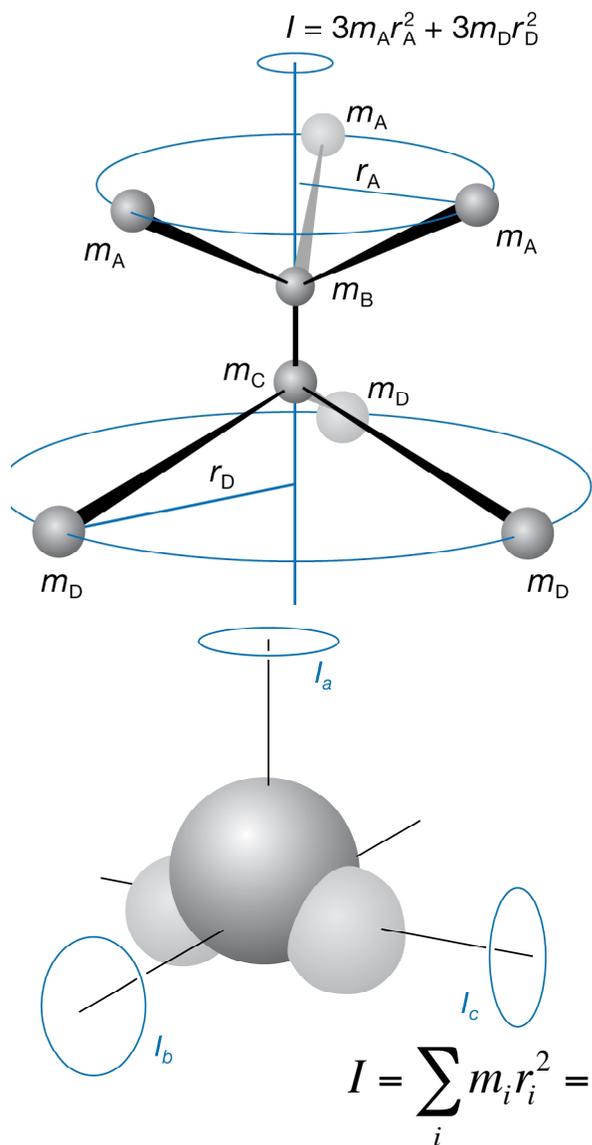


Spectroscopy 1: rotational and vibrational spectra

Pure rotation spectra

Moments of inertia



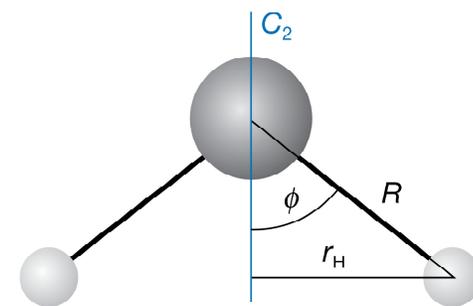
The key molecular parameter required for treating rotational spectra – the **moment of inertia**, I , of the molecule:

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

r_i – the perpendicular distance of the atom I from the axis of rotation. The moment of inertia depends on the masses of the atoms and the molecular geometry, therefore rotational spectroscopy gives information about bond lengths and bond angles.

In general, the rotational properties of any molecule can be expressed in terms of the moments of inertia about three perpendicular axis. The convention is to label the moments of inertia I_a , I_b , and I_c , with the axes chosen so that $I_a \geq I_b \geq I_c$. For the linear molecules, the moment of inertia around the internuclear axis is zero.

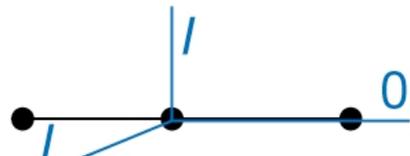
Example. Calculating the moment of inertia of a molecule. Calculate the moment of inertia of an H_2O molecule around the axis defined by the bisector of the HOH angle. HOH = 104.5° , the bond length is 95.7 pm.



