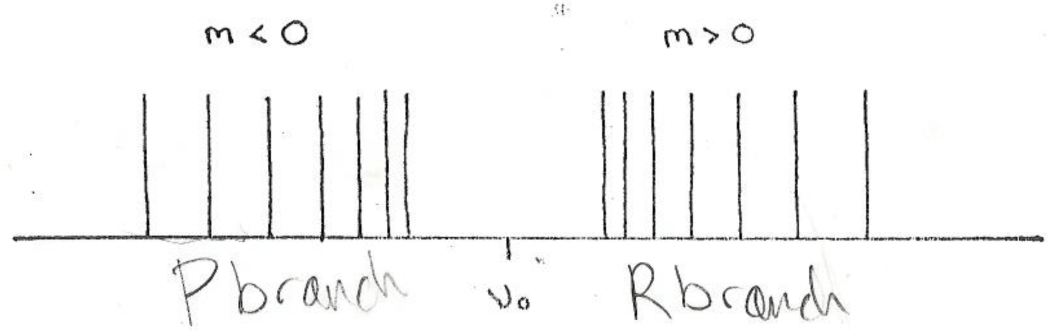
Lines within a band are characterized by;

$$\nu = c + dm + em^2$$ c, d & e are constants.

m can be positive or negative

at $m = 0$ ; $\nu = c$ this corresponds to a missing line between $m = +1$ and $m = -1$.

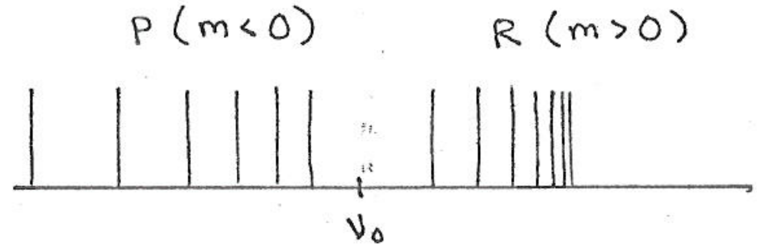
this wavenumber is called the <u>null gap</u> = $\underline{\nu_0}$.



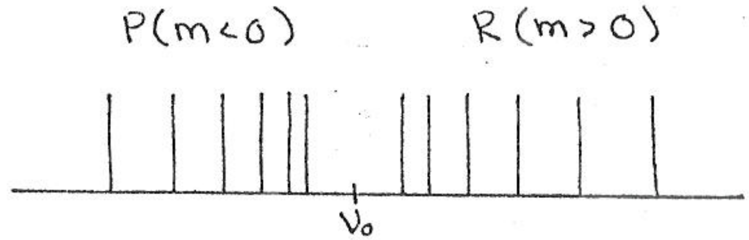

series of lines with $m > 0$ is the R branch $\Delta J = +1$

series of lines with $m < 0$ is the P branch $\Delta J = -1$

P & R branches go in different directions the sign of e is determined by the way the P & R lines draw apart or together.




e is negative




e is positive

* however this depends heavily on d & e terms, because $m^2$ term can dominate and cause the lines to bend back toward the null gap.

$$\nu = \nu_0 + dm + em^2$$

For the CH spectrum, e is negative and the R band reverses after m=7 back toward the null gap.

Since there are different values for $B_v$ from one vibrational state to another, the observed spectra corresponds to transitions, not particular states.

The lines are then represented by

$$\nu_R = \nu_0 + 2B_v' + (3B_v' - B_v'')J + (B_v' - B_v'')J^2 \quad ; \; J = 0, 1, 2 \ldots$$

$$\nu_P = \nu_0 - (B_v' + B_v'')J + (B_v' - B_v'')J^2 \quad ; \; J = 1, 2, 3.$$

$$\nu_Q = \nu_0 + (B_v' - B_v'')J + (B_v' - B_v'')J^2 \quad ; \; J = 1, 2, 3 \ldots$$

R branch $\quad m = -(J+1)$

P branch $\quad m = +J$

Q branch $\quad m = J$

$\Delta J = 0, \pm 1$ and lowest $J$ value is $J = 1$ because $J < \Lambda$

1st line of : $\quad R \rightarrow J = 0$

$P \longrightarrow J = 2$

$Q \longrightarrow J = 1.$

$P(J=1)$ line is missing when a Q branch is present.

# Data Reduction

from recorded $2^{nd}$ order spectra

1) Find null gap : $\nu_o$ is usually between P(1) and R(1)

if P(1) is missing use the Q branch because it often runs right up to null gap depending on the $(B_v' - B_v'')$

$$\nu_Q = \nu_o + (B_v' - B_v'')J(J+1)$$

so J=1 line would be close to $\nu_o$ if $(B_v' - B_v'')$ is small, so look for crowded region.

if $(B_v' - B_v'')$ is large then there will be a region with no peaks.

there is a graphical method, however it requires $B_v$ values - so it time consuming iterative procedure.

also the P & R branches must obey combination relations separately.

