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5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

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Lecture #12: Rotational Assignment of Diatomic Electronic Spectra I

Difficult to establish absolute rotational assignment of real electronic bands because

- * band heads - not all rotational lines are resolved
- * zero-gap is obscured
- * overlap by other bands and atomic lines
- * imperfections such as “perturbations” and “Predissociation”

See Herzberg Diatomics, pp. 168-192

TODAY

1. Nothing known at the start. The Fortrat Parabola - R and P branches fit one parabola but with arbitrary numbering! How do we decide on correct numbering?
- 2. B-value for 1 or 2 states known
one known set of rotational combination differences $\Delta_2F(J)$
“LAGERQVIST STRIP”
- 3. Nothing known. Simultaneous analysis of two bands that the vibrational analysis suggests share a vibrational level in common. Tedious trial and error method.
4. Computer automated analysis of $\left\{ \begin{array}{l} Z' \text{ ————— } \text{ unknown} \\ B'' \text{ ————— } \\ A'' \text{ ————— } \end{array} \right\} \text{ known}$
based on known $\Delta_2F(J)$'s and intensity systematics
5. Loomis-Wood plots: picking out branches (fragmentary patterns)
6. Laser Excited Dispersed Fluorescence (DF) spectrum

Grating spectrograph → ~24" Glass Plate, 10 μ slit

$$\frac{600\text{mm}}{10^{-2}\text{mm}} = 6 \times 10^4 \text{ resolution elements}$$

typically ~10³ rotational lines

in a sense all 10³ lines must be simultaneously assigned

- * several complex decisions, all made correctly
- * enormous redundancy

pattern recognition supplemented by trial and error

Figure 1 a trivial spectrum (SiO), assignable just like a vibration-rotation band in IR

Figure 2 non-trivial. Same molecule. same electronic system. “IMPERFECTIONS”

overlap
 perturbations
 impurities (SiO⁺, SiN)

Image of a trivial spectrum (SiO), assignable just like a
 vibration-rotation band in IR removed due to
 copyright restrictions.

Figure 1

Image of a non-trivial. Same molecule. Same electronic system.
 "Imperfections" removed due to copyright restrictions.

Figure 2

Fortrat parabola - one equation accounts for both R and P branches of ¹Σ⁺ - ¹Σ⁺ system.

$$v(n) = v_0 + (B' + B'')n + (B' - B'')n^2$$

	ΔB	
origin	linear	quadratic
P(J) =	v(-J)	i.e. n = -J
R(J) =	v(J + 1)	i.e. n = J + 1

relativism - any numbering is possible — same parabola, but apparently different equation.
 i.e. let m = n + 2. Then we get

$$v(m) = \underbrace{[v_0 - 2(B' + B'') + 4 \Delta B]}_{\text{new origin term}} + \underbrace{[B' + B'' - 2 \Delta B]}_{\text{new linear}} + \underbrace{\Delta B m^2}_{\text{same quadratic term}}$$

Image removed due to copyright restrictions.
Please see: Fig. 24 in Herzberg, G. *Spectra of Diatomic Molecules*. New York, NY: Van Nostrand, 1950.

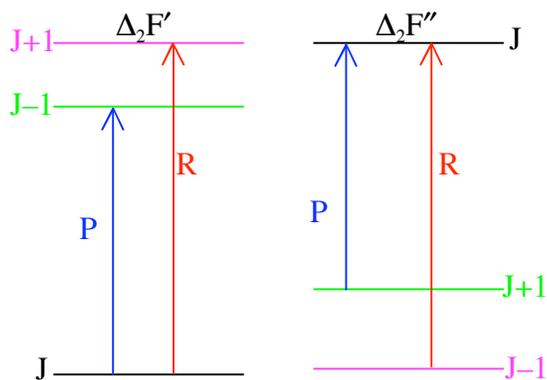
Figure 3

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Please see: Fig. 18 in Herzberg, G. *Spectra of Diatomic Molecules*. New York, NY: Van Nostrand, 1950.

