Physics 780.04 Winter 2009

Answers To Assignment # 4

1. $\nu = 2B = 115271.2 \text{ MHz} = 1.152712 \times 10^{11} \text{ s}^{-1}$

$$B = 5.76356 \times 10^{10} \text{ s}^{-1} = \frac{h}{8\pi^2 \mu R_e^2}$$

$h = 6.62606876 \times 10^{-27}$ erg-s

$m(^{12}C) = 12.0000$ amu $\qquad N_A = 6.02214199 \times 10^{23}$ amu/gm

$m(^{16}O) = 15.99943$ amu

$$\mu^{-1} = m(^{12}C)^{-1} + m(^{16}O)^{-1} \Rightarrow \mu = 6.85704 \text{ amu}$$

$$\mu = 1.1386377 \times 10^{-23} \text{ gm}$$

$$\therefore R_e = \left(\frac{8\pi^2 \mu B}{h}\right)^{-1/2} = 1.1308 \times 10^{-8} \text{ cm} = 1.1308 \text{ Å}$$

or use formula $B(\text{MHz}) = 5.05376 \times 10^5 / I$ (amu-Å^2)

$I = \mu R_e^2$

2. Bernath, p 202 (11a) HCl $\tilde{B}_0 = 10.4 \text{ cm}^{-1}$

$$P_J = (2J+1)\, e^{-hBJ(J+1)/kT} / q_{rot}$$

$$\frac{dP_J}{dJ} = \frac{1}{q_{rot}} \left\{ 2\, e^{-hBJ'(J'+1)/kT} - (2J'+1)^2 \frac{hB}{kT}\, e^{-hBJ'(J'+1)/kT} \right\}$$

$$0 = 2 - (2J'+1)^2\, hB/kT \Rightarrow (2J'+1)^2 = 2kT/hB$$

$$2J'+1 = \sqrt{\frac{2kT}{hB}} \quad \text{or} \quad 2J'+1 \approx 2J' \Rightarrow J' = \sqrt{\frac{kT}{2hB}}$$

(less accurate)

$$\frac{k}{hB} = \frac{k}{hc\tilde{B}} = \frac{\tilde{k}}{\tilde{B}} \qquad \tilde{k} = 0.69504 \text{ cm}^{-1}\text{ K}^{-1}$$

$$\tilde{k}/\tilde{B}_0(\text{HCl}) = 6.68308 \times 10^{-2} \text{ K}^{-1}$$

$$(kT/hB)_{300K} = \left(\frac{\tilde{k}T}{\tilde{B}}\right)_{300K} = 20.04923$$

$J' = 2.7 \Rightarrow J' \approx 3$

Check: $P_J \propto (2J+1)\, e^{-\tilde{B}J(J+1)/\tilde{k}T} = (2J+1)\, e^{-J(J+1)/20.04923}$

$P_2 = \qquad q_{rot} = kT/hB = 20.04923$

$$P_2^{300K} = \frac{5\, e^{-6/20.04923}}{20.04923} = 0.1849$$

Similarly $P_3^{300K} = 0.192 \qquad P_4^{300K} = 0.166$

$$\left(\frac{kT}{hB}\right)_{2000K} = 133.66 = q_{rot}\,(2000\,K)$$

$J' \approx 7.7 = 8 \qquad$ Check $P_7^{2000K} = 0.07381$

$\sim P_8^{2000K} = 0.07422 \quad P_9^{2000K} = 0.07250$

3. Bernath, p 203, problem 20 $\qquad \mathcal{H}' = -\mu E_z \cos\theta$

a) $\langle J M | \underbrace{\cos\theta | J M\rangle}_{} = 0$ since $\langle J\pm 1\, M | J M\rangle = 0$

recursion relation $\cos\theta |JM\rangle = a|J+1, M\rangle + b|J-1, m\rangle$
(see below)

b) $$Y_{JM} = |JM\rangle = \underbrace{\frac{(-1)^M}{\sqrt{2}}\left[\frac{(2J+1)(J-M)!}{(J+M)!}\right]}_{N_{J,M}} P_J^M(\cos\theta)\,\frac{1}{\sqrt{2\pi}}\, e^{iM\varphi}$$

