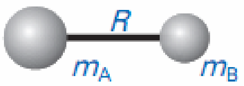
Rotational spectroscopy

Mechanical properties of rotation

Torque: m·**r**

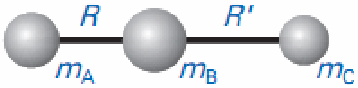
Moment of inertia, ***I***: $\mathbf{I} = \sum_i m_i \mathbf{r}_i^2$

1. *Diatomic molecules*

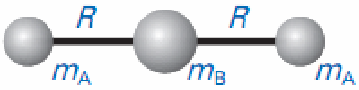


$$I = \mu R^2 \qquad \mu = \frac{m_A m_B}{m}$$

2. *Triatomic linear rotors*

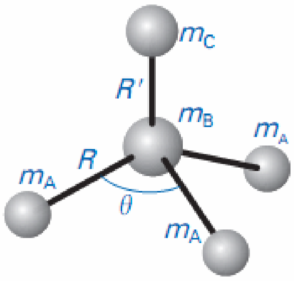


$$I = m_A R^2 + m_C R'^2 - \frac{(m_A R - m_C R')^2}{m}$$



$$I = 2m_A R^2$$

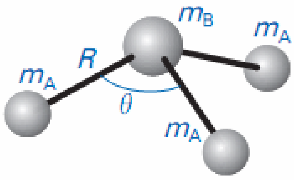
3. *Symmetric rotors*



$$I_{\parallel} = 2m_A(1-\cos\theta)R^2$$

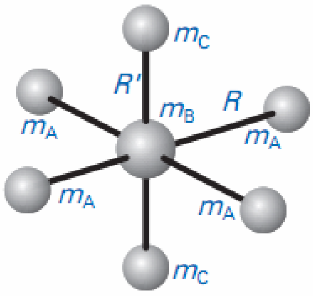
$$I_{\perp} = m_A(1-\cos\theta)R^2 + \frac{m_A}{m}(m_B + m_C)(1 + 2\cos\theta)R^2$$

$$+ \frac{m_C}{m}\left\{(3m_A + m_B)R' + 6m_A R[\tfrac{1}{3}(1+2\cos\theta)]^{1/2}\right\}R'$$



$$I_{\parallel} = 2m_A(1-\cos\theta)R^2$$

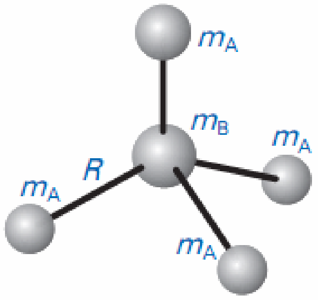
$$I_{\perp} = m_A(1-\cos\theta)R^2 + \frac{m_A m_B}{m}(1 + 2\cos\theta)R^2$$



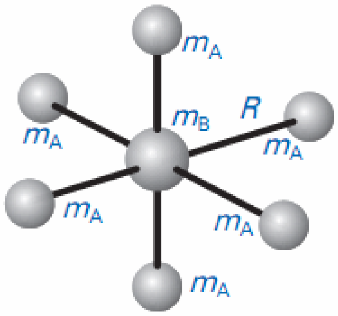
$$I_{\parallel} = 4m_A R^2$$

$$I_{\perp} = 2m_A R^2 + 2m_C R'^2$$

4. *Spherical rotors*



$$I = \tfrac{8}{3} m_A R^2$$



$$I = 4 m_A R^2$$

The moment of inertia of a molecule is a measure of how difficult it is to rotationally accelerate the molecule - the larger the moment of inertia, the smaller the increase in **angular momentum** for a given applied **torque.**

Because I depends on both the mass of the atoms and the geometry of the molecule, the rotational spectroscopy will provide us with information about *bond lengths and bond angles*.

Angular momentum: $\mathbf{J} = \mathbf{I} \cdot \omega$

where $\omega = 2\pi \cdot \nu$, the angular velocity of a rotating object with ν rotational frequency.

