1. Introduction
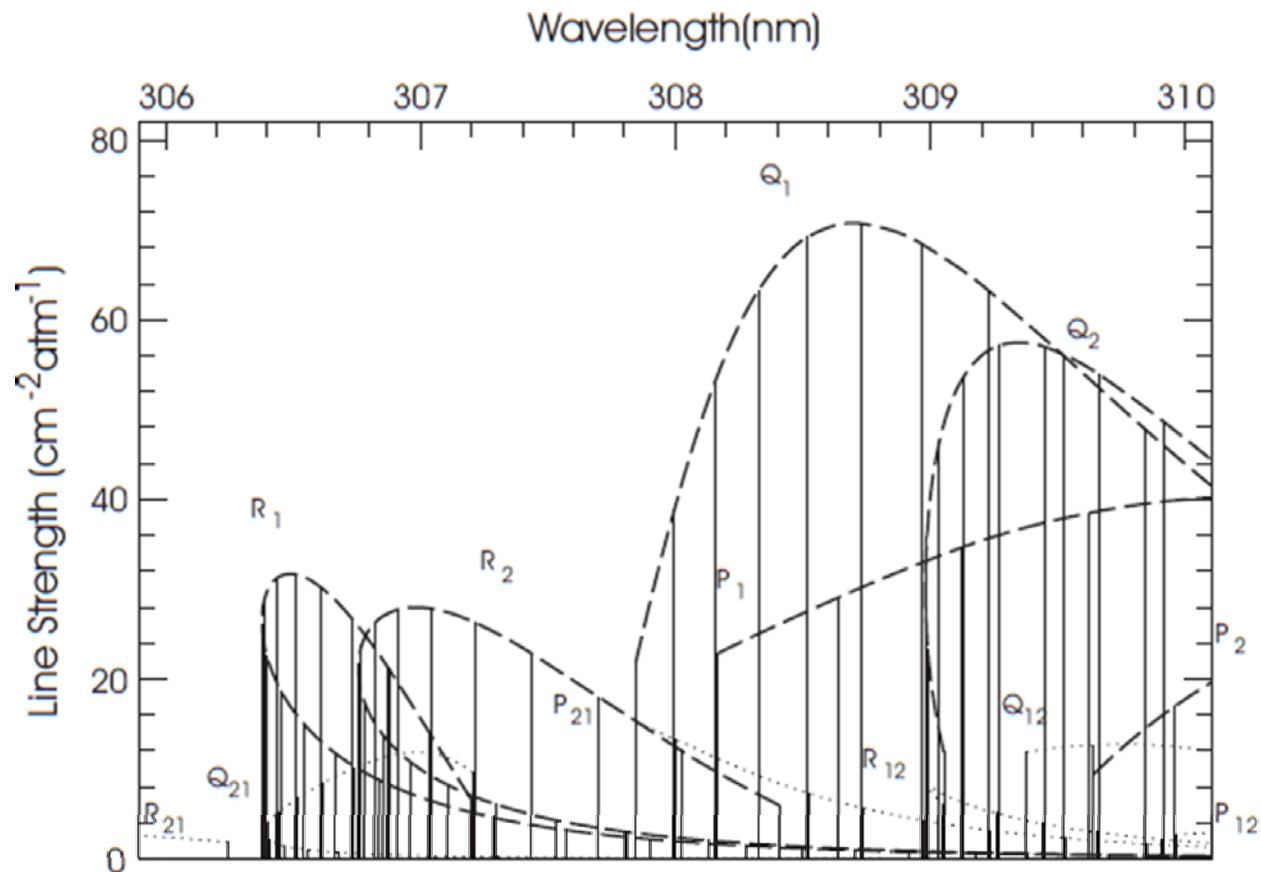
- OH, a prominent flame emitter, absorber.
  Useful for T, X_{OH} measurements.

Selected region of $A^2\Sigma^+ \leftarrow X^2\Pi(0,0)$ band at 2000K

The vibrational structure of the system was gradually recognized.[2-4] It is given in Table 1 which lists the heads of all the bands found until now with an estimate of their intensities according to Tanaka and Koana[4]. For the bands that are underlined, new measurements and a revision of the analysis are given in this report. For the other bands the references indicate where the most complete data can be found. More accurate data on the intensities of a number of bands are given further on in this report (Table 6).

Table 1

V' \ V''	0	1	2	3	4
0	3064 (10)	3428 (7)[1]			
1	2811 (9)	3122 (9)	3185 (6)[1]		
2	2609 (4)[4]	2875 (9)[3]	3185 (6)[3, 5]		
3	2444 (1)[2, 3]	2677 (5)[2, 3]	2945 (7)[3]	3254 (4)[3]	
4		2517 (2)[3]	2753 (4)[3]	3022 (5)[3]	3331 (4)[3]

2. Energy levels

■ Term energies

Angular momentum energy (nuclei + electrons)

$$E(n, v, J) = T_e(n) + G(v) + F(J)$$

elec. q. no. ⟶ | Electronic energy
vib. q. no. ⟶ | Vibrational energy
ang. mom. q. no. ⟶

