- The principal axes of a molecule are defined such that they are centered at center-of-mass and the moment of Inertia tensor is diagonal

$$\overleftrightarrow{I} = \begin{bmatrix} I_{xx} & & 0 \\ & I_{yy} & \\ 0 & & I_{zz} \end{bmatrix}$$

We label the 3 moments of inertia (axes) A, B, C

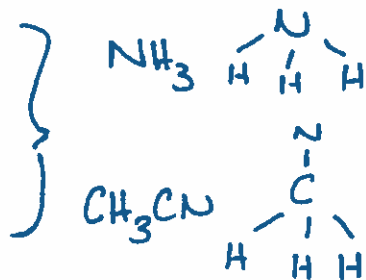$$\ni I_A \leq I_B \leq I_C$$
(Least) $\longrightarrow$ (Greatest)
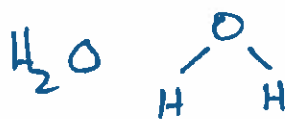
- There are 4 basic types of molecules:

Linear $\qquad$ C – O $\qquad$ $I_A = 0 \qquad I_B = I_C$

Symmetric Top $\qquad$ NH_3 $\qquad$ $I_A = I_B < I_C$ $\quad$ OBLATE

$\qquad$ CH_3CN $\qquad$ $I_A < I_B = I_C$ $\quad$ PROLATE

Asymmetric Top $\qquad$ H_2O $\qquad$ $I_A \neq I_B \neq I_C$

Spherical Top $\qquad$ CH_4 $\qquad$ $I_A = I_B = I_C$

Molecular rotations and vibrations
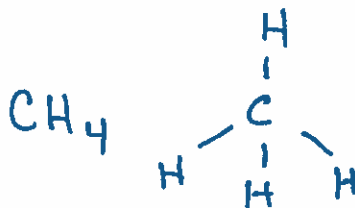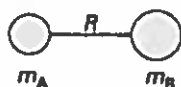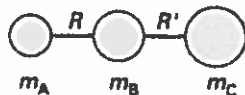
Table 10.1 Moments of inertia†

1. Diatomics

$$I = \frac{m_A m_B}{m} R^2 = \mu R^2$$
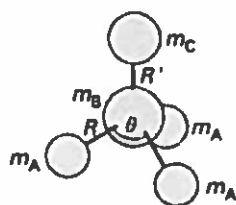
2. Linear rotors

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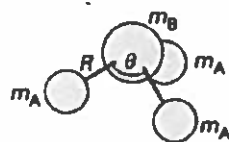$$- \frac{(m_A R - m_C R')^2}{m}$$

$$I = 2m_A R^2$$

3. Symmetric rotors

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

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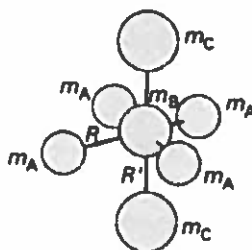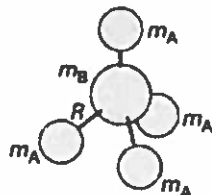

$$I_{\parallel} = 2m_A R^2 (1 - \cos \theta)$$

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

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

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

4. Spherical rotors

$$I = \tfrac{8}{3} m_A R^2$$
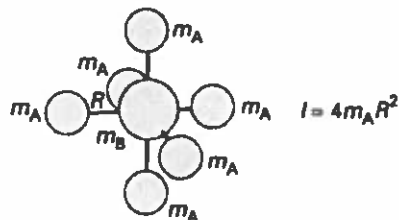
$$I = 4m_A R^2$$

† In each case m is the total mass of the molecule.

