Chemistry 562 **Spring 2012**

Problem Set 5

Due beginning of class on Friday, February 24th

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

1. (a) For a particle with an angular momentum quantum number l=3, work out the magnitude of the angular moment (L) and of its possible projections ($L_z \equiv l_z$) onto the z-axis in units of $\hbar$. Give the angle from the z-axis for the possible values of the projections and sketch a diagram.

   (b) Could we know the projection of L onto the y-axis ($L_y \equiv l_y$) simultaneously with L and L_z? Explain by calculating the commutator.

   (c) Can we know both of the projections onto the l_y and l_x axes? Explain by calculating the commutator.

   (d) Confirm that the wave function for m_l=0 satisfies the Schrödinger equation and find its energy.

2. What is the degeneracy of J=0 and J=1 for a linear, symmetric, and spherical rotor? For each rotor, give the complete set of quantum numbers for each state. (Each state should have a unique set of quantum numbers.)

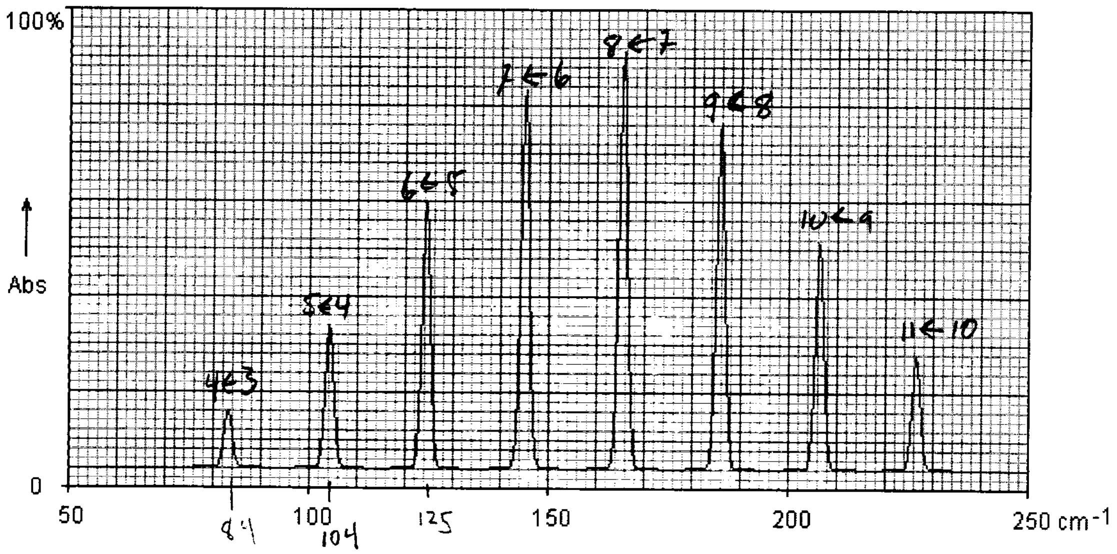
3. (a) What are the selection rules for a pure rotational transition?

   (b) Write the x, y and z components of the transition dipole operator for pure rotations in spherical harmonics.

   (c) Mathematically show that the light-induced transition between the J=0 and J=2, m_J=0 rotational wavefunctions is not allowed. (See Further Information 12.2 for help.)

3

4. The rotational spectrum of $H^{35}Cl$ is shown below.



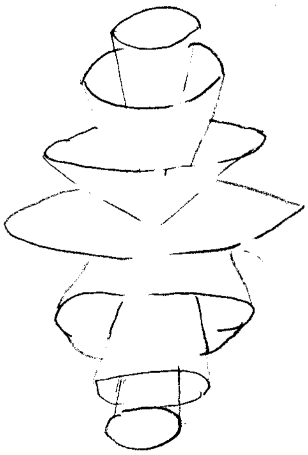
1 (a) Label each peak with the correct transition $J_u \leftarrow J_L$ transition. Note that the first observable transition is $J_u=4 \leftarrow J_L=3$, because the first two transitions are too weak to observe experimentally.

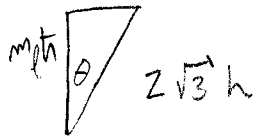
1 (b) Determine a rough value for the rotational constant B for $H^{35}Cl$ from this spectrum. Give your answer in units of cm^{-1}.

1 (c) Calculate the equilibrium bond length for $H^{35}Cl$ in Å from your estimate of B.

