22.4.4: iv. Problem Solutions

Q1
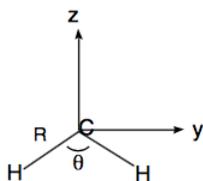
Molecule I	Molecule II	
$R_{CH} = 1.121$Å	$R_{CH} = 1.076$Å	(22.4.4.1)(22.4.4.2)
$\angle_{HCH} = 104°$	$\angle_{HCH} = 136°$	(22.4.4.3)
$y_H = \text{R Sin}\left(\dfrac{\theta}{2}\right) = \pm 0.8834$	$y_H = \pm 0.9976$	(22.4.4.4)
$z_H = \text{R Cos}\left(\dfrac{\theta}{2}\right) = -0.2902$	$z_H = -0.4031$	(22.4.4.5)
Center of Mass(COM):	clearly, $X = Y = 0$,	(22.4.4.6)
$Z = \dfrac{12(0) - 2\text{RCos}\left(\dfrac{\theta}{2}\right)}{14} = -0.0986$	$Z = -0.0576$	(22.4.4.7)

a.

$$I_{xx} = \sum_j m_j(y_j^2 + z_j^2) - M(Y^2 + Z^2) \tag{22.4.4.8}$$

$$T_{xy} = -\sum_j m_j x_j y_j - MXY \tag{22.4.4.9}$$

$I_{xx} = 2(1.121)^2 - 14(-0.0986)^2$	$I_{xx} = 2(1.076)^2 - 14(-0.0576)^2$	(22.4.4.10)
$= 2.377$	$= 2.269$	(22.4.4.11)
$I_{yy} = 2(0.6902)^2 - 14(-0.0986)^2$	$I_{yy} = 2(0.4031)^2 - 14(-0.0576)^2$	(22.4.4.12)
$= 0.8167$	$= 0.2786$	(22.4.4.13)
$I_{zz} = 2(0.8834)^2$	$I_{zz} = 2(0.9976)^2$	(22.4.4.14)
$= 1.561$	$= 1.990$	(22.4.4.15)
$I_{xz} = I_{yz} = I_{xy} = 0$		(22.4.4.16)

b. Since the moment of inertia tensor is already diagonal, the principal moments of inertia have already been determined to be

$(I_a \langle I_b \langle I_c):$		(22.4.4.17)
$I_{yy}\langle I_{zz} \langle I_{xx}$	$I_{yy}\langle I_{zz} \langle I_{xx}$	(22.4.4.18)
$0.8167\langle 1.561\langle 2.377$	$0.2786\langle 1.990\langle 2.269$	(22.4.4.19)

Using the formula: $A = \dfrac{h}{8\pi^2 c I_a} = \dfrac{6.62x10^{-27}}{8\pi^2(3x10^{10})I_a}$

$$A = \frac{16.84}{I_a}\,\text{cm}^{-1}$$

similarly, $B = \cdot\ \text{cm}^{-1}$, and $C = \frac{16.84}{I_c}\ \text{cm}^{-1}$.

So,

	Molecule I	Molecule II	
			(22.4.4.20)
	$y \Rightarrow A = 20.62$	$y \Rightarrow A = 60.45$	(22.4.4.21)
	$z \Rightarrow B = 10.79$	$z \Rightarrow B = 8.46$	(22.4.4.22)
	$x \Rightarrow C = 7.08$	$x \Rightarrow C = 7.42$	(22.4.4.23)

c. Averaging B + C:

$$B = B\frac{B+C}{2} = 8.94 \qquad B = \frac{B+C}{2} = 7.94 \tag{22.4.4.24}$$

$$A - B = 11.68 \qquad\qquad A - B = 52.51 \tag{22.4.4.25}$$

Using the Prolate top formula

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

	Molecule I	Molecule II	
			(22.4.4.26)
	$E = 11.68K^2 + 8.94J(J+1)$	$E = 52,51K^2 + 7.94J(J+1)$	(22.4.4.27)

Levels: J = 0,1,2,... and K = 0,1, ... J
For a given level defined by J and K, there are M_J degeneracies given by: (2J + 1)x

$$\left\{ \begin{array}{l} 1 \text{ for K} = 0 \\ 2 \text{ for K} \neq 0 \end{array} \right\} \tag{22.4.4.28}$$

d.