Most molecules radiate via electric dipole transitions meaning $\langle \psi_i | \hat{\mu}_e | \psi_f \rangle \neq 0$

For this matrix element to be non-zero,

$\mu_e \neq 0$ Permanent Electric Dipole Moment

Examples:

H_2

Symmetric

$\mu_e = 0$

CH_4

Symmetric (Tetrahedral)
$\mu_e = 0$

CO Center of mass

"Asymmetric"

$\mu_e = 0.11 \, D$
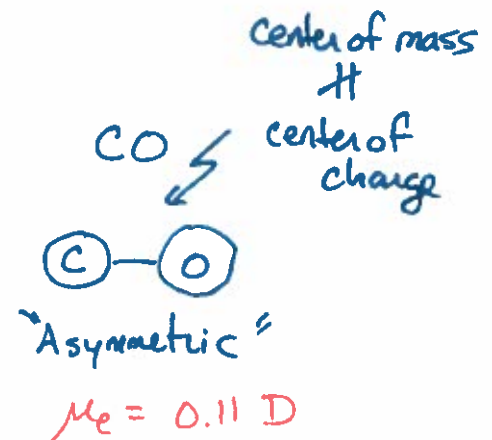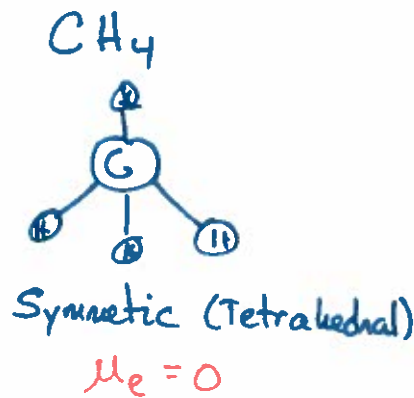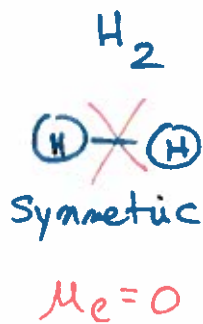
Typical values of $\mu_e = 1 \text{ Debye} = 10^{-18} \text{ esu} \cdot \text{cm}$

Note $\vec{\mu}_e$ is a vector and in general, we need to figure out which orientation $\vec{\mu}_e$ has to determine selection rules for transitions.

The Rigid Rotar

$$m_1 \overset{R}{\text{—}} m_2$$

$$R = \text{CONST}$$

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

$$\hat{H} \psi = E \psi$$

$$H = T + V \qquad \text{set } V = 0 \left(\begin{array}{l} \text{Real molecules} \\ \text{have } V(r) \end{array} \right)$$

$$T = \frac{1}{2} \frac{J^2}{I} \leftarrow \text{angular momentum}$$

$$\Rightarrow \hat{H} \psi = \frac{1}{2} \frac{\hat{J}^2}{I} \psi = E \psi \qquad \psi_{rot} \sim Y_{J M_J}(\theta, \phi)$$

$$\text{so} \quad E = \frac{1}{2I} \cdot \hbar^2 J(J+1) \quad \Longleftarrow \begin{array}{l} \text{Note that} \\ \text{spacing of energy} \\ \text{levels } E \sim \dfrac{J^2}{I} \end{array}$$

Define B such that $E = hB J(J+1)$

$$\underset{\text{"Rotational Constant"}}{\uparrow} \qquad\qquad B = \frac{h}{8\pi^2 I}$$

$$\nu_{J+1 \to J} = \frac{E_{J+1} - E_J}{h} = B \left[(J+1)(J+2) - J(J+1) \right]$$