The moment of inertia of a diatomics

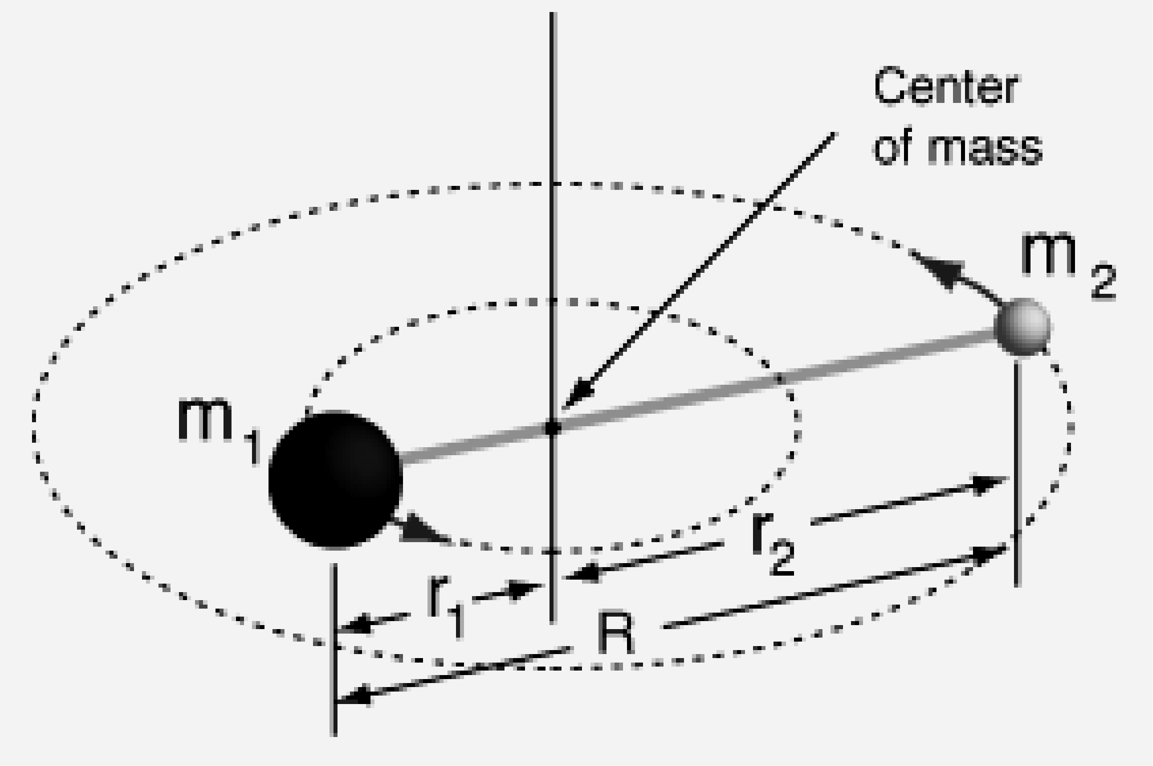


Figure 1. The rotation produces ***I*** perpendicular to the plane of rotation.

The bond distance: $R = r_1 + r_2$

The center of mass has a physical property,

$$r_1 m_1 = r_2 m_2 \qquad 1.$$

The moment of inertia:

$$I = m_1 r_1^2 + m_1 r_2^2 \qquad 2.$$

The radial distances from masscenter can be given by bond length

$$r_1 = \frac{m_2 R}{m_1 + m_2} \qquad r_2 = \frac{m_1 R}{m_1 + m_2} \qquad 3.$$

Substituting r_1 and r_2 into Equation 2. we get for ***I***

$$\mathbf{I} = \frac{m_1 m_2}{m_1 + m_2} \mathbf{R}^2$$

Introducing reduced mass, μ

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad\qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mathbf{I} = \mu \cdot \mathbf{R}^2 \qquad 4.$$

For multi-atom molecules, the reduced mass is determined by replacing the two values of m_i with the total masses of the molecule to both sides of the bond in question. In other words, the multi-atom molecule is calculated as though it is a molecule with two atoms, where each atom is the part of the molecule on either side of the bond.

In general, the rotational properties of any molecule can be expressed using the moments of inertia about three mutually perpendicular axes.

Axes are labelled: I_a, I_b and I_c, choosing the axes in such a way that

$$I_c \geq I_b \leq I_a$$

Note that for *linear molecules*, the moment of inertia around the molecular axis is zero, as all the atoms lie on the axis of rotation so are at zero distance from it.