Molecule I		Molecule II
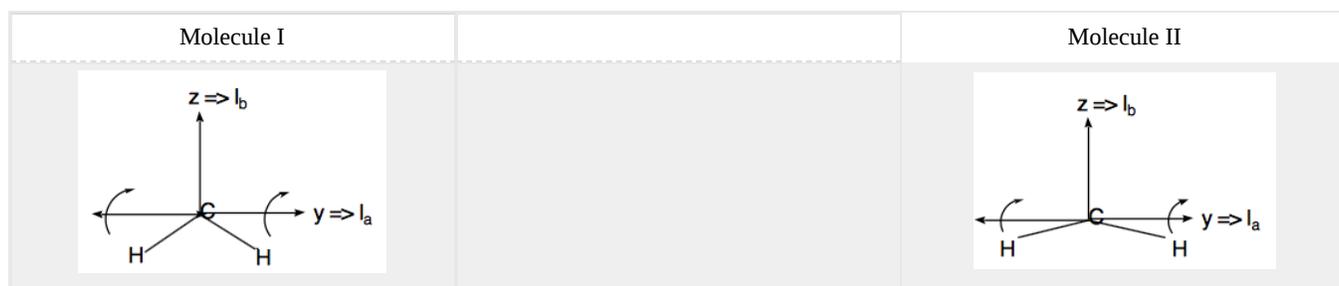
e. Since $\vec{\mu}$ is along Y, $\Delta K = 0$ since K describes rotation about the y axis.
Therefore $\Delta J = \pm 1$
f. **Assume** molecule I is CH_2^- and molecule II is CH_2. Then, $\Delta E = E_{J_j}(CH_2)$, where:
$E(CH_2) = 52.51K^2 + 7.94J(J+1)$, and $E(CH_2) = 11.68K^2 + 8.94J(J+1)$
For R-branches: $J_j = J_i + 1, \Delta K = 0$;

$$\begin{aligned} \Delta E_R &= E_{J_j}(CH_2) - E_{J_i}(CH_2) & (22.4.4.29) \\ &= 7.94(J_i+1)(J_i+1+1) - 8.94J_i(J_i+1) & (22.4.4.30) \\ &= (J_i+1)\{7.94(J_i+1+1) - 8.94J_i\} & (22.4.4.31) \\ &= (J_i+1)\{(7.94-8.94)J_i + 2(7.94)\} & (22.4.4.32) \\ &= (J_i+1)\{-J_i + 15.88\} & (22.4.4.33) \end{aligned}$$

For P-branches: $J_j - 1, \Delta K = 0$;

$$\begin{aligned} \Delta E_P &= E_{J_j}(CH_2) - E_{J_i}(CH_2) & (22.4.4.34) \\ &= 7.94(J_i-1)(J_i-1+1) - 8.94J_i(J_i+1) & (22.4.4.35) \\ &= J_i\{7.94(J_i-1) - 8.94(J_i+1)\} & (22.4.4.36) \\ &= J_i\{(7.94-8.94)J_i - 7.94 - 8.94\} & (22.4.4.37) \\ &= J_i\{-J_i - 16.88\} & (22.4.4.38) \end{aligned}$$

This indicates that the R branch lines occur at energies which grow closer and closer together as J increases (since the 15.88 - J_i term will cancel). The P branch lines occur at energies which lie more and more negative (i.e. to the left of the origin). So, you can predict that if molecule I is CH_2^- and molecule II is CH_2 then the R-branch has a band head and the P-branch does not. This is observed therefore our assumption was correct:

molecule I is CH_2^- and molecule II is CH_2.

g. The band head occurs when $\dfrac{d(\Delta E_R)}{dJ} = 0$.