$$= B\left[\cancel{J^2} + 3J + 2 - \cancel{J^2} - J \right]$$

$$= B \left[2J + 2 \right]$$

$$= 2B(J+1) \quad \text{Linear w/ } J \, !$$

Selection Rules $|\langle \psi_i | \hat{\mu}_c | \psi_p \rangle| \neq 0$ when $\Delta J = \pm 1$
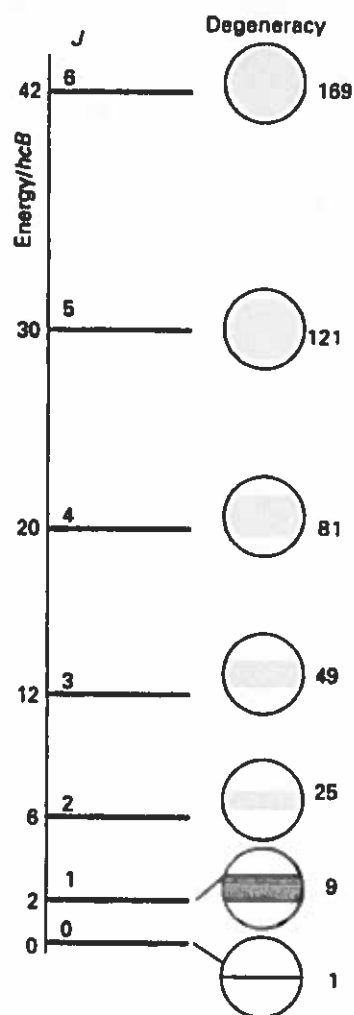
Fig. 10.5 The rotational energy levels and their degeneracies of a spherical rotor. Note the very rapid increase in degeneracy (which at high values of J is proportional to J^2).

Now the main contribution (the term proportional to J^2) comes from the moment of inertia about the figure axis. The perpendicular component continues to contribute because the component of angular momentum about the figure axis is always less than the magnitude of the angular momentum, so even if $|K| = J$, the molecule continues to rotate at least slowly around the perpendicular axis.

There are two special cases that we need to consider. A **spherical rotor** is a rigid molecule that belongs to a cubic (tetrahedral and octahedral) or icosahedral point group. Such molecules have all three moments of inertia equal, so $A = B$. It follows that

$$F(J,K,M_J) = BJ(J+1) \tag{18}$$

and the energy of the molecule is independent of both K and M_J. However, as both quantum numbers are still needed to specify the angular momentum of the molecule, each level is now $(2J+1)^2$-fold degenerate (Fig. 10.5). The K-degeneracy reflects the fact that it is immaterial what component the angular momentum has on the now arbitrary molecular z-axis. A **linear rotor** is a rigid linear molecule, one that belongs to the point group $C_{\infty v}$ or $D_{\infty h}$. In such molecules, the angular momentum vector is necessarily perpendicular to the axis of the molecule, and so $K \equiv 0$ in all states. Substitution of this value in eqn 10.15 gives

$$F(J,M_J) = BJ(J+1) \tag{19}$$

This equation resembles the last one, but note that K does not appear in the specification of the state as it is identically zero. One implication of the absence of K is that the degeneracy of a linear rotor is only $g_J = 2J + 1$, for now only M_J can range over a series of values and K is fixed at zero (Fig. 10.6).

10.4 Centrifugal distortion

The treatment of a molecule as a rigid rotor is only an approximation. As the degree of rotational excitation increases, the bonds are put under stress and are stretched. The increase in moment of inertia that accompanies this **centrifugal distortion** results in a lowering of the rotational constants, and so the energy levels are less far apart at high J than expected on the basis of the rigid rotor assumption. We shall now show that a first approximation to the effect of centrifugal distortion on the energy levels of a linear rotor is obtained by writing

$$F(J,M_J) = BJ(J+1) - DJ^2(J+1)^2 \tag{20}$$

where D, which is called the **centrifugal distortion constant**, depends on the stiffness of the bonds.