Model 1: rigid rotor.
The amplitude of a vibration is small compared to the bond length of the rotating molecule, therefore bond length can be regarded as constant.
We suppose that molecules are *rigid rotors*, bodies that do not distort under the stress of rotation. Rigid rotors can be classified into four types:

Spherical rotors have three equal moments of inertia (e.g. CH_4, SF_6)

$$\mathbf{I}_c = \mathbf{I}_b = \mathbf{I}_a$$

Symmetric rotors have two equal moments of inertia (e.g. CH_3Cl, NH_3, C_6H_6).

$$\mathbf{I}_c = \mathbf{I}_b \neq \mathbf{I}_a$$

Linear rotors have one moment of inertia (that around the molecular axis) equal to zero (e.g.CO_2, HCl, CH≡CH).

$$\mathbf{I}_\mathrm{c} = \mathbf{I}_\mathrm{b} \quad \mathbf{I}_\mathrm{a} = 0$$

Asymmetric rotors have three different moments of inertia.

$$\mathbf{I}_c \neq \mathbf{I}_b \neq \mathbf{I}_a$$

Classical mechanics gives expressions for the energy of a rotating body in terms of the angular momentum, and we may obtain the analogous quantum mechanical expressions by **substitution** of the quantum expressions for angular momentum.

The classical expression for a body rotating about a given axis with angular velocity ω is

$$E = \frac{I\omega^2}{2} \qquad 1.$$

Note the similarity to the classical expression for linear kinetic energy.

$$E_{\text{lin}} = \frac{m\text{v}^2}{2}$$

The moment of inertia is the rotational equivalent of the mass, and the angular velocity replaces the linear velocity. A body free to rotate about three mutually perpendicular axes has an energy given by:

$$E = \frac{I_{\text{a}}\omega_{\text{a}}^2}{2} + \frac{I_{\text{b}}\omega_{\text{b}}^2}{2} + \frac{I_{\text{c}}\omega_{\text{c}}^2}{2} \qquad 2.$$

Equation 2. can be transformed

$$E = \frac{I_{\text{a}}^2\omega_{\text{a}}^2}{2I_{\text{a}}} + \frac{I_b^2\omega_{\text{b}}^2}{2I_b} + \frac{I_c^2\omega_{\text{c}}^2}{2I_c}$$

to substitute angular momentum, *J*.

$$E = \frac{J_{\text{a}}^2}{2I_{\text{a}}} + \frac{J_{\text{b}}^2}{2I_b} + \frac{J_{\text{c}}^2}{2I_c} \qquad 3.$$

For a symmetric rotor Equation 3. takes the form

$$E = \frac{J^2}{2I} \qquad 3a.$$

According to classical theory, radiation of any frequency may be absorbed by a molecule with a permanent dipole moment since there is no restriction on the rotational frequency of the molecule, but quantum theory requires that a molecule may only possess energies given by equation,

$$E_{rot}(J) = J(J+1)\cdot\frac{h^2}{4\pi^2\cdot 2I} = J(J+1)\cdot\frac{h^2}{8\pi^2\cdot I} \qquad 4.$$

and so only *finite quanta of energy* may be absorbed or emitted.

When J^2 in Equation 3a. is replaced by $J(J+1)h^2/(4\pi^2)$, the result is Equation 4., which is the solution of Schrödinger equation for rotation energy.

The magnitude of the angular momentum was given by **quantum number, *J***, which was restricted to positive integral values (and zero).

$J = 0, 1, 2, 3, ...$; and $\Delta J = \pm 1$

Selection rule. A molecule must have a permanent dipole moment, i.e. $\mu \neq 0$, for absorbing microwave radiation.

The rotation energy in Equation 4. is frequently given in wavenumber terms, and a rotation constant B is can be separated.

$$hc\cdot\tilde{v} = J(J+1)\cdot\frac{h^2}{8\pi^2\cdot I}$$

$$\tilde{v} = J(J+1)\cdot\frac{h}{8\pi^2\cdot I\cdot c} = J(J+1)B \qquad 5.$$

The rotation constant, B of a molecule is characteristic to the nature of molecule, and independent of J.
The greater the molecule the higher its moment of inertia and B becomes smaller. If the velocity of light is given in cm/s units the unit of B is cm^{-1}.

