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Department of Physics

Study Material: PHY 512 Atomic & Molecular Spectroscopy

M.Sc (Hons.) Physics 2nd sem

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BOOK: Fundamentals of Molecular Spectroscopy CN Banwell Mc Graw Hill

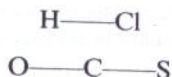
MICROWAVE SPECTROSCOPY

2.1 THE ROTATION OF MOLECULES

We saw in the previous chapter that spectroscopy in the microwave region is concerned with the study of rotating molecules. The rotation of a three-dimensional body may be quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular directions through the centre of gravity—the principal axes of rotation. Thus a body has three principal *moments of inertia*, one about each axis, usually designated I_A , I_B , and I_C .

Molecules may be classified into groups according to the relative values of their three principal moments of inertia—which, it will be seen, is tantamount to classifying them according to their shapes. We shall describe this classification here before discussing the details of the rotational spectra arising from each group.

1. *Linear molecules.* These, as the name implies, are molecules in which all the atoms are arranged in a straight line, such as hydrogen chloride HCl, or carbon oxysulphide OCS, illustrated below. The three directions of rotation may be taken as (a) about the bond axis, (b) end-over-end



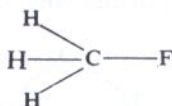
rotation in the plane of the paper, and (c) end-over-end rotation at right angles to the plane. It is self-evident that the moments of (b) and (c) are the same (i.e., $I_B = I_C$) while that of (a) is very small. As an approx-

imation we may say that $I_A = 0$, although it should be noted that this is only an approximation (see p. 46).

Thus for linear molecules we have:

$$I_B = I_C \quad I_A = 0 \quad (2.1)$$

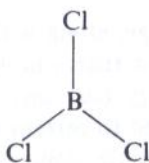
2. *Symmetric tops*. Consider a molecule such as methyl fluoride, where the three hydrogen atoms are bonded tetrahedrally to the carbon, as shown below. As in the case of linear molecules, the end-over-end rotation in,



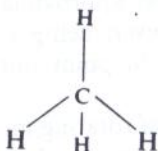
and out of, the plane of the paper are still identical and we have $I_B = I_C$. The moment of inertia about the C—F bond axis (chosen as the main rotational axis since the centre of gravity lies along it) is now not negligible, however, because it involves the rotation of three comparatively massive hydrogen atoms off this axis. Such a molecule spinning about this axis can be imagined as a top, and hence the name of the class. We have then:

$$\text{Symmetric tops: } I_B = I_C \neq I_A \quad I_A \neq 0 \quad (2.2)$$

There are two subdivisions of this class which we may mention: if, as in methyl fluoride above, $I_B = I_C > I_A$, then the molecule is called a *prolate* symmetric top; whereas if $I_B = I_C < I_A$, it is referred to as *oblate*. An example of the latter type is boron trichloride, which, as shown, is planar and symmetrical. In this case $I_A = 2I_B = 2I_C$



3. *Spherical tops*. When a molecule has all three moments of inertia identical, it is called a spherical top. A simple example is the tetrahedral molecule methane CH_4 . We have then:



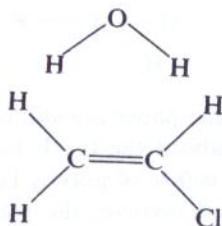
$$\text{Spherical tops: } I_A = I_B = I_C \quad (2.3)$$

In fact these molecules are only of academic interest in this chapter. Since they can have no dipole moment owing to their symmetry, rotation alone can produce no dipole change and hence no rotational spectrum is observable.

4. *Asymmetric tops*. These molecules, to which the majority of substances belong, have all three moments of inertia different:

$$I_A \neq I_B \neq I_C \quad (2.4)$$

Simple examples are water H_2O , and vinyl chloride $\text{CH}_2=\text{CHCl}$.



Perhaps it should be pointed out that one can (and often does) describe the classification of molecules into the four rotational classes in far more rigorous terms than have been used above (see, for example, Herzberg, *Molecular Spectra and Molecular Structure*, vol. II). However, for the purposes of this book the above description is adequate.

2.2 ROTATIONAL SPECTRA

We have seen that rotational energy, along with all other forms of molecular energy, is quantized: this means that a molecule cannot have any arbitrary amount of rotational energy (i.e., any arbitrary value of angular momentum) but its energy is limited to certain definite values depending on the shape and size of the molecule concerned. The permitted energy values—the so-called rotational energy *levels*—may in principle be calculated for any molecule by solving the Schrödinger equation for the system represented by that molecule. For simple molecules the mathematics involved is straightforward but tedious, while for complicated systems it is probably impossible without gross approximations. We shall not concern ourselves unduly with this, however, being content merely to accept the results of existing solutions and to point out where reasonable approximations may lead.

We shall consider each class of rotating molecule in turn, discussing the linear molecule in most detail, because much of its treatment can be directly extended to symmetrical and unsymmetrical molecules.

2.3 DIATOMIC MOLECULES

2.3.1 The Rigid Diatomic Molecule

We start with this, the simplest of all linear molecules, shown in Fig. 2.1. Masses m_1 and m_2 are joined by a rigid bar (the bond) whose length is

$$r_0 = r_1 + r_2 \quad (2.5)$$

The molecule rotates end-over-end about a point C , the centre of gravity: this is defined by the moment, or balancing, equation:

$$m_1 r_1 = m_2 r_2 \quad (2.6)$$

The moment of inertia about C is defined by:

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= m_2 r_2 r_1 + m_1 r_1 r_2 \quad (\text{from (2.6)}) \\ &= r_1 r_2 (m_1 + m_2) \end{aligned} \quad (2.7)$$

But, from (2.5) and (2.6):

$$m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$$

therefore,

$$r_1 = \frac{m_2 r_0}{m_1 + m_2} \quad \text{and} \quad r_2 = \frac{m_1 r_0}{m_1 + m_2} \quad (2.8)$$

Replacing (2.8) into (2.7):

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2 \quad (2.9)$$

where we have written $\mu = m_1 m_2 / (m_1 + m_2)$, and μ is called the *reduced mass* of the system. Equation (2.9) defines the moment of inertia conveniently in terms of the atomic masses and the bond length.

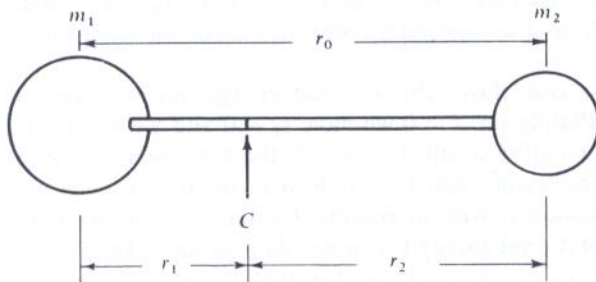


Figure 2.1 A rigid diatomic molecule treated as two masses, m_1 and m_2 , joined by a rigid bar of length $r_0 = r_1 + r_2$.

By the use of the Schrödinger equation it may be shown that the rotational energy levels allowed to the rigid diatomic molecule are given by the expression:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ joules} \quad \text{where } J = 0, 1, 2, \dots \quad (2.10)$$

In this expression h is Planck's constant, and I is the moment of inertia, either I_B or I_C , since both are equal. The quantity J , which can take integral values from zero upwards, is called the *rotational quantum number*: its restriction to integral values arises directly out of the solution to the Schrödinger equation and is by no means arbitrary, and it is this restriction which effectively allows only certain discrete rotational energy levels to the molecule.

Equation (2.10) expresses the allowed energies in joules; we, however, are interested in differences between these energies, or, more particularly, in the corresponding frequency, $\nu = \Delta E/h$ Hz, or wavenumber, $\bar{\nu} = \Delta E/hc$ cm^{-1} , of the radiation emitted or absorbed as a consequence of changes between energy levels. In the rotational region spectra are usually discussed in terms of wavenumber, so it is useful to consider energies expressed in these units. We write:

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots) \quad (2.11)$$

where c , the velocity of light, is here expressed in cm s^{-1} , since the unit of wavenumber is reciprocal *centimetres*.

Equation (2.11) is usually abbreviated to:

$$\varepsilon_J = BJ(J+1) \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots) \quad (2.12)$$

where B , the *rotational constant*, is given by

$$B = \frac{h}{8\pi^2 I_B c} \text{ cm}^{-1} \quad (2.13)$$

in which we have used explicitly the moment of inertia I_B . We might equally well have used I_C and a rotational constant C , but the notation of (2.13) is conventional.

From Eq. (2.12) we can show the allowed energy levels diagrammatically as in Fig. 2.2. Plainly for $J = 0$ we have $\varepsilon_J = 0$ and we would say that the molecule is not rotating at all. For $J = 1$, the rotational energy is $\varepsilon_1 = 2B$ and a rotating molecule then has its lowest angular momentum. We may continue to calculate ε_J with increasing J values and, in principle, there is no limit to the rotational energy the molecule may have. In practice, of course, there comes a point at which the centrifugal force of a rapidly rotating diatomic molecule is greater than the strength of the bond, and the molecule is disrupted, but this point is not reached at normal temperatures.

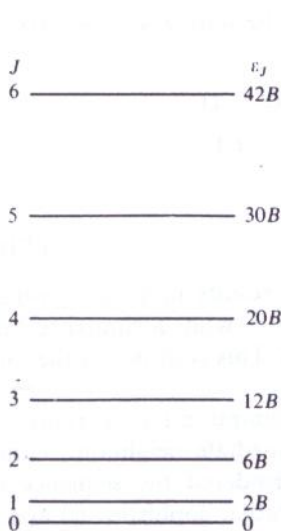


Fig. 2.2

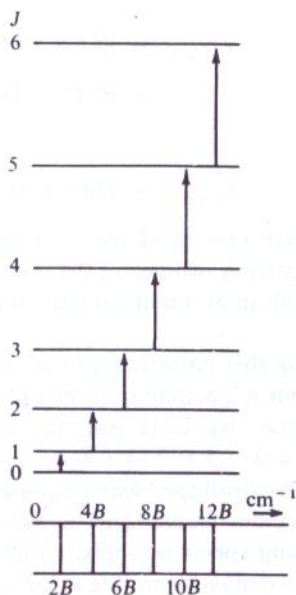


Fig. 2.3

Figure 2.2 The allowed rotational energy levels of a rigid diatomic molecule.

Figure 2.3 Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them.

We now need to consider *differences* between the levels in order to discuss the spectrum. If we imagine the molecule to be in the $J = 0$ state (the *ground rotational state*, in which no rotation occurs), we can let incident radiation be absorbed to raise it to the $J = 1$ state. Plainly the energy absorbed will be:

$$\varepsilon_{J=1} - \varepsilon_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

and, therefore,

$$\bar{\nu}_{J=0 \rightarrow J=1} = 2B \text{ cm}^{-1} \quad (2.14)$$

In other words, an absorption line will appear at $2B \text{ cm}^{-1}$. If now the molecule is raised from the $J = 1$ to the $J = 2$ level by the absorption of more energy, we see immediately:

$$\begin{aligned} \bar{\nu}_{J=1 \rightarrow J=2} &= \varepsilon_{J=2} - \varepsilon_{J=1} \\ &= 6B - 2B = 4B \text{ cm}^{-1} \end{aligned} \quad (2.15)$$

In general, to raise the molecule from the state J to state $J + 1$, we would have:

$$\begin{aligned}\bar{\nu}_{J \rightarrow J+1} &= B(J+1)(J+2) - BJ(J+1) \\ &= B[J^2 + 3J + 2 - (J^2 + J)]\end{aligned}$$

or

$$\bar{\nu}_{J \rightarrow J+1} = 2B(J+1) \text{ cm}^{-1} \quad (2.16)$$

Thus a stepwise raising of the rotational energy results in an absorption spectrum consisting of lines at $2B, 4B, 6B, \dots, \text{cm}^{-1}$, while a similar lowering would result in an identical emission spectrum. This is shown at the foot of Fig. 2.3.

In deriving this pattern we have made the assumption that a transition can occur from a particular level only to its immediate neighbour, either above or below: we have not, for instance, considered the sequence of transitions $J = 0 \rightarrow J = 2 \rightarrow J = 4 \dots$. In fact, a rather sophisticated application of the Schrödinger wave equation shows that, for this molecule, we need only consider transitions in which J changes by one unit—all other transitions being spectroscopically *forbidden*. Such a result is called a *selection rule*, and we may formulate it for the rigid diatomic rotator as:

$$\text{Selection rule: } \Delta J = \pm 1 \quad (2.17)$$

Thus Eq. (2.16) gives the *whole* spectrum to be expected from such a molecule.

Of course, only if the molecule is asymmetric (heteronuclear) will this spectrum be observed, since if it is homonuclear there will be no dipole component change during the rotation, and hence no interaction with radiation. Thus molecules such as HCl and CO will show a rotational spectrum, while N_2 and O_2 will not. Remember also, that rotation about the bond axis was rejected in Sec. 2.1: we can now see that there are two reasons for this. Firstly, the moment of inertia is very small about the bond so, applying Eqs (2.10) or (2.11) we see that the energy levels would be extremely widely spaced: this means that a molecule requires a great deal of energy to be raised from the $J = 0$ to the $J = 1$ state, and such transitions do not occur under normal spectroscopic conditions. Thus diatomic (and all linear) molecules are in the $J = 0$ state for rotation about the bond axis, and they may be said to be not rotating. Secondly, even if such a transition should occur, there will be no dipole change and hence no spectrum.

To conclude this section we shall apply Eq. (2.16) to an observed spectrum in order to determine the moment of inertia and hence the bond length. Gilliam et al.† have measured the first line ($J = 0$) in the rotation

† Gilliam, Johnson, and Gordy, *Physical Review*, **78**, 140 (1950).

spectrum of carbon monoxide as 3.84235 cm^{-1} . Hence from Eq. (2.16):

$$\bar{\nu}_{0 \rightarrow 1} = 3.84235 = 2B \text{ cm}^{-1}$$

or,

$$B = 1.92118 \text{ cm}^{-1}$$

Rewriting Eq. (2.13) as: $I = h/8\pi^2 Bc$, we have

$$I_{\text{CO}} = \frac{6.626 \times 10^{-34}}{8\pi^2 \times 2.99793 \times 10^{10} \times B} = \frac{27.9907 \times 10^{-47}}{B} \text{ kg m}^2$$

$$= 14.5695_4 \times 10^{-47} \text{ kg m}^2$$

where we express the velocity of light in cm s^{-1} , since B is in cm^{-1} . But the moment of inertia is μr^2 (cf. Eq. (2.9)) and, knowing the relative atomic weights (H = 1.0080) to be C = 12.0000, O = 15.9994, and the absolute mass of the hydrogen atom to be $1.67343 \times 10^{-27} \text{ kg}$, we can calculate the masses of carbon and oxygen, respectively, as 19.92168 and $26.56136 \times 10^{-27} \text{ kg}$. The reduced mass is then:

$$\mu = \frac{19.92168 \times 26.56136 \times 10^{-54}}{46.48303 \times 10^{-27}} = 11.38365 \times 10^{-27} \text{ kg}$$

Hence:

$$r^2 = \frac{I}{\mu} = 1.2799 \times 10^{-20} \text{ m}^2$$

and

$$r_{\text{CO}} = 0.1131 \text{ nm (or } 1.131 \text{ \AA)}$$

2.3.2 The Intensities of Spectral Lines

We want now to consider briefly the relative intensities of the spectral lines of Eq. (2.16); for this a prime requirement is plainly a knowledge of the relative probabilities of transition between the various energy levels. Does, for instance, a molecule have more or less chance of making the transition $J = 0 \rightarrow J = 1$ than the transition $J = 1 \rightarrow J = 2$? We mentioned above calculations which show that a change of $\Delta J = \pm 2, \pm 3$, etc., was forbidden—in other words, the transition probability for all these changes is zero. Precisely similar calculations show that the probability of all changes with $\Delta J = \pm 1$ is almost the same—all, to a good approximation, are equally likely to occur.

This does not mean, however, that all spectral lines will be equally intense. Although the intrinsic probability that a single molecule in the $J = 0$ state, say, will move to $J = 1$ is the same as that of a single molecule moving from $J = 1$ to $J = 2$, in an assemblage of molecules, such as in a normal gas sample, there will be different numbers of molecules in each level to begin with, and therefore different total numbers of molecules will carry out transitions between the various levels. In fact, since the intrinsic probabilities are identical, the line intensities will be directly proportional to the initial numbers of molecules in each level.

The first factor governing the population of the levels is the Boltzmann distribution (cf. Sec. 1.7.2). Here we know that the rotational energy in the lowest level is zero, since $J = 0$, so, if we have N_0 molecules in this state, the number in any higher state is given by:

$$N_J/N_0 = \exp(-E_J/kT) = \exp\{-BhcJ(J+1)/kT\} \quad (2.18)$$

where, we must remember, c is the velocity of light in cm s^{-1} when B is in cm^{-1} . A very simple calculation shows how N_J varies with J ; for example, taking a typical value of $B = 2 \text{ cm}^{-1}$, and room temperature (say $T = 300 \text{ K}$), the relative population in the $J = 1$ state is:

$$\begin{aligned} \frac{N_1}{N_0} &= \exp\left\{-\frac{2 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} \times 1 \times 2}{1.38 \times 10^{-23} \times 300}\right\} \\ &= \exp(-0.019) \approx 0.98 \end{aligned}$$

and we see that there are almost as many molecules in the $J = 1$ state, at equilibrium, as in the $J = 0$. In a similar way the two graphs of Fig. 2.4 have been calculated, showing the more rapid decrease of N_J/N_0 with increasing J and with larger B .

A second factor is also required—the possibility of *degeneracy* in the energy states. Degeneracy is the existence of two or more energy states which have exactly the *same* energy. In the case of the diatomic rotator we may approach the problem in terms of its angular momentum.

The defining equations for the energy and angular momentum of a rotator are:

$$E = \frac{1}{2}I\omega^2 \quad \mathbf{P} = I\omega$$

where I is the moment of inertia, ω the rotational frequency (in radians per second), and \mathbf{P} the angular momentum. Rearrangement of these gives

$$\mathbf{P} = \sqrt{2EI}$$

The energy level expression of Eq. (2.10) can be rewritten:

$$2EI = J(J+1) \frac{h^2}{4\pi^2}$$

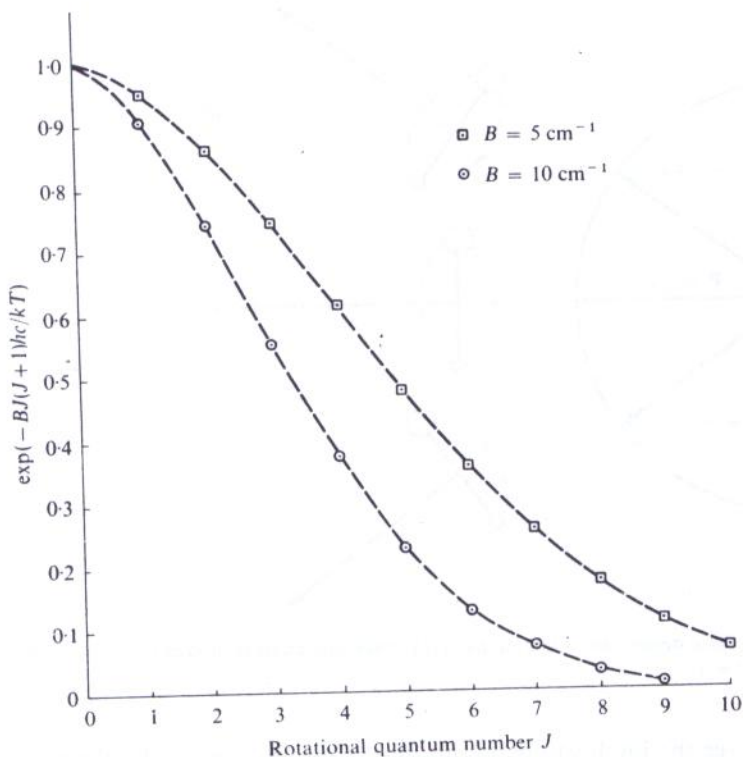


Figure 2.4 The Boltzmann populations of the rotational energy levels of Fig. 2.2. The diagram has been drawn taking values of $B = 5$ and 10 cm^{-1} and $T = 300 \text{ K}$ in Eq. (2.18).

and hence

$$\mathbf{P} = \sqrt{J(J+1)} \frac{h}{2\pi} = \sqrt{J(J+1)} \text{ units} \quad (2.19)$$

where, following convention, we take $h/2\pi$ as the fundamental unit of angular momentum. Thus we see that \mathbf{P} , like E , is quantized.

Throughout the above derivation \mathbf{P} has been printed in bold face type to show that it is a *vector*—i.e., it has *direction* as well as *magnitude*. The direction of the angular momentum vector is conventionally taken to be along the axis about which rotation occurs and it is usually drawn as an arrow of length proportional to the magnitude of the momentum. The number of different directions which an angular momentum vector may take up is limited by a quantum mechanical law which may be stated:

'For integral values of the rotational quantum number (in this case J), the angular momentum vector may only take up directions such that its component along a given reference direction is zero or an integral multiple of angular momentum units.'

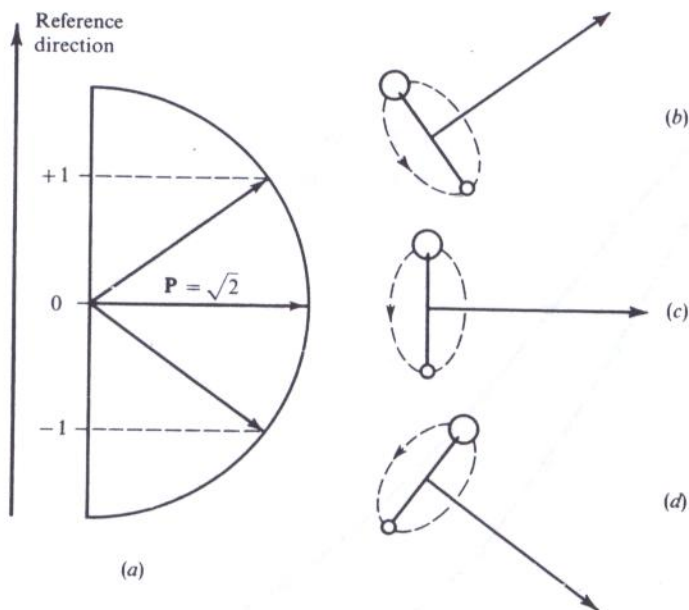


Figure 2.5 The three degenerate orientations of the rotational angular momentum vector for a molecule with $J = 1$.

We can see the implications of this most easily by means of a diagram. In Fig. 2.5 we show the case $J = 1$. Here $P = \sqrt{1 \times 2}$ units $= \sqrt{2}$, and, as Fig. 2.5(a) shows, a vector of length $\sqrt{2}$ ($= 1.41$) can have only *three* integral or zero components along a reference direction (here assumed to be from top to bottom in the plane of the paper): +1, 0, and -1. Thus the angular momentum vector in this instance can be oriented in only three different directions (Fig. 2.5(b)–(d)) with respect to the reference direction. All three rotational directions are, of course, associated with the same angular momentum and hence the same rotational energy: the $J = 1$ level is thus threefold degenerate.

Figure 2.6(a) and (b) shows the situation for $J = 2$ ($P = \sqrt{6}$) and $J = 3$ ($P = 2\sqrt{3}$) with fivefold and sevenfold degeneracy respectively. In general it may readily be seen that *each energy level is $2J + 1$ -fold degenerate*.

Thus we see that, although the molecular population in each level decreases exponentially (Eq. (2.18)), the number of degenerate levels available increases rapidly with J . The total relative population at an energy E_J will plainly be:

$$\text{Population} \propto (2J + 1) \exp(-E_J/kT) \quad (2.20)$$

When this is plotted against J the points fall on a curve of the type shown in Fig. 2.7, indicating that the population rises to a maximum and then

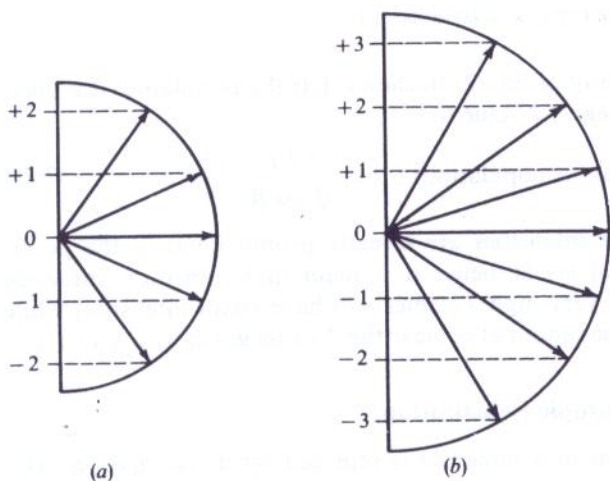


Figure 2.6 The five and seven degenerate rotational orientations for a molecule with $J = 2$ and $J = 3$ respectively.

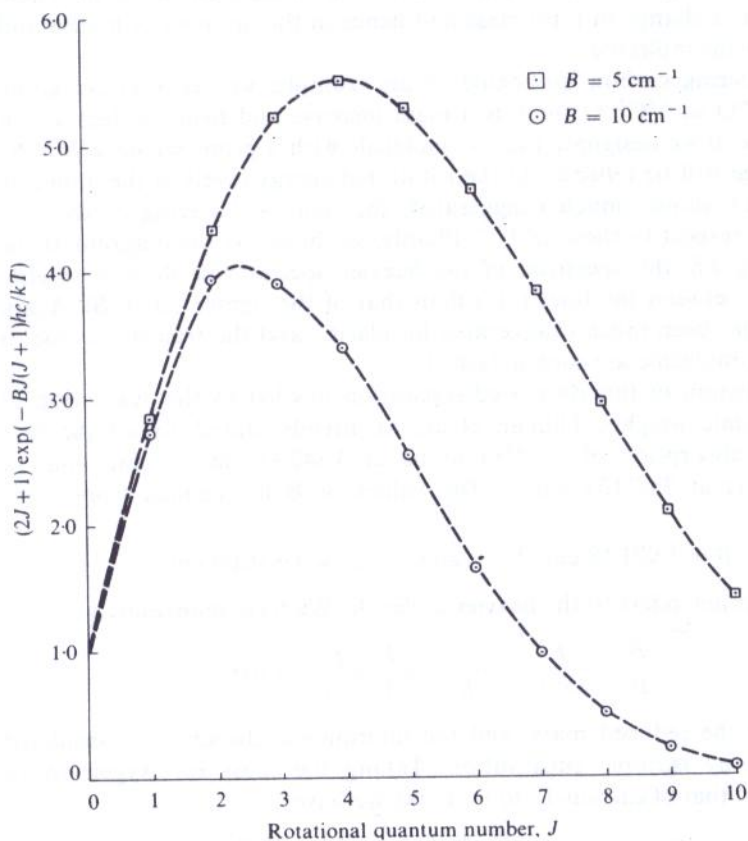


Figure 2.7 The total relative populations, including degeneracy, of the rotational energy levels of a diatomic molecule. The diagram has been drawn for the same conditions as Fig. 2.4.

diminishes. Differentiation of Eq. (2.20) shows that the population is a maximum at the nearest integral J value to:

$$\text{Maximum population: } J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \quad (2.21)$$

We have seen that line intensities are directly proportional to the populations of the rotational levels, hence it is plain that transitions between levels with very low or very high J values will have small intensities while the intensity will be a maximum at or near the J value given by Eq. (2.21).