Consider a diatomic molecule of reduced mass μ (see eqn 10.10). If it is rotating at an angular velocity ω, it will experience a centrifugal force of magnitude $\mu R \omega^2$ that tends to stretch the bond. A bond acts like a spring, and the restoring force obeys Hooke's law to a good approximation, that it is proportional to the displacement from equilibrium, R_0; the magnitude of this restoring force is written $k(R - R_0)$ where k is the force constant (this molecular parameter will figure in the discussion of molecular vibrations later in the chapter). At equilibrium the centrifugal and restoring forces are in balance, and from the
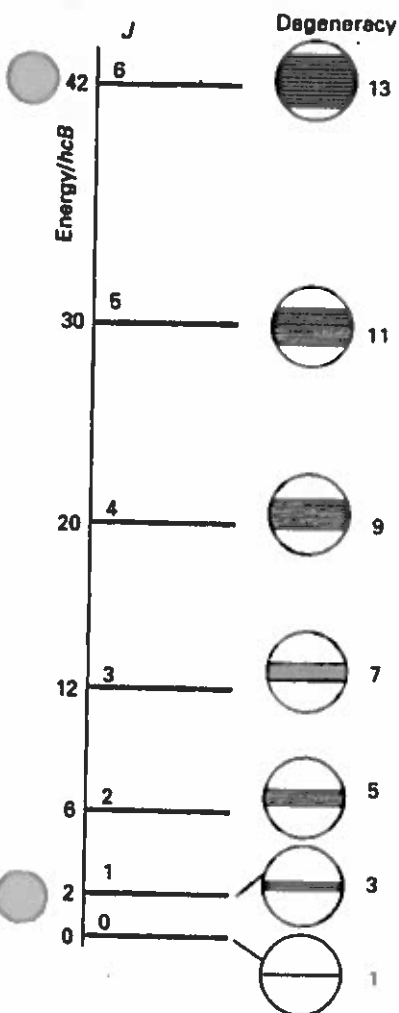
Fig. 10.6 The rotational energy levels and their degeneracies of a linear rotor. Note that the degeneracy increases more slowly (at high values of J the number is proportional to J) than for a spherical rotor, and the rotational states are much more sparse.

condition

$$\mu R \omega^2 = k(R - R_0)$$

we can deduce that

$$R = \frac{kR_0}{k - \mu\omega^2} \approx R_0\left(1 + \frac{\mu\omega^2}{k}\right)$$

This approximation holds for $\mu\omega^2/k \ll 1$, which corresponds to small d ments $(R - R_0 \ll R_0)$. The classical hamiltonian for the molecule is

$$H = \frac{J^2}{2\mu R^2} + \tfrac{1}{2}k(R - R_0)^2$$

where the first term is the rotational kinetic energy and the second is th tial energy arising from the stretching of the bond (recall that $F = -dV$ follows from the introduction of eqn 10.21 into this equation and the $J = \mu R^2 \omega$ that

$$H = \frac{J^2}{2\mu R^2} + \frac{J^4}{2k\mu^2 R^6}$$

Now we confine attention to small displacements and use eqn 10.22 in t

$$\frac{1}{R^2} = \frac{1}{R_0^2}\left(1 - \frac{\mu\omega^2}{k}\right)^2 \approx \frac{1}{R_0^2}\left(1 - \frac{2\mu\omega^2}{k}\right)$$

which, with $J = \mu R^2 \omega$, is equivalent to

$$\frac{1}{R^2} = \frac{1}{R_0^2}\left(1 - \frac{J^2}{k\mu R^4}\right)^2 \approx \frac{1}{R_0^2} - \frac{2J^2}{k\mu R_0^6}$$

With this expression substituted into the first term of eqn 10.23 and R second term approximated by R_0^6, we obtain

$$H \approx \frac{J^2}{2\mu R_0^2} - \frac{J^4}{k\mu^2 R_0^6} + \frac{J^4}{2k\mu^2 R_0^6} = \frac{J^2}{2\mu R_0^2} - \frac{J^4}{2k\mu^2 R_0^6}$$

We can now interpret the J^2 and J^4 terms as operators and immediatel down the eigenvalues:

$$E(J, M_J) \approx \frac{J(J+1)\hbar^2}{2\mu R_0^2} - \frac{J^2(J+1)^2\hbar^4}{2k\mu^2 R_0^6}$$

It follows that the wavenumbers of the rotational terms have the form

$$F(J, M_J) \approx BJ(J+1) - DJ^2(J+1)^2 \qquad D = \frac{\hbar^3}{4\pi kc\mu^2 R_0^6}$$

where D is the centrifugal distortion constant.

The centrifugal distortion constant is larger for molecules with bon have low force constants, for then the centrifugal distortion cause given angular momentum is large. However, because a small force c is often associated with long bond lengths and high reduced mass, the of the latter terms may overcome the effect of changes in k itself.

Fig. 10.3 The physical significance of the quantum numbers J, K, and M_J for a rotating nonlinear molecule.