$R(m-1) - P(-m)$

$$\Delta_2 F' = R(J) - P(J)$$

$$\Delta_2 F = 4 B_v (J + \tfrac{1}{2}).$$

$$\Delta_2 F'' = R(J-1) - P(J+1)$$

| $J$ | $\frac{\Delta_2 F'}{4(J+\frac{1}{2})}$ | $\frac{\Delta_2 F''}{4(J+\frac{1}{2})}$ |
|---|---|---|
| 0 | | |
| 1 | 12.13 | 12.73 |
| 2 | 10.93 | 12.35 |
| 3 | 10.37 | 11.71 |
| 4 | 10.0 | 11.4 |
| 5 | 9.76 | 11.19 |
| 6 | 9.67 | 10.88 |
| 7 | 9.43 | 10.81 |
| 8 | 9.33 | 10.67 |
| 9 | 9.21 | 10.56 |
| 10 | 9.07 | 10.50 |
| 11 | 8.97 | 10.4 |
| 12 | 8.23 | 10.3 |
| 13 | | 10.19 |
| 14 | | |

$\langle B_v' \rangle = 9.81$ $\langle B_v'' \rangle = 11.05$

Finding final average of combination relations;

$$\langle B_v' \rangle_f = \frac{386.06}{40} = 9.65$$

$$\langle B_v'' \rangle_f = \frac{465.57}{42} = 11.09$$

then $(B_v' - B_v'') = -1.44$

$B_v' + B_v'' = 20.74$

[illegible] $m_{head} = \frac{(B_v' + B_v'')}{-2(B_v' - B_v'')} = 7.2$ which is in very good agreement.

From this technique:

$$\langle B_v' \rangle = 9.65 \qquad (12.18)$$

$$\langle B_v'' \rangle = 11.09 \qquad (13.81).$$

$$B_v' - B_v'' = -1.44 \qquad (-1.635)$$

$$B_v' + B_v'' = 20.74 \qquad (26.0).$$

<u>check</u>

$$m_{head} = \frac{B_v' + B_v''}{-2(B_v' - B_v'')} = 7.2$$

5) Draw Fortrat Diagram - using wavenumbers in air

6) Determine wavenumber relation:

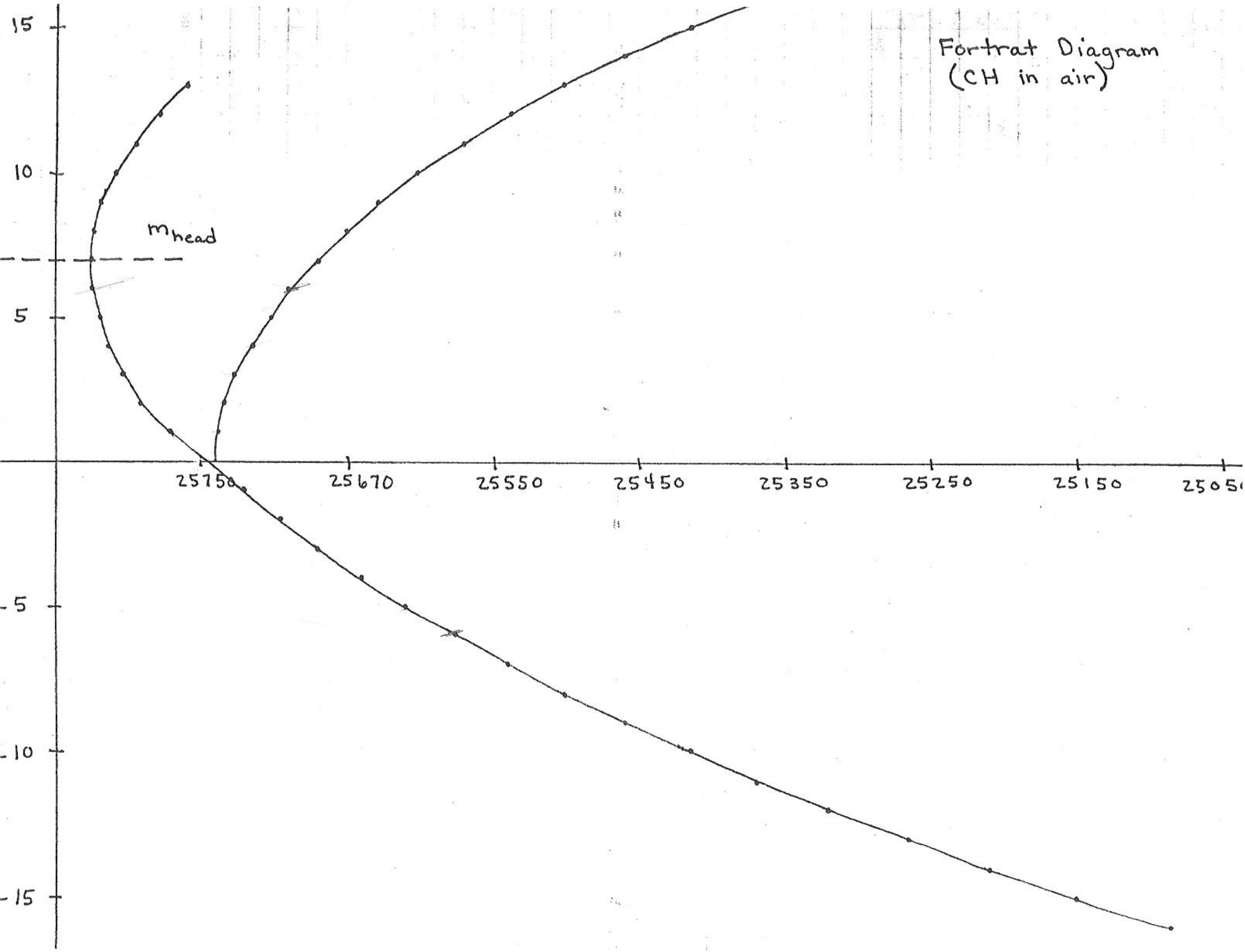
$$\nu_{P,R} = \nu_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2$$

$$\nu_Q = \nu_0 + (B_v' - B_v'')J(J+1)$$

Results:

$$\nu_{P,R} = 25731.5 + 20.74\,m - 1.44\,m^2$$

$$\nu_Q = 25731.5 - 1.44\,J(J+1)$$


Fortrat Diagram
(CH in air)
$m_{head}$
15
10
5
-5
-10
-15
25750
25670
25550
25450
25350
25250
25150
2505

where $\nu_0$ has been corrected to vacuum value:

in order to use this formula, the peak wavenumbers must be converted from air to vacuum values.

