Problem Set 14

Part I

(1)

$$E_{J+1} - E_J = B_e(J+1)(J+2) - B_e J(J+1)$$
$$- \alpha_e(v+\tfrac{1}{2})(J+1)(J+2)$$
$$+ \alpha_e(v+\tfrac{1}{2}) J(J+1)$$
$$- D_e (J+1)^2(J+2)^2$$
$$+ D_e (J)^2(J+1)^2$$

$$E_{J+1} - E_J = 2B_e(J+1) - 2\alpha_e(v+\tfrac{1}{2})(J+1) - 4D_e(J+1)^3$$

For rigid rotor

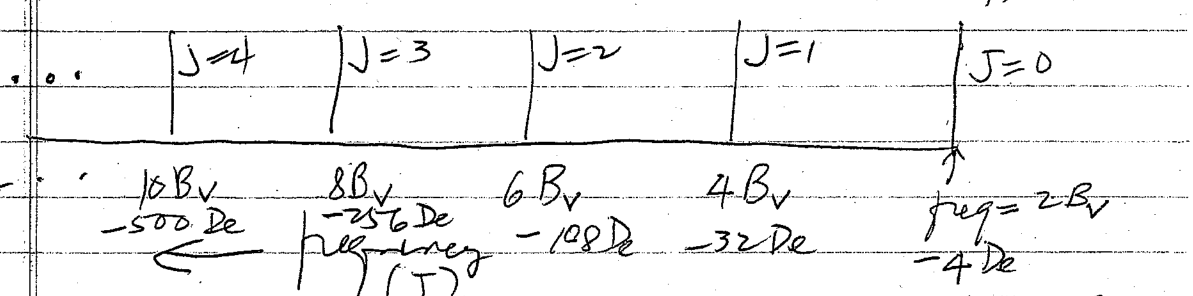
$$E_{J+1} - E_J = 2B_e(J+1)$$

deviation from rigid rotor increases with increasing J

microwave frequency:

$$freq = 2B_e(J+1) - 2\alpha_e(v+\tfrac{1}{2})(J+1) - 4D_e(J+1)^3$$
$$= B_v\, 2(J+1) - 4D_e(J+1)^3$$

can almost neglect, very small

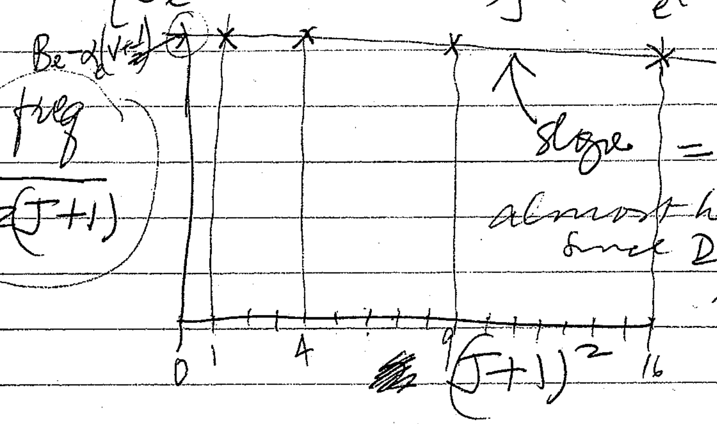


frequency spacing $= freq(J+1) - freq(J) = 2B_v - 4D_e[3J^2+9J+7]$

$$\text{freq} = 2B_e(J+1) - 2\alpha_e(v+\tfrac{1}{2})(J+1) - 4D_e(J+1)^3 + \dots$$

$$\frac{\text{freq}}{2(J+1)} = \left[B_e - \alpha_e(v+\tfrac{1}{2})\right] - 2D_e(J+1)^2$$

Plot $\dfrac{\text{freq}}{2(J+1)}$



slope $= -2D_e$
almost horizontal since D_e is small

intercept $= B_v = B_e - \alpha_e(v+\frac{1}{2})$
slope $= -2D_e$

(2) for $\Delta J = +1$ $J_{upper} = J_{lower} + 1$

$$E_{v=1,J+1} - E_{v=0,J} = \tfrac{3}{2}\nu_e - x_e\nu_e(\tfrac{3}{2})^2 + y_e\nu_e(\tfrac{3}{2})^3$$
$$- \tfrac{1}{2}\nu_e + x_e\nu_e(\tfrac{1}{2})^2 - y_e\nu_e(\tfrac{1}{2})^3$$
$$+ B_e(J+1)(J+2) - B_e J(J+1)$$
$$- D_e(J+1)^2(J+2)^2 + D_e(J)^2(J+1)^2$$
$$- \alpha_e \tfrac{3}{2}(J+1)(J+2) + \alpha_e \tfrac{1}{2} J(J+1)$$

actually can neglect D_e as too small

$$\boxed{\text{freq}_{\text{for } \Delta J=+1} = \nu_e - 2x_e\nu_e + \dots + 2B_e(J+1) - \alpha_e(J^2+4J+3)}$$ neglect $y_e\nu_e$ term

or

$$\text{freq}_{\text{for } \Delta J=\pm 1} = \nu_e - 2x_e\nu_e + 2B_1(J+1) + (B_1-B_0)J(J+1)$$

$$R(J) = \nu_0 + 2B_1 + (3B_1 - B_0)J + (B_1-B_0)J^2$$

high frequency side

R branch

for $\Delta J = -1$ $\quad J_{upper} = J_{lower} - 1$

$$E_{v=1,\,J-1} - E_{v=0,\,J} = \tfrac{3}{2}\nu_e - x_e\nu_e\left(\tfrac{3}{2}\right)^2 + y_e\nu_e\left(\tfrac{3}{2}\right)^3 - \tfrac{1}{2}\nu_e + x_e\nu_e\left(\tfrac{1}{2}\right)^2 - y_e\nu_e\left(\tfrac{1}{2}\right)^3$$

$$+ B_e(J-1)(J) - \alpha_e\tfrac{3}{2}(J-1)J - B_e J(J+1) + \alpha_e \tfrac{1}{2}J(J+1)$$

neglecting De term as too small

low frequency side

$$\boxed{\text{freq for } \Delta J = -1 = \nu_e - 2x_e\nu_e + \cdots - 2B_e J - \alpha_e J(J-2)}$$