2.3.3 The Effect of Isotopic Substitution

When a particular atom in a molecule is replaced by its isotope—an element identical in every way except for its atomic mass—the resulting substance is identical chemically with the original. In particular there is no appreciable change in internuclear distance on isotopic substitution. There is, however, a change in total mass and hence in the moment of inertia and B value for the molecule.

Considering carbon monoxide as an example, we see that on going from $^{12}\text{C}^{16}\text{O}$ to $^{13}\text{C}^{16}\text{O}$ there is a mass increase and hence a decrease in the B value. If we designate the ^{13}C molecule with a prime we have $B > B'$. This change will be reflected in the rotational energy levels of the molecule and Fig. 2.8 shows, much exaggerated, the relative lowering of the ^{13}C levels with respect to those of ^{12}C . Plainly, as shown by the diagram at the foot of Fig. 2.8, the spectrum of the heavier species will show a smaller separation between the lines ($2B'$) than that of the lighter one ($2B$). Again the effect has been much exaggerated for clarity, and the transitions due to the heavier molecule are shown dashed.

Observation of this decreased separation has led to the evaluation of precise atomic weights. Gilliam et al., as already stated, found the first rotational absorption of $^{12}\text{C}^{16}\text{O}$ to be at 3.84235 cm^{-1} , while that of $^{13}\text{C}^{16}\text{O}$ was at 3.67337 cm^{-1} . The values of B determined from these figures are:

$$B = 1.92118 \text{ cm}^{-1} \quad \text{and} \quad B' = 1.83669 \text{ cm}^{-1}$$

where the prime refers to the heavier molecule. We have immediately:

$$\frac{B}{B'} = \frac{h}{8\pi^2 I c} \cdot \frac{8\pi^2 I' c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046$$

where μ is the reduced mass, and the internuclear distance is considered unchanged by isotopic substitution. Taking the mass of oxygen to be 15.9994 and that of carbon-12 to be 12.00, we have:

$$\frac{\mu'}{\mu} = 1.046 = \frac{15.9994m'}{15.9994 + m'} \times \frac{12 + 15.9994}{12 \times 15.9994}$$

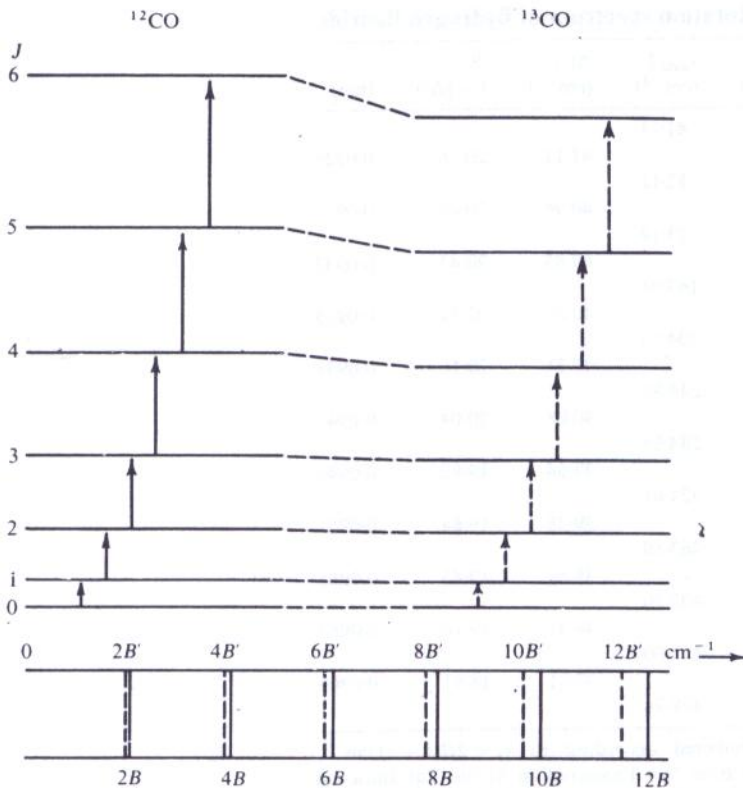


Figure 2.8 The effect of isotopic substitution on the energy levels and hence rotational spectrum of a diatomic molecule such as carbon monoxide.

from which m' , the atomic weight of carbon-13, is found to be 13.0007. This is within 0.02 per cent of the best value obtained in other ways.

It is noteworthy that the data quoted above were obtained by Gilliam et al. from $^{13}\text{C}^{16}\text{O}$ molecules in natural abundance (i.e., about 1 per cent of ordinary carbon monoxide). Thus, besides allowing an extremely precise determination of atomic weights, microwave studies can give directly an estimate of the abundance of isotopes by comparison of absorption intensities.

2.3.4 The Non-Rigid Rotator

At the end of Sec. 2.3.1 we indicated how internuclear distances could be calculated from microwave spectra. It must be admitted that we selected our data carefully at this point—spectral lines for carbon monoxide, other than the first, would not have shown the constant $2B$ separation predicted

Table 2.1 Rotation spectrum of hydrogen fluoride

J	$\bar{\nu}_{\text{obs.}}^\dagger$ (cm^{-1})	$\bar{\nu}_{\text{calc.}}^\ddagger$ (cm^{-1})	$\Delta\bar{\nu}_{\text{obs.}}$ (cm^{-1})	B ($= \frac{1}{2}\Delta\bar{\nu}$)	r (nm)
0	41.08	41.11			
			41.11	20.56	0.0929
1	82.19	82.18			
			40.96	20.48	0.0931
2	123.15	123.14			
			40.85	20.43	0.0932
3	164.00	163.94			
			40.62	20.31	0.0935
4	204.62	204.55			
			40.31	20.16	0.0938
5	244.93	244.89			
			40.08	20.04	0.0941
6	285.01	284.93			
			39.64	19.82	0.0946
7	324.65	324.61			
			39.28	19.64	0.0951
8	363.93	363.89			
			38.89	19.45	0.0955
9	402.82	402.70			
			38.31	19.16	0.0963
10	441.13	441.00			
			37.81	18.91	0.0969
11	478.94	478.74			

\dagger Lines numbered according to $\bar{\nu}_J = 2B(J+1) \text{ cm}^{-1}$. Observed data from 'An Examination of the Far Infra-red Spectrum of Hydrogen Fluoride' by A. A. Mason and A. H. Nielsen, published as Scientific Report No. 5, August 1963, Contract No. AF 19(604)-7981, by kind permission of the authors.

\ddagger See Sec. 2.3.5 for details of the calculation.

by Eq. (2.16). This is shown by the spectrum of hydrogen fluoride given in Table 2.1; it is evident that the separation between successive lines (and hence the apparent B value) decreases steadily with increasing J .

The reason for this decrease may be seen if we calculate internuclear distances from the B values. The calculations are exactly similar to those of Sec. 2.3.1 and the results are shown in column 6 of Table 2.1. Plainly the bond length increases with J and we can see that our assumption of a *rigid* bond is only an approximation; in fact, of course, all bonds are elastic to some extent, and the increase in length with J merely reflects the fact that the more quickly a diatomic molecule rotates the greater is the centrifugal force tending to move the atoms apart.

Before showing how this elasticity may be quantitatively allowed for in rotational spectra, we shall consider briefly two of its consequences. First,

when the bond is elastic, a molecule may have vibrational energy—i.e., the bond will stretch and compress periodically with a certain fundamental frequency dependent upon the masses of the atoms and the elasticity (or force constant) of the bond. If the motion is simple harmonic (which, we shall see in Chapter 3, is usually a very good approximation to the truth) the force constant is given by:

$$k = 4\pi^2 \bar{\omega}^2 c^2 \mu \quad (2.22)$$

where $\bar{\omega}$ is the vibration frequency (expressed in cm^{-1}), and c and μ have their previous definitions. Plainly the variation of B with J is determined by the force constant—the weaker the bond, the more readily will it distort under centrifugal forces.

The second consequence of elasticity is that the quantities r and B vary during a vibration. When these quantities are measured by microwave techniques many hundreds of vibrations occur during a rotation, and hence the measured value is an average. However, from the defining equation of B we have:

$$B = \frac{h}{8\pi^2 I c} = \frac{h}{8\pi^2 c \mu r^2}$$

or

$$B \propto 1/r^2 \quad (2.23)$$

since all other quantities are independent of vibration. Now, although in simple harmonic motion a molecular bond is compressed and extended an equal amount on each side of the equilibrium distance and the average value of the distance is therefore unchanged, the average value of $1/r^2$ is not equal to $1/r_e^2$, where r_e is the equilibrium distance. We can see this most easily by an example. Consider a bond of equilibrium length 0.1 nm vibrating between the limits 0.09 and 0.11 nm. We have:

$$\langle r \rangle_{\text{av.}} = \frac{0.09 + 0.11}{2} = 0.1 = r_e$$

but

$$\left\langle \frac{1}{r^2} \right\rangle_{\text{av.}} = \frac{(1/0.09)^2 + (1/0.11)^2}{2} = 103.05 \text{ nm}^2$$

and therefore $\langle r \rangle_{\text{av.}} = \sqrt{1/103.5} = 0.0985$ nm. The difference, though small, is not negligible compared with the precision with which B can be measured spectroscopically. And in fact the real situation is rather worse. We shall see in Chapter 3 that real vibrations are not simple harmonic, since a real bond may be stretched more easily than it may be compressed, and this usually results in $r_{\text{av.}}$ being greater than $r_{\text{eq.}}$.

It is usual, then, to define three different sets of values for B and r . At the equilibrium separation, r_e , between the nuclei, the rotational constant is B_e ; in the vibrational ground state the average internuclear separation is r_0 associated with a rotational constant B_0 ; while if the molecule has excess vibrational energy the quantities are r_v and B_v , where v is the vibrational quantum number.

During the remainder of this chapter we shall ignore the small differences between B_0 , B_e , and B_v —the discrepancy is most important in the consideration of vibrational spectra in Chapter 3.

We should note, in passing that the rotational spectrum of hydrogen fluoride given in Table 2.1 extends from the microwave well into the infra-red region (cf. Fig. 1.4). This underlines the comment made in Chapter 1 that there is no fundamental distinction between spectral regions, only differences in technique. Since hydrogen fluoride, together with other diatomic hydrides, has a small moment of inertia and hence a large B value, the spacings between rotational energy levels become large and fall into the infra-red region after only a few transitions. Historically, indeed, the moments of inertia and bond lengths of these molecules were first determined from spectral studies using infra-red techniques.

2.3.5 The Spectrum of a Non-Rigid Rotator

The Schrödinger wave equation may be set up for a non-rigid molecule, and the rotational energy levels are found to be:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2 J$$

or

$$\varepsilon_J = E_J/hc = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1} \quad (2.24)$$

where the rotational constant, B , is as defined previously, and the *centrifugal distortion constant* D , is given by:

$$D = \frac{h^3}{32\pi^4 I^2 r^2 kc} \text{ cm}^{-1} \quad (2.25)$$

which is a positive quantity. Equation (2.24) applies for a simple harmonic force field only; if the force field is anharmonic, the expression becomes:

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \dots \text{ cm}^{-1} \quad (2.26)$$

where H , K , etc., are small constants dependent upon the geometry of the molecule. They are, however, negligible compared with D and most modern spectroscopic data are adequately fitted by Eq. (2.24).

From the defining equations of B and D it may be shown directly that

$$D = \frac{16B^3\pi^2\mu c^2}{k} = \frac{4B^3}{\bar{\omega}^2} \quad (2.27)$$

where $\bar{\omega}$ is the vibrational frequency of the bond, and k has been expressed according to Eq. (2.22). We shall see in Chapter 3 that vibrational frequencies are usually of the order of 10^3 cm^{-1} , while B we have found to be of the order of 10 cm^{-1} . Thus we see that D , being of the order 10^{-3} cm^{-1} , is very small compared with B . For small J , therefore, the correction term $DJ^2(J+1)^2$ is almost negligible, while for J values of 10 or more it may become appreciable.

Figure 2.9 shows, much exaggerated, the lowering of rotational levels when passing from the rigid to the non-rigid diatomic molecule. The spectra are also compared, the dashed lines connecting corresponding energy levels and transitions of the rigid and the non-rigid molecules. It should be noted that the selection rule for the latter is still $\Delta J = \pm 1$.

We may easily write an analytical expression for the transitions:

$$\begin{aligned} \varepsilon_{J+1} - \varepsilon_J &= \bar{\nu}_J = B[(J+1)(J+2) - J(J+1)] \\ &\quad - D[(J+1)^2(J+2)^2 - J^2(J+1)^2] \\ &= 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1} \end{aligned} \quad (2.28)$$

where $\bar{\nu}_J$ represents equally the upward transition from J to $J+1$, or the downward from $J+1$ to J . Thus we see analytically, and from Fig. 2.9, that the spectrum of the elastic rotor is similar to that of the rigid molecule except that each line is displaced slightly to low frequency, the displacement increasing with $(J+1)^3$.

A knowledge of D gives rise to two useful items of information. Firstly, it allows us to determine the J value of lines in an observed spectrum. If we have measured a few isolated transitions it is not always easy to determine from which J value they arise; however, fitting Eq. (2.28) to them—provided three consecutive lines have been measured—gives unique values for B , D , and J . The precision of such fitting is shown by Table 2.1 where the wavenumbers are calculated from the equation:

$$\bar{\nu}_J = 41.122(J+1) - 8.52 \times 10^{-3}(J+1)^3 \text{ cm}^{-1} \quad (2.29)$$

Secondly, a knowledge of D enables us to determine—although rather inaccurately—the vibrational frequency of a diatomic molecule. From the above data for hydrogen fluoride and Eq. (2.27) we have:

$$\bar{\omega}^2 = \frac{4B^3}{D} = 16.33 \times 10^6 \text{ (cm}^{-1}\text{)}^2$$

i.e.,

$$\bar{\omega} \approx 4050 \text{ cm}^{-1}$$

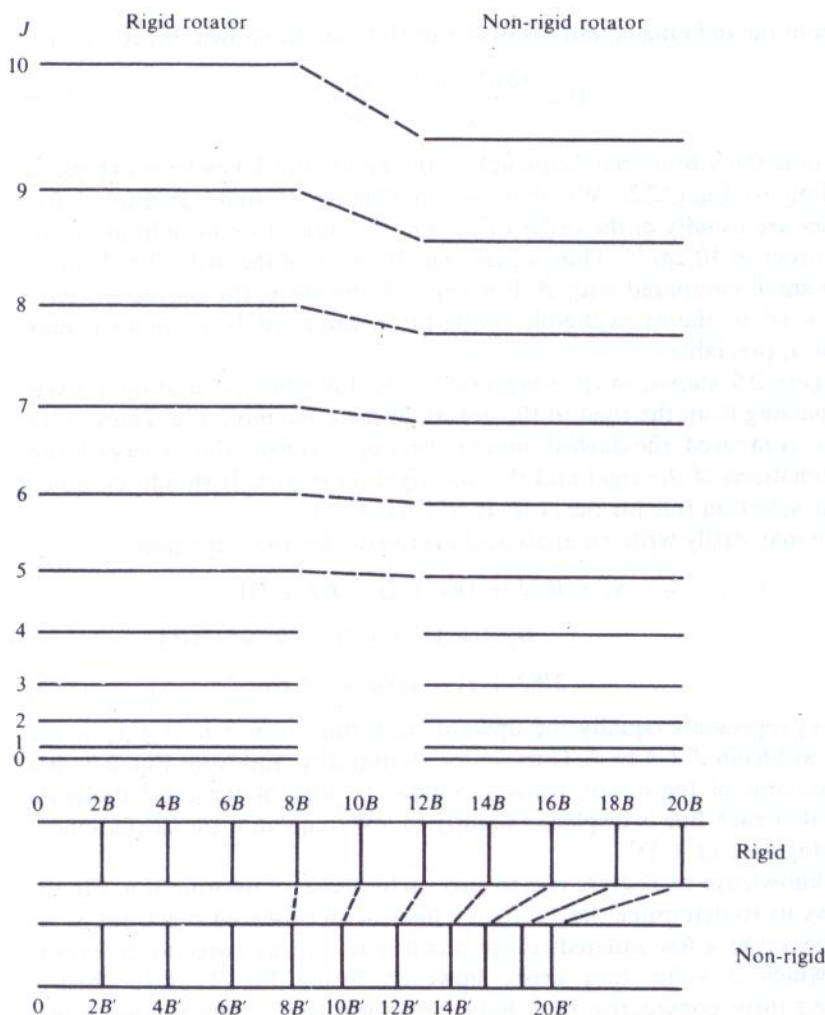


Figure 2.9 The change in rotational energy levels and rotational spectrum when passing from a rigid to a non-rigid diatomic molecule. Levels on the right calculated using $D = 10^{-3}B$.

In the next chapter we shall see that a more precise determination leads to the value 4138.3 cm^{-1} ; the two per cent inaccuracy in the present calculation is due partly to the assumption of simple harmonic motion, and partly to the very small, and hence relatively inaccurate, value of D .

The force constant follows directly:

$$k = 4\pi^2 c^2 \bar{\omega}^2 \mu = 960 \text{ N m}^{-1}$$

which indicates, as expected, that H—F is a relatively strong bond.

2.4 POLYATOMIC MOLECULES

2.4.1 Linear Molecules

We consider first molecules such as carbon oxysulphide OCS, or chloroacetylene $\text{HC}\equiv\text{CCl}$, where all the atoms lie on a straight line, since this type gives rise to a particularly simple spectra in the microwave region. Since $I_B = I_C$; $I_A = 0$, as for diatomic molecules, the energy levels are given by a formula identical with Eq. (2.26), i.e.,

$$\varepsilon_J = BJ(J + 1) - DJ^2(J + 1)^2 + \dots \text{ cm}^{-1} \quad (2.30)$$

and the spectrum will show the same $2B$ separation modified by the distortion constant. In fact, the whole of the discussion on diatomic molecules applies equally to all linear molecules; three points, however, should be underlined:

1. Since the moment of inertia for the end-over-end rotation of a polyatomic linear molecule is considerably greater than that of a diatomic molecule, the B value will be much smaller, and the spectral lines more closely spaced. Thus B values for diatomic molecules are about 10 cm^{-1} , while for triatomic molecules they can be 1 cm^{-1} or less, and for larger molecules smaller still.
2. The molecule must, as usual, possess a dipole moment if it is to exhibit a rotational spectrum. Thus OCS will be microwave active, while OCO (more usually written CO_2) will not. In particular, it should be noted that isotopic substitution does not lead to a dipole moment since the bond lengths and atomic charges are unaltered by the substitution. Thus $^{16}\text{OC}^{18}\text{O}$ is microwave inactive.
3. A non-cyclic polyatomic molecule containing N atoms has altogether $N - 1$ individual bond lengths to be determined. Thus in the triatomic molecule OCS there is the CO distance, r_{CO} , and the CS distance, r_{CS} . On the other hand, there is only *one* moment of inertia for the end-over-end rotation of OCS, and only this one value can be determined from the spectrum. Table 2.2 shows the data for this molecule. Over the four lines observed there is seen to be no appreciable centrifugal distortion, and, taking the value of B as 0.2027 cm^{-1} , we calculate:

$$I_B = \frac{h}{8\pi^2 Bc} = 137.95 \times 10^{-47} \text{ kg m}^2$$

From this one observation it is plainly impossible to deduce the two unknowns, r_{CO} and r_{CS} . The difficulty can be overcome, however, if we study a molecule with different atomic masses but the *same* bond lengths—i.e., an isotopically substituted molecule—since this will have a different moment of inertia.

Table 2.2 Microwave spectrum of carbon oxy-
sulphide

$J \rightarrow J + 1$	$\bar{\nu}_{\text{obs.}} (\text{cm}^{-1})$	$\Delta\bar{\nu}$	$B (\text{cm}^{-1})$
0 → 1	...	2×0.4055	0.2027
1 → 2	0.8109	0.4054	0.2027
2 → 3	1.2163	0.4054	0.2027
3 → 4	1.6217	0.4054	0.2027
4 → 5	2.0271		

Let us consider the rotation of OCS in some detail. Figure 2.10 shows the molecule, where r_{O} , r_{C} , and r_{S} represent the distances of the atoms from the centre of gravity. Consideration of moments gives:

$$m_{\text{O}}r_{\text{O}} + m_{\text{C}}r_{\text{C}} = m_{\text{S}}r_{\text{S}} \quad (2.31)$$

where m_i is the mass of atom i . The moment of inertia is:

$$I = m_{\text{O}}r_{\text{O}}^2 + m_{\text{C}}r_{\text{C}}^2 + m_{\text{S}}r_{\text{S}}^2 \quad (2.32)$$

and we have the further equations:

$$r_{\text{O}} = r_{\text{CO}} + r_{\text{C}} \quad r_{\text{S}} = r_{\text{CS}} - r_{\text{C}} \quad (2.33)$$

where r_{CO} and r_{CS} are the bond lengths of the molecule. It is these we wish to determine. Substituting (2.33) in (2.31) and collecting terms:

$$(m_{\text{C}} + m_{\text{O}} + m_{\text{S}})r_{\text{C}} = m_{\text{S}}r_{\text{CS}} - m_{\text{O}}r_{\text{CO}}$$

or

$$Mr_{\text{C}} = m_{\text{S}}r_{\text{CS}} - m_{\text{O}}r_{\text{CO}} \quad (2.34)$$

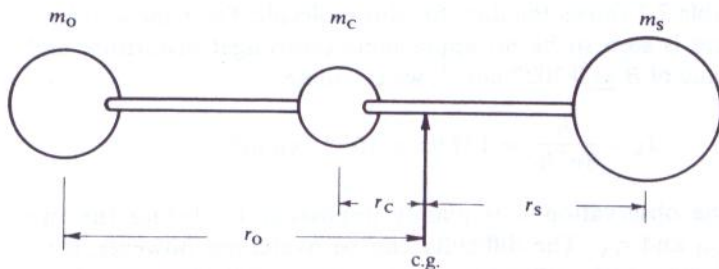


Figure 2.10 The molecule of carbon oxy-sulphide, OCS, showing the distances of each atom from the centre of gravity.

where we write M for the total mass of the molecule. Substituting (2.33) in (2.32):

$$\begin{aligned} I &= m_{\text{O}}(r_{\text{CO}} + r_{\text{C}})^2 + m_{\text{C}}r_{\text{C}}^2 + m_{\text{S}}(r_{\text{CS}} - r_{\text{C}})^2 \\ &= Mr_{\text{C}}^2 + 2r_{\text{C}}(m_{\text{O}}r_{\text{CO}} - m_{\text{S}}r_{\text{CS}}) + m_{\text{O}}r_{\text{CO}}^2 + m_{\text{S}}r_{\text{CS}}^2 \end{aligned}$$

and finally substituting for r_{C} from Eq. (2.34):

$$I = m_{\text{O}}r_{\text{CO}}^2 + m_{\text{S}}r_{\text{CS}}^2 - \frac{(m_{\text{O}}r_{\text{CO}} - m_{\text{S}}r_{\text{CS}})^2}{M} \quad (2.35)$$

Considering now the isotopic molecule, ^{18}OCS , we may write m'_{O} for m_{O} throughout Eq. (2.35):

$$I' = m'_{\text{O}}r_{\text{CO}}^2 + m_{\text{S}}r_{\text{CS}}^2 - \frac{(m'_{\text{O}}r_{\text{CO}} - m_{\text{S}}r_{\text{CS}})^2}{M'} \quad (2.36)$$

and we can now solve for r_{CO} and r_{CS} , provided we have extracted a value for I' from the microwave spectrum of the isotopic molecule. Note that we do *not* need to write r'_{CO} , since we assume that the bond length is unaltered by isotopic substitution. This assumption may be checked by studying the molecules $^{16}\text{OC}^{34}\text{S}$ and $^{18}\text{OC}^{34}\text{S}$, since we would then have four moments of inertia. The bond distances found are quite consistent, and hence justify the assumption.

The extension of the above discussion to molecules with more than three atoms is straightforward; it suffices to say here that microwave studies have led to very precise determinations of many bond lengths in such molecules.

2.4.2 Symmetric Top Molecule

Although the rotational energy levels of this type of molecule are more complicated than those of linear molecules, we shall see that, because of their symmetry, their pure rotational spectra are still relatively simple. Choosing methyl fluoride again as our example we remember that

$$I_{\text{B}} = I_{\text{C}} \neq I_{\text{A}} \quad I_{\text{A}} \neq 0$$

There are now two directions of rotation in which the molecule might absorb or emit energy—that about the main symmetry axis (the C—F bond in this case) and that perpendicular to this axis.

We thus need two quantum numbers to describe the degree of rotation, one for I_{A} and one for I_{B} or I_{C} . However, it turns out to be very convenient mathematically to have a quantum number to represent the *total* angular momentum of the molecule, which is the sum of the separate angular momenta about the two different axes. This is usually chosen to be the quantum number J . Reverting for a moment to *linear* molecules, remember that we there used J to represent the end-over-end rotation of a molecule:

however, this was the *only* sort of rotation allowed, so it is quite consistent to use J , in general, to represent the *total angular momentum*. It is then conventional to use K to represent the angular momentum about the top axis—i.e., about the C—F bond in this case.