▪ Separation of terms: Born-Oppenheimer approximation

▪ $G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2$

▪ Sources of T_e, ω_e, $\omega_e x_e$ ➡ Herzberg

▪ Overall system : $A^2\Sigma^+ \leftarrow X^2\Pi$

in [cm^{-1}]

$A^2\Sigma^+$	T_e	ω_e	$\omega_e x_e$	$X^2\Pi$	T_e	ω_e	$\omega_e x_e$
	32682.0	3184.28	97.84		0.0	3735.21	82.21

Let's first look at the upper state ➡ Hund's case b!
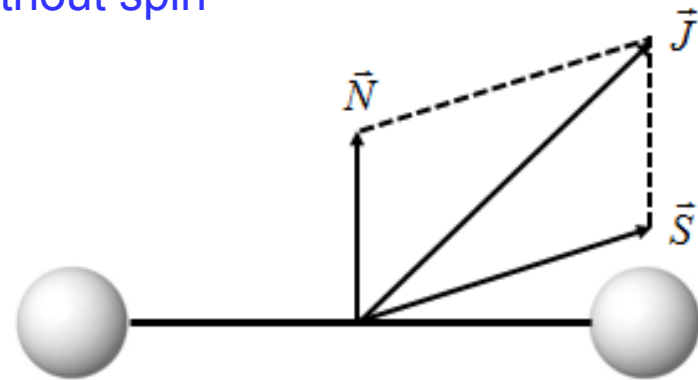
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2. Energy levels

- Hund's case b ($\Lambda=0$, $S\neq0$) – more standard, especially for hydrides

Recall:

- Σ, Ω not rigorously defined

- N = angular momentum without spin

- S = 1/2-integer values

- J = N+S, N+S-1, …, |N-S|

- i = 1, 2, …
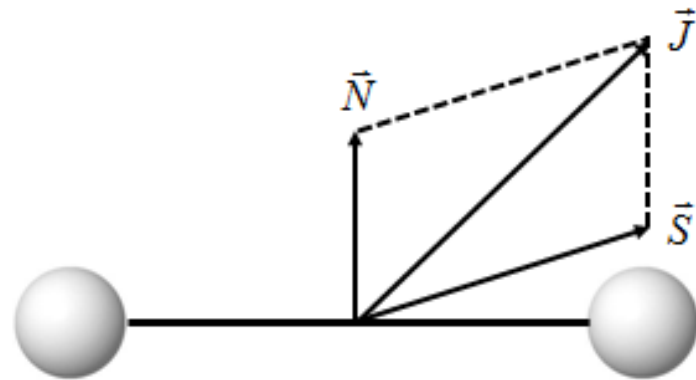
  $F_i(N)$ = rotational term energy

Now, specifically, for OH?

2. Energy levels

- The upper state is $A^2\Sigma^+$

For OH:

- $\Lambda = 0$, $\therefore$ Σ not defined $\Rightarrow$ use Hund's case b

- $N = 0, 1, 2, \ldots$

- $S = 1/2$

- $J = N \pm 1/2$

- F_1 denotes $J = N + 1/2$

F_2 denotes $J = N - 1/2$

Common to write either $F_1(N)$ or $F_1(J)$

2. Energy levels

- The upper state: A$^2\Sigma^+$
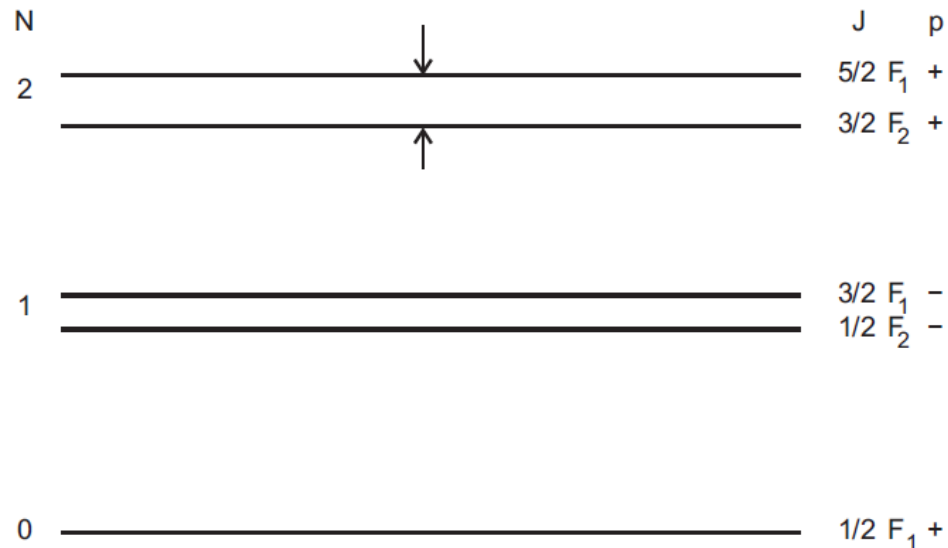
$$F_1(N) = B_v N(N+1) - D_v\left[N(N+1)\right]^2 + \gamma_v N$$

$$F_2(N) = B_v N(N+1) - D_v\left[N(N+1)\right]^2 - \gamma_v (N+1)$$

$$\left(\text{splitting constant } \gamma_v \approx 0.1\,\text{cm}^{-1} \text{ for OH } A^2\Sigma^+\right)$$