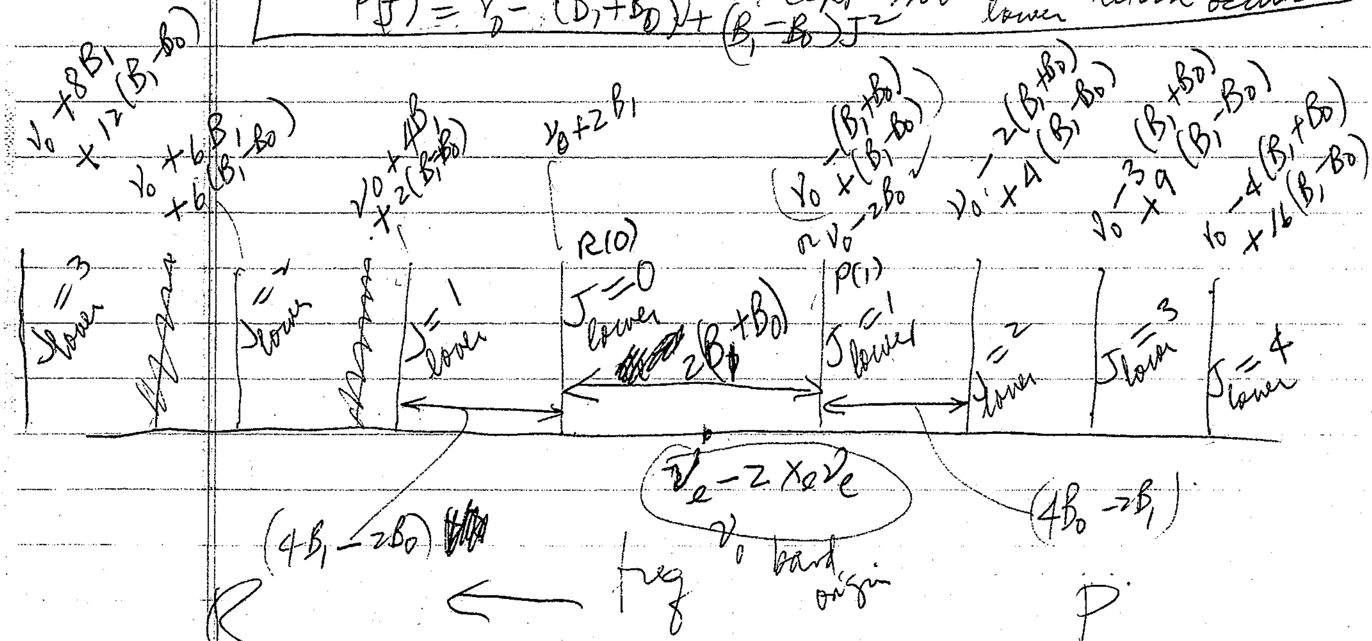
neglecting $y_e\nu_e$ as too small also

except no $J_{lower}=0$ term can occur

or

$$\boxed{\text{freq for } \Delta J=-1 = \underbrace{\nu_e - 2x_e\nu_e}_{\nu_0} + \cdots + (B_1 - B_0)J^2 - (B_1+B_0)J}$$

$P(J) = \nu_0 - (B_1+B_0)J + (B_1-B_0)J^2$ except no $J_{lower}=0$ term can occur



low frequency side (P branch)

spacing between two peaks closest to the band origin $= \nu[P(1)] - \nu[P(2)]$ (J_{lower})

$$= \nu_0 - 2B_0 - [\nu_0 + 2B_1 - 6B_0] = 4B_0 - 2B_1$$

high frequency side (R branch)

spacing between two peaks closest to the band origin $= \nu[R(1)] - \nu[R(0)]$

$$= (\nu_0 + 6B_1 - 2B_0) - [\nu_0 + 2B_1] = 4B_1 - 2B_0$$

spacing between two peaks of same J_{lower}

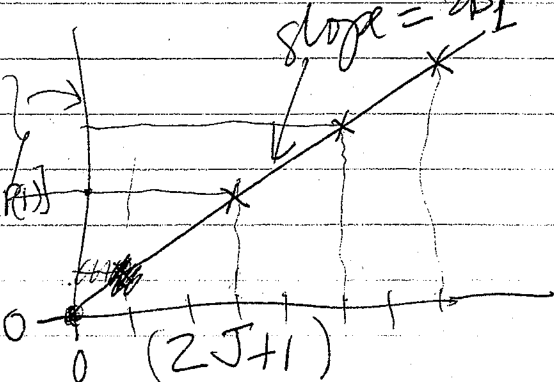
$$= \nu[R(J_{lower})] - \nu[P(J_{lower})]$$

$$= \nu_0 + 2B_1 + (3B_1 - B_0)J + (B_1 - B_0)J^2$$
$$- \{\nu_0 - (B_1 + B_0)J + (B_1 - B_0)J^2\}$$

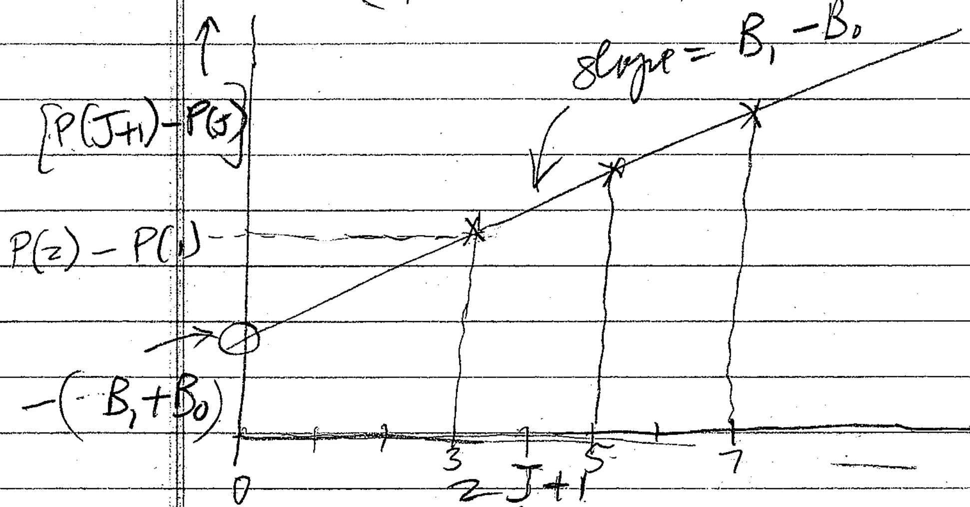
$$= 2B_1 + [(3B_1 - B_0) + (B_1 + B_0)]J = 2B_1 + 4B_1 J$$

$$= 2B_1(2J+1)$$

Plot $\{\nu[R(J)] - \nu[P(J)]\}$



$$P(J+1) - P(J) = \nu_0 - (B_1 + B_0)(J+1) + (B_1 - B_0)(J+1)^2$$
$$- \left[\nu_0 - (B_1 + B_0) J + (B_1 - B_0) J^2 \right]$$
$$= -(B_1 + B_0) + (B_1 - B_0)(2J+1)$$