Let us briefly consider what values are allowed to K and J . Both must, by the conditions of quantum mechanics, be integral or zero. The total angular momentum can be as large as we like, that is, J can be 0, 1, 2, ..., ∞ (except, of course, for the theoretical possibility that a real molecule will be disrupted at very high rotational speeds). Once we have chosen J , however, K is rather more limited. Let us consider the case when $J = 3$. Plainly the rotational energy can be divided in several ways between motion about the main symmetry axis and motion perpendicular to this. If *all* the rotation is about the axis, $K = 3$; but note that K cannot be greater than J since J is the *total* angular momentum. Equally we could have $K = 2, 1$, or 0, in which case the motion perpendicular to the axis increases accordingly. Additionally, however, K can be negative—we can imagine positive and negative values of K to correspond with clockwise and anticlockwise rotation about the symmetry axis—and so can have values $-1, -2$, or -3 .

In general, then, for a total angular momentum J , we see that K can take values:

$$K = J, J - 1, J - 2, \dots, 0, \dots, -(J - 1), -J \quad (2.37)$$

which is a total of $2J + 1$ values altogether. This figure of $2J + 1$ is important and will recur.

If we take first the case of a *rigid* symmetric top—i.e., one in which the bonds are supposed not to stretch under centrifugal forces—the Schrödinger equation may be solved to give the allowed energy levels for rotation as:

$$\varepsilon_{J, K} = E_{J, K}/hc = BJ(J + 1) + (A - B)K^2 \quad \text{cm}^{-1} \quad (2.38)$$

where, as before,

$$B = \frac{h}{8\pi^2 I_B c} \quad \text{and} \quad A = \frac{h}{8\pi^2 I_A c}$$

Note that the energy depends on K^2 , so that it is immaterial whether the top spins clockwise or anticlockwise: the energy is the same for a given angular momentum. For all $K > 0$, therefore, the rotational energy levels are *doubly degenerate*.

The selection rules for this molecule may be shown to be:

$$\Delta J = \pm 1 \quad (\text{as before}) \quad \text{and} \quad \Delta K = 0 \quad (2.39)$$

and, when these are applied to Eq. (2.38), the spectrum is given by:

$$\begin{aligned}\varepsilon_{J+1, K} - \varepsilon_{J, K} = \bar{\nu}_{J, K} &= B(J+1)(J+2) + (A-B)K^2 \\ &\quad - [BJ(J+1) + (A-B)K^2] \\ &= 2B(J+1) \text{ cm}^{-1}\end{aligned}\quad (2.40)$$

Thus the spectrum is independent of K , and hence rotational changes about the symmetry axis do not give rise to a rotational spectrum. The reason for this is quite evident—rotation about the symmetry axis does not change the dipole moment perpendicular to the axis (which always remains zero), and hence the rotation cannot interact with radiation. Equation (2.40) shows that the spectrum is just the same as for a linear molecule and that only one moment of inertia—that for end-over-end rotation—can be measured.

Both Eqs (2.38) and (2.40) are for a rigid molecule, however, and we have already seen that microwave spectroscopy is well able to detect the departure of real molecules from this idealized state. When centrifugal stretching is taken into account, the energy levels become:

$$\begin{aligned}\varepsilon_{J, K} &= BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 \\ &\quad - D_{JK} J(J+1)K^2 - D_K K^4 \text{ cm}^{-1}\end{aligned}\quad (2.41)$$

where, in an obvious notation, D_J , D_{JK} , and D_K are small correction terms for non-rigidity. The selection rules are unchanged (Eq. (2.39)), and so the spectrum is:

$$\begin{aligned}\bar{\nu}_{J, K} = \varepsilon_{J+1, K} - \varepsilon_{J, K} \\ &= 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 \text{ cm}^{-1}\end{aligned}\quad (2.42)$$

We see that the spectrum will be basically that of a linear molecule (including centrifugal stretching) with an additional term depending on K^2 .

It is easy to see why this spectrum now depends on the axial rotation (i.e., depends on K), although such rotation produces no dipole change. Figure 2.11 illustrates methyl fluoride for (a) $K = 0$, no axial rotation, and (b) $K > 0$, the molecule rotating about the symmetry axis. We see, from the much exaggerated diagram, that axial rotation widens the HCH angles and stretches the C—H bonds. The distorted molecule (b) has a different moment of inertia for end-over-end rotation from (a). If we write Eq. (2.42) as:

$$\bar{\nu}_{JK} = 2(J+1)[B - 2D_J(J+1)^2 - D_{JK}K^2] \text{ cm}^{-1}$$

we can see more clearly that the centrifugal distortion constants D_J and D_{JK} can be considered as correction terms to the rotational constant B , and hence as perturbing the moment of inertia I_B .

Since each value of J is associated with $2J + 1$ values of K , we see that each line characterized by a certain J value must have $2J + 1$ components.

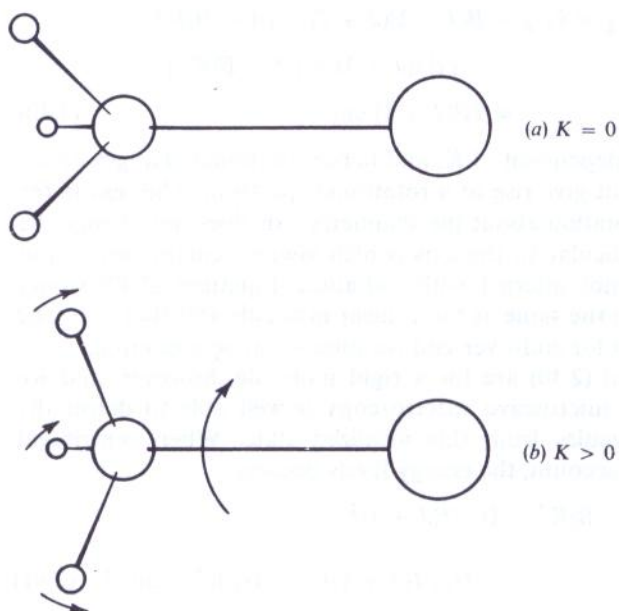


Figure 2.11 The influence of axial rotation on the moment of inertia of a symmetric top molecule, e.g., methyl fluoride, CH_3F . In (a) there is no axial rotation ($K = 0$), and in (b) $K > 0$.

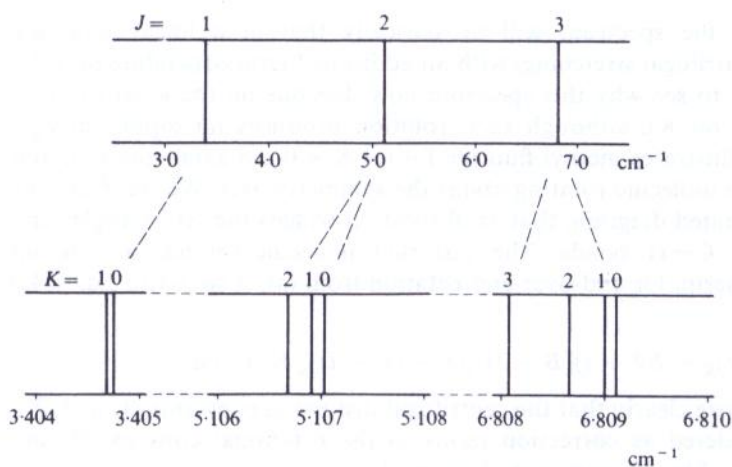


Figure 2.12 A diagrammatic representation of the rotational spectrum of the symmetric top molecule methyl fluoride, CH_3F .

However, since K only appears as K^2 in Eq. (2.42), there will be only $J + 1$ different frequencies, all those with $K > 0$ being doubly degenerate. We may tabulate a few lines as follows:

$$\begin{aligned}
 J = 0, K = 0 & \quad \bar{\nu}_{JK} = 2B - 4D_J \quad \text{cm}^{-1} \\
 J = 1, K = 0 & \quad \bar{\nu}_{JK} = 4B - 32D_J \\
 & \quad K = \pm 1 \quad \bar{\nu}_{JK} = 4B - 32D_J - 4D_{JK} \\
 J = 2, K = 0 & \quad \bar{\nu}_{JK} = 6B - 108D_J \\
 & \quad K = \pm 1 \quad \bar{\nu}_{JK} = 6B - 108D_J - 6D_{JK} \\
 & \quad K = \pm 2 \quad \bar{\nu}_{JK} = 6B - 108D_J - 24D_{JK}, \quad \text{etc.}
 \end{aligned} \tag{2.43}$$

Let us now compare these with the observed spectrum of methyl fluoride. This is shown as a line diagram in Fig. 2.12, and the frequencies are tabulated in Table 2.3. Fitting these data to equations such as (2.43) leads directly to:

$$\begin{aligned}
 B &= 0.851204 \text{ cm}^{-1} \\
 D_J &= 2.00 \times 10^{-6} \text{ cm}^{-1} \\
 D_{JK} &= 1.47 \times 10^{-5} \text{ cm}^{-1}
 \end{aligned}$$

The calculated frequencies of Table 2.3 show how precisely such measurements may now be made.

Once again each spectrum examined yields only one value of B , but the spectra of isotopic molecules can, in principle, give sufficient information for the calculation of all the bond lengths and angles of symmetric top molecules, together with estimates of the force constant of each bond.

Table 2.3 Microwave spectrum of methyl fluoride

J	K	$\bar{\nu}_{\text{obs.}} \dagger (\text{cm}^{-1})$	$\bar{\nu}_{\text{calc.}} (\text{cm}^{-1})$
1	0	3.40475	3.404752
	1	3.40470	3.404693
2	0	5.10701	5.107008
	1	5.10692	5.106920
	2	5.10665	5.106655
3	0	6.80912	6.809120
	1	6.80900	6.809002
	2	6.80865	6.808649
	3	6.80806	6.808062

† Taken from W. Gordy, *Physical Review*, **93**, 406 (1954), by kind permission of the author.

Table 2.4 Some molecular data determined by microwave spectroscopy

Molecule	Type	Bond length (nm)	Bond angle (deg.)	Dipole moment† (debyes)
NaCl	Diatomic	0.23606 ± 0.00001	—	8.5 ± 0.2
COS	Linear	$\left\{ \begin{array}{l} 0.1164 \pm 0.0001 \text{ (CO)} \\ 0.1559 \pm 0.0001 \text{ (CS)} \end{array} \right.$	—	0.712 ± 0.004
HCN	Linear	$\left\{ \begin{array}{l} 0.106317 \pm 0.000005 \text{ (CH)} \\ 0.115535 \pm 0.000006 \text{ (CN)} \end{array} \right.$	—	2.986 ± 0.004
NH ₃	Sym. Top	0.1008 ± 0.0004	107.3 ± 0.2	1.47 ± 0.01
CH ₃ Cl	Sym. Top	$\left\{ \begin{array}{l} 0.10959 \pm 0.00005 \text{ (CH)} \\ 0.17812 \pm 0.00005 \text{ (CCl)} \end{array} \right.$	108.0 ± 0.2 (HCH)	1.871 ± 0.005
H ₂ O	Asym. Top	0.09584 ± 0.00005	104.5 ± 0.3	1.846 ± 0.005
O ₃	Asym. Top	0.1278 ± 0.0002	116.8 ± 0.5	0.53 ± 0.02

† Measured from the Stark effect, cf. Sec. 2.5.2.

2.4.3 Asymmetric Top Molecules

Since spherical tops show no microwave spectrum (cf. Sec. 2.1(3)) the only other class of molecule of interest here is the asymmetric top which has (Sec. 2.1(4)) all three moments of inertia different. These molecules will not detain us long since their rotational energy levels and spectra are very complex—in fact, no analytical expressions can be written for them corresponding to Eqs (2.24) and (2.28) for linear or Eqs (2.41) and (2.42) for symmetric top molecules. Each molecule and spectrum must, therefore, be treated as a separate case, and much tedious computation is necessary before structural parameters can be determined. The best method of attack so far has been to consider the asymmetric top as falling somewhere between the oblate and prolate symmetric top; interpolation between the two sets of energy levels of the latter leads to a first approximation of the energy levels—and hence spectrum—of the asymmetric molecule. It suffices to say that arbitrary methods such as this have been quite successful, and much very precise structural data have been published.

In order to give an idea of the precision of such measurements, we collect in Table 2.4 some molecular data determined by microwave methods, including examples from diatomic and linear molecules, symmetric tops, and asymmetric tops.

2.5 TECHNIQUES AND INSTRUMENTATION

2.5.1 Outline

It is not proposed here to give more than a brief outline of the techniques of microwave spectroscopy since detailed accounts are available in some of the books listed in the bibliography. Microwave spectroscopy, of course, fol-

lows the usual pattern: source, monochromator, beam direction, sample, and detector. We shall discuss each in turn.

1. *The source and monochromator.* The usual source in this region is the klystron valve which, since it emits radiation of only a very narrow frequency range, is called 'monochromatic' and acts as its own monochromator. The actual emission frequency is variable electronically and hence a spectrum may be scanned over a limited range of frequencies using a single klystron.

One slight disadvantage of this source is that the total energy radiated is very small—of the order of milliwatts only. However, since all this is concentrated into a narrow frequency band a sharply tuned detector can be sufficiently activated to produce a strong signal.

2. *Beam direction.* This is achieved by the use of 'waveguides'—hollow tubes of copper or silver, usually of rectangular cross-section—inside which the radiation is confined. The waveguides may be gently tapered or bent to allow focusing and directing of the radiation. Atmospheric absorption of the beam is considerable, so the system must be efficiently evacuated.

3. *Sample and sample space.* In almost all microwave studies so far the sample has been gaseous. However, pressures of 0.01 mmHg are sufficient to give a reasonable absorption spectrum, so many substances which are usually thought of as solid or liquid may be examined provided their vapour pressures are above this value. The sample is retained by very thin mica windows in a piece of evacuated waveguide.

4. *Detector.* It is possible to use an ordinary superheterodyne radio receiver as detector, provided this may be tuned to the appropriate high frequency; however, a simple crystal detector is found to be more sensitive and easier to use. This detects the radiation focused upon it by the waveguide, and the signal it gives is amplified electronically for display on an oscilloscope, or for permanent record on paper.

2.5.2 The Stark Effect

We cannot leave the subject of microwave spectroscopy without a brief description of the Stark effect and its applications. A more detailed discussion is to be found in the books by Kroto and by Townes and Schawlow mentioned in the bibliography.

Experimentally the Stark effect requires the placing of an electric field, either perpendicular or parallel to the direction of the radiation beam, across the sample. Practically it is simpler to have a perpendicular field. We shall consider three advantages of this field.

1. A molecule exhibiting a rotational spectrum must have an electric dipole moment, and so its rotational energy levels will be perturbed by the

application of an exterior field since interaction will occur. Put simply, the absorption lines of the spectrum will be shifted by an amount depending on the extent of the interaction, and thus depending on both E , the applied field, and μ , the dipole moment. For a linear molecule the shift is found to be:

$$\Delta\nu \propto (\mu E)^2 \quad (\text{linear molecule})$$

while for a symmetric top:

$$\Delta\nu \propto \mu E \quad (\text{symmetric top})$$

Thus we have immediately a very accurate method of determining dipole moments, simply by observation of the Stark shift. More important, the measurement is made on very dilute gas samples, so the dipole moment observed may be taken to be that of the actual molecule, uncomplicated by molecular interactions, solvent effects, etc. Some values determined in this way are included in Table 2.4.

2. The second valuable application of the Stark effect is in the assignment of observed spectral lines to particular J values. We have seen that, in the absence of marked departure from rigidity and good resolving power, the assignment of J values is not always obvious. The line of lowest frequency which we observe *may* happen to correspond with $J = 0$, or it may be that it is the first observable line of a series, either because earlier lines are intrinsically very weak or because of limitations in the apparatus used. However, we have seen that each line is $2J + 1$ degenerate because rotations can occur in $2J + 1$ orientations in space without violating quantum laws. In the absence of any orienting effect these transitions have precisely the same frequency, but a Stark field constitutes an orienting effect, and splits the degeneracy; thus multiplet structure is observed for all lines with $J > 0$. The number of components depends on J , and hence unambiguous assignments can be made.
3. The final application is purely an instrumental one, but is especially interesting in that it has its counterpart in other spectral regions. We have already referred to the concept of signal-to-noise ratio in Chapter 1; that part of the noise which arises from random fluctuations in the background radiation may be removed by modulating the beam by means of the Stark effect as explained below.

Imagine the application of a Stark field in a periodic manner such as the 'square-wave' variation of Fig. 2.13; while the field is switched on the signal is modified in the way described in 1 and 2 above. If we arrange the modulation frequency to be some 100 to 1000 Hz, and construct the amplifier so that it amplifies only the component of the signal which has the modulated frequency, stray radiation which has not been through the modulating field will be completely ignored. This results in a great improvement of the signal-to-noise ratio.

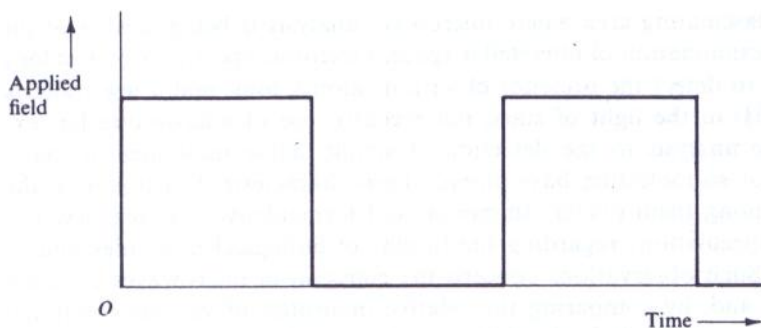


Figure 2.13 A 'square wave' potential as used for Stark modulation.

A further refinement is to arrange for both the modulated and unmodulated parts to be amplified separately and displayed on the same oscilloscope—the modulated part on the upper half, say, and the unmodulated on the lower. This much facilitates the measurement of the Stark splittings discussed in 1 and 2 above.

2.6 CHEMICAL ANALYSIS BY MICROWAVE SPECTROSCOPY

Improvements and simplifications in the techniques of microwave spectroscopy are now allowing it to move away from being purely a specialist research instrument towards becoming a technique for routine analysis. Even though effectively limited to gaseous samples, it has much to offer in this respect, since it is a highly sensitive (0.01 mmHg pressure is adequate) and specific analytical tool.

The microwave spectrum of a substance is very rich in lines since many rotational levels are populated at room temperatures, but since the lines are very sharp and their positions can be measured with great accuracy, observation of just a few of them is sufficient, after comparison with tabulated data, to establish the presence of a previously examined substance in a sample. And the technique is quantitative, since the intensity of a spectrum observed under given conditions is directly dependent on the amount of substance present. Thus mixtures can be readily analysed.

It is the *whole* molecule, by virtue of its moment(s) of inertia, which is examined by microwave spectroscopy. This means that the technique cannot detect the presence of particular molecular groupings in a sample, like $-\text{OH}$ or $-\text{CH}_3$ (cf. the chapters on infra-red, raman, and magnetic resonance spectroscopy later), but it can readily distinguish the presence of isotopes in a sample, and it can even detect different conformational isomers, provided they have different moments of inertia.

One fascinating area where microwave analysis is being used is in the chemical examination of interstellar space. Electronic spectroscopy has long been able to detect the presence of various atoms, ions, and a few radicals (e.g., —OH) in the light of stars, but recently, use of microwaves has extended the analysis to the detection of simple stable molecules in space. Some 30 or so molecules have already been characterized in this way, the earliest among them (water, ammonia, and formaldehyde) giving new impetus to speculations regarding the origins of biological molecules and of life itself. Such observations concern the emission of microwaves by these molecules and, by comparing the relative intensities of various rotational transitions, particularly in the spectrum of ammonia, accurate estimates can be made of the temperature of interstellar material.

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PROBLEMS

(Useful constants: $h = 6.626 \times 10^{-34}$ J s; $k = 1.381 \times 10^{-23}$ J K⁻¹; $c = 2.998 \times 10^8$ m s⁻¹; $8\pi^2 = 78.956$; atomic masses: $^1\text{H} = 1.673 \times 10^{-27}$ kg; $^2\text{D} = 3.344 \times 10^{-27}$ kg; $^{19}\text{F} = 31.55 \times 10^{-27}$ kg; $^{35}\text{Cl} = 58.06 \times 10^{-27}$ kg; $^{37}\text{Cl} = 61.38 \times 10^{-27}$ kg; $^{79}\text{Br} = 131.03 \times 10^{-27}$ kg.)

- 2.1 The rotational spectrum of $^{79}\text{Br}^{19}\text{F}$ shows a series of equidistant lines spaced 0.71433 cm⁻¹ apart. Calculate the rotational constant B , and hence the moment of inertia and bond length of the molecule. Determine the wavenumber of the $J = 9 \rightarrow J = 10$ transition, and find which transition gives rise to the most intense spectral line at room temperature (say 300 K).
 2.2 Using your answers to Prob. 2.1, calculate the number of revolutions per second which the BrF molecule undergoes when in (a) the $J = 0$ state, (b) the $J = 1$ state, and (c) the $J = 10$ state.

Hint: Use $E = \frac{1}{2}I\omega^2$ in conjunction with Eqs (2.10) and (2.13), but remember that here ω is in radians per second.

- 2.3 The rotational constant for H^{35}Cl is observed to be 10.5909 cm⁻¹. What are the values of B for H^{37}Cl and for $^2\text{D}^{35}\text{Cl}$?

- 2.4 Three consecutive lines in the rotational spectrum of H^{79}Br are observed at 84.544 , 101.355 and 118.112 cm⁻¹. Assign the lines to their appropriate $J'' \rightarrow J'$ transitions, then

deduce values for B and D , and hence evaluate the bond length and approximate vibrational frequency of the molecule.

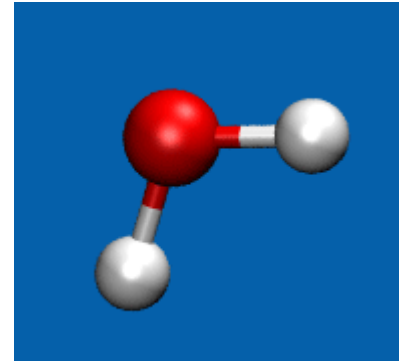
2.5 Sketch a diagram similar to that of Fig. 2.7, using $B = 5 \text{ cm}^{-1}$ and a temperature of 1600 K.

Note: Find the maximum and calculate only two or three points on either side—don't attempt to carry out the calculation for every value of J .

2.6 The bond lengths of the linear molecule $\text{H}-\text{C}\equiv\text{N}$ are given in Table 2.4. Calculate I and B for HCN and for DCN, using relative atomic masses of $\text{H} = 1$, $\text{D} = 2$, $\text{C} = 12$ and $\text{N} = 14$.

2.7 The diatomic molecule HCl has a B value of 10.593 cm^{-1} and a centrifugal distortion constant D of $5.3 \times 10^{-4} \text{ cm}^{-1}$. Estimate the vibrational frequency and force constant of the molecule. The observed vibrational frequency is 2991 cm^{-1} ; explain the discrepancy.

Rotational spectroscopy



- Involve transitions between rotational states of the molecules (**gaseous state!**)
- Energy difference between rotational levels of molecules has the same order of magnitude with **microwave energy**
- Rotational spectroscopy is called **pure rotational spectroscopy**, to distinguish it from **roto-vibrational spectroscopy** (the molecule changes its state of vibration and rotation simultaneously) and **vibronic spectroscopy** (the molecule changes its electronic state and vibrational state simultaneously)

Molecules do not rotate around an arbitrary axis!

Generally, the rotation is around the mass center of the molecule.