for pure case b

- ∴ the spin-splitting is $\gamma_v(2N+1)$ ➡ function of v; increases with N

$\gamma_v(2N+1) \sim 0.1(5) \sim 0.5\,\text{cm}^{-1}$ for N$_2$
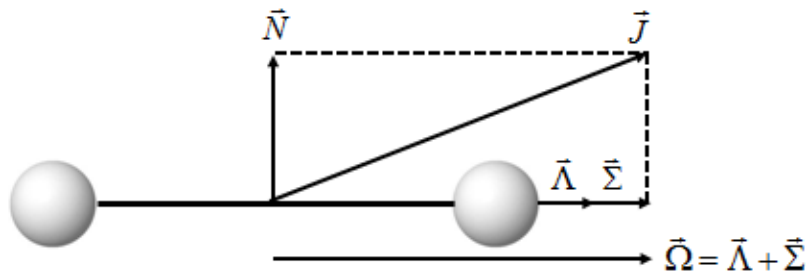Compare with $\Delta\nu_D(1800K) = 0.23\,\text{cm}^{-1}$

Notes:

- Progression for A$^2\Sigma^+$

- "+" denotes positive "parity" for even N [wave function symmetry]

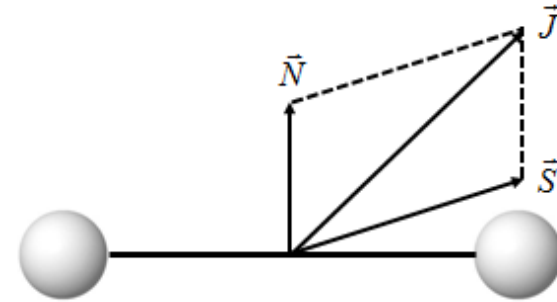- Importance? Selection rules require parity change in transition

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2. Energy levels

■ The ground state: $X^2\Pi$ (Λ=1, S=1/2)

Hund's case *a*
$\Lambda \neq 0$, S $\neq$ 0, Σ defined

Hund's case *b*
$\Lambda = 0$, S $\neq$ 0, Σ not defined

✎ Note:

1. Rules less strong for hydrides

2. OH behaves like Hund's a @ low N
              like Hund's b @ large N

    ➡ at large N, $\vec{L}$ couples more to N, Λ is less defined, S decouples from A-axis

3. Result? OH $X^2\Pi$ is termed "intermediate case"

2. Energy levels

- The ground state: X$^2\Pi$

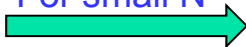 ✎ Notes:

  3. For "intermediate/transition cases"

  $$F_1(N) = B_v\left\{(N+1)^2 - \Lambda^2 - \frac{1}{2}\left[4(N+1)^2 + Y_v(Y_v-4)\Lambda^2\right]^{1/2}\right\} - D_v\left[N(N+1)\right]^2$$

  $$F_2(N) = B_v\left\{N^2 - \Lambda^2 + \frac{1}{2}\left[4N^2 + Y_v(Y_v-4)\Lambda^2\right]^{1/2}\right\} - D_v\left[N(N+1)\right]^2$$

  where $Y_v \equiv A/B_v$ (< 0 for OH); A is effectively the moment of inertia
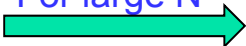
  Note: $F_1(N) < F_2(N)$

  For small N → Behaves like Hund's a, i.e., symmetric top, with spin splitting ΛA

  For large N → Behaves like Hund's b, with small (declining) effect from spin

  $$F_1 \to B_v\left[(N+1)^2 - \Lambda^2 - (N+1)\right]$$
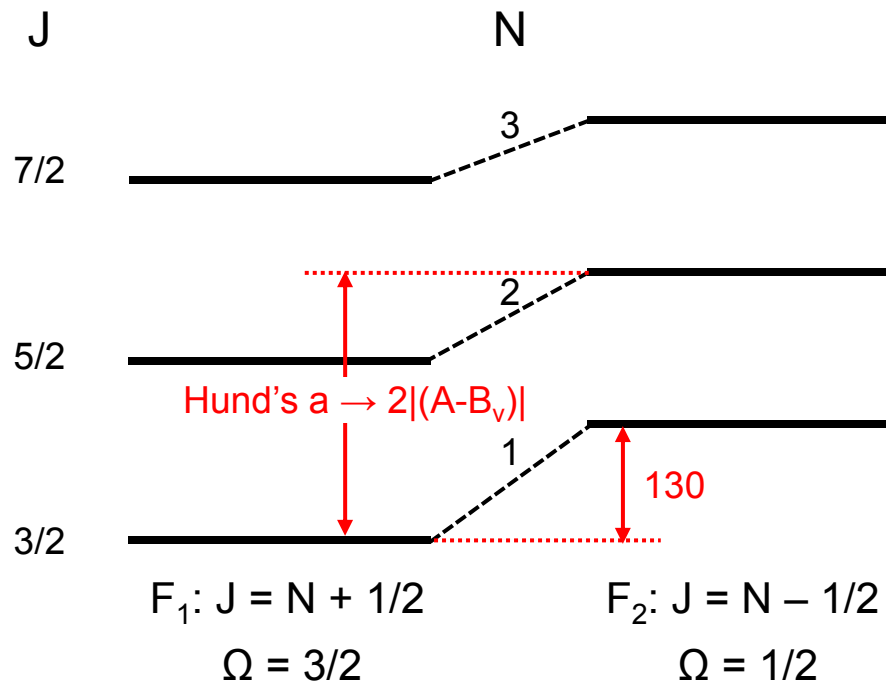
  $$F_2 \to B_v\left[N^2 - \Lambda^2 + N\right]$$