System can only absorb that quantum of energy or wavenumber of microwave radiation, which can be given as the difference between two subsequent levels of rotation level series, $J_1 - J_2$.

In this notation J_1 and J_2 mean the lower level and upper level respectively, and the difference between them is

$$J_2 - J_1 = 1 \qquad 6.$$

Transition $J_1 \rightarrow J_2$:

$$\tilde{\nu} = \frac{\Delta E}{hc} = BJ_2(J_2+1) - BJ_1(J_1+1) = B \cdot \left(J_2^2 + J_2 - J_1^2 - J_1\right)$$

From Eq. 6.: $J_2 = 1 + J_1$ and $J_2^2 = (1 + J_1)^2$

$$\tilde{\nu} = B \cdot \left(J_2^2 + J_2 - J_1^2 - J_1\right) = B\left(1 + 2J_1 + J_1^2 + 1 + J_1 - J_1^2 - J_1\right) = 2B \cdot (J_1 + 1) \qquad 7.$$

The wavenumber can be phrased either by lower rotation level

$$\tilde{\nu} = 2B \cdot (J_1 + 1) \qquad 7.$$

or by upper rotation level.

$$\tilde{\nu} = 2B \cdot J_2 \qquad 7a.$$

This wavenumber equals to the peak position of one band in the vibrational spectrum.

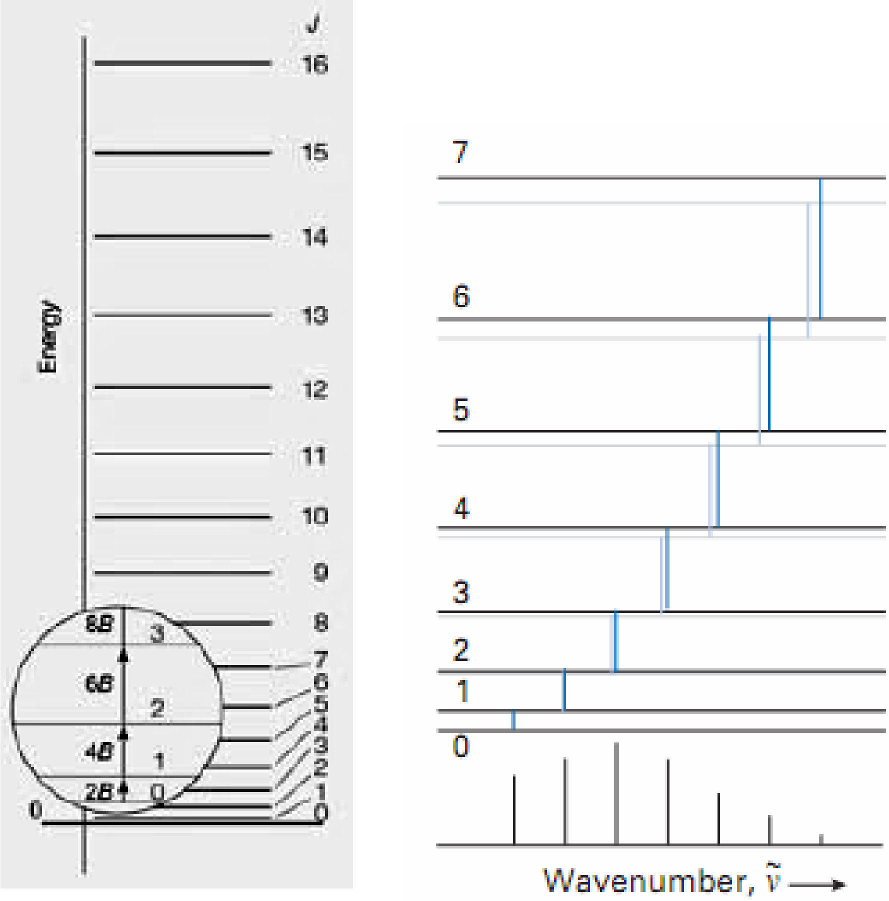


Figure 2. Energy level spacing for linear or spherical rotor.

