3 Rotational Spectroscopy

3.1 Classifications of Rotors

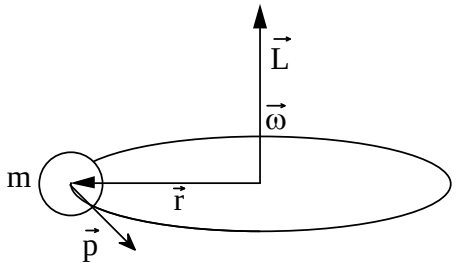
I will begin this subject by looking at the rotational motion of molecules in general. I will first classify molecules into different types according to the nature of their rotational motion. We will then look at a few of these types in somewhat more detail.

Last semester, I discussed the quantum mechanics of the Rigid Rotor. During that discussion, I made a brief digression comparing linear and rotational motion.

Linear Motion	**Rotational Motion**
x	θ
m	I
$v = dx/dt$	$\omega = d\theta/dt$
$\mathbf{p} = m\mathbf{v}$	$\mathbf{L} = I\boldsymbol{\omega}$

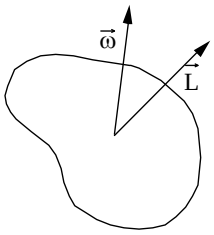
The expression for angular momentum, $\mathbf{L} = I\boldsymbol{\omega}$, in rotational motion is analogous to $\mathbf{p} = m\mathbf{v}$ in linear motion.

For the rotational motion of a single particle about a point, both $\boldsymbol{\omega}$ and $\mathbf{L}$ are vectors which point out of the plane of rotation in the same direction.



This will be true for a diatomic molecule if one neglects any angular momentum of the electrons.

For an extended object however (which includes non-linear polyatomic molecules), $\boldsymbol{\omega}$ and $\mathbf{L}$ need not point in the same direction.



You can see in this case, rather than being a single number, $\mathbf{I}$ must be represented by a 3 × 3 matrix

$$\mathbf{L} = I\boldsymbol{\omega}$$

written explicitly as

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

$\mathbf{I}$ is called the moment of inertia tensor.

One can derive the form of the moment of inertia tensor for a collection of nuclei rotating in space using the definition of angular momentum.

Consider a collection of nuclei of mass m_α located at positions $\mathbf{r}_\alpha$ relative to the origin in a Cartesian coordinate system. The collection of nuclei is rotating with angular velocity $\boldsymbol{\omega}$.

The angular momentum is given by

$$\mathbf{L} = \sum_\alpha \mathbf{r}_\alpha \times \mathbf{p}_\alpha = \sum_\alpha m_\alpha \mathbf{r}_\alpha \times \left(\boldsymbol{\omega} \times \mathbf{r}_\alpha\right)$$

Where we used that:

$$\mathbf{p}_\alpha = m_\alpha \mathbf{v}_\alpha = m_\alpha \left(\boldsymbol{\omega} \times \mathbf{r}_\alpha\right)$$

To simplify this, we need to use the cross product identity

$$\mathbf{P} \times \left(\mathbf{Q} \times \mathbf{R}\right) = \mathbf{Q}\left(\mathbf{P} \cdot \mathbf{R}\right) - \mathbf{R}\left(\mathbf{P} \cdot \mathbf{Q}\right)$$

This gives

$$\mathbf{L} = \sum_\alpha m_\alpha \left(\boldsymbol{\omega}\left(\mathbf{r}_\alpha \cdot \mathbf{r}_\alpha\right) - \mathbf{r}_\alpha \left(\mathbf{r}_\alpha \cdot \boldsymbol{\omega}\right)\right)$$

$$= \sum_\alpha m_\alpha \left(\boldsymbol{\omega}\left(x_\alpha^2 + y_\alpha^2 + z_\alpha^2\right) - \mathbf{r}_\alpha \left(x_\alpha \omega_x + y_\alpha \omega_y + z_\alpha \omega_z\right)\right)$$

Writing out the vector components gives

$$L = \sum_\alpha m_\alpha \Big[\omega_x \left(x_\alpha^2 + y_\alpha^2 + z_\alpha^2\right)\hat{\mathrm{e}}_1 + \omega_y \left(x_\alpha^2 + y_\alpha^2 + z_\alpha^2\right)\hat{\mathrm{e}}_2 + \omega_z \left(x_\alpha^2 + y_\alpha^2 + z_\alpha^2\right)\hat{\mathrm{e}}_3$$

$$- x_\alpha \left(x_\alpha \omega_x + y_\alpha \omega_y + z_\alpha \omega_z\right)\hat{\mathrm{e}}_1 - y_\alpha \left(x_\alpha \omega_x + y_\alpha \omega_y + z_\alpha \omega_z\right)\hat{\mathrm{e}}_2 - z_\alpha \left(x_\alpha \omega_x + y_\alpha \omega_y + z_\alpha \omega_z\right)\hat{\mathrm{e}}_3 \Big]$$

This can be written in matrix form as:

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} \sum_\alpha m_\alpha \left(y_\alpha^2 + z_\alpha^2\right) & -\sum_\alpha m_\alpha x_\alpha y_\alpha & -\sum_\alpha m_\alpha x_\alpha z_\alpha \\ -\sum_\alpha m_\alpha y_\alpha x_\alpha & \sum_\alpha m_\alpha \left(x_\alpha^2 + z_\alpha^2\right) & -\sum_\alpha m_\alpha y_\alpha z_\alpha \\ -\sum_\alpha m_\alpha z_\alpha x_\alpha & -\sum_\alpha m_\alpha z_\alpha y_\alpha & \sum_\alpha m_\alpha \left(x_\alpha^2 + y_\alpha^2\right) \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

The diagonal elements of this matrix are referred to as the **moments of inertia**

$$I_{xx} = \sum_\alpha m_\alpha \left(y_\alpha^2 + z_\alpha^2\right) = \sum_\alpha m_\alpha r_{x\perp}^2$$

$$I_{yy} = \sum_\alpha m_\alpha \left(x_\alpha^2 + z_\alpha^2\right) = \sum_\alpha m_\alpha r_{y\perp}^2$$

$$I_{zz} = \sum_\alpha m_\alpha \left(x_\alpha^2 + y_\alpha^2\right) = \sum_\alpha m_\alpha r_{z\perp}^2$$

Note that the moment of inertia with respect to an axis involves the squares of the perpendicular distances of the masses from that axis (*e.g.*, $r_{x\perp}^2$ from the *x*-axis).