Figure 4 Sometimes situation is even worse because part of Fortrat parabola is obscured or blended — can only resolve fragments of branches which may or may not be related to same Fortrat equation. To join fragments, pick out fragments of branches and extrapolate to try to join up pieces.

How is correct absolute numbering established?

1. zero gap (usually obscured)
2. perturbations - level shift or intensity anomaly at J' or J''
3. combination differences $\Delta_2 F'(J) = R(J) - P(J) = B'(4J + 2)$ [common lower level]
 $\Delta_2 F''(J) = R(J - 1) - P(J + 1) = B''(4J + 2)$ [common upper level]



- a. discovered by trial and error
- b. either $\Delta_2 F'$ or $\Delta_2 F''$ known from analysis of other bands or microwave spectrum
- c. laser excited dispersed fluorescence (DF).

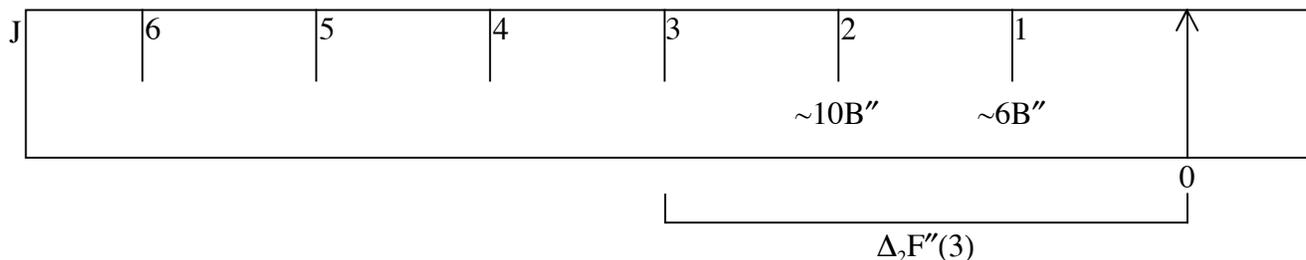
Example of easy case: all $\Delta_2 F''(J)$ known (but $\Delta_2 F'(J)$ not yet known)

Method of LAGERQVIST STRIPS - useful for DkO on Exam 1 [could be computerized].

1. Plot line positions and intensities on long roll of graph paper, typically 1 cm^{-1} per cm.
2. Prepare a Combination-Difference “ruler” (assume lower state C.D.’s are known).

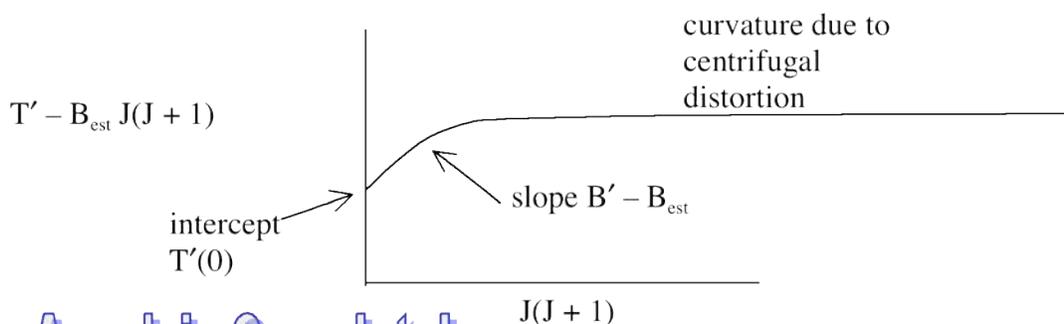
$$R(J - 1) - P(J + 1) = \Delta_2 F'' = B''(4J + 2) - \underbrace{D''(8J^3 + 12J^2 + 12J + J)}$$

high accuracy needed so D'' must be included



3. Use ruler to find the $P(J + 1)$ line related to (and, by definition to red of) $R(J - 1)$ line.
 - * Place arrow on one member of a group of lines that **seem to form a branch**.
 - * Note which lines of correct (i.e. expected Hönl-London relative intensity factor) coincide with one of the ruler markings. Most such coincidences are spurious.