$$\nu_{vac.} = \nu_{air} \cdot \frac{n_{vac.}}{n_{air.}}$$

for the wavelength range 3850 Å to 4100 Å index of refraction

$$n_{air} \cong 1.0003 \qquad \text{approximately constant}$$

* is was irrelevant when determining $B_v$ values because used differences.

7) Draw Fortrat Diagram - with vacuum corrected experimental values and with calculated values from correlation.

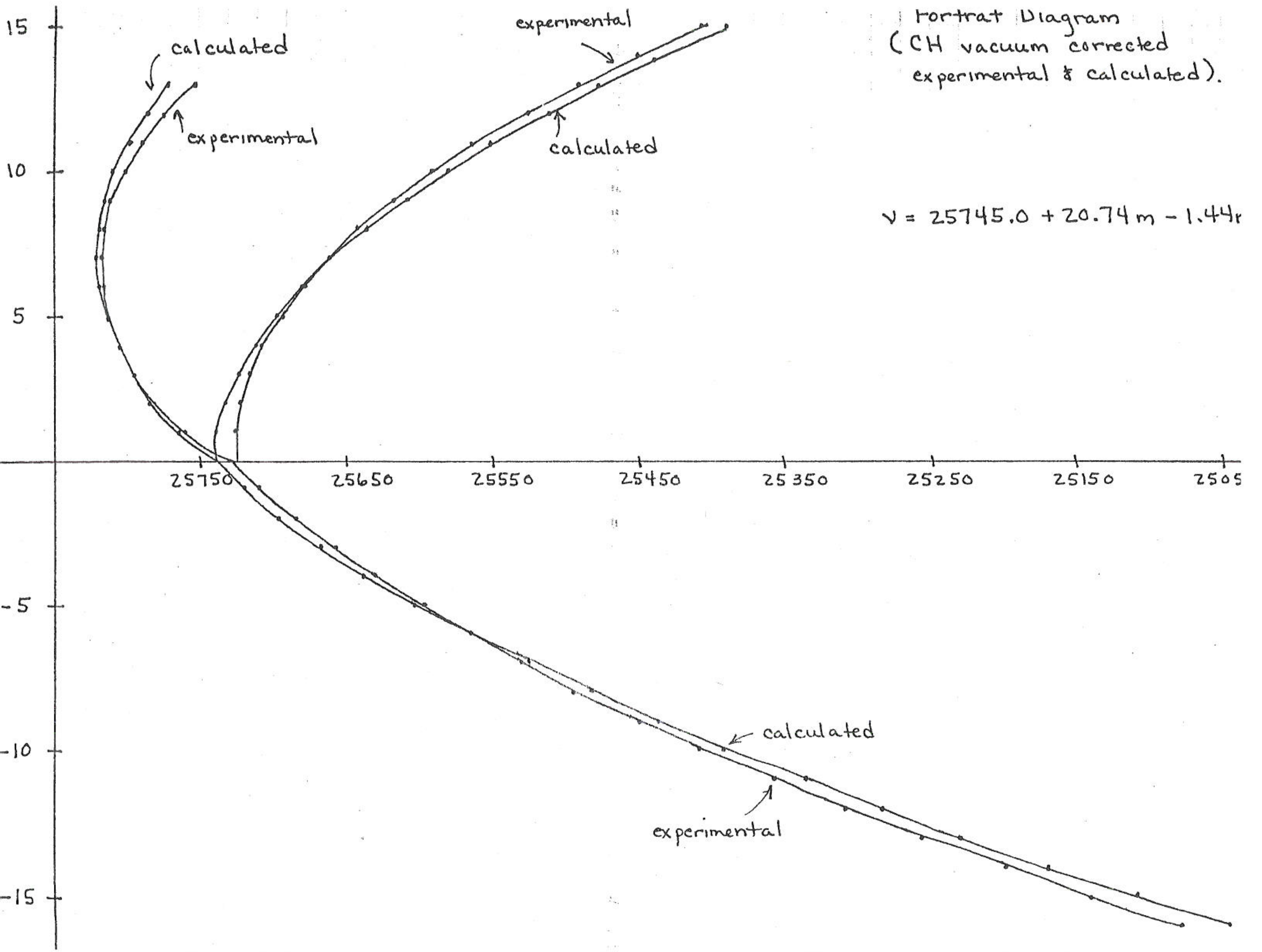
$$\nu_{P,R} = 25745.0 + 20.74\,m - 1.44\,m^2$$

$$\nu_Q = 25745.0 - 1.44\,J(J+1)$$

have determined $\nu_0$ null gap from R(J=0) line & $B_v'$ value

$$\nu_R(J=0) = \nu_0 + 2B_v' \quad , \quad B_v' = 9.65$$

$$\nu_0 = 25745.0$$


Fortrat Diagram
(CH vacuum corrected
experimental & calculated).
ν = 25745.0 + 20.74 m - 1.44r
calculated
experimental
experimental
calculated
calculated
experimental
15
10
5
-5
-10
-15
25750
25650
25550
25450
25350
25250
25150
2505

* this is possible because all wavenumber values are based on R(J=6) head at 3872 Å, not the null gap.