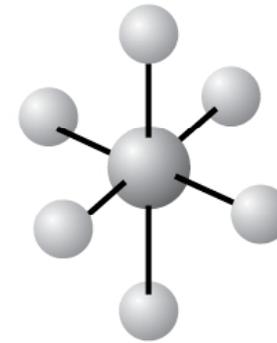
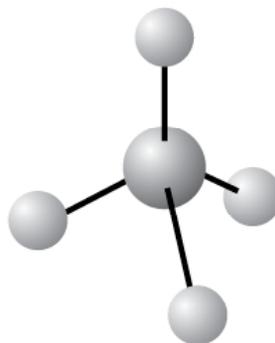
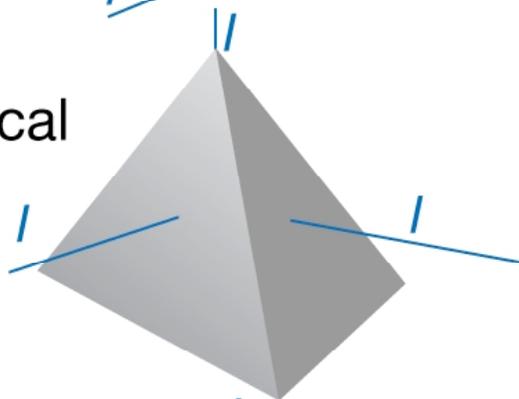
$$I = \sum_i m_i r_i^2 = m_H r_H^2 + 0 + m_H r_H^2 = 2m_H r_H^2 = 2m_H R^2 \sin^2 \phi = 1.91 \times 10^{-47} \text{ kgm}^2$$

Initially, we suppose that molecules are **rigid rotors**, bodies that do not distort under the stress of rotation. Rigid rotors are classified into four types:

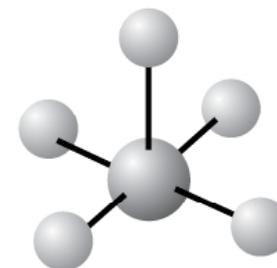
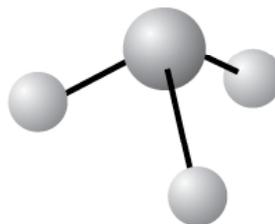
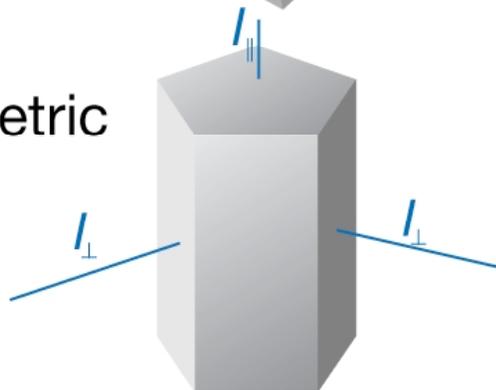
Linear



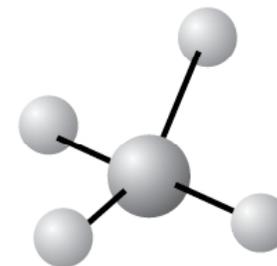
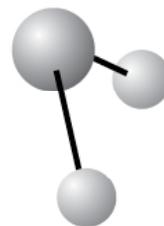
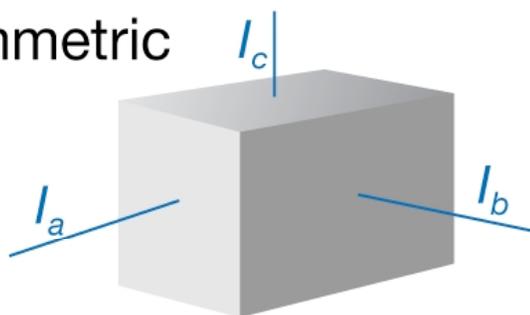
Spherical rotor



Symmetric rotor



Asymmetric rotor



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

Symmetric rotors – two equal moments of inertia (NH_3 , CH_3Cl).