The off-diagonal terms in this matrix are called the **products of inertia**:

$$I_{xy} = -\sum_\alpha m_\alpha x_\alpha y_\alpha$$

$$I_{xz} = -\sum_\alpha m_\alpha x_\alpha z_\alpha$$

$$I_{yz} = -\sum_\alpha m_\alpha y_\alpha z_\alpha$$

The matrix is called the **moment of inertia tensor**.

Because the moment of inertia tensor is a real symmetric matrix, one can prove that it is always possible to find an orthogonal transformation matrix **X** that transforms the moment of inertia tensor **I** into diagonal form.

$$\mathbf{I}' = \mathbf{X}^{-1}\mathbf{I}\mathbf{X}$$

The matrix **X** represents a rotation of the coordinate system, which can be written as

$$\mathbf{r}' = \mathbf{X}^{-1}\mathbf{r} \text{ or } \qquad \mathbf{r} = \mathbf{X}\mathbf{r}'$$

(One can show that the columns of the matrix **X** are made up of the normalized eigenvectors of **I**).

The new coordinate system is called the ***principle axis system*** and the **I'** matrix is a diagonal matrix given by

$$\mathbf{I}' = \begin{pmatrix} I_{x'x'} & 0 & 0 \\ 0 & I_{y'y'} & 0 \\ 0 & 0 & I_{z'z'} \end{pmatrix}$$

Usually the use of the principle axis system is assumed, so the primes are dropped and

$$I_x = I_{x'x'} \quad I_y = I_{y'y'} \quad I_z = I_{z'z'}$$

In the principle axis system one can always write

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} I_x & 0 & 0 \\ 0 & I_y & 0 \\ 0 & 0 & I_z \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

Which axis is labeled *x*, *y*, and *z* is chosen by a set of geometrical conventions. For example, the *z*-axis is always chosen to be the highest order axis of rotational symmetry, and the *x*-axis is out of the plane for a planar molecule.

With the moment of inertia tensor in diagonal form like this, the different components of the angular momentum can simply be written

$$L_x = I_x\omega_x \qquad L_y = I_y\omega_y \qquad L_z = I_z\omega_z$$

The total angular momentum vector can be constructed from these three projections on the principle axes.

The rotational kinetic energy can be written as:

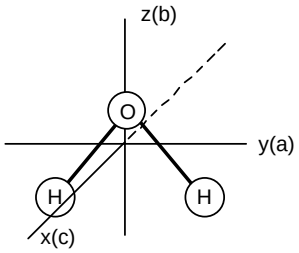
$$E_{rot} = \frac{1}{2}\left[I_x \omega_x^2 + I_y \omega_y^2 + I_z \omega_z^2 \right]$$

$$= \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z}$$

An alternative labeling scheme for the principal axes is based upon the magnitudes of the moments of inertia. In this case, the axes are labeled *A*, *B*, and *C* according to the requirement that

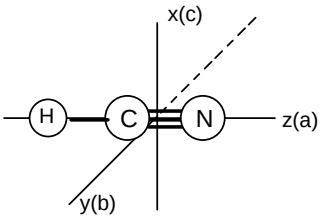
$$I_A \le I_B \le I_C$$

It is not obvious in this case which one is *A*, *B*, and *C* from simply looking at the molecule. One must calculate the moments of inertia. It is important to realize that this is simply another way of labeling the axes. They are the same set of three axes, however.

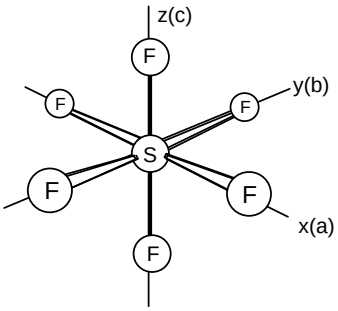


All molecules can be classified on the basis of their three moments of inertia. There are 5 different cases:

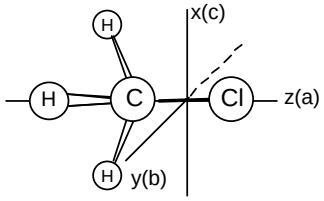
1. **Linear Molecules**, $I_A = 0$, $I_B = I_C$ *e.g.*, HCN



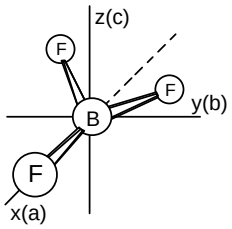
2. **Spherical Tops**, $I_A = I_B = I_C$ *e.g.*, SF_6 and CH_4



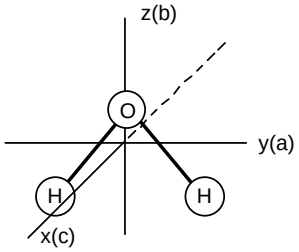
3. **Prolate Symmetric Tops**, $I_A < I_B = I_C$ *e.g.*, CH_3Cl



4. **Oblate Symmetric Tops**, $I_A = I_B < I_C$ *e.g.*, BF_3



5. **Asymmetric Tops,** $I_A < I_B < I_C$ *e.g.*, H_2O



Group theory can be used to classify the rotational properties of molecules. There are three important rules to remember:

- Molecules in the groups O_h, T_d, and I_h are spherical tops.
- Molecules in $C_{\infty v}$ and $D_{\infty h}$ are linear.
- All symmetric top molecules must have a C_n axis with n>2.

You can see that H_2O only has a C_2 axis and is an asymmetric top.

3.2 Linear Molecules

I have already laid much of the foundation for discussing rotational spectroscopy of diatomic molecules, and linear molecule rotation is essentially the same as that of diatomic rotation.

