}}\underbrace{-\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r^2}\psi_{n,l}}_{\text{Potential energy term}} = E_{n,l}\psi_{n,l} \Leftrightarrow \mathbf{H}\psi_{n,l} = E_{n,l}\psi_{n,l}$$

Z is atomic number

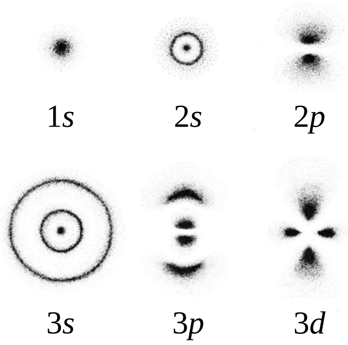
- $\psi_{n,l}$ are electronic wavefunctions
- $|\psi_{n,l}|^2$ gives the electronic charge distribution (probability density function)
- Each wavefunction has an energy $E_{n,l}$ (eigenvalue) associated with it
- n is the principal quantum number. The distance between the electron and the nucleus scales as n^2. Furthermore electron energies scales as $\mathrm{E}\propto 1/\mathrm{n}^2$
- l is the angular momentum quantum number. Atomic orbitals corresponding to states with l = 0,1,2,3,… are denoted by the letters s,p,d,f,… respectively

Example: Hydrogen atom

Energy level diagram

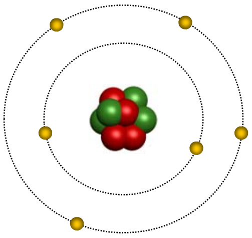


Corresponding electron probability density functions, $|\psi_{n,l}|^2$

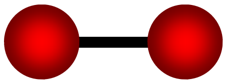


Molecular structure basics

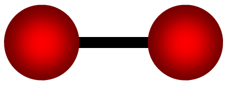
Molecular energy structure



Electronic energy

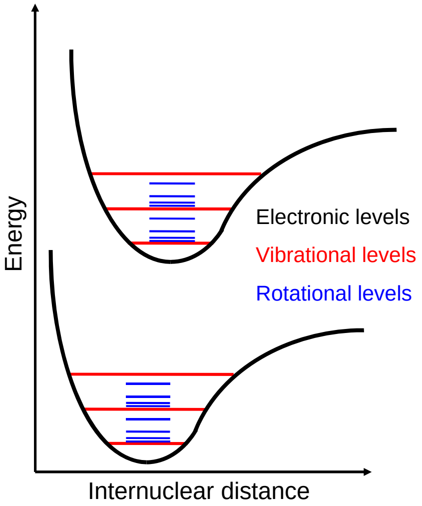


Vibrational energy



Rotational energy

Energy level diagram



Quantum mechanics - Molecules

The Schrödinger equation:

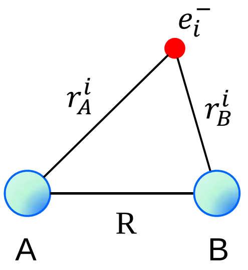
$$-\frac{\hbar^2}{2m}\nabla^2\psi_n(\vec{r})+V(\vec{r})\psi_n(\vec{r})=E_n\psi_n(\vec{r})\Leftrightarrow \mathbf{H}\psi_n(\vec{r})=E_n\psi_n$$

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

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

The Born-Oppenheimer 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**.



$$V(R) = -\frac{e^2}{4\pi\varepsilon_0}\left(\sum_i \frac{Z_A}{r_{Ai}} + \sum_i \frac{Z_B}{r_{Bi}} - \frac{1}{2}\sum_i \sum_{i \neq j} \frac{1}{r_{ij}}\right)$$

all electrons

Solve SE: $\left[-\frac{\hbar^2}{2m}\Delta_i + V(R)\right]\psi = E_n\psi \quad \Rightarrow E_n$