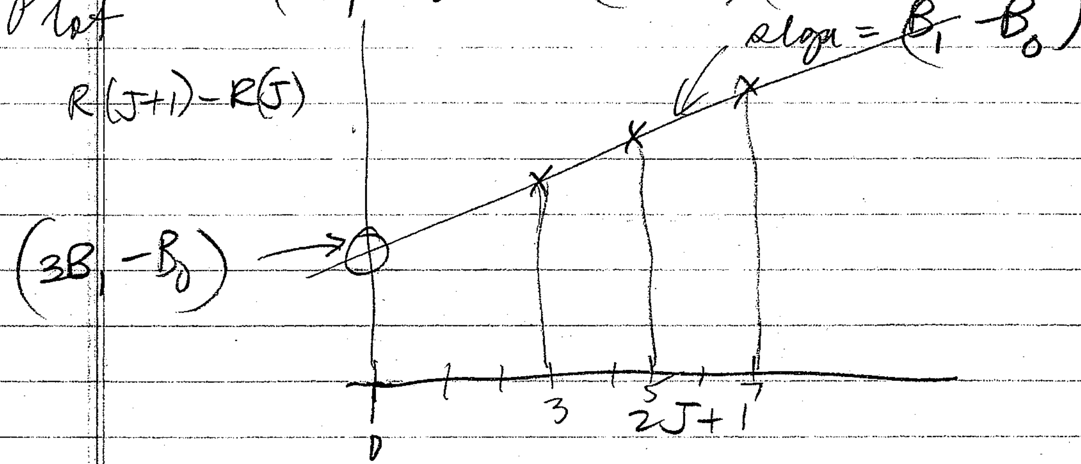


intercept $= -(B_1 + B_0)$
slope $= B_1 - B_0$

(slope − intercept) $= 2B_1$
(intercept + slope) $= -2B_0$

$$R(J+1) - R(J) = \nu_0 + 2B_1 + (3B_1 - B_0)(J+1) + (B_1 - B_0)(J+1)^2$$
$$- \left[\nu_0 + 2B_1 + (3B_1 - B_0)J + (B_1 - B_0)J^2\right]$$
$$= (3B_1 - B_0) + (B_1 - B_0)(2J+1)$$

Plot



$$\text{intercept} - \text{slope} = (3B_1 - B_0) - (B_1 - B_0)$$
$$= 2B_1$$
$$\text{intercept} - 3(\text{slope}) = (3B_1 - B_0) - 3(B_1 - B_0)$$
$$= 2B_0$$

To get $\nu_0 = \nu_e - 2\cancel{x_e}\, x_e$ after you have B_0 and B_1

$$P(1) = \nu_0 - 2B_0 \longrightarrow \nu_0 = P(1) + 2B_0$$
$$R(0) = \nu_0 + 2B_1 \longrightarrow \nu_0 = R(0) - 2B_1$$

(3) $E'^{\text{upper}}_{v=0} - E''^{\text{lower}}_{v''=0} =$ (neglect D_e and $y_e\nu_e$ as too small)

$$\underbrace{\left[U_{\Lambda'}(R_e') - U_{\Lambda''}(R_e'')\right]}_{T_e(\Lambda'\text{ state})} + \frac{1}{2}(\nu_e' - \nu_e'') - \frac{1}{4}(x_e\nu_e' - x_e\nu_e'')$$

$$+ B_0' J'(J'+1) - B_0'' J''(J''+1)$$

(a) For $J' = J''+1$ or $\Delta J = +1$ lines

$$E'_{v=0} - E''_{v''=0} = \underbrace{T_e + \frac{1}{2}(\nu_e' - \nu_e'') - \frac{1}{4}(x_e\nu_e' - x_e\nu_e'')}_{\nu_{00}\text{ band orig.}}$$

$$+ B_0'(J''+1)(J''+2) - B_0'' J''(J''+1)$$

$J''^2 + 3J'' + 2 \qquad J''^2 + J''$

$R(J'')$

$$\boxed{E'_{v=0} - E''_{v''=0} = \nu_{00} + 2B_0' + (3B_0' - B_0'')J'' + (B_0' - B_0'')(J'')^2}$$

high freq. side

(b) For $J' = J''-1$ $\Delta J = -1$ lines

$J^2 - J \qquad J^2 + J$

$$E'_{v'=0} - E''_{v''=0} = \nu_{00} + B_0'(J''-1)(J'') - B_0'' J''(J''+1)$$

$$\boxed{E'_{v'=0} - E''_{v''=0} = \nu_{00} - (B_0' + B_0'')J'' + (B_0' - B_0'')J''^2}$$

$P(J'')$ low freq. side

spacing between adjacent peaks in low freq. side:

$$P(J''+1) - P(J'') = \nu_{00} - (B_0' + B_0'')(J''+1 - J'') + (B_0' - B_0'')\left[(J''+1)^2 - J''^2\right]$$

$$= -(B_0' + B_0'') + (B_0' - B_0'')(2J''+1)$$

(c) $E'_{v'=1} - E''_{v''=0} = [U_A'(R_e') - U_A''(R_e'')] + \frac{3}{2}\nu_e' - \frac{1}{2}\nu_e''$
$- \frac{9}{4}(x_e\nu_e') + \frac{1}{4}x_e\nu_e'' + B_1' J'(J'+1) - B_0'' J''(J''+1)$

$= \nu_{10} + B_1' J'(J'+1) - B_0'' J''(J''+1)$

band origin stands for $T_e(A') + (\frac{3}{2}\nu_e' - \frac{1}{2}\nu_e'') - \frac{9}{4}x_e\nu_e' + \frac{1}{4}x_e\nu_e''$

(a) For $J' = J''+1$ or $\Delta J = +1$ lines

$$\underbrace{E'_{v'=1} - E''_{v''=0}}_{R(J'')} = \nu_{10} + B_1'(J''+1)(J''+2) - B_0'' J''(J''+1)$$

$$R(J'') = \nu_{10} + 2B_1' + (3B_1' - B_0'')J'' + (B_1' - B_0'')(J'')^2$$

high freq side

(b) For $J' = J''-1$ or $\Delta J = -1$ lines

$$\underbrace{E'_{v'=1} - E''_{v''=0}}_{P(J'')} = \nu_{10} + B_1'(J''-1)(J'') - B_0'' J''(J''+1)$$

$$P(J'') = \nu_{10} - (B_1' + B_0'')J'' + (B_1' - B_0'')(J'')^2$$

low freq. end

spacing between adjacent peaks in low frequency side:

$$P(J''+1) - P(J'') = -(B_1' + B_0'')(J''+1-J'') + (B_1' - B_0'')[(J''+1)^2 - J''^2]$$

$$= -(B_1' + B_0'') + (B_1' - B_0'')(2J''+1)$$

Given the $(E'_{v'=0} - E''_{v''=0})$ list of frequencies that is, the values $P(J'')$ and $R(J'')$ $J''=1,2,3,\ldots$ $J''=0,1,2,\ldots$ what can we make straight line plots of data?