3.2.1 Level Spacing

In general, we write the ***classical*** expression for the kinetic energy as

$$E_K = \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2$$

Recall that in a diatomic molecule, $I_A = 0$ and $I_B = I_C = I$. We can therefore write

$$E_K = \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2$$

$$= \frac{J_B^2}{2I} + \frac{J_C^2}{2I} = \frac{J^2}{2I}$$

The quantum mechanical Hamiltonian for a linear rigid rotor is just

$$\hat{H} = \frac{\hat{J}^2}{2I}$$

We have already solved this problem:

$$\hat{H} Y_J^m(\theta,\varphi) = \frac{\hat{J}^2}{2I} Y_J^m(\theta,\varphi) = E Y_J^m(\theta,\varphi)$$

$$= \frac{\hbar^2}{2I} J(J+1) Y_J^m(\theta,\varphi) = BJ(J+1) Y_J^m(\theta,\varphi)$$

where

$$B = \frac{\hbar^2}{2I} = \frac{h^2}{8\pi^2 I} \qquad \text{(in Joules)}$$

Often spectroscopists use $F(J)$ to express the rotational energy levels as a function of the quantum number J in units of MHz or in cm^{-1}.

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

Unfortunately, the same symbol B is used whether expressed in Joules, MHz, or cm^{-1}.

Remember that for a linear molecule, $I_A = 0$ and $I_B = I_C = I$. The moment of inertia, I, will simply be

$$I = \sum_\alpha m_\alpha r^2$$

where r is the distance of the atom from the center of mass.

3.2.2 Selection Rules

In our earlier discussion of selection rules for a diatomic, we started with the transition moment integral

$$\textit{Intensity} \propto \left(\int \psi_2^* \hat{\mu}_z \psi_1 d\tau \right)^2 \qquad \text{(or the equivalent with } \mu_x \text{ or } \mu_y\text{)}$$

After putting in the wave functions as products of vibrational, rotational and electronic parts, we get that the integral can be written as:

$$\iiint \psi_{2el}^*(q_i;R) \psi_{2vib}^*(R) \psi_{2rot}^*(\theta,\varphi) \hat{\mu}_z(q_i,R) \psi_{1el}(q_i;R) \psi_{1vib}(R) \psi_{1rot}(\theta,\varphi)\, d\tau_{q_i}\, d\tau_R\, d\tau_{\theta,\varphi}$$

Where q_i are the electron coordinates and R the distance between the nuclei. The dipole moment which is given in the laboratory frame of reference as $\mu_z(q_i,R)$ and depends on both the electron and the nuclear positions can be written in the molecular frame of reference as

$$\mu_\eta(q_i,R)\cos\theta$$

Rearranging terms and grouping them together gives:

$$\iint \psi^*_{2el}(q_i;R)\psi^*_{2vib}(R)\hat{\mu}_\eta(q_i,R)\psi_{1el}(q_i;R)\psi_{1vib}(R)d\tau_{q_i}\, d\tau_R \int \psi^*_{2rot}(\theta,\varphi)\cos\theta\psi_{1rot}(\theta,\varphi)\, d\tau_{\theta,\varphi}$$

If we now realize that for pure rotational transitions we do not change electronic or vibrational level we can rewrite this as:

$$\iint \psi^*_{1el}(q_i;R)\psi^*_{1vib}(R)\hat{\mu}_\eta(q_i,R)\psi_{1el}(q_i;R)\psi_{1vib}(R)d\tau_{q_i}\, d\tau_R \int \psi^*_{2rot}(\theta,\varphi)\cos\vartheta\psi_{1rot}(\theta,\varphi)\, d\tau_{\theta,\varphi}$$

This double integral gives the mean value of the dipole moment, averaged over the electronic and nuclear coordinates. This is also known as the permanent dipole moment, μ_e, of the molecule. We can thus write:

$$\mu_e \int \psi^*_{2rot}(\theta,\varphi)\cos\theta\psi_{1rot}(\theta,\varphi)\, d\tau_{\theta,\varphi}$$

You can see that one requirement for pure rotational transitions is that the molecule has a permanent dipole moment, μ_e.

Thus, molecules such as O=C=O, Cl – Cl, H-C≡C-H which have no dipole moment, have no pure rotational spectra.

The other requirement is that the integral is non-zero. We can use rigid rotor wave functions for evaluating this integral.

Recall that:

$$\psi_{RR} = Y_J^m(\theta,\varphi) = N_{Jm}P_J^{|m|}(\cos\theta)e^{im\varphi}$$

where

$$N_{Jm} = \left[\frac{(2J+1)}{4\pi}\frac{(J-|m|)!}{(J+|m|)!}\right]^{\frac{1}{2}}$$

Remember that the $P_J^{|m|}(\cos\theta)$ are the associated Legendre polynomials.

Putting this into the integral yields

$$\int \psi^*_{2rot}(\theta,\varphi)\cos\theta\psi_{1rot}(\theta,\varphi)\, d\tau_{\theta,\varphi} = \int N_{J'm'}P_{J'}^{|m'|}(\cos\theta)e^{-im'\varphi}\cos\theta N_{J''m''}P_{J''}^{|m''|}(\cos\theta)e^{im''\varphi}d\tau_{\theta,\varphi}$$

$$= N_{J'm'}N_{J''m''}\int P_{J'}^{|m'|}(\cos\theta)\cos\theta P_{J''}^{|m''|}(\cos\theta)d\tau_\theta \int e^{-im'\varphi}e^{im''\varphi}d\tau_\varphi$$

Note: It is spectroscopic convention to label the upper state quantum number by a single prime and the lower state quantum number by a double prime. When indicating a transition between two states, the convention is to write the upper state first and the lower state second. An arrow is used to indicate absorption, $J' \leftarrow J''$ or emission, $J' \rightarrow J''$. When no prime is indicated, the quantum number refers to the lower state.

The integral over φ will be zero unless *m*'' =*m*' in which case it will be 2π. This gives rise to the *m* selection rule **Δ*m* = 0.** This Δ*m* selection rule results from our choice of radiation along the *z*-direction. If we chose the *x* or *y* component, we could get **Δ*m* = ±1.** This arises from the relation between the molecule fixed dipole moment and the projection on the different axes. We know that

$$\mu_z = \mu_\eta \cos\theta$$

$$\mu_y = \mu_\eta \sin\theta \sin\varphi$$

$$\mu_x = \mu_\eta \sin\theta \cos\varphi$$

If you used one of the latter two components, you would get a $\sin\varphi$ or $\cos\varphi$ in the φ integral, and this would give Δ*m* = ±1.