The rotational axis must allow the conservation of kinetic angular momentum.

$$\vec{M} = \sum_{\alpha} \vec{R}_{\alpha} \times \vec{p}_{\alpha} = \text{const}$$

Molecular Energy Levels

i.e., typically $\Delta E_{el} \gg \Delta E_{vib} \gg \Delta E_{rot}$

Different electronic states
(electronic arrangements)

ΔE_{el}

ΔE_{vib}

ΔE_{rot}

Electronic

Vibrational

Rotational

$\Delta E \approx 2 \times 10^4 - 10^6 \text{ cm}^{-1}$

$10^2 - 5 \times 10^3 \text{ cm}^{-1}$

3 - 300 GHz

(0.1 - 10 cm^{-1})

Transitions at $\lambda \approx$ 500 - 100 nm

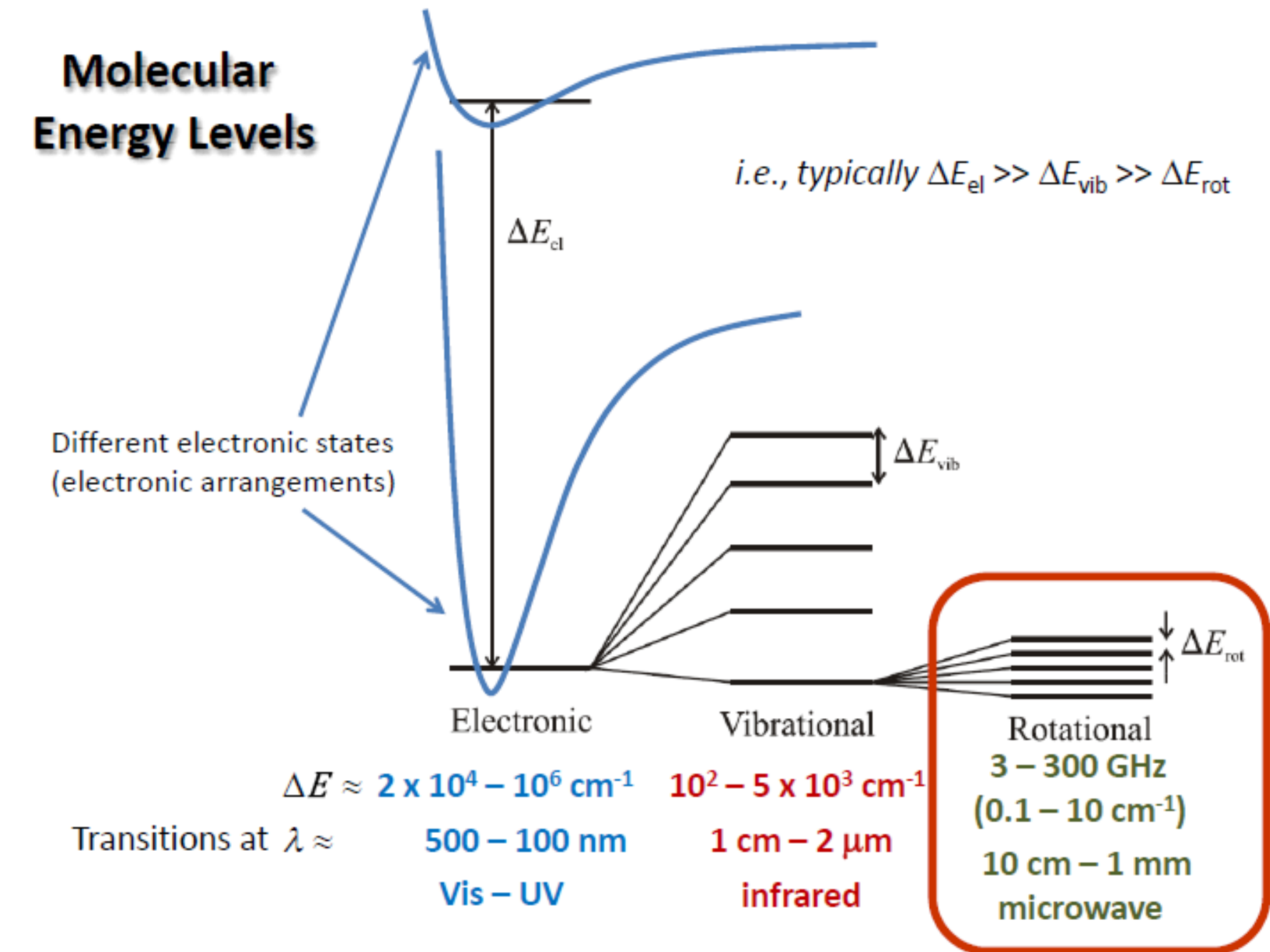
1 cm - 2 μm

10 cm - 1 mm

Vis - UV

infrared

microwave



Rotational spectroscopy

>130 molecules / ions have been identified in interstellar space by their rotational emission spectra (*rf*-astronomy)

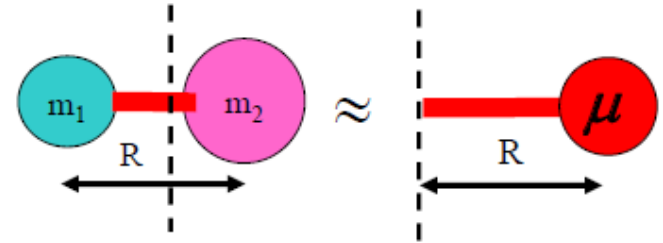
H ₂	C ₃	c-C ₃ H	C ₆	C ₆ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₅ N?	HC ₉ N	CH ₃ OC ₂ H ₆	<u>HC₁₁N</u>
AlF	C ₂ H	I-C ₃ H	C ₄ H	I-H ₂ C ₄	CH ₂ CHCN	HCOOCH ₃	CH ₃ CH ₂ CN	(CH ₃) ₂ CO			
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄	CH ₃ C ₂ H	CH ₃ COOH?	(CH ₃) ₂ O	NH ₂ CH ₂ COOH			
C ₂	C ₂ S	C ₃ O	I-C ₃ H ₂	CH ₃ CN	HC ₅ N	<u>C₇H</u>	CH ₃ CH ₂ OH	<u>CH₂CH₂CHO</u>			
CH	CH ₂	C ₃ S	c-C ₃ H ₂	CH ₃ NC	HCOCH ₃	<u>H₂C₈</u>	HC ₇ N				
CH ⁺	HCN	C ₂ H ₂	CH ₂ CN	CH ₃ OH	NH ₂ CH ₃	<u>CH₂OHCO</u>	C ₈ H				
CN	HCO	CH ₂ D ⁺	CH ₄	CH ₃ SH	<u>c-C₂H₄O</u>	<u>CH₂CHCHO</u>					
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	<u>CH₂CHOH</u>						
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO							
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO							
CSi	H ₂ O	HNCS	H ₂ CHN	C ₆ N							
HCl	H ₂ S	HOCO ⁺	H ₂ C ₂ O	<u>HC₄N</u>							
KCl	HNC	H ₂ CO	H ₂ NCN								
NH	HNO	H ₂ CN	HNC ₃								
NO	MgCN	H ₂ CS	SiH ₄								
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺								

NIST & National Radio Astronomy Lab.

Rotation of diatomic molecule - Classical description

Diatomic molecule = a system formed by 2 different masses linked together with a rigid connector (rigid rotor = the bond length is assumed to be fixed!).

The system rotation around the mass center is equivalent with the rotation of a particle with the mass μ (reduced mass) around the center of mass.



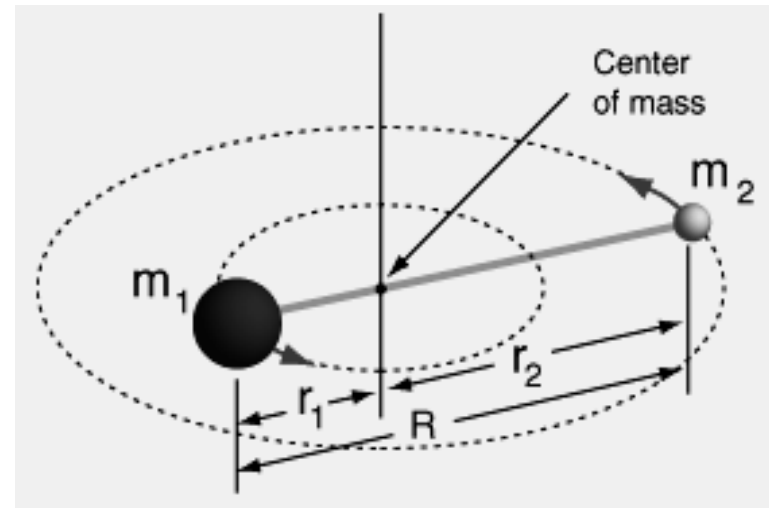
The moment of inertia:
$$\mathbf{I} = \sum_i m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2 = \mu R^2 = \frac{m_1 m_2}{m_1 + m_2} R^2$$

Moment of inertia (I) is the rotational equivalent of mass (m).
Angular velocity (ω) is the equivalent of linear velocity (v).

$E_r \rightarrow$ rotational kinetic energy

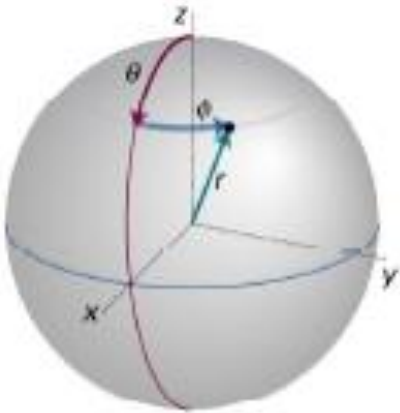
$L = I\omega \rightarrow$ angular momentum

$$E_c = \frac{mv^2}{2} = \frac{p^2}{2m} \quad \leftrightarrow \quad E_r = \frac{I\omega^2}{2} = \frac{L^2}{2I}$$



Quantum rotation: The diatomic rigid rotor

The rigid rotor represents the quantum mechanical “particle on a sphere” problem:



Rotational energy is purely kinetic energy (no potential):

$$\hat{H}\Psi = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x}) \quad \hat{p} = -i\hbar\nabla \quad \nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \quad \text{nabla}$$

Schrodinger equation:
$$\hat{H}\Psi = -\frac{\hbar^2}{2\mu} \nabla^2 \Psi = E\Psi$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Laplacian operator in cartesian coordinate

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

spherical coordinate

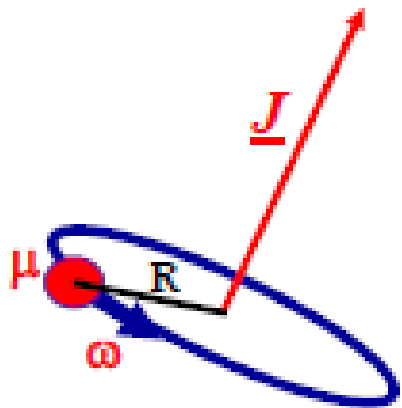
For $r = \text{constant}$ ($\frac{\partial}{\partial r} = 0$), Schrodinger equation simplifies to:

$$-\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = EY(\theta, \phi)$$

The solutions resemble those of the "particle on a ring":

$$Y_{lm_l}(\theta, \phi) = \Theta_{lm_l}(\theta)\Psi_{m_l}(\phi) \quad \rightarrow \text{separation of variable}$$

$$\Psi(\phi+2\pi) = \Psi(\phi) \quad \rightarrow \text{cyclic boundary conditions}$$



$$\left\{ \begin{array}{l} \Psi_{m_J}(\phi) = \frac{e^{im_J\phi}}{\sqrt{2\pi}} \quad \rightarrow \text{wavefunctions (rotational)} \\ E_{\text{rot}}(J, m_J) = J(J+1) \frac{\hbar^2}{2I} \quad \rightarrow \text{eigenvalues (energy)} \end{array} \right.$$

$J = 0, 1, 2, 3, \dots$ (rotational quantum number)

$m_J = 0, \pm 1, \pm 2, \dots, \pm J$ (projection of J)

$$E_{\text{rot}J} = hcBJ(J+1) \quad \rightarrow \text{the rotational energy of a molecule}$$

$$B = \frac{h}{8\pi^2 c \cdot I} = \frac{h}{8\pi^2 c \cdot \mu R^2} \quad \rightarrow \text{rotational constant (in cm}^{-1}\text{)}$$

	\tilde{B}
H ₂	60.85 cm ⁻¹
CO	1.93 cm ⁻¹
HCl	10.59 cm ⁻¹

Obs:

→ Rotational energy levels get more widely space with increasing J !

$$E_{\text{rot}J} = hcBJ(J+1)$$

$$E_{\text{rot}5} = hc \cdot 30B$$

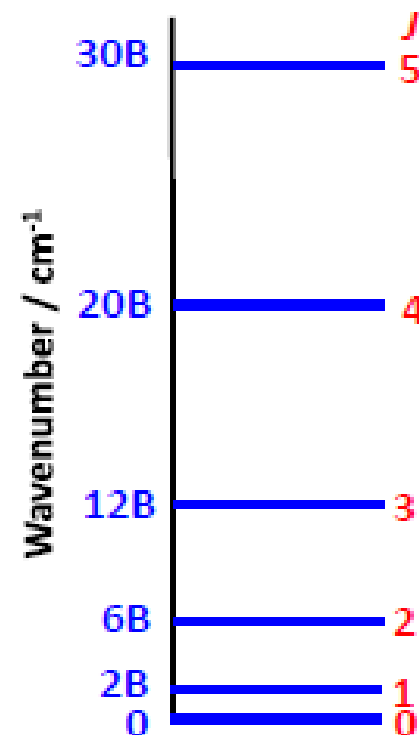
$$E_{\text{rot}4} = hc \cdot 20B$$

$$E_{\text{rot}3} = hc \cdot 12B$$

$$E_{\text{rot}2} = hc \cdot 6B$$

$$E_{\text{rot}1} = hc \cdot 2B$$

$$E_{\text{rot}0} = 0$$



$$E_{\text{rot}0} = 0$$

→ There is no zero point energy associated with rotation!

Obs:

$$B = \frac{h}{8\pi^2 c \cdot \mu R^2}$$

- For large molecules (μ): - the moment of inertia (I) is high,
- the rotational constant (B) is small

For large molecules the rotational levels are closer than for small molecules.

- From rotational spectra we can obtain some information about geometrical structure of molecule (r):

For diatomic molecule we can calculate the length of bond!

- Diatomic molecules rotations can partial apply to linear polyatomic molecules.

- An isotopic effect could be observed: $B \sim 1/(\mu R^2)$

$$\frac{\tilde{B}_{H^{35}Cl}}{\tilde{B}_{H^{37}Cl}} = \frac{\mu_{H^{37}Cl}}{\mu_{H^{35}Cl}} = \frac{37u \cdot u}{38u} \cdot \frac{36u}{35u} = 1.0015$$

Rotational wavefunctions

General solution:

$$\Psi_{m_J}(\phi) = \frac{e^{im_J\phi}}{\sqrt{2\pi}}$$

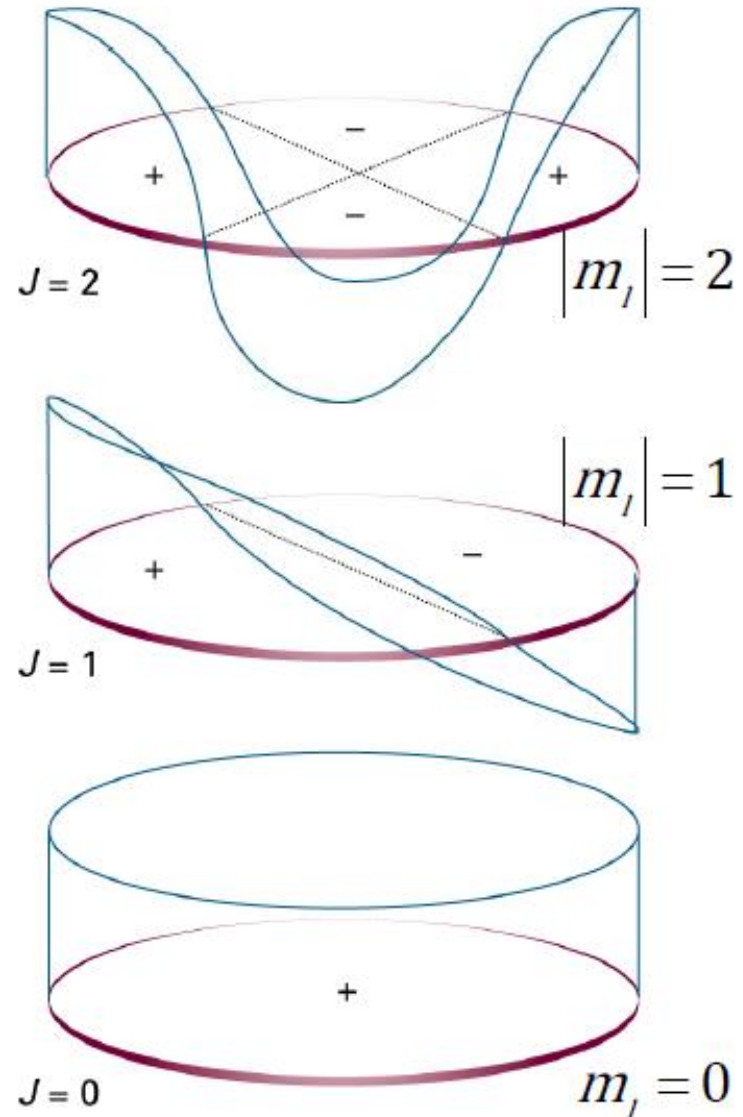
$m_J = 0, \pm 1, \pm 2, \pm 3 \dots$ when imposing cyclic boundary conditions:

$$\Psi(\phi + 2\pi) = \Psi(\phi)$$

Rotational wavefunctions are imaginary functions!

It is useful to **plot the real part** to see their symmetries: odd and even J levels have opposite parity.

Rotational wave functions parity = $(-1)^J$



Degeneracy of Rotational Levels

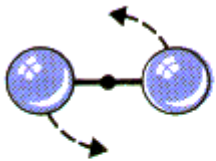
In the absence of external fields energy of rotational levels only determined by J (all $m_J = -J, \dots, +J$) share the same energy. Therefore, **rotational levels** exhibits $(2J+1)$ fold **degeneracy** (arising from the projection quantum number m_J).

Both the magnitude and direction (projection) of rotational angular momentum is quantized. This is reflected in the **two quantum numbers**:

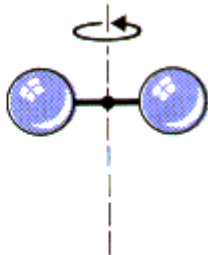
J (magnitude)

m_J (direction/projection).

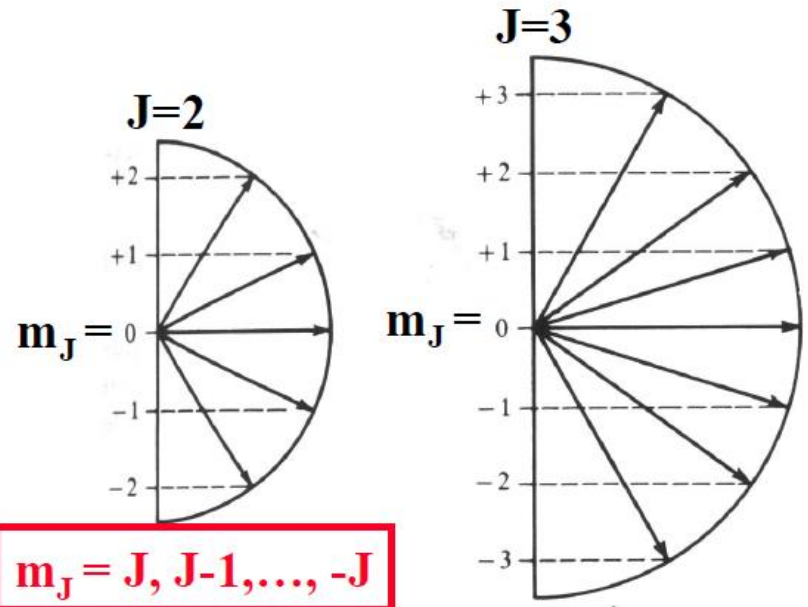
Taking the surface normal as the quantization axis, $m_J = 0$ corresponds to **out-of-plane rotation** and $m_J = J$ corresponds to **in-plane rotation**.

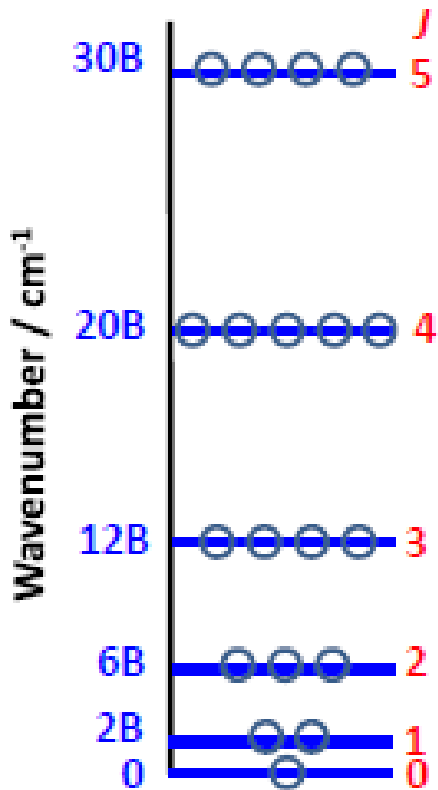


Rotation in the plane of the paper



Rotation out of the plane of the paper.





Populations of rotational levels

$$N_j = N_0 g_j \exp\left(-\frac{E_j}{kT}\right)$$

Boltzmann distribution

$$g_J = 2J + 1$$

degeneracy

$$E_{\text{rot}J} = hcBJ(J + 1)$$

rotational energy

$$N_j = N_0 (2J + 1) \exp\left(-\frac{hcBJ(J + 1)}{kT}\right)$$

The most populated level occurs for: $\frac{dN_J}{dJ} = 0$

$$\frac{dN_J}{dJ} = N_0 \left[2 - (2J + 1)^2 \frac{hcB}{kT} \right] \exp\left(-\frac{hcBJ(J + 1)}{kT}\right) = 0$$

$$2 - (2J_{\text{max}} + 1)^2 \frac{hcB}{kT} = 0$$

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

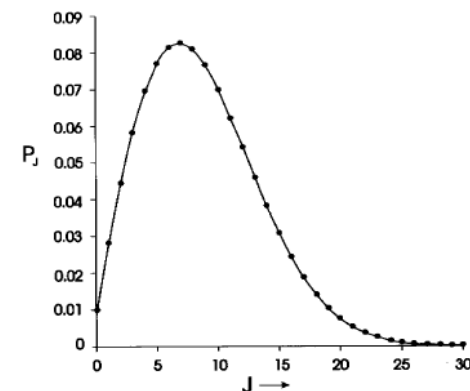


Figure 6.16. Distribution of population among rotational states of CO at room temperature.

Rotational spectroscopy (*Microwave spectroscopy*)

Molecules can absorb energy from microwave range in order to **change their rotational state** ($h\nu = \Delta E_{\text{rot}} = E_{\text{rot(sup)}} - E_{\text{rot(inf)}}$).

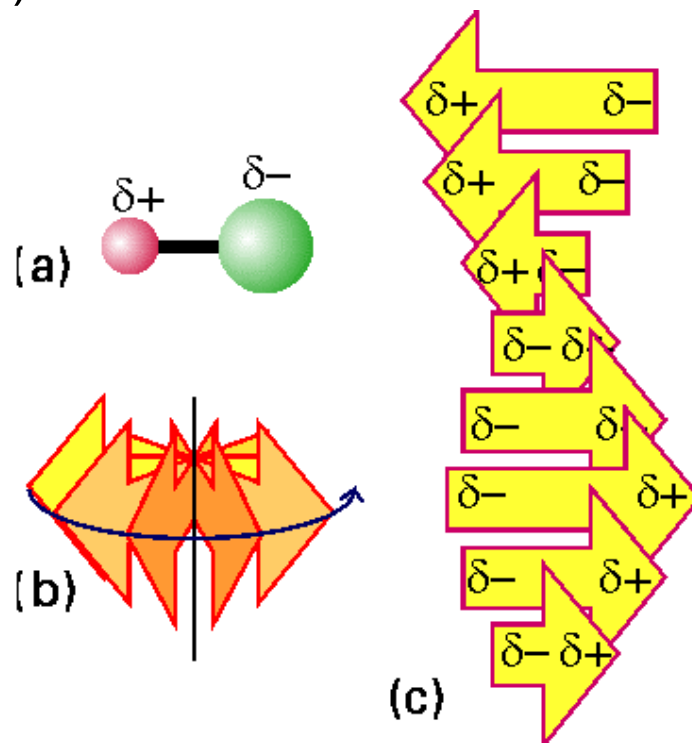
Gross Selection Rule:

For a molecule to exhibit a pure rotational spectrum it must possess a **permanent dipole moment**. (otherwise the photon has no means of interacting “nothing to grab hold of”)

→ a **molecule must be polar** to be able to interact with microwave.

→ a polar rotor appears to have an oscillating electric dipole.

Homonuclear diatomic molecules such as O_2 , H_2 , do not have a dipole moment and, hence, **no pure rotational spectrum!**



Specific Selection Rule:

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

Only for diatomic molecules (linear molecules)!

The specific selection rule derive from conservation of angular momentum.

But need to change parity (see rotational wavefunctions)!

Schrödinger equation explains the specific selection rule ($\Delta J = \pm 1$):

$$\mu_r = \int \Psi_f \mu \Psi_i$$

f - final state, i initial state

μ_r - transition dipole moment

The molecule absorbed microwave radiation (change its rotational state) only if integral is non-zero ($\Delta J = \pm 1$): the rotational transition is allowed!

If the integral is zero, the transition is forbidden!