  ⇒ $F_1 - F_2 \to B_v\left[(N+1)^2 - N^2 - (2N+1)\right] \to 0$

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2. Energy levels

- The ground state: $X^2\Pi$

  ✎ Notes:

    4. Some similarity to symmetric top

J (left column)

J
7/2
5/2
3/2

N (middle column): 3, 2, 1

Hund's a → $2|(A-B_v)|$

130

F_1: J = N + 1/2 Ω = 3/2

F_2: J = N − 1/2 Ω = 1/2

Showed earlier that $F_1 < F_2$

J (right column): 5/2, 3/2, 1/2

$T_e = T_0 + A\Lambda\Sigma$

For OH, A = -140 cm^{-1}

➡ $T_e = T_0 + (-140)(1)(1/2)$, $\Sigma = 1/2$
            $+ (-140)(1)(-1/2)$, $\Sigma = -1/2$

➡ $\Delta T_e = \underline{140}$ cm^{-1}

Not too far off the 130 cm^{-1} spacing for minimum J

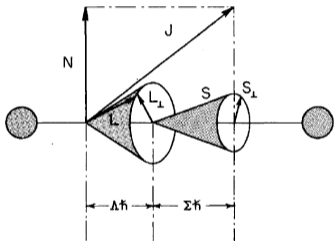Recall: Hund's case **a** has constant difference of $2(A-B_v)$ for same J

$F(J) = BJ(J+1) + (A-B)\Omega^2$

$(A–B)\Omega^2 \approx -158.5\Omega^2$

(A for OH~ -140, B ~ 18.5), Ω = 3/2, 1/2

➡ Ω = 3/2 state lower by $\underline{316}$ cm^{-1}

Actual spacing is only 188 cm^{-1}, reflects that <u>hydrides quickly go to Hund's case **b**</u>

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2. Energy levels

- The ground state: $X^2\Pi$
  - Notes:
    5. Role of Λ-doubling
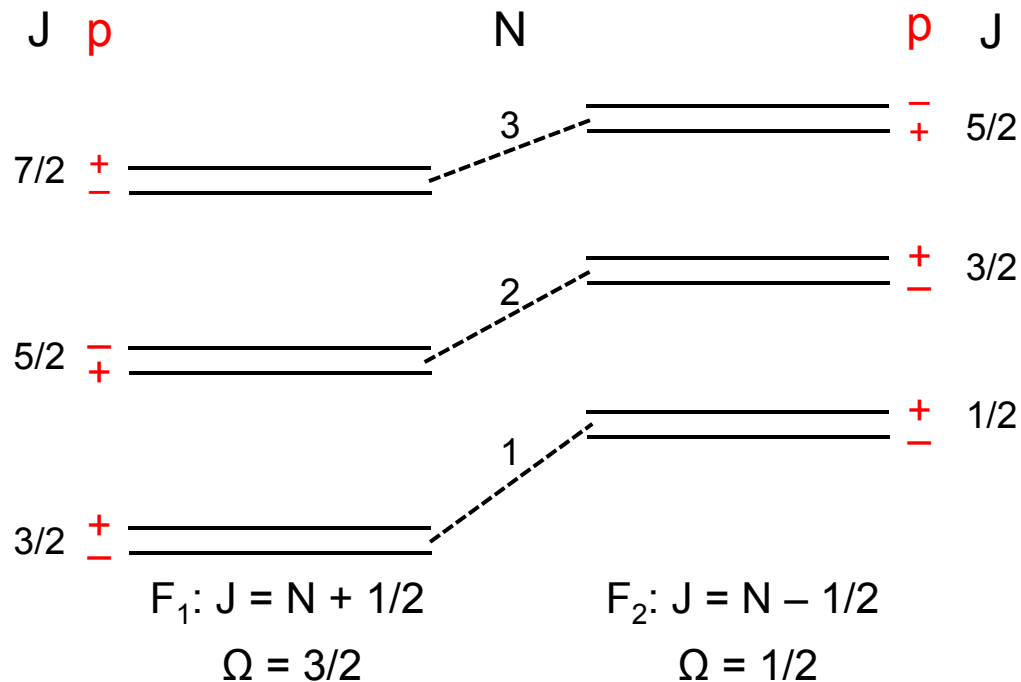
$$F_{ic} = F_i(J) + \delta_c J(J+1)$$
$$F_{id} = F_i(J) + \delta_d J(J+1)$$
$$F_{id} < F_{ic}$$

- $F_{ic}(J) - F_{id}(J) \approx 0.04$ cm^{-1} for typical J in OH
- c and d have different parity (p)
- Splitting decreases with increasing N

F_1: $J = N + 1/2$ F_2: $J = N - 1/2$

$\Omega = 3/2$ $\Omega = 1/2$

Showed earlier that $F_1 < F_2$

Now let's proceed to draw transitions, but first let's give a primer on transition notation.