To help evaluate the integral over θ which gives the *J* selection rules, one can make use of a recursion formula that relates different Legendre polynomials to one another.

$$\cos\theta P_J^{|m|}(\cos\theta) = \frac{J+|m|}{2J+1} P_{J-1}^{|m|}(\cos\theta) + \frac{J-|m|+1}{2J+1} P_{J+1}^{|m|}(\cos\theta)$$

Using this recursion relation in the θ part of the integral gives

$$\int P_{J'}^{|m'|}(\cos\theta)\cos\theta P_{J''}^{|m''|}(\cos\theta)d\tau_\theta = \left(\frac{J''+|m''|}{2J+1}\right)\int P_{J'}^{|m'|}(\cos\theta)P_{J''-1}^{|m''|}(\cos\theta)d\tau_\theta + \left(\frac{J''-|m''|+1}{2J+1}\right)\int P_{J'}^{|m'|}(\cos\theta)P_{J''+1}^{|m''|}(\cos\theta)d\tau_\theta$$

Remember that the eigenfunctions of a Hermitian operator form a complete orthonormal set. This means that eigenfunctions corresponding to different eigenvalues are orthogonal.

Thus, the first integral on the right will be zero unless *J*' = *J*'' - 1 or *J*'-*J*'' = -1. This gives rise to the selection rule that Δ*J* = -1.

Once can see that the second integral will be equal to zero unless *J*' = *J*''+1. This gives rise to the selection rule that Δ*J* = 1

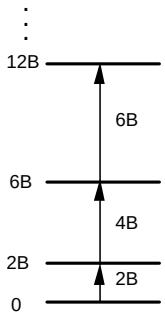
Together we have: **Δ*J* = ± 1 Δ*m* = 0, ±1**

So in addition to the requirement of a permanent dipole moment for pure rotational transitions, the rotational selection rules require that Δ*J* = ± 1 and Δ*m* = 0, ±1. Because in the absence of a magnetic field the states of different *m* are degenerate, the Δ*m* = 0, ±1 selection rule has no effect on the energies of the transitions in the spectrum. We will therefore ignore it for the moment. Note that this is true both for pure rotational transitions and vibration-rotation transitions, since the same integral is involved.

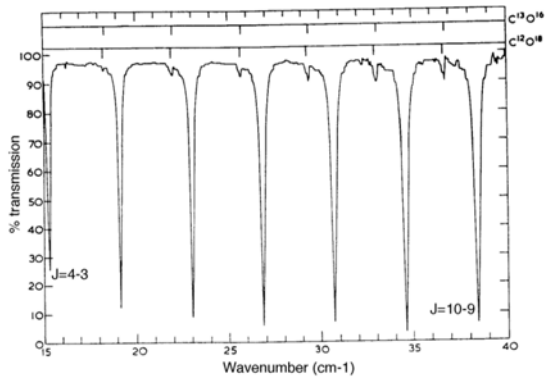
The selection rule Δ*J* = ± 1 results in the following transition frequencies:

$$\begin{aligned} \nu_{J+1\leftarrow J} &= F(J') - F(J'') = F(J+1) - F(J) \\ &= B(J+1)(J+2) - BJ(J+1) \\ &= 2B(J+1) \end{aligned}$$

Thus, the first transition, *J* = 1←0, occurs at 2*B*. The others are spaced at multiples of 2*B*.



Example: Rotational Spectrum of CO.



Note the isotope peaks; different isotopes have different rotational constants. From analysis of this spectrum, one could get the rotational constant *B*, which gives the moment of inertia, *I*, which in turn will provide r_e. This is the most accurate way to determine bond lengths.

The expression that we derived for the energies of the rotational levels was in the rigid rotor approximation where we have neglected vibration rotation interaction and centrifugal distortion.
Recall our general expression for the energy levels of a diatomic:

$$F(\mathrm{v},J)=\frac{E_{vJ}}{hc}=\omega_e\left(\mathrm{v}+\frac{1}{2}\right)+B_eJ\left(J+1\right)-\omega_ex_e\left(\mathrm{v}+\frac{1}{2}\right)^2-\alpha\left(\mathrm{v}+\frac{1}{2}\right)J\left(J+1\right)-DJ^2\left(J+1\right)^2$$

It is important to note that the number of terms here is simply determined by how many terms we carry in the perturbation theory treatment to derive it. One can take this out to higher order terms if one likes.

One can rewrite this expression in the following way

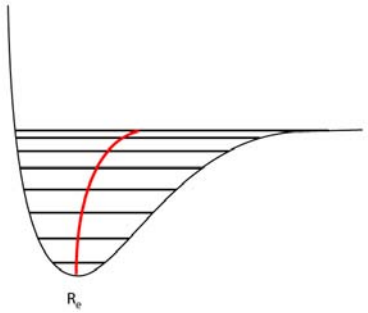
$$F(\mathrm{v},J)=\omega_e\left(\mathrm{v}+\frac{1}{2}\right)-\omega_ex_e\left(\mathrm{v}+\frac{1}{2}\right)^2+B_{\mathrm{v}}J\left(J+1\right)-DJ^2\left(J+1\right)^2$$

where

$$B_{\mathrm{v}}=B_e-\alpha\left(\mathrm{v}+\frac{1}{2}\right)$$

One can have pure rotational transitions in excited vibrational states, and this expression accounts for the change in the *B* rotational constant with increasing vibrational quantum number as well as the effects of centrifugal distortion. (Higher order treatments include the vibrational dependence of *D* as well).

As we discussed earlier in the course, the fact that the rotational constant is dependent on the vibrational level reflects the fact that there is anharmonicity in the potential that makes the average bond length increase with increasing vibrational quantum number. This makes the effective rotational constant depend upon the vibrational quantum number, v.



The frequency for a pure rotational transition comes from taking the difference in energy levels:

$$\nu_{J+1\leftarrow J} = F(J') - F(J'') = F(J+1) - F(J)$$

$$= B_v(J+1)(J+2) - D(J+1)^2(J+2)^2 - B_v J(J+1) + DJ^2(J+1)^2$$

$$= 2B_v(J+1) - 4D(J+1)^3$$

You can see that the transition frequencies are slightly lowered by centrifugal distortion.

