

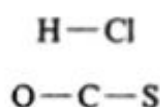
MICROWAVE SPECTROSCOPY

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

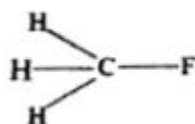


The three directions of rotation may be taken as (a) about the bond axis, (b) end-over-end rotation in the plane of the paper, and (c) end-over-end rotation at right angles to the plane. It is self-evident that the moments of (b) and (c) are the same (that is $I_B = I_C$) while that of (a) is very small. As an approximation we may say that $I_A = 0$, although it should be noted that this *is* only an approximation (see Sec. 2.3.1).

Thus for linear molecules we have:

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

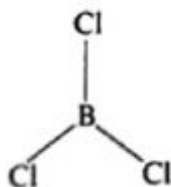
2. *Symmetric tops*. Consider a molecule such as methyl fluoride, where the three hydrogen atoms are bonded tetrahedrally to the carbon, as shown below:



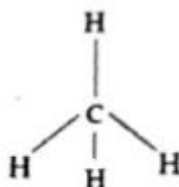
As in the case of linear molecules, the end-over-end rotation in, and out of, the plane of the paper are still identical and we have $I_B = I_C$. The moment of inertia about the C—F bond axis (chosen as the main rotational axis since the centre of gravity lies along it) is now not negligible, however, 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:



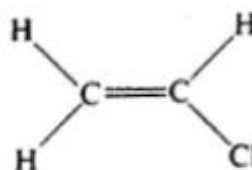
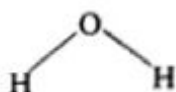
$$\text{Spherical tops: } I_A = I_B = I_C \quad (2.3)$$

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 for 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:

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

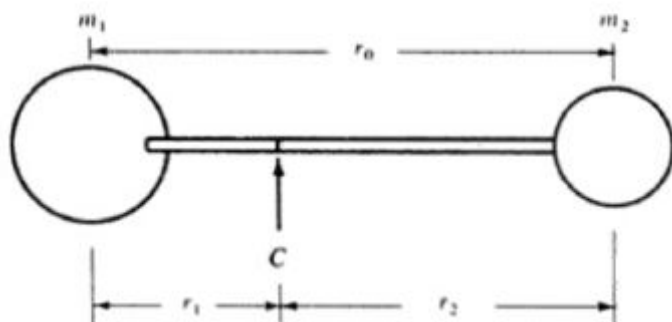


Figure 2.1 A rigid diatomic molecule treated as two masses, m_1 and m_2 , joined by a rigid bar of length $r_0 = r_1 + r_2$.

The moment of inertia about C is defined by:

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

However, from Eqs (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) in (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.

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:

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

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) expressed 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:

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

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:

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

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

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

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.

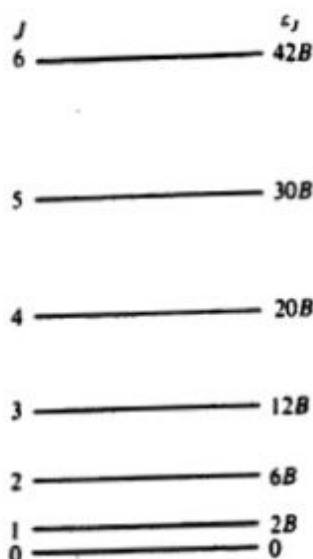


Figure 2.2 The allowed rotational energies of a rigid diatomic molecule.

From Eq. (2.12) we can show the allowed energy levels diagrammatically as in Fig. 2.2. Plainly for $J = 0$ we have $\epsilon_J = 0$ and we would say that the molecule is not rotating at all. For $J = 1$, the rotational energy is $\epsilon_1 = 2B$ 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.

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:

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

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:

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

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

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

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

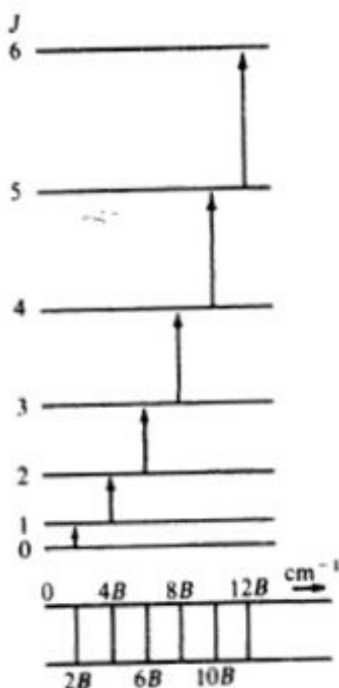


Figure 2.3 Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them.

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 spectrum of carbon monoxide as $3.842\,35\text{ cm}^{-1}$. Hence, from Eq. (2.16):

$$\bar{\nu}_{0 \rightarrow 1} = 3.842\,35 = 2B \text{ cm}^{-1}$$

or

$$B = 1.921\,18 \text{ cm}^{-1}$$

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

$$\begin{aligned} I_{\text{CO}} &= \frac{6.626 \times 10^{-34}}{8\pi^2 \times 2.997\,93 \times 10^{10} \times B} = \frac{27.9907 \times 10^{-47}}{B} \text{ kg m}^2 \\ &= 14.5695_4 \times 10^{-47} \text{ kg m}^2 \end{aligned}$$

where we express the velocity of light in cm s^{-1} , since B is in cm^{-1} . However, the moment of inertia is μr^2 (cf. Eq. (2.9)) and, knowing the relative atomic weights ($\text{H} = 1.0080$) to be $\text{C} = 12.0000$, $\text{O} = 15.9994$, and the absolute mass of the hydrogen atom to be $1.673\,43 \times 10^{-27} \text{ kg}$, we can calculate the masses of carbon and oxygen, respectively, as $19.921\,68$ and $26.561\,36 \times 10^{-27} \text{ kg}$. The reduced mass is then:

$$\mu = \frac{19.921\,68 \times 26.561\,36 \times 10^{-54}}{46.483\,03 \times 10^{-27}} = 11.383\,65 \times 10^{-27} \text{ kg}$$