$$\begin{aligned} \frac{d(\Delta E_R)}{dJ} &= \frac{d}{dJ}[(J_i+1)\{-J_i+15.88\}] = 0 & (22.4.4.39) \\ &= \frac{d}{dJ}\left(-J_i^2 - J_i + 15.88J_i + 15.88\right) = 0 & (22.4.4.40) \\ &= -2J_i + 14.88 = 0 & (22.4.4.41) \\ \therefore\quad & J_i = 7.44, \text{ so } J = 7 \text{ or } 8. & (22.4.4.42) \end{aligned}$$

At J = 7.44:

$$\begin{aligned} \Delta E_R &= (J+1)\{-J+15.88\} & (22.4.4.43) \\ \Delta E_R &= (7.44+1)\{-7.44+15.88\} = (8.44)(8.44) = 71.2\text{cm}^{-1}\text{above the origin.} & (22.4.4.44) \end{aligned}$$

Q2

a.

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2,z^2
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R_x,R_y)	(xz,yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		(x^2-y^2,xy)
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x,y)	
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		
$\Gamma_{C\text{-}H}$	6	0	0	0	0	2	0	0	0	6	2	0		

b. The number of irreducible representations may be found by using the following formula:

$$n_{irrep} = \frac{1}{g}\sum_R \xi_{red}(R)\xi_{irrep}(R), \tag{22.4.4.45}$$

$$\text{where } g = \text{the order of the point group (24 for } D_{6h}). \tag{22.4.4.46}$$

$$n_{A_{1g}} = \frac{1}{24}\sum_R \Gamma_{C-H}(R)\dot{A}_{1g}(R) \tag{22.4.4.47}$$

$$= \frac{1}{24}\{(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1)+\ldots \tag{22.4.4.48}$$

$$+(3)(0)(1)+(3)(2)(1)+(1)(0)(1)+(2)(0)(1)+\ldots \tag{22.4.4.49}$$

$$+(2)(0)(1)+(1)(6)(1)+(3)(2)(1)+(3)(0)(1)\} \tag{22.4.4.50}$$

$$= 1 \tag{22.4.4.51}$$

$$n_{A_{2g}} = \frac{1}{24}\{(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1)+\ldots \tag{22.4.4.52}$$

$$+(3)(0)(-1)+(3)(2)(-1)+(1)(0)(1)+(2)(0)(1)+\ldots \tag{22.4.4.53}$$

$$+(2)(0)(1)+(1)(6)(1)+(3)(2)(-1)+(3)(0)(-1)\} \tag{22.4.4.54}$$

$$= 0 \tag{22.4.4.55}$$

$$n_{B_{1g}} = \frac{1}{24}\{(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1)+\ldots \tag{22.4.4.56}$$

$$+(3)(0)(1)+(3)(2)(-1)+(1)(0)(1)+(2)(0)(-1)+\ldots \tag{22.4.4.57}$$

$$+(2)(0)(1)+(1)(6)(-1)+(3)(2)(1)+(3)(0)(-1)\} \tag{22.4.4.58}$$

$$= 0 \tag{22.4.4.59}$$

$$n_{B_{2g}} = \frac{1}{24}\{(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1)+\ldots \tag{22.4.4.60}$$

$$+(3)(0)(-1)+(3)(2)(1)+(1)(0)(1)+(2)(0)(-1)+\ldots \tag{22.4.4.61}$$

$$+(2)(0)(1)+(1)(6)(-1)+(3)(2)(-1)+(3)(0)(1)\} \tag{22.4.4.62}$$

$$= 0 \tag{22.4.4.63}$$

$$n_{E_{1g}} = \frac{1}{24}\{(1)(6)(2)+(2)(0)(1)+(2)(0)(-1)+(1)(0)(-2)+\ldots \tag{22.4.4.64}$$

$$+(3)(0)(0)+(3)(2)(0)+(1)(0)(2)+(2)(0)(1)+\ldots \tag{22.4.4.65}$$

$$+(2)(0)(-1)+(1)(6)(-2)+(3)(2)(0)+(3)(0)(0)\} \tag{22.4.4.66}$$

$$= 0 \tag{22.4.4.67}$$

$$n_{E_{2g}} = \frac{1}{24}\{(1)(6)(2)+(2)(0)(-1)+(2)(0)(-1)+(1)(0)(2)+\ldots \tag{22.4.4.68}$$