8) Determine internuclear spacing:

$$B_v' = B_e - \alpha_e(v' + \tfrac{1}{2}) = 9.65$$

$$B_v'' = B_e - \alpha_e(v'' + \tfrac{1}{2}) = 11.09$$

the CH 3850 Å to 4020 Å band is a 0,0 transition

$$v' = v'' = 0$$

using $\alpha_e$ values from Hertzberg:

$$\alpha_e(^2\Sigma^-) = .485$$

$$\alpha_e(^2\Pi) = .534$$

$$\alpha_e = \sqrt{\frac{8\pi^2 \mu x_e \omega_e c}{h}}$$

$B_e' = 9.893$ — actual values $B_e(^2\Sigma^-) = 12.89$

$B_e'' = 11.357$ — $B_e(^2\Pi) = 14.46$

using $B_e = \frac{h}{8\pi^2 c \mu r_e^2}$  $\mu = \frac{m_C m_H}{m_C + m_H}$

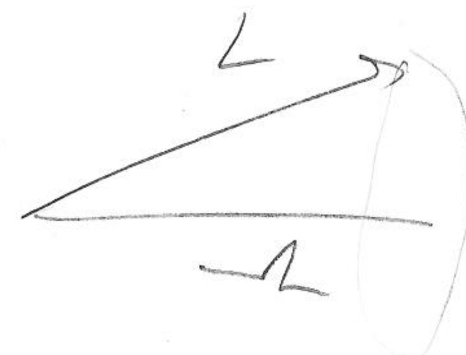
| | | actual values |
|---|---|---|
| $r_e'$ | $= 1.35$ Å | 1.18 Å |
| $r_e''$ | $= 1.26$ Å | 1.12 Å |

9) Rotational Temperature:

determine this from Boltzman's Law about populations in different J states. - intensity relationships

however did not have any of the required information so used from Hertzberg, for unresolved band lines.

$$\Delta \nu_{max} (P \& R) = \sqrt{\frac{8BkT}{hc}}$$



$R_{max} (J=6) = 25826.4$

$P_{max} (J=7) = 25541.6$  $\bar{B_e} = 10.625$

$T_{rot.} = 1373°K$

if $P_{max} (J=10) = 25417.9$

$T_{rot.} = 2825°K$

Recommendations :

1) take spectra in $2^{nd}$ order.

2) use Broida spectrum & Hertzberg book.

3) may have to do the spectrum more than once.

4) take a peak reference point rather than guess at $\nu_0$.

Q lines are present when $\Lambda \neq 0$, $\Lambda = m_L$,
$L$ = electronic orbital angular momentum.

For CH the transition is $^2\Sigma^- (\Lambda = 0) \rightarrow {}^2\Pi (\Lambda = 1)$

$\Lambda \neq 0$ corresponds to another allowable transition

$$\Delta J = 0, \pm 1$$

Diatomic Molecule can be represented by Vibrating Rotator

because vibrations & rotations occur simultaneously

define

$$B_v = \frac{h}{8\pi^2 c \mu} \overline{\left[ \frac{1}{r^2} \right]}$$

where $B_v = B_e - \alpha_e (v + \tfrac{1}{2})$. $v$ = vibration state

so that vibration & rotation terms are combined in an average approximation.

* have neglected higher order terms.

Results: using the Broida spectra determined the peak species and m numbers. – too complicated

i) Q branch
ii) have $\Lambda$ splitting and spin splitting in Q, P and R branchs.
iii) Have R branch bending back toward null gap.

using the P(2) and R(1) lines made $\nu_0$ estimate;

$$\nu_0 = 25726.8 \ cm^{-1}$$

* using the R(7) head at 3872 Å as reference to determine wavelengths.

from this data $(B_v' - B_v'') \sim -1.6$ which is small, so Q(1) line should be very close to $\nu_0$.

A new null gap was placed at
$\nu_0 = 25739.2$

2) Compile wavenumbers of each peak & determine the 1st and 2nd differences of peaks.

$$\nu = \nu_o + dm + em^2$$

$$\Delta\nu = \nu(m+1) - \nu(m)$$

$$\Delta^2\nu = \Delta\nu(m+1) - \Delta\nu(m)$$ should be relatively constant

| | m | ν | ν corr. | Δν | Δ²ν |
|---|---|---|---|---|---|
| | ⋮ | | | | |
| | 4 | 25814.8 | 25807.1 | 9.6 | 2.5 |
| | 3 | 25805.2 | 25797.5 | 12.1 | 8.7 |
| | 2 | 25793.1 | 25785.3 | 20.8 | |
| | 1 | 25772.3 | 25764.3 | | |
| $\nu_o$ | 0 | 25739.3 | 25731.5 | | |
| | -1 | — | | | |
| | -2 | 25695.9 | 25688.2 | 26.3 | 2.1. |
| | -3 | 25669.6 | 25661.9 | 28.4 | |
| | -4 | 25641.2 | 25633.5 | | |
| | ⋮ | | | | |

$$\nu_{vacuum} = \nu_{air} \cdot \frac{n_{vac.}}{n_{air}}$$

After assuming $\nu_0$ value between a P(2) line and R(1) line & using R(m=7) head value at 3772 Å, $\nu_0$ = 25728.6.
& got $B_v' - B_v''$ = −1.3, which is small, so reassigned $\nu_0$ to close to Q(J=1) line