Linear rotors – have one moment of inertia (the one about the molecular axis) equal to zero (CO_2 , HCl , OCS , $\text{HC}\equiv\text{CH}$).

Assymmetric rotors – have three different moments of inertia (H_2O , H_2CO , CH_3OH).

The explicit expressions for the moment of inertia of some symmetrical molecules are given in Table 12.1 (p. 450 in Atkins).

The rotational energy levels

The rotational levels of a rigid rotor may be obtained by solving the appropriate Schrödinger equation. Alternatively (a short cut), we consider the classical expression for the energy of a rotating body, express it in terms of the angular momentum, and then import the quantum mechanical properties of the angular momentum in the equation. The classical

expression for the energy:

$$E_a = \frac{1}{2} I_a \omega_a^2$$

ω_a – the angular velocity (in radians per second, rad s^{-1}) about an axis a , I_a – the corresponding moment of inertia. A body free to rotate about three axes has an energy

$$E = \frac{1}{2} I_a \omega_a^2 + \frac{1}{2} I_b \omega_b^2 + \frac{1}{2} I_c \omega_c^2$$

Because $J_a = I_a \omega_a$,

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

Spherical rotors (there are two or more C_n axis with $n > 2$: T_d , O_h)

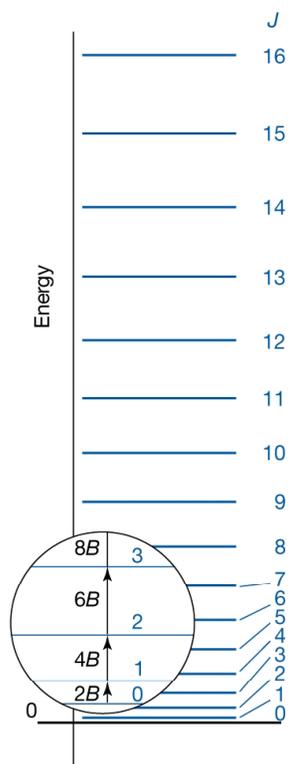
When all three moments of inertia are equal to some value I , the classical expression for

the energy is
$$E = \frac{J_a^2 + J_b^2 + J_c^2}{2I} = \frac{J^2}{2I}$$

J is the magnitude of the angular momentum. For the quantum mechanical rotor:

$$J^2 \rightarrow J(J+1)\hbar^2 \quad J = 0, 1, 2, \dots$$

$$E_J = J(J+1)\frac{\hbar^2}{2I} \quad J = 0, 1, 2, \dots$$



The resulting ladder of energy levels is shown on the figure. The energy is normally expressed in terms of the rotational constant, B , of the molecule:

$$hcB = \frac{\hbar^2}{2I} \quad B = \frac{\hbar}{4\pi cI} \quad E_J = hcBJ(J+1) \quad J = 0, 1, \dots$$

The rotational constant is a wavenumber (units are cm^{-1}). The energy of a rotational state is normally reported as the **rotational term**, $F(J)$, a wavenumber, by division by hc :

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

The separation of adjacent levels is $F(J) - F(J-1) = 2BJ$

Because the rotational constant decreases as I increases, large molecules have closely spaced rotational energy levels. For example, for CCl_4 , $I = 4.85 \times 10^{-45} \text{ kg m}^2$, $B \approx 0.06 \text{ cm}^{-1}$.

