CHAPTER 3

ROTO-VIBRATIONAL SPECTROSCOPY

3.1 BORN-OPPENHEIMER APPROXIMATION

The Hamiltonian H or a diatomic or polyatomic molecule is the sum of the kinetic energy T and the potential energy V.

In a molecule the **kinetic energy** T consists of contributions T_e and T_n from the motions of the electrons and nuclei, respectively..

The **potential energy** comprises two terms, V_{ee} and V_{nn} due to coulombic repulsions between the electrons and between the nuclei, respectively, and a third term V_{en} due to attractive forces between the electrons and nuclei.

So, the Hamiltonian H has the form:

$$H = T + V = T_e + T_n + V_{ee} + V_{nn} + V_{en}$$

For fixed nuclei $T_n = 0$ and $V_{nn} = cost$, and there is a set of electronic wave functions ψ_e which satisfy the Schrodinger equation:

$$H_e \psi_e = E_e \psi_e$$

where $H_e = T_e + V_{ee} + V_{en}$

3.1 BORN-OPPENHEIMER APPROXIMATION

$$H_e = T_e + V_{en} + V_{en}$$

Since H_e depends on nuclear coordinates, because of the V_{en}, so do ψ_e and E_e will depend on nuclear coordinates.

In the **Born–Oppenheimer approximation** proposed in 1927, it is assumed that vibrating nuclei move so slowly compared with electrons.

In other words, the electrons "adjust“ instantaneously to any nuclear motion: they are said to follow the nuclei. .

For this reason, E_e can be treated as part of the potential field in which the nuclei move, so that:

$$H_n = T_n + V_{nn} + E_e$$

and the Schrodinger equation for nuclear motion will be:

$$H_n \psi_n = E_n \psi_n$$

3.1 BORN-OPPENHEIMER APPROXIMATION

It follows from the Born–Oppenheimer approximation that the total wave function ψ can be factorized:

$$\psi = \psi_e(q, Q)\psi_n(Q)$$

where the q are electron coordinates and Q as well as q.

Impose it as a solution of the Schrodinger equation of the nuclei-electron system:

$$H\psi = E\psi$$

It follows:

$$E = E_e + E_n$$

The wave function ψ_n can be factorized further into a vibrational part ψ_v and a rotational part ψ_r:

$$\psi_n = \psi_v\psi_r$$

3.1 BORN-OPPENHEIMER APPROXIMATION

similarly, as we saw for a centrosymmetric finite potential in which the wave function is factorized into a radial part and an angular part.

Thus, it follows that the energy of the nuclei can be expressed as the sum of a contribution E_v given by vibration and one E_r given by rotation, $E_n = E_v + E_r$.

In summary, the wave function of a molecule can be factorized as:

$$\psi = \psi_e \psi_v \psi_r$$

and its energy eigenvalues as:

$$E = E_e + E_v + E_r$$

In conclusion, it is for these reasons that we can treat electronic, vibrational and rotational spectroscopy separately.

3.2 ROTATIONAL SPECTROSCOPY

3.2.1 The rigid rotor

A useful approximate model for the end-over-end rotation of a diatomic molecule is that of the rigid rotor in which the bond joining the nuclei is regarded as a rigid, weightless rod.

To study the rotational spectra of molecules, it is useful to classify them according to the **main moments of inertia**.

The moment of inertia I of a molecule referred to any axis passing through its center of mass is defined as:

$$I = \sum_i m_i r_i^2$$

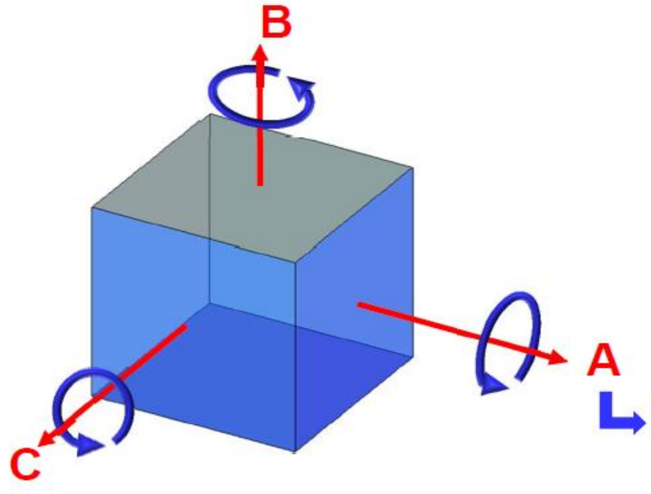
where m_i are the masses of the single atoms and r_i their distances from the axis.

One can always find one axis, called the $c - axis$, about which the moment of inertia has its maximum value, and another axis, labeled the $c - axis$, about which I has its minimum value. It can be shown that the a and c axes must be mutually perpendicular.

3.2 ROTATIONAL SPECTROSCOPY

3.2.1 The rigid rotor

These two axes, together with another axis that is perpendicular to both ($b - axis$), constitute the principal axes of inertia referred to the principal moments of inertia I_a, I_b and I_c.



Thus, according to convention, the principal axes are ordered:

$$I_c \geq I_b \geq I_a$$

Depending on the relative size of the inertia moments, I_a, I_b and I_c, rotors can de divided into four classes: linear rotors, symmetric tops, spherical tops and asymmetric rotors.

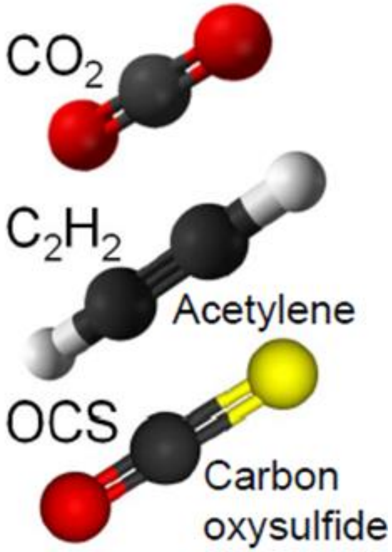
3.2 ROTATIONAL SPECTROSCOPY

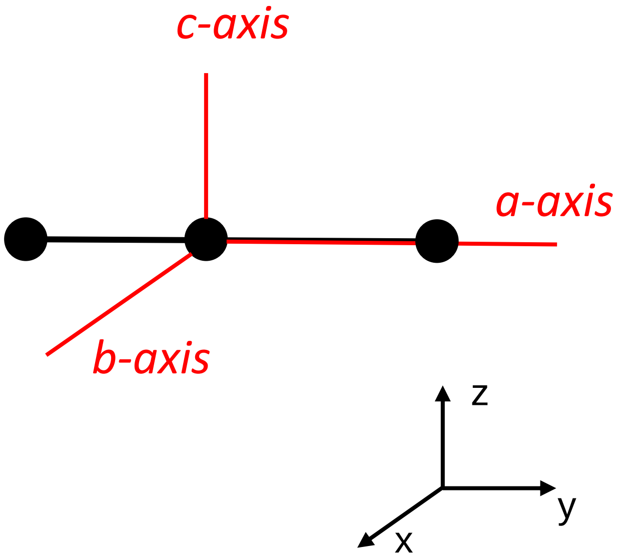
3.2.2 Linear rotors. Frequencies. Selection rules. Intensity

For a linear rotor:

$$I_b = I_c$$
$$I_a = 0$$

where $b - axis$ and $c - axis$ may be in any direction perpendicular to the internuclear $\mathrm{a} - axis$

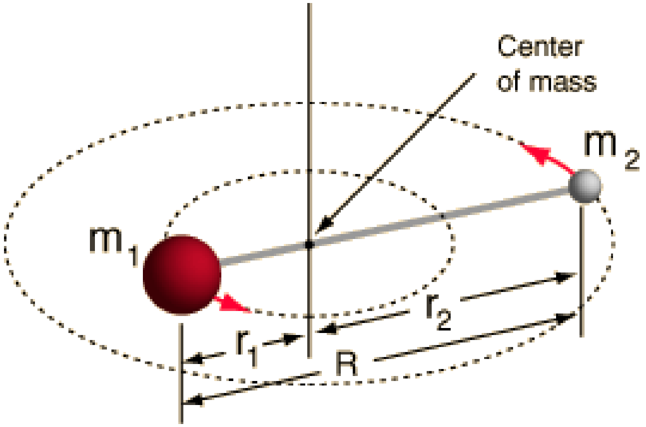




3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. **Frequencies.** Selection rules. Intensity

This rigid rotor model has two masses m_1 e m_2 attached to each other with a fixed distance between the two masses.



In the Solid-State Physics course (**Chapter 5, paragraph 5.5.2**) we set the Schrodinger equation for a centrosymmetric potential in spherical coordinates.

We separate the eigenfunction in an angular part $\Upsilon(\theta, \varphi)$ and a radial part $R(r)$.

The angular part has been expressed in terms of the Legendrian operator Λ^2 .

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. **Frequencies.** Selection rules. Intensity

$$\frac{1}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial R(r)}{\partial r} + \Lambda^2\Upsilon(\theta,\varphi) = -\frac{2mr^2E}{\hbar^2}$$

At r fixed, we determined the angular part of the wave function by solving angular part of Schrodinger equation.

$$\Lambda^2\Upsilon(\theta,\varphi) = \mathcal{E}\Upsilon(\theta,\varphi)$$

where $\mathcal{E}$ are the energy eigenvalues of the angular part.

This is the equation typically solved for the angular momentum operator in spherical coordinates, and the eigenfunctions are spherical harmonics :

$$\Upsilon_J^m(\theta,\varphi) = A_{J,m_J}e^{im_J\varphi}P_J(cos\theta)$$

where $P_l(cos\theta)$ are Legendre polynomials in sine and cosine terms, and J and m_J are integers. Fixed $J = 0,1,2,\ldots$, m_J assumes only the following values:, $-J+1 \ldots J, J+1$.

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. **Frequencies.** Selection rules. Intensity

J is the total angular momentum and m_J is the z-component of angular momentum. Hereafter, we will omit the subscript J of the quantum number m_J.

The eigenvalues are :

$$\mathcal{E} = J(J+1)$$

For linear rotors, we can use the same model by introducing the reduced mass

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

With this assumption, the rotational energies are :

$$E_r = \frac{h^2}{8\pi^2 \mu r^2} J(J+1)$$

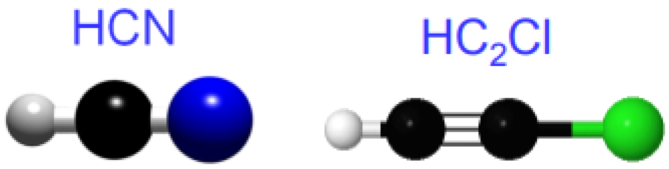
Being the moment of inertia for the reduced mass defined as $I = \mu r^2$:

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

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. **Frequencies.** Selection rules. Intensity

The same expression is valid for any linear polyatomic molecule but, since I is larger than that of a diatomic molecule, rotational energy levels E_r are much closer to each other.



In spectroscopy, the measurable physical quantity is the frequency (not energy). Then, the rotational energy levels E_r are usually converted in angular frequency dividing E_r by $\hbar$:

$$F(J) = \frac{E_r}{\hbar} = \frac{\hbar}{2I}J(J+1) = BJ(J+1)$$

$F(J)$ and B have the same unit as the angular frequency.

B is also known as the rotational constant.

Its estimation by appropriate spectroscopic techniques allows the calculation of internuclear distances.

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. Selection rules. Intensity

A **selection rule**, or transition rule, formally constrains the possible transitions of a system from one quantum state to another.

A selection rule consists of two parts: a general and a specific one.

The general selection rule constrains the requirements for a given spectrum to be observable.

Once the general selection rule is verified, the specific selection rule is applied to the atom or molecules to determine whether a certain transition within the spectrum can occur.

Selection rules determine all possible transitions between quantum levels as a result of the absorption or emission of electromagnetic radiation.

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. Selection rules. Intensity

The electromagnetic radiation has an oscillating electric field $E_0\cos(\omega t)$ that interacts with the molecule through a dipole transition.

In the **Chapter 1**, we have defined the dipole matrix element between two states u_a and u_b as:

$$D_{ab} = \int u_a^* \boldsymbol{\mu} u_b d\tau$$

where $\boldsymbol{\mu} = -e\boldsymbol{r}$ is the dipole operator.

Consider an electric field oriented along the z-axis (in the laboratory frame). We can evaluate the interaction between the transition dipole along $x -$,$y -$ or $z -$axis of the molecule with the radiation field.

If $\boldsymbol{D_{ab}}$ is zero, the transition is forbidden.

The selection rule determines the condition for $\boldsymbol{D_{ab} \neq 0}$.

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. Selection rules. Intensity

For a rigid rotor with the effective mass approximation, the eigenstates of the Schrodinger equation are spherical harmonics $\Upsilon_m^J(\theta, \varphi)$ and then the dipole matrix element for the transition $|J', m'\rangle \rightarrow |J, m\rangle$ is:

$$D_{J,m\rightarrow J',m'} = \int_0^{2\pi}\int_0^{\pi} \Upsilon_{J'}^{m'*}(\theta, \varphi)\boldsymbol{\mu}\,\Upsilon_J^m(\theta, \varphi)sen\theta d\theta d\varphi$$

$$D_{ab} = \int u_a^* \boldsymbol{\mu} u_b d\tau$$

We notice immediately that the molecule must have a **permanent dipole moment** to have a rotational spectrum (the general selection rule).

So heteronuclear diatomic molecules (CO, NO, HF) have a rotational spectrum, while homonuclear diatomic molecules (H_2, N_2, Cl_2) cannot have a rotational spectrum.

Similarly, asymmetric polyatomic linear molecules such as $\mathrm{O = C = S}$, $\mathrm{H - C \equiv N}$ (namely, without a center of inversion) can have rotational transitions, while symmetrical polyatomic linear molecules (ovvero con un centro di inversione) such as $\mathrm{S = C = S}$ e $\mathrm{H - C \equiv C - H}$ (with a center of inversion) cannot not have a pure rotational spectrum.

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. **Selection rules.** Intensity

We replace in the the dipole matrix element $D_{J,m\to J',m'}$ the expression of harmonic spheres in terms of Legendre polynomials. Then, we use the canonical substitution $x = cos\theta$, leading to:

$$Y_J^m(\theta,\varphi) = A_{J,m_J} e^{im_J\varphi} P_J(cos\theta)$$

$$D_{J,m\to J',m'} = A_{J,m} A_{J',m'} \mu \int_0^{2\pi} e^{i(m-m')\varphi} d\varphi \int_{-1}^{1} P_{J'}(x) P_J(x)\, dx$$

The integral in the φ variable is nonzero only when $m = m'$, namely $\boldsymbol{\Delta m = 0}$.

This represents the first part of the specific selection rule for rotational transitions.