Again using R(m=7) head ; $\nu_0$ = 25739.2
$\lambda_0$ = 3885.1

| J | m | ν | ν_corr | Δν | Δ²ν |
|---|---|---|---|---|---|
| 13 | 14 | too close to $\nu_0$ | | | |
| 12 | 13 | 25761.6. | 25753.9 | 21.3 | |
| 11 | 12 | 25782.9. | 25775.2 | 16.0 | 5.3 |
| 10 | 11 | 25798.9. | 25791.2. | 12.7 | 3.3. |
| 9 | 10 | 25811.6. | 25803.9 | 7.5 | 5.2 |
| 8 | 9 | 25819.1 | 25811.4 | 5.3 | 2.2 |
| 7 | 8 | 25824.4 | 25816.7 | 2.0 | 3.3 |
| 6 | 7 | 25826.4 | 25818.7 | 2.0 | 0 |
| 5 | 6 | 25824.4 | 25816.7 | 3.2 | 1.2 |
| 4 | 5 | 25821.2 | 25813.5. | 6.4 | 3.2 |
| 3 | 4 | 25814.8 | 25807.1 | 9.6 | 3.2 |
| 2 | 3 | 25805.2 | 25797.5 | 12.1 | 2.5 |
| 1 | 2 | 25793.1 | 25785.3 | 20.2 | 8.7. |
| 0 | 1 | 25772.8 | 25764.? | | |
| | 0 | 25739.2 | 25731.5. | | |
| 1 | −1 | (25720.3) ? | (25712.6) ? | | |
| 2 | −2 | 25695.9 | 25688.2 | 26.3 | |
| 3 | −3 | 25669.6 | 25661.9. | 28.4 | 2.1 |
| 4 | −4 | 25641.2. | 25633.5. | 31.6 | 3.2 |
| 5 | −5 | 25609.6. | 25601.9 | 34.5 | 2.9 |
| 6 | −6 | 25575.1 | 25567.4 | 33.5 | −1.0 |
| 7 | −7 | 25541.6. | 25533.9. | 39.6 | 6.1 |
| 8 | −8 | 25502.0 | 25494.3. | 40.5. | .9 |
| 9 | −9 | 25461.5. | 25453.9 | 43.6. | 3.1 |
| | −10 | 25417.9 | 25410.3. | 47.4 | 2.8 |
| | −11 | 25370.5. | 25362.9 | 50.3 | 2.9 |
| | −12 | 25320.2. | 25312.6 | 56.3 | 6.0 |
| | −13 | 25267.9 | 25260.3 | 57.0 | 1.0 |
| | −14 | 25210.9. | 25203.3. | 59.9 | 2.9 |
| | −15 | 25151.0 | 25143.5. | 63.6 | 3.7 |
| | −16 | 25087.4. | 25079.9. | 68.3 | 4.7 |
| | −17 | 25019.1 | 25011.6. | | |

$\overline{\Delta^2 \nu_{RR}}$ = 3.256

$(B_v' - B_v'')$ = 1.628

| J | $\nu$ | $\nu_{corr}$ | $\Delta\nu$ | $\Delta^2\nu$ |
|---|---|---|---|---|
| 1 | 25737.2 | 25729.5 | 3.2 | |
| 2 | 25734.0 | 25726.3 | 7.4 | 4.2 |
| 3 | 25726.6 | 25718.9 | 9.5 | 2.1 |
| 4 | 25717.1 | 25709.4 | 11.6 | 2.1 |
| 5 | 25705.5 | 25697.8 | 14.8 | 3.2 |
| 6 | 25690.7 | 25683.1 | 17.9 | 3.1 |
| 7 | 25672.8 | 25665.1 | 20.1 | 2.2 |
| 8 | 25652.7 | 25645.0 | 23.1 | 3.0 |
| 9 | 25629.6 | 25621.9 | 27.3 | 3.2 |
| 10 | 25602.3 | 25594.6 | 30.4 | 3.1 |
| 11 | 25571.9 | 25564.2 | 32.4 | 2.0 |
| 12 | 25539.5 | 25531.8 | 36.5 | 4.1 |
| 13 | 25503.0 | 25495.4 | 41.6 | 5.1 |
| 14 | 25461.4 | 25453.9 | 45.5 | 3.9 |
| 15 | 25415.9 | 25408.3 | 50.5 | 5.0 |
| 16 | 25365.4 | 25357.8 | 53.5 | 3.0 |
| 17 | 25309.9 | 25302.3 | | |

$\overline{\Delta^2\nu_Q} = 3.287 = 2e$ ; $e = (B_v' - B_v'') = 1.64$.

from the average value of $\Delta^2\nu$, can determine e from

$$\nu_{P,R} = \nu_0 + \underbrace{(B_v' + B_v'')}_{=d} m + \underbrace{(B_v' - B_v'')}_{=e} m^2$$

$$\overline{\Delta^2\nu} = 2e = 2(B_v' - B_v'')$$ like 2nd derivative $\frac{d^2\nu}{dm^2} = 2e$.

for a ballpark estimate of $(B_v' + B_v'')$

$$\Delta\nu\,(m=+1 \;\&\; m=-1) = 2d. = 2(B_v' + B_v'').$$

then solve for $B_v'$ & $B_v''$ ball park values.