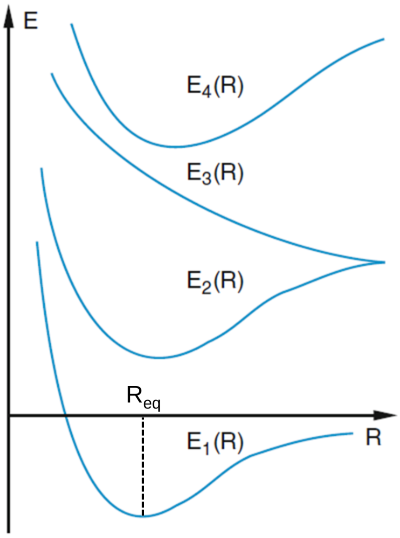
The total energy also contains the potential energy due to the interaction between the nuclei:

$$E_{tot}(R) = E_n + V_{nuc-nuc}(R) \qquad V_{nuc-nuc}(R) = \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R}$$

(Z: atomic number)

Repeat the calculation for different R ⇒ Potential energy curve

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

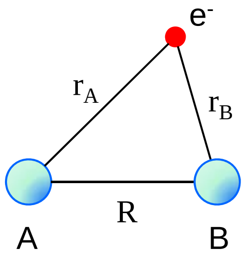
It also means $\psi_{molecule} = \psi_{e-} \cdot \Psi_{nuclei}$

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

The B-O approximation is not a bad one in almost all cases and it simplifies the calculations enormously!

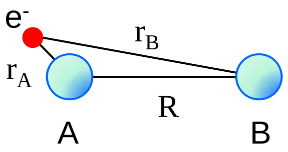
The molecular orbital approximation

Consider the simplest molecule, i.e. H_2^+
And assume that the nuclei are clamped at a given distance R (B-O approx.)



$$V(R) = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B}\right)$$

Let $r_A << r_B$ $$V(R) \approx -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A}\right)$$



This is the potential of a hydrogen atom!
Its ground state orbital is 1s

Write an approximative wavefunction then of two 1s-orbitals

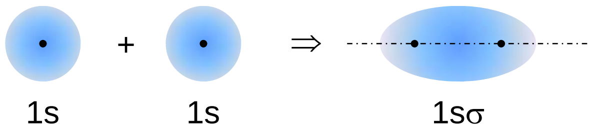
$$\Psi = N[\psi_{1s}(A) + \psi_{1s}(B)]$$

Linear combination of atomic orbitals (LCAO)

Linear combination of atomic orbitals (LCAO)

$$\Psi = N[\psi_{1s}(A) + \psi_{1s}(B)]$$

This particular orbital is called a σ-orbital



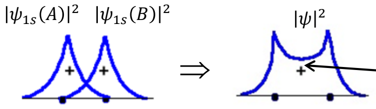
Cylindrical symmetry

The electron probability distribution is given by $|\psi|^2$

$$|\psi|^2 = N^2(|\psi_{1s}(A)|^2 + |\psi_{1s}(B)|^2 + 2\psi_{1s}(A)\psi_{1s}(B))$$

Constructive interference
(overlap density)

$\psi_{1s}(A) \propto e^{-r_A/a_0}$ $\psi_{1s}(B) \propto e^{-r_B/a_0}$



Symmetric charge distribution

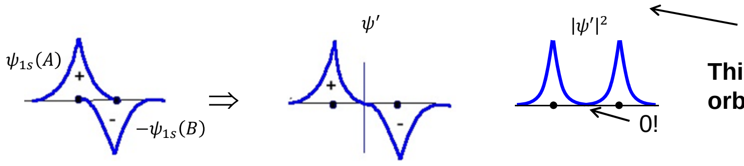
Enhanced e^- probability here ⇒ stronger binding

The H_2^+ electron is a 1sσ electron in ground state.
This is a bonding orbital.

Antibonding orbitals

$\psi' = N[\psi_{1s}(A) - \psi_{1s}(B)]$ This is another possible linear combination of the two 1s orbitals

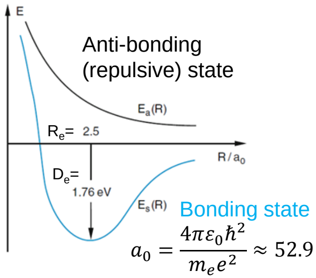
$$|\psi'|^2 = N^2(|\psi_{1s}(A)|^2 + |\psi_{1s}(B)|^2 - 2\psi_{1s}(A)\psi_{1s}(B))$$