Integrating into the variable φ with $m = m'$ condition:

$$D_{J,m\to J',m} = 2\pi\mu A_{J,m} A_{J',m} \int_{-1}^{1} P_{J'}(x) P_J(x)\, dx$$

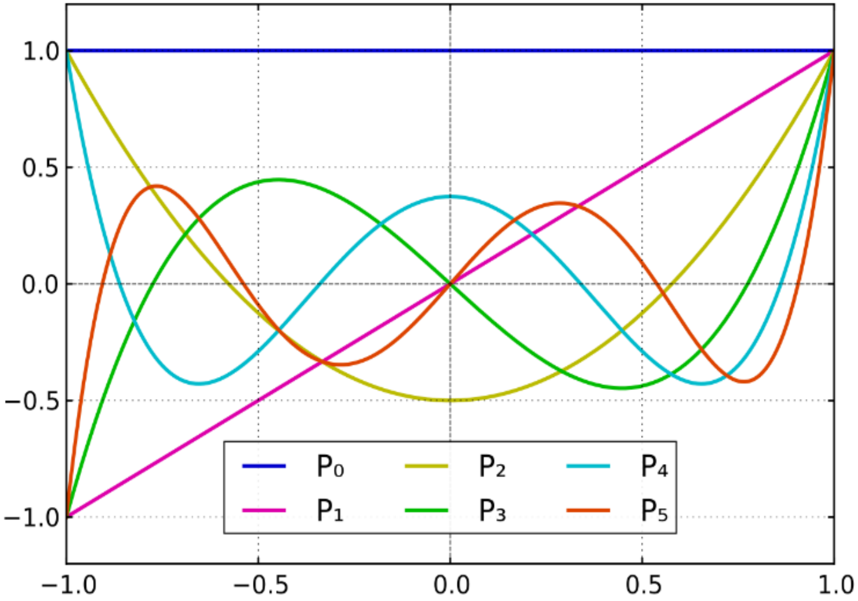
3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. Selection rules. Intensity

$$D_{J,m\rightarrow J',m} = 2\pi\mu A_{J,m}A_{J',m}\int_{-1}^{1} P_{J'}(x)P_{J}(x)\,dx$$

At this point it would be necessary to calculate all products among all possible combinations (J, J').

The first 5 Legendre polynomials are represented in Figure:



Qualitatively, if we consider the symmetry of the polynomials with respect to the point $x = 0$ based on even or odd indexes, it is worth noticing that the integral will be non-null only when $\boldsymbol{J' = J+1}$ or $\boldsymbol{J' = J-1}$.

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. **Selection rules.** Intensity

It then follows that the specific selection rule for rotational transitions is:

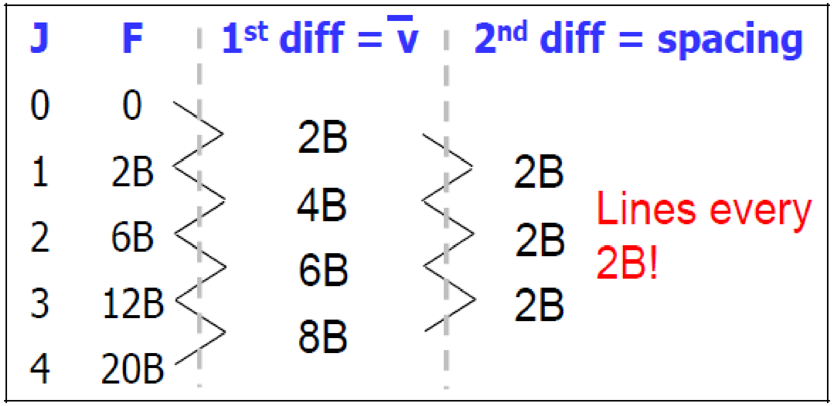
$$\boldsymbol{\Delta J = \pm 1} \qquad \text{and} \qquad \boldsymbol{\Delta m = 0}$$

The transition angular frequencies are then given by:

$$F(J) = BJ(J+1)$$

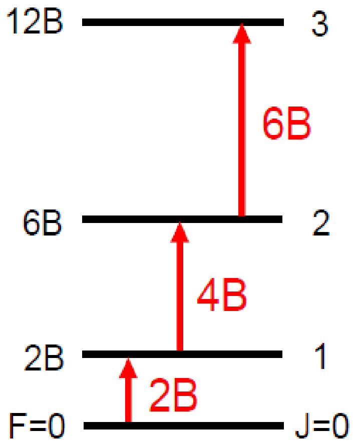
$$\omega = F(J+1) - F(J) = B(J+1)(J+2) - BJ(J+1) = B(J+1)(J+2-J) = 2B(J+1)$$

The rotational spectra of heteronuclear diatomic molecules are the easiest to be recognized and analyzed because they consist of equally spaced absorption lines.



J	F	1st diff = $\bar{v}$	2nd diff = spacing
0	0		
		2B	
1	2B		2B
		4B	
2	6B		2B
		6B	
3	12B		2B
		8B	
4	20B		

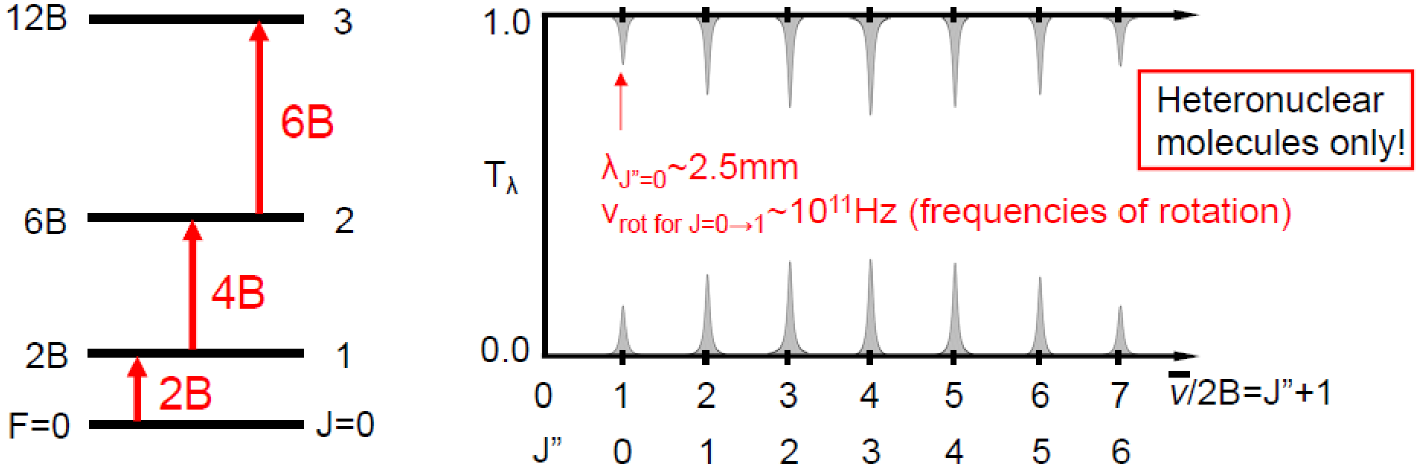
Lines every 2B!



3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. **Selection rules.** Intensity

A rotational spectrum of a heteronuclear diatomic molecule appears as:



By measuring the frequency spacing between two adiacent lines of the comb, it is possible to determine the rotational constant B and then the length of the chemical bond.

Measured spectra → Physical characteristics of molecule

Line spacing =2B → $B = \dfrac{h}{8\pi^2 Ic}$ → $I = \mu r_e^2$ → r_e Accurately!

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. Selection rules. Intensity

The intensities of the rotational lines depend on the population of the lowest energy state of the transition.

The population N_J of the J-th level with respect to N_0 is given by the Boltzmann distribution:

$$\frac{N_J}{N_0} = (2J+1)e^{-\frac{E_r}{KT}}$$

where $(2J+1)$ is the degeneration of the J-th level.

Degeneration arises from the fact that in the absence of an electric or magnetic field, $(2J+1)$ degenerate levels corresponding to the same energy eigenvalue are possible, resulting from the number of possible values for m_J.

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. Selection rules. Intensity

$$\frac{N_J}{N_0} = (2J+1)e^{-\frac{E_r}{KT}}$$

$$E_r = \frac{\hbar^2}{2I}J(J+1)$$

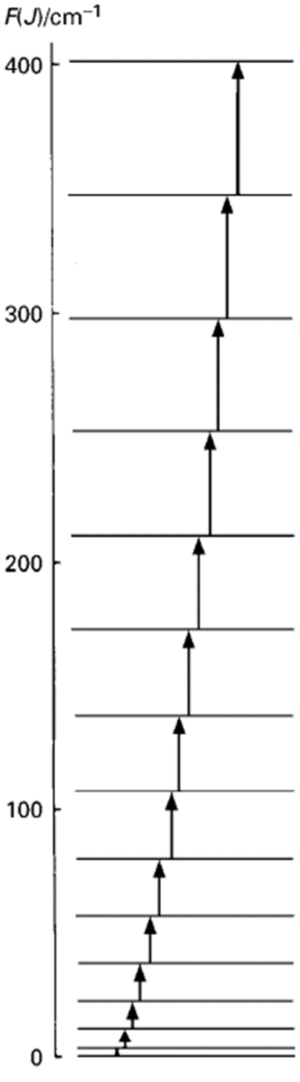
It is immediately observed that $\frac{N_J}{N_0}$ consists of two opposite terms: as J increases, the term $(2J+1)$ increases, while the term $e^{-\frac{E_r}{KT}}$ rapidly decreases.

The result is that starting from small values of J, the $(2J+1)$ term dominates: $\frac{N_J}{N_0}$ increases as J increases. Then a maximum is reached as a trade-off; after that, the exponential term becomes dominant and $\frac{N_J}{N_0}$ goes quickly to zero.

In the next slide, the values of three terms $(2J+1)$, $e^{-\frac{E_r}{KT}}$ and $\frac{N_J}{N_0}$ are shown for increasing J values, calculated for the CO molecule:

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. Selection rules. Intensity



J	$(2J+1)$	$\exp\left(\frac{-E_r}{kT}\right)$	$\frac{N_J}{N_0}$	$\tilde{\nu}/\mathrm{cm}^{-1}$
14	29	0.138	4.00	57.7
13	27	0.180	4.86	53.8
12	25	0.230	5.75	50.0
11	23	0.288	6.62	46.1
10	21	0.355	7.46	42.3
9	19	0.428	8.13	38.4
8	17	0.507	8.62	34.6
7	15	0.590	8.85	30.8
6	13	0.673	8.75	26.9
5	11	0.754	8.29	23.1
4	9	0.828	7.45	19.2
3	7	0.893	6.25	15.4
2	5	0.945	4.73	11.5
1	3	0.981	2.94	7.69
0	1	1.00	1.00	3.84

$$E_r = \frac{\hbar^2}{2\mu r^2} J(J+1)$$

$$\frac{N_J}{N_0} = (2J+1)e^{-\frac{E_r}{KT}}$$

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. Selection rules. Intensity

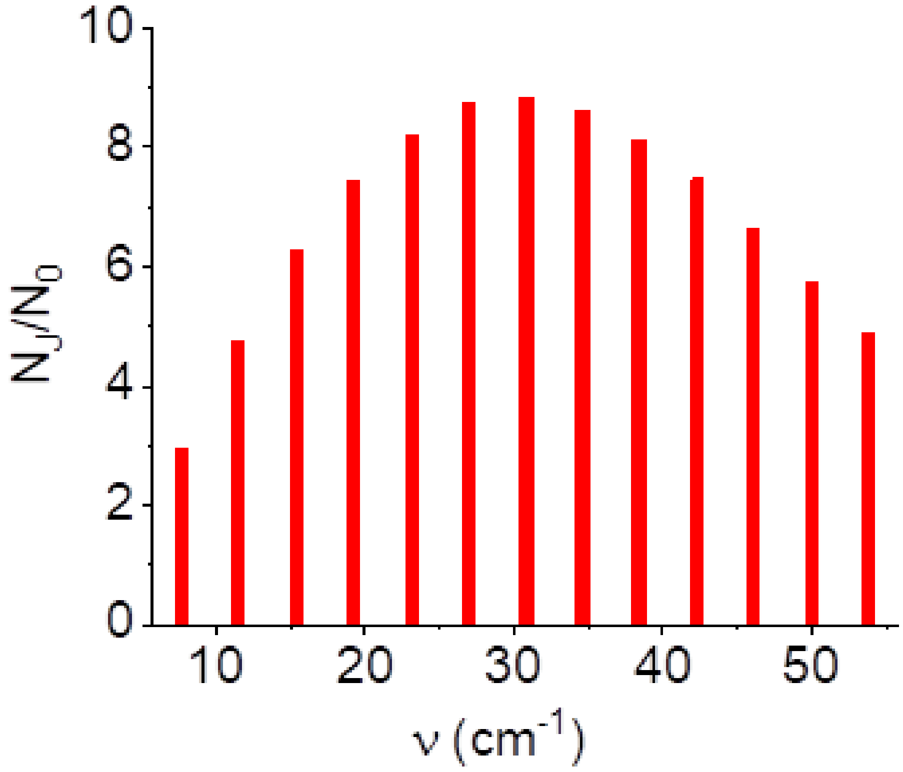
Let's plot the $\frac{N_J}{N_0}$ values as a function of the wavenumbers (and then J):

The population shows a maximum at the value $J = J_{max}$, calculated by solving the equation:

$$\frac{d\left(\frac{N_J}{N_0}\right)}{dJ} = 0$$

The result is:

$$J_{max} = \sqrt{\frac{KT}{2hB}} - \frac{1}{2}$$



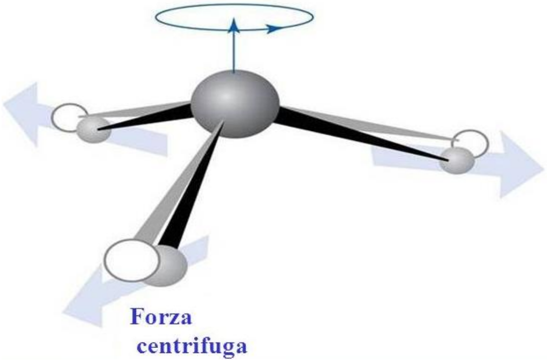
For the rotational spectrum of CO molecule, $J_{max} = 7$.

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. Selection rules. Intensity

Centrifugal distortion

The centrifugal distortion is related to the changing bond length of a molecule. A real molecule does not behave as a rigid rotor that has a rigid rod for a chemical bond, but rather acts as if it has a spring for a chemical bond.



In fact, the chemical bond cannot be assumed as rigid. It can be represented (in elastic approximation) by a spring that connects the nuclei, as we will see in **Chapter 3.3**.

As the rotational velocity of a molecule increases (that is, as the J increases), its bond length increases and its moment of inertia increases. In other words, the faster rate of spin increases the centrifugal force pushing outward on the molecules resulting in a longer average bond length.

The spring stretches, r increases and so B decreases. As a result, the frequency spacing is not more constant, but decreases at high J values.

$$B = \frac{\hbar}{2I}$$

3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. Selection rules. Intensity

Centrifugal distortion

This effect is taken into account by introducing a second order correction for $F(J)$

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

where D is the **centrifugal distortion constant** and is always positive for diatomic molecules.

The transition frequencies are now given by:

$$\begin{aligned}&\omega = F(J+1) - F(J)\\&= B(J+1)(J+2) - D(J+1)^2(J+2)^2 - BJ(J+1) + DJ^2(J+1)^2\\&= 2B(J+1) + D(J+1)^2(J^2 - J^2 - 4J - 4) = 2B(J+1) - 4D(J+1)^3\end{aligned}$$

The centrifugal distortion constant depends on the stiffness of the bond, and it is not surprising that it can be related to the vibration wavenumber.