- * move ruler arrow to next consecutive member of the tentative branch fragment. Look for coincidences with next higher or next lower number on C. D. ruler. Remember to look both to red and blue of arrowed line. Far fewer spurious matches will occur.
- * Repeat procedure a few times until a *bona fide* match at consecutive J-values occurs for each member of the tentative branch. You have found and identified (with correct absolute J's) R(J - 1) (to blue) and P(J + 1) (to red) pairs of lines terminating on common upper state rotational levels.
- * Plot "term values" (or "reduced term values") of each upper state rotational level vs. J(J + 1). Calculate term value by adding to R(J - 1) the lower state rotational energy $F''(J - 1) = B''(J - 1)(J) - D''(J - 1)^2(J)^2$. A "reduced" term value is $T'(J) - B'_{\text{est}} J(J + 1)$, which gives a useful scale expansion.



Analysis Complete!

More difficult case — nothing known about $\Delta_2 F'$ or $\Delta_2 F''$.

Must find two (speculatively) linked vibrational bands, say (0,0) and (1,0) in order to establish absolute rotational numbering of either band.

2 problems:

1. Correct relative numbering in R and P branch regions of Fortrat parabola. Must extrapolate accurately from one branch fragment back through head region to pick up other branch fragment. It is easy to miss by ± 1 or 2 J-units (typically must test ~ 5 relative numberings of 2nd branch fragment).
2. Absolute J numbering.

Observed Lines

0,0	1,0
30003.5	30502.2
2.7	1.2
1.8	500.0
30000.7	498.6
29999.4	97.0
97.9	95.2
71.3	70.0
67.8	66.2
64.0	62.2
60.1	58.0
56.0	53.6
51.7	49.0

Diagram annotations: A pink bracket labeled 'trial' groups the top five lines of the 0,0 band. A red bracket labeled 'correct' groups the top five lines of the 1,0 band. A red bracket labeled 'R' is between the 30000.7 and 29999.4 lines in the 0,0 band. A red bracket labeled 'R' is between the 498.6 and 97.0 lines in the 1,0 band. A blue bracket labeled 'P' is between the 71.3 and 51.7 lines in the 0,0 band. A blue bracket labeled 'P' is between the 70.0 and 49.0 lines in the 1,0 band.

Here is a 6 step procedure using the line list.

- adopt arbitrary numbering for the P-branches of 2 linked bands.

$$\begin{array}{l} P_1 \quad J_1^{\text{trial}} \\ P_2 \quad J_2^{\text{trial}} \end{array}$$

- Extrapolate to R_1 and R_2 regions using Fortrat Equation. Use trial numbering for R_1 and R_2 suggested by extrapolation. Uncertainty in J is ± 2 for both. 25 possibilities for R_1 (5 possibilities) \times R_2 (5 possibilities)!

- Calculate set of combination differences for common vibrational level.

i.e. for $(0,0) + (1,0) \rightarrow v'' = 0$ level
trial C.D.'s (see Figure on next page).