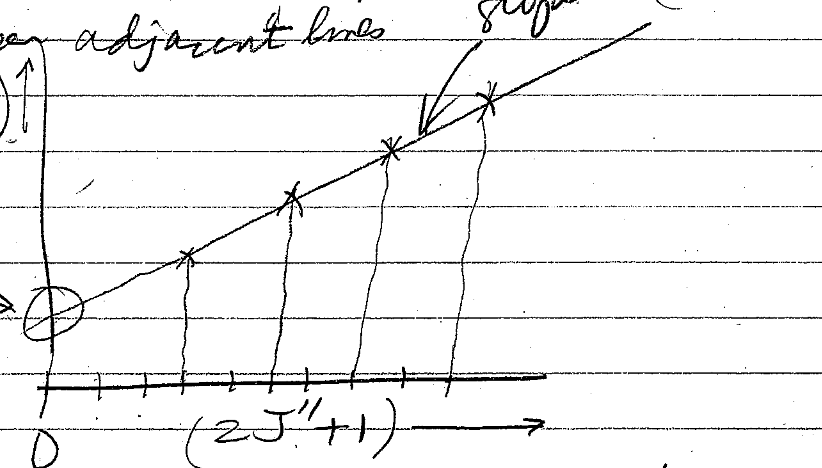
J''	$P(J'')$	$R(J'')$
0	—	
1		
2		
3		

frequencies

given all such numbers

from spacing between adjacent lines

$P(J''+1) - P(J'')$



$b = -B_0' - B_0''$

$m = B_0' - B_0''$

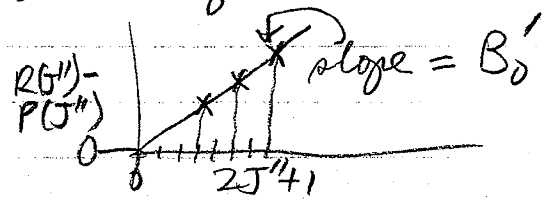
$b + m = -2B_0''$ = slope + intercept

$m - b = 2B_0'$ = slope − intercept

can get both B_0' and B_0'' from straight line plot

From $R(J'') - P(J'') = 2B_0' + 2B_0'J'' = B_0'(2J''+1)$

can get B_0'



From $P(1) = \nu_{00} - (B_0' + B_0'')1 + (B_0' - B_0'')1^2$
$\qquad = \nu_{00} - 2B_0''$

$R(0) = \nu_{00} + 2B_0'$.

Can get $\nu_{00} = T_e(\nu') + \frac{1}{2}(\nu_e' - \nu_e'') - \frac{1}{4}(x_e\nu_e' - x_e\nu_e'')$
if we first get B_0' or B_0'' from previous plots.

(4) Rotational Raman, ending in same v, i.e. $v' = v'' = 0$

$E_{v'J'} - E_{v''J''} = B_0[J'(J'+1) - J''(J''+1)]$

$\Delta J = +2 \qquad J' = J'' + 2 \qquad$ S branch (begins with $J'' = 0$)

$S(J'') = B_0[\underbrace{(J''+2)(J''+3)}_{J^2+5J+6} - \underbrace{J''(J''+1)}_{-J^2-J}]$

$\qquad = B_0(4J'' + 6)$

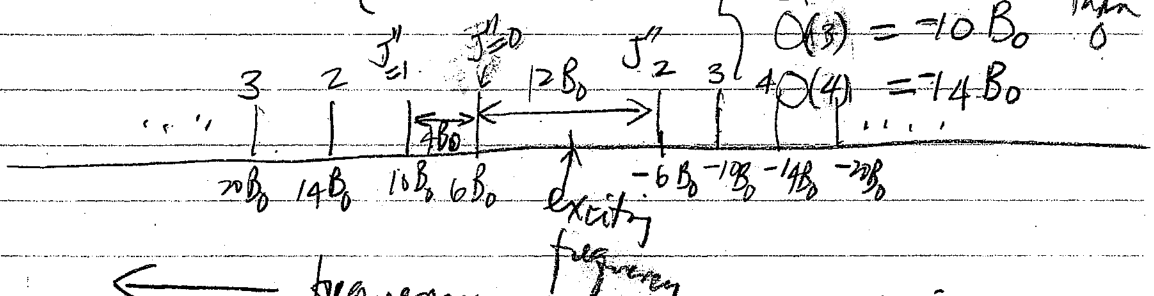
$\begin{cases} S(0) = 6B_0 \\ S(1) = 10B_0 \\ S(2) = 14B_0 \end{cases}$

$\Delta J = -2 \qquad J' = J'' - 2 \qquad$ O branch (begins with $J'' = 2$ since J' cannot be less than 0)

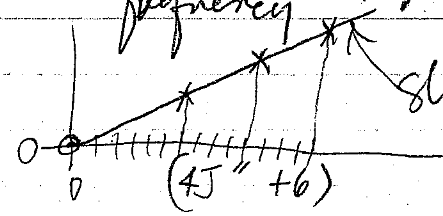
$O(J'') = B_0[\underbrace{(J''-2)(J''-1)}_{J^2-3J+2} - \underbrace{J''(J''+1)}_{-J^2-J}]$

$\qquad = -B_0(4J'' + 2)$

$\begin{cases} O(2) = -6B_0 \\ O(3) = -10B_0 \\ O(4) = -14B_0 \end{cases}$

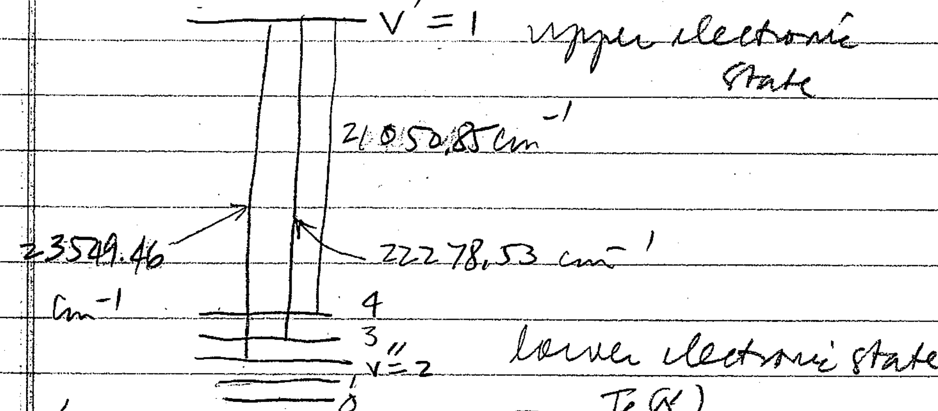


Plot $S(J'')$



slope $= B_0$ line passes through origin

5



$$21050.85 = E'_{v'=1} - E_{v''=4} = \overbrace{U_1(R_e') - U_{4''}(R_e'')}^{T_e(\Lambda')} + \frac{3}{2}\nu_e' - \frac{9}{2}\nu_e'' - \left(\frac{3}{2}\right)^2 x_e\nu_e' + \left(\frac{9}{2}\right)^2 x_e\nu_e''$$