Symmetric rotors (groups $C_n, C_{nv}, C_{nh}, S_n, D_n, D_{nh}, D_{nd}; n > 2$)

In symmetric rotors, two moments of inertia are equal but different from the third; the unique axis of the molecule is its **principal axis**. The unique moment of inertia (about the principal axis) is denoted as I_{\parallel} and the other two as I_{\perp} . If $I_{\parallel} > I_{\perp}$, the rotor is **oblate** (like a pancake or C_6H_6); If $I_{\parallel} < I_{\perp}$, the rotor is **prolate** (like a cigar or CH_3Cl). The classical

expression for the energy becomes

$$E = \frac{J_b^2 + J_c^2}{2I_{\perp}} + \frac{J_a^2}{2I_{\parallel}}$$

With

$$J^2 = J_a^2 + J_b^2 + J_c^2,$$

$$E = \frac{J^2 - J_a^2}{2I_{\perp}} + \frac{J_a^2}{2I_{\parallel}} = \frac{J^2}{2I_{\perp}} + \left(\frac{1}{2I_{\parallel}} - \frac{1}{2I_{\perp}} \right) J_a^2$$

The quantum expression is generated by replacing J^2 by $J(J+1)\hbar^2$, where J is the angular momentum quantum number. The component of angular momentum about any axis is

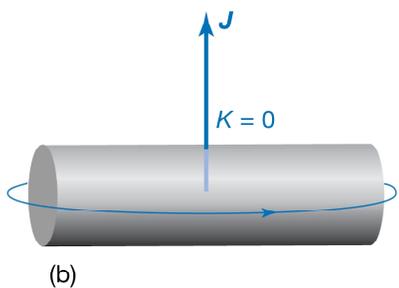
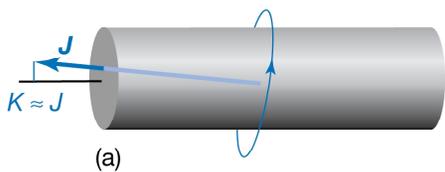
restricted to the values $K\hbar$, with $K = 0, \pm 1, \dots, \pm J$. K is the quantum number for a component on the principal axis. Therefore, we replace J_a^2 by $K^2\hbar^2$.

Then, the rotational terms are

$$F(J, K) = BJ(J+1) + (A - B)K^2 \quad J = 0, 1, 2, \dots \quad K = 0, \pm 1, \dots, \pm J$$

$$A = \frac{\hbar^2}{4\pi c I_{\parallel}} \quad B = \frac{\hbar^2}{4\pi c I_{\perp}}$$

The equation shows the dependence of the energy levels on the two distinct moments of inertia of the molecule. When $K = 0$, there is no component of angular momentum about the principal axis, and the energy levels will depend only on I_{\perp} .



When $K = \pm J$, almost all the angular momentum arises from rotation around the principal axis, and the energy levels are determined largely by I_{\parallel} . The sign of K does not affect the energy because opposite values of K correspond to opposite senses of rotation, and the energy does not depend on the sense of rotation.

Example. Calculating the rotational energy levels of a molecule. A $^{14}\text{NH}_3$ molecule is a symmetric rotor with bond length 101.2 pm and HNH bond angle 106.7° . Calculate rotational terms.

For a symmetric rotor, like NH_3

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

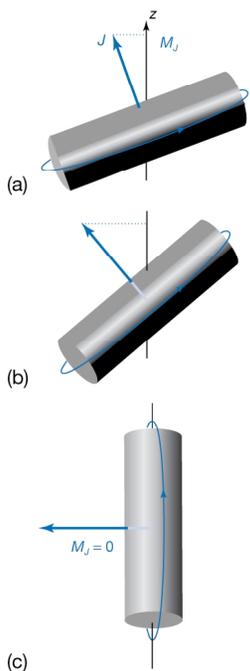
Using $m_A = 1.0078$ u, $m_B = 14.0031$ u, $R = 101.2$ pm, $\theta = 106.7^\circ$, we obtain $I_{\parallel} = 4.4128 \times 10^{-47}$ kg m² $I_{\perp} = 2.8059 \times 10^{-47}$ kg m²

$$A = 6.344 \text{ cm}^{-1} \quad B = 9.977 \text{ cm}^{-1}$$

$$F(J,K)/\text{cm}^{-1} = 9.977J(J+1) - 3.633K^2$$

$$F(J,K)/\text{GHz} = 299.1J(J+1) - 108.9K^2$$

For $J = 1$, the energy needed for the molecule to rotate mainly about its principal axis ($K = \pm J$) is 16.32 cm^{-1} (489.3 GHz), but end-over end rotation ($K = 0$) corresponds to 19.95 cm^{-1} (598.1 GHz).