Table 1. for rotation levels

J	$\tilde{\nu}\,/\,\mathrm{cm}^{-1}$	$\Delta\tilde{\nu}\,/\,\mathrm{cm}^{-1}$
1	$4B$	
2	$6B$	$2B$
3	$8B$	$2B$
4	$10B$	$2B$

The rotational levels are not equidistant, which can be seen from the second column of Table 1.

Peak separation Δv.
The rotation spectra contains peak series with peak separation equal to each other.

$$\Delta\tilde{\nu} = 2B\cdot\left(J_1+1\right) - 2BJ_1 = 2B \qquad 8.$$

The result given in Eq. 8 originates from Eq. 7.

Equation 4. for $E_{rot}(J)$ is only approximate. In order to provide a better description of the energy levels of a diatomic molecule, *a centrifugal distortion term* is added to the energy.
This takes into account of the fact that as a real molecule rotates faster and faster (i.e. with more energy), the bond stretches a little (if you swing a weight attached to a piece of elastic in a circle, you can observe the same effect on a macroscopic scale).

$$E_{rot}(J) = J(J+1)\cdot B - D_J J^2 (J+1)^2 \qquad 9.$$

D_J is called the *centrifugal distortion constant*, and is several orders of magnitude smaller than B.

The spectrum
Separations of rotational energy levels correspond to the *microwave region* of the electromagnetic spectrum.