Using this more accurate expression, one can now obtain not only the rotational constant *B*, but also the vibration rotation interaction constant □ and the centrifugal distortion constant *D*.

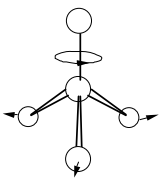
3.3 Spherical Tops

In general, one would expect spherical top molecules not to show any pure rotational transitions because they do not have any permanent dipole moment (which is a requirement for having a pure rotational spectrum).

You can see this by simply looking at the character tables for the point groups T_d, and O_h. There is no translational coordinate (*i.e.*, *x*, *y*, or *z*) which belongs to the totally symmetric representation. Remember, that the symmetry of different components of the dipole moment are the same as a translation in that direction. Thus we would not expect there to be any dipole moment and hence no rotational spectrum.

However, for spherical top molecules which have only C_3 axes of symmetry, there can be a slight dipole moment induced by centrifugal distortion.

Consider the molecule CH_4 for example. Rotation about any of the 4 C_3 axes will push out the off axis hydrogens slightly but does not effect the hydrogen that is on the axis. This results in a very small dipole moment and hence a weak rotational spectrum. I will not take the time to discuss this in detail.



3.4 Symmetric Tops

Now let's turn to the more complex problem of symmetric top rotational motion. Although more complex than that of linear molecules, among polyatomics the rotational motion of symmetric tops is the simplest to understand. My discussion will focus on ***prolate symmetric tops***, although I will mention oblate tops at several points.

Recall that in a prolate symmetric top, $I_A < I_B = I_C$. The two identical moments are usually called I_B. We call the axis of highest symmetry in a symmetric top, the ***figure axis.***

In the quantum mechanical picture of symmetric top rotation, one has to consider which operators commute with each other, since this determines which quantities can be simultaneously well defined. Moreover, the quantities whose operators commute with the Hamiltonian will be independent of time and will be represented by "good" quantum numbers.

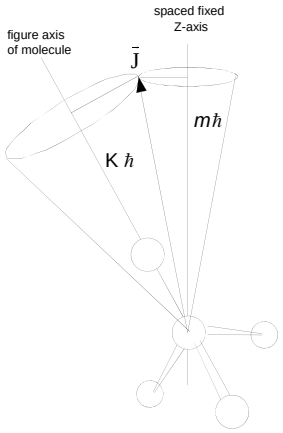
Recall that for rigid diatomic molecules, the operators $\hat{H}, \hat{J}^2, \hat{J}_z$ all commute with each other. Remember that J_Z represents the projection of **J** on the spaced fixed *z*-axis. We therefore had two good rotational quantum numbers *J*, and *m*, although the energy depends only on *J*.

For a symmetric top molecule we will find that there is another operator that commutes with these three, *i.e.* the operator representing the projection of *J* on the figure axis. This operator is given the symbol J_z (lower case *z*) or J_a.

Thus, there will be an additional good quantum number, which is denoted *K*, that represents a constant projection of the total angular momentum on the figure axis of the molecule.

In the quantum mechanical problem of the symmetric top, the total angular momentum of the molecule must simultaneously maintain a constant projection on the spaced fixed *z*-axis as well as on the figure axis of the molecule.

We therefore have the following picture:



We get two cones, constrained by the need to have constant projections of *J*. The relative sizes of these cones are simply related to the projection quantum numbers *K* and *m*. We should realize that the ***J*** vector is not fixed in space, it simply has a fixed length and a fixed projection on the space fixed *z*-axis.

In a symmetric top, we will see that the energy now depends upon two of the three good quantum numbers, *i.e*. *J*, which corresponds to the total angular momentum, and *K*, which corresponds to the projection of *J* on the figure axis. It is still true that in the absence of magnetic fields, the energy doesn't depend upon *m* since

space is isotropic. The fact that the molecule is not isotropic means that the energy will depend upon *K*. If the molecule was isotropic (*i.e.*, a spherical top) the energy would not depend upon *K*.

3.4.1 Hamiltonian and Energy Levels

To treat the quantum mechanical problem of the symmetric top, one has to write down the classical expression for the total energy and then substitute the corresponding operators to get the Hamiltonian. One must then find the eigenvalues and eigenfunctions of the Hamiltonian.

The classical expression for the energy of a rigid prolate symmetric top is:

$$E = \frac{J_A^2}{2I_A} + \frac{J_B^2}{2I_B} + \frac{J_C^2}{2I_C}$$

$$= \frac{J_A^2}{2I_A} + \frac{1}{2I_B}\left(J_B^2 + J_C^2\right)$$

Since $I_B = I_C$

We could also write this

$$E = \frac{J_z^2}{2I_A} + \frac{1}{2I_B}\left(J_x^2 + J_y^2\right)$$

since for a prolate symmetric top, $a \leftrightarrow z$, $b \leftrightarrow x$, and $c \leftrightarrow y$.

(Remember that lower case *x*, *y*, *z* are molecule fixed coordinates, uppercase *X*, *Y*, *Z* are spaced fixed coordinates)

We know that

$$J_x^2 + J_y^2 + J_z^2 = J^2 \qquad \text{or} \qquad J_x^2 + J_y^2 = J^2 - J_z^2$$

We can therefore write

$$E = \frac{J_z^2}{2I_A} + \frac{1}{2I_B}\left(J^2 - J_z^2\right)$$

Rearranging this gives

$$E = \frac{J^2}{2I_B} + \left(\frac{1}{2I_A} - \frac{1}{2I_B}\right)J_z^2$$

The corresponding quantum mechanical Hamiltonian is therefore:

$$\hat{H} = \frac{\hat{J}^2}{2I_B} + \left(\frac{1}{2I_A} - \frac{1}{2I_B}\right)\hat{J}_z^2$$

Because we are dealing with non-linear molecules, the eigenfunctions of this Hamiltonian will depend upon three angles, the so-called Euler angles θ, φ, and χ. The first two are those of a spherical polar coordinate system that describe the orientation of the figure axis (which is fixed in the molecule) with respect to the

space-fixed *X*, *Y*, and *Z* axes. Another angle, χ, is needed, to describe the orientation of the molecule about its figure axis. (The spinning motion of a symmetric top about its top axis involves a change in χ.)