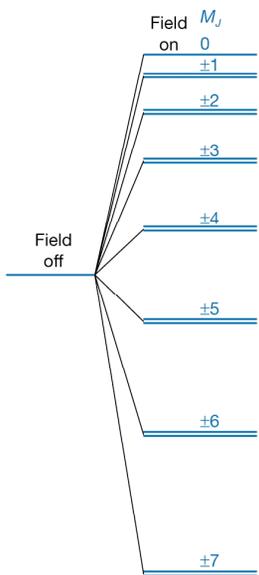
Linear rotors

For a linear rotor the rotation occurs only about an axis perpendicular to the line of atoms; there is zero angular momentum around the internuclear line. Therefore, the component of angular momentum around the principal axis of a linear rotor is zero and $K = 0$. The rotational terms of linear molecule are therefore

$$F(J) = BJ(J + 1) \quad J = 0, 1, 2, \dots$$

Degeneracies and the Stark effect

The energy of a symmetric rotor depends on J and K and each level except those with $K = 0$ is doubly degenerate: the states with K and $-K$ have the same energy. Meanwhile, the angular momentum of the molecule has a component on an external, laboratory-fixed axis. This component is quantized, with permitted values $M_J \hbar$, $M_J = 0, \pm 1, \dots, \pm J$, giving $2J + 1$ values in all. The quantum number M_J does not appear in the expression for the energy, but it is necessary for a complete specification of the rotor. All $2J + 1$ orientations of the rotating molecule have the same energy and it follows that a symmetric rotor level is $2(2J + 1)$ -fold degenerate for $K \neq 0$ and $(2J + 1)$ -fold degenerate for $K = 0$. A linear rotor always has $K = 0$, but the angular momentum may still have $2J + 1$ components on the laboratory axis, so its degeneracy is $2J + 1$.

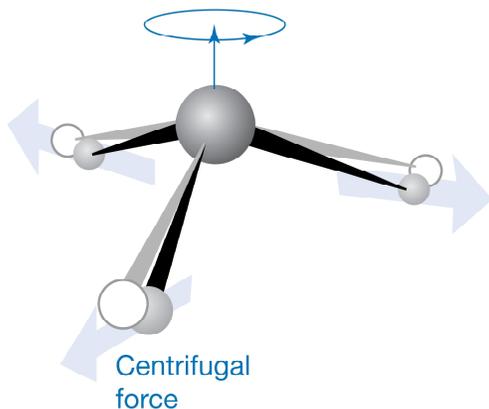


A spherical rotor – a version of a symmetric rotor with $A = B$: the quantum number K may still take any of $2J + 1$ values, but the energy is independent of K . Therefore, in addition to a $(2J + 1)$ -fold degeneracy arising from its orientation in space, the rotor also has a $(2J + 1)$ -fold degeneracy with respect to an arbitrary axis in the molecule. The overall degeneracy is then $(2J + 1)^2$. The degeneracy due to M_J (the orientation of the rotation in space) is partly removed when an electric field is applied to a polar molecule. The splitting of states by an electric field is called the **Stark effect**. For a linear rotor in an electric field \mathcal{E} , the energy of the state $|J, M_J\rangle$ is given by

$$E(J, M_J) = hcBJ(J + 1) + a(J, M_J)\mu^2 \mathcal{E}^2$$

$$a(J, M_J) = \frac{J(J + 1) - 3M_J^2}{2hcBJ(J + 1)(2J - 1)(2J + 3)}$$

The energy of a state with quantum number M_J depends on the square of the permanent electric dipole moment, μ . Therefore, the observation of the Stark effect can be used to measure this property. The technique is limited to molecules that are sufficiently volatile to be studied by microwave spectroscopy.



