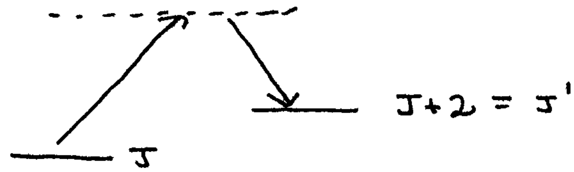
Physics 780.04 — Winter Quarter 2009

Dr. Herbst

Answers to Set # 5

1\.

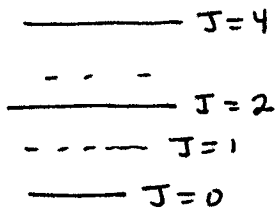


'Stokes'

$$\frac{\Delta E_J}{h} = B\left[(J+2)(J+3) - J(J+1)\right]$$

$$\frac{\Delta E_J}{h} = 2B(2J+3) = \Delta\nu_J$$

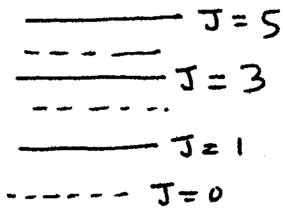
C_2 $\quad {}^1\Sigma_g^+$



even J ONLY

$$\frac{\Delta\nu_2}{\Delta\nu_0} = \frac{2B(4+3)}{2B(3)} = \frac{7}{3}$$

O_2 $\quad {}^3\Sigma_g^-$



odd J only

$$\frac{\Delta\nu_3}{\Delta\nu_1} = \frac{2B(6+3)}{2B(2+3)} = \frac{9}{5}$$

CO all J's allowed

$$\frac{\Delta\nu_1}{\Delta\nu_0} = \frac{2B(2+3)}{2B(0+3)} = \frac{5}{3}$$

Ratios tell us if all J's allowed (CO), if only even J's allowed (C_2), or if only odd J's allowed (O_2).

2\. Deslandres Table $\quad \tilde{\nu} = \tilde{T}_e' - \tilde{T}_e'' + (\tilde{G}_{v'} - \tilde{G}_{v''}) + \tilde{F}_{v'}(J') - \tilde{F}_{v''}(J'')$

(a) (cm^{-1})

$$\tilde{\nu} = 21{,}757.619 + \tilde{\omega}_e'(v'+\tfrac{1}{2}) - \tilde{\omega}_e' x_e'(v'+\tfrac{1}{2})^2 - \left[\tilde{\omega}_e''(v''+\tfrac{1}{2}) - \tilde{\omega}_e'' x_e''(v''+\tfrac{1}{2})^2\right]$$

$$\tilde{\nu} = 21{,}757.619 + 246.317(v'+\tfrac{1}{2}) - 2.231(v'+\tfrac{1}{2})^2 - \left[266.459(v''+\tfrac{1}{2}) - 1.035(v''+\tfrac{1}{2})^2\right.$$

$v' \backslash v''$	0	Δ''_{1-0}	1	Δ''_{2-1}	2	Δ''_{3-2}	3
0	21747.249	264.389	21482.860	262.319	21220.541	260.249	20960.292
Δ'_{1-0}	241.855		241.855		241.855		241.855
1	21989.104	264.389	21724.715	262.319	21462.396	260.249	21202.147
Δ'_{2-1}	237.393		237.393		237.393		237.393
2	22226.497	"	21962.108	"	21699.789	"	21439.540
Δ'_{3-2}	232.931		232.931		232.931		232.931
3	22459.428	"	22195.039	"	21932.720	"	21672.471

(b) $v' = 1 \quad v'' = 0$

P-branch $\tilde{\nu}_P(J) = \tilde{\nu}_{1-0} - (\tilde{B}_1' + \tilde{B}_0'')J + (\tilde{B}_1' - \tilde{B}_0'')J^2$

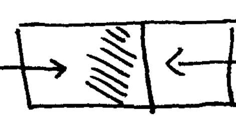
R-branch $\tilde{\nu}_R(J) = \tilde{\nu}_{1-0} + (\tilde{B}_1' + \tilde{B}_0'')(J+1) + (\tilde{B}_1' - \tilde{B}_0'')(J+1)^2$

$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e(v+1/2)$ X state: $\tilde{B}_0'' = \tilde{B}_e'' - \dfrac{\tilde{\alpha}_e''}{2} = 0.108471 \text{ cm}^{-1}$