Results:

$$\overline{\Delta^2\nu_{P,R}} = 3.256 \quad , (B_v' - B_v'') = -1.628$$

$$\overline{\Delta^2\nu_{Q}} = 3.287 \quad , (B_v' - B_v'') = -1.64$$

then using $\Delta\nu\,(m=+1, m=-1) = 52$ ; $(B_v' + B_v'') = 26.0$

* However the $P(m=-1)$ line should be missing, used a $P(1)$ value from Broida spectrum.

From $(B_v' - B_v'') = -1.635$

$(B_v' + B_v'') = 26.0$

$B_v' = 12.183$
$B_v'' = 13.817$ ball park values, not accurate.

<u>check</u>

$m_{head} = 7$ $\quad m_{head} = \dfrac{B_v' + B_v''}{-2(B_v' - B_v'')}$. from $\dfrac{d\nu}{dm} = 0$.

$m_{head} = 7.95$

4) More accurate technique to solve for $B_v'$ & $B_v''$ :

combination relations:

if have only P & R branch:

$$R(J-1) - P(J+1) = \Delta_2 F''(J) = 4 B_v''(J + 1/2)$$

$$R(J) - P(J) = \Delta_2 F'(J) = 4 B_v'(J + 1/2)$$

if have Q branch also :

$$\Delta_1 F' = R(J) - Q(J) = Q(J+1) - P(J+1) \qquad \Delta_1 F' = 2B_v'(J+1)$$

$$\Delta_1 F'' = R(J) - Q(J+1) = Q(J) - P(J+1) \qquad \Delta_1 F'' = 2B_v''(J+1)$$

$$R(J) = \nu_R = \nu_0 + 2B_v' + (3B_v' - B_v'')J + (B_v' - B_v'')J^2$$

$$P(J) = \nu_P = \nu_0 - (B_v' + B_v'')J + (B_v' - B_v'')J^2$$

$$Q(J) = \nu_Q = \nu_0 + (B_v' - B_v'')J + (B_v' - B_v'')J^2$$

* even with a Q branch, the P & R relationships still hold.

| J | R(J) | Q(J) | P(J) | $\frac{\Delta_1 F'(R,Q)}{2(J+1)}$ | $\frac{\Delta_1 F'(P,Q)}{2(J+1)}$ | $\frac{\Delta_1 F''(R,Q)}{2(J+1)}$ | $\frac{\Delta_1 F''(P,Q)}{2(J+1)}$ |
|---|---|---|---|---|---|---|---|
| 0 | 25772.3 | | | | | | |
| 1 | 25793.1 | 25737.2 | | 13.97 | 9.53 | 14.78 | 10.32 |
| 2 | 25805.2 | 25734.0 | 25695.9 | 11.86 | 9.5 | 13.1 | 10.73 |
| 3 | 25814.8 | 25726.6 | 25669.6 | 11.0 | 9.49 | 12.2 | 10.68 |
| 4 | 25821.2 | 25717.1 | 25641.2 | 10.4 | 9.59 | 11.57 | 10.75 |
| 5 | 25824.4 | 25705.5 | 25609.6 | 9.9 | 9.63 | 11.14 | 10.87 |
| 6 | 25826.4 | 25690.7 | 25575.1 | 9.7 | 9.37 | 10.97 | 10.65 |
| 7 | 25824.4 | 25672.8 | 25541.6. | 9.5 | 9.42 | 10.73 | 10.68 |