$$\Delta_2 F''(J) = v(J+1) - v(-J) \quad \text{lower state}$$

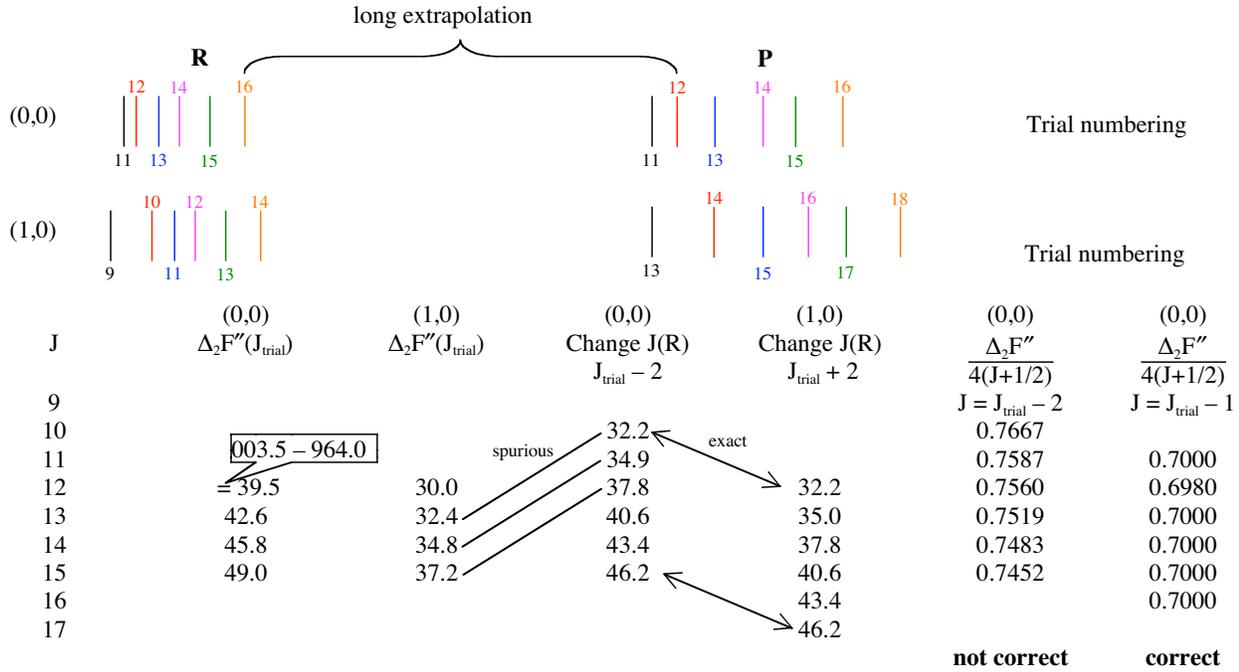
or

$$\Delta_2 F'(J) = v(J) - v(-J-1) \quad \text{upper state}$$

See figure (next page) that describes how set of C.D.'s will look normal but that there cannot be agreement between those for 2 linked bands unless absolute numbering is correct.

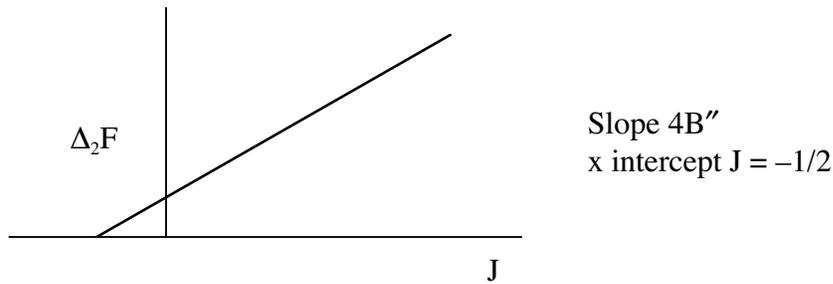
- Look for agreement between any of the C.D.'s for the two bands. If none exists, try changing the trial numberings of R_1 and/or R_2 ~25 combinations! Recalculate C.D.'s until agreement is found. Tedious.
- Agreement is found (columns 3 and 4). Note that spurious agreement is easy to obtain if data quality is poor. For example, see alternative near agreement between columns 2 and 3.

This establishes the correct relative R,P branch numberings in both linked bands. However, the relative numbering may differ from the correct absolute numbering by a different integer in each band. No problem.



6. Graphical method for determining absolute numbering in each band. $\Delta_2 F''(J) = B''(4J + 2)$

Plot $\Delta_2 F$ vs. J :



C.D. plot (with scale expansion).

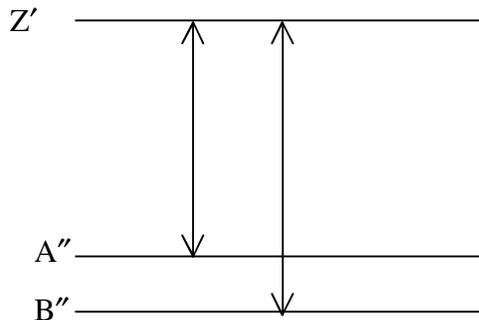
If J^{trial} is wrong:

- * B not sufficiently constant (see centrifugal distortion effects)
- * intercept is not $-1/2$

This procedure could easily be computerized.