3. Allowed radiative transitions

- Transition notations

Full description: $A^2\Sigma^+$ (v')←$X^2\Pi$ (v") $^Y X_{\alpha\beta}$(N" or J")

$$^{Y}X_{\alpha\beta}\left(N" \text{ or } J"\right)$$

where Y – ΔN (O, P, Q, R, S for ΔN = -2 to +2)

X – ΔJ (P, Q, R for ΔJ = -1, 0, +1)

α = i in F_i'; i.e., 1 for F_1, 2 for F_2

β = i in $F_i"$; i.e., 1 for F_1, 2 for F_2

✎ Notes:

Strongest trans.
e.g., $R_1(7)$ or R_17

1. Y suppressed when ΔN = ΔJ
2. β suppressed when α = β
3. Both N" and J" are used

Example: $^SR_{21}$:

ΔJ = +1, ΔN = +2

F' = F_2(N')

F" = F_1(N")

- General selection rules

  - Parity must change + → – or – → +
  - ΔJ = 0, $\pm$1
  - No Q (J = 0) transitions, J = 0 → J = 0 not allowed

$$O_{12}(K) = F_1(K-2) - f'_2(K) \qquad J-1 \to J \qquad (5a)$$

$$P_1(K) = F_1(K-1) - f_1(K) \qquad J-1 \to J \qquad (5b)$$

$$P_2(K) = F_2(K-1) - f_2(K) \qquad J-1 \to J \qquad (5c)$$

$$P_{12}(K) = F_1(K-1) - f_2(K) \qquad J \to J \qquad (5d)$$

$$Q_1(K) = F_1(K) - f'_1(K) \qquad J \to J \qquad (5e)$$

$$Q_{21}(K) = F_2(K) - f'_1(K) \qquad J-1 \to J \qquad (5f)$$

$$Q_2(K) = F_2(K) - f'_2(K) \qquad J \to J \qquad (5g)$$

$$Q_{12}(K) = F_1(K) - f'_2(K) \qquad J+1 \to J \qquad (5h)$$

$$R_1(K) = F_1(K+1) - f_1(K) \qquad J+1 \to J \qquad (5i)$$

$$R_{21}(K) = F_2(K+1) - f_1(K) \qquad J \to J \qquad (5j)$$

$$R_2(K) = F_2(K+1) - f_2(K) \qquad J+1 \to J \qquad (5k)$$

$$S_{21}(K) = F_2(K+2) - f'_1(K) \qquad J+1 \to J \qquad (5l)$$

The following remarks will make it easier to utilize the results of the earlier papers.

In the previous publications often different notations were used. In the papers by Heurlinger[9], Watson[10, 14], Fortrat[13], Dieke[2], the numbering of the lines is $K+1$ of the final state and the indices 1 and 2 of the levels are interchanged, e.g. $R_2(5)$ of the present paper was $R_1(6)$.

Mulliken[17] uses the notation for case (a), i.e. he numbers the lines, and names the branches by their J values. He indicates by a prefixed superscript the type of branch as follows:

Present paper O_{12} P_1 P_2 P_{12} Q_1 Q_{21} Q_2 Q_{12} R_1 R_{21} R_2 S_{21}

Mulliken $^{P}P_P$ P_1 P_2 ^{P}Q $Q_1{}^{Q}_P$ $Q_2{}^{Q}_B$ $R_1{}^{R}_Q$ $R_2{}^{R}R$

The later papers usually use a notation similar to Mulliken's notation or the one adopted in the present paper.

3. Allowed radiative transitions

- Allowed transitions

Allowed rotational transitions from N"=13 in the $A^2\Sigma^+ \leftarrow X^2\Pi$ system