$$+(3)(0)(0)+(3)(2)(0)+(1)(0)(2)+(2)(0)(-1)+\ldots \tag{22.4.4.69}$$

$$+(2)(0)(-1)+(1)(6)(2)+(3)(2)(0)+(3)(0)(0)\} \tag{22.4.4.70}$$

$$= \quad 0 \tag{22.4.4.71}$$

$$n_{A_{1u}} = \quad \frac{1}{24}\{(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1)+\ldots \tag{22.4.4.72}$$

$$+(3)(0)(1)+(3)(2)(1)+(1)(0)(-1)+(2)(0)(-1)+\ldots \tag{22.4.4.73}$$
$$+(2)(0)(-1)+(1)(6)(-1)+(3)(2)(-1)+(3)(0)(-1)\} \tag{22.4.4.74}$$

$$= \quad 0 \tag{22.4.4.75}$$

$$n_{A_{2u}} = \quad \frac{1}{24}\{(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1)+\ldots \tag{22.4.4.76}$$

$$+(3)(0)(-1)+(3)(2)(-1)+(1)(0)(-1)+(2)(0)(-1)+\ldots \tag{22.4.4.77}$$
$$+(2)(0)(-1)+(1)(6)(-1)+(3)(2)(1)+(3)(0)(1)\} \tag{22.4.4.78}$$

$$= \quad 0 \tag{22.4.4.79}$$

$$n_{B_{1u}} = \quad \frac{1}{24}\{(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1)+\ldots \tag{22.4.4.80}$$

$$+(3)(0)(1)+(3)(2)(-1)+(1)(0)(-1)+(2)(0)(1)+\ldots \tag{22.4.4.81}$$
$$+(2)(0)(-1)+(1)(6)(1)+(3)(2)(-1)+(3)(0)(1)\} \tag{22.4.4.82}$$

$$= \quad 0 \tag{22.4.4.83}$$

$$n_{B_{2u}} = \quad \frac{1}{24}\{(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1)+\ldots \tag{22.4.4.84}$$

$$+(3)(0)(-1)+(3)(2)(1)+(1)(0)(-1)+(2)(0)(1)+\ldots \tag{22.4.4.85}$$
$$+(2)(0)(-1)+(1)(6)(1)+(3)(2)(1)+(3)(0)(-1)\} \tag{22.4.4.86}$$

$$= \quad 1 \tag{22.4.4.87}$$

$$n_{E_{1u}} = \quad \frac{1}{24}\{(1)(6)(2)+(2)(0)(1)+(2)(0)(-1)+(1)(0)(-2)+\ldots \tag{22.4.4.88}$$

$$+(3)(0)(0)+(3)(2)(0)+(1)(0)(-2)+(2)(0)(-1)+\ldots \tag{22.4.4.89}$$
$$+(2)(0)(1)+(1)(6)(2)+(3)(2)(0)+(3)(0)(0)\} \tag{22.4.4.90}$$

$$= \quad 1 \tag{22.4.4.91}$$

$$n_{E_{2u}} = \quad \frac{1}{24}\{(1)(6)(2)+(2)(0)(-1)+(2)(0)(-1)+(1)(0)(2)+\ldots \tag{22.4.4.92}$$

$$+(3)(0)(0)+(3)(2)(0)+(1)(0)(-2)+(2)(0)(1)+\ldots \tag{22.4.4.93}$$
$$+(2)(0)(1)+(1)(6)(-2)+(3)(2)(0)+(3)(0)(0)\} \tag{22.4.4.94}$$

$$= \quad 0 \tag{22.4.4.95}$$

We see that $\Gamma_{C-H} = A_{1g} \oplus E_{2g} \oplus B_{2u} \oplus E_{1u}$

c. x and y $\Rightarrow E_{1u}$, z $\Rightarrow A_{2u}$, so, the ground state A_{1g} level can be excited to the degenerate E_{1u} level by coupling through the x or y transition dipoles. Therefore E_{1u} is infrared active and $\perp$ polarized.

d. $(x^2 + y^2, z^2) \Rightarrow A_{1g}, (xz, yz) \Rightarrow E_{1g}, (x^2 - y^2, xy) \Rightarrow E_{2g}$, so, the ground sate A_{1g} level can be excited to the degenerate E_{2g} level by coupling through the $x^2 - y^2$ or xy transitions or be excited to the degenerate A_{1g} level by coupling through the xz or yz transitions. Therefore A_{1g} and E_{2g} are Raman active.