$$22278.53 = E'_{v'=1} - E_{v''=3} = T_e(\Lambda') + \frac{3}{2}\nu_e' - \frac{7}{2}\nu_e'' - \left(\frac{3}{2}\right)^2 x_e\nu_e' + \left(\frac{7}{2}\right)^2 x_e\nu_e''$$

$$23549.46 = E'_{v'=1} - E_{v''=2} = T_e(\Lambda') + \frac{3}{2}\nu_e' - \frac{5}{2}\nu_e'' - \left(\frac{3}{2}\right)^2 x_e\nu_e' + \left(\frac{5}{2}\right)^2 x_e\nu_e''$$

$\leftarrow 2 \qquad \leftarrow 3$

$$23549.46 - 22278.53 = -\frac{5}{2}\nu_e'' + \left(\frac{5}{2}\right)^2 x_e\nu_e'' + \frac{7}{2}\nu_e'' - \left(\frac{7}{2}\right)^2 x_e\nu_e''$$
$$= \nu_e'' - x_e\nu_e''\left[\left(\frac{7}{2}\right)^2 - \left(\frac{5}{2}\right)^2\right] = 1270.93$$

$\leftarrow 3 \qquad \leftarrow 4$

$$22278.53 - 21050.85 = -\frac{7}{2}\nu_e'' + \left(\frac{7}{2}\right)^2 x_e\nu_e'' + \frac{9}{2}\nu_e'' - \left(\frac{9}{2}\right)^2 x_e\nu_e''$$
$$= \nu_e'' - x_e\nu_e''\left[\left(\frac{9}{2}\right)^2 - \left(\frac{7}{2}\right)^2\right] = 1227.68$$

$\leftarrow 1 \qquad \leftarrow 2$

next layer spacing $= -\frac{3}{2}\nu_e'' + \left(\frac{3}{2}\right)^2 x_e\nu_e'' + \frac{5}{2}\nu_e'' - \left(\frac{5}{2}\right)^2 x_e\nu_e''$

$$= \nu_e'' - x_e\nu_e''\left[\left(\frac{5}{2}\right)^2 - \left(\frac{3}{2}\right)^2\right] =$$

$\leftarrow 0 \qquad \leftarrow 1$

next spacing $= -\frac{1}{2}\nu_e'' + \left(\frac{1}{2}\right)^2 x_e\nu_e'' + \frac{3}{2}\nu_e'' - \left(\frac{3}{2}\right)^2 x_e\nu_e''$

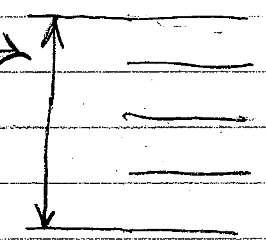
$$= \nu_e'' - x_e\nu_e''\left[\left(\frac{3}{2}\right)^2 - \left(\frac{1}{2}\right)^2\right]$$

If we sum over these spacings up to the $v''=4$ to $v''=1$, we get

$$4\nu_e'' - x_e\nu_e''\left\{\left(\tfrac{9}{2}\right)^2 - \cancel{\left(\tfrac{7}{2}\right)^2} + \cancel{\left(\tfrac{7}{2}\right)^2} - \cancel{\left(\tfrac{5}{2}\right)^2} + \cancel{\left(\tfrac{5}{2}\right)^2} - \cancel{\left(\tfrac{3}{2}\right)^2} + \cancel{\left(\tfrac{3}{2}\right)^2} - \left(\tfrac{1}{2}\right)^2\right\}$$

$$= 4\nu_e'' - x_e\nu_e''\left\{\left(\tfrac{9}{2}\right)^2 - \left(\tfrac{1}{2}\right)^2\right\}$$

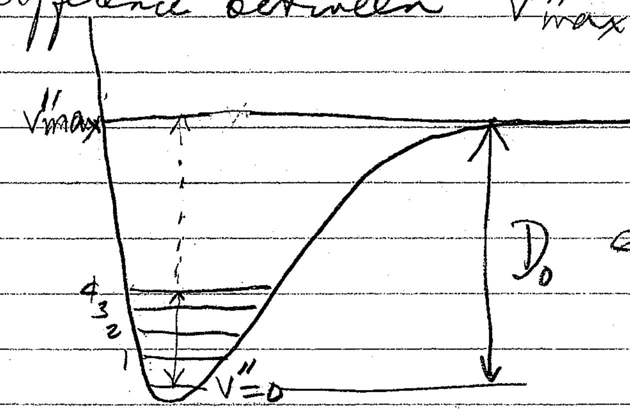
This is the gap between $v''=0$ and $v''=4$ levels



$v''=4$ $\quad \frac{9}{2}\nu_e'' - \left(\frac{9}{2}\right)^2 x_e\nu_e''$

$v''=0$ $\quad \frac{1}{2}\nu_e'' - \left(\frac{1}{2}\right)^2 x_e\nu_e''$

So if keep doing this sum through all the $v''=1$ to $v''=0$ through $v''=1$ to v''_{max}, we should get all the way to the difference between v''_{max} and $v''=0$ which is

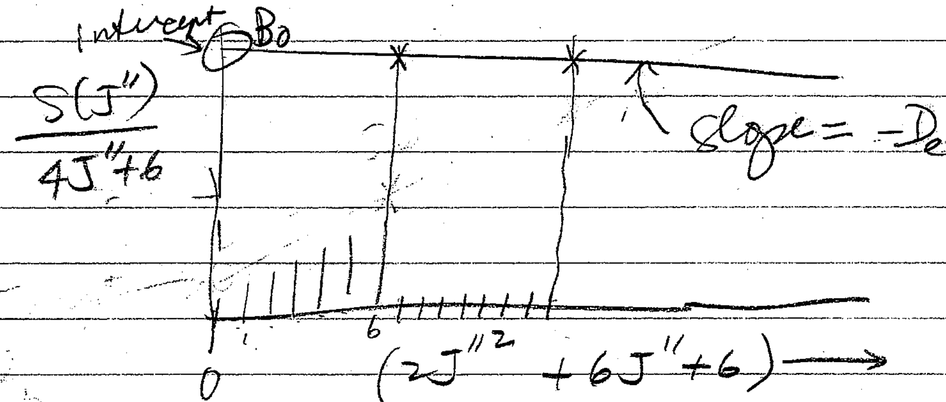


the dissociation energy.