Thus $\psi = \psi(\theta, \varphi, \chi)$

These eigenfunctions will be simultaneous eigenfunctions of $\hat{H}, \hat{J}^2, \hat{J}_Z$ and $\hat{J}_z$ since these operators commute. In addition to representing states having a fixed value of the energy, these eigenfunctions can be characterized by 3 rotational quantum numbers, *J*, *m*, and *K*. The first two have their usual meaning, while the third represents the projection of *J* on the figure axis.

It is important to note the analogy between $\hat{J}_Z$ and $\hat{J}_z$. Recall that the operator for J_Z is given by

$$\hat{J}_Z = -i\hbar \frac{\partial}{\partial \varphi}$$

One could show that

$$\hat{J}_z = -i\hbar \frac{\partial}{\partial \chi}$$

If we substituted into the Hamiltonian the $\hat{J}^2$ and $\hat{J}_z$ operators, we would find that we could separate the Hamiltonian into separate parts that depend upon θ, φ, and χ. Thus the eigenfunctions will be products of separate functions of θ, φ, and χ.

We already know what the solutions to the φ and χ parts are. Remember that the eigenfunctions for

$\hat{J}_Z = -i\hbar \frac{\partial}{\partial \varphi}$ are simply $\psi(\varphi) = e^{im\varphi}$

In the same way, the eigenfunctions of

$\hat{J}_z = -i\hbar \frac{\partial}{\partial \chi}$ are $\psi(\chi) = e^{iK\chi}$

This set of eigenfunctions will therefore have the form

$$\psi_{J,K,m}(\theta, \varphi, \chi) = \left(\frac{2J+1}{8\pi^2}\right)^{\frac{1}{2}} e^{im\varphi} d^J_{mK}(\theta) e^{iK\chi}$$

It is clear that these functions are eigenfunctions of J_Z and J_z since multiplication by a function of φ will not affect the eigenvalue equation for these operators.

The functions $d^J_{mK}(\theta)$ are hypergeometric functions of $\sin^2(\theta/2)$. They are rarely listed explicitly since the actual functions are usually not needed for calculations. It is sufficient to know the eigenvalues for each of the angular momentum operators with these functions.

Although I haven't given you expressions for these functions $d^J_{mK}(\theta)$ it is important to know that if one sets *K*=0, these functions simply become the spherical harmonics. This makes physical sense in that if there is no rotation about the figure axis, the system behaves just like a diatomic molecule.

The important thing to realize is that the wave functions for a symmetric top depend upon 3 rotational quantum numbers (rather than two for linear molecules).

- ***J*** is the total angular momentum quantum number as in the case of linear molecules.
- ***m*** is the quantum number for the projection of the total angular momentum on the spaced fixed Z-axis (as before).
- ***K*** is quantum number for the projection of the total angular momentum on the figure axis of the molecule.

We already know what the eigenvalues are for the $\hat{J}^2$ and $\hat{J}_Z$ operators. Because $\hat{J}_z$ is also a projection operator, one can treat it in an analogous manner to $\hat{J}_Z$.

We will have the following set of eigenvalue equations:

$$\hat{H}\,\psi_{J,K,m}(\theta,\varphi,\chi) = E\,\psi_{J,K,m}(\theta,\varphi,\chi)$$
$$\hat{J}^2\,\psi_{J,K,m}(\theta,\varphi,\chi) = \hbar^2 J(J+1)\,\psi_{J,K,m}(\theta,\varphi,\chi)$$
$$\hat{J}_Z\,\psi_{J,K,m}(\theta,\varphi,\chi) = \hbar m\,\psi_{J,K,m}(\theta,\varphi,\chi)$$
$$\hat{J}_z\,\psi_{J,K,m}(\theta,\varphi,\chi) = \hbar K\,\psi_{J,K,m}(\theta,\varphi,\chi)$$

where $\hbar K$ is the projection of *J* on the figure axis.

Given the expressions for the eigenvalues of the angular momentum operators for a symmetric top, it is simple to determine the expression for the energy levels.

$$\hat{H}\,\psi_{J,K,m}(\theta,\varphi,\chi) = \left[\frac{\hat{J}^2}{2I_B} + \left(\frac{1}{2I_A} - \frac{1}{2I_B}\right)\hat{J}_z^2\right]\psi_{J,K,m}(\theta,\varphi,\chi)$$

$$= \left[\frac{\hbar^2}{2I_B}J(J+1) + \left(\frac{\hbar^2}{2I_A} - \frac{\hbar^2}{2I_B}\right)K^2\right]\psi_{J,K,m}(\theta,\varphi,\chi)$$

In units of cm^{-1}, the energy levels for a ***prolate*** symmetric top are given by

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

The corresponding levels of an ***oblate*** symmetric top can be obtained by simply substituting *C* for *A*:

$$E = BJ(J+1) + (C-B)K^2$$

The rotational constants *A*, *B*, and *C*, in units of cm^{-1}, are defined by:

$$A = \frac{h}{8\pi^2 c I_A} \qquad B = \frac{h}{8\pi^2 c I_B} \qquad C = \frac{h}{8\pi^2 c I_C}$$

Remember that the convention in labeling the axes was that $I_A<I_B<I_C$. Because the rotational constants *A*, *B*, and *C* are inversely proportional to the moments of inertia I_A, I_B, I_C their ordering is reversed

$$A \geq B \geq C$$

Since the *K* quantum number is a projection of *J*, it can only take on the values

$K = -J, -J+1, \ldots -1, 0, 1, \ldots J-1, J$

Another way to look at this is that $J \geq |K|$

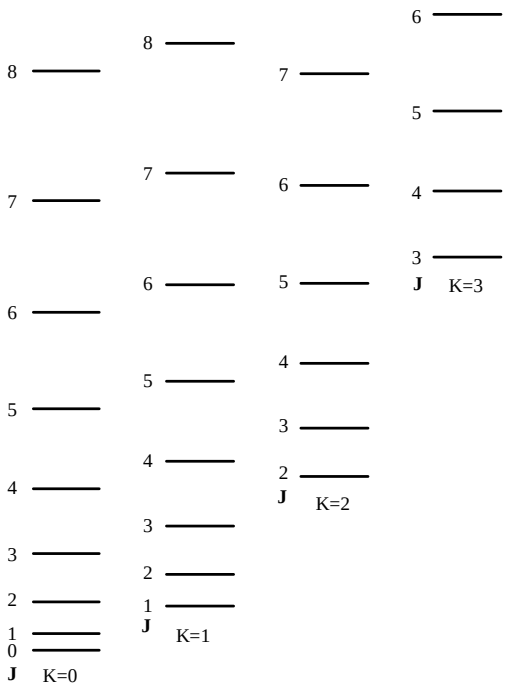
Notice that in the energy levels expressions above, the *K* quantum number enters in as K^2. This means that the *+K* and the *-K* levels with the same $|K|$ have the same energy (*i.e.*, the direction of rotation doesn't affect the energy). For this reason one usually leaves off the sign designation.