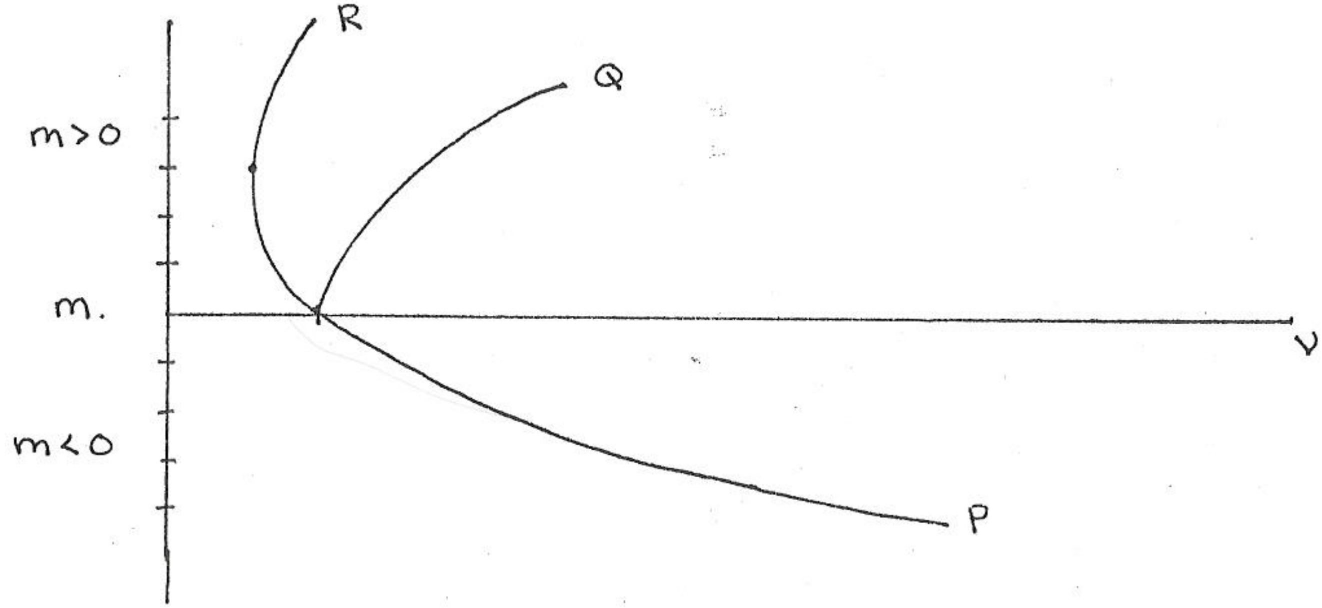
| J | R(J) | Q(J) | P(J) | $\frac{\Delta_1 F'(R,Q)}{2(J+1)}$ | $\frac{\Delta F_1''(P,Q)}{2(J+1)}$ | $\frac{\Delta F_1'(R,Q)}{2(J+1)}$ | $\frac{\Delta F_1''(P,Q)}{2(J+1)}$ |
|---|---|---|---|---|---|---|---|
| 0 | 25772.3 | | | | | 17.4 | |
| 1 | 25793.1 | 25737.2 | (25720.3) | 13.97 | 9.53. | 14.78 | 10.32 |
| 2 | 25805.2 | 25734.0 | 25695.9 | 11.86 | 9.5. | 13.1 | 10.73. |
| 3 | 25814.8. | 25726.6 | 25669.6. | 11.0 | 9.49. | 12.2 | 10.68 |
| 4 | 25821.2 | 25717.1 | 25641.2 | 10.4 | 9.59. | 11.57. | 10.75 |
| 5 | 25824.4 | 25705.5 | 25609.6 | 9.9. | 9.63 | 11.14 | 10.87 |
| 6 | 25826.4 | 25690.7 | 25575.1 | 9.7. | 9.37. | 10.97 | 10.65. |
| 7 | 25824.4 | 25672.8 | 25541.6 | 9.48. | 9.42. | 10.73 | 10.68 |
| 8 | 25819.1 | 25652.7 | 25502.0 | 9.24 | 9.34 | 10.53 | 10.62 |
| 9. | 25811.6 | 25629.6 | 25461.5. | 9.1. | 9.22 | 10.47 | 10.59. |
| 10 | 25798.9 | 25602.3 | 25417.9 | 8.94 | 9.15. | 10.32 | 10.54 |
| 11 | 25782.9 | 25571.9 | 25370.5. | 8.79 | 9.14 | 10.14 | 10.49 |
| 12 | 25761.6 | 25539.5 | 25320.2 | 8.54 | 9.04 | 9.94 | 10.45. |
| 13 | | 25503.0 | 25267.9 | | 8.95 | | 10.43. |
| 14 | | 25461.4 | 25210.9 | | 8.8[illegible] | | 10.35. |
| 15 | | 25415.9 | 25151.0 | | 8.69. | | 10.27 |
| 16 | | 25365.4 | 25087.4 | | 8.55. | | 10.2 |
| 17 | | 25309.9. | 25019.1. | | | | |