Centrifugal distortion

We have treated molecules as rigid rotors. However, the atoms in rotating molecules are subject to centrifugal forces that tend to distort the molecular geometry and change the moments of inertia. For example, centrifugal distortion stretches the bond in a diatomic molecule and hence increases the moment of inertia.

As a result, centrifugal distortion reduces the rotational constant and the energy levels are slightly closer than the rigid-rotor expressions predict: $F(J) = BJ(J+1) - D_J J^2(J+1)^2$
 D_J – the **centrifugal distortion constant**. It is large when the bond is easily stretched. For a diatomic molecule,

$$D_J \approx \frac{4B^3}{\tilde{\nu}^2}$$

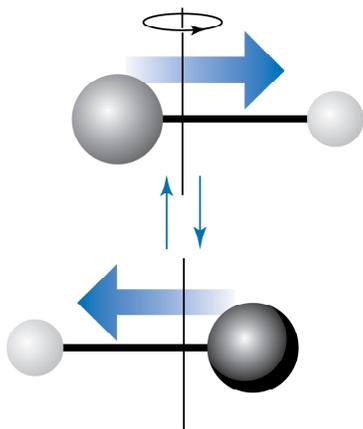
Hence the observation of the convergence of the rotational levels can be interpreted in terms of the flexibility of the bond.

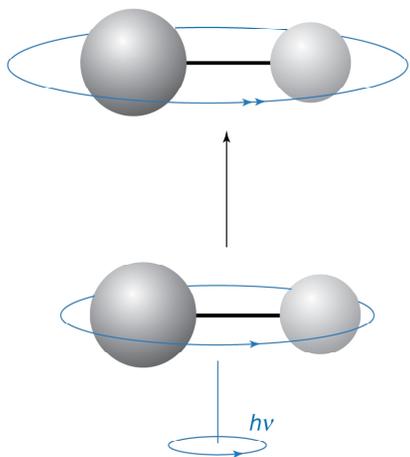
Rotational transitions

Typical values of B for small molecules are in the range of 0.1 - 10 cm^{-1} , so rotational transitions lie in the microwave region of the spectrum. The transitions are detected by monitoring the net absorption of microwave radiation.

Rotational selection rules

For a molecule to give a pure rotational spectrum, it must be polar. The classical basis: a polar molecules appears to possess a fluctuating dipole moment when rotating, a nonpolar molecule does not. Homonuclear diatomic molecules and symmetrical linear molecules (CO_2) are rotationally inactive. Spherical rotors cannot have electric dipole moments unless they become distorted by rotation, so they also inactive except in special cases. An example of a spherical rotor that does become sufficiently distorted for it to acquire a dipole moment – SiH_4 . Of the molecules N_2 , CO_2 , OCS , H_2O , $\text{CH}_2=\text{CH}_2$, C_6H_6 , only OCS and H_2O are polar, so only these two molecules have microwave spectra.





The specific rotational selection rules are found by evaluating the transition dipole moment between rotational states. For example, for a linear molecule, the transition moment vanishes unless

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

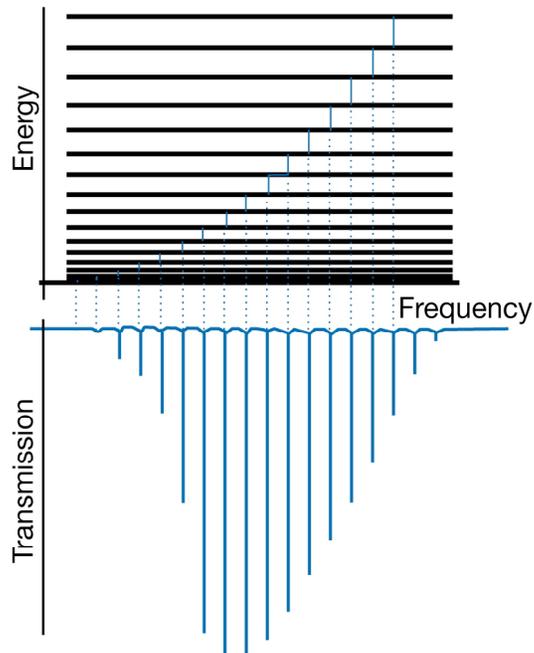
The transition $\Delta J = +1$ corresponds to absorption and the transition $\Delta J = -1$ corresponds to emission. The allowed change in J in each case arises from the conservation of angular momentum when a photon, a spin-1 particle, is emitted or absorbed.