Rotational transitions

$$\bar{\nu}_{r(J_1 \rightarrow J_2)} = \frac{\Delta E_{\text{rot}J}}{hc} = \frac{E_{\text{rot}J_2} - E_{\text{rot}J_1}}{hc}$$

$$E_{\text{rot}J} = hcBJ(J+1)$$

$$\bar{\nu}_{r(J_1 \rightarrow J_2)} = BJ_2(J_2+1) - BJ_1(J_1+1)$$

$$\bar{\nu}_{r(J_1 \rightarrow J_2)} = B \cdot (J_2^2 + J_2 - J_1^2 - J_1)$$

$$J_2 = J_1 + 1$$

$$\bar{\nu}_{r(J_1 \rightarrow J_1+1)} = B(1 + 2J_1 + J_1^2 + 1 + J_1 - J_1^2 - J_1)$$

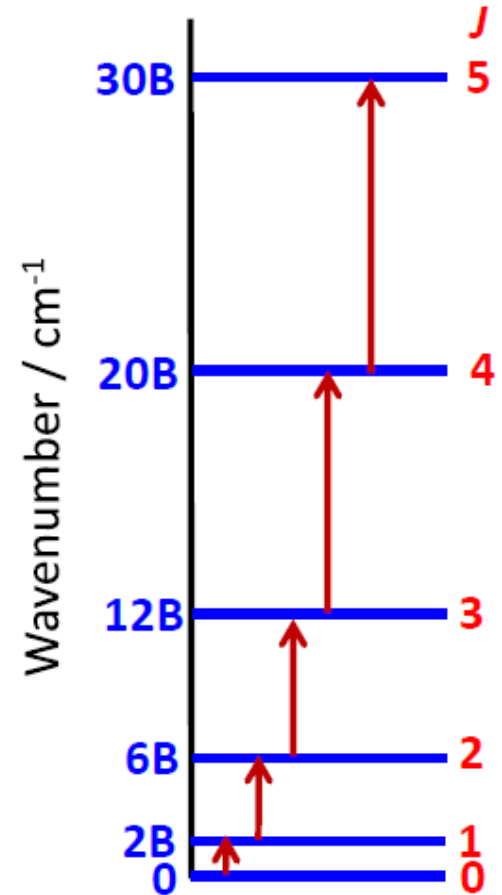
$$\bar{\nu}_{r(J_1 \rightarrow J_1+1)} = 2B \cdot (J_1 + 1)$$

$\bar{\nu}_r$ rotational transition wavenumber

J_1 rotational quantum number of inferior state

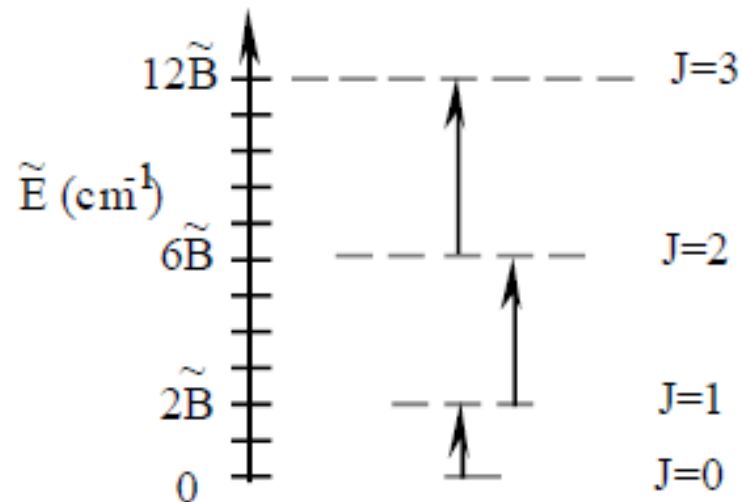
J_2 rotational quantum number of superior state

$$\bar{\nu}_{r(J_2-1 \rightarrow J_2)} = 2B \cdot J_2$$

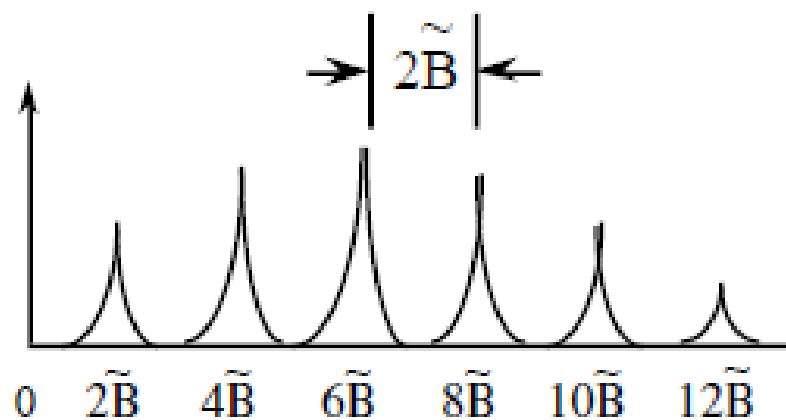


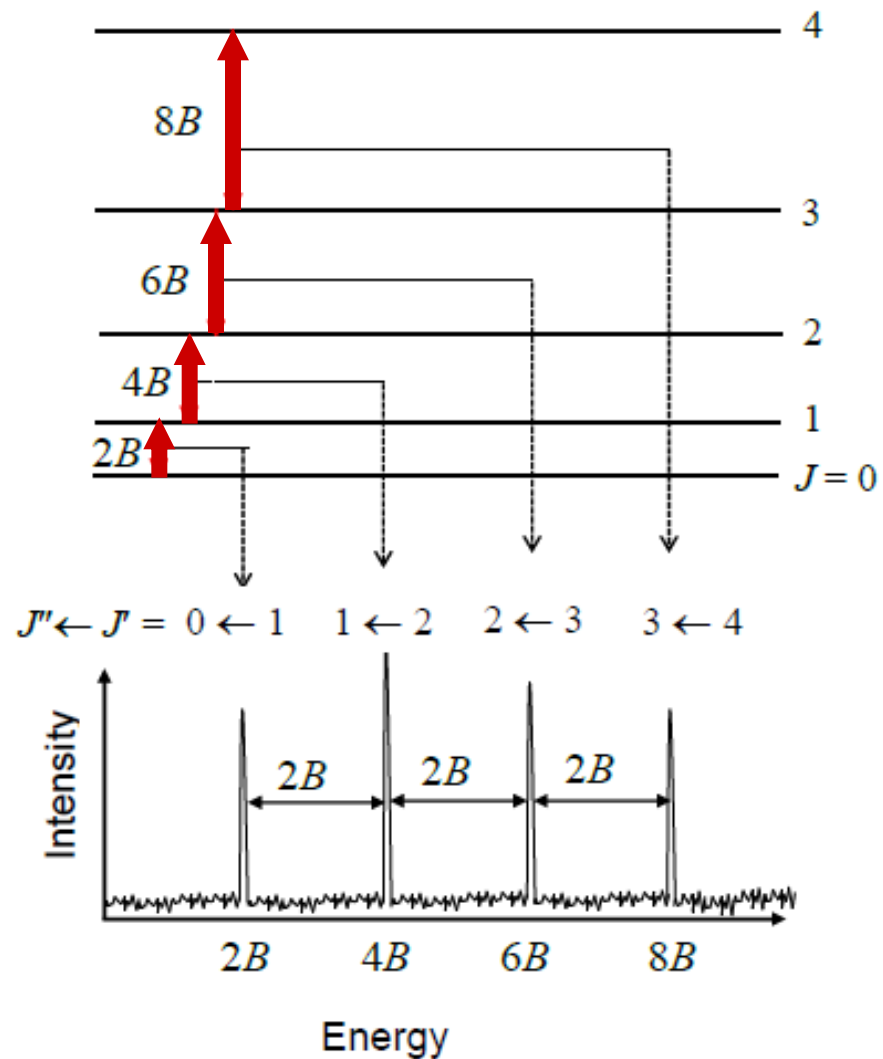
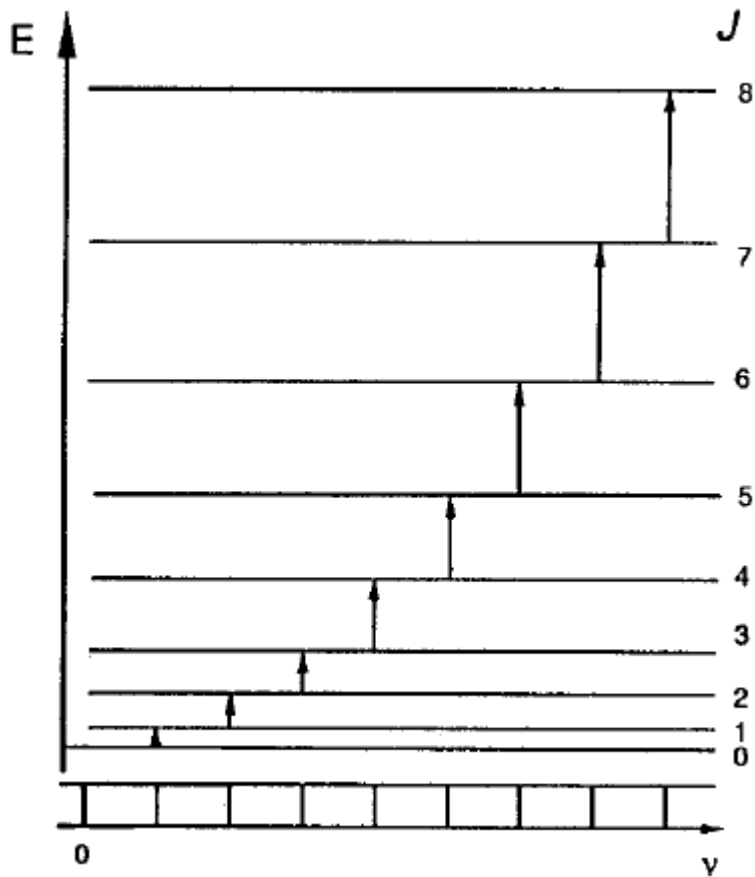
Rotational spectra have a lot of peaks ($\bar{\nu}_r$) spaced by $2B$ ($\Delta\bar{\nu}_r$).

$$\begin{array}{l} \bar{\nu}_{r(0 \rightarrow 1)} = 2B \\ \bar{\nu}_{r(1 \rightarrow 2)} = 4B \\ \bar{\nu}_{r(2 \rightarrow 3)} = 6B \\ \bar{\nu}_{r(3 \rightarrow 4)} = 8B \end{array} \left. \begin{array}{l} \Delta\bar{\nu}_r = 2B \\ \Delta\bar{\nu}_r = 2B \\ \Delta\bar{\nu}_r = 2B \end{array} \right\}$$



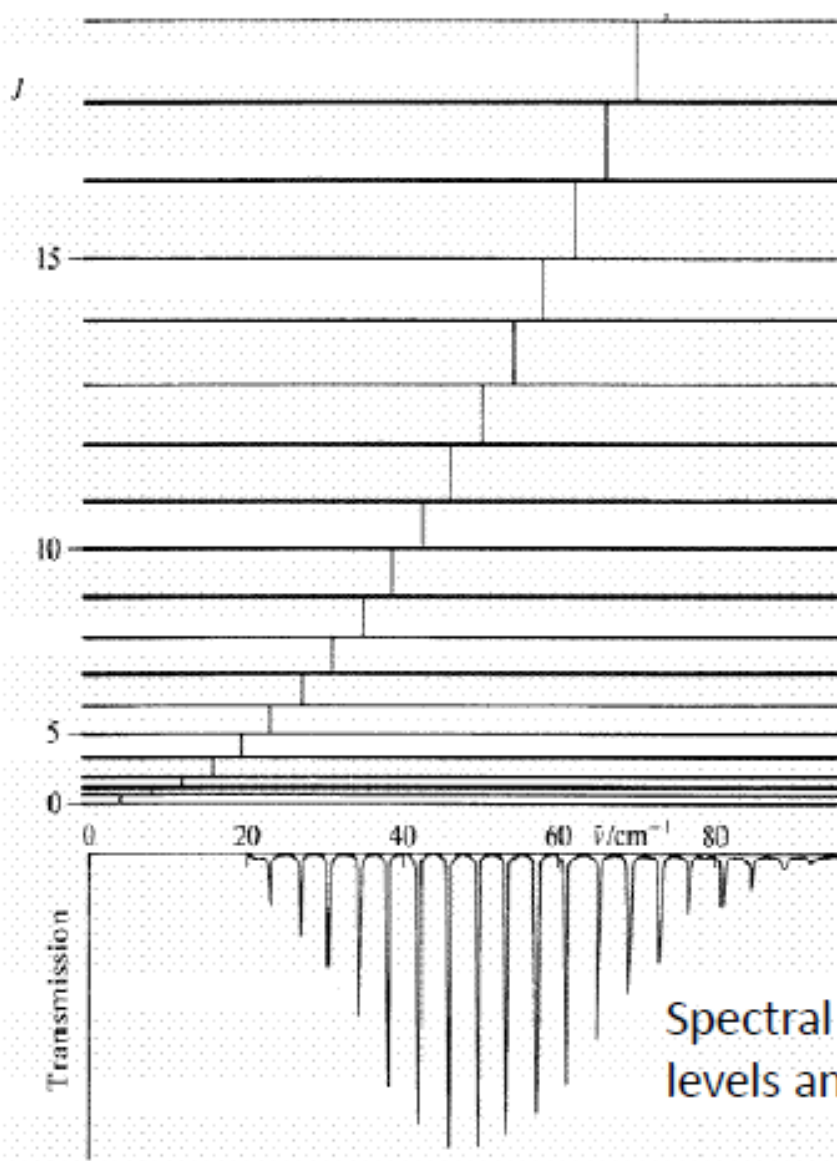
J_1	E (cm^{-1})	$\bar{\nu}_r$ (cm^{-1})	$\Delta\bar{\nu}_r$ (cm^{-1})
0	0		
1	$2B$	$2B$	
2	$6B$	$4B$	$2B$
3	$12B$	$6B$	$2B$





The rotational transitions are separated by $2B$ in the observed spectrum!

Rotational Spectrum of CO



Rotational spectrum of CO (300K)

$$\begin{aligned} \tilde{\nu} &= F_{J+1} - F_J \\ &= \tilde{B}(J+1)(J+2) - \tilde{B}J(J+1) \\ &= 2\tilde{B}(J+1) \end{aligned}$$

Transitions in the microwave region:
 $1\text{-}100 \text{ cm}^{-1}$ ($\lambda = 1 \text{ cm} - 100 \mu\text{m}$)

Lines spaced by $2\tilde{B}$

$F_J = E_J/hc$ rotational spectral terms

Spectral Profile governed by population of lower levels and J dependence of the transition strength.

Beyond the Rigid Rotor: Centrifugal Distortion

The rigid rotor model holds for rigid rotors.

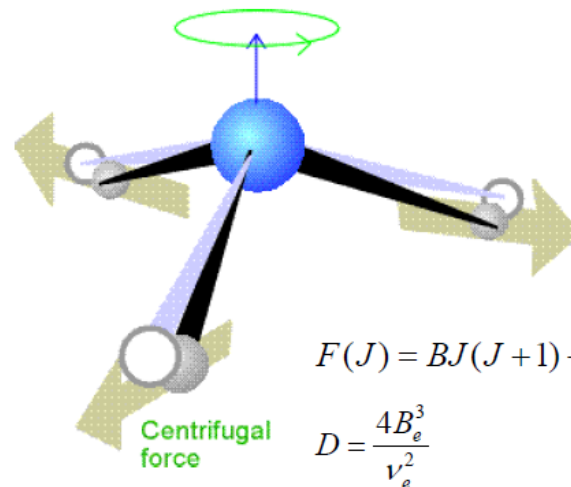
Molecules are *not* rigid rotors – their bonds stretch during rotation

As a result, the moment of inertia I change with J .

For real molecule, the rotational constant B depend on rotational quantum number J !

It is more convenient to treat centrifugal distortion as a perturbation to the rigid rotor terms.

In real rotational spectra the peaks are not perfectly equidistant:
centrifugal distortion (D).



- The effect of rotation on a molecule. The centrifugal force arising from rotation distorts the molecule, opening out bond angles and stretching bonds slightly. The effect is to increase the moment of inertia of the molecule and hence to decrease its rotational constant.

Centrifugal Distortion in diatomic molecules

When J increase (molecule rotates faster) the bond length increase \rightarrow the moment of inertia increase \rightarrow the rotational constant B decrease.

$$B' = B - D \cdot J(J+1)$$

The rotational energy becomes:

$$E_{\text{rot}}(J) = hc \cdot [J(J+1) \cdot B - D \cdot J^2(J+1)^2]$$

D : the centrifugal distortion constant (in cm^{-1})

$$D = \frac{4 \cdot B^3}{\bar{\nu}_0^2} \quad (\text{cm}^{-1})$$

$\bar{\nu}_0$: the wavenumber of harmonic oscillator!

In this case, **the wavenumber of rotational transition** ($J \rightarrow J+1$) is:

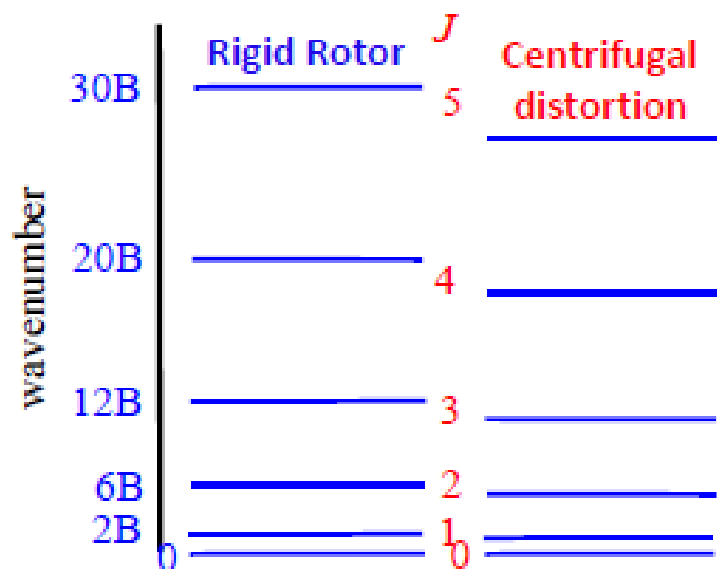
$$\bar{\nu}_{\text{rj}} = \frac{\Delta E}{hc} = 2B(J+1) - 4D(J+1)^3$$

The centrifugal distortion constant D is much smaller than B !

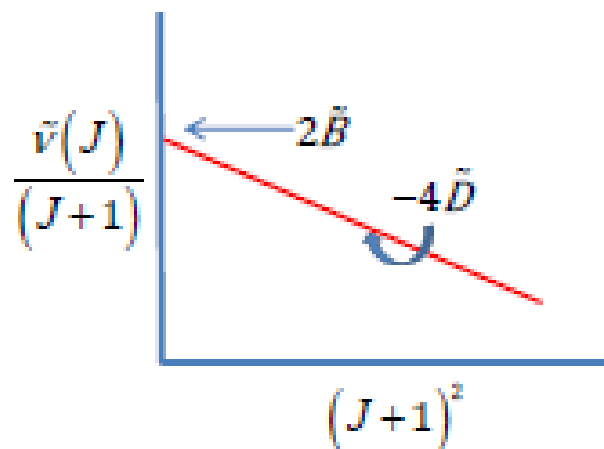
in cm^{-1}	\tilde{B}	\tilde{D}
H^{35}Cl	10.44	0.0005282
$^{12}\text{C}^{16}\text{O}$	1.923	0.0000061
HCN	1.478	0.0000029

The rotational energy levels of real molecule shrink together.

The peaks (rotational transitions) from rotational spectra of real molecule are not equidistant!



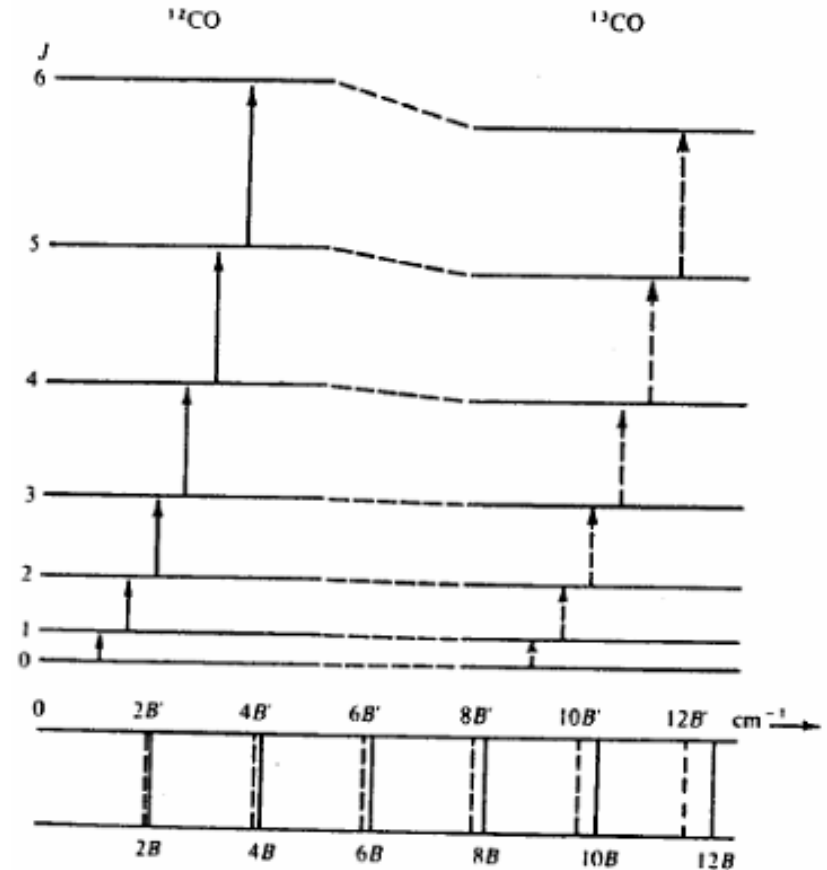
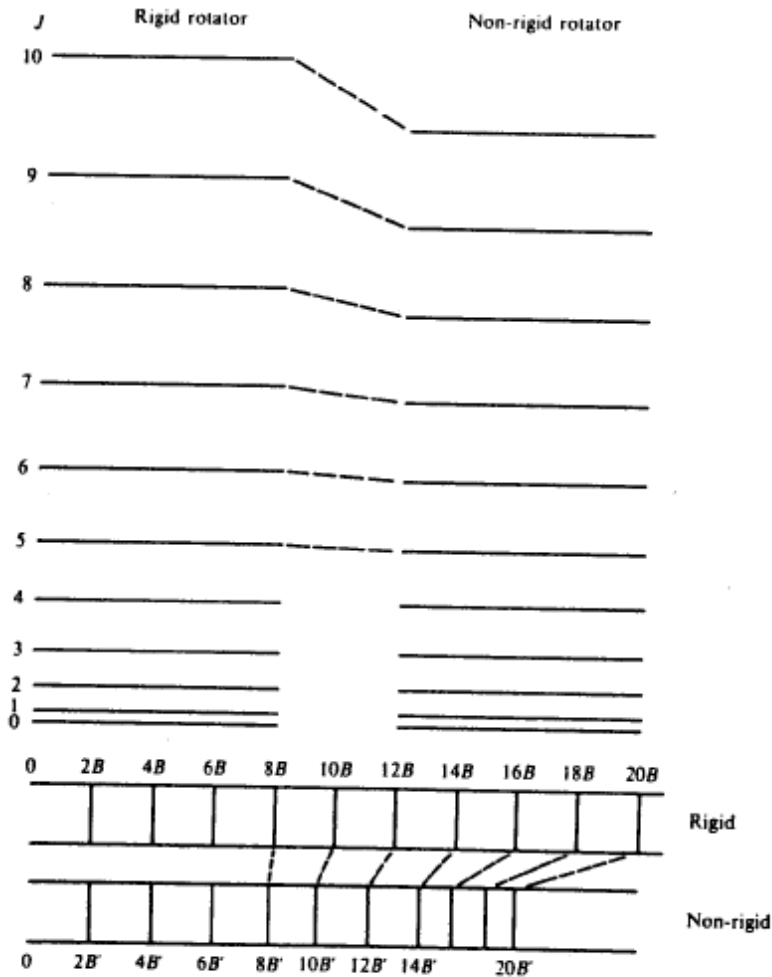
$$\bar{\nu}_r = 2B(J+1) - 4D(J+1)^3$$



B and **D** constants can be calculated from the graph function: $\frac{\bar{\nu}_r}{(J+1)} = f(J+1)^2$

$$\frac{\bar{\nu}_r}{(J+1)} = 2B - 4D(J+1)^2 \quad \longrightarrow \quad \text{slope} = -4D; \quad \text{y intercept} = 2B$$

$$E_{\text{rot}}(J) = hc \cdot [J(J+1) \cdot B - D_J J^2(J+1)^2]$$



The effect of isotopic substitution on the energy levels and rotational spectrum of a diatomic such as carbon monoxide.

The change in rotational energy levels and spectrum when passing from a rigid to a non-rigid diatomic molecule. Energy levels on the right are calculated using $D = 10^{-3}B$.

$$\bar{\nu}_r = 2B(J+1) - 4D(J+1)^3$$

$$B = \frac{h}{8\pi^2 \cdot I \cdot c}$$

$$D = \frac{4 \cdot B^3}{\bar{\nu}_0^2}$$

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

Independent activity

a) The molecule $^{23}\text{Na}^1\text{H}$ (rigid rotor) is found to undergo a rotational transition from $J = 0$ to $J = 1$ when it absorbs a photon of frequency $2.94 \cdot 10^{11}$ Hz.

b) What is the equilibrium bond length of the molecule?

c) Calculate the wavenumber of the most intense rotational transition at room temperature.

d) Calculate the difference (in cm^{-1}) between energy of the fifth rotational level of NaH considering rigid rotor and non-rigid rotor ($D = 0.0003 \text{ cm}^{-1}$) approximations.

$$\bar{\nu}_r = 2B(J+1) - 4D(J+1)^3$$

$$B = \frac{h}{8\pi^2 c \cdot \mu R^2}$$

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

$$E_{\text{rot}}(J) = hc \cdot [J(J+1) \cdot B - D_J J^2 (J+1)^2]$$

$$1 \text{ u} = 1.67 \cdot 10^{-27} \text{ kg} \quad k = 1.38 \cdot 10^{-23} \text{ J/K} \quad c = 3 \cdot 10^8 \text{ m/s}, h = 6.626 \cdot 10^{-34} \text{ J}\cdot\text{s}$$

Rotation of polyatomic molecules

The moment of inertia I of a system about an axis passing through the center of mass is given by:

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

The **polyatomic molecules can be classified** on the basis of their moments of inertia about three mutually perpendicular axes through the center of mass (principal axes).

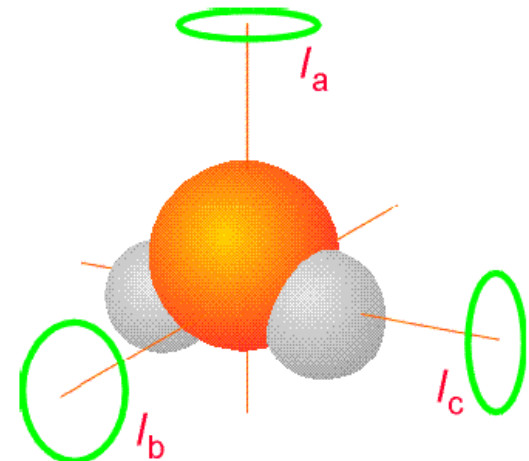
a, b, c : three axes

I_a, I_b, I_c : three moments of inertia

($I_c = I_{\max}$)

$$I_c > I_b > I_a$$

- An asymmetric rotor has three different moments of inertia; all three rotation axes coincide at the centre of mass of the molecule.

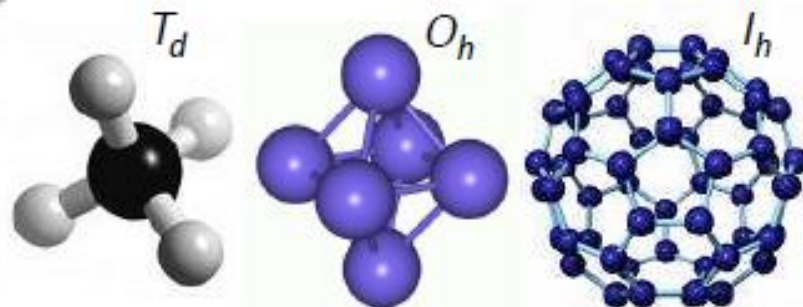


General Classification of Molecules

I. Spherical tops:

$$I_a = I_b = I_c$$

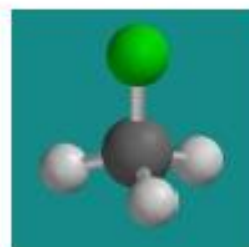
Zero dipole moment
∴ no rotational spectrum



II. Symmetric tops: (two identical I_i)

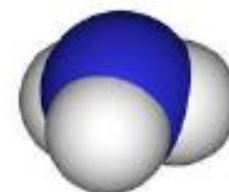
a) Prolate tops:

$$I_a < I_b = I_c$$



b) Oblate tops:

$$I_a = I_b < I_c$$



III. Asymmetric tops:

$$I_a < I_b < I_c$$



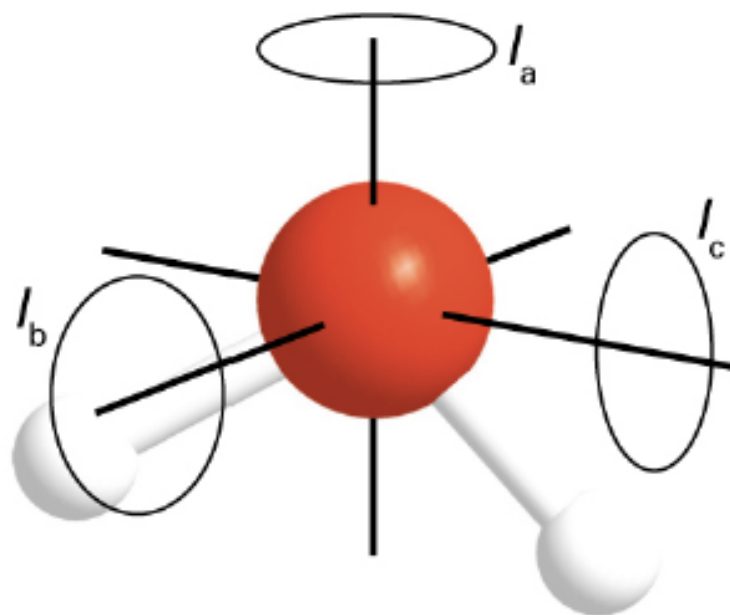
Rotational terms

For diatomics we defined a rotational constant $\tilde{B} \propto \frac{1}{I} = \frac{1}{\mu R^2}$

In general we require three such rotational constants:

as wavenumbers: $\tilde{A} = \frac{h}{8\pi^2 c I_a}$ $\tilde{B} = \frac{h}{8\pi^2 c I_b}$ $\tilde{C} = \frac{h}{8\pi^2 c I_c}$

$$\tilde{A} \geq \tilde{B} \geq \tilde{C}$$



H₂O molecule

$$\tilde{A} = 27.9 \text{ cm}^{-1}$$

$$\tilde{B} = 14.5 \text{ cm}^{-1}$$

$$\tilde{C} = 9.3 \text{ cm}^{-1}$$

But, we can no longer relate these constants explicitly to individual bond lengths within the molecule.