Fig. 10.4 When $K = 0$ the rotation of the molecule is entirely about an axis that is perpendicular to its figure axis. When K has its maximum value (of J), most of the rotational motion is around the figure axis.

This hamiltonian can be expressed in terms of the operator $J^2 = J_x^2 +$ for the magnitude of the angular momentum, when it becomes

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

It follows that in order to establish the eigenvalues of this hamiltonian need do is to import the eigenvalues of the operators J^2 and J_z, whic established in Chapter 4. It is conventional to use K for the quantum specifying the component of angular momentum on the internal figure a molecule and to reserve M_J for its component on the laboratory fixed Then we can write the eigenvalues of H as

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

with

$$J = 0, 1, 2, \ldots \qquad K = J, J-1, \ldots, -J \qquad M_J = J, J-1, \ldots, -$$

It is important to note that although the component of angular momen the laboratory axis does not appear explicitly in the hamiltonian, it is ne less required to specify the complete angular momentum state of the m (Fig. 10.3). Its absence from the expression for E is consistent with the fa in the absence of external fields, the energy of the molecule is indepen the orientation of its angular momentum in space. The significance quantum number K is that it tells us how the total angular momentum molecule is distributed over the molecular axes: when $|K| \approx J$, then alm whole of the molecule's angular momentum is around its figure axis (Fig. if $|K| \approx 0$, then most of its angular momentum is about an axis perpendic the figure axis. Note that the energy depends on K^2, so the energy is indepe of the direction of rotation about the figure axis, as is physically plausib

It is a further convention in the discussion of molecular rotation to e: the energy in terms of the rotational constants A and B:

$$A = \frac{\hbar}{4\pi c I_\parallel} \qquad B = \frac{\hbar}{4\pi c I_\perp}$$

Then, with $E(J, K, M_J) = hcF(J, K, M_J)$, where F is a wavenumber,

$$F(J, K, M_J) = BJ(J+1) + (A-B)K^2$$

The degeneracy of each level with $K \neq 0$ is $g_J = 2(2J+1)$, because M take $2J+1$ different values for a given value of J, and K can be either po or negative. If $K = 0$, $g_J = 2J+1$ because K then has only a single $\vee$ When $K = 0$, the motion is entirely around an axis perpendicular t figure axis, and

$$F(J, 0, M_J) = BJ(J+1)$$

As expected, the energy of rotation now depends solely on the mome inertia about that perpendicular axis. When $|K| = J$, its maximum value,
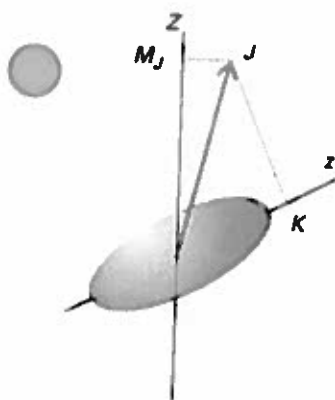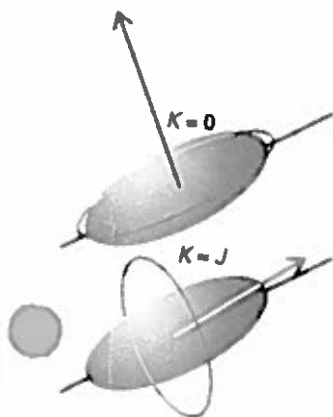
$$F(J, \pm J, M_J) = AJ^2 + BJ$$

Homonuclear Example : H_2

$$\mu_e = 0$$

<u>BuT</u> Electric Quadrupole transitions are allowed

$\langle \psi_i | \hat{Q}_e | \psi_f \rangle \neq 0 \Rightarrow \Delta J = \pm 2$

E/k

~512K ———————————— J = 2
                              para

         28 μm

171 K ———————————— J = 1
                              ortho

0 K ———————————— J = 0
                              para

Common misconception is
that H_2 does not radiate
easily because $\mu_e = 0$.
Not true!