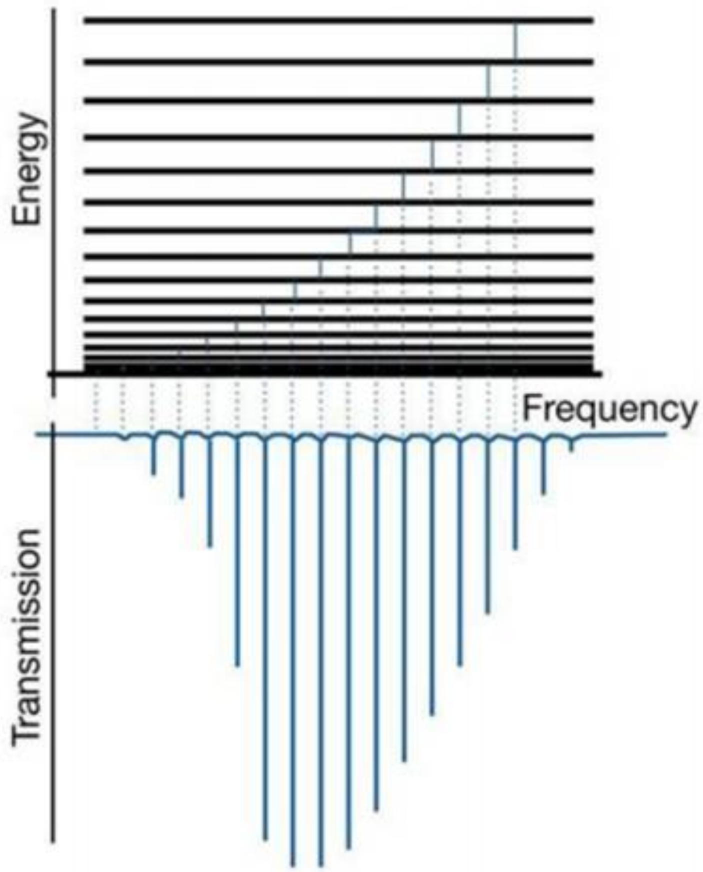
3.2 ROTATIONAL SPECTROSCOPY

3.2.2 Linear rotors. Frequencies. Selection rules. Intensity

Centrifugal distortion

Rotational Levels

Rotational Spectrum



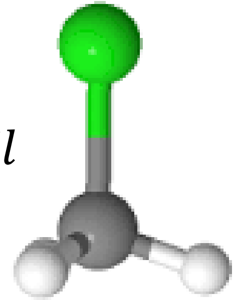
3.2 ROTATIONAL SPECTROSCOPY

3.2.3 Symmetrical rotor molecules. Prolates. Oblates

In symmetrical rotor molecules two principal moments of inertia are the same, and the third different.

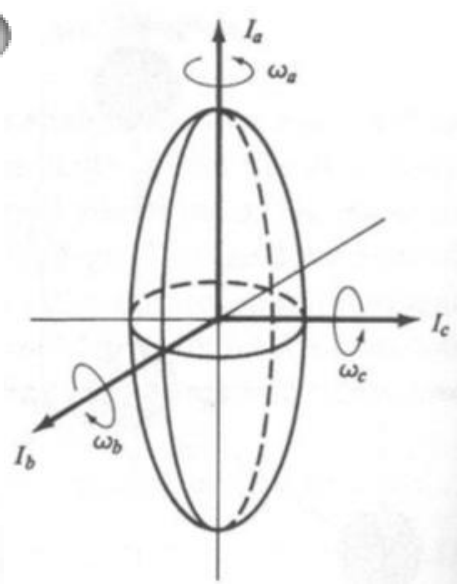
We distinguish two subcategories:

CH_3Cl



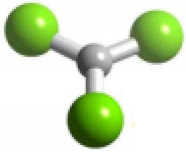
Prolates

$$I_b = I_c > I_a$$

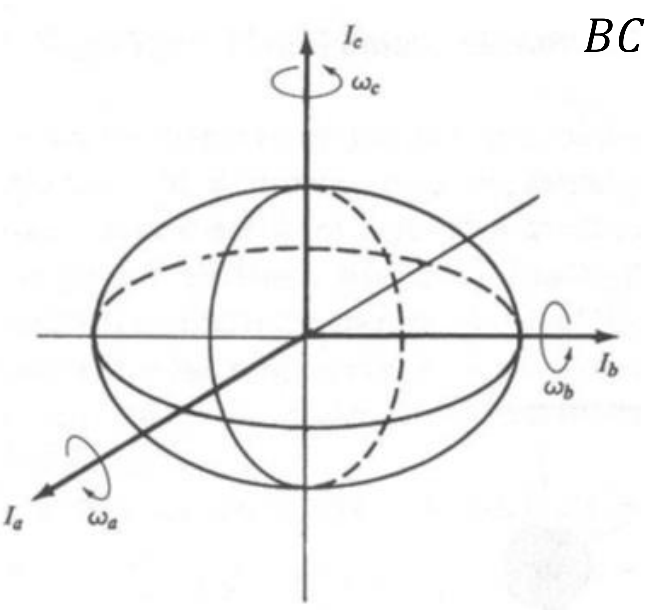


Oblates

$$I_b = I_a > I_c$$



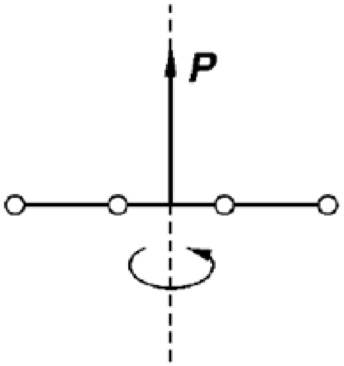
BCl_3



3.2 ROTATIONAL SPECTROSCOPY

3.2.3 Symmetrical rotor molecules. Prolates. Oblates

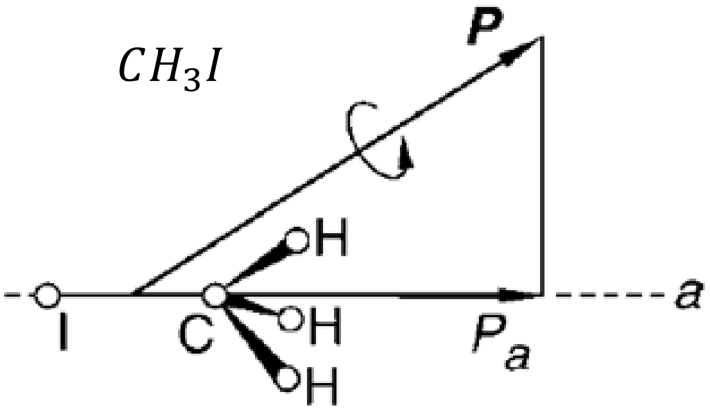
In a diatomic or linear polyatomic molecule, the rotational angular momentum vector $\vec{P}$ lies along the axis of rotation.



In a **prolate** symmetric rotor, $\vec{P}$ need not be perpendicular to the a axis.

In general, it takes up any direction in space and the molecule rotates around $\vec{P}$.

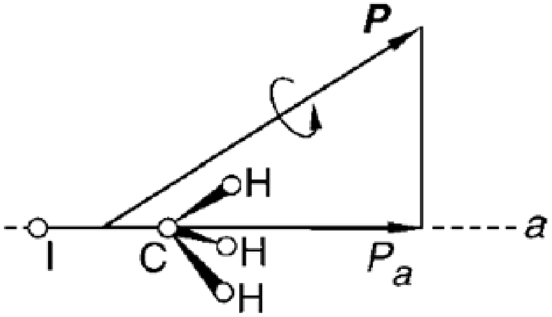
CH_3I



3.2 ROTATIONAL SPECTROSCOPY

3.2.3 Symmetrical rotor molecules. Prolates. Oblates

We identify a component of $\vec{P}$ along the a axis P_a (and therefore a moment of inertia I_a) and a component $P_\perp$ orthogonal to the a ax is (with a moment of inertia $I_\perp$).



Using the classical relation between the angular momentum P, moment of inertia I and rotational energy E_r:

$$E_r = \frac{P^2}{2I}$$

We can rewrite it considering the two contributions of $\vec{P}$:

$$E_r = \frac{{P_a}^2}{2I_a} + \frac{{P_\perp}^2}{2I_\perp}$$

In our case, ${P_\perp}^2 = {P_b}^2 + {P_c}^2$ and so:

$$E_r = \frac{{P_a}^2}{2I_a} + \frac{{P_b}^2 + {P_c}^2}{2I_\perp}$$

3.2 ROTATIONAL SPECTROSCOPY

3.2.3 Symmetrical rotor molecules. Prolates. Oblates

On the other hand, the following relation for the rotational angular momentum vector must be verified:

$$P^2 = {P_a}^2 + {P_b}^2 + {P_c}^2$$

$$E_r = \frac{{P_a}^2}{2I_a} + \frac{{P_b}^2 + {P_c}^2}{2I_\perp}$$

Replacing ${P_b}^2 + {P_c}^2 = P^2 - {P_a}^2$ one obtain:

$$E_r = \frac{P^2}{2I_\perp} + {P_a}^2\left(\frac{1}{2I_a} - \frac{1}{2I_\perp}\right)$$

If we replace the square of the classical angular momentum with the eigenvalues of the angular momentum operator:

$$P^2 \to J(J+1)\hbar^2$$

we get:

$$E_r = \frac{J(J+1)\hbar^2}{2I_\perp} + {P_a}^2\left(\frac{1}{2I_a} - \frac{1}{2I_\perp}\right)$$

3.2 ROTATIONAL SPECTROSCOPY

3.2.3 Symmetrical rotor molecules. Prolates. Oblates

We can then define as before:

$$F(J) = \frac{E_r}{\hbar} = \frac{J(J+1)\hbar}{2I_{\perp}} + {P_a}^2\left(\frac{1}{2I_a\hbar} - \frac{1}{2I_{\perp}\hbar}\right)$$

We note that the first terms describe the rotation around an axis orthogonal to the a axis, which can be or the b axis or the b axis having the same moment of inertia $I_b = I_c = I_{\perp}$. This is the analogous case of a diatomic molecule.

Using the result obtained for the diatomic molecule:

$$F(J) = BJ(J+1) + {P_a}^2\left(\frac{1}{2I_a\hbar} - \frac{1}{2I_{\mathrm{b}}\hbar}\right)$$

where

$$B = \frac{\hbar}{2I_b}$$

3.2 ROTATIONAL SPECTROSCOPY

3.2.3 Symmetrical rotor molecules. Prolates. Oblates

P_a represents the projection of angular momentum on the a axis. It can be quantized and can take only the values:

$$F(J) = BJ(J+1) + {P_a}^2\left(\frac{1}{2I_a h} - \frac{1}{2I_\perp h}\right)$$

$$P_a = K\hbar$$

where $K = -J, \dots, 0, \dots J$ is a second rotational quantum number (as for the quantum number m).

So, replacing it in the previous expression, we have:

$$F(J,K) = BJ(J+1) + K^2(A-B)$$

$$F(J) = BJ(J+1) + {P_a}^2\left(\frac{1}{2I_a\hbar} - \frac{1}{2I_\mathrm{b}\hbar}\right)$$

where

$$A = \frac{\hbar}{2\,I_a}$$

For **oblate** rotors, the description is the same as long as you replace the c axis with the a axis. Following the same steps, the result is:

$$F(J,K) = BJ(J+1) + K^2(C-B) \qquad \text{con } C = \frac{\hbar}{2I_c}$$

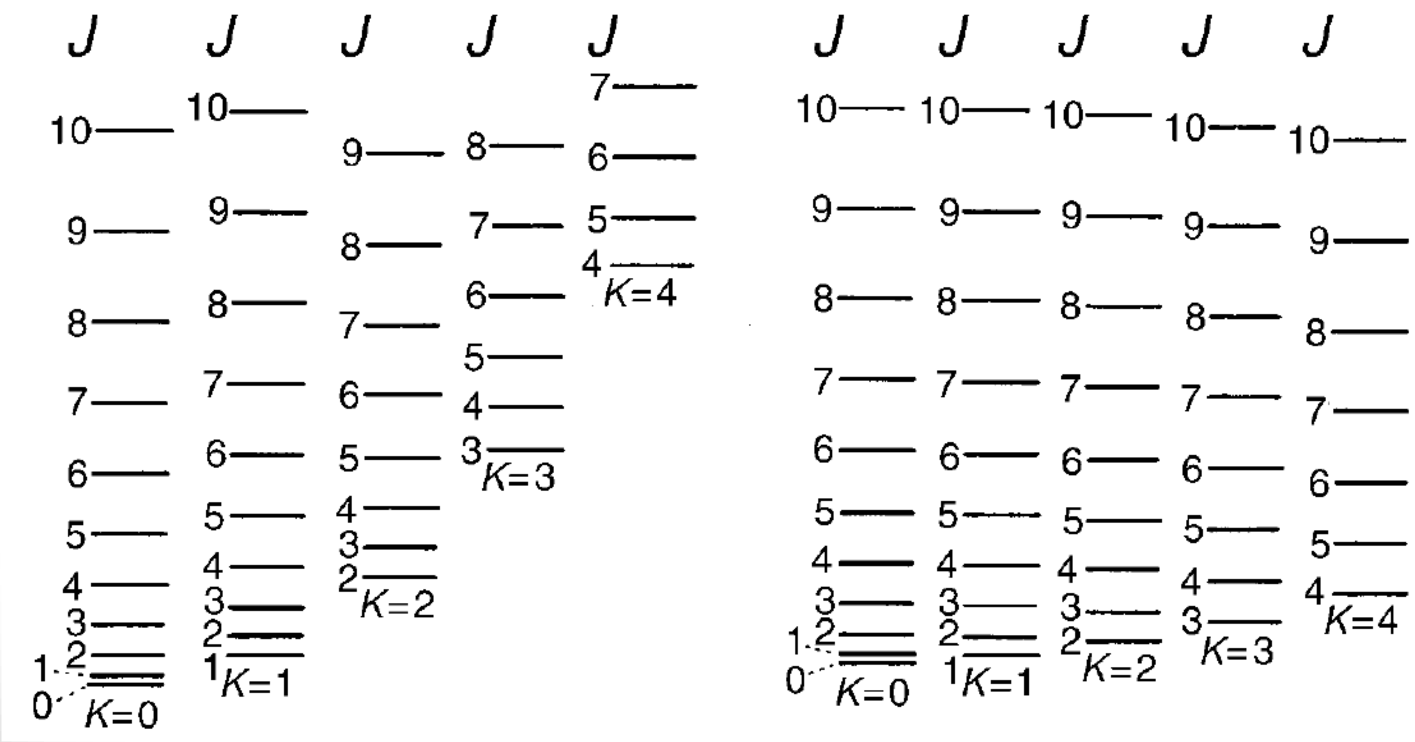
3.2 ROTATIONAL SPECTROSCOPY

3.2.3 Symmetrical rotor molecules. Prolates. Oblates

The rotational energy levels for a prolate and an oblate symmetric rotor are shown schematically in Figure:

prolate rotors

oblate rotors



3.2 ROTATIONAL SPECTROSCOPY

3.2.3 Symmetrical rotor molecules. Prolates. Oblates

$$F(J,K) = BJ(J+1) + K^2(A-B) \qquad \text{prolate rotors}$$

$$F(J,K) = BJ(J+1) + K^2(C-B) \qquad \text{oblate rotors}$$

Although these present a much more complex picture than those for a linear molecule the fact that the selection rules:

$$\Delta J = \pm 1 \qquad \text{and} \qquad \Delta K = 0$$

results in the expression for the transition frequencies or wavenumbers:

$$\omega = F(J+1,K) - F(J) = 2B(J+1)$$

This is the same as for a diatomic or linear polyatomic molecule and, again, the transitions show an equal spacing of $2B$.

The effects of centrifugal distortion are not included.