State or level
⬇
a specific v",J",N",and Λ-coupling
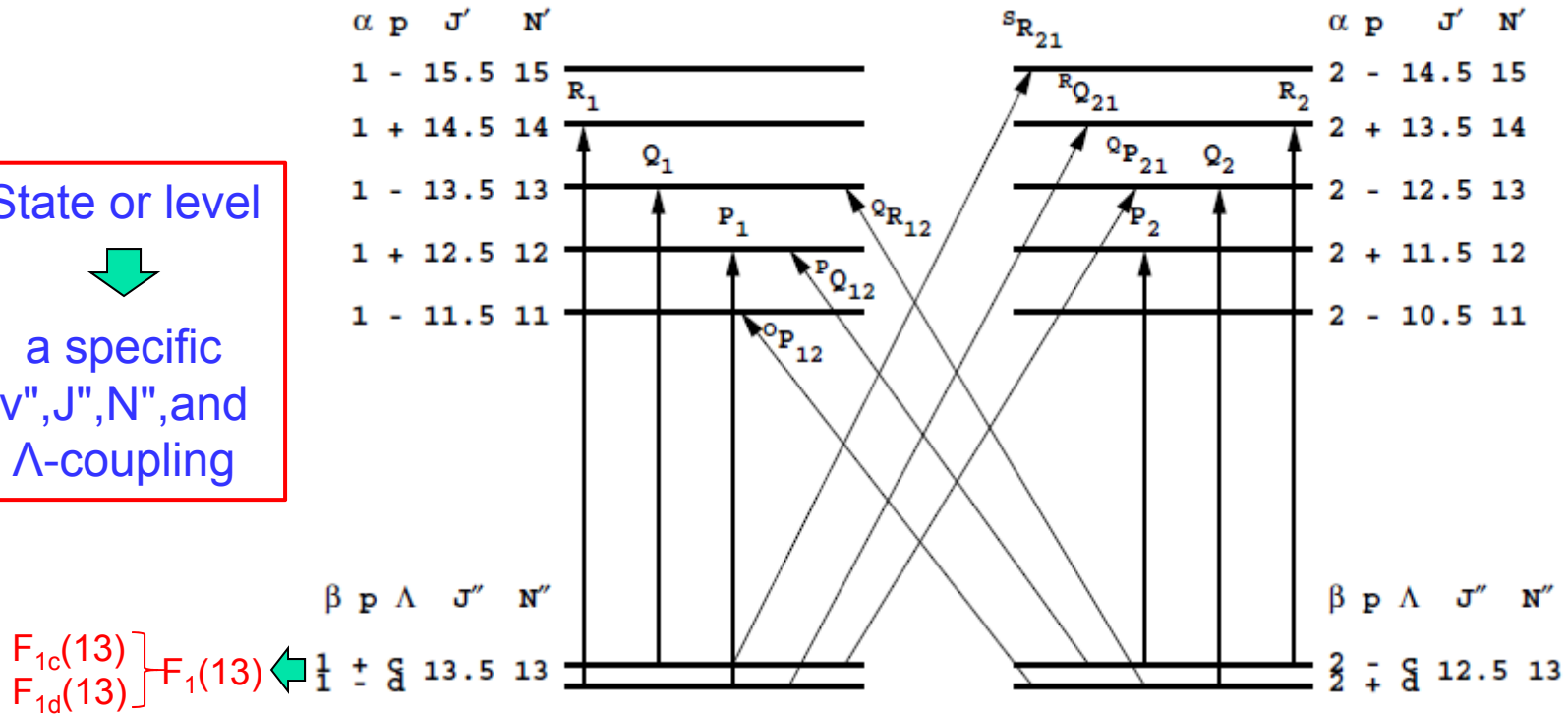
- 12 bands possible (3 originating from each *lambda-doubled, spin-split* X state)
- Main branches: α = β; Cross-branches: α ≠ β
- Cross-branches weaken as N increases

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3. Allowed radiative transitions

- Allowed transitions

Allowed rotational transitions from N"=13 in the $A^2\Sigma^+ \leftarrow X^2\Pi$ system
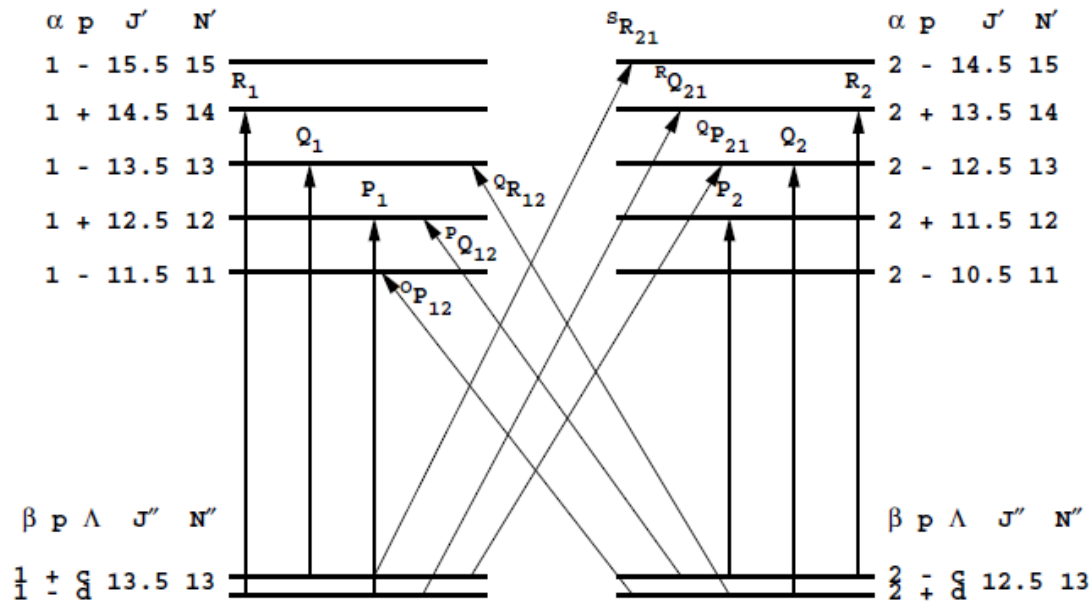
✎ Notes:

- A given J" (or N") has 12 branches (6 are strong; $\Delta J = \Delta N$)
- $+ \leftrightarrow -$ rule on parity
- $F_{1c} - F_{1d} \approx 0.04N(N+1)$ for OH ➡ for N~10, Λ-doubling is ~ $4 cm^{-1}$, giving clear separation
- If upper state has Λ-doubling, we get <u>twice</u> as many lines!