Prolate tops

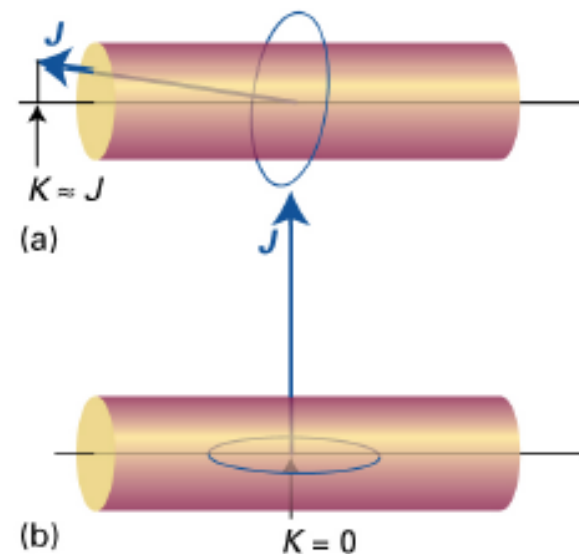
$$F_{J,K} = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$$

$$J = 0, 1, 2, 3, \dots$$

$$K = 0, \pm 1, \pm 2, \dots, \pm J$$

Levels labelled J_{K_a}

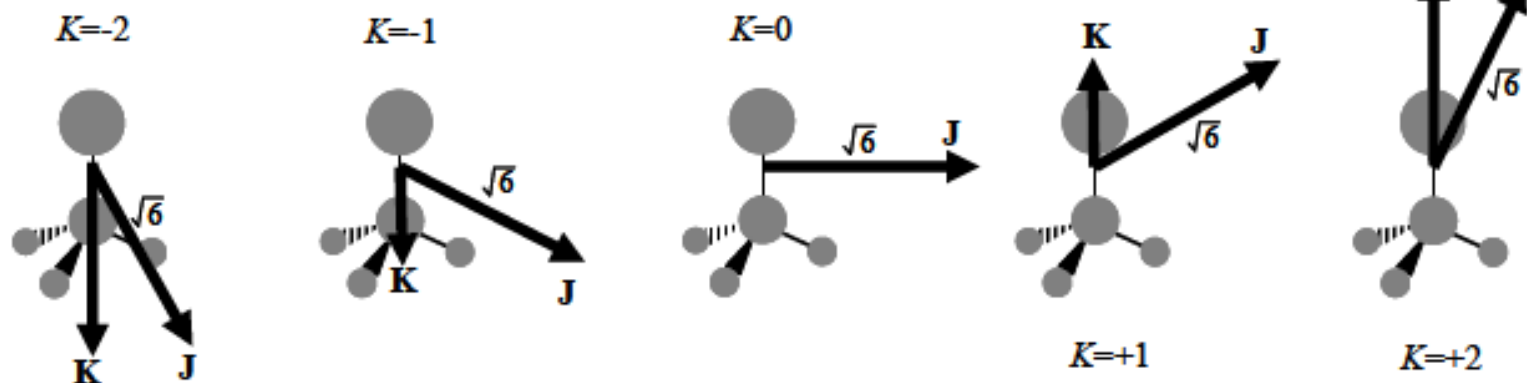
J is the *total angular momentum*
or *rotational quantum number* and
 K_a the *projection quantum number*
(for projection on the unique, a axis).



$$|\vec{J}| = \sqrt{J(J+1)} \hbar$$

$$J_a = K \hbar$$

$J = 2$



n.b., Each level has $2J+1$ degeneracy (arising from M_J)

In addition, each level $K > 0$ has extra two-fold degeneracy ($\pm K$)

Oblate tops

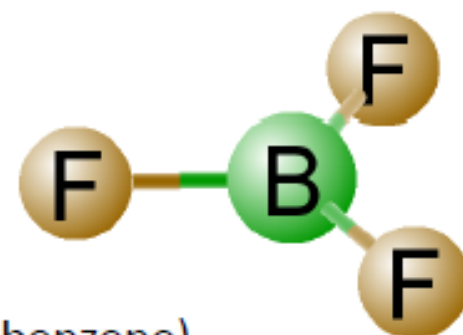
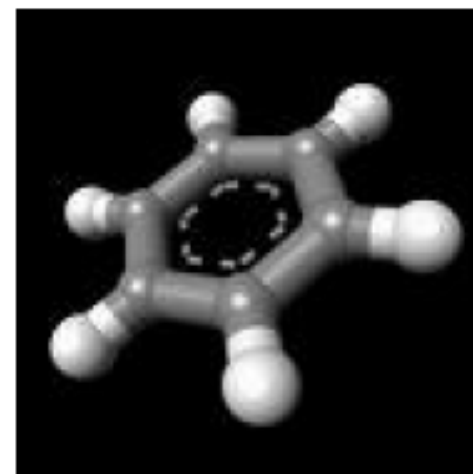
$$F_{J,K} = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2$$

$$J = 0, 1, 2, 3, \dots$$

$$K = 0, \pm 1, \pm 2, \dots \pm J$$

Levels labelled J_{Kc}

J is the *total angular momentum*
or *rotational quantum number* and
 K_c the *projection quantum number*
(for projection on the unique, c axis).

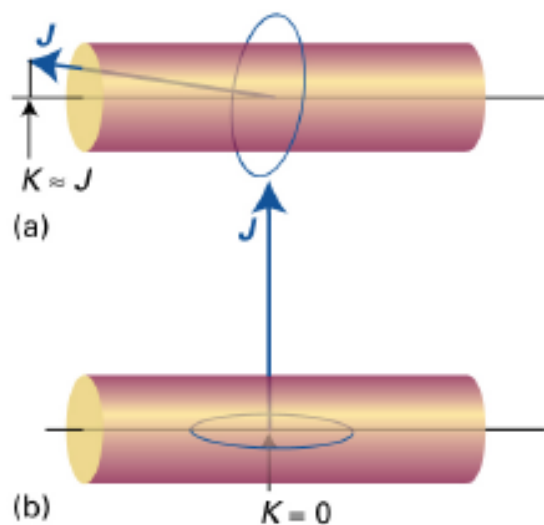


Oblate tops are typically flat
“discus” – like molecules (e.g., benzene)

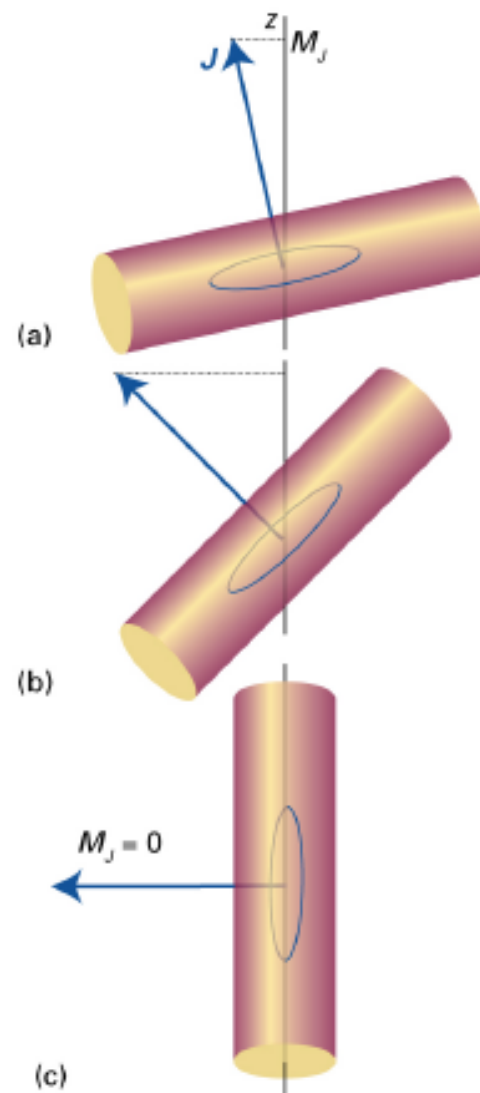
n.b., Each level has $2J+1$ degeneracy (arising from M_J)
In addition, each level $K > 0$ has extra two-fold degeneracy ($\pm K$)

Don't confuse various projections

$$|\vec{J}| = \sqrt{J(J+1)} \hbar$$



K refers to a projection on a body-fixed axis
(in this case, for a prolate top, the a axis)

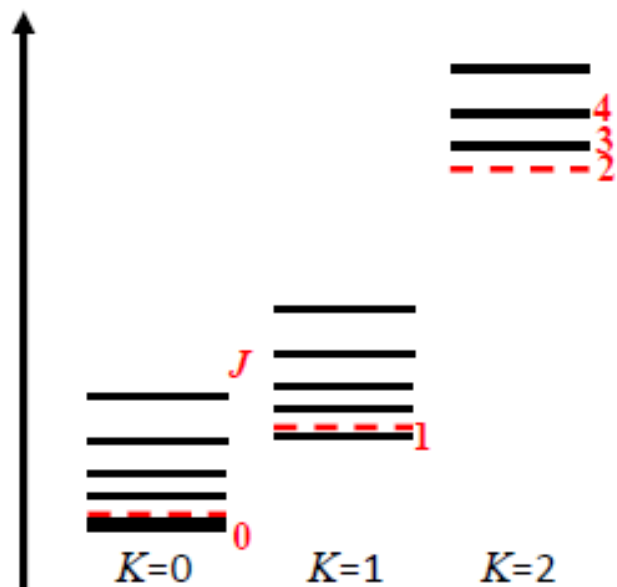


M_J refers to a projection on a space-fixed axis

Energy levels for Symmetric tops

Prolate top terms

$$F_{J,K} = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2 > 0$$

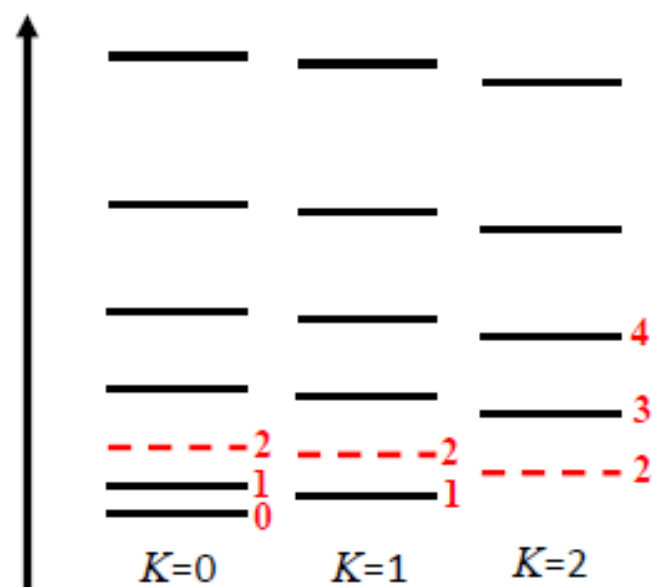


K - stacks

For a given *J*, energy **increases** with *K*

Oblate top terms

$$F_{J,K} = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2 < 0$$



K - stacks

For a given *J*, energy **decreases** with *K*

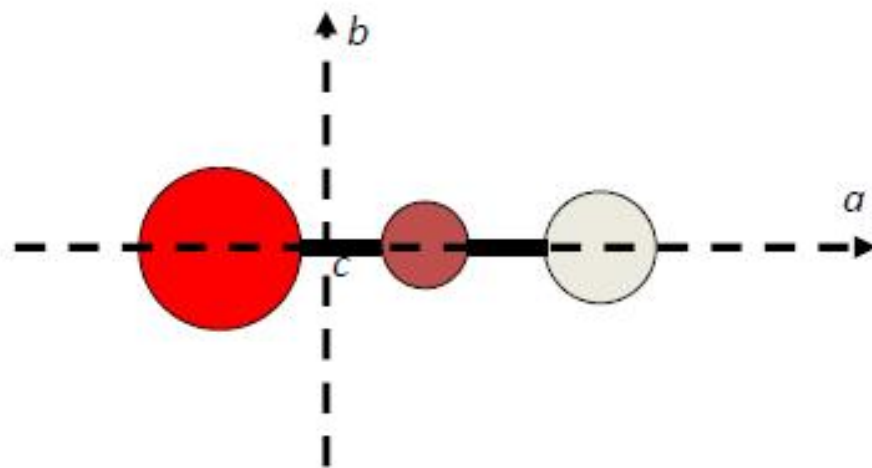
Linear Molecules ($C_{\infty v}$, $D_{\infty h}$)

Special, limiting case of prolate top:

$$I_a = 0, \text{ hence } \tilde{A} = \infty$$

Only $K = 0$ exists, so

$$F_J = \tilde{B}J(J+1) \quad J = 0, 1, 2, 3, \dots$$

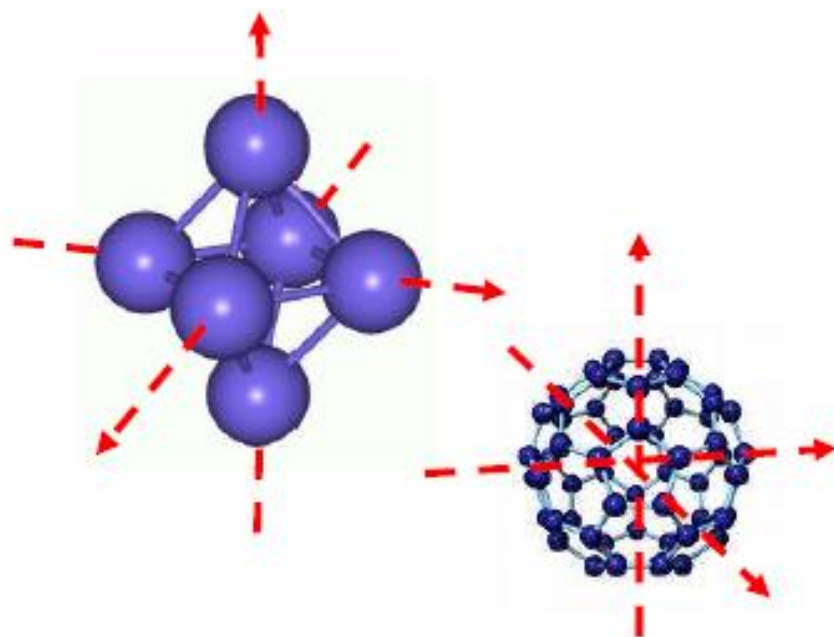


Spherical Tops (T_d , O_h , I_h)

$$\tilde{A} = \tilde{B} = \tilde{C}$$

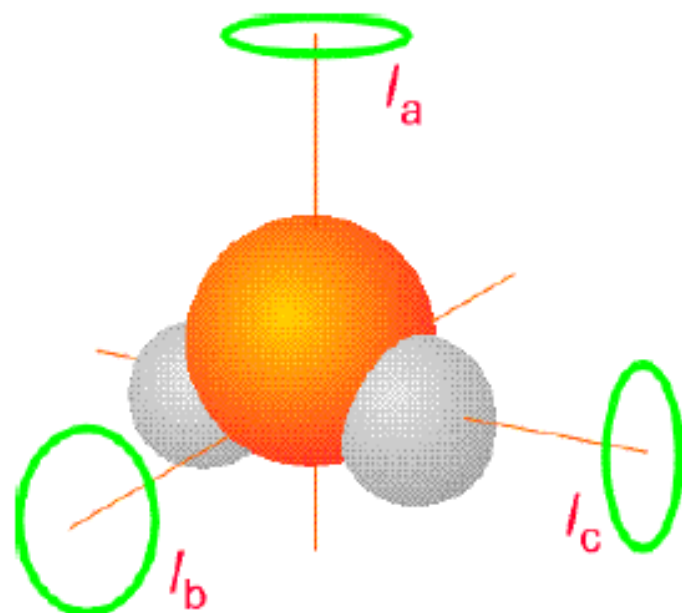
$$F_J = \tilde{B}J(J+1) \quad J = 0, 1, 2, 3, \dots$$

$$\text{Degeneracy} = (2J+1)^2$$

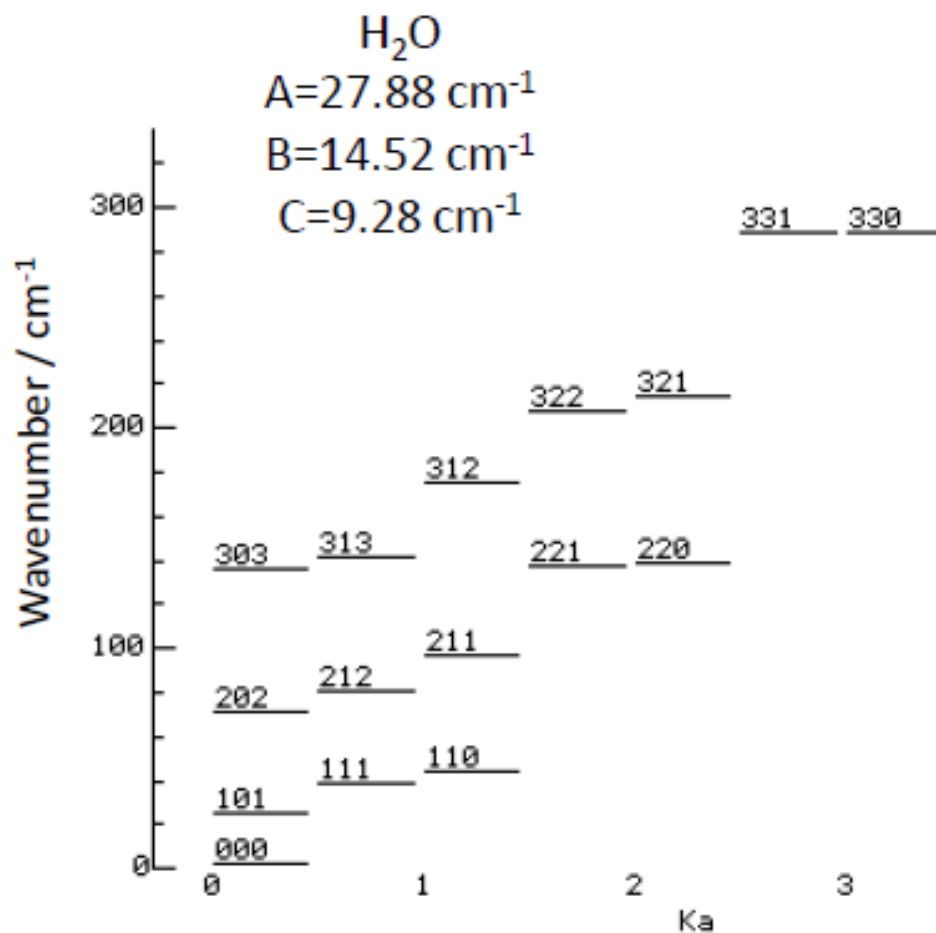


Asymmetric tops

Alas for the vast majority of molecules there is no simple general analytical form for the rotational levels. Some molecules are described as “near prolate” and “near oblate” tops. In general, terms can be derived by matrix diagonalisation.



$$J_{K_a, K_c}, \text{ e.g., } 2_{21}$$



Rotational Spectroscopy

- I. **Gross Selection rule:** To exhibit a pure rotational spectrum a molecule *must possess a permanent dipole moment*.

Homonuclear diatomic molecules such as O₂, H₂, etc. do not have a dipole moment and, hence, **no pure rotational spectrum!**

- II. **Specific Selection Rule:** During a transition the allowed changes in the J , K quantum numbers are:

$$\Delta J = \pm 1 \quad \Delta K = 0$$

(arises from quantum theory, but you can think of this as a combination of conservation of angular momentum and parity)

Spectra of Symmetric tops

prolate

oblate

Terms: $F_{J,K} = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$ $F_{J,K} = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2$

Allowed
transitions:

$$\tilde{\nu} = F_{J+1,K} - F_{J,K}$$

$$i.e., \quad \tilde{\nu} = 2\tilde{B}(J+1)$$

Within the rigid rotor approximation spectra of prolate & oblate tops are the same as for linear molecules (and indeed spherical tops):

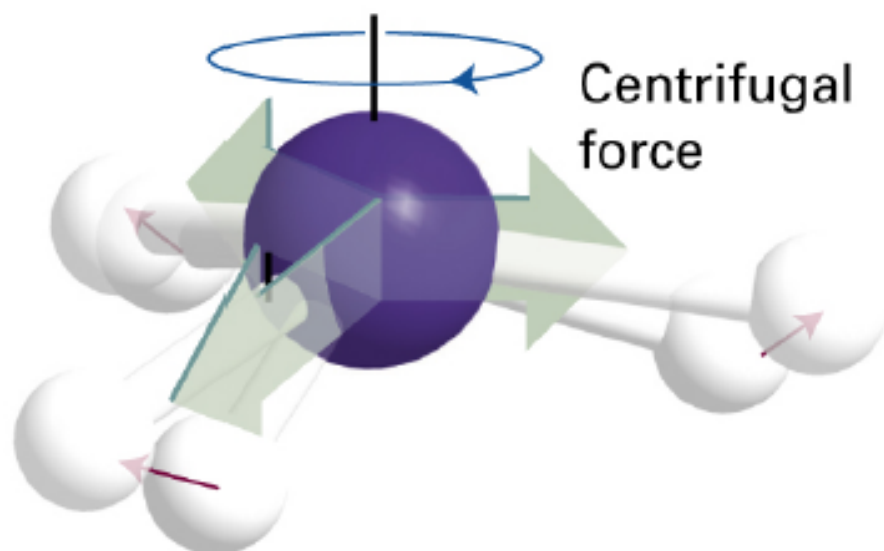
i.e., Equally spaced lines with separation = $2\tilde{B}$

We thus obtain no information on the unique axis (a for prolate, c for oblate) *i.e.*, nothing about the other rotational constants.

Beyond the Rigid Rotor: Centrifugal Distortion

The rigid rotor model holds for, well, rigid rotors.

Molecules, unfortunately, are *not* rigid rotors – their bonds stretch during rotation.



As a result, the various I (and thus rotational constants) *change* with J .

It is more convenient (*i.e.*, easier) to treat centrifugal distortion as a perturbation to the rigid rotor terms.

Centrifugal Distortion in symmetric tops

Prolate tops:

$$F(J, K) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2 - \tilde{D}_J J^2(J+1)^2 - \tilde{D}_{JK} J(J+1)K^2 - \tilde{D}_K K^4,$$

Oblate tops:

$$F(J, K) = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2 - \tilde{D}_J J^2(J+1)^2 - \tilde{D}_{JK} J(J+1)K^2 - \tilde{D}_K K^4,$$

Rigid rotor terms

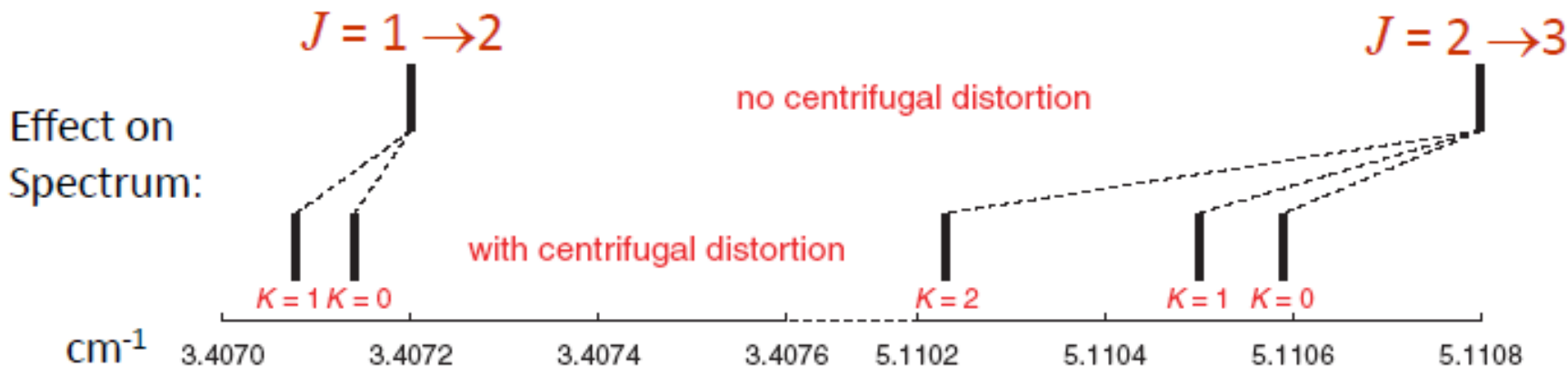
Centrifugal distortion terms

i.e., three distortion constants!

$$\Delta J = \pm 1 \quad \Delta K = 0$$

Transitions occur at:

$$\begin{aligned} \tilde{\nu} &= F(J+1, K) - F(J, K) \\ &= 2(\tilde{B} - \tilde{D}_{JK}K^2)(J+1) - 4\tilde{D}_J(J+1)^3 \end{aligned}$$



Roto-vibrational IR spectroscopy

In the IR absorption spectra recorded at **high resolution**, the vibrational bands have a **structure of lines** due to **rotational** transitions ($J_1 \rightarrow J_2$) that occur *simultaneously* with the **vibrational** transition ($v_1 \rightarrow v_2$).