$A_{EQ} \sim \nu^5$ and because

H_2 is small and light

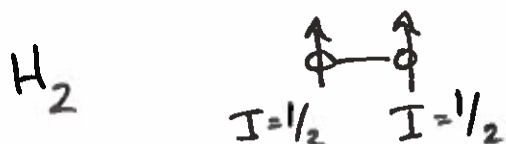$\Rightarrow E \sim \frac{1}{I}$ is widely spaced

and ν J=2→0 is high

A_{2-0} for H_2 is only 3 orders of magnitude smaller

than A_{1-0} for CO!

Real reason is Boltzmann : $\dfrac{n_{J=2}}{n_{J=0}} = \dfrac{g_{J=2}}{g_{J=0}} \cdot e^{-512K/T}$

In 10 K gas, H_2 J=2 is <u>not</u> <u>collisionally</u> <u>excited</u>.

Spin Statistics

H_2 $\updownarrow \quad \hat{\phi}$
     $I = 1/2 \quad I = 1/2$

Interchange of identical $I = 1/2$ nuclei
obey Fermi-Dirac statistics

$$\hat{P}(\Psi_{tot}) = -\Psi_{tot}$$

$$\Psi_{tot} = \Psi_{electronic} \; \Psi_{vib.} \; \Psi_{rot} \; \Psi_{nuc}$$

$\hat{P}(\Psi_{elec}) = +$ for $^1\Sigma^+$ electronic state

$\hat{P}(\Psi_{vib}) = +$ for $v = 0$ $\left[1^{st} \text{ Hermite polynomial is symmetric} \atop \hat{P} \sim (-1)^v \right]$

$\Psi_{nuc} = \begin{cases} |\uparrow\uparrow\rangle & \text{Symmetric} \\ |\downarrow\downarrow\rangle & \text{Symmetric} \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) & \text{Symmetric} \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) & \text{Anti-symmetric} \end{cases}$ $\hat{P}(\Psi_{rot}) = -$ "ORTHO"

$\Rightarrow \hat{P}(\Psi_{rot}) = +$ "PARA"

$$\hat{P}(\Psi_{rot}) = (-1)^J \quad \text{since} \quad \Psi_{rot} \sim Y_J^{M_J}(\theta, \phi)$$

So

$J = 0, 2, 4 \ldots$ EVEN ARE PARA Levels
$J = 1, 3, 5 \ldots$ ODD ARE ORTHO LEVELS

Note that the Parity of Electric Quadrupole transitions does not change.

- Real molecules have $V(r)$

  Solutions by Dunham $\Rightarrow$ Dunham coefficients.

  A popular parametrization is an angular (see Townes & Schawlow)
  momentum expansion

$$\nu = BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3 \cdots$$

$\underbrace{}$ Centrifugal distortion

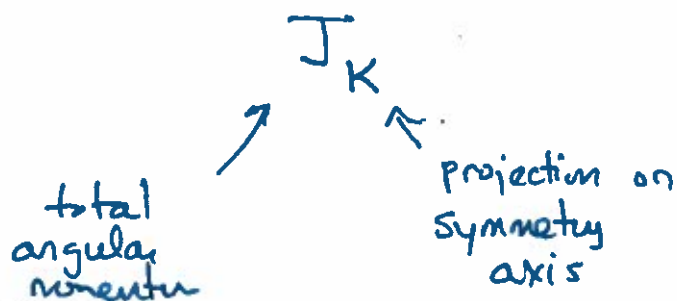$\uparrow$ sextant distortion constant etc.

Symmetric Tops

Classical Problem:

Constants of motion are

① TOTAL angular momentum

② Proj. onto top symmetry axis

Quantum Problem

① 2 "good" quantum numbers

$$J_K$$

$\nearrow$ total angular momentu

$\nwarrow$ projection on symmetry axis

- Obviously $K \leq J$

  $N.B.$ There are 2 projections of J onto axis: $\pm K$ which are degenerate!

$$|\langle \psi_i | \hat{\mu_e} | \psi_f \rangle| \neq 0 \Rightarrow \Delta J = 0, \pm 1 \quad \underline{\Delta K = 0}$$