Part II $\quad J' = J''+2$ transitions

(1) $$S(J'') = B_0[(J''+2)(J''+3) - J''(J''+1)]$$
$$- D_e[(J''+2)^2(J''+3)^2 - J''^2(J''+1)^2]$$
$$= B_0(4J''+6) - D_e(8J^3+36J^2+60J+36)$$
$$S(J'') = B_0(4J''+6) - D_e(4J''+6)(2J''^2+6J''+6)$$

$$\frac{S(J'')}{4J''+6} = B_0 - D_e(2J''^2+6J''+6)$$



answers: $B_0 =$ $\qquad D_e =$

Part II

(2) Vibrational term is

$v=5$ —— 6745.52

$v=4$ ——

$v=3$ ——

$v=2$ ——

$v=1$ ——

$v=0$ —— 0.0

$$G_v = \left(v+\tfrac{1}{2}\right)\nu_e - x_e \nu_e \left(v+\tfrac{1}{2}\right)^2$$

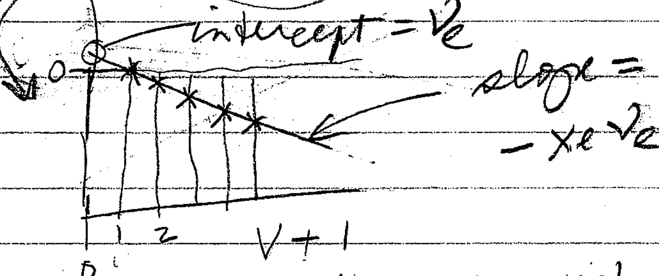
relative to $v=0$

$$- \left(\tfrac{1}{2}\right)\nu_e + x_e\nu_e\left(\tfrac{1}{2}\right)^2$$

$$= v \cdot \nu_e - x_e \nu_e (v^2 + v)$$

$$\frac{\text{given freq spacing}}{v} = \nu_e - x_e \nu_e (v+1)$$

v	ordinate		abscissa
0	0		1
1	1406.51		2
2	$\frac{2788.17}{2}$		3
3	$\frac{4139.71}{3}$		4
4	$\frac{5458.41}{4}$		5
5	$\frac{6745.52}{5}$		6



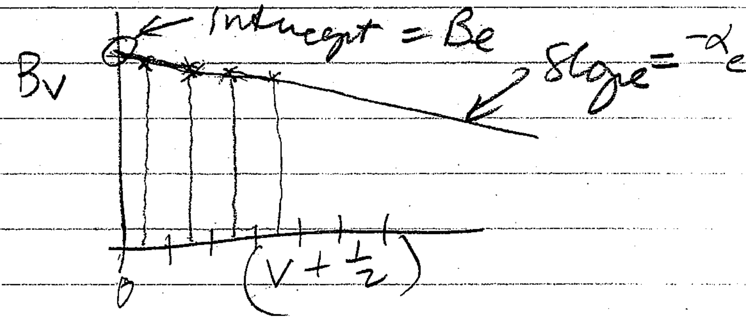
answers: $\nu_e = 1444.7\ cm^{-1}$ $x_e\nu_e = 15.69\ cm^{-1}$

rotational constants are

B_0 B_1 B_2 etc

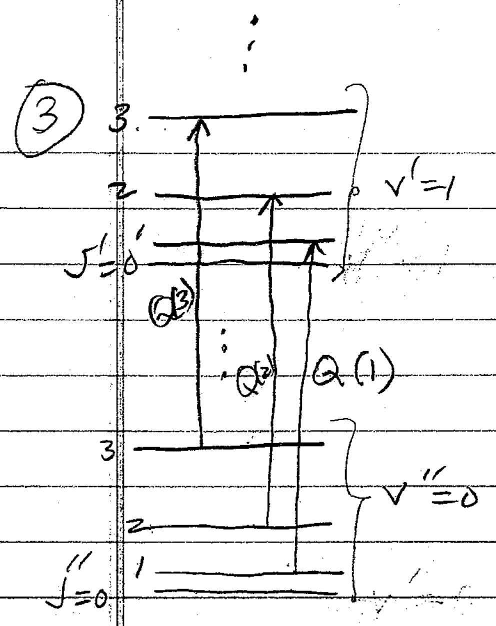
$$B_v = B_e - \alpha_e \left(v+\tfrac{1}{2}\right)$$

ordinate	abscissa
1.4574	0.5
1.4366	1.5
1.4173	2.5
1.3937	3.5
1.3772	4.5
1.3561	5.5

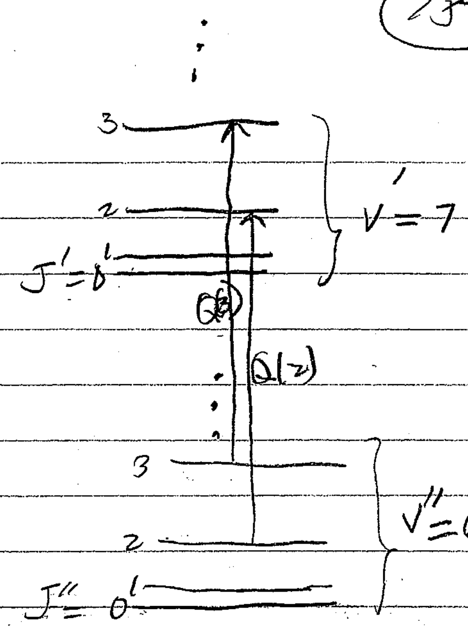


answers are: $B_e = 1.4667\ cm^{-1}$ $\alpha_e = 0.01992\ cm^{-1}$

3



$\Delta J = 0$ $^{15}N_2$



$\Delta J = 0$ $^{15}N_2$

spin of $^{15}N = \frac{1}{2}$
from hand-out on nuclear spin angular momentum
$Z=7$ 7 protons 8 neutrons in ^{15}N

$$\left.\begin{array}{l} \text{protons } (1s_{1/2})^2 (1p_{3/2})^4 (1p_{1/2})^1 \\ \text{neutrons } (1s_{1/2})^2 (1p_{3/2})^4 (1p_{1/2})^2 \end{array}\right\} \text{net spin} = 1/2$$

Pauli exclusion principle: Ψ_{TOTAL} must be antisymmetric with respect to interchange of ^{15}N nuclei in $^{15}N_2$ molecule

$$\Psi_{TOTAL} = \underset{\substack{\text{elec. space} \\ \Lambda=0}}{\psi} \cdot \underset{\substack{\text{elec spin} \\ S, M_S}}{\psi} \cdot \psi_{vib,v} \cdot Y_{J,M_J}(\theta,\phi) \cdot \underset{\substack{\text{nucl spin} \\ I, M_I}}{\psi} \cdot F(X_{CM})G(Y_{CM})D(Z_{CM})$$