When the transition moment is evaluated for all possible relative orientations of the molecule to the line of flight of the photon, the total $J+1 \leftrightarrow J$ transition intensity is proportional to

$$|\mu_{J+1,J}|^2 = \left(\frac{J+1}{2J+1} \right) \mu_0^2 \rightarrow \frac{1}{2} \mu_0^2 \quad \text{for} \quad J \gg 1$$

μ_0 – the permanent electric dipole moment of the molecule. The intensity is proportional to the square of the permanent electric dipole moment – strongly polar molecules give rise to much more intense rotational lines than less polar molecules.

An additional selection rule for symmetric rotors: $\Delta K = 0$.



The appearance of rotational spectra

When these selection rules are applied to the expressions for the energy levels of a rigid symmetric or linear rotor, it follows that the wavenumbers of the allowed $J + 1 \leftarrow J$ absorptions are

$$\tilde{\nu}(J + 1 \leftarrow J) = 2B(J + 1) \quad J = 0, 1, 2, \dots$$

When centrifugal distortion is taken into account

$$\tilde{\nu}(J + 1 \leftarrow J) = 2B(J + 1) - 4D_J(J + 1)^3$$

The second term is typically very small and the spectrum appears with nearly equally spaced peaks. The spectrum consists of a series of lines with wavenumbers $2B, 4B, 6B, \dots$ and of separation $2B$. The measurement of the line spacing gives B , and hence the moment of inertia perpendicular to the principal axis of the molecule. The masses of atoms are known – it is simple to deduce the bond length of a diatomic molecule. In the case of a polyatomic molecule (OCS, NH_3) the analysis gives only a single quantity I_{\perp} and it is not possible to infer both bond lengths (OCS) or the bond length and bond angle (NH_3). The use of isotopically substituted molecules can overcome this difficulty. Rotational spectrum is then measured for ABC and A'BC and it is assumed that $R(\text{A-B}) = R(\text{A}'\text{-B})$. Then two moments of inertia are obtained (for ABC and A'BC), which gives two equations with two unknowns, $R(\text{A-B})$ and $R(\text{B-C})$. The assumption that bond lengths are unchanged by isotopic substitution is only an approximation, but a very good one in most cases.

Example. Predicting the appearance of a rotational spectrum.

Predict the form of the rotational spectrum of NH₃.

We calculated the energy levels in the previous example. The NH₃ molecule is a polar symmetric rotor, so the selection rules are $\Delta J = \pm 1$, $\Delta K = 0$. For absorption, $\Delta J = +1$; $B = 9.977 \text{ cm}^{-1}$:

J	0	1	2	3	...
$\tilde{\nu}/\text{cm}^{-1}$	19.95	39.91	59.86	79.82	...
ν/GHz	598.1	1197	1795	2393	...

The line spacing is 19.95 cm^{-1} (598.1 GHz).