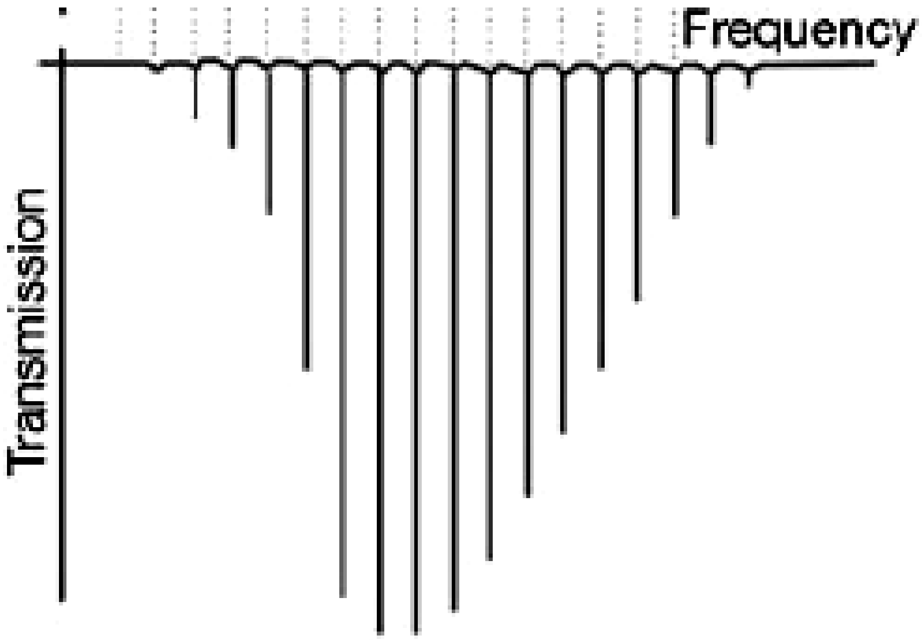


Figure 3. Rotational Spectrum of NH_3

Example

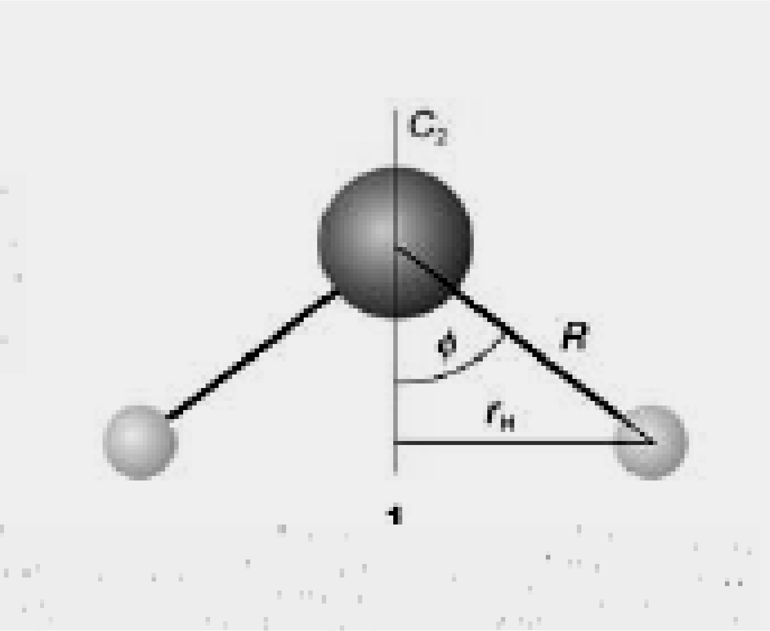


Figure 4. To the moment of inertia of water.

Calculate the moment of inertia of water by using data

the HOH bond angle, $2\Phi=104.5^{\circ}$,
the HO bond length, $R = 95.4$ pm
the mass of proton $m_H = 1.67\ 10^{-27}$ kg

We add up moments of inertia of two hydrogen and one oxygen atoms

$$I = m_H r_H^2 + 0 + m_H r_H^2 = 2 m_H r_H^2$$

The oxygen atom is on the axis therefore it has zero moment of inertia.

$$r_H = R \cdot \sin\Phi = 95.4 \cdot 10^{-12} \cdot \sin 52.25 = 7.54 \cdot 10^{-11}\,\mathrm{m}$$

$$I = 2 \cdot 1.67 \cdot 10^{-27} \cdot \left(7.54 \cdot 10^{-11}\right)^2 = 1.9 \cdot 10^{-47}\,\mathrm{kgm}^2$$

Rotational-vibrational fine structure

In gas phase the fine structure belonging to a vibration band shows rotation fine splitting. In some cases, a single vibration transition appears as triplet band containing P, Q, R branches, as a result of vibration rotation interaction.
Vibration alters the length and angular momentum of rotating bond periodically.

This interaction can be described by the sum of vibrational and rotational energies.