1 a) $L = \sqrt{l(l+1)}\,\hbar$ $\quad l=3 \quad L = \sqrt{3(4)}\,\hbar = 2\sqrt{3}\,\hbar$

$l_z = m_l \hbar \qquad l_z = -3, -2, -1, 0, 1, 2, 3$





$\cos\theta_{m_l} = \dfrac{m_l \hbar}{2\sqrt{3}\,\hbar}$

m_l	θ_{m_l}
3	30
2	54.7
1	73.2
0	90
-1	106.8
-2	125.3
-3	150

b) $[\hat{L}_y, \hat{L}_z]\psi = \hat{L}_y \hat{L}_z \psi - \hat{L}_z \hat{L}_y \psi$

$\hat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$

$\hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

$\psi \equiv \psi(x,y,z)$

$[\hat{L}_y, \hat{L}_z]\psi = -\hbar^2\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\psi + \hbar^2\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\psi$

$= -\hbar^2\left(z\frac{\partial}{\partial x} x\frac{\partial}{\partial y}\psi - z\frac{\partial}{\partial x} y\frac{\partial}{\partial x}\psi - x\frac{\partial}{\partial z} x\frac{\partial}{\partial y}\psi + x\frac{\partial}{\partial z} y\frac{\partial}{\partial x}\psi\right)$

$+\hbar^2\left(x\frac{\partial}{\partial y} z\frac{\partial}{\partial x}\psi - x\frac{\partial}{\partial y} x\frac{\partial}{\partial z}\psi - y\frac{\partial}{\partial x} z\frac{\partial}{\partial x}\psi + y\frac{\partial}{\partial x} x\frac{\partial}{\partial z}\psi\right)$

1 b) $$[\hat{L}_y, \hat{L}_z]\psi = -\hbar^2\left(z\left(\frac{\partial x}{\partial x}\frac{\partial \psi}{\partial y} + x\frac{\partial^2\psi}{\partial x\partial y}\right) - zy\frac{\partial^2\psi}{\partial x^2} - x^2\frac{\partial^2\psi}{\partial y\partial z} + xy\frac{\partial^2\psi}{\partial x\partial z}\right) + \hbar^2\left(xz\frac{\partial^2\psi}{\partial x\partial y} - x^2\frac{\partial^2\psi}{\partial y\partial z} - yz\frac{\partial^2\psi}{\partial x^2} + y\left(\frac{\partial x}{\partial x}\frac{\partial\psi}{\partial z} + x\frac{\partial^2\psi}{\partial x\partial z}\right)\right)$$

$$= \hbar^2\left(-z\frac{\partial\psi}{\partial y} \cancel{- xz\frac{\partial^2\psi}{\partial x\partial y}} \cancel{+ zy\frac{\partial^2\psi}{\partial x^2}} \cancel{+ x^2\frac{\partial^2\psi}{\partial y\partial z}} \cancel{- xy\frac{\partial^2\psi}{\partial x\partial z}} \cancel{+ xz\frac{\partial^2\psi}{\partial x\partial y}} \cancel{- x^2\frac{\partial^2\psi}{\partial y\partial z}} \cancel{- yz\frac{\partial^2\psi}{\partial x^2}} + y\frac{\partial\psi}{\partial z} \cancel{+ xy\frac{\partial^2\psi}{\partial x\partial z}}\right) = \hbar^2\left(y\frac{\partial\psi}{\partial z} - z\frac{\partial\psi}{\partial y}\right) = i\hbar\,\frac{\hbar}{i}\left(y\frac{\partial\psi}{\partial z} - z\frac{\partial\psi}{\partial y}\right)$$

$$= i\hbar\hat{L}_x$$

1 c) definition of $x, y,$ and z are arbitrary (except for RHR), so

$$[L_y, L_x] = -i\hbar\hat{L}_z$$

1d) $\hat{H}\psi = E\psi$ $\qquad \psi = Y_{l=3, m_l=0} = \left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta - 3\cos\theta)$

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\right)$$

$$\hat{H}\psi = \frac{-\hbar^2}{2mr^2}\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\left(5\cos^3\theta - 3\cos\theta\right)$$

$$= \frac{-\hbar^2}{2I}\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\left(-5\cdot 3\cos^2\theta\sin\theta + 3\sin\theta\right)$$

$$= \frac{-\hbar^2}{2I}\frac{1}{\sin\theta}\frac{d}{d\theta}\left(-15\cos^2\theta\sin^2\theta + 3\sin^2\theta\right)$$

$$= \frac{-\hbar^2}{2I}\frac{1}{\sin\theta}\frac{d}{d\theta}\left(-15\cos^2\theta + 15\cos^4\theta + 3 - 3\cos^2\theta\right)$$

$$= \frac{-\hbar^2}{2I}\frac{1}{\sin\theta}\left(+30\cos\theta\sin\theta - 60\cos^3\theta\sin\theta + 6\cos\theta\sin\theta\right)$$

$$= \frac{-\hbar^2}{2I}\left(30\cos\theta - 60\cos^3\theta + 6\cos\theta\right) = \frac{+\hbar^2}{2I}\left(60\cos^3\theta - 36\cos\theta\right)$$

$$= \frac{\hbar^2}{2I}\cdot 12\left(5\cos^3\theta - 3\cos\theta\right) = \frac{6\hbar^2}{I}\psi$$