B state $\tilde{B}_1' = \tilde{B}_e' - \alpha_e' \dfrac{3}{2} = 0.098115 \text{ cm}^{-1}$

$\tilde{B}_1' - \tilde{B}_0'' < 0$ $\therefore$ bandhead occurs for R branch since quadratic term catches up to linear term and cancels it.

degraded to lower $\tilde{\nu}$ or higher λ



bandhead at higher $\tilde{\nu}$ than band origin

$\tilde{\nu} \rightarrow$

(c) $\tilde{\nu}_R(1-0) = \tilde{\nu}_{1-0} + a(J+1) + b(J+1)^2$ $\quad a = \tilde{B}_1' + \tilde{B}_0''$

$b = \tilde{B}_1' - \tilde{B}_0''$

$$\frac{d\tilde{\nu}_R}{dJ} = 0 = a + 2b(J+1)$$

$$\therefore 1 + J = \frac{a}{-2b} = \frac{\tilde{B}_1' + \tilde{B}_0''}{2(\tilde{B}_0'' - \tilde{B}_1')} = \frac{0.206586 \text{ cm}^{-1}}{2 \times (\underbrace{0.010356 \text{ cm}^{-1}}_{-b})}$$

$1 + J \approx 9.97 \rightarrow 10 \quad J \approx 9$

Check: $\tilde{\nu}_R(J) = \tilde{\nu}(1-0) + a(J+1) + b(J+1)^2$

$\tilde{\nu}(1-0) = \Delta\hat{T}_e + \tilde{G}_1' - \tilde{G}_0'' = 21989.104 \text{ cm}^{-1}$ (Deslandres Table)

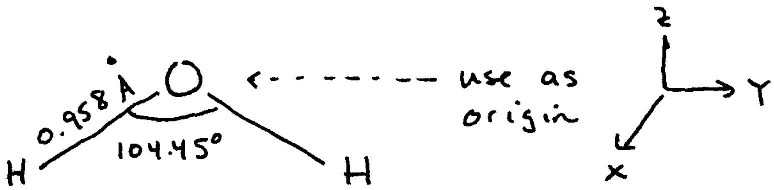
$\tilde{\nu}_R(8-7) = 21990.094 \text{ cm}^{-1}$

$\tilde{\nu}_R(9-8) = 21990.124 \text{ cm}^{-1}$

$\tilde{\nu}_R(10-9) = \boxed{21990.134} \text{ cm}^{-1} \leftarrow$ head

$\tilde{\nu}_R(11-10) = 21990.123 \text{ cm}^{-1}$

(3.)



$m_{O^{16}} = 15.99491$ amu

$m_{H^1} = 1.007825$ amu

$M = m_O + 2m_H = 18.01056$ amu

(a) molecule in yz plane

Center of Mass: $X_{cm} = Y_{cm} = 0$ (symmetry)

$$M Z_{cm} = 2m_H\left[-0.958 \cos\frac{104.45^\circ}{2}\right] \Rightarrow Z_{cm} = -0.06568 \text{ Å}$$

(below O atom)

<u>Moments of Inertia</u>

$$I_{zz} = \sum_i m_i\left[(x_i - X_{cm})^2 + (y_i - Y_{cm})^2\right] = \sum_i m_i y_i^2$$

$$I_{zz} = 2m_H\left[0.958 \sin\frac{104.45^\circ}{2}\right]^2 = 1.15575 \text{ amu Å}^2$$

$$I_{yy} = \sum_i m_i\left[(X_i - X_{cm})^2 + (Z_i - Z_{cm})^2\right] = \sum_i m_i (Z_i - Z_{cm})^2$$

$$I_{yy} = m_O(-Z_{cm})^2 + 2m_H\left(-0.958\cos\frac{104.45^\circ}{2} - Z_{cm}\right)^2$$

$$I_{yy} = 0.61645 \text{ amu-Å}^2$$

$$I_{xx} = \sum_i m_i\left[(y_i - Y_{cm})^2 + (z_i - Z_{cm})^2\right] = I_{yy} + I_{zz}$$

$$I_{xx} = 1.77220 \text{ amu-Å}^2$$

<u>Products of Inertia</u>

All $x_i = 0$, $X_{cm} = 0$ $\qquad I_{xy} = -\sum_i m_i(x_i - X_{cm})(y_i - Y_{cm}) = 0$