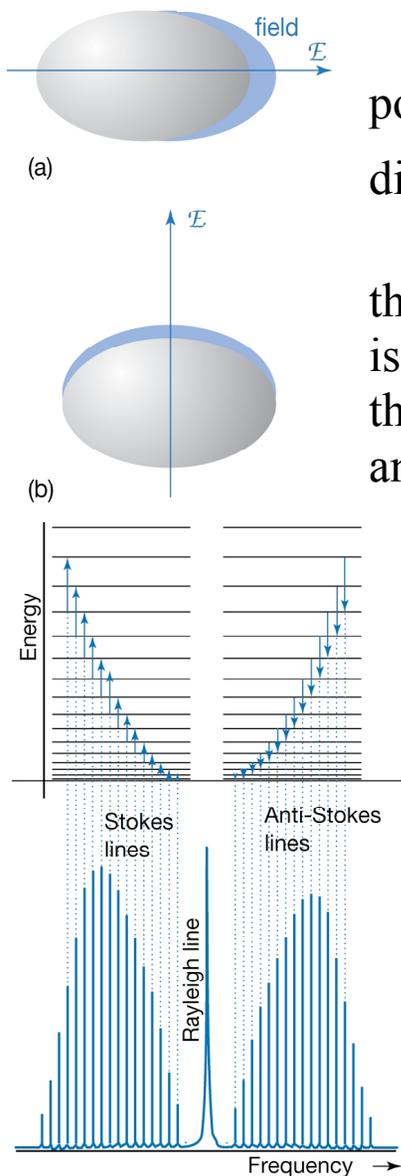
The intensities of spectral lines increase with increasing J and pass through a maximum. The most important reason – the existence of a maximum in the population of rotational levels. The Boltzmann distribution implies that the population of each state decays exponentially with decreasing J , but the degeneracy of the levels increases $N_J \propto Ng_J e^{-E_J/kT}$ N – the total number of molecules in the sample J , g_J – the degeneracy of the level J . The value of J corresponding to a maximum of this expression is found by treating J as a continuous variable, differentiating with respect to J , and setting the result equal to zero.

$$J_{\max} \approx \left(\frac{kT}{2hcB} \right)^{1/2} - \frac{1}{2}$$

For a typical molecule (OCS, $B = 0.2 \text{ cm}^{-1}$) at room temperature $kT \approx 1000hcB$ and $J_{\max} \approx 22$. However, it must be taken into account that the intensity of each transition also depends on J .

Rotational Raman spectra

The gross selection rule: *the molecule must be anisotropically polarizable.*



The distortion of a molecule in an electric field is determined by its polarizability α . If the strength of the field is \mathcal{E} , the molecule acquires an induced dipole moment:

$$\mu = \alpha \mathcal{E}$$

An atom is isotropically polarizable – the same distortion is induced whatever the direction of the applied field. The polarizability of a spherical rotor is also isotropic. However, non-spherical rotors have polarizabilities that do depend on the direction of the field relative to the molecule – these molecules are anisotropically polarizable. All linear molecules and diatomics (including

homonuclear) are therefore rotationally Raman active and the technique can be used to study many of the molecules that are inaccessible to microwave spectroscopy. However, spherical rotors (CH_4 , SF_6) are rotationally Raman inactive as well as microwave inactive. The specific rotational Raman selection rules are:

$$\text{Linear rotors: } \Delta J = 0, \pm 2$$

$$\text{Symmetric rotors: } \Delta J = 0, \pm 1, \pm 2 \quad \Delta K = 0$$

We can predict the form of the Raman spectrum of a linear rotor by applying the selection rule $\Delta J = \pm 2$. For $\Delta J = +2$, the scattered radiation leaves the molecule in a higher rotational state, so the wavenumber of the incident radiation, $\tilde{\nu}_i$, is decreased: Stokes lines:

$$\tilde{\nu}(J+2 \leftarrow J) = \tilde{\nu}_i - \{F(J+2) - F(J)\} = \tilde{\nu}_i - 2B(2J+3)$$

For $\Delta J = -2$, anti-Stokes lines are observed:

$$\tilde{\nu}(J-2 \leftarrow J) = \tilde{\nu}_i + \{F(J) - F(J-2)\} = \tilde{\nu}_i + 2B(2J-1)$$

The separation of adjacent lines is $4B$ in both regions.