Note also that *m* does not enter into the energy level expression. This is because J_Z did not appear in the Hamiltonian. In the absence of an external field, there is nothing to make the energy different in one direction in space than in another, thus there is a 2*J*+1 fold degeneracy with respect to the *m* quantum number (*i.e*. the *Z*-projection in space). However, if one puts a molecule in an electric or magnetic field, the degeneracy would split and states with different *m* would have different energies.

The pattern of energy levels of a symmetric top is fairly simple. For a given value of *K*, the energy level structure looks like that of a linear molecule apart from an offset of $(A-B)K^2$ for a prolate top and $(C-B)K^2$ of an oblate top. This is shown in the figure below.

You can see that each value of *K* has its own stack of energy levels, the spacing of which is just $BJ(J+1)$, which is the same as a linear molecule. Notice that each stack starts at successively higher values of *J.* This is because of the restriction that *J* ≥ *K*. Also note that because $(A-B)$ is a positive value (by definition of the ordering of the rotational constants), the offset of each successive *K* stack (*i.e*., increasing *K*) is positive. That means for fixed *J*, the levels increase with *K*.

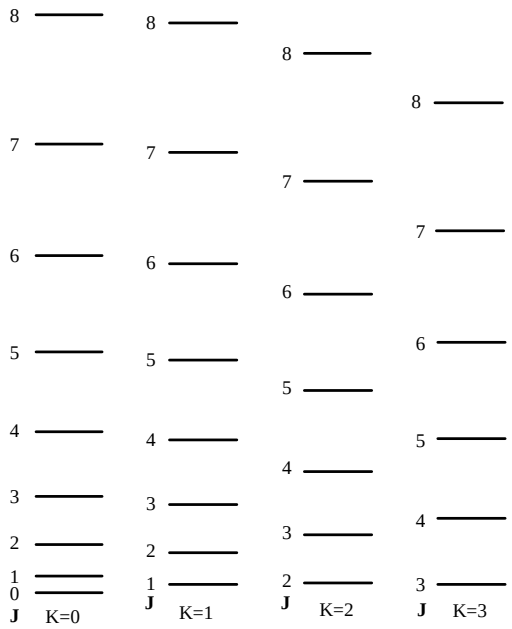
The major difference in the oblate top is that because $(C-B)$ is negative, each successive *K* stack is lower in energy. You might not see this immediately from looking at the diagram above since each stack starts at a higher *J* level (since *K* must be greater than or equal to *J*). Nevertheless, you can see that for fixed *J*, the levels get lower in energy with increasing *K*.



Prolate Symmetric Top Energy Levels

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

The levels of an oblate symmetric top are shown in the figure below:



Oblate Symmetric Top Energy Levels

$$E = BJ(J+1) + (C-B)K^2$$

3.4.2 Selection Rules and Spectra

I will not derive the selection rules for symmetric tops, but in principle it is no different than for a diatomic molecule. One has to evaluate the transition moment integral using the appropriate eigenfunctions.

The result is $\Delta J = \pm 1 \qquad \Delta m = 0, \pm 1 \qquad \Delta K = 0$

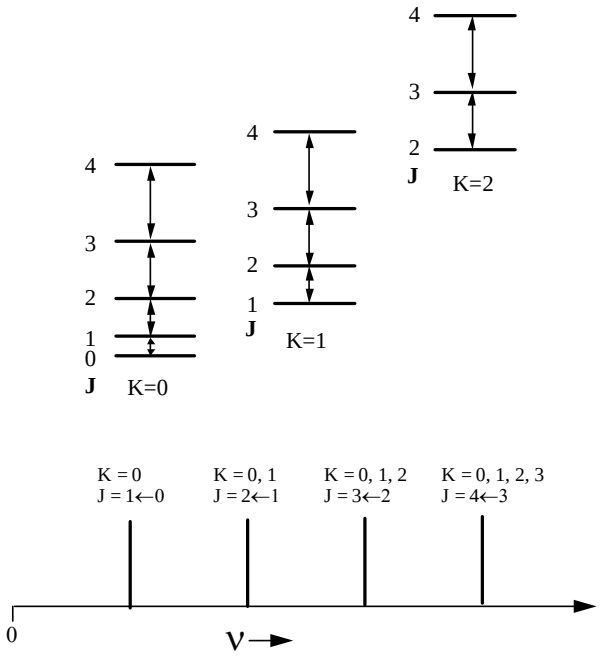
This is for pure rotational spectra. We will soon see that the rotational selection rules will be different for vibration-rotation spectra.

- The ΔJ selection rule is the same as a linear molecule.
- The Δm selection rule has no effect on the spectra since the m levels are all degenerate.
- The ΔK selection rule restricts transitions to states within the same K stack. From a physical point of view, the ΔK selection rule comes from the fact that because there is no dipole moment perpendicular to the axis, you cannot induce any angular momentum parallel to the axis (which is what is needed to change K).

Neglecting centrifugal distortion, the transition frequencies are simply given by

$$\begin{aligned} \nu_{J+1,K \leftarrow J,K} &= F(J+1,K) - F(J,K) \\ &= B(J+1)(J+2) + (A-B)K^2 - BJ(J+1) - (A-B)K^2 \\ &= 2B(J+1) \end{aligned}$$

This is shown schematically below.



Note the superposition of several transitions at the same frequency. This is because the *B* constant is independent of the value of *K*. If one takes into consideration centrifugal distortion, the overlapping transitions will be shifted from one another.