Also $I_{xz} = 0$ $\qquad I_{yz} = -\sum_i m_i(y_i - Y_{cm})(z_i - Z_{cm})$

$$= -\sum_i m_i y_i (z_i - Z_{cm})$$

$$I_{yz} = -\left\{ m_H y_H (z_H - z_{cm}) + m_H(-y_H)(z_H - z_{cm}) + m_o (0)(0 - z_{cm}) \right\} = 0$$

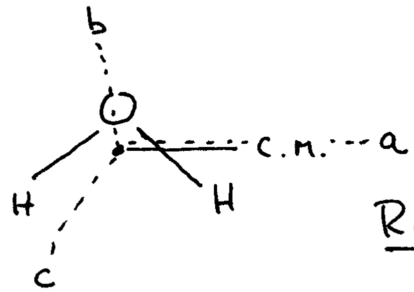
$\therefore$ I_{xx}, I_{yy}, I_{zz} principal moments of inertia

$I_a < I_b < I_c$

$I_{yy} = I_a = 0.61645 \text{ amu-}\mathring{A}^2$

$I_{zz} = I_b = 1.15575 \text{ amu-}\mathring{A}^2$

$I_{xx} = I_c = 1.77220 \text{ amu-}\mathring{A}^2$



Rotational Constants

$$\underset{(\text{MHz})}{\text{Rot. Con.}} = \frac{5.05376 \times 10^5}{I_i \; (\text{amu-}\mathring{A}^2)}$$

$\therefore$ $A = 819,820 \text{ MHz} = 819.820 \text{ GHz}$

$B = 437,270 \text{ MHz} = 437.270 \text{ GHz}$

$C = 285,170 \text{ MHz} = 285.170 \text{ GHz}$

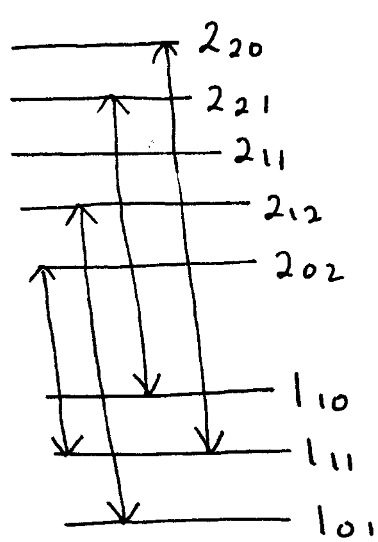
$$K = \frac{2B - A - C}{A - C} = -0.431$$

(b) Dipole Moment (see diagram above) can only be in b-direction

$\therefore$ $\mu = \mu_b$ only $\Rightarrow$ b-type transitions / selection rules

strongest transitions: $\Delta K_a = \pm 1$ $\quad \Delta K_c = \pm 1, \pm 3$ $\quad (\Delta J = 0, \pm 1)$

(c)



2_{20}: $2A + 2B + 2C + 2\left[(B-C)^2 + (A-C)(A-B)\right]^{1/2}$

2_{21}: $4A + B + C$

2_{11}: $A + 4B + C$

2_{12}: $A + B + 4C$

2_{02}: $2A + 2B + 2C - 2\left[(B-C)^2 + (A-C)(A-B)\right]^{1/2}$

1_{10}: $A + B$

1_{11}: $A + C$

1_{01}: $B + C$

Transition	Frequency (GHz)	Transition	Frequency (GHz)
$2_{02}-1_{11}$	1025.25	$2_{21}-1_{10}$	2744.63
$2_{12}-1_{01}$	1675.33	$2_{20}-1_{11}$	2933.81

(4) $B_0 = \dfrac{h}{8\pi^2 \mu R_0^2}$ assume $R_0(^{12}CO) = R_0(^{13}CO) \equiv R_0$

Masses ^{12}C 12.0000 ^{13}C 13.00335 ^{16}O 15.99491 amu

$$\frac{B_0(^{13}CO)}{B_0(^{12}CO)} = \frac{\mu(^{12}CO)}{\mu(^{13}CO)} \qquad \mu^{-1} = m_C^{-1} + m_O^{-1}$$

$$= \left[\frac{m(^{12}C) + m(O)}{m(^{12}C)\,m(O)}\right]^{-1} \frac{m(^{13}C) + m(O)}{m(^{13}C)\,m(O)}$$

$$= 0.955914$$

$$B_0(^{13}CO) = 0.955914 \times 57.6 \text{ GHz}$$

$$= 55.06 \text{ GHz}$$

$$\nu(J=1\to 0) = 2B_0 = 110.1 \text{ GHz} \quad {}^{13}CO$$