3.2 ROTATIONAL SPECTROSCOPY

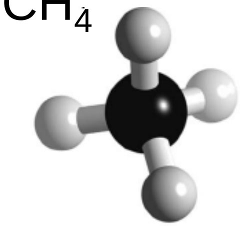
3.2.4 Spherical rotor molecules

In Spherical rotor molecules three principal moments of inertia are the same

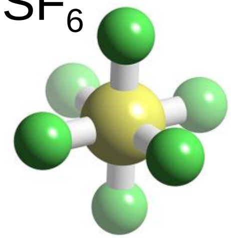
$$I_b = I_c = I_a$$

Examples of spherical rotor molecules are:

CH_4



SF_6



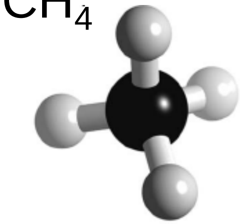
We tend to think of a spherical rotor molecule as having no permanent dipole moment and, therefore, no rotational spectra.

However, rotation about any of the C3 axes (i.e. any of the four axes in methane containing a C–H bond) results in a centrifugal distortion in which the other three hydrogen atoms are thrown outwards slightly from the axis.

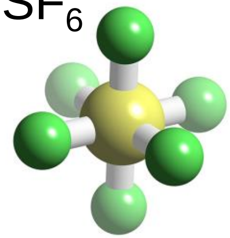
3.2 ROTATIONAL SPECTROSCOPY

3.2.4 Spherical rotor molecules

CH_4



SF_6



This converts the molecule into a symmetric rotor and gives it a small dipole moment resulting in a very weak rotational spectrum.

Neglecting centrifugal distortion, the rotation term values for a spherical rotor are given by:

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

This is an identical expression to that for a diatomic or linear polyatomic molecule and, as the rotational selection rule is the same, namely: $\Delta J = \pm 1$, and the transition wavenumbers or frequencies are given by:

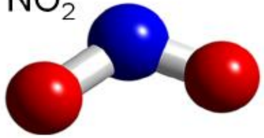
$$\upsilon = F(J+1) - F(J) = 2B(J+1)$$

3.2 ROTATIONAL SPECTROSCOPY

3.2.5 Asymmetric rotor molecules

H_2O

NO_2



Asymmetric rotor molecules have three different moments of inertia:

$$I_b \neq I_c \neq I_a$$

Although these molecules form much the largest group we shall take up the smallest space in considering their rotational spectra.

The reason for this is that there are no closed formulae for their rotational term values. Instead, these term values can be determined accurately only by a matrix diagonalization for each value of J, which remains a good quantum number.

At a simple level, the rotational transitions of near-symmetric rotors are easier to understand. For a prolate or oblate near-symmetric rotor the rotational term values are given, approximately, by:

$$F(J,K) \simeq \tilde{B}J(J+1) + K^2\left(A-\tilde{B}\right) \qquad \text{for a prolate rotor}$$

$$F(J,K) \simeq \tilde{B}J(J+1) + K^2\left(C-\tilde{B}\right) \qquad \text{for an oblate rotor}$$

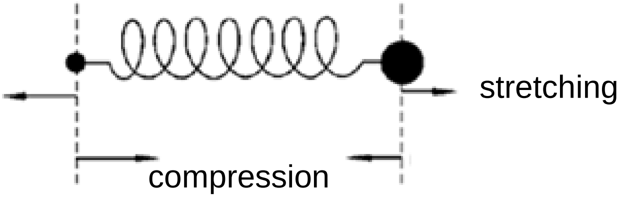
where $\tilde{B} = \frac{1}{2}(B+C)$ for a prolate rotor

$\tilde{B} = \frac{1}{2}(B+A)$ for an oblate rotor

3.3 VIBRATIONAL SPECTROSCOPY

3.3.1 Harmonic oscillator

A model to describe the vibrations of a diatomic molecule is to consider the interatomic chemical bond as a harmonic oscillator:



For small displacements, stretching and bond compressions follow Hooke's law:

$$Force = -\frac{dV(x)}{dx} = -kx$$

where V is the potential, k is the spring constant and $x = r - r_e$ is the displacement with respect to the equilibrium length r_e.

Integrating it, $V(x) = \frac{1}{2}kx^2$.

The Hamiltonian of the harmonic oscillator will be:

$$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

where μ is the reduced mass of the nuclei.

3.3 VIBRATIONAL SPECTROSCOPY

3.3.1 Harmonic oscillator

The energy eigenvalues of the Schrodinger equation (and so the vibrational energy levels of a diatomic molecule treated in the harmonic oscillator approximation) are:

$$E_n = \hbar\omega\left(v + \frac{1}{2}\right)$$

where $v = 0,12,..$ and ω are the classical angular frequencies given by:

$$\omega = \sqrt{\frac{k}{\mu}}$$

So, the vibrational levels are equispaced BY $\hbar\omega$ and the lowest energy level corresponding to $v = 0$ has energy $E_0 = \frac{\hbar\omega}{2}$.

Eigenfunctions ψ_v are in the form:

$$\psi_v = \sqrt{\frac{1}{2^v v!\sqrt{\pi}}}H_v(y)e^{-\frac{y^2}{2}}$$

where $H_v(y)$ are **Hermite polynomials** and $y = \sqrt{\frac{4\pi^2 v\omega}{h}}x$

3.3 VIBRATIONAL SPECTROSCOPY

3.3.1 Harmonic oscillator

The Hermite polynomials are:

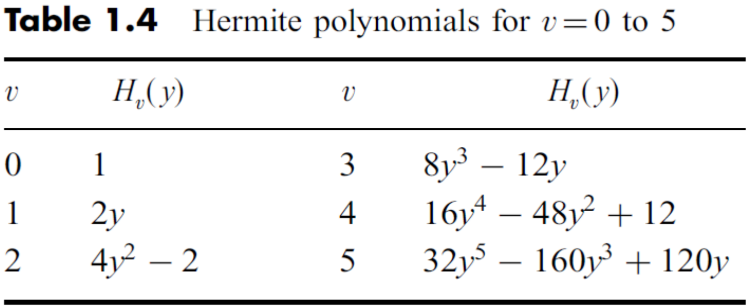


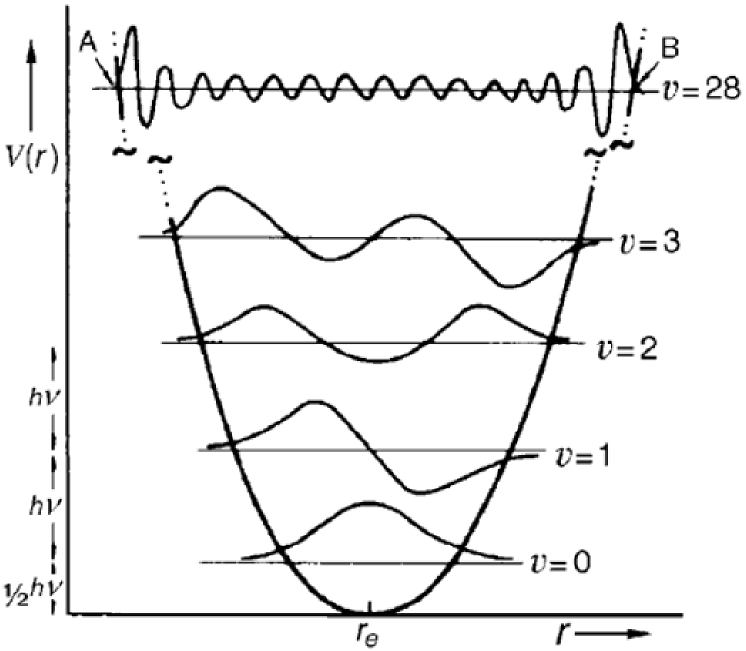
Table 1.4 Hermite polynomials for $v = 0$ to 5

v	$H_v(y)$	v	$H_v(y)$
0	1	3	$8y^3 - 12y$
1	$2y$	4	$16y^4 - 48y^2 + 12$
2	$4y^2 - 2$	5	$32y^5 - 160y^3 + 120y$

Figure shows the potential $V(r)$ as a function of the bond length r.

r_e represents the equilibrium length of the bond.

The energy levels and the corresponding wave functions for $v = 0,1,2,3$ and 28 are also represented.



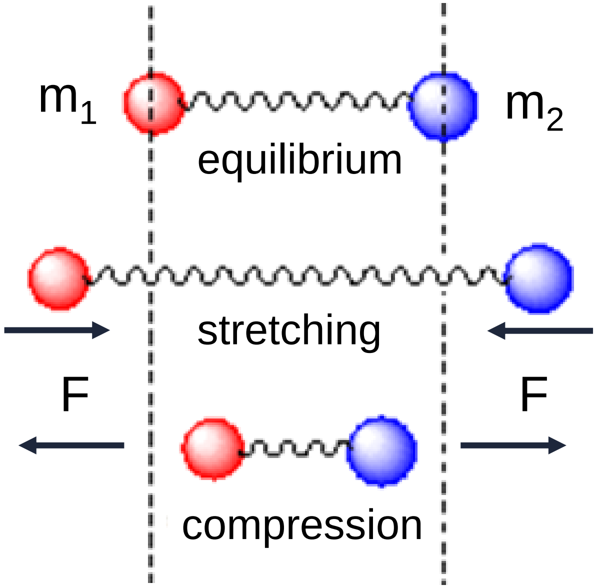
3.3 VIBRATIONAL SPECTROSCOPY

3.3.1 Harmonic oscillator

k values represent the strength of the bond.

Physically, the strength of the spring representing the bond is affected by a subtle balance of nuclear repulsions, electron repulsions and electron–nuclear attractions.

None of these is affected by nuclear mass and, therefore, k is not affected by isotopic substitution.



Just as for rotation it is convenient to use term values instead of energy levels. Vibrational term values $G(\upsilon)$ invariably have dimensions of wavenumber, so we have

$$G(\upsilon) = \frac{E_\upsilon}{\hbar} = \omega\left(\upsilon + \frac{1}{2}\right)$$

which allows to describe energy levels in terms of frequencies, i.e. a measurable quantity.

3.3 VIBRATIONAL SPECTROSCOPY

3.3.2 Infrared spectra

The transition moment for a transition between lower and upper states with wave functions u_a and u_b is given by:

$$D_{ab} = \int u_a^* \boldsymbol{\mu} u_b dx$$

where $\boldsymbol{\mu} = -e\boldsymbol{x}$ is the dipole moment operator and x is the displacement of the internuclear distance from equilibrium.

The dipole moment $\boldsymbol{\mu}$ is zero for a homonuclear diatomic molecule, resulting in $D_{ab} = 0$, and all vibrational transitions being forbidden.

The eigenstates are the functions ψ_v :

$$D_{v'v''} = \int \psi_{v'}^* \boldsymbol{\mu} \psi_{v''} dx$$

$$\psi_v = \sqrt{\frac{1}{2^v v! \sqrt{\pi}}} H_v(y) e^{-\frac{y^2}{2}}$$

For a heteronuclear diatomic molecule, $\mu \neq 0$ and varies with x.

3.3 VIBRATIONAL SPECTROSCOPY

3.3.2 Infrared spectra

For small displacements, you can expand μ in Taylor series around the equilibrium configuration (identified by subscript e):

$$\boldsymbol{\mu} = \boldsymbol{\mu_e} + \left(\frac{d\boldsymbol{\mu}}{dx}\right)_e x + \frac{1}{2!}\left(\frac{d^2\boldsymbol{\mu}}{dx^2}\right)_e x^2 + \cdots$$

The transition moment now becomes:

$$D_{v'v''} = \boldsymbol{\mu_e} \int \psi_{v'}^* \psi_{v''} dx + \left(\frac{d\boldsymbol{\mu}}{dx}\right)_e \int \psi_{v'}^* x \psi_{v''} dx + \cdots$$

$$D_{v'v''} = \int \psi_{v'}^* \boldsymbol{\mu} \psi_{v''} dx$$

Since $\psi_{\nu'}$ and $\psi_{\nu''}$ are eigenfunctions of the same hamiltonian, when $\nu' \neq \nu''$:

$$\int \psi_{v'}^* \psi_{v''} dx = 0$$

Thus:

$$D_{v'v''} = \left(\frac{d\boldsymbol{\mu}}{dx}\right)_e \int \psi_{v'}^* x \psi_{v''} dx + \cdots$$

3.3 VIBRATIONAL SPECTROSCOPY

3.3.2 Infrared spectra

$$\psi_v = \sqrt{\frac{1}{2^v v! \sqrt{\pi}}} H_v(y) e^{-\frac{y^2}{2}}$$

Using the expressions found for ψ_v it can be shown that $D_{v'v''}$ is non-zero if:

$$\Delta v = \pm 1$$

This constitutes the vibrational selection rule.

In the harmonic oscillator, where all level spacings are equal, all transitions obeying this selection rule are coincident at a wavenumber ω.

At the thermal equilibrium, the population N_ν of the ν-th vibrational level is related to N_0 of the lowest energy level by the Boltzmann factor:

$$\frac{N_v}{N_0} = e^{-\frac{E_v}{KT}}$$

Each vibrational transition observed in the gas phase gives rise to what is called a ‘**band**’ in the spectrum..

The word ‘**line**’ is reserved for describing a transition between rotational levels associated with the two vibrational levels giving rise to the fine structure of a band.

3.3 VIBRATIONAL SPECTROSCOPY

3.3.3 Electrical and mechanical harmonicity

Taylor's series expansion of the electric dipole moment $\boldsymbol{\mu}$ contains terms in x to the second and higher powers.

$$\boldsymbol{\mu} = \boldsymbol{\mu_e} + \left(\frac{d\boldsymbol{\mu}}{dx}\right)_e x + \frac{1}{2!}\left(\frac{d^2\boldsymbol{\mu}}{dx^2}\right)_e x^2 + \cdots$$

The effect of higher terms is known as anharmonicity and, because this particular kind of anharmonicity is concerned with electrical properties of a molecule, it is referred to as electrical anharmonicity.

One effect of it is to cause the vibrational selection rule $\Delta v = \pm 1, \pm 2, \pm 3, \ldots$

Since electrical anharmonicity is usually small, the effect is to make only a very small contribution to the intensities of $\Delta v = \pm 2, \pm 3, \ldots$.

These transitions are known as vibrational overtones.

When the transition $\Delta v = \pm 1$is observed, we refer as **fundamental vibrational band**

3.3 VIBRATIONAL SPECTROSCOPY

3.3.3 Electrical and mechanical harmonicity

Just as the electrical behaviour of a real diatomic molecule is not accurately harmonic, neither is its mechanical behaviour.

The potential function, vibrational energy levels and wave functions were derived by assuming that vibrational motion obeys Hooke's law, but this assumption is reasonable only when r is not very different from r_e (i.e. when x is small).

$$Forza\ di\ richiamo = -\frac{dV(x)}{dx} = -kx$$

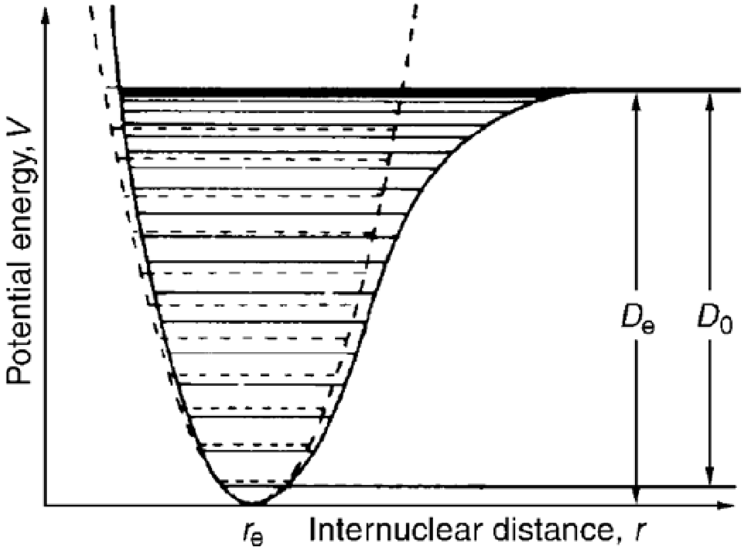
where V is the potential, k is the elastic constant and $x = r - r_e$ is the displacement with respect to the equilibrium length r_e.