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

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

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:

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

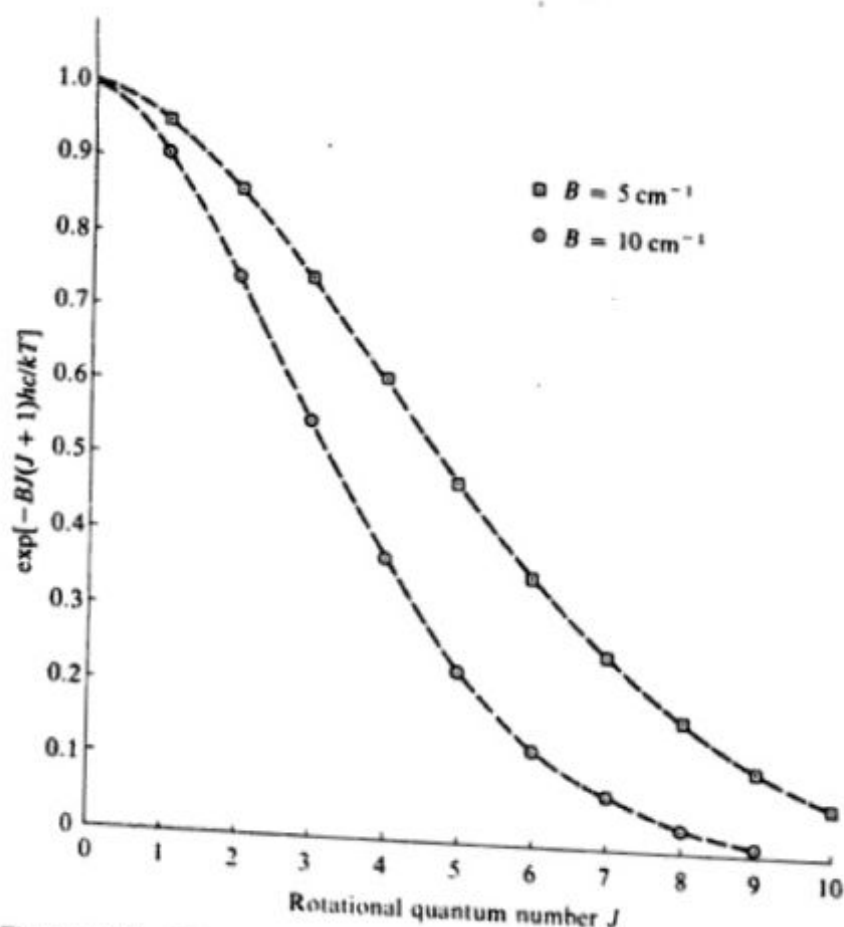


Figure 2.4 The Boltzmann populations of the rotational energy levels of Fig. 2.2. The diagram has been drawn taking values of $B = 5$ and 10 cm^{-1} and $T = 300 \text{ K}$ in Eq. (2.18).

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:

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

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.

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 $\mathbf{P} = \sqrt{1 \times 2} \text{ units} = \sqrt{2}$, 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

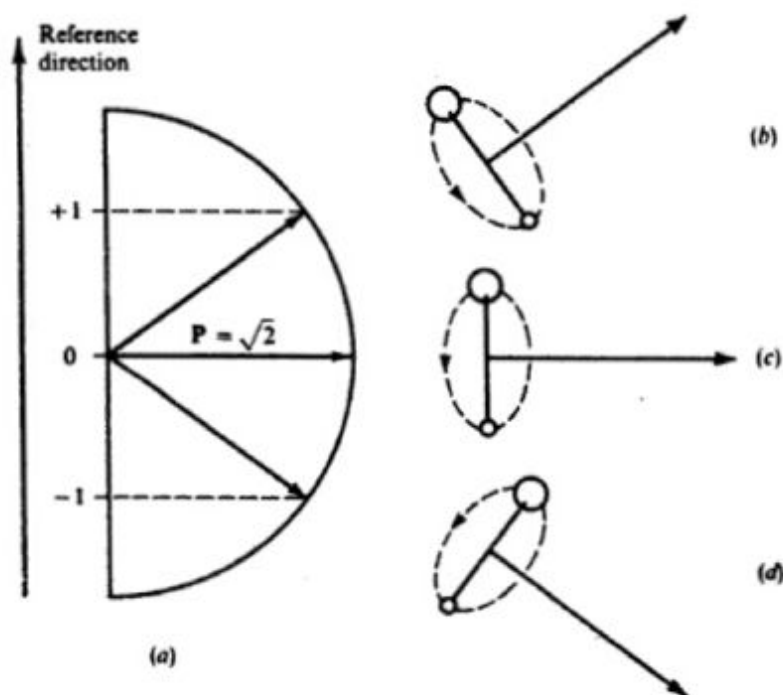


Figure 2.5 The three degenerate orientations of the rotational angular momentum vector for a molecule with $J = 1$.