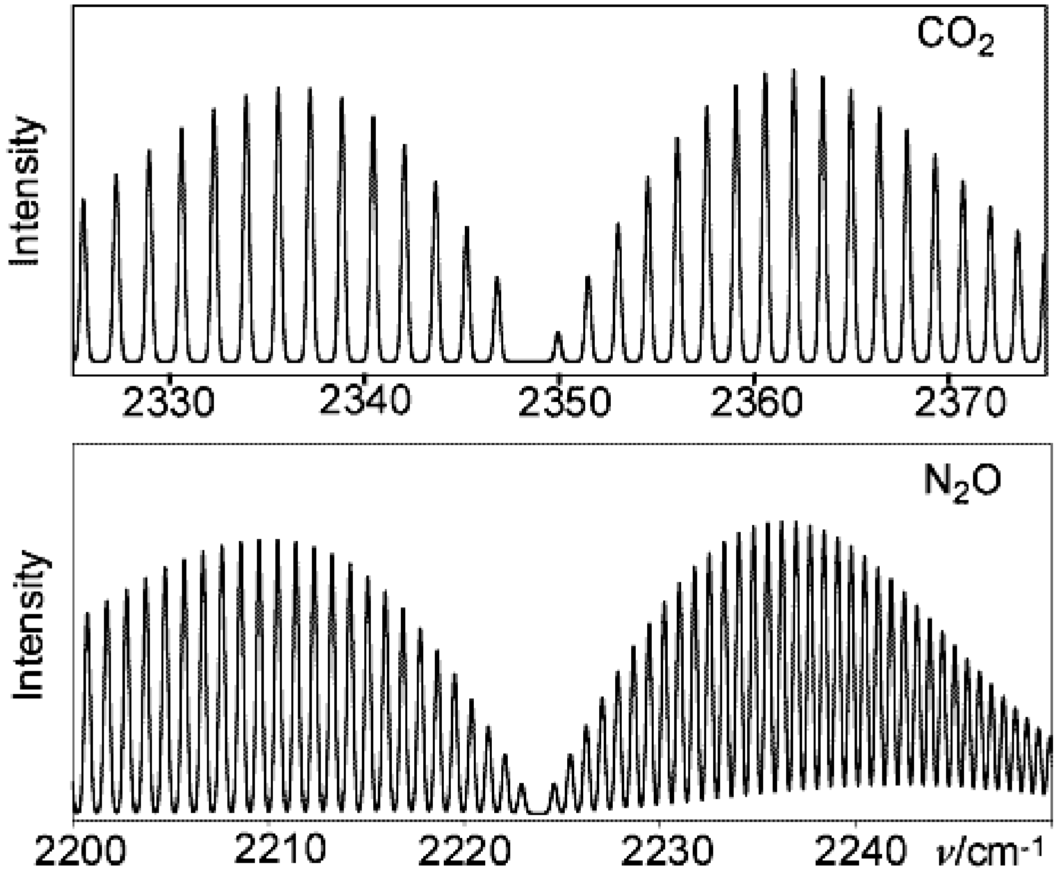


Figure 5. Infrared vibration-rotation bands of CO_2 and N_2O are shown.

The rotation quantum number J changes by ±1 during the vibrational transition of a diatomic molecule, and selection rules also allow $\Delta J = 0$.

The combined rotation vibration terms given in wavenumber

$$\tilde{\mathrm{v}}(\mathrm{v}, J) = (\mathrm{v} + 1/2)\tilde{\mathrm{v}}_{\mathrm{v}} + BJ(J+1)$$

Transition P:

$$\mathrm{v} \rightarrow \mathrm{v}+1 \qquad\qquad J+1 \rightarrow J$$

$$\tilde{\mathrm{v}}(\mathrm{v}, J) = (\mathrm{v} + 3/2 - \mathrm{v} - 1/2)\tilde{\mathrm{v}}_{\mathrm{v}} + B(J(J+1) - (J+1)\cdot(J+2))$$

$$\tilde{\mathrm{v}}(\mathrm{v}, J) = \tilde{\mathrm{v}}_{\mathrm{v}} - 2B(J+1) \qquad 10.$$

The result in Eq. 10 can be seen in Fig. 6., the lowest energy branch.