$$(2J+1)\cos\theta\, P_J^M = (J+M)\,P_{J-1}^M + (J-M+1)\,P_{J+1}^M$$

$$E^{(2)} = \sum_{J'=J\pm 1} \frac{|\mathcal{H}_{JM;J'M}|^2}{E_J - E_{J'}} \qquad E_{J+1} - E_J = 2hB(J+1)$$

$$\mathcal{H}_{J'M;JM} = -\mu E_z \langle J'M|\cos\theta|JM\rangle$$

$$\langle J+1\, M|\cos\theta|JM\rangle = \int_{\theta=0}^{\pi} N_{J+1,M}^{*}\, P_{J+1}^{M\,*}\cos\theta\, N_{JM}\, P_J^M \sin\theta\, d\theta \times \frac{1}{2\pi}\int_0^{2\pi} 1 \cdot d\varphi$$

$$\langle J+1, M|\cos\theta|J M\rangle = \frac{N_{JM}}{N_{J+1,M}} \int N^2_{J+1,M} \, P^M_{J+1} \left[\frac{J-M+1}{2J+1}\right] P^M_{J+1}$$

$$\times \sin\theta \, d\theta$$

$$= \frac{N_{JM}}{N_{J+1,M}} \left(\frac{J-M+1}{2J+1}\right) \cdot 1$$

$$= \left[\frac{2J+1}{2J+3} \frac{(J-M)!}{(J+1-M)!} \frac{(J+M+1)!}{(J+M)!}\right]^{1/2} \frac{J-M+1}{2J+1}$$

$$= \left[\frac{(J+1+M)(J+1-M)^2}{(2J+1)(2J+3)(J+1-M)}\right]^{1/2}$$

$$= \left[\frac{(J+1)^2 - M^2}{(2J+1)(2J+3)}\right]^{1/2}$$

$$E^{(2)}_{J\neq 0} = + \frac{|\mathcal{H}_{J+1,J}|^2}{E_J - E_{J+1}} + \frac{|\mathcal{H}_{J-1,J}|^2}{E_J - E_{J-1}}$$

$$= \frac{1}{2hB}\left[\frac{|\mathcal{H}_{J+1,J}|^2}{-(J+1)} + \frac{|\mathcal{H}_{J-1,J}|^2}{J}\right]$$

$$= \frac{\mu^2 E_z^2}{2hB}\left[-\frac{(J+1)^2 - M^2}{(J+1)(2J+1)(2J+3)} + \frac{J^2 - M^2}{J(2J-1)(2J+1)}\right]$$

To simplify:

1st rationalize : $E^{(2)} = \frac{\mu^2 E_z^2}{2hB}\left\{\frac{[M^2-(J+1)^2]J(2J-1) + (J^2-M^2)[(J+1)(2J+3)]}{J(J+1)(2J-1)(2J+1)(2J+3)}\right\}$

$$\text{Numerator} = M^2 J(2J-1) - M^2(J+1)(2J+3) - (J+1)^2 J(2J-1) + J^2(J+1)(2J+3)$$

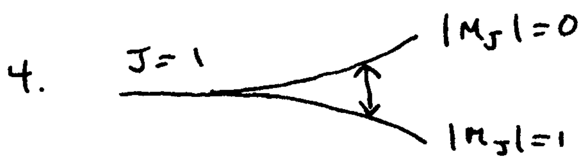
$$= M^2[-6J-3] + J(J+1)\left[-(J+1)(2J-1) + J(2J+3)\right]$$

$$= -3M^2(2J+1) + J(J+1)[2J+1]$$

$$\therefore E^{(2)}_{J\neq 0} = \frac{\mu^2 E_z^2}{2hB}\left[\frac{J(J+1) - 3M^2}{J(J+1)(2J-1)(2J+3)}\right]$$

$J=0$ use only 1st term $\quad E^{(2)}_{J=0} = -\mu^2 E_z^2/6hB$

4.



$$E^{(2)} = \frac{\mu^2 E_z^2}{2hB} \frac{J(J+1) - 3M_J^2}{J(J+1)(2J-1)(2J+3)}$$

$$E^{(2)}_{J=1, M_J=0} = \frac{\mu^2 E_z^2}{10hB} \qquad E^{(2)}_{J=1, |M|=1} = -\frac{\mu^2 E_z^2}{20hB}$$