At room temperature - only the **vibrational ground state** ($v = 0$) is **populated**.

- **the rotational levels with $J > 0$ are populated**: the rotational level with maximum population have a rotational quantum number different from zero ($J_{\max} \neq 0$)!

$$E_{\text{tot}} = E_{\text{vibr}} + E_{\text{rot}}$$

IR radiation : $300 - 4.000 \text{ cm}^{-1}$

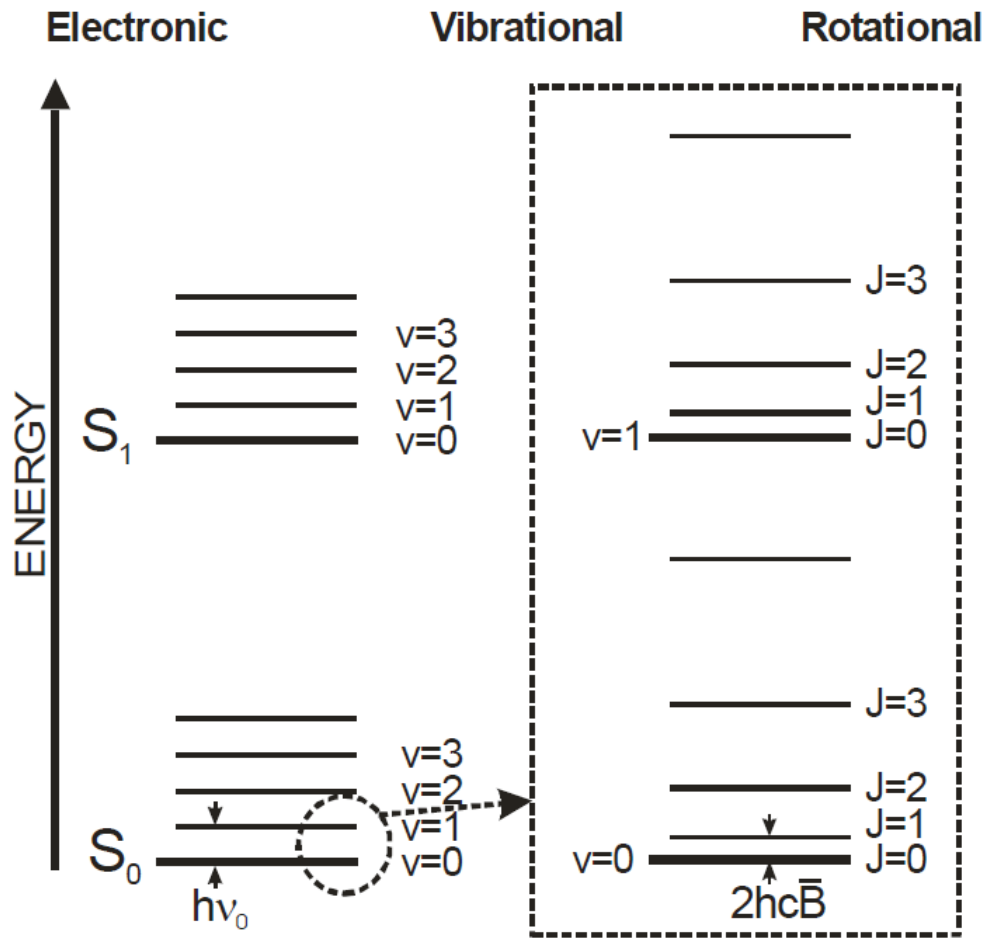
$$E_{\text{tot}} = h \cdot c \cdot \bar{\nu}_0 \left(v + \frac{1}{2} \right) + h \cdot c \cdot B \cdot J(J+1) + \dots$$

$$\sim 1.000 \text{ cm}^{-1} \quad \sim 1 - 10 \text{ cm}^{-1}$$

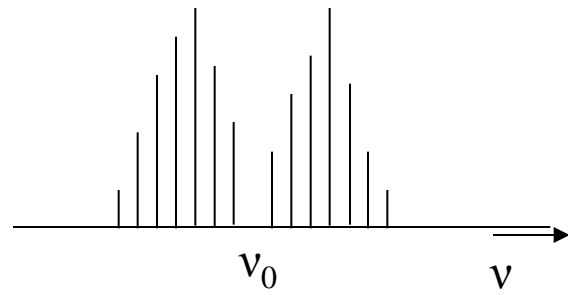
$$v = 0, 1, 2, \dots \quad J = 0, 1, 2, \dots$$

If the molecule (in **vibrational ground state**) *absorbed infrared radiation*, it will pass on an **excited vibrational** level ($\Delta v = +1$).

In the same time, the molecule can pass on **another rotational level** of excited vibration level (characterized by a *different rotational quantum number* than the initial) ($\Delta J = \pm 1$)



The spectrum consists of **lines** that appear at the **frequency** corresponding to **transitions**, having the *intensity proportional to the number of molecules that have made that transition.*



Pure vibrational spectrum: one line at ν_0 .

Pure rotational spectrum: several lines separated by $2B$.

Roto-vibrational spectrum : several lines separated by $2B$, grouped into two branches (P and R), apart in ν_0 zone

(exception: for polyatomic molecule Q branch (ν_0) could appear!)

Roto-vibrational spectra of diatomic molecules

Consider the molecule as an **harmonic oscillator and a rigid rotor**.

The **selection rules** for **roto-vibrational transition** are:

$$\Delta v = \pm 1 \quad \Delta J = \pm 1$$

The **energy absorbed by molecule** is equal with the sum of vibrational and rotational energy changes.

$$E_{abs} = \Delta E_{vib} + \Delta E_{rot}$$

$$E(v, J) = h \cdot c \cdot \left[\bar{\nu}_0 \left(v + \frac{1}{2} \right) + B \cdot J(J+1) \right]$$

$$h \cdot c \cdot \bar{\nu} = E_2 - E_1 = E(v_2, J_2) - E(v_1, J_1) \rightarrow \text{absorbed energy}$$

$$\bar{\nu} = \frac{E_2 - E_1}{h \cdot c} = \left[\bar{\nu}_0 \left(v_2 + \frac{1}{2} \right) + B \cdot J_2(J_2 + 1) \right] - \left[\bar{\nu}_0 \left(v_1 + \frac{1}{2} \right) + B \cdot J_1(J_1 + 1) \right]$$

At **room temperature**: $v_1 = 0$ and $\Delta v = +1$ so $v_2 = 1$

$$\bar{\nu} = \bar{\nu}_0 + B \cdot [J_2(J_2 + 1) - J_1(J_1 + 1)] \quad \leftarrow \text{wavenumber of roto-vibrational transition}$$

The rotational levels with $J \neq 0$ are populated, thus transitions with $\Delta J = 1$ and $\Delta J = -1$ may occur.

$$\Delta J = +1 \rightarrow J_2 = J_1 + 1$$

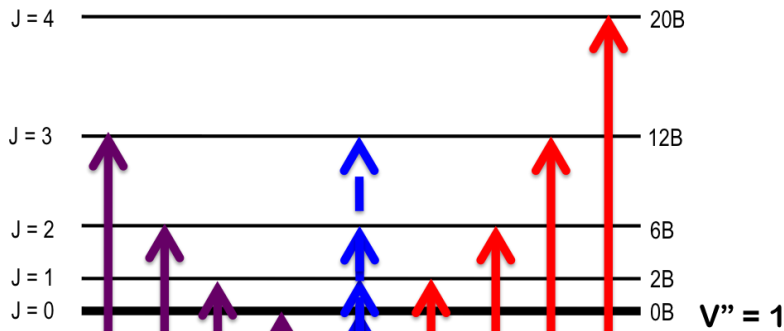
$$\bar{\nu}_R = \bar{\nu}_0 + 2 \cdot B \cdot (J_1 + 1)$$

R branch ($J_1 = 0, 1, 2, \dots$)

$$\Delta J = -1 \rightarrow J_2 = J_1 - 1$$

$$\bar{\nu}_P = \bar{\nu}_0 - 2 \cdot B \cdot J_1$$

P branch ($J_1 = 1, 2, 3, \dots$)

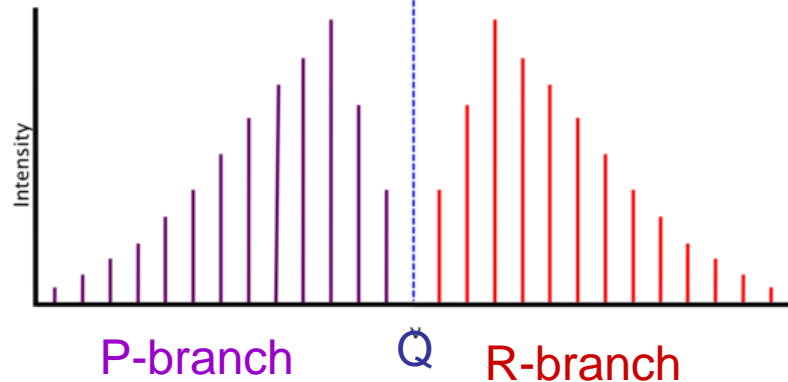
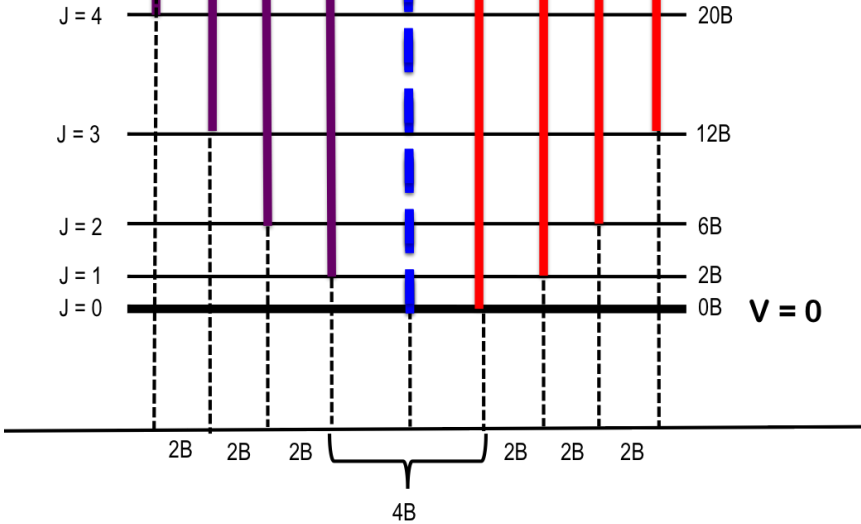


Selection rules: $\Delta J = 0, \pm 1$
 $\Delta v = 1$

If $\Delta J = +1$ we obtained **R branch** (“rich”, the molecule gain rotational energy)

If $\Delta J = -1$ we obtained **P branch** (“poor”, the molecule lose rotational energy)

If $\Delta J = 0$ we obtained **Q branch** (for perpendicular vibrations in polyatomic molecules: ex. *NCN bend*)



The lines of the P-branch (purple arrows) and R-branch (red arrows) are separated by $2B$, thus the bond length can be deduced!

$$\bar{\nu}_{P,J} = \bar{\nu}_0 - 2 \cdot B \cdot J$$

$$J = 1, 2, 3, \dots$$

$$\bar{\nu}_{R,J} = \bar{\nu}_0 + 2 \cdot B \cdot (J + 1)$$

$$J = 0, 1, 2,$$

$$\bar{\nu}_{P,1} = \bar{\nu}_0 - 2 \cdot B$$

$$\bar{\nu}_{P,2} = \bar{\nu}_0 - 4 \cdot B$$

$$\bar{\nu}_{P,3} = \bar{\nu}_0 - 6 \cdot B$$

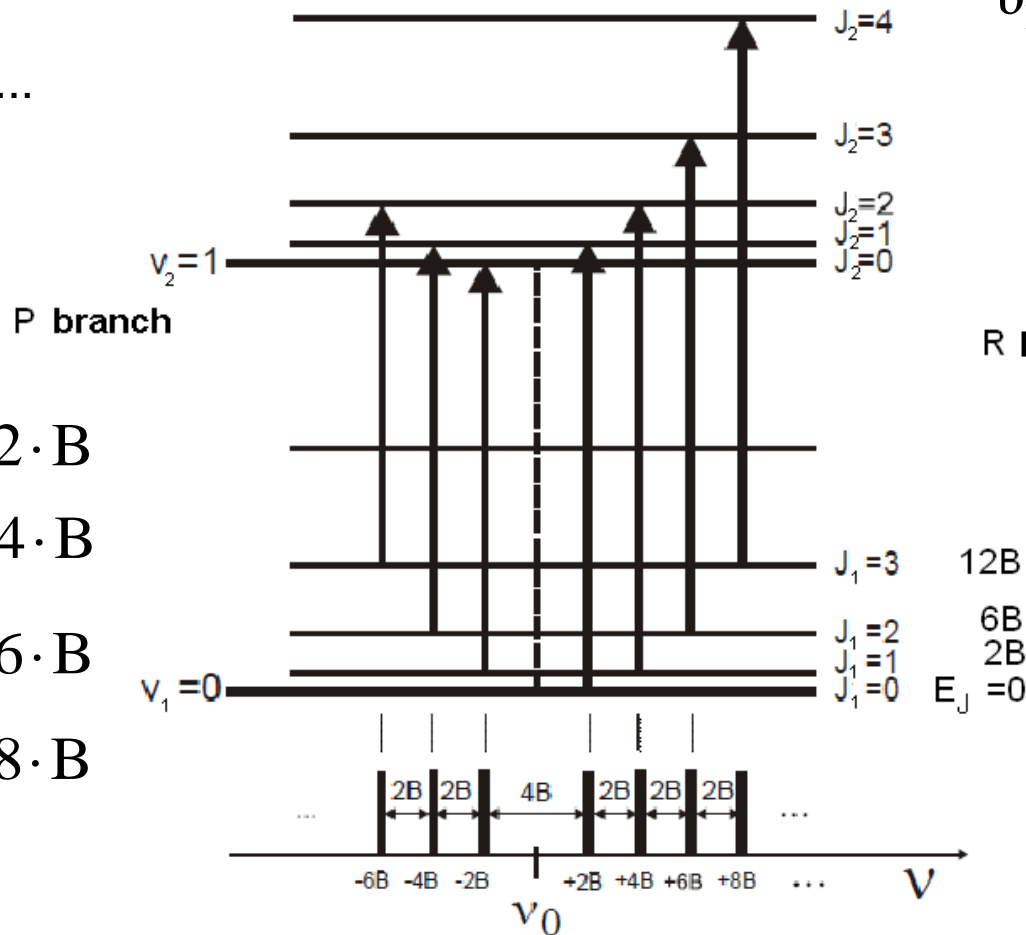
$$\bar{\nu}_{P,4} = \bar{\nu}_0 - 8 \cdot B$$

$$\bar{\nu}_{R,0} = \bar{\nu}_0 + 2 \cdot B$$

$$\bar{\nu}_{R,1} = \bar{\nu}_0 + 4 \cdot B$$

$$\bar{\nu}_{R,2} = \bar{\nu}_0 + 6 \cdot B$$

$$\bar{\nu}_{R,3} = \bar{\nu}_0 + 8 \cdot B$$



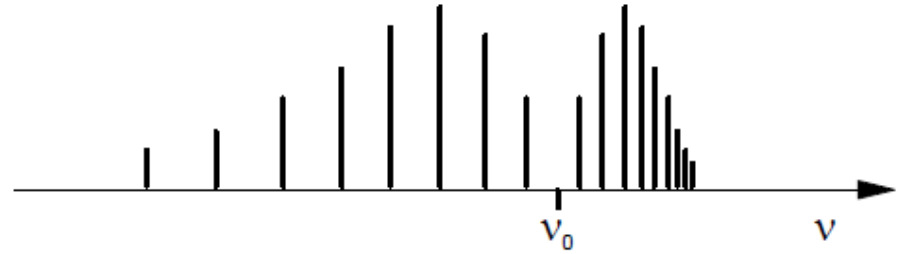
Q branch ($\Delta J = 0$) could appear in IR spectrum of polyatomic molecule!

Q transition ($\Delta J = 0$) is allowed only for vibrations that involved a **perpendicular dipole moment change** (to the symmetry axis of the molecule).

$$\text{Q branch } (\Delta J = 0): \quad \bar{\nu}_Q = \bar{\nu}_0$$

For real molecule: vibration and rotation are not independent!

Two effects appear:



1) roto-vibrational coupling

Diatomic molecule: molecule vibrates \rightarrow the bonds length (r) are changing \rightarrow the moment of inertia changes \rightarrow the rotational constant B changes

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right)$$

$\alpha_e \rightarrow$ roto-vibrational coupling constant

$B_e \rightarrow$ rotational constant for rigid and independent rotor

Each vibrational level have different rotational constant, so $B_0 \neq B_1!$

In this case the energy of roto-vibrational level is:

$$E(v, J) = h \cdot c \cdot \left[\bar{\nu}_0 \left(v + \frac{1}{2} \right) + B_v \cdot J(J+1) \right]$$

$$E(v, J) = h \cdot c \cdot \left[\bar{\nu}_0 \left(v + \frac{1}{2} \right) + B_e \cdot J(J+1) - \alpha_e \left(v + \frac{1}{2} \right) J(J+1) \right]$$

2) centrifugal distortion

When the rotation velocity increase (J increase) → the bond length increase → the moment of inertia increase → the rotational constant B decrease

$$B_J = B_e - D \cdot J(J+1) \quad D \rightarrow \text{centrifugal distortion constant}$$

In this case the energy of roto-vibrational level is:

$$E(v, J) = h \cdot c \cdot \left[\bar{\nu}_0 \left(v + \frac{1}{2} \right) + B_J \cdot J(J+1) \right]$$
$$E(v, J) = h \cdot c \cdot \left[\bar{\nu}_0 \left(v + \frac{1}{2} \right) + B_e \cdot J(J+1) - DJ^2(J+1)^2 \right]$$

Considering **both effects**, the energy of a particular roto-vibrational level is:

$$E_{v,J} = h \cdot c \left[\bar{\nu}_0 \left(v + \frac{1}{2} \right) + B_e J \cdot (J+1) - \alpha_e \left(v + \frac{1}{2} \right) J \cdot (J+1) - D [J(J+1)]^2 \right]$$

$$E_{v,J} = h \cdot c \left[\bar{\nu}_0 \left(v + \frac{1}{2} \right) + B_e J \cdot (J+1) - \alpha_e \left(v + \frac{1}{2} \right) J \cdot (J+1) - D [J(J+1)]^2 \right]$$

We can consider: $E_{v,J} = hc [\bar{\nu}_0 (v + 1/2) + B_{v,J} J(J+1)]$

where: $B_{v,J} = B_e - \alpha_e (v + \frac{1}{2}) - DJ(J+1)$

P branch: $(\Delta v = 1, \Delta J = -1)$ $(v = 0 \text{ and } J = 1, 2, 3 \dots)$

$$\bar{\nu}_{P,J} = \frac{1}{hc} (E_{(1,J-1)} - E_{(0,J)}) = \bar{\nu}_0 + (B_1 - B_0)J^2 - (B_1 + B_0)J$$

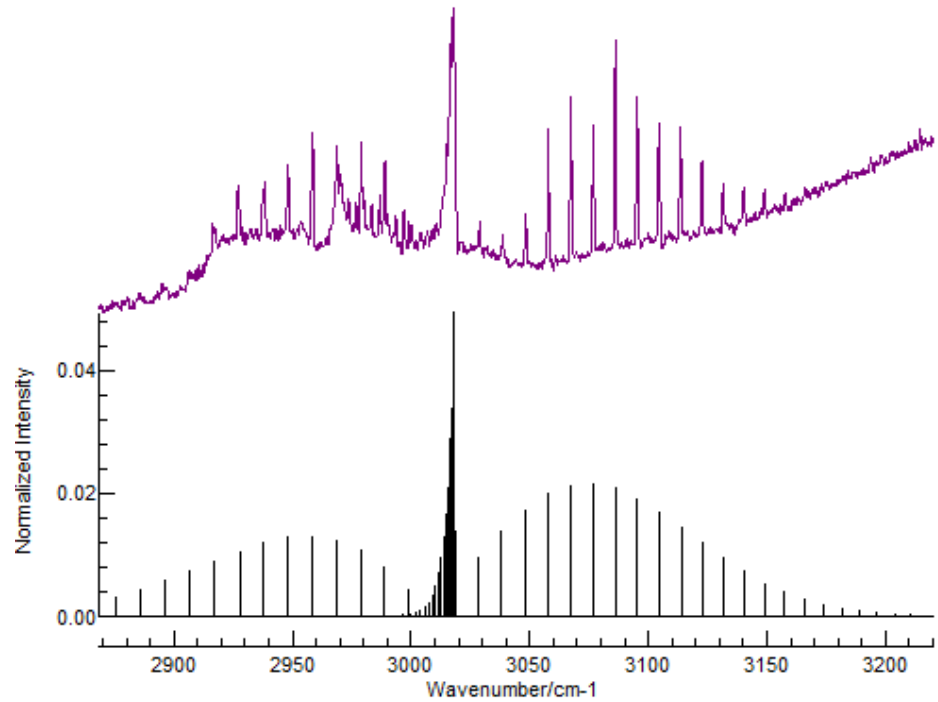
Q branch : $(\Delta v = 1, \Delta J = 0)$ $(v = 0 \text{ și } J = 1, 2, 3 \dots)$ (if observable)

$$\bar{\nu}_{Q,J} = \frac{1}{hc} (E_{(v+1,J)} - E_{(v,J)}) = \bar{\nu}_0 + (B_1 - B_0)J(J+1)$$

R branch: $(\Delta v = 1, \Delta J = +1)$ $(v = 0 \text{ și } J = 0, 1, 2, 3 \dots)$

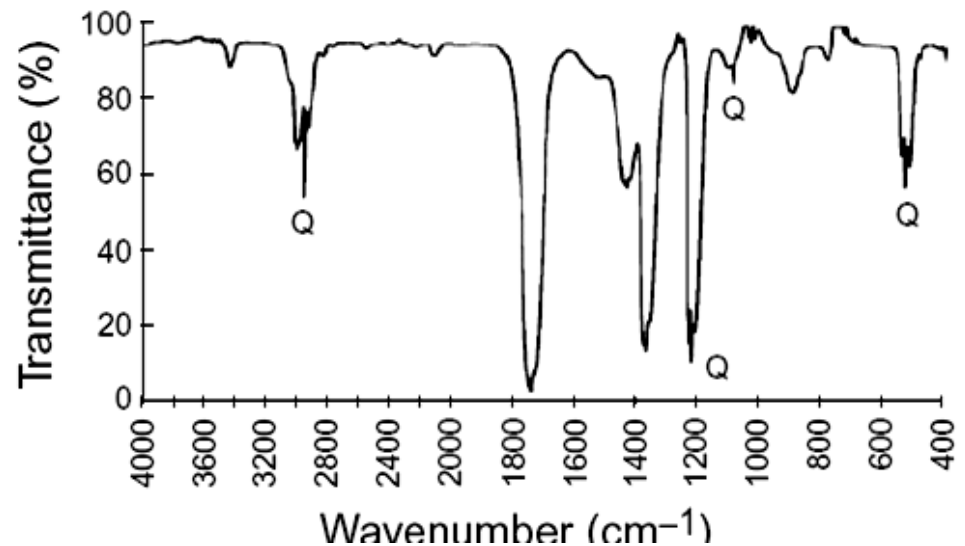
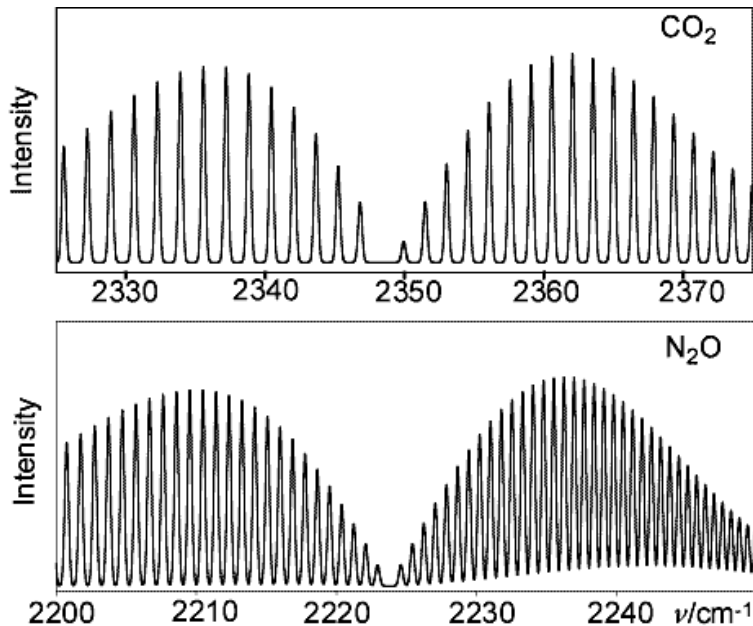
$$\bar{\nu}_{R,J} = \frac{1}{hc} (E_{(1,J+1)} - E_{(0,J)}) = \bar{\nu}_0 + (B_1 - B_0)(J+1)^2 + (B_1 + B_0)(J+1)$$

Part of the rotational-vibrational spectrum of methane (CH_4) gas (from FTIR), showing the presence of P-, Q- and R- branches (purple, top)



A simulation of the rotational-vibrational spectrum of methane (CH_4). Frequency is on the x-axis, and transmittance on the y-axis (black, down).

Interference from the absorption band of water can be seen $> 3150\text{cm}^{-1}$.