$\langle B_v' \rangle = 10.08$  $\langle B_v'' \rangle = 9.22$

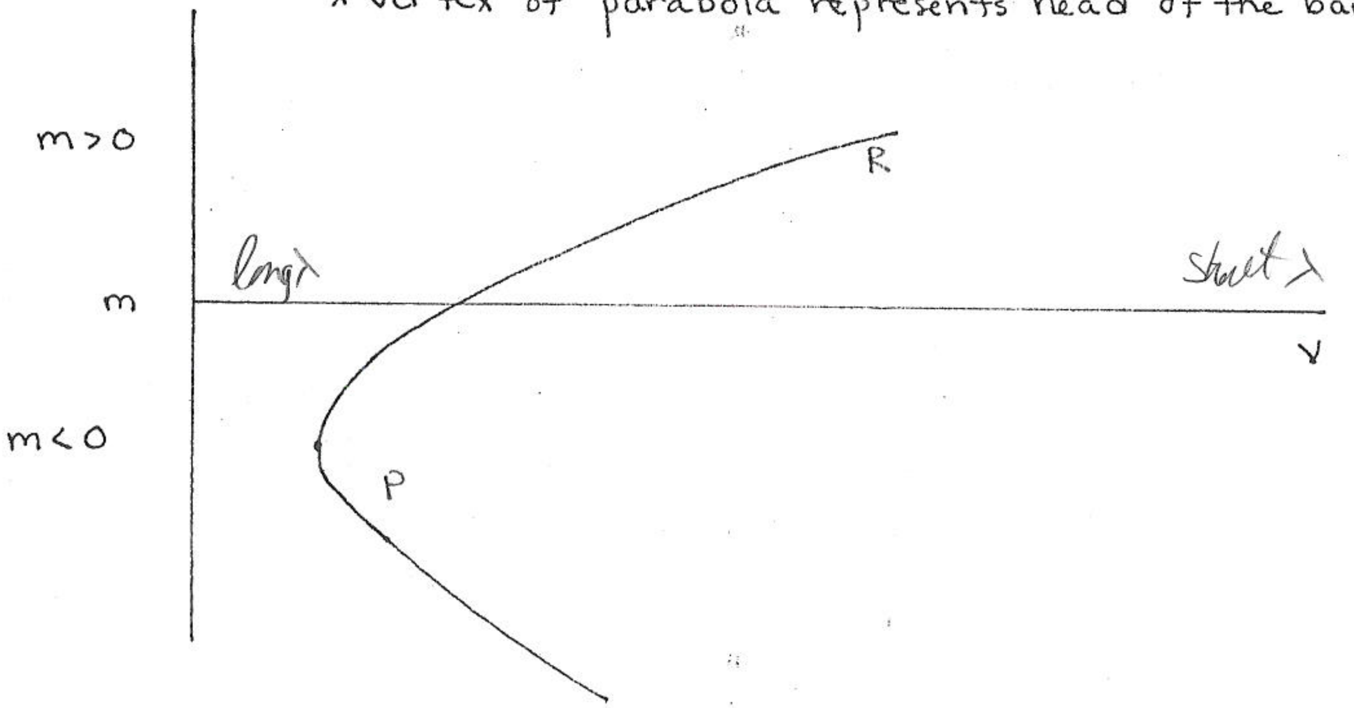
$\langle B_v' \rangle = 11.79$

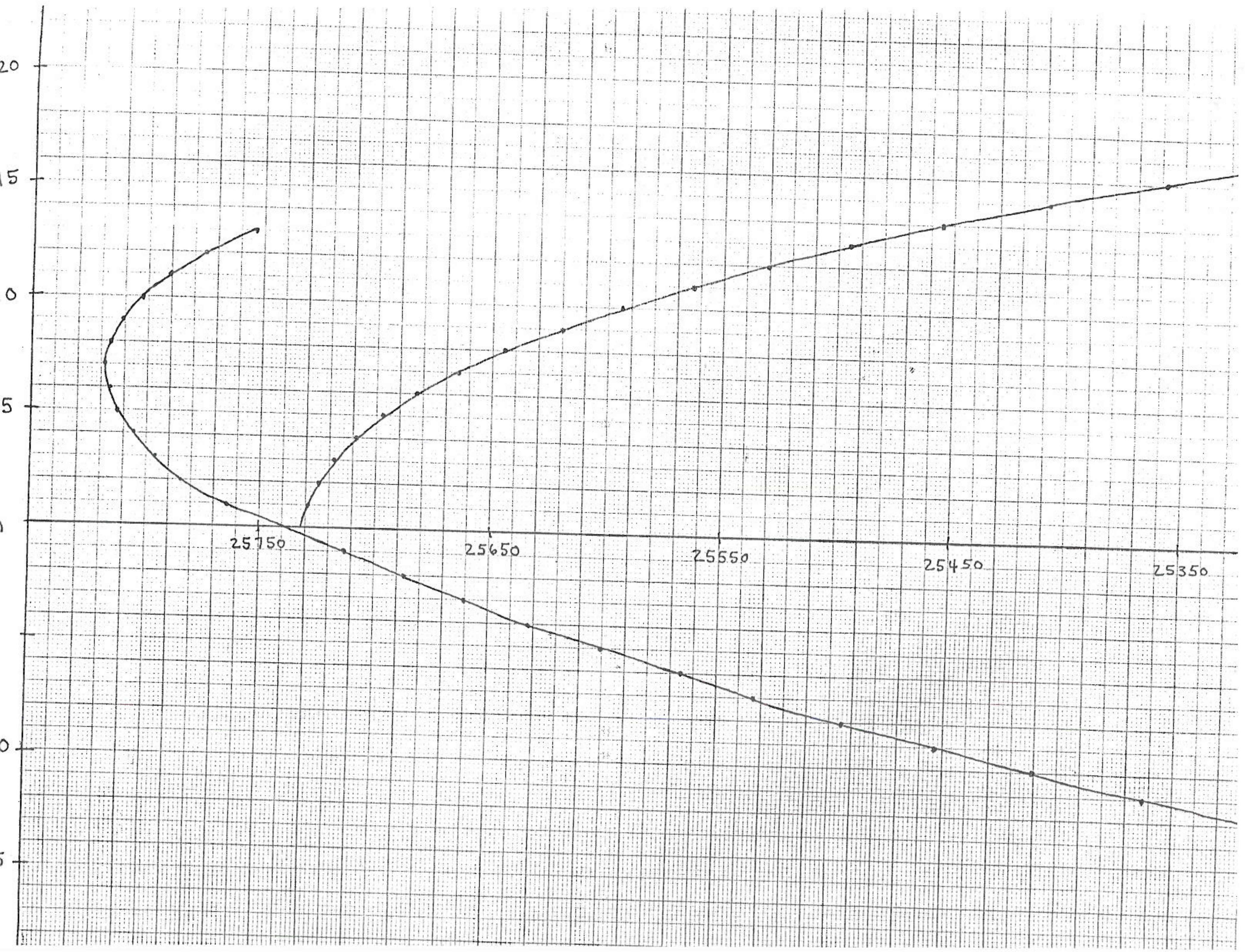
$\langle B_v'' \rangle = 10.54$

The formula for these lines represents a parabola, called Fortrat parabola.




* vertex of parabola represents head of the band




20
15
0
5
0
25750
25650
25550
25450
25350