$B = 2 \times 10^4$ MHz

$$\nu = \Delta E/h = \frac{3\mu^2 E_z^2}{20 h^2 B} = \frac{3}{20B}\left(\frac{\mu E_z}{h}\right)^2$$

$$1 \text{ MHz} = \Big[\underbrace{0.50348\, \mu(D)\, E_z(V/cm)}_{MHz^2}\Big]^2 \frac{3}{20(2 \times 10^4 \text{ MHz})}$$

$$\frac{1 \text{ MHz} \times 20 \times 2 \times 10^4 \text{ MHz}}{3 \cdot (.50348 \times 1 \times 10^3 \frac{MHz}{D})^2} = \mu^2(D)$$

$\mu(D) = 0.725$ Debye

5. $^{35}Cl_2$ $\quad i = 3/2$ fermions $\quad \psi_A = \underbrace{\psi_{elec}}_{symm} \underbrace{\psi_{rot}}_{(-1)^J} \psi_{ns}$

ortho states $g_I^o = (i+1)(2i+1) = 10$ $(I = 3, 1)$ symm

$\Rightarrow$ J odd

para states $g_I^p = i(2i+1) = 6$ $(I = 2, 0)$ anti

$\Rightarrow$ J even

<u>Para</u> ($g_I^p = 6$)

J = 4 —— $g = 6 \times 9 = 54$

J = 2 —— $g = 6 \times 5 = 30$

J = 0 —— $g = 6 \times 1 = 6$

<u>Ortho</u> ($g_I^o = 10$)

J = 3 —— $g = 10 \times 7 = 70$

J = 1 —— $g = 10 \times 3 = 30$

6. $\tilde{\nu}(J) = \tilde{\nu}_0 + \tilde{B}_v' \, J'(J'+1) - \tilde{B}_v'' \, J''(J''+1)$

$J' = J'' = J$

$$\tilde{\nu}_Q(J) = \tilde{\nu}_0 + \tilde{B}_{v'} \, J(J+1) - \tilde{B}_{v''} \, J(J+1)$$

$$= \tilde{\nu}_0 + (\tilde{B}_{v'} - \tilde{B}_{v''})J + (\tilde{B}_{v'} - \tilde{B}_{v''})J^2$$

$\therefore$ all J near origin

7. Method I $\quad \dfrac{E_{v,max}}{h} \cong \dfrac{D_e}{h} = \omega_e(V_{max} + \tfrac{1}{2}) - \omega_e x_e (V_{max} + \tfrac{1}{2})^2$

$x_e = h\omega_e / 4D_e$

$$\frac{D_e}{h} = \omega_e(V_{max} + \tfrac{1}{2}) - \frac{h\omega_e^2}{4D_e}(V_{max} + \tfrac{1}{2})^2$$

$$(V_{max} + \tfrac{1}{2})^2 - \frac{4D_e}{h\omega_e}(V_{max} + \tfrac{1}{2}) + 4D_e^2/(h\omega_e)^2 = 0$$

$$\left[(V_{max} + \tfrac{1}{2}) - \frac{2D_e}{h\omega_e}\right]^2 = 0 \qquad V_{max} + \tfrac{1}{2} = 2D_e/h\omega_e$$

$$V_{max} \approx 2D_e/h\omega_e - \tfrac{1}{2} = \frac{1}{2x_e} - \tfrac{1}{2}$$

No. vib. levels $= V_{max} + 1 \approx \dfrac{1}{2x_e} + \tfrac{1}{2} \approx \dfrac{1}{2x_e} = \dfrac{2D_e}{h\omega_e}$

Method II

$$\frac{E_{v+1} - E_v}{h} = \omega_e - \omega_e x_e (v+1)$$

Assume $\Delta E_{v+1,v} = 0$ when $v = V_{max}$

$$0 = \omega_e - 2\omega_e x_e (V_{max} + 1)$$

$$\frac{\omega_e}{2\omega_e x_e} = V_{max} + 1 = \frac{1}{2x_e} = \frac{2D_e}{h\omega_e}$$

$H_2\,(X\,{}^1\Sigma_g^+)$ $\quad \omega_e = 4395\ \text{cm}^{-1}$, $\quad D_e = 4.75\ \text{eV}$ $\Rightarrow$ Est. no. $= 17$, Actual no. $= 14$