Q3

a.

$$\frac{d}{dr}\left(\frac{F}{r}\right) = \quad \frac{F'}{r} - \frac{F}{r^2} \tag{22.4.4.96}$$

$$r^2\frac{d}{dr}\left(\frac{F}{r}\right) = \quad rF' - F \tag{22.4.4.97}$$

$$\frac{d}{dr}\left(r^2\frac{d}{dr}\left(\frac{F}{r}\right)\right) = \quad F' - F' + rF'' \tag{22.4.4.98}$$

So,

$$\frac{-\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\left(\frac{F}{r}\right)\right) = \frac{-\hbar^2}{2\mu}\frac{F''}{r}$$

Rewriting the radial Schrödinger equation with the substitution: $R = \dfrac{F}{r}$ gives:

$$\frac{-h^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d(Fr^{-1})}{dr}\right) + \frac{J(J+1)\hbar^2}{2\mu r^2}\left(\frac{F}{r}\right) + \frac{1}{2}k(r-r_e)^2\left(\frac{F}{r}\right) = \left(\frac{F}{r}\right)$$

Using the above derived identity gives:

$$\frac{-\hbar^2}{2\mu}\frac{F''}{r} + \frac{J(J+1)\hbar^2}{2\mu r^2}\left(\frac{F}{r}\right) + \frac{1}{2}k(r-r_e)^2\left(\frac{F}{r}\right) = E\left(\frac{F}{r}\right)$$

Cancelling out an r^{-1}:

$$\frac{-\hbar^2}{2\mu}F'' + \frac{J(J+1)\hbar^2}{2\mu r^2}F + \frac{1}{2}k(r-r_e)^2 F = EF$$

b.

$$\frac{1}{r^2} = \frac{1}{(r_e+\Delta r)^2} = \frac{1}{r_e^2\left(1+\dfrac{\Delta r}{r_e}\right)} \approx \frac{1}{r_e^2}\left(1 - \frac{2\Delta r}{r_e} + \frac{3\Delta r^2}{r_e^2}\right)$$

So,

$$\frac{J(J+1)\hbar^2}{2\mu r^2} \approx \frac{J(J+1)\hbar^2}{2\mu r_e^2}\left(1 - \frac{2\Delta r}{r_e} + \frac{3\Delta r^2}{r_e^2}\right)$$

c. Using this substitution we now have:

$$\frac{-\hbar^2}{2\mu}F'' + \frac{J(J+1)\hbar^2}{2\mu r_e^2}\left(1 - \frac{2\Delta r}{r_e} + \frac{3\Delta r^2}{r_e^2}\right)F + \frac{1}{2}k(r-r_e)^2 F = EF$$

Now, regroup the terms which are linear and quadratic in $\Delta r = r - r_e$:

$$\frac{1}{2}k\Delta r^2 + \frac{J(J+1)\hbar^2}{2\mu r_e^2}\frac{3}{r_e^2}\Delta r^2 - \frac{J(J+1)\hbar^2}{2\mu r_e^2}\frac{2}{r_e}\Delta r$$

$$= \left(\frac{1}{2}k + \frac{J(J+1)\hbar^2}{2\mu r_e^2}\frac{3}{r_e^2}\right)\Delta r^2 - \left(\frac{J(J+1)\hbar^2}{2\mu r_e^2}\frac{2}{r_e}\right)\Delta r$$

Now, we must complete the square:

$$a\Delta r^2 - b\Delta r = a\left(\Delta r - \frac{b}{2a}\right)^2 - \frac{b^2}{4a}.$$