$P_{AB}\Psi_{TOTAL} = -\Psi_{TOTAL}$ if A and B are indistinguishable fermions (such as spin ½ ^{15}N)

$P_{AB} \underset{\substack{\text{elec space} \\ \Lambda=0}}{\psi} = + \underset{\substack{\text{elec space} \\ \Lambda=0}}{\psi}$ just like H_2 molecule in Prob Set 12.
where A and B enter into the electronic wavefunction since electron coordinates in atomic orbitals are on A+B

$P_{AB}\ \psi_{\substack{elec\\spin}} = +\psi_{\substack{elec\\spin}}$ since no A or B in $\psi_{\substack{elec\\spin}}$, it cannot change sign

$P_{AB}\ \psi_{vib,v} = +\psi_{vib,v}(R_{AB})$ since $(R_{AB}-R_e)$ does not change sign

$P_{AB}\ \psi_{\substack{rot\\J,M_J}} = P_{AB}\ Y_{JM_J}(\theta,\phi) = (-1)^J Y_{JM_J}(\theta,\phi)$ changes sign for odd J only

$P_{AB}\ \psi_{\substack{nucl\\spin\ I,M_I}}$: $P_{AB}\ \alpha(A)\cdot\alpha(B) = +\alpha(A)\cdot\alpha(B)$

$P_{AB}\ \beta(A)\cdot\beta(B) = +\beta(A)\cdot\beta(B)$

$P_{AB}\ [\alpha(A)\beta(B) + \beta(A)\alpha(B)]/\sqrt{2} = +(\quad)/\sqrt{2}$

$I_{TOTAL}=1$ three of these

$P_{AB}\ [\alpha(A)\cdot\beta(B) - \beta(A)\cdot\alpha(B)]/\sqrt{2} = -(\quad)/\sqrt{2}$ one only for $I_{TOTAL}=0$

$P_{AB}(F\cdot G\cdot D)_{translation} = +(F\cdot G\cdot D)_{translation}$, since these functions are entirely in center of mass coordinates

$$X_{CM} = \frac{m_A X_A + m_B X_B}{(m_A + m_B)}$$

interchanging A and B does not change the sign of X_{CM} and therefore cannot affect the sign of the function $\sqrt{\frac{2}{L_1}}\sin\left(\frac{n_x\pi}{L_1}X_{CM}\right)$

Thus the only parts that can change sign are rotation and nuclear spin. Must choose only those products of these functions that change sign

$$Y_{J\,odd,M}(\theta,\phi)\cdot\begin{cases}\alpha(A)\cdot\alpha(B)\\ \text{or } \beta(A)\cdot\beta(B)\\ \text{or } [\alpha(A)\cdot\beta(B)+\beta(A)\cdot\alpha(B)]/\sqrt{2}\end{cases}$$

$$Y_{J\,even,M}(\theta,\phi)\cdot[\alpha(A)\cdot\beta(B) - \beta(A)\cdot\alpha(B)]/\sqrt{2}$$

We see that there are 3 nuclear spin states associated with odd J and only 1 nuclear spin state with even J. This fact alone would make Q(J odd) three times as intense as the closest Q(J even), if all states have equal likelihood.

For ^{14}N the nuclear spin is 1, resulting from

7 protons $(1S_{1/2})^2(1P_{3/2})^4(1P_{1/2})^1$ } total angular momentum of a ^{14}N nucleus is $\frac{1}{2}+\frac{1}{2}=1$

7 neutrons $(1S_{1/2})^2(1P_{3/2})^4(1P_{1/2})^1$

Integer value of I makes ^{14}N a boson

Pauli exclusion principle states that Ψ_{TOTAL} must be symmetric with respect to interchange of two indistinguishable bosons.

We already have seen that the only parts of the Ψ_{TOTAL} of N_2 molecule that change sign upon P_{AB} are rotation and nuclear spin. From Prob-Set 12 you found the product functions that are eigenfunctions of I^2_{TOTAL} and also M_I.

$$P_{AB}\left\{\begin{array}{l} \alpha(A)\cdot\alpha(B) \\ \beta(A)\cdot\beta(B) \\ \gamma(A)\cdot\gamma(B) \\ [\alpha(A)\beta(B)+\beta(A)\alpha(B)]/\sqrt{2} \\ [\alpha(A)\gamma(B)+\gamma(A)\cdot\alpha(B)]/\sqrt{2} \\ [\beta(A)\gamma(B)+\gamma(A)\cdot\beta(B)]/\sqrt{2} \end{array}\right\}$$

no change in sign

6 functions for 6 states

$$P_{AB}\left\{\begin{array}{l} [\alpha(A)\beta(B)-\beta(A)\cdot\alpha(B)]/\sqrt{2} \\ [\alpha(A)\cdot\gamma(B)-\gamma(A)\cdot\alpha(B)]/\sqrt{2} \\ [\beta(A)\cdot\gamma(B)-\gamma(A)\cdot\beta(B)]/\sqrt{2} \end{array}\right\} \rightarrow$$

change in sign

3 functions for 3 nuclear spin states

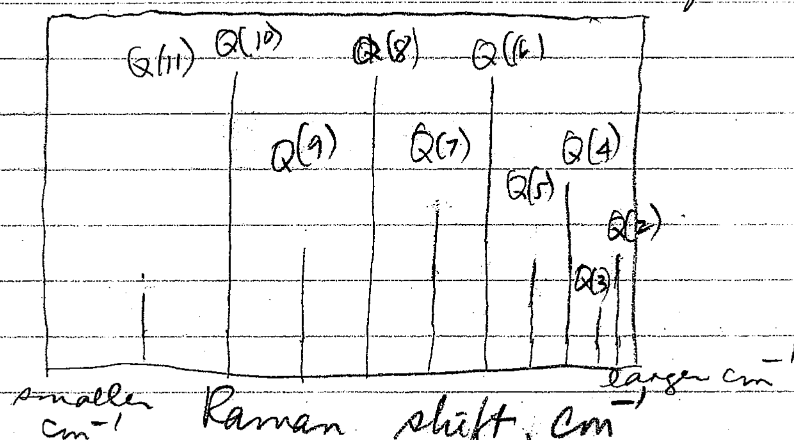
For $^{14}N_2$ $P_{AB}\Psi_{TOTAL}$ can only lead to no change in sign if the products are

$Y_{J odd, M_J}(\theta,\phi) \cdot \psi_{nucl\ spin\ antisym.}$ or else $Y_{J even, M_J}(\theta,\phi) \cdot \psi_{nucl\ spin\ sym.}$

there are 3 of these

there are 6 of these

For $^{14}N_2$ the more intense peaks are for even J:

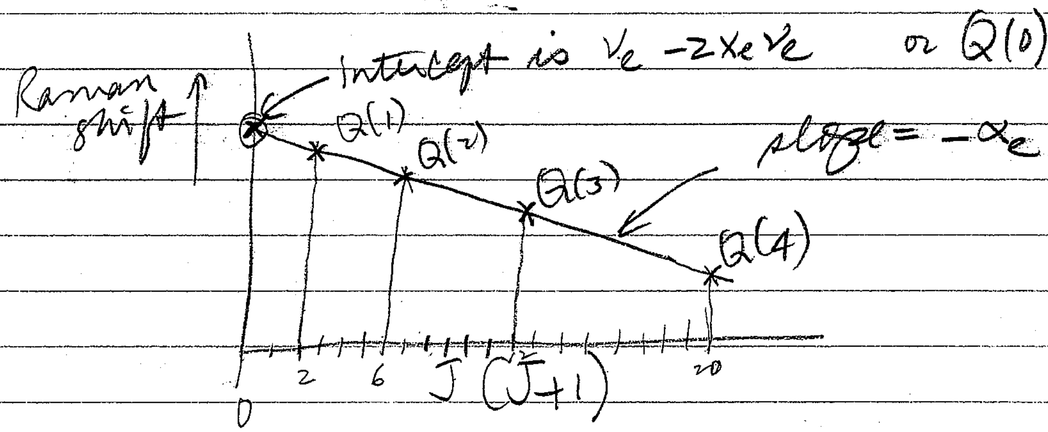


expected $^{14}N_2$ Raman spectrum

$Q(J)$ frequency of Raman shift is given by:

$$E_{v'=1,J} - E_{v''=0,J} = \left(\tfrac{3}{2}\nu_e\right) - x_e\nu_e\left(\tfrac{3}{2}\right)^2 - \alpha_e\left(\tfrac{3}{2}\right)J(J+1) - \left[\tfrac{1}{2}\nu_e - x_e\nu_e\left(\tfrac{1}{2}\right)^2 - \alpha_e\left(\tfrac{1}{2}\right)J(J+1)\right]$$

$$= \nu_e - 2x_e\nu_e - \alpha_e J(J+1)$$



largest Raman shift is $Q(0)$, decreasing with increasing J

Part II continued

④ We see from number ⑤ of Part I that

$$1270.87 = T_e(\Lambda') + \tfrac{3}{2}\nu_e' - (\tfrac{3}{2})^2 x_e\nu_e' - (2+\tfrac{1}{2})\nu_e'' - (2+\tfrac{1}{2})^2 x_e\nu_e''$$

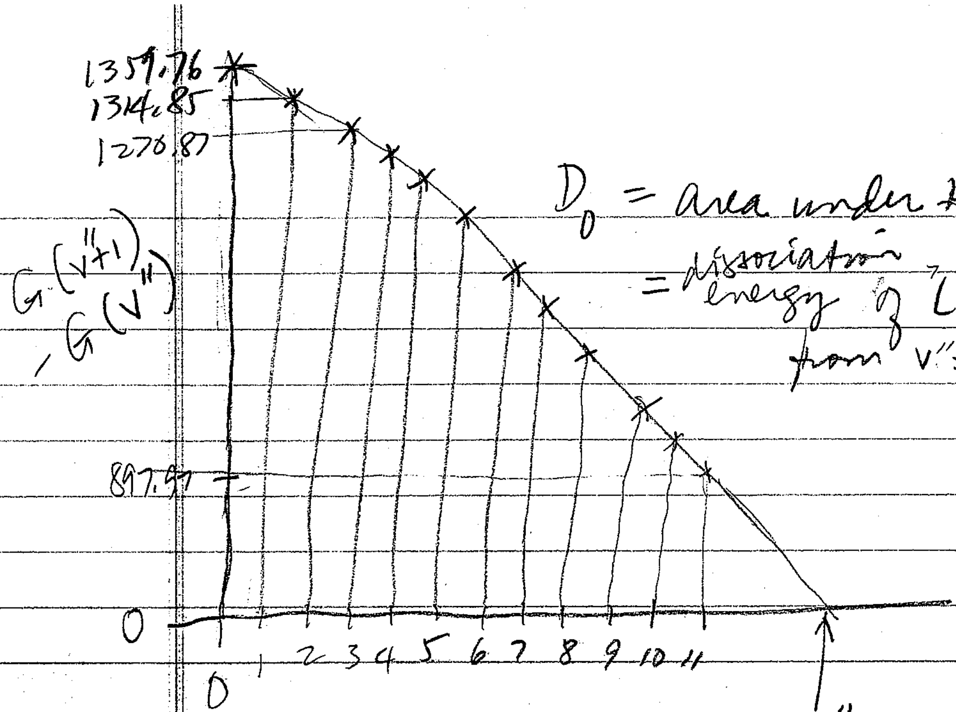
$$- \left[T_e(\Lambda') + \tfrac{3}{2}\nu_e' - (\tfrac{3}{2})^2 x_e\nu_e' - (3+\tfrac{1}{2})\nu_e'' - (3+\tfrac{1}{2})^2 x_e\nu_e'' \right]$$

$$= -G_{v''+\frac{1}{2}}(v''=2) + G_{v''+\frac{1}{2}}(v''=3)$$

for Λ'' state, the lower electronic state

Therefore we identify all the other frequencies as

From the given Table III cm^{-1}	$v''+\frac{1}{2}$	assignment
1359.76	$0+\frac{1}{2}$	$G_{v''+\frac{1}{2}}(v''=1) - G_{v''+\frac{1}{2}}(v''=0)$
1314.85	$1+\frac{1}{2}$	$G_{v''+\frac{1}{2}}(v''=2) - G_{v''+\frac{1}{2}}(v''=1)$
1270.87	$2+\frac{1}{2}$	$G_{v''+\frac{1}{2}}(v''=3) - G_{v''+\frac{1}{2}}(v''=2)$
1227.82	$3+\frac{1}{2}$	
1185.40	$4+\frac{1}{2}$	
1143.83	$5+\frac{1}{2}$	
1102.63	$6+\frac{1}{2}$	
1061.74	$7+\frac{1}{2}$	
1021.16	$8+\frac{1}{2}$	
980.42	$9+\frac{1}{2}$	
939.97	$10+\frac{1}{2}$	
897.97	$11+\frac{1}{2}$	$G_{v''+\frac{1}{2}}(v''=12) - G_{v''+\frac{1}{2}}(v''=11)$



D_0 = area under the curve
= dissociation energy of LiH, measured from $v''=0$ level,

$$\sum_{v''=0}^{v''_{max}} \left[G(v''+1) - G(v'')\right] \cong \text{area under the straight line}$$

$= \frac{1}{2}(32)(1359.76)$
$= 21756.16 \text{ cm}^{-1}$