3. Allowed radiative transitions

- Allowed transitions

Allowed rotational transitions from N"=13 in the $A^2\Sigma^+\leftarrow X^2\Sigma^+$ system
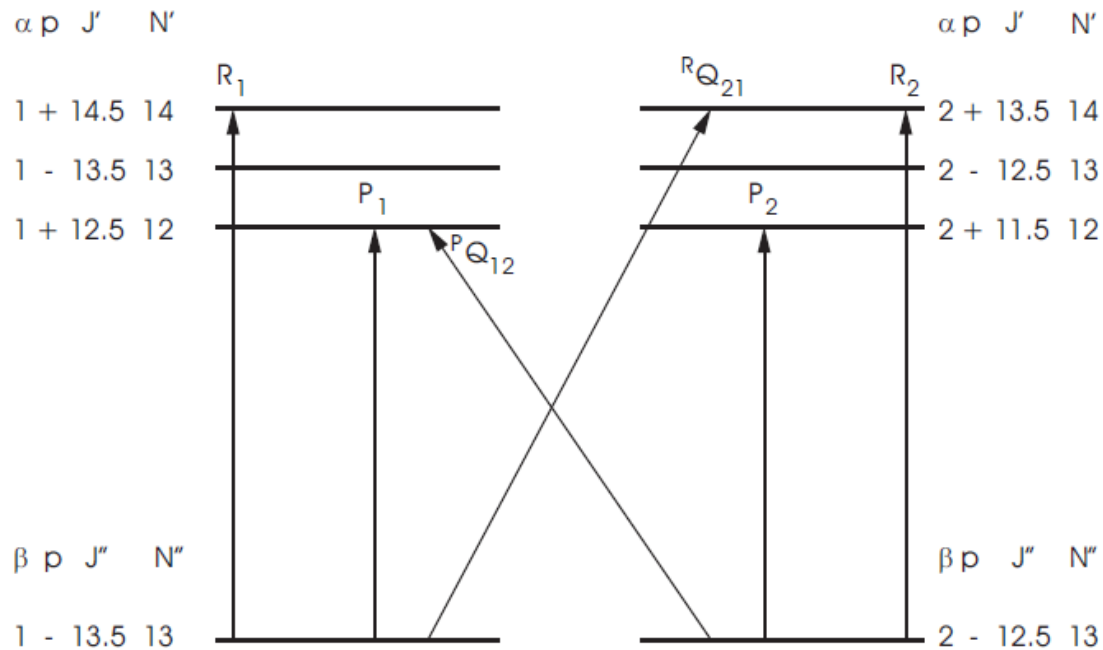

- Note:
  1. The effect of the parity selection rule in reducing the number of allowed main branches to 4
  2. The simplification when $\Lambda=0$ in lower state, i.e., no Λ-doubling

4.1. Oscillator strengths

- Absorption oscillator strength

elec. osc. strength   F-C factor   H-L factor

$$f_{(n'',v'',\Sigma'',J'',\Lambda''),(n',v',\Sigma',J',\Lambda')} = f_{n''n'}\, q_{v''v'}\, \frac{S_{J''J'}}{2J''+1}$$

elec.   vib.   spin   ang. mom.   Λ-doubling

or in shorthand notation $\quad f_{J''J'} = \underbrace{f_{n''n'}\, q_{v''v'}}\, \dfrac{S_{J''J'}}{2J''+1}$

$\qquad\qquad\qquad\qquad\qquad = f_{v''v'}$ = band oscillator strength

For OH A$^2\Sigma^+$–X$^2\Pi$

(v',v")	$f_{v'v''}$
(0,0)	0.00096
(1,0)	0.00028

✏ Notes: $q_{v''v'}$ and $S_{J''J'}$ are normalized

- $\displaystyle\sum_{v'} q_{v''v'} = 1$

- $\displaystyle\sum_{J'} S_{J''J'} = (2J''+1)\underbrace{(2S+1)}\,\delta$

  $\underbrace{}_{g''_{el}=4 \text{ for } X^2\Pi}$

  ⌐1 for Λ = 0 (Σ state), 2 otherwise

this sum includes the S values for all states with J"

4.1. Oscillator strengths

- *Is $S_{J''J'} = S_{J'J''}$?* ➤ Yes, for our normalization scheme!
  - From $g_1 f_{12} = g_2 f_{21}$, and recognizing that $2J+1$ is the ultimate (non removable) degeneracy at the state level, we can write, for a specific transition between single states

  $$\left(2J''+1\right) \cdot f_{el}'' \cdot q_{v''v'} \cdot \frac{S_{J''J'}}{2J''+1} = \left(2J'+1\right) \cdot f_{el}' \cdot q_{v'v''} \cdot \frac{S_{J'J''}}{2J'+1}$$

  In this way, there are no remaining electronic degeneracy and we require, for detailed balance, that $f_{el}'' = f_{el}'$, $q_{v''v'} = q_{v'v''}$ and $S_{J''J'} = S_{J'J''}$

- *Do we always enforce $\sum_{J'} S_{J''J'} = \left(2J''+1\right)$ for a state?* ➤ No!
  - But note we do enforce $\sum_{J'} S_{J''J'} = \left(2J''+1\right)\left(2S+1\right)\delta$ (14.17)

    and $\sum_{J''} S_{J''J'} = \left(2J'+1\right)\left(2S+1\right)\delta$ (14.19)

    where, for OH $A^2\Sigma \leftarrow X^2\Pi$, $(2S+1) = 2$ and $\delta = 2$.