Destructive interference

This is an anti-bonding orbital designated 1sσ*

PECs based on LCAO



$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \approx 52.9 \text{ pm}$$

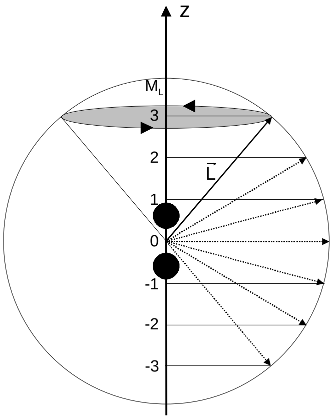
Electronic structure

- 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



Electronic spin

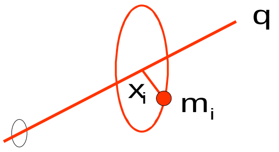
- Molecules also have spin angular momentum. S precesses around the internuclear axis
- S can have 2S+1 different projections, Σ, on the internuclear axis
- 2S+1 = multiplicity of the state
- Spin-orbit interaction between Λ and Σ
- Total angular momentum: Ω = Λ + Σ

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

Molecular rotation

Quantum mechanical picture

Classical mechanics:

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

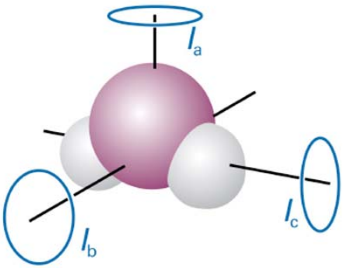
Quantum mechanics: (J_q is an operator of the angular momentum)

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

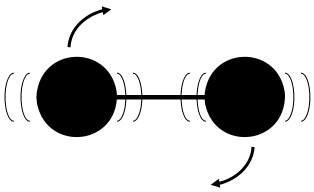
There is no potential energy associated with pure rotational motion

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: ~10^{-15} s
Vibrations: ~10^{-14} s
Rotations: ~10^{-13}-10^{-12} s

Diatomic molecules

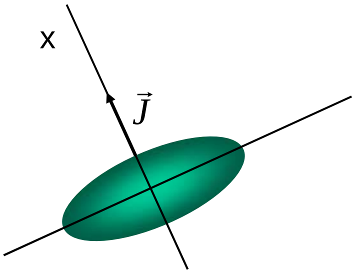
$$\mathbf{H} = \frac{\mathbf{J}^2}{2I} \quad \Rightarrow \text{eigenvalues: } E(J, M_J) = \frac{J(J+1)\hbar^2}{2I}$$

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

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

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

2J+1 possible M_J values for each rotational level
⇒ 2J+1-fold degenerate.



The rotational constant, B:

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

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

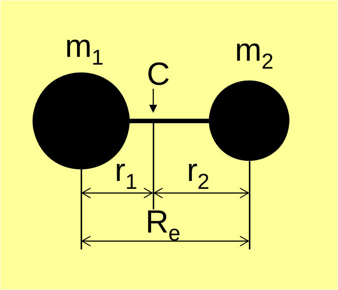
Energy levels for a diatomic molecule

Solutions to the Schrödinger equation:

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

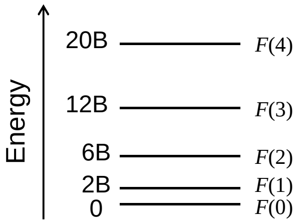
$$I = \mu R_e^2$$

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



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

J=0, 1, 2, …. ⇒



The energy separation increases with increasing J

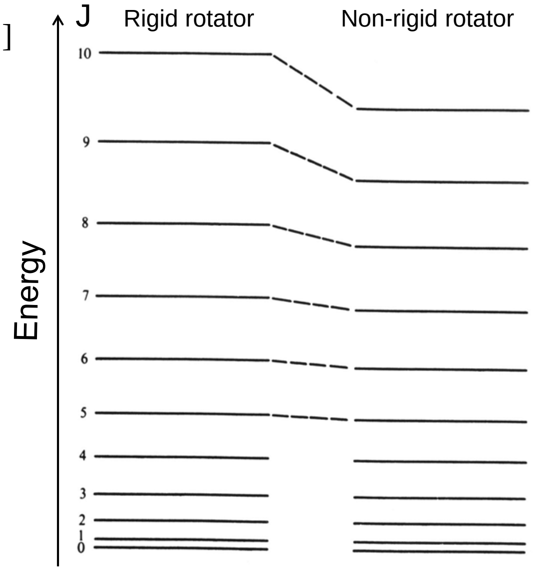
Energy levels for non-rigid rotator

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

D centrifugal distortion constant

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

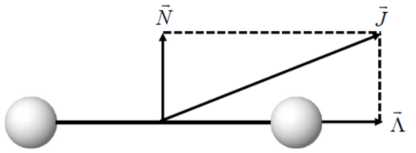
F(18) = 682,72 cm^{-1} for N_2
with D-correction



Coupling of rotational and electronic modes

no electronic spin (S = 0)

- Taken into account also the electrons revolving about the nuclei $\Rightarrow$ moment of inertia about the internuclear axis $\Rightarrow$ Angular momentum $\vec{\Lambda}$ directed along the internuclear axis



$\vec{N}$: Angular momentum of nuclei

$\vec{\Lambda}$: Projection of electron orbital angular momentum

$\vec{J}$: Total angular momentum; $\vec{J} = \vec{N} + \vec{\Lambda}$

- The rotational levels of such a symmetric top are the same as those of a simple linear rotor, except that all levels are shifted upwards in energy by a factor (A-B)Λ^2

$$F(J) = BJ(J + 1) + (A - B)\Lambda^2$$

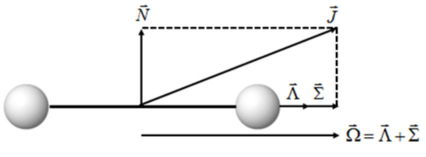
(Λ is the orbital angular momentum quantum number)

Levels with J < Λ are absent and each level is split into two sublevels (Λ-doubling)

Coupling of rotational and electronic modes

with non-zero electronic spin (S $\neq$ 0)

For strong coupling of the spin to the internuclear axis (Hund's coupling case a) the projections of the spin and electron orbital angular momentum onto the internuclear axis forms a net component $\vec{\Omega} = \vec{\Lambda} + \vec{\Sigma}$



$\vec{N}$: Angular momentum of nuclei

$\vec{\Lambda}$: Projection of electron orbital angular momentum

$\vec{\Sigma}$: Projection of electron spin

$\vec{J}$: Total angular momentum; $\vec{J} = \vec{N} + \vec{\Omega}$

Since $\Lambda \neq 0$ there is an associated magnetic field due to the net current about the axis. This field interacts with the spinning electrons. This leads to **spin-orbit coupling** and thus spin-splitting of energy levels.

$$F(J) = BJ(J + 1) + (A - B)\Omega^2$$

NB: The model is just an approximation! The coupling may change as J ranges from low to high levels!

Vibrational energy levels

Solutions to Schrödinger equation for harmonic oscillator:

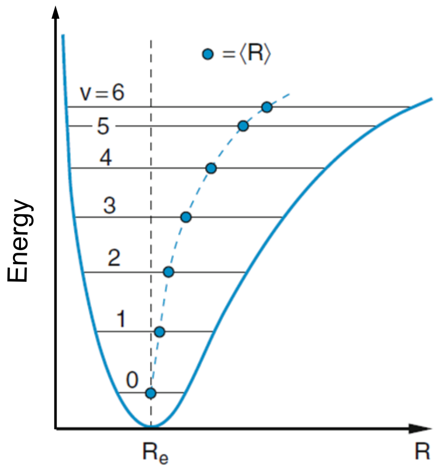
$$G(v) = \omega_e \left(v + \frac{1}{2}\right) \quad (\mathrm{cm}^{-1})$$

G(0) = 0.5ω_e, G(1) = 1.5ω_e, G(2)= 2.5ω_e

A better description of the energy 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.



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

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.