So,

$$\left(\frac{1}{2}k + \frac{J(J+1)\hbar^2}{2\mu r_e^2}\frac{3}{r_e^2}\right)\left(\Delta r - \frac{\dfrac{J(J+1)\hbar^2}{2\mu r_e^2}\dfrac{1}{r_e}}{\dfrac{1}{2}k + \dfrac{J(J+1)\hbar^2}{2\mu r_e^2}\dfrac{3}{r_e^2}}\right)^2 - \frac{\left(\dfrac{J(J+1)\hbar^2}{2\mu r_e^2}\dfrac{1}{r_e}\right)^2}{\dfrac{1}{2}k + \dfrac{J(J+1)\hbar^2}{2\mu r_e^2}\dfrac{3}{r_e^2}}$$

Now, redefine the first term as $\frac{1}{2}k$, second term as $(r - \bar{r}_e)^2$, and the third term as $-\Delta$ giving:

$$\frac{1}{2}\bar{k}(r - \bar{r}_e)^2 - \Delta$$

From:

$$\frac{-\hbar^2}{2\mu}F'' + \frac{J(J+1)\hbar^2}{2\mu r_e^2}\left(1 - \frac{2\Delta r}{r_e} + \frac{3\Delta r^2}{r_e^2}\right)F + \frac{1}{2}k(r - r_e)^2 F = EF, \qquad (22.4.4.100)$$

$$\frac{-\hbar^2}{2\mu}F'' + \frac{J(J+1)\hbar^2}{2\mu r_e}F + \left(\frac{J(J+1)\hbar^2}{2\mu r_e^2}\left(-\frac{2\Delta r}{r_e} + \frac{3\Delta r^2}{r_e^2}\right) + \frac{1}{2}k\Delta r^2\right)F = EF \qquad (22.4.4.101)$$

and making the above substitution result in:

$$\frac{-\hbar^2}{2\mu}F'' + \frac{J(J+1)\hbar^2}{2\mu r_e^2}F + \left(\frac{1}{2}\bar{k}(r - \bar{r}_e)^2 - \Delta\right)F = EF,$$

or,

$$\frac{-\hbar^2}{2\mu}F'' + \frac{1}{2}\bar{k}(r - r\bar{r}_e)^2 F = \left(E - \frac{J(J+1)\hbar^2}{2\mu r_e^2} + \Delta\right)F.$$

d. Since the above is nothing but a harmonic oscillator differential equation in x with force constant $\bar{k}$ and equilibrium bond length $\bar{r}_e$, we know that:

$$\frac{-\hbar^2}{2\mu}F'' + \frac{1}{2}\bar{k}(r - \bar{r}_e)^2 F \varepsilon F, \text{ has energy levels:} \qquad (22.4.4.102)$$

$$\varepsilon = \hbar\sqrt{\frac{\bar{k}}{\mu}}\left(v + \frac{1}{2}\right), \text{ v} = 0, 1, 2, \ldots \qquad (22.4.4.103)$$

So,

$$E + \Delta. - \frac{J(J+1)\hbar^2}{2\mu r_e^2} = \varepsilon \qquad (22.4.4.104)$$

tell us that:

$$E = \hbar\sqrt{\frac{\bar{k}}{\mu}}\left(v+\frac{1}{2}\right) + \frac{J(J+1)\hbar^2}{2\mu r_e^2} - \Delta. \tag{22.4.4.105}$$

As J increases, $\bar{r}_e$ increases because of the centrifugal force pushing the two atoms apart. On the other hand $\bar{k}$ increases which inicates that the molecule finds it more difficult to stretch against both the centrifugal and Hooke's Law (spring) Harmonic force field. The total energy level (labeled by J and v) will equal a rigid rotor componenet $\dfrac{J(J+1)\hbar^2}{2\mu r_e^2}$ plus a Harmonic oscillator part $\hbar\sqrt{\dfrac{\bar{k}}{\mu}}\left(v+\dfrac{1}{2}\right)$ (which has a force constant $\bar{k}$ which increases with J).