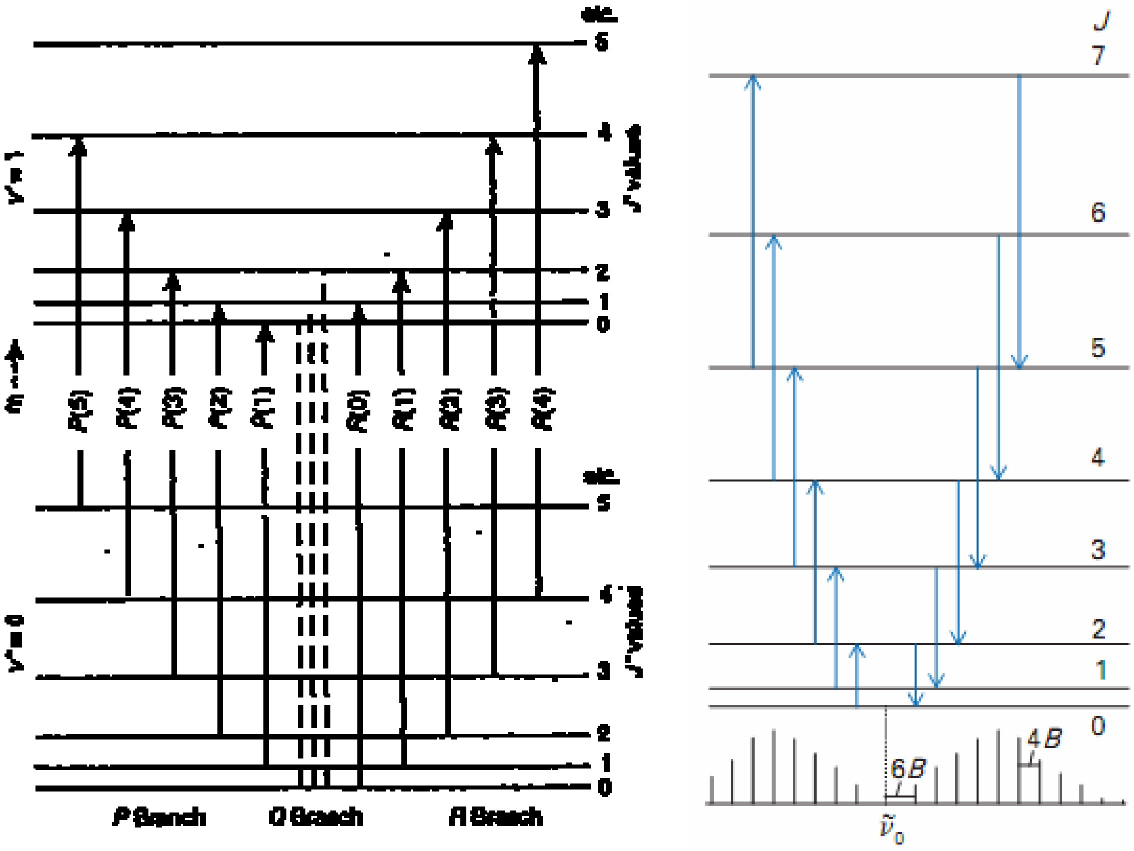


Figure 6. Transitions between the lowest vibrational state, denoted v=0, and the next highest vibrational state (v=1). Each vibrational state has many rotational levels denoted by a rotational quantum number (J' for the upper vibrational state, and J'' for the lower). The spacing between rotational levels of the same vibrational state has been greatly exaggerated for clarity.

Transition Q (in some cases forbidden):

$\mathrm{v} \rightarrow \mathrm{v}+1 \qquad\qquad J \rightarrow J$

$$\tilde{\mathrm{v}}(\mathrm{v}, J) = \tilde{\mathrm{v}}_{\mathrm{v}} \qquad 11.$$

Transition R:

$\mathrm{v} \rightarrow \mathrm{v}+1 \qquad\qquad J \rightarrow J+1$

$$\tilde{\mathrm{v}}(\mathrm{v}, J) = \tilde{\mathrm{v}}_{\mathrm{v}} + B((J+1)\cdot(J+2) - J(J+1))$$

$$\tilde{\mathrm{v}}(\mathrm{v}, J) = \tilde{\mathrm{v}}_{\mathrm{v}} + 2B(J+1) \qquad 12.$$

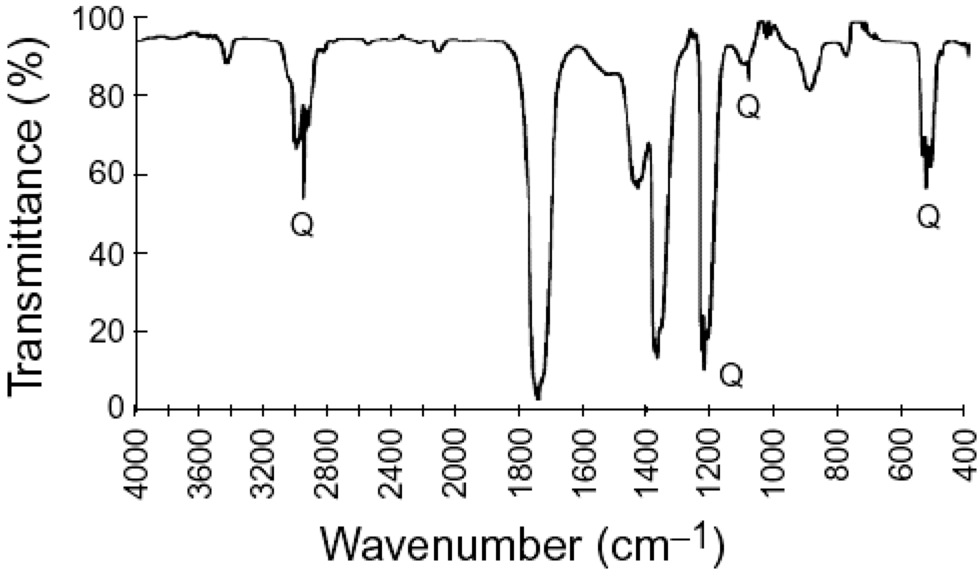


Figure. 7. Vapour spectrum of acetone with characteristic Q-branch slitting, denoted by Q.