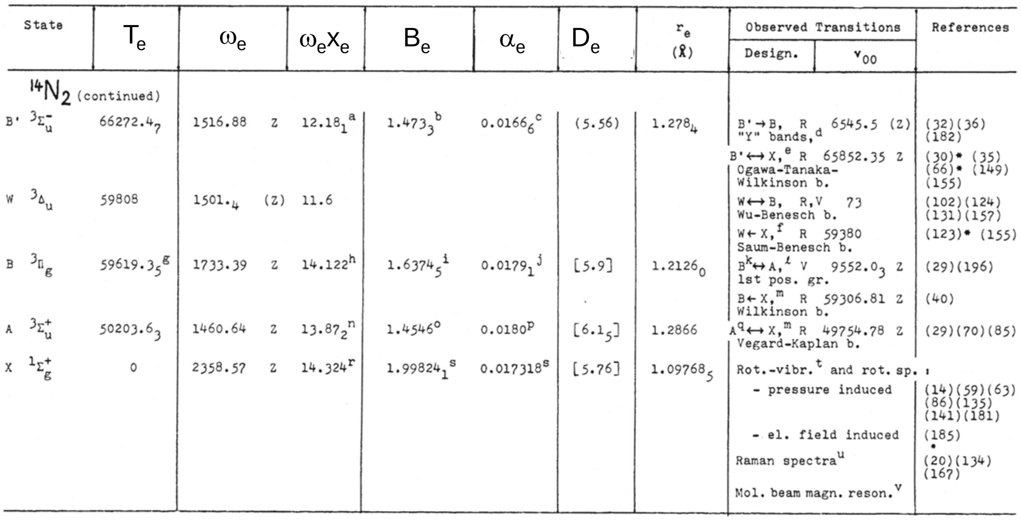
The rotational constant B_v in a vibrational state v, can be expressed as

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

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



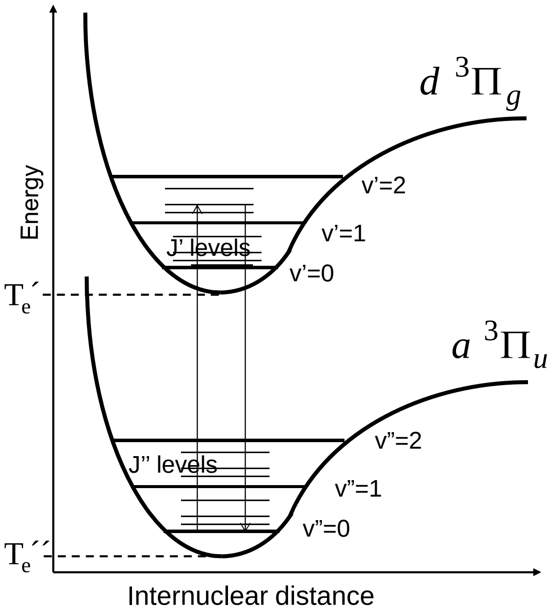
State	T_e	ω_e	$\omega_e x_e$	B_e	α_e	D_e	r_e (Å)	Observed Transitions: Design.	Observed Transitions: ν_{00}	References
$^{14}N_2$ (continued)										
B' $^3\Sigma_u^-$	66272.4_7	1516.88 Z	$12.18_1{}^a$	$1.473_3{}^b$	$0.0166_6{}^c$	(5.56)	1.278_4	B'→B, R "Y" bands,^{d}	6545.5 (Z)	(32)(36) (182)
								B'↔X,^{e} R Ogawa-Tanaka-Wilkinson b.	65852.35 Z	(30)* (35) (66)* (149) (155)
W $^3\Delta_u$	59808	$1501._4$ (Z)	11.6					W↔B, R,V Wu-Benesch b.	73	(102)(124) (131)(157)
								W←X,^{f} R 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 1st pos. gr.	9552.0_3 Z	(29)(196)
								B←X,^{m} R 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 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) (86)(135) (141)(181)
								- el. field induced		(185)
								Raman spectra^u		(20)(134) (167)
								Mol. beam magn. reson.^{v}		

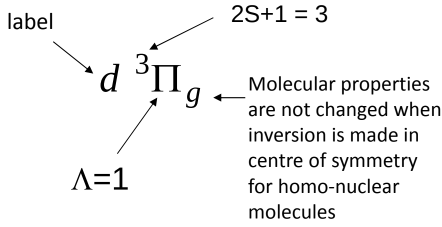
From Huber and Herzberg: "Constants of diatomic molecules"