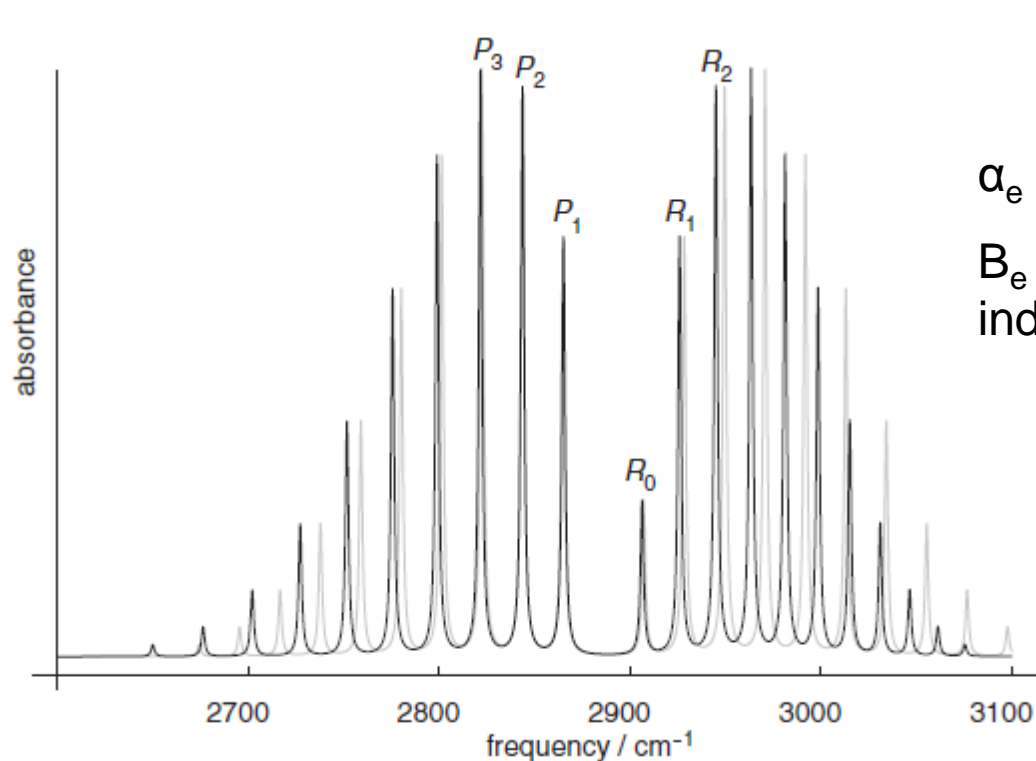


Roto-vibrational coupling effect is higher than centrifugal distortion!

Because of anharmonicity, the bond length is higher in $v = 1$ state than in $v = 0$ state ($r_1 > r_0$), so $\mathbf{B}_1 < \mathbf{B}_0$ (with 1-2%).

In **R branch** the distances between lines **decrease** (when J increase).

In **P branch** the distances between lines **increase** (when J increase).



$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right)$$

α_e → roto-vibrational coupling constant

B_e → rotational constant for rigid and independent rotor

$$B_0 = B_e - \frac{1}{2} \alpha_e$$

$$B_1 = B_e - \frac{3}{2} \alpha_e$$

$$\alpha_e = B_0 - B_1$$

gray - calculated spectrum (supposed $B_0 = B_1$)

black - experimental spectrum (real molecule!)

$$E_{v,J} = hc[\bar{\nu}_0(v + 1/2) + B_e J(J + 1)]$$

$$\text{Rigid rotor: } B_0 = B_1 = B_e$$

P branch: $\Delta J = -1$

$$E_{(v=1,J=0)} - E_{(v=0,J=1)} = hc[\bar{\nu}_0 + B_e(0) - B_e(2)] = hc[\bar{\nu}_0 - 2B_e] = hc\bar{\nu}_{P1}$$

$$E_{(v=1,J=1)} - E_{(v=0,J=2)} = hc[\bar{\nu}_0 + B_e(2) - B_e(6)] = hc[\bar{\nu}_0 - 4B_e] = hc\bar{\nu}_{P2}$$

$$E_{(v=1,J=2)} - E_{(v=0,J=3)} = hc[\bar{\nu}_0 + B_e(6) - B_e(12)] = hc[\bar{\nu}_0 - 6B_e] = hc\bar{\nu}_{P3}$$

R branch: $\Delta J = +1$

$$E_{(v=1,J=1)} - E_{(v=0,J=0)} = hc[\bar{\nu}_0 + B_e(2) - B_e(0)] = hc[\bar{\nu}_0 + 2B_e] = hc\bar{\nu}_{R0}$$

$$E_{(v=1,J=2)} - E_{(v=0,J=1)} = hc[\bar{\nu}_0 + B_e(6) - B_e(2)] = hc[\bar{\nu}_0 + 4B_e] = hc\bar{\nu}_{R1}$$

$$E_{(v=1,J=3)} - E_{(v=0,J=2)} = hc[\bar{\nu}_0 + B_e(12) - B_e(6)] = hc[\bar{\nu}_0 + 6B_e] = hc\bar{\nu}_{R2}$$

$$E_{v,J} = hc[\bar{\nu}_0(v + 1/2) + B_v J(J + 1)]$$

$$\text{Non-rigid rotor: } B_0 \neq B_1 \quad (B_0 > B_1)$$

P branch: $\Delta J = -1$

$$E_{(v=1,J=0)} - E_{(v=0,J=1)} = hc[\bar{\nu}_0 + B_1(0) - B_0(2)] = hc[\bar{\nu}_0 - 2B_0] = hc\bar{\nu}_{P1}$$

$$E_{(v=1,J=1)} - E_{(v=0,J=2)} = hc[\bar{\nu}_0 + B_1(2) - B_0(6)] = hc[\bar{\nu}_0 + 2B_1 - 6B_0] = hc\bar{\nu}_{P2}$$

$$E_{(v=1,J=2)} - E_{(v=0,J=3)} = hc[\bar{\nu}_0 + B_1(6) - B_0(12)] = hc[\bar{\nu}_0 + 6B_1 - 12B_0] = hc\bar{\nu}_{P3}$$

R branch: $\Delta J = +1$

$$E_{(v=1,J=1)} - E_{(v=0,J=0)} = hc[\bar{\nu}_0 + B_1(2) - B_0(0)] = hc[\bar{\nu}_0 + 2B_1] = hc\bar{\nu}_{R0}$$

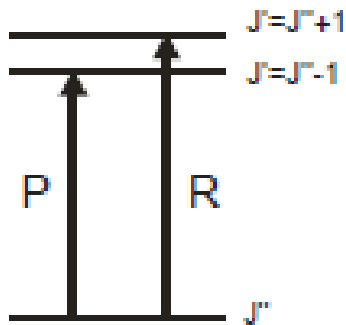
$$E_{(v=1,J=2)} - E_{(v=0,J=1)} = hc[\bar{\nu}_0 + B_1(6) - B_0(2)] = hc[\bar{\nu}_0 + 6B_1 - 2B_0] = hc\bar{\nu}_{R1}$$

$$E_{(v=1,J=3)} - E_{(v=0,J=2)} = hc[\bar{\nu}_0 + B_1(12) - B_0(6)] = hc[\bar{\nu}_0 + 12B_1 - 6B_0] = hc\bar{\nu}_{R2}$$

The lab analysis of roto-vibrational spectra

Difference combination method is based on the determination of difference between wavenumbers of two transitions with a common energy level (initial or final)

Same (J'') initial level



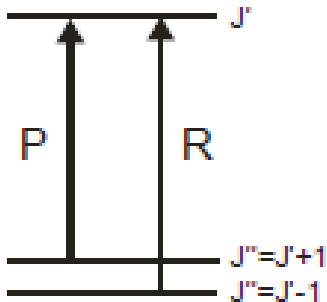
$$\bar{\nu}_{RJ} - \bar{\nu}_{PJ} = B_1(4J + 2)$$

$$B_1 = B_e - \frac{3}{2}\alpha_e$$

$$B_1 = \frac{\bar{\nu}_{RJ} - \bar{\nu}_{PJ}}{(4J + 2)}$$

B_1 rotation constant of superior vibrational level (B')

Same (J') final level



$$\bar{\nu}_{R(J-1)} - \bar{\nu}_{P(J+1)} = B_0(4J + 2)$$

$$B_0 = B_e - \frac{1}{2}\alpha_e$$

$$B_0 = \frac{\bar{\nu}_{R(J-1)} - \bar{\nu}_{P(J+1)}}{(4J + 2)}$$

B_0 rotation constant of inferior vibrational level (B'')

$$\alpha_e = B_0 - B_1$$

$$B_e = \frac{3B_0 - B_1}{2}$$

Only the gaseous molecules have rotational fine structure!

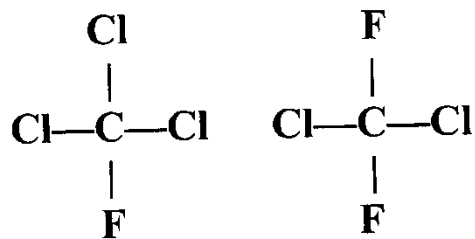
In liquid state the molecular rotations are partially blocked by molecular interactions → the rotational fine structure disappears or appears like an envelope of P, Q, R structure.

If the solvents are increasing polarity, we will obtain different spectra

-unpolar solvents (FC 75 ($C_8F_{16}O$) and Freon 113)
→ envelope of rotational bands

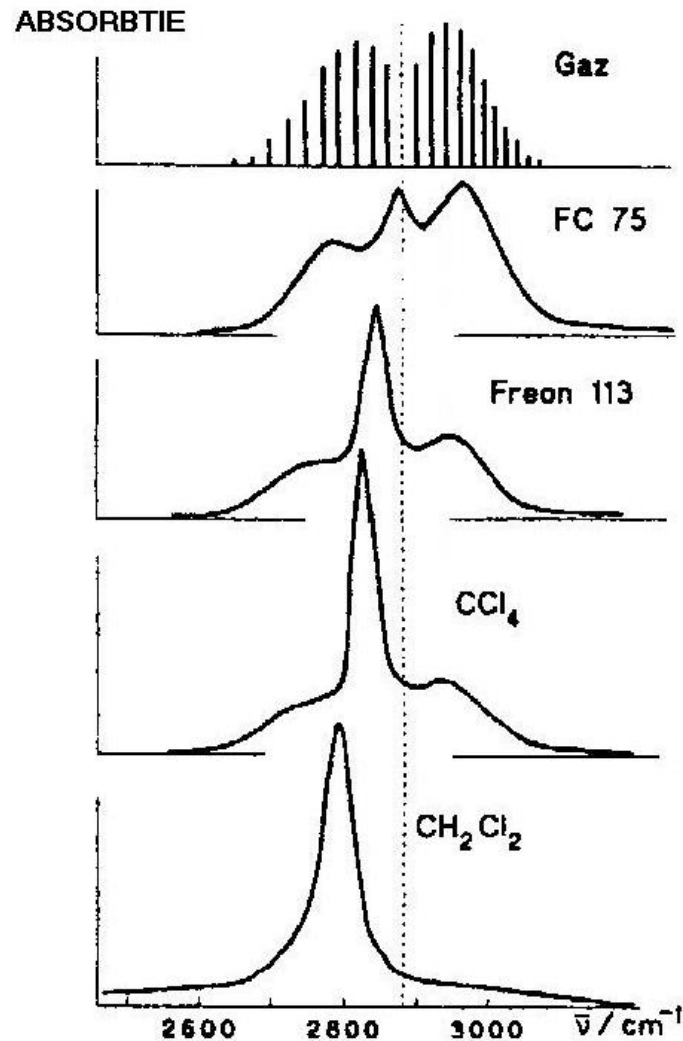
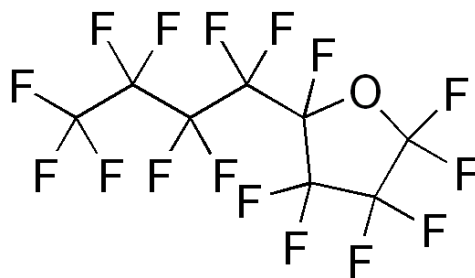
-polar solvents (dichloromethane: CH_2Cl_2)
→ the rotational bands disappear completely.

The H-Cl bond force constant decrease from unpolar solvents to polar solvents. Therefore, the maximum of principal band shift to lower frequencies.



Freon-11

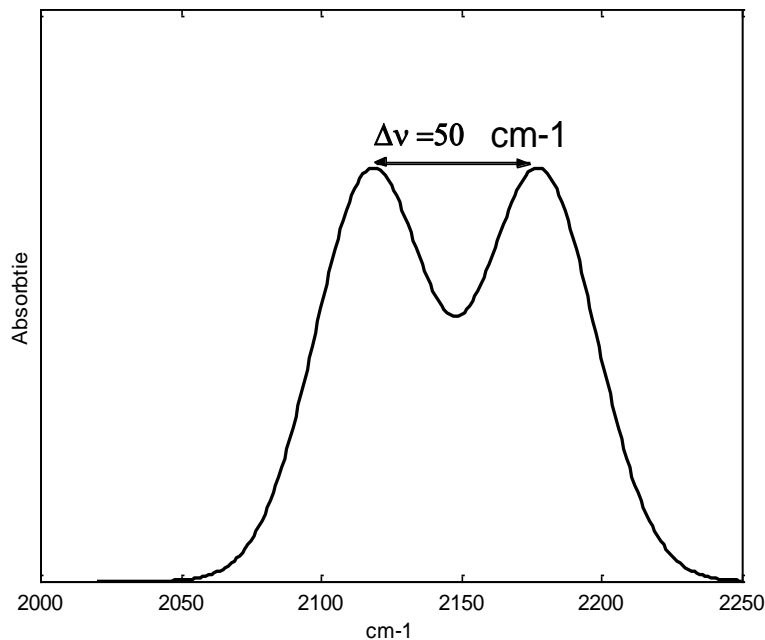
Freon-12



Rotational fine structure (HCl - gas)

Pure vibrational band (HCl in CH_2Cl_2 - liquid)

Lower resolution roto-vibrational spectrum → the rotational structure do not appear!



Still rotational constant B could be calculated with formula:

$$\Delta\bar{\nu} = \sqrt{\frac{8kTB}{hc}}$$

$\Delta\bar{\nu}$ = the distance between the 2 maxima (the envelopes of R and P branch).

Ex: For $T = 300 \text{ K}$ and $\Delta\nu = 50 \text{ cm}^{-1}$ rotational constant is $B = 1,51 \text{ cm}^{-1}$

Independent activity:

Calculate the distance (in wavenumbers) between the transitions ($\Delta J = \pm 1$) that start from the most populated rotational level of lower vibrational level (the two maxima from the figure). Consider the molecule as an harmonic oscillator and a rigid rotor:

$$E(\nu, J) = h \cdot c \cdot \left[\bar{\nu}_0 \left(\nu + \frac{1}{2} \right) + B \cdot J(J+1) \right]$$

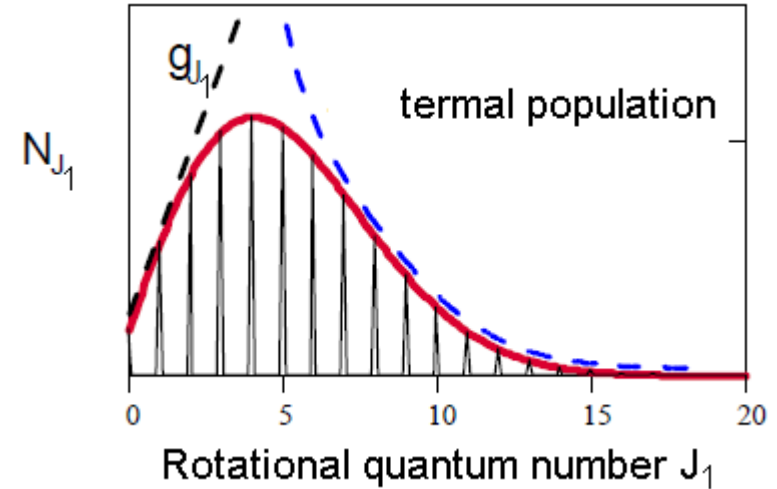
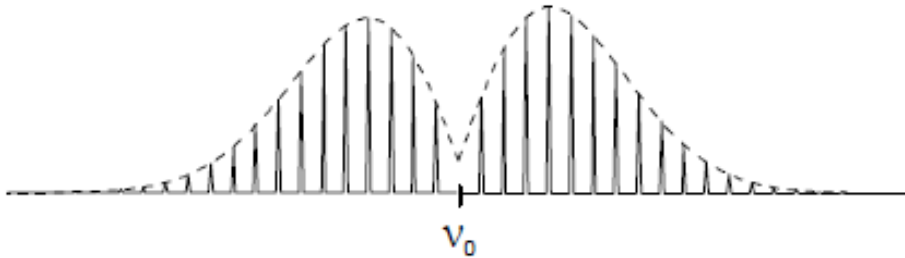
$$J_{\max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

Usually superior level (v_2, J_2) is not populated, so *the roto-vibrational transitions intensity depends on the lower level population (v_1, J_1)* .

$$\Delta N = N(v_1, J_1) - N(v_2, J_2) \approx N(v_1, J_1)$$

$$N(v_1, J_1) = N_0 g(J_1) \exp\left(-\frac{E_{v_1} + E_{J_1}}{k \cdot T}\right)$$

$$N(v_1, J_1) = N_0 (2J_1 + 1) \exp\left[-\frac{hc}{kT} \left(\bar{\nu}_0 \left(v_1 + \frac{1}{2}\right) + B \cdot J_1 (J_1 + 1)\right)\right]$$



Relative amplitude of roto-vibrational lines is related mainly to the population of rotational levels.

At room temperature:

- vibrational states 0 and 1:

$$N_1/N_0 = (1/1) \exp[-10^{-18}J / (1.38 \cdot 10^{-23}J/K \cdot 300K)] = 0 \quad (\text{all the population is in the lower state})$$

- rotational states 0 and 1:

$$N_1/N_0 = (3/1) \exp[-10^{-21}J / (1.38 \cdot 10^{-23}J/K \cdot 300K)] = 2.4 \quad (\text{two and a half larger population at state } J = 1 \text{ than at state } J = 0)$$

Determination of temperature through spectroscopy:

There are two types of temperature: one that can be measured through thermal equilibrium of the medium with a thermometer or a thermocouple, and one that is determined through spectroscopy.

To a first approximation, the height of the peaks in the roto-vibrational spectrum depends on the population of the state where the absorption/emission line is originated.

For rotational lines, the population is proportional to:

$$N_J = N_0 g(J) \exp\left(\frac{-E_J}{k \cdot T}\right) = N_0 (2J + 1) \exp\left(\frac{-h \cdot c \cdot B_e J(J + 1)}{k \cdot T}\right)$$

$$N_J = N_0 (2J + 1) \exp\left(\frac{-h \cdot c \cdot B_e (J^2 + J)}{k \cdot T}\right)$$

$(2J + 1)$ comes from the *degeneracy of rotational states* and $E_J = B_e J(J+1)$

The rotational quantum number (J_{\max}) corresponding to maximum intensity line can be calculated by taking the first derivative of the expression with respect to J and setting it to 0.

$$N_J = N_0(2J + 1) \exp\left(\frac{-h \cdot c \cdot B_e}{k \cdot T} (J^2 + J)\right)$$

$$\frac{dN_J}{dJ} = 2N_0 \exp\left(\frac{-h \cdot c \cdot B_e}{k \cdot T} (J^2 + J)\right) + N_0(2J + 1) \left(\frac{-h \cdot c \cdot B_e}{k \cdot T} (2J + 1)\right) \exp\left(\frac{-h \cdot c \cdot B_e}{k \cdot T} (J^2 + J)\right)$$

$$\frac{dN_J}{dJ} = 0 \Rightarrow 2 + (2J + 1) \left(\frac{-h \cdot c \cdot B_e}{k \cdot T} (2J + 1)\right) = 0$$

$$2kT - hcB_e \cdot (4J^2 + 2J + 1) = 0$$

$$4hcB_e J^2 + 2hcB_e J + (hcB_e - 2kT) = 0$$

$$J = -\frac{1}{2} \pm \sqrt{\frac{kT}{2hcB_e}}$$

Since $J \geq 0$:

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

$$J_{\max} = -\frac{1}{2} + \sqrt{\frac{k_B T}{2B_e}}$$

We can calculate which line will be the largest for a given temperature, or if we know which is the strongest line, we can calculate the temperature.

For the example of HCl absorption, the largest lines were the 4th of the R branch, and the 3rd of the P branch.

R branch, $\Delta J = +1$

0→1	
1→2	
2→3	
3→4	originated in 3rd state

P branch, $\Delta J = -1$

1→0	
2→1	
3→2	originated in 3rd state

Then:

$$3 + \frac{1}{2} = \sqrt{\frac{k_B T}{2B_e}} = \sqrt{\frac{1.38 \times 10^{-23} T}{2 \times 2 \times 10^{-22}}} \quad T = 355K$$

Problems:

1. a) From the following wavenumbers of the P and R branches of the $0 \rightarrow 1$ infrared vibrational band of $^1\text{H}^{127}\text{I}$, obtain the values for the rotational constants B_0 , B_1 and B_e (in cm^{-1}), the band center ν_0 (in cm^{-1}) and the vibration-rotation interaction constant α_e (in cm^{-1}).

Transition Frequency (cm^{-1})		Transition Frequency (cm^{-1})	
R(0)	2242	P(1)	2217
R(1)	2254	P(2)	2204
R(2)	2265.5	P(3)	2190.5
R(3)	2276.5	P(4)	2176.5

b) What value results for the internuclear distance r_0 (in Å)?

How does the value for r_e compare with the value $r_e = 1.607775$ Å for $^2\text{H}^{127}\text{I}$?

How should it compare? Why?

c) What fraction of the HI molecules are in the $v = 0; 1; 2$ states at 300 K and at 1500 K?

2. Which of the following set of molecules, O_2 , HF, CCl_4 , H_2O and CO, would exhibit a microwave spectrum ?

A molecule requires a permanent dipole moment to exhibit a microwave spectrum. Thus HF, H_2O and CO would have such a spectrum, whilst O_2 and CCl_4 would not.

Will CO and O_2 give rotational fine structure in an infra-red spectrum ?

To give a line in an infra-red spectrum, the molecule must exhibit a change in dipole moment during a vibration.

To get rotational fine structure the molecule must also have a permanent dipole moment.

Thus the vibrational lines in the IR spectrum of CO will have rotational fine structure, but O_2 will not give an IR spectrum at all.

3. The rotational constant for the ground vibrational state ($v = 0$) for $^{12}C^{16}O$ is $1,9314 \text{ cm}^{-1}$. In a microwave spectrum of $^{12}C^{16}O$, what will be the spacing between absorption lines? (used the rigid rotor approximation)

For the rigid rotor approximation, microwave absorption lines appear at $2B$, $4B$, $6B$ etc. giving the line separation = $2B$.

Therefore, the absorption lines would be separated by $2 \cdot 1,9314 = 3,8628 \text{ cm}^{-1}$.

4. The rotational constant for the ground vibrational state ($v = 0$) for $^{12}\text{C}^{16}\text{O}$, denoted B_0 , is $1,9314 \text{ cm}^{-1}$. Using the rigid rotor approximation, calculate the equilibrium internuclear distance.

For the rigid rotor approximation, the energy of a rotational level J is given by

$$E(J) = h \cdot c \cdot B J(J+1)$$

and the wavenumber of an absorption line as

$$\bar{\nu}_{J \rightarrow J+1} = \Delta E / h \cdot c = [E(J+1) - E(J)] / h \cdot c = 2 B (J+1)$$

where the rotational constant $B = \frac{h}{8\pi^2 \cdot I \cdot c} \text{ cm}^{-1}$ (c is in units of $\text{cm} \cdot \text{s}^{-1}$),

and the moment of inertia, $I = \mu r_e^2$. Thus, $r_e = \sqrt{\frac{h}{8\pi^2 c \mu B}}$

For $^{12}\text{C}^{16}\text{O}$, $\mu = [12 \cdot 16 / (12+16)] \cdot 1,6606 \cdot 10^{-27} = 1,13850 \cdot 10^{-26} \text{ kg}$

In its ground vibrational state ($v=0$), the rotational constant is given as $B = B_0 = 1,9314 \text{ cm}^{-1}$, thus,

$$r_e = \sqrt{\frac{6,6262 \cdot 10^{-34}}{8 \cdot \pi^2 \cdot 2,9979 \cdot 10^{10} \cdot 1,1385 \cdot 10^{-26} \cdot 1,9314}} \quad r_e = 0,11283 \cdot 10^{-9} \text{ m} = \mathbf{0,1128 \text{ nm}}$$

5. For the first vibrationally excited state ($v = 1$) of $^{12}\text{C}^{16}\text{O}$, the rotational constant, denoted B_1 , is $1,6116 \text{ cm}^{-1}$. Again using the rigid rotor approximation, calculate the equilibrium bond distance for this state.

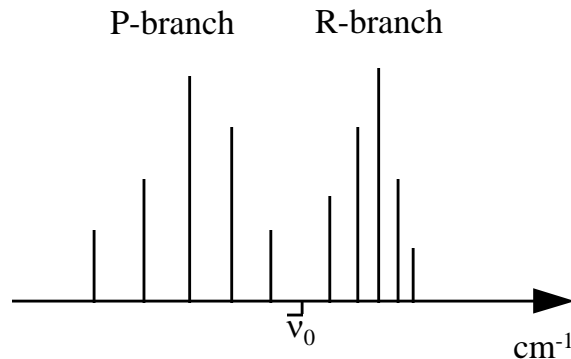
Similar to question (4), except that in the first vibrational state ($v=1$), the rotational constant $B = B_1 = 1,6116 \text{ cm}^{-1}$. Thus ,

$$r_e = \sqrt{\frac{6,6262 \cdot 10^{-34}}{8 \cdot \pi^2 \cdot 2,9979 \cdot 10^{10} \cdot 1,1385 \cdot 10^{-26} \cdot 1,6116}} \quad r_e = 0,12352 \cdot 10^{-9} \text{ m} = \mathbf{0,1235 \text{ nm}}$$

6. How will manifest the change in the equilibrium internuclear distance (hence the change in rotational constant) in the rotational fine structure of the infra-red spectrum ?

When the molecule is in its lowest vibrational state ($v=0$), it has an equilibrium bond length of $0,1128 \text{ nm}$ corresponding to a rotational constant, $B_0 = 1,9314 \text{ cm}^{-1}$. When vibrationally excited to its first vibrational state ($v = 1$), it has an increased equilibrium bond length of $0,1235 \text{ nm}$, and a lower rotational constant, $B_1 = 1,6116 \text{ cm}^{-1}$. This will be the observed in the rotational fine structure of the fundamental vibrational peak $\bar{\nu}_0 = \Delta G (v = 0 \rightarrow 1)$ of the IR spectrum.

Since $B_0 > B_1$, we would observe lines getting wider spaced in the P-branch and closer in the R-branch, as depicted in the spectrum below.



http://rkt.chem.ox.ac.uk/tutorials/rotation/rot_spectra.html