Alternative approach useful for extremely complex bands. Computer automated analysis based on model-free TERM VALUE method.

Start with two fully characterized vibrational levels A'' and B'' in order to automatically characterize an unknown level Z' linked to both A'' and B'' .



takes advantage of known lower level combination differences and term values.

1. Prepare energy-ordered transition lists for $Z'-A''$ and $Z'-B''$ bands.
2. Search $Z'-A''$ list for all pairs of lines differing by preset tolerance from given A'' state $\Delta_2 F''_A$. Make list of possible R(J-1), P(J+1) pairs for that J.
3. Add to each observed transition frequency the known A'' state term value. This gives set of trial $Z'(J)$ term values.

both same
to preset
tolerance

$$\begin{cases} T_{Z'}(J') = T_{A'}(J'-1) + R_{\text{trial}}(J'-1) \\ T_{Z'}(J') = T_{A'}(J'+1) + P_{\text{trial}}(J'+1) \end{cases}$$

4. Attempt to verify by searching for all $\Delta_2 F_B''(J)$ (at same J-values) in Z'-B'' list.

Find all pairs with $\Delta_2 F_B''(J)$ difference to present tolerance. Prepare new list of feasible R(J-1), P(J+1) pairs for Z'-B''.

5. Convert each Z'-B'' line pair into a Z' state term value for that J'.
6. Compare $T_{Z'}(J')$ term values from Z'-A'' and Z'-B'' bands.

Collect only those special quartets of lines [P,R from Z'-A'' and P,R from Z'-B''] which have term values $T_{Z'}(J')$ which agree within preset tolerance.

7. Require reasonable (Hönl-London factors) intensity relationships

$$\begin{aligned} & I_R/I_p \text{ within band} \\ & I_{R_{Z-A}}/I_{R_{Z-B}} \text{ populations (in absorption) and/or F-C factors.} \end{aligned}$$

See Figure 5 term value method summary.

L. Hagland et. al., On the Band Spectrum of YbH and YbD
Ark. f. Fys. **32**, 321 (1966)

+500	+546	+1678	+1735	+.10+.14	+18568.26
+2	+0	+3	+2	-.09	
+497	+541	+1675	+1731	+.02+.10	+18577.29
+0	+1	+3	+0	+.08	
+253	+315	+1362	+1412	+.02-.12	+19292.79
+4	+4	+4	+4	+.01	
+195	+254	+1304	+1349	+.14-.06	+19456.09
+3	+2	+0	+2	+.05	
+193	+253	+1301	+1346	+.10-.09	+19461.29
+2	+4	+6	+0	-.10	
+139	+206	+1204	+1299	-.05-.10	+19589.32
+1	+2	+0	+0	-.13	

Figure 5 List obtained when employing the computer program to pick out branches. The list represents a specific J-number. The feasible term values of an upper rotational level are found at the far right, each preceded by the indices of the four lines which connect with the proposed level. The individual errors of the combination differences are also given and, on the line below, the difference between $T'_A(J)$ and $T'_B(J)$. On this line one also finds the intensity figures of the four lines. The preset limit of the errors of the combination differences was $\pm 0.15 \text{ cm}^{-1}$ and of the term values $\pm 0.15 \text{ cm}^{-1}$.

Rotational Assignment of a ${}^1\Sigma^-1\Sigma$ Band

The Fortrat equation is

$$v(n) = v_0 + (B' + B'')n + (B' - B'')n^2$$

$$R(J) = v(n) \quad n = J + 1$$

$$P(J) = v(n) \quad n = -J$$

$$\begin{aligned} \Delta_2 F'(J) &= R(J) - P(J) = (B' + B'')[J + 1 - (-J)] + (B' - B'')[J + 1]^2 - (-J)^2 \\ &= (4J + 2)B' \end{aligned}$$

$$\begin{aligned} \Delta_2 F''(J) &= R(J - 1) - P(J + 1) = (B' + B'')[J - (-J - 1)] + (B' - B'')[J - 1]^2 - (J + 1)^2 \\ &= (4J + 2)B'' \end{aligned}$$