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

Nomenclature and band structure

Rovibronic transitions





For transitions between J-levels
ΔJ = -1, 0, or +1 (not J = 0 to J = 0)

ΔJ = -1 is called a P-branch
ΔJ = 0 is called a Q-branch
ΔJ = +1 is called an R-branch

Rovibronic transitions

Spectrum for a symmetric top (Λ≠0, S=0) and ΔΛ = 0 transitions

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

Upper state energy: $E' = T_e' + G(v') + B'J'(J'+1) + (A' - B')\Lambda^2$

Lower state energy: $E'' = T_e'' + G(v'') + B''J''(J''+1) + (A'' - B'')\Lambda^2$

$$P(J'') = \underbrace{T_e' - T_e'' + G(v') - G(v'') + (A' - A'' - B' + B'')\Lambda^2}_{\tilde{\nu}_{00}} - (B' + B'')J + (B' - B'')J^2$$

$\tilde{\nu}_{00}$ (a constant called band origin)

$$P(J'') = \tilde{\nu}_{00} - (B' + B'')J + (B' - B'')J^2$$

$$Q(J'') = \tilde{\nu}_{00} + (B' - B'')J + (B' - B'')J^2$$

$$R(J'') = \tilde{\nu}_{00} + (B' + B'')(J+1) + (B' - B'')(J+1)^2$$

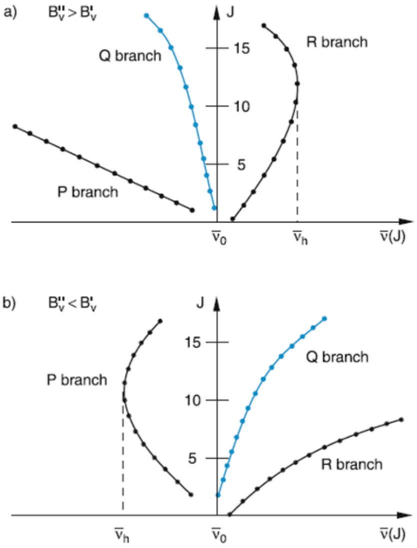
$m_P = -J$
$m_Q = J$
$m_R = J + 1$

➡

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 $b = B' - B''$

Fortrat diagrams

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 $b = B' - B''$

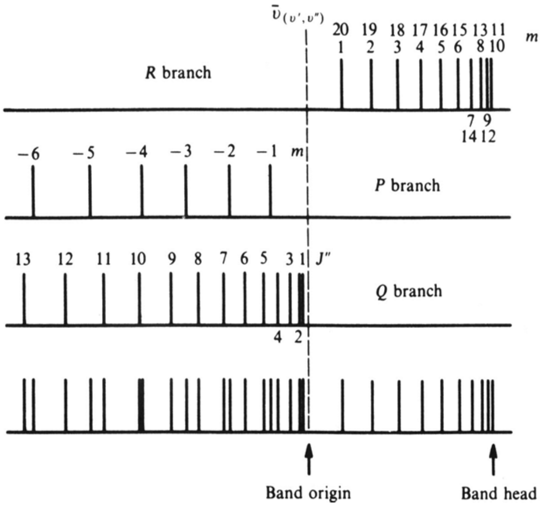


Plotting the results of these expressions in diagrams with m(or J) vs $\tilde{\nu}$ results in a so-called Fortrat daigram.

When B'' > B' there is a bandhead in the R-branch (see panel a)

When B'' < B' there is a bandhead in the P-branch (see panel b)

Band structure (2)