At large values of r we know that the molecule dissociates: two neutral atoms are formed and, since they do not influence each other, the force constant is zero and r can then be increased to infinity with no further change of the potential energy V.

Therefore, the potential energy curve flattens out at $V = D_e$, where D_e is the dissociation energy measured relative to the equilibrium potential energy.

3.3 VIBRATIONAL SPECTROSCOPY

3.3.3 Electrical and mechanical harmonicity



As dissociation is approached the force constant $k \to 0$ and the bond gets weaker. The effect is to make the potential energy curve shallower than for a harmonic oscillator, when $r > r_e$.

At small values of r, the positive charges on the two nuclei cause mutual repulsion, which increasingly opposes their approaching each other. Consequently, the potential energy curve is steeper than for a harmonic oscillator, as the figure also shows.

3.3 VIBRATIONAL SPECTROSCOPY

3.3.3 Electrical and mechanical harmonicity

The deviations found in the curve for a real molecule from that resulting from the harmonic oscillator approximation are due to mechanical anharmonicity.

A molecule may show both electrical and mechanical anharmonicity, but the latter is generally much more important, and it is usual to define a harmonic oscillator as one which is harmonic in the mechanical sense.

One effect of mechanical anharmonicity is to modify the $\Delta \upsilon = \pm 1$ selection rule to $\Delta \upsilon = \pm 1, \ \pm 2, \pm 3, \ldots$ but the overtone transitions with $\Delta \upsilon = \pm 2, \pm 3, \ldots$ are usually weak compared with those with $\Delta \upsilon = \pm 1$.

However, unlike electrical anharmonicity, mechanical anharmonicity modifies the vibrational term values and wave functions.

The harmonic oscillator term values are modified to a power series in $\left(\upsilon + \frac{1}{2}\right)$:

$$G(\upsilon) = \omega_e \left(\upsilon + \frac{1}{2}\right) - \omega_e x_e \left(\upsilon + \frac{1}{2}\right)^2 + \omega_e y_e \left(\upsilon + \frac{1}{2}\right)^3 + \cdots$$

where ω_e is the angular frequency of the classical oscillator.

3.3 VIBRATIONAL SPECTROSCOPY

3.3.3 Electrical and mechanical harmonicity

$$G(v) = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + \omega_e y_e\left(v+\frac{1}{2}\right)^3 + \cdots$$

The terms $\omega_e x_e$, $\omega_e y_e$, … are anharmonic constants and are written in this way because sometimes the function $G(v)$ is expressed in the form:

$$G(v) = \omega_e\left[\left(v+\frac{1}{2}\right) - x_e\left(v+\frac{1}{2}\right)^2 + y_e\left(v+\frac{1}{2}\right)^3 + \cdots\right]$$

The reason for the negative sign in the second term of the expansion is that the constant x_e has the same sign for all diatomic molecules and, when the negative sign is included, x_e is always positive. Further terms in the expansion may be positive or negative.

The transition frequencies are given by:

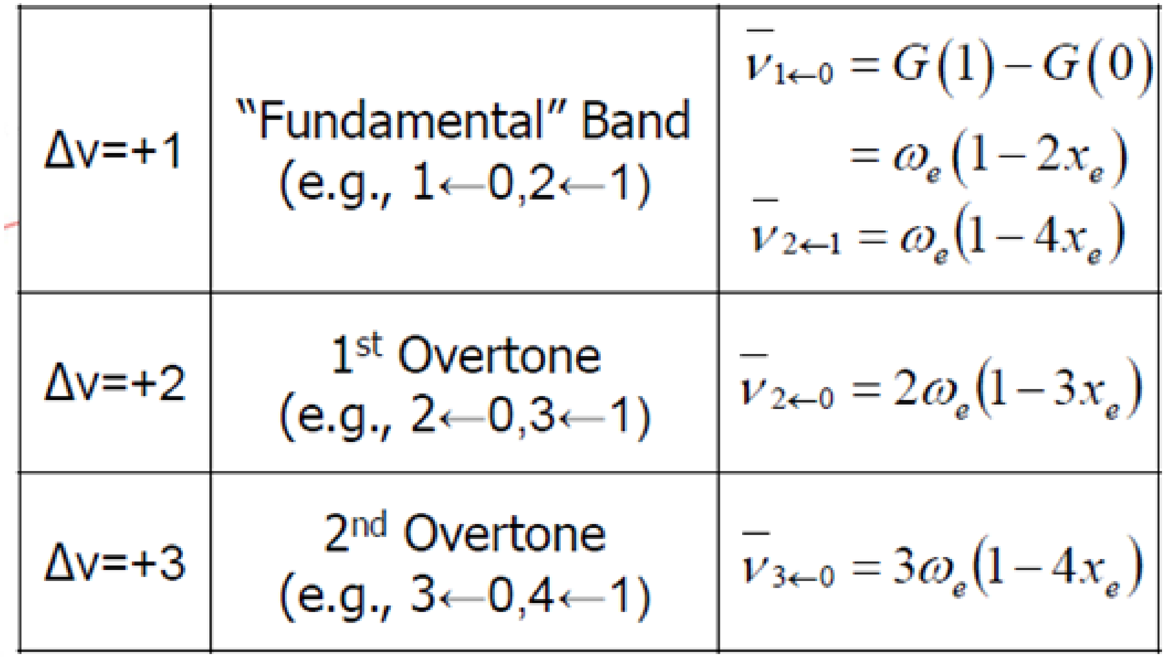
$$\omega = G(v+1) - G(v) = \omega_e - 2\omega_e x_e(v+1) + \omega_e y_e\left(3v^2 + 6v + \frac{13}{4}\right)$$

3.3 VIBRATIONAL SPECTROSCOPY

3.3.3 Electrical and mechanical harmonicity

If we consider only the first correction for the anarmonicity ($y_e = 0$):

$$\omega = G(v+1) - G(v) = \omega_e - 2\omega_e x_e (v+1)$$

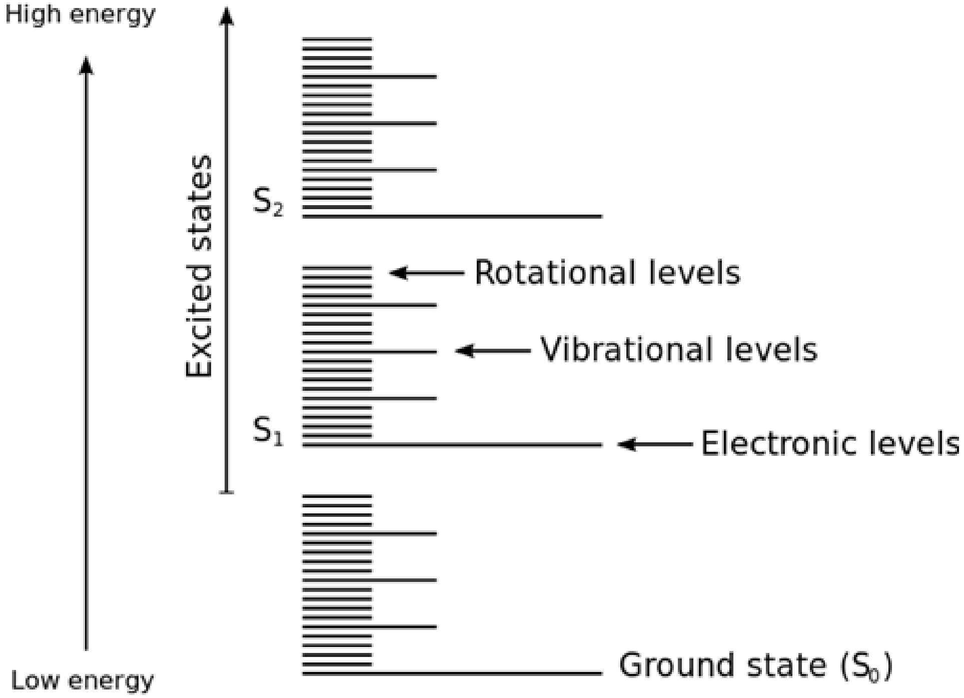


Δv=+1	"Fundamental" Band (e.g., 1←0,2←1)	$\bar{\nu}_{1\leftarrow 0} = G(1) - G(0)$ $= \omega_e(1-2x_e)$ $\bar{\nu}_{2\leftarrow 1} = \omega_e(1-4x_e)$
Δv=+2	1st Overtone (e.g., 2←0,3←1)	$\bar{\nu}_{2\leftarrow 0} = 2\omega_e(1-3x_e)$
Δv=+3	2nd Overtone (e.g., 3←0,4←1)	$\bar{\nu}_{3\leftarrow 0} = 3\omega_e(1-4x_e)$

3.4 ROTO-VIBRATIONAL SPECTROSCOPY

3.4.1 P-, R- and Q-branch structures

Energy differences between rotational energy levels are smaller than differences between vibrational levels, which in turn are smaller than differences in energy between electronic levels.



Therefore, there is a stack of rotational energy levels associated with each vibrational level.

3.4 ROTO-VIBRATIONAL SPECTROSCOPY

3.4.1 P-, R- and Q-branch structures

In rotational spectroscopy we observe transitions between rotational energy levels associated with the same vibrational level (usually $\upsilon = 0$).

In roto-vibrational spectroscopy, considering the selection rules $\Delta\upsilon = \pm 1$ e $\Delta J = \pm 1$, transitions can occur between stacks of rotational energy levels associated with two different vibrational levels.

When a molecule has both vibrational and rotational energy the total term values S are given by the sum of the rotational term values $F(J)$ and the vibrational term values $G(n)$:

$$S = G(\upsilon) + F(J) = \omega_e\left(\upsilon + \frac{1}{2}\right) - \omega_e x_e\left(\upsilon + \frac{1}{2}\right)^2 + BJ(J+1) - DJ^2(J+1)^2$$

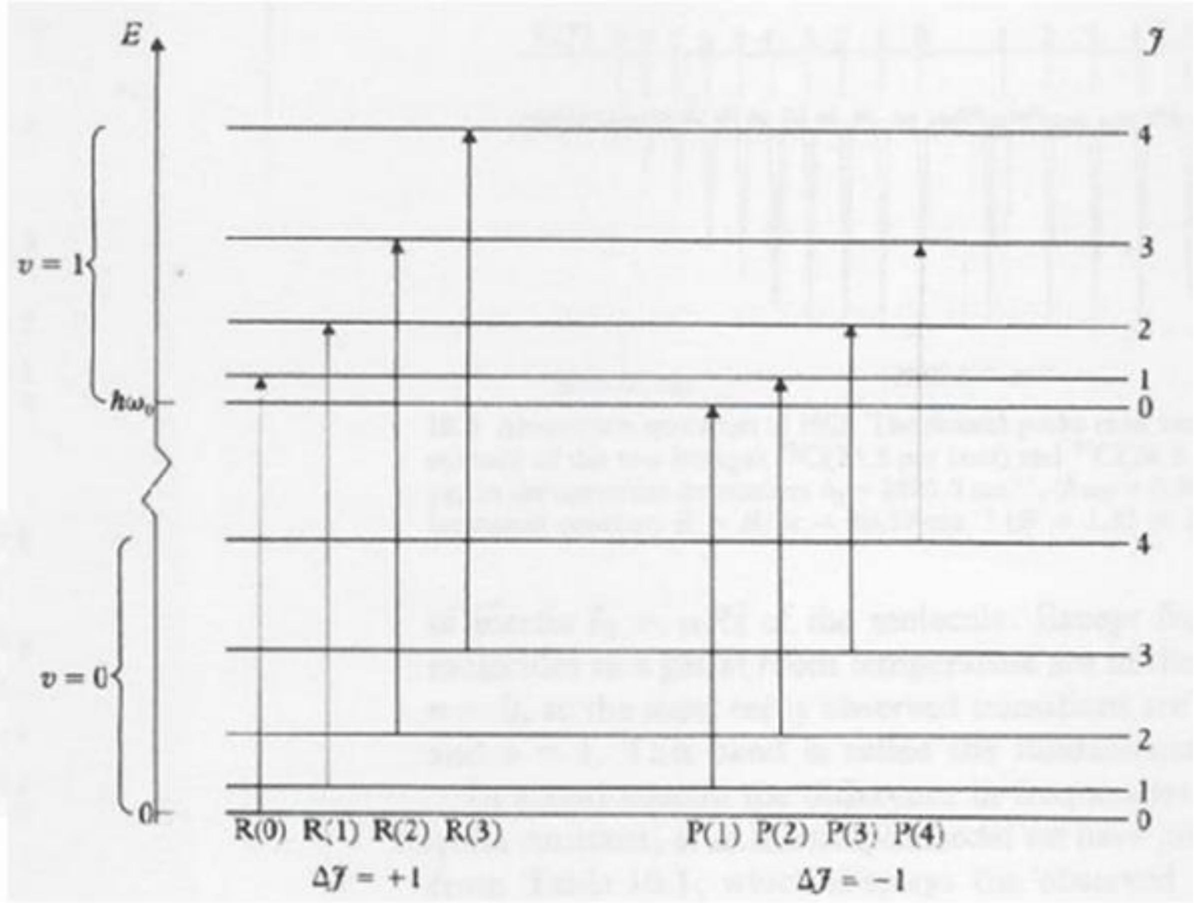
The rotational part of the transition is subject to the same selection rules as pure rotational transitions.

Therefore, in absorption ($\Delta\upsilon = +1$), you will have transitions

- $\boldsymbol{\Delta J = +1}$ that will form the $\boldsymbol{R-branch}$
- $\boldsymbol{\Delta J = -1}$ that will form the $\boldsymbol{P-branch}$

3.4 ROTO-VIBRATIONAL SPECTROSCOPY

3.4.1 P-, R- and Q-branch structures



Each transition of the $\boldsymbol{R - branch}$ is labelled $R(J)$ while each transition of $\boldsymbol{P - branch}$ with $P(J)$, where J represents the lowest state value.

3.4 ROTO-VIBRATIONAL SPECTROSCOPY

3.4.1 P-, R- and Q-branch structures

If we neglect centrifugal distortion and second-order terms ($x_e \sim 0$), the angular frequencies of the $\boldsymbol{R-branch}$ transitions ($\nu = 1 \rightarrow \nu = 0$) will be:

$$S = G(v) + F(J) = \omega_e\left(v + \frac{1}{2}\right) + BJ(J+1)$$

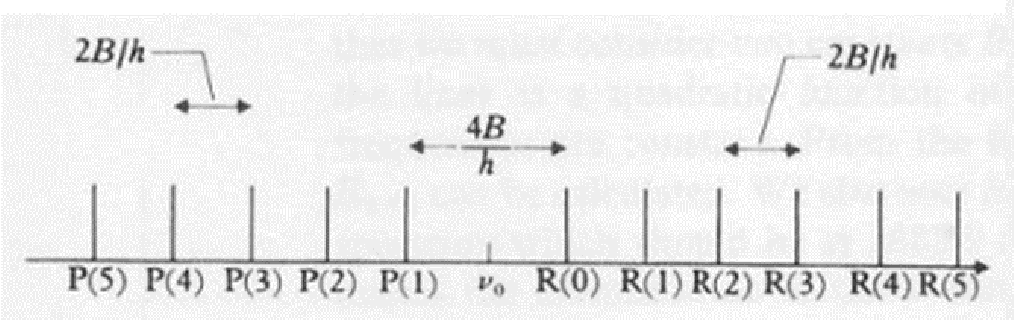
$$\omega[R(J)\,] = \frac{3}{2}\omega_e + B(J+1)(J+2) - \frac{1}{2}\omega_e - BJ(J+1) = \omega_e + 2B(J+1)$$

where ω_e is the angular frequency of the pure vibrational transition.