$$E = \frac{6\hbar^2}{I}$$

2) linear

$$\frac{E}{hc} = BJ(J+1)$$

J	K=0	M_L	E	
0	0	0	0	D = 1
1	0	-1	2B	
1	0	0	2B	D = 3
1	0	1	2B	

$$\frac{E}{hc} = BJ(J+1) + (A-B)K^2$$

Symmetric

J	K	M_L	E	
0	0	0	0	D = 1
1	1	0	2B + (A - B)	
1	1	1	2B + (A - B)	
1	1	-1	2B + (A - B)	D = 6
1	-1	0	2B + (A - B)	
1	-1	1	2B + (A - B)	
1	-1	-1	2B + (A - B)	
1	0	0	2B	
1	0	1	2B	D = 3
1	0	-1	2B	

Spherical

$E = BJ(J+1)$

J	K	M_J	E
0	0	0	0
1	-1	-1	2B
1	-1	0	2B
1	-1	1	2B
1	0	-1	2B
1	0	0	2B
1	0	1	2B
1	1	-1	2B
1	1	0	2B
1	1	1	2B

D = 1

D = 9

3) a) $\Delta J = \pm 1$

$\Delta M_J = 0, \pm 1$

b) $\mu_x = \mu_0 \sin\theta \cos\phi$

$\mu_y = \mu_0 \sin\theta \sin\phi$

$\mu_z = \mu_0 \cos\theta \quad \Rightarrow \mu_0 \left(\frac{4\pi}{3}\right)^{1/2} Y_{l=0, m_l=0}$

$Y_{1,1} = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \, e^{+i\phi} \qquad Y_{1,-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \, e^{-i\phi}$

$\cos\phi = \frac{1}{2}(e^{i\phi} + e^{-i\phi})$

$\sin\phi = \frac{-1}{2} i (e^{i\phi} - e^{-i\phi})$

$\sin\theta \cos\phi = \frac{1}{2}\left(-\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \, e^{i\phi} + \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \, e^{-i\phi}\right)\left(\frac{8\pi}{3}\right)^{1/2}$

$= \frac{1}{2}\left(\frac{8\pi}{3}\right)^{1/2} \left(-Y_{1,1} + Y_{1,-1}\right)$

$\sin\theta \sin\phi = \frac{1}{2}\left(\frac{8\pi}{3}\right) \left(Y_{1,1} - i Y_{1,-1}\right)$

$$Y_{J=0,\ M_J=0} = \left(\frac{1}{4\pi}\right)^{1/2}$$

$$Y_{J=2,\ M_J=0} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$\vec{\mu}_z = \int Y_{J=2,M_J=0}(\theta,\phi)\ \hat{\mu}_z\ Y_{J=2,M_J=0}\ d\tau$$

$$= \int Y_{2,0}\ Y_{1,0}\ Y_{0,0}\ d\tau \qquad = \underline{\underline{0}}$$

$M_{J_F} \stackrel{?}{=} M_{J_z} + M_{J_i}$ $\qquad 0 = 0 + 0\ \checkmark$

but $\quad 1 \llcorner 2 \quad$ 1, 2, 0 improper triangle

$$\vec{\mu}_y = \int Y_{2,0}(Y_{1,1} - Y_{1,-1})Y_{0,0}\ d\tau = \int Y_{2,0}Y_{1,1}Y_{0,0} - \int Y_{2,0}Y_{1,-1}Y_{0,0}\ d\tau$$

$$0 \neq 0 + 0 \qquad 0 \neq -1 + 0$$

$$\Downarrow \qquad\qquad \Downarrow$$

$$0 \quad - \quad 0 = \underline{\underline{0}}$$

$$\vec{\mu}_x = \int Y_{2,0}(Y_{1,1} + Y_{1,-1})Y_{0,0}\ d\tau = \int Y_{2,0}Y_{1,1}Y_{0,0}\ d\tau + \int Y_{2,0}Y_{1,-1}Y_{0,0}\ d\tau$$

$\Downarrow$ (same integrals) $\Downarrow$

$$0 \quad + \quad 0 = \underline{\underline{0}}$$

$\vec{\mu} = \vec{\mu}_x + \vec{\mu}_y + \vec{\mu}_z = 0$ Forbidden Transition

#6) $2B = 20\ cm^{-1}$

$$B = 10\ cm^{-1} = \frac{\hbar^2}{2\mu Re^2} \qquad Re = \sqrt{\frac{\hbar^2}{2\mu B}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1 \cdot 35}{1+35} = \frac{35}{36}\ amu$$

$$Re = \left(\frac{2 \cdot \frac{35}{36} \frac{1}{6.022 \times 10^{26}} \frac{mol}{Kg} hcB}{\hbar^2}\right)^{-1/2} = 1.3 \times 10^{-10}\ m$$

$$= 1.3\ \text{Å}$$