$\nu_{P,R} = \nu(v',v'') + (B'+B'')\ m + (B'-B'')\ m^2$

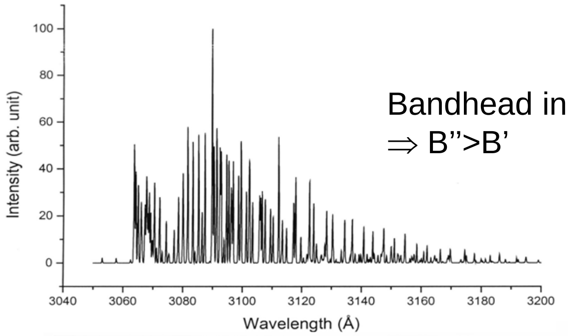
$\nu(v',v'')$ is the band origin

m = -1,-2,-3 for P-branch
m = 1,2, 3 for R-branch

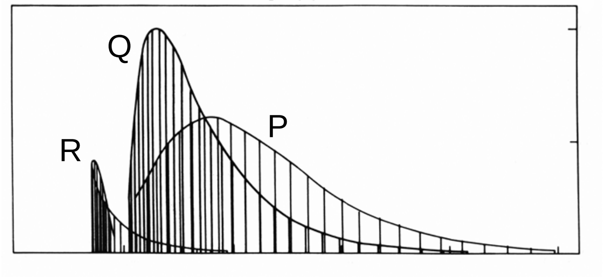
B' < B'' ⇔ band head in R-branch
⇔ degradation towards red

B' > B'' ⇔ band head in P-branch
⇔ degradation towards violet

Absorption spectrum of OH



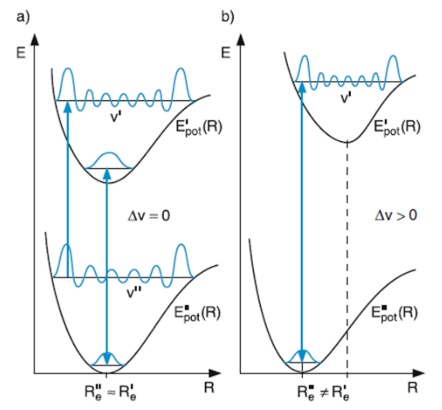
Bandhead in the R-branch
⇒ B''>B'



Vibrational structure

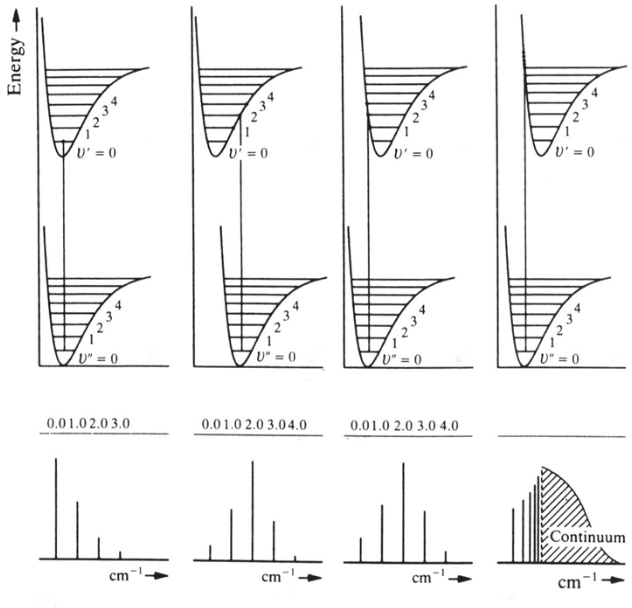
The strength of a vibrational transition depends on the overlap between the vibrational wave functions in the two states (the FCF).

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 Δv = 0 transitions
b) FCF maximum for Δv > 0 transitions

Vibrational band structure



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

Population distributions

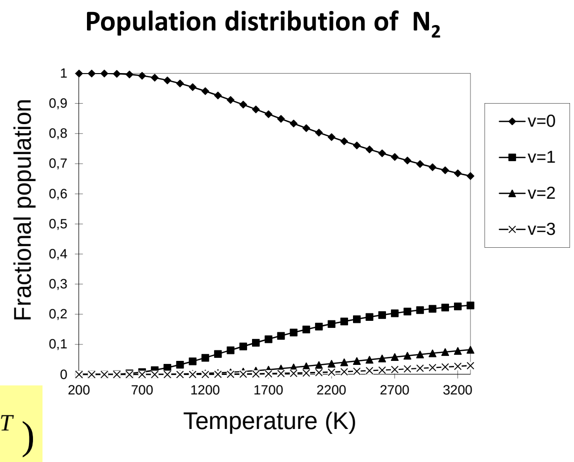
Vibrational population distributions

The population distribution may generally be written

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

The vibrational population distribution can be calculated as

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



Rotational population distribution

The rotational population distribution can be calculated as

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

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

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

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

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

Rotational population distribution