Similarly, the angular frequencies of the $\boldsymbol{P-branch}$ transitions ($\nu = 1 \rightarrow \nu = 0$) will be:

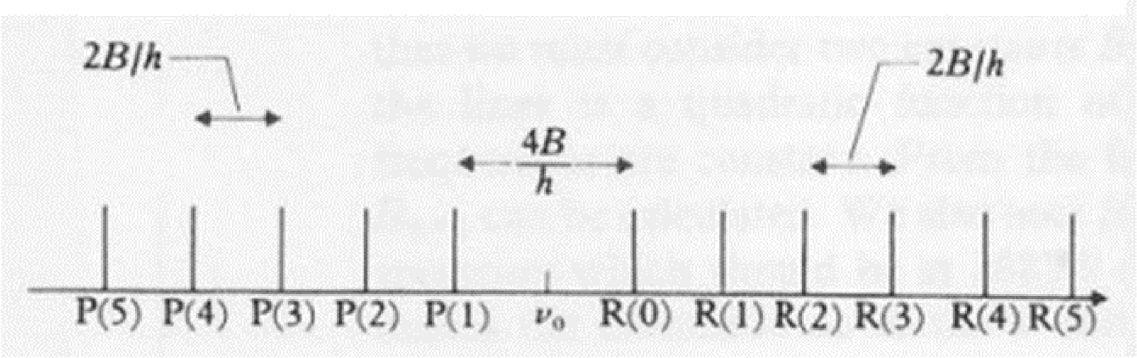
$$\omega[P(J)\,] = \frac{3}{2}\omega_e + BJ(J-1) - \frac{1}{2}\omega_e - BJ(J+1) = \omega_e - 2BJ$$

It follows that the spacing between adjacent $\boldsymbol{R-branch}$ lines and also between adjacent $\boldsymbol{P-branch}$ lines is $2B$:



3.4 ROTO-VIBRATIONAL SPECTROSCOPY

3.4.1 P-, R- and Q-branch structures



The spacing between the first $\boldsymbol{P-branch}$ transition, $P(1)$, and the first $\boldsymbol{R-branch}$ transition, $R(0)$, is equal to:

$$\omega[R(0)\,] - \omega[P(1)] = 4B$$

$$\omega[R(J)\,] = \omega_e + 2B(J+1)$$

$$\omega[P(J)\,] = \omega_e - 2BJ$$

By measuring the central frequency ω_e it is possible to derive the spring constant k, while from the measurement of the separation between two adjacent lines it is possible to determine the equilibrium distance between the two atoms.

3.4 ROTO-VIBRATIONAL SPECTROSCOPY

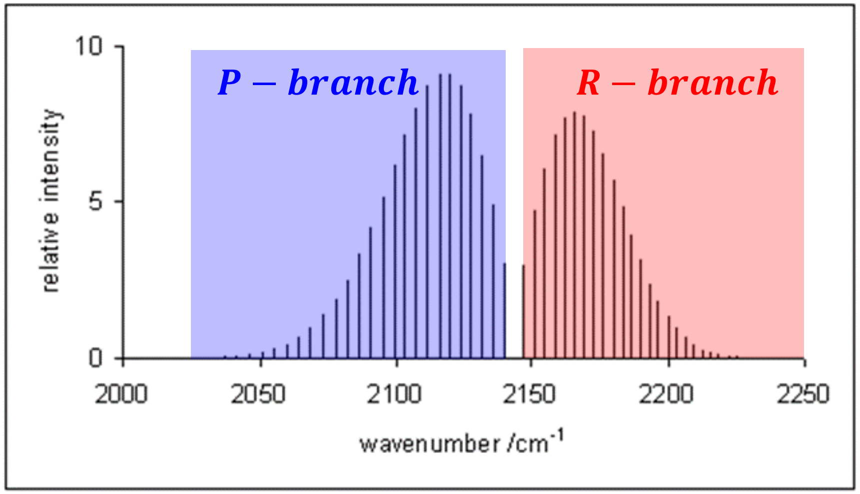
3.4.1 P-, R- and Q-branch structures

The intensity distribution among rotational transitions in a vibration–rotation band is governed principally by the Boltzmann distribution of population among the initial states, giving:

$$\frac{N_J}{N_0} = (2J+1)e^{-\frac{B\hbar J(J+1)}{KT}}$$

where J represents the initial energy level of the transition.

Ultimately, the P- and R-branches will appear as two bands:



3.4 ROTO-VIBRATIONAL SPECTROSCOPY

3.4.1 P-, R- and Q-branch structures

Since transitions with $\Delta J = 0$ are forbitten means that purely vibrational transitions are not allowed.

If they were allowed, they would all be at the center of the gap between P- and R-band.

The molecules that allow these transitions are those that have an electronic angular momentum in the ground electronic state.

An example is nitric oxide (NO).

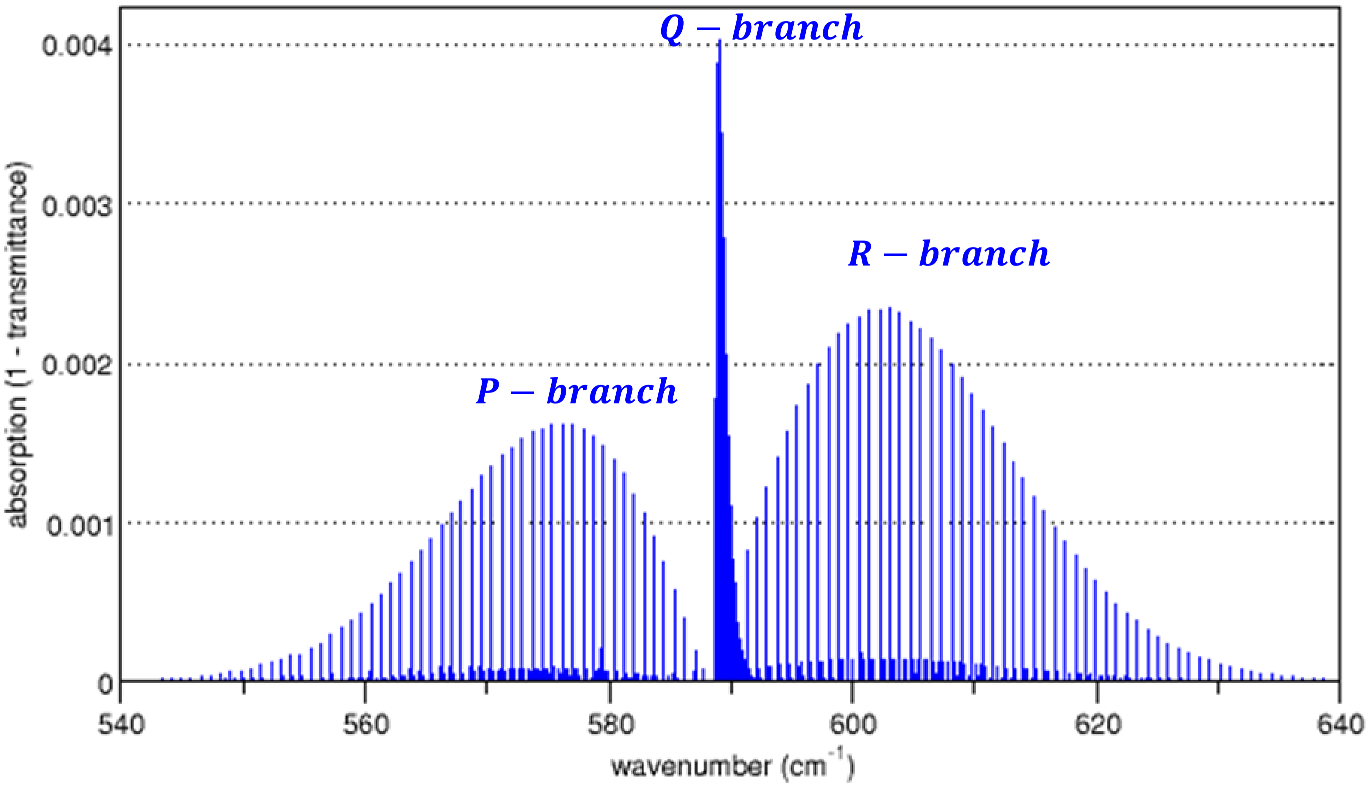
The rotational selection rule for this molecule is:

$$\Delta J = 0, \pm 1$$

and together with $\boldsymbol{R} -$ and $\boldsymbol{P - branch}$ we will have a very intense and narrow branch that corresponds to the transitions $\Delta J = 0$, named as $\boldsymbol{Q - branch}$

3.4 ROTO-VIBRATIONAL SPECTROSCOPY

3.4.1 P-, R- and Q-branch structures



3.4 ROTO-VIBRATIONAL SPECTROSCOPY

3.4.2 Branches asymmetry

The two bands are not quite symmetrical but shows a convergence in the R-branch and a divergence in the P-branch. .

This asymmetry is mainly because the B parameter depends on the frequency of the vibrational level, so it is necessary to introduce B_0 for all rotational levels of the fundamental vibration band $(\nu = 0)$ and B_1 for all rotational levels of the first overtone band $(\nu = 1)$.

In the analysis of roto-vibrational spectra it is possible to separate the two contributions.

The method is known as **the method of combination differences**: differences in wavenumber between transitions with a common upper state are dependent on properties of the lower states only.

Similarly, differences in wavenumber between transitions with a common lower state are dependent on properties of the upper states only.

For example, transitions $R(0)$ and $P(2)$ have a common upper state with $J' = 1$, then $\omega[R(0)\,] - \omega[P(2)]$ must be a function of B_1 only.

The same will be for transitions $R(1)$ and $P(3)$.

3.4 ROTO-VIBRATIONAL SPECTROSCOPY

3.4.2 Branches asymmetry

Generalizing:

$$\begin{aligned}&\omega[R(J-1)\,]-\omega[P(J+1)]\\&=\omega_e+B_0J(J+1)-B_1J(J-1)-[\omega_e+B_0J(J+1)-B_1(J+1)(J+2)]\\&=B_1(J+1)(J+2)-B_1J(J-1)=4B_1\left(J+\frac{1}{2}\right)\end{aligned}$$

Similarly, since all pairs of transitions $R(J)$ and $P(J)$ have common lower states, $\omega[R(J)\,]-\omega[P(J)]$ is a function of B_0 only and we have:

$$\begin{aligned}&\omega[R(J)\,]-\omega[P(J)]\\&=\omega_e+B_0(J+1)(J+2)-B_1J(J+1)-[\omega_e+B_0J(J-1)-B_1J(J+1)]\\&=B_0(J+1)(J+2)-B_0J(J-1)=4B_0\left(J+\frac{1}{2}\right)\end{aligned}$$

The band centre is not quite midway between $R(0)$ and $P(1)$ but its wavenumber ω_e can be obtained from:

$$\omega[R(0)]=\omega_e+2B_0$$

$$\omega[P(1)]=\omega_e-2B_1$$

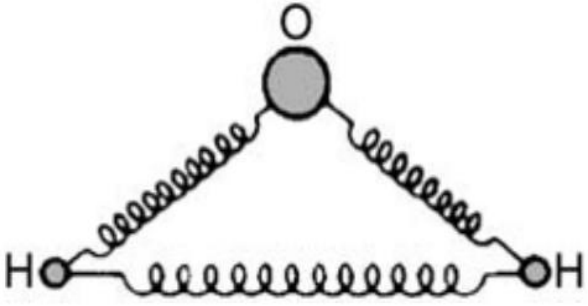
therefore: $\omega_e=\omega[R(0)]-2B_0=\omega[P(1)]+2B_1$

3.5 POLYATOMIC MOLECULES

3.5.1 Normal modes of vibration

Classically, we can think of the vibrational motions of a molecule as being those of a set of balls representing the nuclei, of various masses, connected by Hooke's law springs representing the various forces acting between the nuclei. .

This modelling for the H_2O molecule is shown in the Figure:



The stronger forces between the bonded O and H nuclei are represented by strong springs which provide resistance to stretching the bonds.

The weaker force between the non-bonded hydrogen nuclei is represented by a weaker spring which provides resistance to an increase or decrease of the HOH angle.

3.5 POLYATOMIC MOLECULES

3.5.1 Normal modes of vibration

Even with this simple model it is clear that if one of the nuclei is given a sudden displacement it is very likely that the whole molecule will undergo a very complicated motion, a Lissajous motion, consisting of a mixture of angle-bending and bond-stretching.

The Lissajous motion can always be broken down into a combination of the so-called normal vibrations of the system which, in the Lissajous motion, are superimposed in varying proportions..

A normal mode of vibration is one in which all the nuclei undergo harmonic motion, have the same frequency of oscillation and move in phase but generally with different amplitudes.

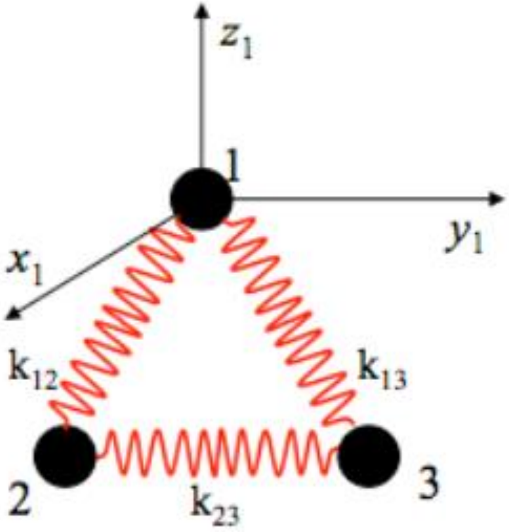
The form of the normal vibrations may be obtained from a knowledge of the bond lengths and angles and of the bond-stretching and angle-bending force constants, which are a measure of the strengths of the various springs in the ball-and-spring model.

3.5 POLYATOMIC MOLECULES

3.5.1 Normal modes of vibration

By the absorption of a photon, let's suppose to excite a vibration of the molecule represented in the Figure, assuming a displacement only for the atom **1**, that is, $\vec{r}_1 \neq 0$ only.

The origin point of the reference frame is in the equilibrium position of the atom **1**.



For small displacements, the force $\overrightarrow{F^1}$ acting upon the atom **1** will be:

$$\begin{cases} F_x^1 = -k_{xx}^{11}x_1 - k_{xy}^{11}y_1 - k_{xz}^{11}z_1 \\ F_y^1 = -k_{yx}^{11}x_1 - k_{yy}^{11}y_1 - k_{yz}^{11}z_1 \\ F_z^1 = -k_{zx}^{11}x_1 - k_{zy}^{11}y_1 - k_{zz}^{11}z_1 \end{cases}$$

In a more compact form:

$$F_\alpha^1 = -\sum_{\beta=1}^{3} k_{\alpha\beta}^{11} x_\beta^1$$

3.5 POLYATOMIC MOLECULES

3.5.1 Normal modes of vibration

$$F_\alpha^1 = -\sum_{\beta=1}^{3} k_{\alpha\beta}^{11} x_\beta^1$$

where $x_\beta^1 = (x_1, y_1, z_1)$ and $k_{\alpha\beta}^{11}$ is the stiffness tensor relative to the component α of the elastic force acting upon the atom **1** caused by a displacement along the direction β.