3.4.3 Effects of Centrifugal Distortion

If we include the effects of centrifugal distortion of a symmetric top, the energy level expression becomes

$$F(J,K) = BJ(J+1) - D_J J^2 (J+1)^2 + (A-B)K^2 - D_K K^4 - D_{JK} J(J+1)K^2$$

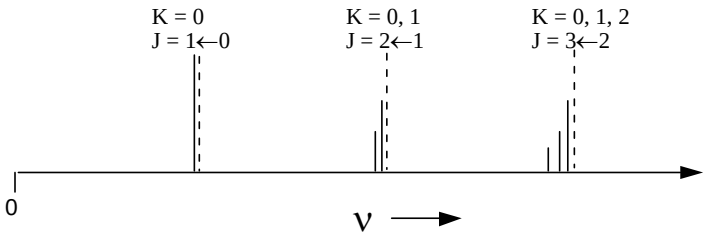
There are now 3 centrifugal distortion constants, D_J, D_K, and D_{JK}.

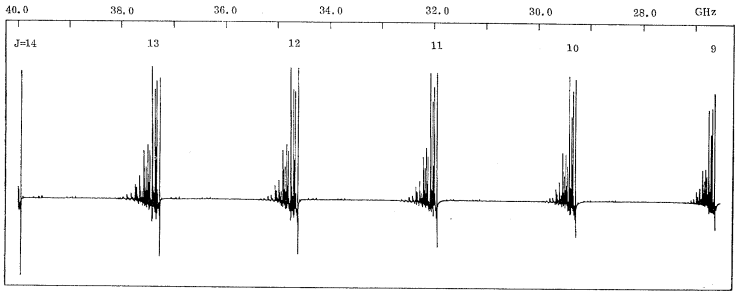
You can see that because of the selection rule $\Delta K = 0$, all of the terms which depend only on *K* will drop out when one takes the difference in energy levels. The transition frequencies are given by

$$\nu_{J+1,K\leftarrow J,K} = F(J+1,K) - F(J,K)$$

$$= 2B(J+1) - 4D_J (J+1)^3 - 2D_{JK} (J+1)K^2$$

The constant D_{JK} splits out the transitions with different *K* for a given $J+1\leftarrow J$ which in the absence of centrifugal distortion would fall on top of one another.





Part of the microwave spectrum of cyanodiacetylne

3.5 Asymmetric Tops

Asymmetric top molecules have $I_A < I_B < I_C$ with no two moments equal to one another.

The rigid rotor Hamiltonian can be written:

$$\hat{H} = \frac{\hat{J}_A^2}{2I_A} + \frac{\hat{J}_B^2}{2I_B} + \frac{\hat{J}_C^2}{2I_C}$$

The Schrödinger equation for the asymmetric top has no general analytical solutions and must be solved numerically.

If two of the rotational constants are nearly equal, the spectrum will resemble that of a symmetric top with some of the lines split due to asymmetry. One way to think of an asymmetric top is that the quantum numbers corresponding to the +*K* and -*K* levels that were degenerate in the symmetric top are no longer degenerate.

The degree of asymmetry can be quantified by an asymmetry parameter, called "Ray's asymmetry parameter", κ, which can take values from -1 to +1. The asymmetry parameter is defined as

$$\kappa = \frac{2B - A - C}{A - C}$$

You can see from this definition that for a: **prolate top:** $B = C$ and $\kappa = -1$
oblate top: $A = B$ and $\kappa = +1$

For a slightly asymmetric top the splitting between these levels is given by

$$\Delta E = \frac{b^K (J+K)!}{8^{K-1}(J-K)!\left[(K-1)!\right]^2}$$

With for a slightly asymmetric prolate top:

$$b_p = \frac{\kappa + 1}{\kappa - 3}$$

Note that b_p is zero for a prolate symmetric top and increases as the molecule becomes more asymmetric.

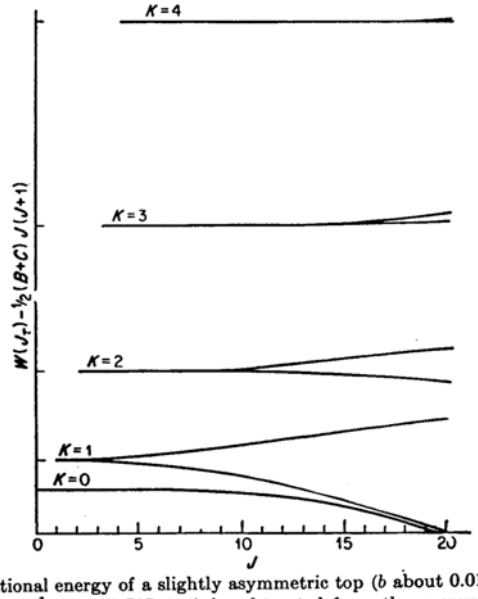
The corresponding definition for an oblate top is:

$$b_o = \frac{\kappa - 1}{\kappa + 3}$$

If the asymmetry is somewhat small, the spectrum can be analyzed as a symmetric top spectrum taking the asymmetry splitting into account.

The figure below shows this splitting for a slightly asymmetric prolate top (b_p = 0.01). Here the energy levels are plotted with the pure *J* contribution to the energy subtracted off.
There is no analytical formula, however, to relate the energies of the levels to the *J* and *K* quantum numbers.

Rotational levels of asymmetric tops only have only two "good" quantum numbers (that is quantum numbers that correspond to conserved quantities), and that is the total angular momentum quantum number, *J* and the projection of *J* on the space fixed *z*-axis, *m*.



Rotational energy of a slightly asymmetric top (*b* about 0.01) as a function of *J*. [The term $\frac{1}{2}(B + C)J(J + 1)$ is subtracted from the energy, *i.e.*, the deviations of the curves from horizontal lines represent the deviations from the levels of the symmetric top.] (*From Dieke and Kistiakowsky*)

The quantum number *K* is no longer a good quantum number insofar as the projection of *J* on the principal axis is no longer a conserved quantity. However, the levels of an asymmetric top are often labeled by the *K* quantum numbers corresponding to the levels of a prolate or oblate symmetric top, K_A, and K_C.

A notation that you will often see is J_{K_A,K_C} to designate the rotational levels of an asymmetric top.