- *When is there a problem?*
  - Everything is okay for Σ-Σ and Π-Π, where there are equal "elec. degeneracies", i,e., $g''_{el} = g'_{el}$. But for Σ-Π (as in OH), we have an issue. In the $X^2\Pi$ state, $g_{el} = 4$ (2 for spin and 2 for Λ-doubling), meaning each J is split into 4 states. Inspection of our H-L tables for $S_{J''J'}$ for OH $A^2\Sigma \leftarrow X^2\Pi$ (absorption) confirms $\Sigma S_{J''J'}$ from each state is $2J''+1$. All is well. But, in the upper state, $^2\Sigma$, we have a degeneracy g'_{el} of 2 (for spin), not 4, and now we will find that the sum of $\sum_{J''} S_{J'J''}$ is twice $2J'+1$ for a single J' when we use the H-L values for $S_{J''J'}$ for $S_{J'J''}$. However, as there are 2 states with J', the overall sum $\sum_{J''} S_{J'J''} = \left(2J'+1\right)4$ as required by (14.19)

4.1. Oscillator strengths

- Absorption oscillator strength for f_{00} in OH $A^2\Sigma^+$–$X^2\Pi$

Source	f_{00}
Oldenberg, et al. (1938)	0.00095 ± 0.00014
Dyne (1958)	0.00054 ± 0.0001
Carrington (1959)	0.00107 ± 0.00043
Lapp (1961)	0.00100 ± 0.0006
Bennett, et al. (1963)	0.00078 ± 0.00008
Golden, et al. (1963)	0.00071 ± 0.00011
Engleman, et al. (1973)	0.00096
Bennett, et al. (1964)	0.0008 ± 0.00008
Anketell, et al. (1967)	0.00148 ± 0.00013

4.1. Oscillator strengths

- Absorption oscillator strength

Transition	$S_{J''J'}/(2J''+1)$	$\Sigma F_1(J)$	$\Sigma F_2(J)$	$\Sigma[F_1(J)+F_2(J)]$
$Q_{12}(0.5)$	0.667	0	2	2
$Q_2(0.5)$	0.667			
$R_{12}(0.5)$	0.333			
$R_2(0.5)$	0.333			
$P_1(1.5)$	0.588	2	2	4
$P_{12}(1.5)$	0.078			
$P_{21}(1.5)$	0.392			
$P_2(1.5)$	0.275			
$Q_1(1.5)$	0.562			
$Q_{12}(1.5)$	0.372			
$Q_{21}(1.5)$	0.246			
$Q_2(1.5)$	0.678			
$R_1(1.5)$	0.165			
$R_{12}(1.5)$	0.235			
$R_{21}(1.5)$	0.047			
$R_2(1.5)$	0.353			
$P_1(2.5)$	0.530	2	2	4
$P_{12}(2.5)$	0.070			
$P_{21}(2.5)$	0.242			
$P_2(2.5)$	0.358			
$Q_1(2.5)$	0.708			
$Q_{12}(2.5)$	0.263			
$Q_{21}(2.5)$	0.214			
$Q_2(2.5)$	0.757			
$R_1(2.5)$	0.256			
$R_{12}(2.5)$	0.173			
$R_{21}(2.5)$	0.050			
$R_2(2.5)$	0.379			

Transition	$S_{J''J'}/(2J''+1)$	$\Sigma F_1(J)$	$\Sigma F_2(J)$	$\Sigma[F_1(J)+F_2(J)]$
$P_1(3.5)$	0.515	2	2	4
$P_{12}(3.5)$	0.056			
$P_{21}(3.5)$	0.167			
$P_2(3.5)$	0.405			
$Q_1(3.5)$	0.790			
$Q_{12}(3.5)$	0.195			
$Q_{21}(3.5)$	0.170			
$Q_2(3.5)$	0.814			
$R_1(3.5)$	0.316			
$R_{12}(3.5)$	0.131			
$R_{21}(3.5)$	0.044			
$R_2(3.5)$	0.402			
$P_1(9.5)$	0.511	2	2	4
$P_{12}(9.5)$	0.016			
$P_{21}(9.5)$	0.038			
$P_2(9.5)$	0.488			
$Q_1(9.5)$	0.947			
$Q_{12}(9.5)$	0.050			
$Q_{21}(9.5)$	0.048			
$Q_2(9.5)$	0.950			
$R_1(9.5)$	0.441			
$R_{12}(9.5)$	0.035			
$R_{21}(9.5)$	0.014			
$R_2(9.5)$	0.462			

Hönl-London factors for selected OH transitions