Including the case of the other two atoms (**2** e **3**), a homogeneous system with a 9×9 coefficient matrix is obtained

$$\begin{cases} F_x^1 = -k_{xx}^{11} x_1 \; \ldots -k_{xx}^{12} x_2 \; \ldots -k_{xz}^{13} z_3 \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \\ F_z^3 = -k_{zx}^{31} x_1 \; \ldots -k_{zx}^{32} x_2 \; \ldots -k_{zz}^{13} z_3 \end{cases}$$

For N atoms, it can be written compactly:

$$F_\alpha^i = -\sum_{\beta=1}^{3} \sum_{j=1}^{N} k_{\alpha\beta}^{ij} x_\beta^j$$

with $i, j = 1, \ldots, N$ and $\alpha, \beta = 1,2,3$

3.5 POLYATOMIC MOLECULES

3.5.1 Normal modes of vibration

The question now is: are there any solutions resulting in N atoms that vibrate all at the same frequency ω? In other words, we want to determine the normal modes of vibration such that, if m_j is the mass of the j-th atom, must result:

$$\begin{cases} F_x^1 = -\omega^2 m_1 x_1 \\ \dots\dots\dots\dots\dots\dots\dots.. \\ F_z^N = -\omega^2 m_N z_N \end{cases}$$

that can be rewritten as:

$$F_\alpha^i = -\omega^2 \sum_{\beta=1}^{3} \sum_{j=1}^{N} m_j x_\beta^j \delta_{\alpha\beta} \delta_{ij}$$

$$F_\alpha^i = -\sum_{\beta=1}^{3} \sum_{j=1}^{N} k_{\alpha\beta}^{ij} x_\beta^j$$

If the two expressions are imposed to be equal:

$$\sum_{\beta=1}^{3} \sum_{j=1}^{N} \left(k_{\alpha\beta}^{11} - \omega^2 m_j \delta_{\alpha\beta} \delta_{ij}\right) x_\beta^j = 0$$

3.5 POLYATOMIC MOLECULES

3.5.1 Normal modes of vibration

which has non-trivial solutions if and only if the determinant of the $3N \times 3N$ matrix coefficient is equal to zero:

$$\begin{vmatrix} k_{xx}^{11} - \omega^2 m_1 & k_{xy}^{11} & \dots & k_{zz}^{1N} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ k_{xx}^{1N} & k_{xy}^{1N} & \dots & k_{zz}^{NN} - \omega^2 m_N \end{vmatrix} = 0$$

This equation has $3N$ roots $\omega_1 \dots \omega_{3N}$ representing the normal modes of the molecule.

Some of these roots are always null:

- 6 roots in a generic molecule (3 translations of the center of mass and 3 rotations)
- 5 roots in a linear molecule (the rotation around the axis with a moment of inertia I = 0 is "frozen").

Ultimately, a molecule has:

- $\mathbf{3N - 5}$ normal modes of vibration if it is **linear**
- $\mathbf{3N - 6}$ normal modes of vibration if it is **non-linear**

3.5 POLYATOMIC MOLECULES

3.5.2 Group vibrations

In an approximation which is analogous to that which we have used for a diatomic molecule, each of the vibrations of a polyatomic molecule can be regarded as harmonic.

Quantum mechanical treatment in the harmonic oscillator approximation shows that the vibrational term values $G(v_i)$ associated with each normal vibration i, all taken to be nondegenerate, are given by:

$$G(v_i) = \omega_i \left(v_i + \frac{1}{2} \right)$$

where ω_i is the classical vibration wavenumber and v_i the vibrational quantum number which can take the values 0; 1; 2; 3; . . . .

In general, for vibrations with a degree of degeneracy d_i, the previous expression becomes:

$$G(v_i) = \omega_i \left(v_i + \frac{d_i}{2} \right)$$

3.5 POLYATOMIC MOLECULES

3.5.2 Group vibrations

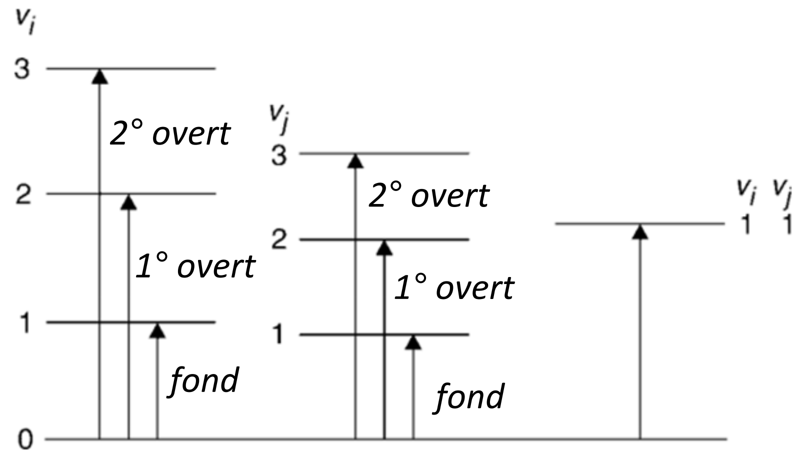
As for a diatomic molecule, the general harmonic oscillator selection rule for infrared vibrational transitions is:

$$\Delta v_i = \pm 1$$

for each vibration, with $\Delta v_i = \pm 2, \pm 3$ overtone transitions allowed, but generally weak, when account is taken of anharmonicity.

In addition there is the possibility of combination tones involving transitions to vibrationally excited states in which more than one normal vibration is excited.

Fundamental, overtone and combination tone transitions involving two vibrations v_i and v_j are illustrated in Figure.



vibration v_i vibration v_j combination tone $v_i + v_j$

3.5 POLYATOMIC MOLECULES

3.5.2 Group vibrations

For vibrational transitions to be allowed in the infrared spectrum there is an additional requirement that there must be an accompanying change of dipole moment.

These requirements necessitate further selection rules which depend on the symmetry properties of the molecule concerned.

However, their intensities depend on the magnitudes of the change of dipole moment : these may be so small for some vibrations that, although the transitions are allowed, they are too weak to be observed.

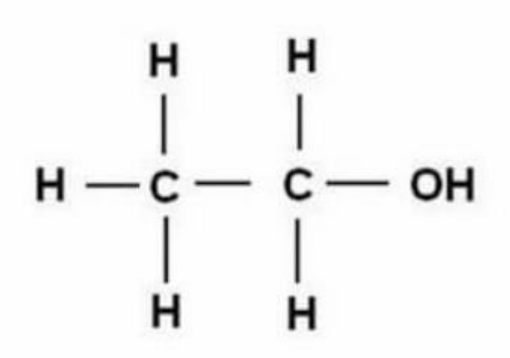
Although, in general, a normal mode of vibration involves movement of all the atoms in a molecule there are circumstances in which movement is more or less localized in a part of the molecule.

For example, if the vibration involves the stretching or bending of a terminal $X-Y$ group, where X is heavy compared with Y, the corresponding vibration wavenumbers are almost independent of the rest of the molecule to which $X-Y$ is attached.

3.5 POLYATOMIC MOLECULES

3.5.2 Group vibrations

For example,, In ethyl alcohol CH_3CH_2OH the motions of the hydrogen atom of the OH group are approximately those that it would have if it were attached to an infinite mass by a bond whose force constants are typical of an OH bond.



For this reason, we speak of a typical wavenumber of an OH-stretching vibration, for which the symbol $\upsilon(OH)$ is used, which can vary from 3590 to 3650 cm^{-1}.

The wavenumber range is small and reflects the relatively slight dependence on the part of the molecule in the immediate neighborhood of the group.

Such a typical wavenumber is called a **group wavenumber** or, incorrectly, but commonly, a group frequency.

Another group wavenumber of the OH group is the bending, or deformation, vibration which is typically in the 1050 cm^{-1} to 1200 cm^{-1} range.

3.5 POLYATOMIC MOLECULES

3.5.2 Group vibrations

Other general circumstances in which normal vibrations tend to be localized in a particular group of atoms arise when there is a chain of atoms in which the force constant between two of them is very different from those between other atoms in the chain.

For example, in the molecule $HC \equiv C - CH = CH_2$ the force constants in the $C - C$, $C = C$ e $C \equiv C$ bonds are quite dissimilar.

It follows that the stretchings of the bonds are not strongly coupled and that each stretching vibration wavenumber is typical of the $C - C$, $C = C$ e $C \equiv C$ group.

Not all parts of a molecule are characterized by group vibrations. Many normal modes involve strong coupling between stretching or bending motions of atoms in a straight chain, a branched chain or a ring. .

Such vibrations are called **skeletal vibrations** and tend to be specific to a particular molecule.

For this reason, the region where skeletal vibrations mostly occur, from about 1300 cm^{-1} to low wavenumber, is sometimes called the **fingerprint region**.

3.5 POLYATOMIC MOLECULES

3.5.2 Group vibrations

Skeletal vibrations

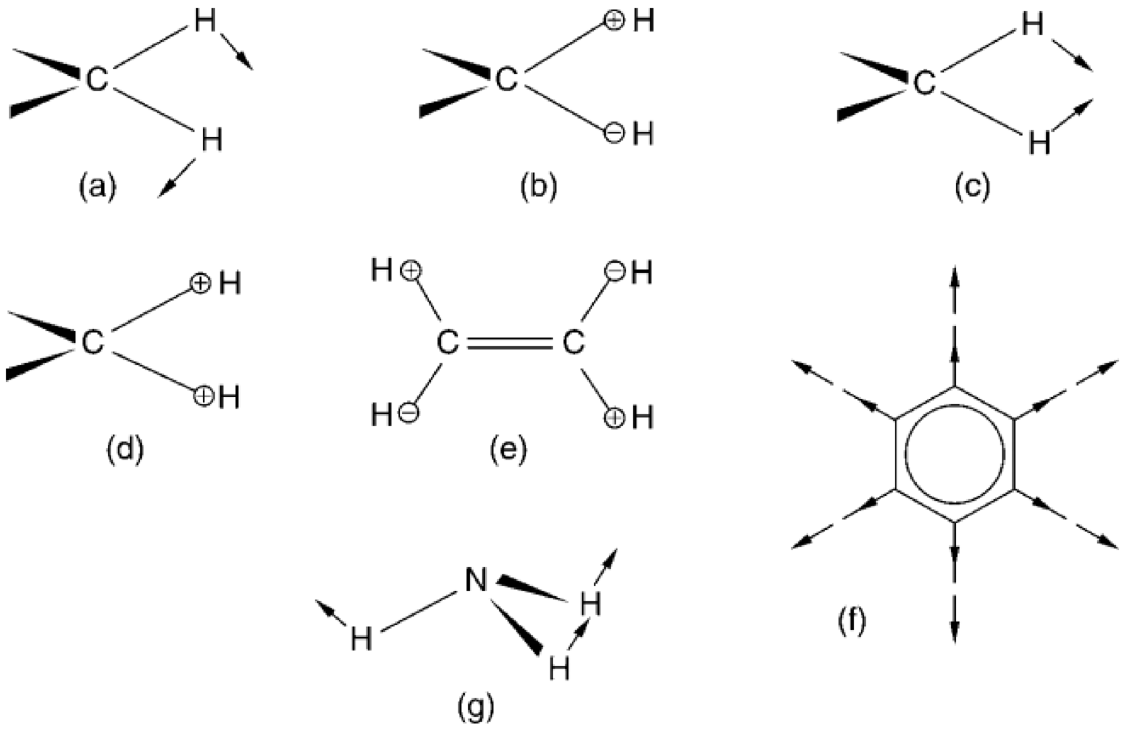


Figure 6.13 Illustration of (a) rocking, (b) twisting, (c) scissoring and (d) wagging vibrations in a CH_2 group. Also shown are (e) the torsional vibration in ethylene, (f) the ring-breathing vibration in benzene and (g) the inversion, or umbrella, vibration in ammonia

3.5 POLYATOMIC MOLECULES

3.5.2 Group vibrations

In the infrared spectrum the intensity of absorption due to a particular vibration depends on the change of dipole moment during the vibration, similar to that for a diatomic molecule.

For example, the stretching vibration of the strongly polar $C = O$ bond gives a strong absorption band, whereas that of the $C = C$ bond gives a weak band.

Indeed, if the $C = C$ bond is in a symmetrical molecule such as $H_2C = CH_2$ there is no change of dipole moment at all and the vibration is infrared inactive.

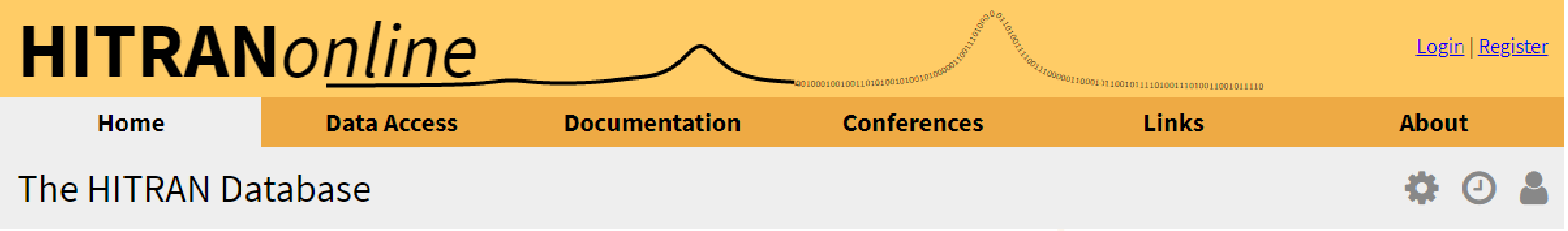
If the $C = C$ bond is in, say, $HFC = CH_2$, there is a small change of dipole moment due to stretching of the bond but clearly not as large a change as that due to stretching of the $C - F$ bond.

Just as group vibration wavenumbers are fairly constant from one molecule to another, so are their intensities.

For example, if a molecule were being tested for the presence of a $C - F$, bond there must be not only an infrared absorption band due to bond-stretching at about 1100 cm cm^{-1}, but also it must be intense.