Suppose that the numbering is incorrect by m units. This is quite plausible because the form of the Fortrat equation is independent of m :

$$n' = n + m$$

$$v(n') = [v_0 - (B' + B'')m + (B' - B'')m^2] + (B' + B'' - 2m\Delta B)n' + \Delta Bn'^2.$$

The apparent combination differences would be $[v(n' - 1) - v(-n')]$ and $[v(n' - 2) - v(-n' - 1)]$.

$$\Delta_2 F'(J) = [B' - m\Delta B](4J + 2)$$

$$\Delta_2 F''(J) = [B'' - m\Delta B](4J + 2).$$

A plot of $\Delta_2 F$ vs. J gives a straight line with slope $4(B - m\Delta B)$ and intercept $J = -1/2$. This means that a single band cannot be given a unique numbering unless B' or B'' is known in advance.

To remove this numbering ambiguity, it is necessary to analyze simultaneously two bands linked by a common upper or lower state vibrational level.

Suppose we think we have the A-X (0,0) and (1,0) bands. Then we expect a common set of lower state combination differences. So we are interested in $\Delta_2 F''$. We seek agreement in $\Delta_2 F''$ for the two bands. This can only occur if both bands are correctly numbered.

$$\text{For } (0,0) \quad \Delta B = B'_0 - B''_0 \equiv \Delta B_{00}$$

$$(1,0) \quad \Delta B = B'_1 - B''_0 \equiv B'_0 - \alpha'_e - B''_0 = \Delta B_{00} - \alpha'_e$$

$$\Delta_2 F''(1,0)(J) = [B''_0 - m(\Delta B_{00}) + m\alpha'_e](4J + 2)$$

$$\Delta_2 F''(0,0)(J) = [B''_0 - m(\Delta B_{00}) + 0](4J + 2)$$

These two sets of $\Delta_2 F''(J)$ can only be identical if $m = 0$.

This requires that $R(J-1) - P(J+1)$ must be measured with a precision better than $(\alpha'_e/2)(4J+2)$. For typical values of α and J_{\max} of 0.002 cm^{-1} and 20, this amounts to a required precision of $\sim 0.08 \text{ cm}^{-1}$ in the measured separation of two lines $82B \approx 80 \text{ cm}^{-1}$ apart!

However, there are additional ambiguities which must be overcome before an absolute rotational numbering becomes evident.

Suppose you can pick out several series of regularly spaced lines. The first problem is to discover which branch fragments belong to the same band. This is accomplished by fitting each fragment to a Fortrat type quadratic equation. The absolute numbering is irrelevant at this stage – simply pick arbitrary consecutive integer running numberings.

1. Fragments with the same n^2 coefficient probably belong to the same vibronic band.
2. Two fragments with the same n^2 coefficient must be combined by extrapolating from the region of one fragment to that of the other. This extrapolation, using the arbitrary numbering of one fragment and the fitted values of the constant, linear, and quadratic terms, is probably not going to give a definitive numbering of the second fragment relative to the first. It is also possible that the two fragments belong to the same branch, to R and P branches of the same band, or to different bands and the proposed linkage is spurious. All plausible numberings of the second fragment relative to the first must be examined. This means that a set of trial combination differences must be computed for each trial numbering of the second fragment. Which of these is correct may be established only by finding exact agreement between combination differences for two linked bands. If the 2nd-fragment numbering is uncertain by ± 2 units, 5 sets of combination differences must be computed.
3. Suppose that the two bands really are linked and that the R and P branches in each have the correct relative numberings. There is still no reason to expect that either band has the correct absolute J-numbering or even that the integer error in numbering is the same for both bands. Trial and error to the rescue!

Relative intensities, perturbations, and prior expectations for reasonable values of B' , B'' help to limit the number of possibilities that must be tested. However, when $B' - B''$ is small, an enormous number of possible numberings must be tested.

Prior knowledge of B' or B'' or the use of laser fluorescence techniques make the assignment process vastly less tedious.

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Please see: Figure 1 in Herzberg, G. I., et al. "Band of Spectra of YbH and YbD." *Phys Scr* 32 (1966): 321-69.

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