3.6 HITRAN DATABASE

https://hitran.org/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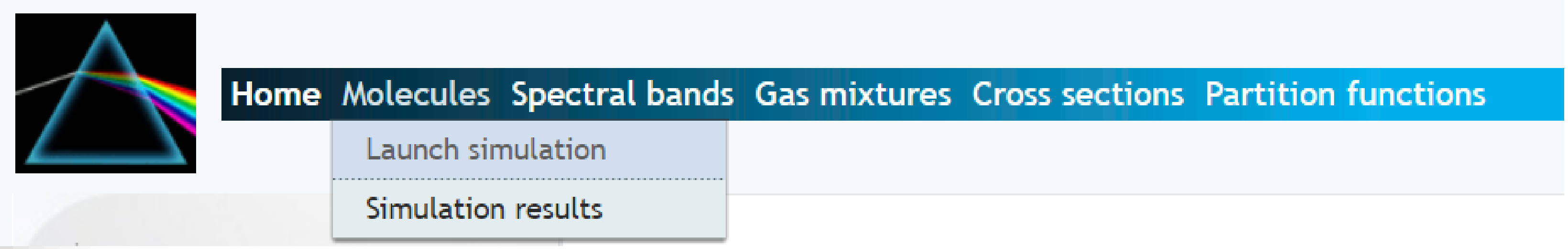
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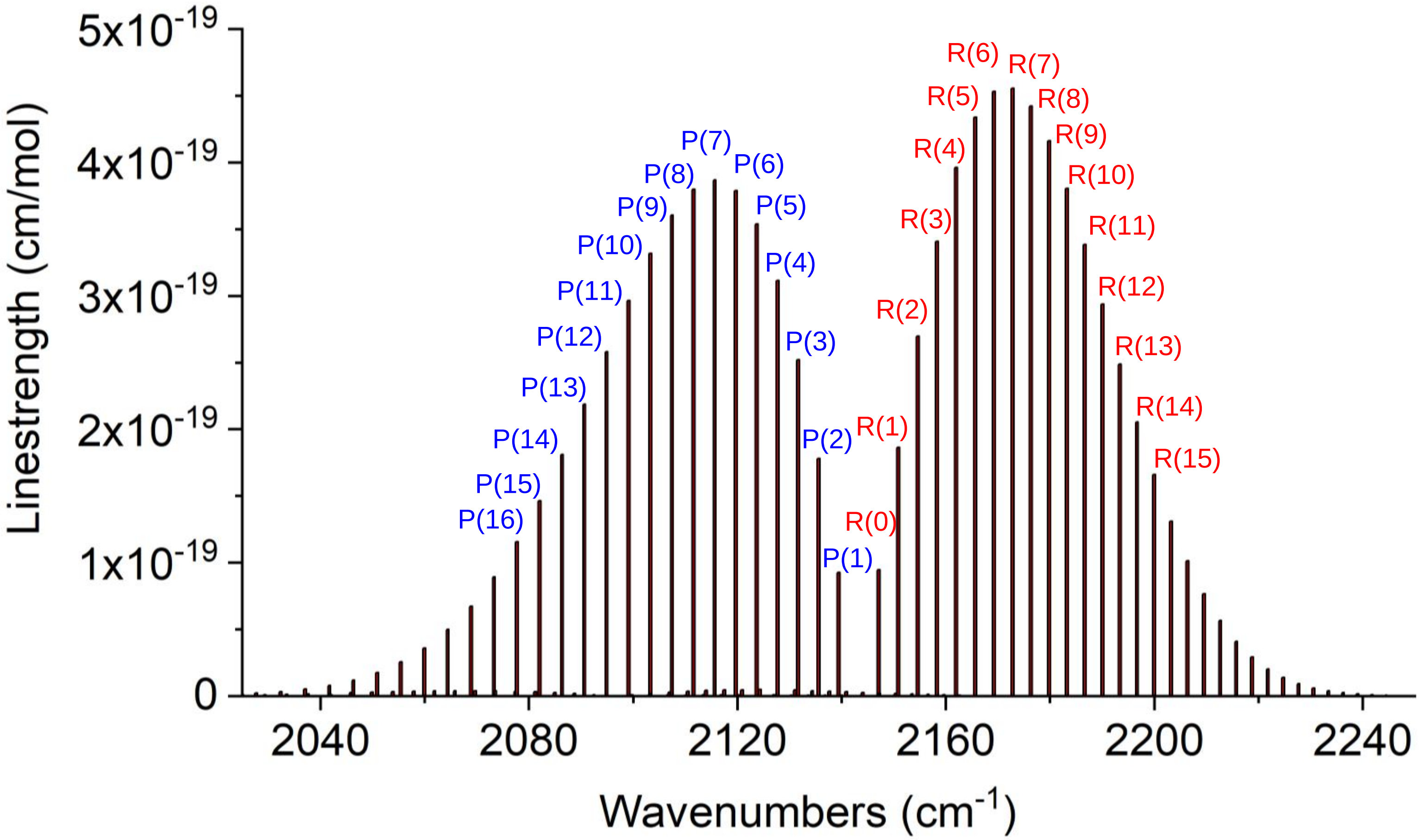
Launch simulation

Simulation results

3.7 EXAMPLE: FUNDAMENTAL BAND OF CO



3.7 EXAMPLE: FUNDAMENTAL BAND OF CO

We determine the rotational constant B.

Apply **the method of combination differences**: differences in wavenumber between transitions with a common upper state are dependent on properties of the lower states only.

$$\omega[R(J-1)\,] - \omega[P(J+1)] = 4B_1\left(J+\frac{1}{2}\right)$$

Similarly, differences in wavenumber between transitions with a common lower state are dependent on properties of the upper states only.

$$\omega[R(J)\,] - \omega[P(J)] = 4B_0\left(J+\frac{1}{2}\right)$$

First wee need to convert the wavenumbers to angular frequency because B_0 and B_1 were defined in units of angular frequency.

The angular frequency ω is related to the frequency υ

$$\omega = 2\pi\upsilon$$

which in turn is related to the wavelength λ and the wavenumber $\tilde{\upsilon}$:

$$\upsilon = \frac{c}{\lambda} = c\tilde{\upsilon}$$

where c is the speed of light.

3.7 EXAMPLE: FUNDAMENTAL BAND OF CO

Then merging both expressions:

$$\omega = 2\pi c\tilde{\nu}$$

Since $\tilde{\nu}$ is in [cm^{-1}], $c = 0.03\, THz \cdot cm$

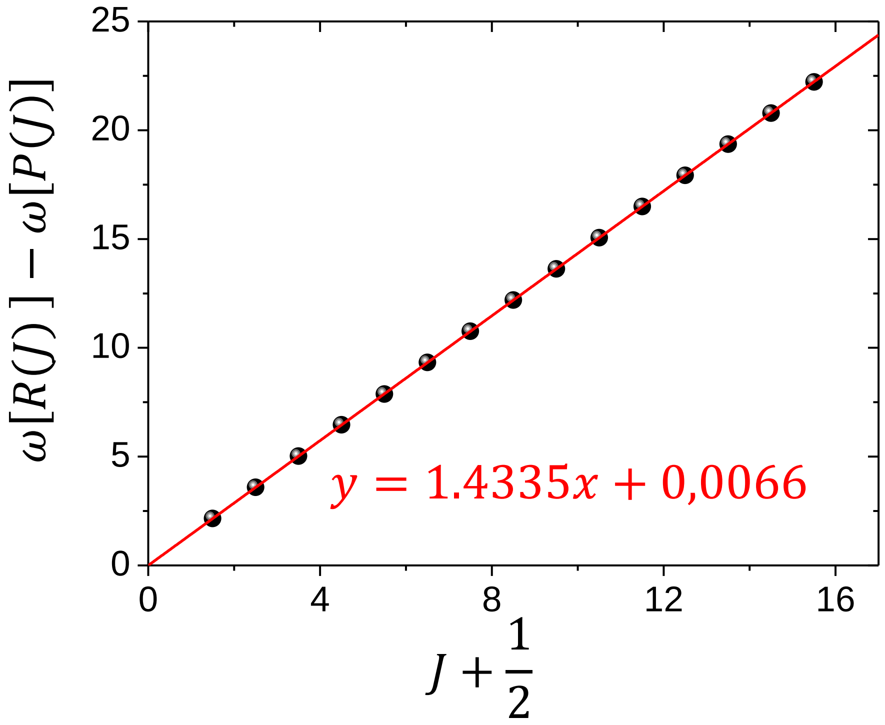
Linea	**$\tilde{\nu}$ (cm^{-1})**	**ω (THz)**
P(1)	2139,43	403,069
P(2)	2135,55	402,338
P(3)	2131,63	401,599
P(4)	2127,68	400,855
P(5)	2123,79	400,122
P(6)	2119,68	399,348
P(7)	2115,63	398,585
P(8)	2111,54	397,814
P(9)	2107,42	397,038
P(10)	2103,27	396,256
P(11)	2099,08	395,467
P(12)	2094,86	394,672
P(13)	2090,61	393,871
P(14)	2086,32	393,063
P(15)	2082	392,249
P(16)	2077,65	391,429

Linea	**$\tilde{\nu}$ (cm^{-1})**	**ω (THz)**
R(0)	2147,08	404,510
R(1)	2150,86	405,222
R(2)	2154,59	405,925
R(3)	2158,3	406,624
R(4)	2161,97	407,315
R(5)	2165,6	407,999
R(6)	2169,2	408,677
R(7)	2172,76	409,348
R(8)	2176,28	410,011
R(9)	2179,77	410,669
R(10)	2183,22	411,319
R(11)	2186,64	411,963
R(12)	2190,02	412,600
R(13)	2193,36	413,229
R(14)	2196,66	413,851
R(15)	2199,93	414,467

3.7 EXAMPLE: FUNDAMENTAL BAND OF CO

Determine B_0 : $$\omega[R(J)\,] - \omega[P(J)] = 4B_0\left(J + \frac{1}{2}\right)$$

J		
1	R(1)-P(1)	2,153
2	R(2)-P(2)	3,587
3	R(3)-P(3)	5,025
4	R(4)-P(4)	6,460
5	R(5)-P(5)	7,877
6	R(6)-P(6)	9,330
7	R(7)-P(7)	10,763
8	R(8)-P(8)	12,197
9	R(9)-P(9)	13,631
10	R(10)-P(10)	15,063
11	R(11)-P(11)	16,496
12	R(12)-P(12)	17,928
13	R(13)-P(13)	19,358
14	R(14)-P(14)	20,788
15	R(15)-P(15)	22,218

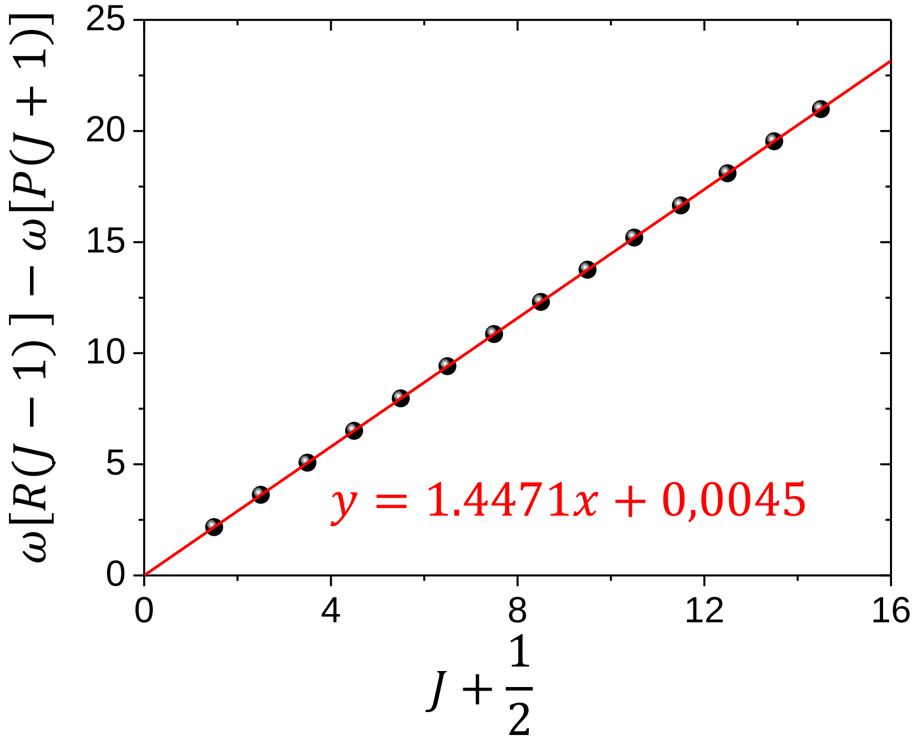


$$B_0 = 0.358\,THz$$

3.7 EXAMPLE: FUNDAMENTAL BAND OF CO

Determine B_1 : $$\omega[R(J-1)\,] - \omega[P(J+1)] = 4B_1\left(J + \frac{1}{2}\right)$$

J		
1	R(0)-P(2)	2,172
2	R(1)-P(3)	3,623
3	R(2)-P(4)	5,070
4	R(3)-P(5)	6,502
5	R(4)-P(6)	7,967
6	R(5)-P(7)	9,414
7	R(6)-P(8)	10,863
8	R(7)-P(9)	12,310
9	R(8)-P(10)	13,755
10	R(9)-P(11)	15,202
11	R(10)-P(12)	16,647
12	R(11)-P(13)	18,092
13	R(12)-P(14)	19,537
14	R(13)-P(15)	20,980



$$B_1 = 0.362\,THz$$

3.7 EXAMPLE: FUNDAMENTAL BAND OF CO

Once the rotational constant is known, we can determine the length of the bond $C - O$. The rotational constant B is defined as:

$$B = \frac{h}{4\pi I} = \frac{h}{4\pi \mu r^2}$$

where the reduced mass μ is defined as:

$$\mu = \frac{m_{\mathrm{C}} m_{\mathrm{O}}}{m_{\mathrm{C}} + m_{\mathrm{O}}}$$

Knowing that: $m_{\mathrm{C}} = 12u$ is the mass of the carbon atom

$m_{\mathrm{O}} = 16u$ is the mass of the oxygen atom

with $u = 1.66 \cdot 10^{-27}\,\mathrm{kg}$ unified atomic mass unit

The reduced mass will be:

$$\mu = \frac{m_{\mathrm{C}} m_{\mathrm{O}}}{m_{\mathrm{C}} + m_{\mathrm{O}}} = \frac{12 \cdot 16u^2}{28u} = 6.86\,u$$

3.7 EXAMPLE: FUNDAMENTAL BAND OF CO

Ultimately we can determine the length of the bond $C-O$ by using the expression $B_{0,1}[Hz] = \frac{h[\boldsymbol{J\cdot s}]}{4\pi\mu[\boldsymbol{kg}]r^2[\boldsymbol{m^2}]}$, with $h = 6{,}626 \cdot 10^{-34}\,J \cdot s$:

$$r = \sqrt{\frac{h}{4\pi\mu B_{0,1}}}$$

Using $B_0 = 0.358\,THz$:

$$r_0 = \sqrt{\frac{h}{4\pi\mu B_{0,1}}} = \sqrt{\frac{6{,}626 \cdot 10^{-34}\,J \cdot s}{4 \cdot 3.14 \cdot 6.86 \cdot 1.66 \cdot 10^{-27}\,\mathrm{kg} \cdot 0.358 \cdot 10^{12}\,Hz}} = 113.72\,pm$$

Using $B_1 = 0.362\,THz$:

$$r_1 = \sqrt{\frac{h}{4\pi\mu B_{0,1}}} = \sqrt{\frac{6{,}626 \cdot 10^{-34}\,J \cdot s}{4 \cdot 3.14 \cdot 6.86 \cdot 1.66 \cdot 10^{-27}\,\mathrm{kg} \cdot 0.358 \cdot 10^{12}\,Hz}}$$
$$= 113.18\,pm$$

3.7 EXAMPLE: FUNDAMENTAL BAND OF CO

We can now determine the classical frequency of vibration:

$$\omega_e = \omega[R(0)] - 2B_0 = \omega[P(1)] + 2B_1$$

Replacing:

$$\omega_{e,0} = \omega[R(0)] - 2B_0 = 404{,}510\, THz - 0.716\, THz = 403{,}794\, THz$$

$$\omega_{e,1} = \omega[P(1)] + 2B_1 = 403{,}069\, THz + 0.724\, THz = 403{,}793\, THz$$

Note the classical frequency of vibration, we can determine the spring constant k :

$$k = \omega_e^2 \mu$$

Substituting the obtained values:

$$k = 403.79^2 \cdot 10^{24} Hz \cdot 6.86 \cdot 1.66 \cdot 10^{-27}\,\text{kg} = 1.855.96\ \frac{N}{m}$$